INTERACTION OF SECOND-PHASE PARTICLES WITH A
CRYSTAL GROWING FROM THE MELT

by

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ABSTRACT

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PATRICK FRANCOIS AUBOURG

Submitted to the Department of Materials, Science and Engineering on May 5, 1978 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

The interaction of second-phase particles with a solidification front has been experimentally and theoretically studied.

The critical velocity, \( V_c \), i.e., the maximum growth rate for which a particle is pushed by a growing crystal--has been measured with an horizontal set-up for various particles (Au, Cu, Ni, Zn, CuO, Ge, glass, mica, ranging in size between 1 and 200 µm) in low and high entropy of fusion organics (CBr\(_4\), d-camphor, thymol, naphthalene, durene). The critical velocity, \( V_c \), was inversely proportional to the viscosity of the melt; \( V_c \) was lower in low entropy of fusion organics than in high entropy of fusion organics having the same viscosity; \( V_c \) decreased with increasing particle size as \( R^{-n} \) with \( n \) equal to unity for small spherical particles (1 to 30 µm) and increasing with particle size.

The origin of the disjoining force between solid and particle has been discussed. It has been shown experimentally that this force was not of electrostatic origin. The disjoining force was due to dispersion forces and has been estimated from optical data, using Lifshitz's macroscopic theory. For the water-ice system, the Hamaker constant for short interaction distances has been computed for several oxides and metallic particles (\(-9\times10^{-20}J\) for gold, \(-.15\times10^{-20}J\) for SiO\(_2\)).

Expressions of the critical velocity have been derived for small and large spheres, smooth or rough, and subjected or not to an external field. These expressions were in good agreement with experimental observations. Small irregularities on the surface of the particles were found to increase the critical velocity by several orders of magnitude. The influence of differences in thermal conductivity between
particles and matrix has been treated numerically. When the particles had a higher (lower) thermal conductivity than the matrix, in the case of macroscopically smooth solidification fronts, the front dimpled (rised) behind the particle. The critical velocity was reduced (increased), and the coefficient \( n \) was increased (reduced). The larger the particle the more pronounced was this effect.
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CHAPTER 1

INTRODUCTION

It has been observed for more than a century that crystals growing in a liquid containing foreign particles can sometimes push these particles for long distances ahead of the solid-liquid interface. The ability of a particle to be pushed is a function of the growth rate, the properties of the crystal, as well as the nature, size, and shape of the particle. A solidification front can have, therefore, a purification and a classification role. This phenomenon has been observed in crystals growing both from the melt and from supersaturated solutions, and has been studied not only by crystal growers but also by geologists and civil engineers. The latter have been mainly interested in the behavior of soil particles at an ice-water interface to explain the formation of ice-lenses and frost-heaving.

The presence of second-phase impurities can have a strong influence on the properties of the crystallized solid; and the problem of the rejection of dissolved impurities and second-phase particles is critical for obtaining pure materials and materials with controlled phase assemblages. It has been suggested, for example, that incorporation of the small heterogeneous nuclei that are present in most liquid metals is a source of dislocations in the melt-grown crystals.

Another example of the importance of second phase particles is given by recent research conducted by NASA: metallic superconductors can be hardened by second-phase ceramic particles. To avoid segregation and obtain a uniform distribution of particles, these composites were grown
in a micro-gravity environment. Even in a zero gravity environment, however, if the particles are pushed by the solidification front, clustering and segregation of the particles can occur during solidification.

While the problem of the rejection of dissolved solutes at a solidification front has been extensively investigated and is well understood, the companion problem of the behavior of second-phase particles has not received as much attention and theoretical explanations of the phenomenon are still incomplete.

The present study consists of three parts: The first part (Chapters 2, 3, 4) is a critical literature review of the experimental data on particles pushing and of the various theoretical analyses. The nature of the forces between solid, liquid and particles is discussed in detail in this part, and the different existing methods used to compute van der Waals forces are presented in detail since they represent the major contribution to rejection forces. A critical analysis of the theoretical derivations is given, and the different proposed equations are compared.

The second part (Chapters 5 and 6) consists of experimental measurements on particle pushing and of optical measurements necessary to compute the van der Waals forces. The results on particle pushing are given in terms of the "critical velocities", $V_c$, that is the growth rate below which a particle is pushed by the solidification front and above which it is entrapped. This study includes data for various organic materials of both low and high entropy of fusion, for various particles and various growth geometries.
The third part (Chapters 7, 8, 9) is a theoretical and mathematical discussion of the phenomenon. First the forces acting on a particle pushed by a solidification front are computed for various geometries of the front. Then the exact differential equation that a solidification front must satisfy when it pushes a particle is presented, and expressions for the critical velocities of particles are derived. These expressions are compared with experimental values. Finally, the influence of a difference in thermal properties between matrix and particle is discussed.

Before proceeding, it should be noted that the understanding of the forces between a solidification front and second-phase particles not only would allow us to predict which particles will be entrapped and under what conditions, but also would help us understand many other related problems such as adhesion, interactions of biological cells, cleaning, strength of aggregates, etc.
CHAPTER 2

LITERATURE REVIEW - EXPERIMENTAL OBSERVATIONS

The experimental studies can be classified in two groups. In the first one, the rejection of a small particle at a solidification front is studied either by varying the growth rate in order to determine the maximum rate at which a particle is pushed (critical velocity) or by varying the pressure exerted by or on the particle and measuring the maximum pressure at which entrapment occurs. In the second group of experiments, a crystal is grown between two plates and the minimum pressure at which the crystal stops growing ("crystallization pressure") is measured. Since a thin liquid film must always exist between the obstacle and the crystal, for the crystal to continue to grow, these studies are related to the determination of disjoining pressure, i.e., the pressure existing in a thin film in excess of the hydrostatic pressure. A critical review of the experimental work, prior to 1959 has been given by Khaimov-Mal'kov (1,2,3).

2.1. Interaction of a Small Particle with a Crystal-Liquid Interface

2.1.1. Entrapment Pressure

The first systematic study of particle rejection was done by Shubnikov (4) on an alum crystal (KAl (SO₄)₂; 12 H₂O) pushing a glass bead formed at the end of a thin glass fiber (Figure 2-1). The fiber acted as a spring and the crystallization force was taken to be the force corresponding to the deflection when the ball began to enter in the crystal. Such measurements are not very precise: In most cases a funnel of liquid is formed under the particle (2,3) and the contact area is not accurately known. The reported pressure can, therefore, be too small, in some cases
(1) CRYSTAL HOLDER
(2) GROWING CRYSTAL
(3) SUPERSATURATED SOLUTION
(4) GLASS FIBER
(5) GLASS BEAD.

FIGURE 2-1 SHUBNIKOV'S EXPERIMENT
by several orders of magnitude. The formation of such a funnel of liquid behind a particle can easily be understood for crystals grown from a supersaturated solution as a lens of depleted liquid that will not mix readily with the rest of the solution is formed behind the particle. Another uncertainty in this measurement is the definition of the time at which the glass bead begins to be entrapped since free particles resting in a cusp at a crystal surface can be pushed for long distances without being entrapped. This approach to entrapment is, however, very interesting as it allows the investigator to change one parameter at a time. In the case of an alum crystal and a glass bead, the entrapment pressure was found to be about 0.5 atm. (2). This value is corrected to take into account the very small area of contact due to cusping of the front behind the bead.

2.1.2. Critical Velocity

The first reported systematic measurements of critical velocities were done by Sparsi and Pikurov (5,6). They studied the crystallization of various organics (salol, azobenzene, benzil, naphthalene) in the presence of suspensions of lycopodium (a fine organic sulfur powder found in spores), carbon, Al$_2$O$_3$, Cr$_2$O$_3$ and starch. They introduced the concept of a critical growth rate and showed that it depended upon the various particle-organic combinations.

In this country, the first measurements are those of Corte (7) for an ice-water interface. Various particles (glass, calcite, rutile, mica ...) of different size and shape were used. Corte's results are summarized in Figures 2-2 and 2-3. The experiments were run in a large container with a horizontal ice front moving upward. All the materials used had a
Figure 2-2 Percentage by weight of particles (diameter 0.149 - 0.290 mm) carried at least 1 cm under various freezing rates. Water - ice system (Ref. 7)
Figure 2-3 Critical freezing rate as a function of particle size - water-ice system (Ref. 7)
density of 2.5 to 3.3 g/cm$^3$ except rutile which had a density of about 5 g/cm$^3$. Shale and mica particles were both in the shape of flakes, but the shale particles were 5 to 10 times thicker than the mica. One can see in Figure 2-2 that the measured velocity generally increased with decreasing pressure exerted by the particle on the front—i.e., the spherical glass beads had a lower critical velocity than the broken glass fragments—and the shale particles had a lower critical velocity than the light mica flakes for the same maximum diameter. Such an explanation would agree with the observation that a particle, upon contact with the solidification front, will rotate to present the largest cross section to the front. The surface properties of mica are, however, so drastically different from those of other materials that this alone could explain the observed difference in critical velocity.

The effect of particle size on critical velocity is shown in Figure 2-3. Corte's original graph has been modified to plot the highest growth rates at which all the particles of a given size range were pushed (i.e., critical velocity) as a function of the size of the largest particles of the group (and not the smallest as was done by Corte). The critical velocity, $V_c$, increases with decreasing particle size as $1/d^n$ where $d$ is the largest dimension of the particles and $n$ varies between 1.4 and 1.7.

Corte's data are qualitatively very interesting as they show the influence of size and nature of the particles, but quantitatively they should be used with caution as the critical velocities were determined on pile ups of particles, 3 to 20 particles thick; and the size, shape and nature of the particles were only approximately defined. This last point is apparent in the range of values given for the densities (for example,
the density of rutile was given as 4.1 to 5.3 g/cm$^3$).

Hoekstra and Miller (8) studied the rejection of Pyrex spheres by an ice front using again a vertical growth geometry. Their results are given in Figure 2-4. More results on the ice-water system, using the same vertical geometry, were gathered by Bolling and Cissé (9, 10) who studied the rejection of metallic spheres (tungsten, silver, copper). Since the thermal conductivity of these particles is much larger than that of the surrounding water, one would expect that they would modify the equilibrium shape of the solidification front and possibly give quite different results. This was not the case, however, as shown in Figure 2-4. For some ranges of particle size the critical velocity varied as $1/R^n$ with $n$ between 2 and 3, but the overall variation for a large range of radii was more complex. The effect of density was shown with copper particles, comparing air-free particles with those which trapped some air bubbles; the lighter air-laden particles were pushed at higher velocities. It was also found that particles pushed at grain boundaries were entrapped at higher critical velocities. This result tends to confirm Corte's conclusion that the critical velocity increases when the area of contact between particle and solid increases, i.e., when the pressure applied by the particle decreases. Cissé and Bolling also studied the solidification of salol (11) and found similar results.

Uhlmann, Chalmers and Jackson (12, 13) studied the solidification of water and of several organics (salol, thymol and orthoterphenyl) with various particles. They used a very thin sample mounted between two microscope slides. The solidification front in this case was vertical
FIGURE 2-4 CRITICAL VELOCITIES IN THE SYSTEM WATER-ICE
1 - G. F. BOLLING AND J. CISSÉ - VERTICAL GROWTH
   (REF. 9-10)
2 - P. HOEKSTRA AND R.D. MILLER - VERTICAL GROWTH
   (REF. 8)
3 - J. AGUIRRE-PUENTE, M.A. AZOUNI - HORIZONTAL
   GROWTH (REF. 14)
and the particles were resting against the bottom slide. Gravity was not
directly a factor in these experiments but the interpretation of the
results may be complicated by the friction of the particles against the
glass slide. Their results (Table 2-1) showed that the critical velocities
generally increased in the order orthoterphenyl, salol, thymol, which is
the order of decreasing viscosity (respectively 30, 8.5 and 5.0 centi-
poise at melting point); but the critical velocities did not change by the
same amount for various particles in the different liquids. In fact, if
the particles are classified in order of increasing critical velocity,
the order is practically reversed in going from thymol to salol. It was
also observed that for small particles (< 15 μm) the critical velocity was
independent of the size of the particles and for larger particles $V_c$
decreased with increasing size. Finally, Uhlmann et al. showed that this
effect could not be explained by a simple Coulombic interaction: In
most systems nearly all particles were charged, but in a given system
particles with charges varying in magnitude by a factor of 10 and of both
signs were all trapped in the same range of velocities.

An horizontal growth technique has been used by Aguirre-Puente (14)
and by Omenyi (15, 16). The critical velocities found by Aguirre-Puente
for the ice-water-silica system (Figure 2-4) were larger than the values
reported previously by Bolling and Cissé, for vertical growth, and this
difference may be partially due to the effect of gravity. Some other
difference must however exist between the two experiments since, in the
region where the two sets of data overlap, the difference in critical
velocities increases for decreasing particle size; and this result is in
<table>
<thead>
<tr>
<th>Orthoterphenyl</th>
<th>Salol</th>
<th>Thymol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Particle</strong></td>
<td><strong>$V_c$ ($\mu$/sec)</strong></td>
<td><strong>Particle</strong></td>
</tr>
<tr>
<td>AgI</td>
<td>not pushed</td>
<td>AgI</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.3</td>
<td>Graphite</td>
</tr>
<tr>
<td>MgO</td>
<td>0.5</td>
<td>Silt</td>
</tr>
<tr>
<td>Silt</td>
<td>0.7</td>
<td>Si</td>
</tr>
<tr>
<td>Si</td>
<td>0.8</td>
<td>Sn</td>
</tr>
<tr>
<td>Sn</td>
<td>1</td>
<td>Diamond, 0-2(\mu)</td>
</tr>
<tr>
<td>Diamond, 0-2(\mu)</td>
<td>1.3</td>
<td>Diamond, 3-5(\mu)</td>
</tr>
<tr>
<td>Diamond, 3-5(\mu)</td>
<td>1.4</td>
<td>Ni</td>
</tr>
<tr>
<td>Ni</td>
<td>2</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.5</td>
<td>MgO</td>
</tr>
<tr>
<td>Zn</td>
<td>2.5</td>
<td>Zn</td>
</tr>
</tbody>
</table>

**Note:** In an ice-water system, all the solid particles are pushed at more than 20 $\mu$m/sec, liquid particles (Xylene, 1-2 $\mu$m) are pushed at 13 $\mu$m/sec.

Table 2-1. Critical velocities for particle-organic matrix systems classified in order of increasing critical velocity (Ref. 13)
contradiction with theoretical considerations that show that the effect of gravity decreases when the particle size decreases. Omenyi studied the solidification of naphthalene and biphenyl: acetal and nylon particles were pushed (Figure 2-5 and 2-6) and teflon and silicon-coated glass beads were not. The coefficient n varies between .3 and .7 in naphthalene and .4 and 2 in biphenyl. Also shown in Figure 2-5 are the results of Zubko et al. (17) for various particles in naphthalene. These data were obtained with a vertical set-up.

More recently Kuo and Wilcox (18, 19) studied the rejection of various particles (carbon, silicon, copper, ...) in naphthalene, camphor, salol and bensophenone. Both horizontal and vertical geometries were used. In the horizontal zone melting experiments, a 1 cm i.d. pyrex tube was rotated at 30 to 50 r.p.m. to keep the particles in suspension. Their main goal was to obtain practical information to develop an industrial separation process. Therefore they studied mainly the influence of stirring, interface shape and gas bubbles on entrapment. They observed that stirring increased the critical velocities by a factor of 2 or 3, and that if the solidification front was convex particles were trapped more readily along the tube wall. This result has been confirmed by our experiments to be described in Chapter 5 below. Contrary to Bolling and Cissé's observations, carbon particles were preferentially trapped at grain boundaries during solidification of salol, and there was no preferential entrapment or rejection at grain boundaries with naphthalene. These studies on particle separation (particle chromatography) had been continued by Chen (20, 21). The results were not very encouraging from the viewpoint of particle chromatography since the particles were trapped over a fairly
FIGURE 2-5 CRITICAL VELOCITIES IN NAPHTHALENE
1. S.N. OMENYI HORIZONTAL GROWTH (REF. 15)
2. A.M. ZUBKO, et al VERTICAL GROWTH (REF. 17)
FIGURE 2-6 CRITICAL VELOCITY IN BIPHENYL (REF. 15)
large range of velocities.

Chen also studied the influence on critical velocity of the force exerted by a particle on the solidification front. By using steel or iron particles coated with gold, silver or aluminum, the force exerted by the particle could be modified by applying a magnetic field. By this technique, in a vertical growth experiment, the apparent weight of the particles was increased by a factor of up to 1.4. Contrary to intuition, he found that the critical velocity was an increasing function of load—i.e., that the higher the force with which the particle pressed on the front, the better it was pushed! These results should, however, be regarded with caution since no correlation was found for silver coated particles and the correlation for gold coated particles was only weak. In fact, as noted by Chen, a stronger correlation was observed between critical velocity and the number of the experiment (classified chronologically).

Very few experimental results exist for the solidification of metals. Myer and Fleming (22, 23) observed segregation of silica particles during dendritic solidification of an iron-copper alloy. The particles were concentrated in the interdendritic spaces. The lateral growth rate of the dendrite was very low and no attempt was made to measure it. Livingston and Cline (24), while working on the solidification of copper-lead alloys, observed that liquid droplets of lead could be pushed ahead of the interface at growth rates of up to 100 \( \mu m/s \).

The only systematic study is due to Zubko et al. (17). They used a vertical set up. The particles studied were quite large (diameter of 2 to
3 mm) and the growth rate was varied between 14 and 280 μm/s. Their results are shown on Table 2.2. They explained their results exclusively on the base of a thermal argument: If the particles have a higher thermal conductivity than the matrix, the solidification front behind the particle will be cusped and the particles will be entrapped. They did not attempt to measure accurately a critical velocity and captured particles might have been pushed at growth rates lower than 14 μm/s.

The problem of liquid or solid particle migration in solids in a temperature gradient is related, at least in appearance, to the present problem. It has been extensively studied by people interested in the storage of radioactive materials (25, 26, 27). The migration rates were very slow and migration was explained by the presence of a third liquid or gaseous phase.

In conclusion, these various experimental data are difficult to compare since the experimental details are not always known and since with the exception of a few studies, the exact shape and surface finish of the particles is not given. One can, however, make the following observations from this fairly large collection of experimental results:

- The critical velocity is a function of the system solid-particle and of the size and shape of the particles. It increases with decreasing particle size and varies approximately as 1/R^n, where R is the particle radius. Most generally the exponent, n, is not constant and increases with increasing particle size.

- The critical velocity is generally a decreasing function of the melt viscosity.
<table>
<thead>
<tr>
<th>Matrix</th>
<th>Thermal conductivity of matrix, $k_m$ (W/m·°C)</th>
<th>Density of Particle, $\rho$ (kg/m³)</th>
<th>Thermal conductivity of particle, $k_p$ (W/m·°C)</th>
<th>Density $\rho_p$ (kg/m³)</th>
<th>Experimental result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>112.6</td>
<td>7140</td>
<td>W</td>
<td>167</td>
<td>19300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ta</td>
<td>54</td>
<td>16600</td>
</tr>
<tr>
<td>Bi</td>
<td>8.4</td>
<td>9800</td>
<td>W</td>
<td>167</td>
<td>19300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ta</td>
<td>54</td>
<td>16600</td>
</tr>
<tr>
<td>Sn</td>
<td>65.7 or 33.5</td>
<td>7300</td>
<td>W</td>
<td>167</td>
<td>19300</td>
</tr>
<tr>
<td></td>
<td>or 33.5</td>
<td></td>
<td>Ta</td>
<td>54</td>
<td>16600</td>
</tr>
<tr>
<td></td>
<td>33.5</td>
<td></td>
<td>Mo</td>
<td>145</td>
<td>10200</td>
</tr>
</tbody>
</table>

Particles not wetted by the melt

Particles wetted by the melt

| Sn    | 65.7                            | 7300            | Fe                              | 84              | 7860            | >1 Capture      |
|       |                                 |                 | Ni                              | 82.9            | 8900            | >1 Capture      |
|       |                                 |                 | Cr                              | 29              | 7190            | <1 Repulsion    |

Table 2-2. Results of Zubko et al (17) on metallic systems.

Vertical geometry, growth rate >14 µm/sec.
- Critical velocities measured with an horizontal set up are generally larger than those measured with a vertical set up.

- Large pile-ups of particles can be pushed but there is no published result on the critical velocity of a particle in a pile-up versus a single particle.

- In no case were investigators able to observe the liquid film that must exist between solid and particle.

- The curvature of the front behind a particle increases until the particle is trapped but fairly curved fronts may push a particle.

- A particle can be pushed for a certain distance before it is entrapped.

The system ice-water has been one of the most widely studied due to its practical importance; it may, however, be one of the most difficult to treat theoretically due to the highly polar nature of water and to uncertainty concerning the nature of the ice-water interface (the possible existence of an ordered layer of water adjacent to the ice surface).

2.2. Interaction Between a Solidification Front and a Large Obstacle:

Crystallization Pressure

Having observed that a growing crystal can push particles, investigators tried to measure the pressure under which a crystal stops growing (2, 3, 28). The pressure measured by this technique was much larger than the one measured by Shubnikov's technique. For an alum crystal (Figure 2-7), the crystallization pressure increased with supersaturation (or supercooling) up to about 40 kg/cm$^2$ for a supersaturation of $C/C_0 = 1.9$ and was different for different crystal faces. Khaimov-Mal'kov (3) showed
Figure 2-7 Measurement of Crystallization Pressure
that the growth rate of a covered face decreased with increasing pressure. The decrease was initially very fast for small loads and then smaller for increasing loads.

These studies are obviously a limiting case of entrapment of small particles: for a small particle to be entrapped it is not necessary that the crystal behind the particle stops growing completely but simply that it does not grow as fast as the rest of the front.

2.3. **Stability of Liquid Films - Disjoining Pressure**

If a particle is pushed ahead of a solidification front, there must always be a film of liquid between the solid and the particle. The problem of the stability of thin films and particularly free soap films has been studied extensively. From hydrostatic considerations, a free film should not be stable as the radius of curvature at the edge of the film is smaller than at the nearly flat center, and capillary effects should suck the central portion of the film toward the edges. The fact that the film remains stable implies the existence of a force balancing these capillary forces. Deryagin and co-workers, who studied extensively the phenomenon, called this force the disjoining pressure, $\Pi$ (29).

The notion of disjoining pressure is easier to grasp in the case of a thin liquid film between two solids. If $P_e$, is the pressure that must be applied to the two solids, to maintain an equilibrium gap thickness, $h$, in addition to hydrostatic and capillary forces, and if the hydrostatic pressure in the thin film is $P_f$, the disjoining pressure $\Pi$ is equal to:

$$\Pi = P_e - P_f$$  \hspace{1cm} (2.1)
Π is positive if one must press the two solids to keep them together, i.e., if the gap, h, has a tendency to widen if no force is applied. The notion of disjoining pressure is somewhat confusing, however, since it is often not clear from published articles if the pressure is supported by the liquid, in excess of the hydrostatic pressure, or if it is supported by the solids. Π is essentially a jump in pressure at each of the two surfaces adjacent to the thin liquid layer (Figure 2-8) i.e., a pressure supported by the solids.

In the case of free films, unless the notion of surface membranes is introduced, the nature of the disjoining pressure is harder to visualize. The pressure tensor in the thin liquid film must be viewed as anisotropic. The normal component of pressure, in the z direction is constant (equilibrium) but the horizontal component varies with position (30). The relevance of the work on disjoining pressure to the problem of particle pushing has been recognized only recently (20, 31, 32).

Disjoining pressure can be due to various mechanisms, as will be discussed in Chapter 3. In recent articles, Deryagin and his coworkers have reviewed some of these mechanism, including structural effects (33), and the adsorption of components in binary solutions (34, 35) and in the case of electrolytes (36).

Deryagin and his group were the first ones to study systematically the influence of pressure and solutes on the thickness and stability of free films. They studied also films formed on a solid and between two solids. In their measurements on free films, the films were formed between two bubbles (37, 38, 39). The pressure was determined either
FIGURE 2.8 DISJOINING PRESSURE, $\Pi$, IN A THIN FILM
directly or from measurements of the radii of curvature of the bubbles and use of the Laplace's equation relating pressure to surface tension and curvature. The thickness of the film was measured by interferometric techniques (this method has also been used in the case of transparent solids).

Free films were only found to be stable in the presence of dissolved surface active substances. The equilibrium thickness of the film was of the order of a few tens of nm. With pure water, no film was ever observed and the two bubbles burst together immediately. It is interesting to note, however, that if instead of using a quartz holder, the bubbles were held in a pyrex ring, enough ions were dissolved after a few minutes of contact to form films that took a few seconds to break. The thickness of the film decreased with increasing pressure. The stability of these films is due to the repulsion of ionic layers. The molecular or van der Waals forces are always destabilizing these films as the dispersion forces are always attractive between two identical bodies.

The case of wetting films was studied by Deryagin et al. (40). They studied the formation of water films on mica and glass substrates. The film thickness decreased with increasing pressure and reached a value of 30 nm for small pressures (6 g/m$^2$ for glass, 14 g/cm$^2$ for mica). Measurement of $\xi$ potential showed that in water, the surface of air bubbles as well as of glass and mica were charged negatively and even in the case of pure water, part of the disjoining action may be attributed to ionic layers. These results have been confirmed by more recent work (41).
The stability of films between two solids has been studied both between a flat surface and a sphere and between two cylinders at right angles (in first approximation, both geometries are equivalent). Only few measurements exist on a liquid film between two solids and most data have been taken on two solids separated by an air or vacuum gap. These experiments are quite difficult and extreme care is required to overcome the problems of: (a) vibration, as very small forces must be measured; (b) cleanliness and flatness of the surface, as very small gaps are used; and (c) static charges, as electrostatic forces must be negligible.

In spite of these difficulties, measurements on quartz surfaces, done during the last 15 years by various research groups are in fair agreement. Experimental techniques and data have been reviewed by Israelachvili and Tabor (42). By using freshly cleaved mica (43), they were able to measure the van der Waals forces down to gap thicknesses of 1.5 nm. In mica, the forces were non retarded (vary as $1/d^2$) for distances, $d$, less than 10 nm and retarded (vary as $1/d^3$) for $d$ larger than 50 nm. The Hamaker constants were respectively, $A = 1.35 \times 10^{-19}$ J and $B = 9.7 \times 10^{-29}$ J.m for mica and $A = 3.4 \times 10^{-21}$ J and $B = 6.6$ to $20.0 \times 10^{-29}$ J.m for silica. At short distances, the attraction between two mica plates was therefore nearly two orders of magnitude larger than between two quartz plates.

Measurements of the force between two solids separated by a liquid layer have been obtained on crossed wires. In most cases, however, the distance between the wires could not be measured and Deryagin and co-workers measured only the adhesion forces and the force barrier preventing contact for various electrolyte solutions (38, 39). Only
recently were they able to measure the gap thickness (41). In their latest experiment they measured the van der Waals forces between quartz and platinum wires. For the case of quartz, their results are in agreement with previous experimental data. They found Hamaker constants (see Chapter 3) equal to $A = 0.45 \times 10^{-19}$ J and $B = 1.02 \times 10^{-28}$ J.m. For platinum wire, $A = 2 \times 10^{-19}$ J and $B = 10.5 \times 10^{-28}$ J.m. The value of B is close to that computed from theoretical considerations.

Other data in the literature concern the forces between two mica cylinders separated by a KNO$_3$ solution (45). Due to the electrolytic nature of KNO$_3$, two different kinds of forces are active. At large distances the interaction is dominated by attractive van der Waals forces, but a smaller distances, repulsion forces due to double layer interaction become predominant. There is therefore a stable gap thickness. The thickness of the liquid film decreases with increasing ionic concentration. This phenomenon is of extreme importance in colloid stability and has been studied extensively. It is well explained by DLVO theory (Deryagin, Landeau, Vervey and Overbeek). This problem is not, however, of direct interest to us as it always involves charged double layers and electrolytes.
CHAPTER 3

LITERATURE SURVEY - FORCES ACTING ON A PARTICLE

To predict and compute the critical velocity of a particle in a given system, it is necessary to know the various forces acting on the particle while it is pushed by the solidification front. For steady-state rejection to occur, the sum of these various forces must be zero, and the critical velocity will be reached when these forces cannot be balanced any more.

When the solidification front is growing at a velocity \( V \), a particle pushed by the front moves, in the liquid at the same velocity \( V \) and is therefore subjected to a drag force, \( F_D \). This force is due to two factors: first to the penetration of the particle in the liquid as the fluid flow is deviated by the particle and as the component of the velocity normal to the particle becomes zero. This contribution to drag is, however, very small relative to the second term, the drag due to flow or diffusion of fresh liquid behind the particle. As the particle is very close to the solidification front, the standard Stokes' equations for drag force are not applicable and a new formula was derived by Carrier (12). For a spherical particle of radius \( R \), at a distance \( h_0 \) from a flat front growing at a velocity \( V \) from a melt of viscosity \( \eta \), the drag force, \( F_D \) is:

\[
F_D = 6\pi\eta \frac{VR^2}{h_0}
\]  

(3.1)

This formula will be discussed in more details in Chapter 7.

The particle is also subjected to gravitational forces in a vertical setup or to frictional force in an horizontal setup. Furthermore, in a horizontal setup, where the particles are resting against the top or bottom walls of the cell, the particles may be attracted electrostatically to the glass walls.
The force between particles and solidification front (disjoining force) can be due to at least four different mechanisms (33).

a. **Ionic Electrostatic** - This force is due to the overlapping of double ionic layers. It was shown previously that this term is the major contributor to the stability of thin films of solutions of electrolytes.

b. **Dispersion or Molecular** - This force (van der Waals forces) is due to fluctuating electromagnetic fields and play a major role in the stability of films that do not contain ions.

c. **Structural** - This force is due to the existence of a boundary layer of liquid with a structure modified under the influence of surface forces. The layer of liquid can be modified by a variation in the energy of intermolecular bonds and by a variation in the mode of arrangement of the molecules. This mechanism is only important in the case of polar liquids. This term was found to be the major term to explain the stability of very thin films of water on glass, mica or metals (33).

d. **Adsorption** - This force is due to the overlapping of the adsorption layers of another component (dissolved molecules).

In all the discussions of critical velocity, the matrix material was assumed non polar and pure so that the structural and adsorption terms can be neglected. The adsorption term could, however, play an important role since it has been shown recently (46) that the concentration of impurities will be larger behind a particle being pushed than in the bulk of the liquid. In the same respect, the concentration of absorbed gases is larger behind a particle and small gas bubbles can be nucleated between solidification front and particle; the bubbles favor the pushing of the
particles, widening the thickness of the gap between particle and front. This mechanism was reported to be operative for copper particles pushed by an ice front growing from air saturated water (47). This contribution can, however, be limited by degasing the liquid or by successive growth and melt of the matrix prior to measurement of critical velocities.

3.1. Ionic–Electrostatic Forces

In many cases, the particles are charged; if the solidification front is also charged, the particle can be either repelled or attracted by the front. A simple electrostatic computation shows that the force between a charged plane and a charge sphere of radius \( R \), is independent of the separation.

\[
F = \frac{4\pi \sigma_1 \sigma_2 R^2}{2\varepsilon_0 \varepsilon}
\]  

(3.2)

where \( \sigma_1 \) is the surface charge density; \( \varepsilon_0 \) the dielectric constant of vacuum (\( = 1/36\pi \times 10^9 \) u. S.I.R.); and \( \varepsilon \) is the relative dielectric constant of the medium between particle and front. Considering that the area occupied by a molecule is about \( 10^{-19} \) m\(^2\) and that 1 molecule in 1000 is charged with a charge of one electron (\( 1.6 \times 10^{-19} \) C), the charge density \( \sigma \) is equal to \( \frac{1.6 \times 10^{-19}}{10^{-19}} \times \frac{1}{1000} = 1.6 \times 10^{-3} \) C/m\(^2\). Choosing the dielectric constant equal to 3, the force between a particle of radius 1 \( \mu \)m and the front would be equal to

\[
F = 6 \times 10^{-6} \text{ N}
\]

This force would therefore be much larger than the molecular disjoining force discussed later in this chapter since for a 1 \( \mu \)m particle this force is less than \( 10^{-8} \) N. In this computation, however, the charge densities were chosen arbitrarily and were certainly too large. Furthermore, if the
front is charged, the melt must also be slightly ionized and the simple electrostatic model is not valid. Models involving the existence of charged double layer must be considered (48, 49); and this double layer has the effect of reducing significantly the interaction between solids. The expression for the force is much more difficult to derive, and the force is found to vary as \((R/h)^2\) where \(h\) is the separation sphere front. An exact computation requires knowledge of the ionic species present and their concentrations. Since this information is not available one must resort to an experimental approach.

Deryagin and Churaev (33) studied the relative magnitude of the various components of the disjoining force. In the case of water and mica or glass solids, the stability of the water film is determined by the ionic electrostatic component for thick films (>70 nm) and by the structural component for thin films (<10 nm). For pure non-polar liquids, they found that the electrostatic effects were small.

Uhlmann et al. (13) showed that rejection of particles was not due to an electrostatic effect since particles with charges varying by an order of magnitude and even of different sign had about the same critical velocity.

In our discussion of rejection of particles, the ionic electrostatic effect will therefore be neglected.

In the following section, a thermodynamic argument will be presented to explain why particles are rejected by a growing front and then the nature of the molecular rejection force will be discussed in more detail.
3.2. Thermodynamic Argument – Surface Energy

If the interfacial free energy solid-particle, $\sigma_{SP}$, is greater than the sum of the surface free energies solid-liquid, $\sigma_{SL}$, and liquid-particle, $\sigma_{LP}$, the configuration with the lowest energy is achieved when the particle is surrounded by liquid. The condition for entrapment appears therefore extremely simple: with the notation:

$$\Delta \sigma_{\infty} = \sigma_{SP} - (\sigma_{SL} + \sigma_{LP}) \tag{3.3}$$

a particle will always be entrapped if:

$$\Delta \sigma_{\infty} < 0 \tag{3.4}$$

This argument, already presented in the 1940's to discuss the stability of thin liquid films (50) has been used extensively by Neumann (51, 16). It can, however, only tell us if a particle will be rejected or entrapped at infinitely low growth rate; intuitively, however, the larger $\Delta \sigma_{\infty}$, the more likely the particle will be to be pushed and the higher will be the critical velocity.

To predict a critical velocity, this argument can be refined by considering that the surface energy of a thin film, $\sigma$, is a function of the thickness of the film (50, 40). Uhlmann, Chalmers, and Jackson (12, 13) assumed that the difference $\Delta \sigma = \sigma(h) - (\sigma_{SL} + \sigma_{LP})$, varied with the distance $h$, between solid and particle as:

$$\Delta \sigma = \Delta \sigma_{\infty} \times \left(\frac{h}{\delta}\right)^n \tag{3.5}$$

where $\delta$ is the minimum separation between solid and particle, corresponding to contact and is equal to a molecular diameter, i.e., a few $\AA$; and $n$ is a positive number chosen equal to 4 or 5 (5 was used in the numerical ...
culations). For thick films, the surface free energy of the film, \( \sigma \), is equal to \((\sigma_{SL} + \sigma_{LP})\) and at contact \( \sigma \) is equal to \( \sigma_{SP} \).

This formalism and the value of \( n \) can be derived from the relation existing between disjoining pressure, \( \Pi_m \) and surface tension (50)

\[
\frac{\partial \Pi_m}{\partial h} = \frac{1}{h} \frac{\partial \sigma}{\partial h}
\]

(3.6)

As will be seen later, (Equations 3.29 and 3.30), the disjoining pressure due to van der Waals forces, \( \Pi_m \), is equal to \(-A_{12}/6\pi h^3\) for short distances and \(-B_{12}/h^4\) for large distances where \( A_{12} \) and \( B_{12} \) are the non-retarded and retarded Hamaker constants. By integration of Equation (3.6), the surface free energy of the film can be written, for short distances,

\[
\sigma(h) = (\sigma_{SL} + \sigma_{LP}) - \frac{A_{12}}{4\pi h^2}
\]

(3.7)

and for large distances,

\[
\sigma(h) = (\sigma_{SL} + \sigma_{LP}) - \frac{4B_{12}}{3h^3}
\]

(3.8)

These expressions have the same form as Equation (3.5). For short distances, therefore, \( n \) equals 2 and

\[
\Delta \sigma_\infty = \frac{-A}{4\pi h^2}
\]

(3.9)

and for large distances (retarded forces), \( n \) equals 3 and

\[
\Delta \sigma_\infty = \frac{-4B}{3h^3}
\]

(3.10)

The repulsive interaction occurring at very short distances, varies like \( 1/h^m \) with \( m = 7 \) to 9 and a similar derivation would give a value of 6 to 8 for \( n \). Uhlmann et al. (13) used an average value of 4 to 5. As the
liquid film must be, at least several molecules thick, it would seem more appropriate to consider the attractive force only and choose $n$ equal to 2 or 3. This change in the value of $n$ will only have the effect of reducing the critical velocities computed by Uhlmann et al. by a factor of 1.5.

The main difficulty with this approach is the determination of $\Delta \sigma_\infty$. The free energy solid-melt, $\sigma_{SL}$, can be measured directly. The various experimental techniques and data for a number of systems have been reviewed by Jones (52). The most reliable techniques are, either the measurement of the undercooling at a curved interface and computation of $\sigma_{SL}$ from the Gibbs-Thomson equation relating curvature, undercooling and surface tension, or the observation of the shape of a grain boundary groove at the solid-melt interface.

The surface tension $\sigma_{SL}$ can also be estimated semi-empirically and Turnbull (53) suggested a relation of the form

$$\sigma_{SL} = K \Omega L n_s$$  \hspace{1cm} (3.11)

where $\Omega$ is the molecular volume; $L$ is the latent heat of fusion per unit volume; $n_s$ is the number density of molecules in the surface; and $K$ is an empirical constant equal to about 1/2 for metals and about 1/3 for non metals. These values were computed from nucleation data. Recent computations (54), using a more accurate derivation, showed that for non metals, $K$ could be as low as 0.25. If $a_o$ is the molecular diameter, the molecular volume $\Omega = a_o^3$ and $n_s \approx 1/a_o^2$; and Equation (3.11) can be written

$$\sigma_{SL} = K \cdot a_o \cdot L$$  \hspace{1cm} (3.12)
More recently, Spaepen (55) modelled the solid-melt interface on a computer, considering that the surface energy is only due to a difference in configurational entropy between solid and liquid. He obtained an expression having the form of Equation 3.11, with \( K = 0.86 \). When experimental surface free energy values (52), determined from grain-boundary grooving at crystal-liquid interfaces and not from nucleation experiment are used, \( K \) is found to vary between 0.33 and 1.3. The fact that these values are larger than those measured from nucleation experiments is surprising since, for macroscopic samples, \( \sigma \) is a decreasing function of temperature. Equation (3.12) gives therefore a good estimate of \( \sigma_{SL} \) considering that the errors reported for the measurements of surface tension are at least \( \pm 10 \) to 20\% and that the approximation used for \( \Omega \) and \( n_s \) are fairly crude. Jones (52) suggested that \( K \) is an increasing function of \( (L/T_m) \) where \( T_m \) is the melting point. The existing data are, however, insufficient to confirm such a relation.

The other two surface free energies, \( \sigma_{SP} \) and \( \sigma_{LP} \), needed to compute \( \Delta \sigma_\infty \) are more difficult to determine. In discussing the thermodynamics and imperfections of solid surfaces, Dunning (56) reviewed the several ways in which surface energies had been measured. Measurements had been mostly done in high energy solids and the values measured by different methods were often very different. For example, the surface energy of freshly cleaved mica was until recently considered very high \( (>4000 \text{ mJ/m}^2) \) but is now considered to be only moderate \( (308 \text{ mJ/m}^2) \). Neumann, however, suggested that they can be determined from contact angle measurements using an equation of state approach (51). For a given solid, liquid,
vapor system (respectively S, L, V), the surface energy $\sigma_{LV}$ can be measured by a sessile or pendant drop technique, and if the liquid does not spread on the solid, the surface free energies are related to the contact angle $\theta$ by Young's equation:

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \theta$$

(3.13)

A third relation or measurement is necessary to determine the surface energies since Equation (3.13) defines only the difference $\sigma_{SV} - \sigma_{SL}$. The existence of a second relation between the surface energies, similar to an equation of state, was demonstrated by Ward and Neumann (51). By studying the relation between wetting angles, $\theta$, and $\sigma_{LV}$ for a series of liquids on a low surface energy solid, Neumann (51) was able to show that the surface energies were related by the following empirical relation:

$$\sigma_{SL} = \frac{(\sqrt{\sigma_{SV}} - \sqrt{\sigma_{LV}})^2}{1 - 0.015 \frac{\sqrt{\sigma_{SV} \sigma_{LV}}}{\sigma_{LV}}}$$

(3.14)

To obtain this equation, it is assumed that:

1. The solid has a lower surface energy than all the liquids considered. No adsorbed film is therefore formed on the surface of the solid and $\sigma_{SV}$ is independent of the liquid used, i.e. $\sigma_{SV} = \sigma_S$

2. The surface tension $\sigma_{SL}$ equals zero when the liquid spreads on the solid (i.e., $\theta = 0$). $\sigma_{SL}$ and $\sigma_{SV}$ can therefore be determined by simply measuring one contact angle and $\sigma_{LV}$.

This technique was applied by Omenyi and Neumann (15, 16) to the case of particle pushing. They studied the rejection of low surface energy particles in two organics, naphthalene and biphenyl. The contact angle, $\theta$, was measured at room temperature using a sessile drop of water or
glycerol (high surface energy liquids) on a solid sample of organic material and particle material. The surface tension of the liquids were measured and $\sigma_{SV}$ was computed with the help of Equation (3.13) and (3.14). The liquids used had a higher surface tension than the solids so that $\sigma_{SV}$ was independent of the liquid used, i.e., $\sigma_{SV} = \sigma_S$. The values $\sigma_S$ measured at room temperature were then extrapolated to the melting temperature of the organics. The surface tension of the liquid organic, $\sigma_{LV}$, was measured (or a literature value was used) near the melting point and $\sigma_{SL}$ and $\sigma_{PL}$ were computed by Equation (3.14). $\sigma_{PS}$ was computed by assuming that Equation (3.14) was still valid if the third phase was another solid instead of a liquid (i.e., $\sigma_{LV}$ was replaced by $\sigma_{PV}$).

The resulting $\Delta\sigma_\infty$ were then computed. It was found that $\Delta\sigma_\infty$ is positive, for acetal and nylon particles, and that $\Delta\sigma_\infty$ is negative for polystyrene, teflon and silicone (silicone coated glass particles were used). Experimental work showed that the first two types of particles were pushed and the last three entrapped even at growth rates "well below 5 $\mu$m/s". This technique was therefore highly successful.

It should be noted, however, that the values of the crystal-liquid surface tension found by using Equation (3.14) are 0.59 mJ/m$^2$ for naphthalene and 0.64 mJ/m$^2$ for biphenyl. These values are two orders of magnitude lower than the experimental values reported by Jones (52), respectively 61 + 11 mJ/m$^2$ for naphthalene and 50 + 10 mJ/m$^2$ for diphenyl. Furthermore, the experimental values are in fair agreement with the prediction of Equation 3.12 since the $K$ values computed from these experimental data are respectively 0.7 to 1.0 for naphthalene and 0.6 to 0.9 for diphenyl. This
discrepancy between the surface free energy values measured experimentally and those computed by Neumann's method casts strong doubts on the validity of this approach for the prediction of solid-melt surface energy—either the extrapolation procedure used to compute the surface energy of the solid at its melting point is invalid or Equation (3.14) which was derived from data on polymeric solids is not valid for other materials. The values reported for the surface energies particle-solid organic, \( \sigma_{PS} \), are also very low (0.0 to 4.4 mJ/m\(^2\)), suggesting that Equation (3.14) may not be applicable to two solids.

Since Equation (3.14) was derived from measurements of melting angles on various polymeric materials, including teflon, it can be assumed that the values for the surface tension particle-vapor, \( \sigma_{PV} \), derived using Equation (3.14) are valid. The success of the model in predicting entrapment or pushing may be due to the fact that for all the polymeric materials used, \( \sigma_{SP} \) does not vary much and that the sign of \( \Delta \sigma_\infty \) is directly related to the magnitude of \( \sigma_{PV} \). A comparison of the values of \( \sigma_{PV} \) (Table 3-1) shows that the particle with large surface free energy \( \sigma_{PV} \) were pushed (acetal, nylon) whereas the particles with low surface free energy were entrapped.

Another method of estimating the surface free energy between two media (1) and (2) has been proposed by Good and Garifalco (see for example, Ref. 57). They introduced an interaction parameter \( \phi \) that can be computed, at least approximately, from ionization constants and dipolar forces, and

\[
\sigma_{12} = \sigma_1 + \sigma_2 - 2 \phi \sqrt{\sigma_1 \sigma_2} \tag{3.15}
\]
<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma_{PV}$ in mJ/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetal</td>
<td>45.7 - 46.6</td>
</tr>
<tr>
<td>nylon</td>
<td>44.3 - 45.8</td>
</tr>
<tr>
<td>polystyrene</td>
<td>31.7 - 32.5</td>
</tr>
<tr>
<td>siliconed glass</td>
<td>18.7 - 18.8</td>
</tr>
<tr>
<td>teflon</td>
<td>18.3 - 20.7</td>
</tr>
</tbody>
</table>

Table 3-1. Surface free energy of various particles, measured by Omenyi and Neumann (15-16)
Using a simplified quasi-lattice model, Good and Elbing (57) showed that

$$\phi = \frac{\varepsilon_{12}}{\sqrt{\varepsilon_{11}\varepsilon_{22}}} \quad (3.16)$$

where the $\varepsilon_{ij}$ are the molecular pair interaction energies. In the case of a solid and its own melt, to a good approximation $\varepsilon_{11} = \varepsilon_{12} = \varepsilon_{22}$ and $\phi = 1$. Using the values found by Neumann for naphthalene, $\sigma_{SV} = 26.4$ mJ/m$^2$ and $\sigma_{LV} = 32.6$, the solid melt surface energy computed with Equation (3.15) found to be very low: $\sigma_{SL} = 0.33$ mJ/m$^2$. This value is in good agreement with the value derived by Neumann. It should be noted, however, that surface entropy is ignored in this model. The models of Good cannot therefore be applied to the solid-melt interface without modifications, since the largest contribution to this interfacial free energy may be entropic (55).

Fowkes (58) also proposed a formula similar to Equation (3.15), but he expanded the surface energies in a series of terms corresponding to each type of molecular interaction: dispersion force contribution, hydrogen bond, metallic bond, etc. He argued that interactions between different kinds of molecules could only occur through interaction of forces common to both. For example, the surface tension of mercury is due to dispersion forces and to intermetallic interactions; at the interface mercury-hydrocarbon, only the dispersion forces could interact, the molecules of hydrocarbon being unaffected by the metallic bond and

$$\sigma_{\text{Hg-hydro.C}} = \sigma_{\text{Hg}} + \sigma_{\text{hydro.C}} - 2\sqrt{\sigma_{\text{Hg}}^{\text{d}} \sigma_{\text{hydro.C}}^{\text{d}}} \quad (3.17)$$

where the $\sigma^{\text{d}}$ are the dispersion force components of the surface tensions.
This approach is, however, complex in practice, as it necessitates for each system a series of surface tension measurements to determine the dispersion force component. This determination is made possible by the fact that for liquid saturated hydrocarbons, the intermolecular attraction is due almost entirely to London dispersion forces; and the dispersion component of the surface tension is obtained by measuring the surface tension of the interface material, hydrocarbon.

In conclusion, the thermodynamic approaches are theoretically interesting but the experimental difficulty of determining the various surface energies make its use impractical. Furthermore, unless the surface free energy of the thin liquid film is considered to be a function of its thickness, this approach will only allow predictions whether particles will be pushed or entrapped at infinitely small growth rates.

3.3. Molecular Forces

To study the molecular or van der Waal forces between solid, liquid and particle, two different approaches can be used. The first one, historically, is the microscopic approach, where the forces between two atoms or molecules are determined from molecular parameters (polarizability, oscillator strength) and the force between two macroscopic bodies is obtained by summing these elementary forces over all the pairs of atoms or molecules. The second or macroscopic approach treats the media as a continuum and the forces between macroscopic bodies are obtained by solving Maxwell's equations with the proper boundary conditions; the resulting forces are functions of the geometry and of the dielectric properties of the media. Both approaches have been reviewed and compared in several recent articles.
(42, 59-62), and only the most important features will be discussed here.

3.3.1. Microscopic Approach

In the microscopic approach, the forces between macroscopic bodies are computed by summing the intermolecular (or interatomic) forces over all the pairs of molecules (or atoms). In the rest of this chapter the word molecule will be systematically used with the understanding that one should read molecule or atom. The first step in computing the macroscopic forces is therefore to determine the long-distance forces between two molecules. Historically, these forces have been separated into three categories:

a. The orientation or Keesom forces due to dipole-dipole interaction. The energy of interaction, \( U \), between two dipoles of permanent dipole moment \( \mu_1 \) and \( \mu_2 \) is

\[
U = -\frac{2 \mu_1 \mu_2}{3kT \ d^6}
\]  

(3.18)

where \( k \) is Boltzmann's constant, \( T \) is the absolute temperature and \( d \) is the distance between the molecules.

b. The induction or Debye forces due to dipole-induced dipole interaction between a molecule with a permanent dipole \( \mu_1 \) and a non-polar molecule. Here again, the interaction energy varies as \( d^{-6} \) and is function of the polarizability, \( \alpha \), of the molecules:

\[
U = -\frac{\mu_1^2 \alpha_2}{d^6}
\]  

(3.19)

c. The dispersion or London forces due to induced dipole-induced dipole interaction between two non-polar molecules: even though the time average of the dipole moment of the molecules is zero, at any instant, there exists a finite dipole moment determined by the instantaneous position of the electrons. This dipole moment generates an electric field which
polarizes nearby non-polar molecules. Averaging these interactions over a finite period of time, one finds an interaction energy varying as \( d^{-6} \):

\[
U = -\frac{C_{12}}{d^6}
\]  
(3.20)

By treating the molecules as isotropic harmonic oscillators, of characteristic frequency \( \omega_i \) and polarizability \( \alpha_i \), London found that

\[
C_{12} = \frac{3\hbar}{2} \frac{\omega_1 \omega_2}{\omega_1 + \omega_2} \alpha_1 \alpha_2
\]  
(3.21)

where \( \hbar \) is Planck's constant divided by \( 2\pi \), and the constant \( C_{12} \) is generally referred to as the London constant. Many more sophisticated treatments have been used to derive \( C_{12} \) (for reviews, see Refs. 42, 60, 61, 62) by introducing multiple characteristic frequencies each with an effective number of electrons relaxing (oscillator strength). The role of a medium other than vacuum between the two molecules has also been investigated, the polarizabilities being replaced by the polarizabilities in this medium (excess polarizabilities).

When each molecule has only one characteristic frequency, \( \omega_j \), for absorption and emission of radiation, \( \omega_j \) is often identified with the frequency corresponding to the ionization potential, \( I_j : \omega_j = I_j/\hbar \). This result is not really justified theoretically but the London constants computed in this fashion are consistent with other measurements. In many cases, the simple London expression, (3.21), may be a sufficient approximation.

When the distance, \( d \), between the molecules becomes large (\( d > 50 - 100 \) nm), the interactions cannot be considered instantaneous and the time needed for the electrostatic field of the first atom to reach the second
and return may be comparable with the fluctuation period itself. Equation (3.20) must be replaced by an equation taking into account these "retardation" effects; the interaction energy is reduced and varies as \( d^{-7} \):

\[
U = -\frac{K_{12}}{d^7}
\]  

(3.22)

This is valid for \( d > \frac{\lambda}{2\pi} \), where \( \lambda \) is the characteristic absorption wavelengths of the molecules \( i \). The retarded London constant, \( K_{12} \) is equal to:

\[
K_{12} = \frac{23}{4\pi} \hbar c \alpha_1(0) \alpha_2(0)
\]  

(3.23)

where \( \alpha_i(0) \) are the static polarizabilities.

Dispersion forces are generally much larger than orientation or induction forces except for the case of strongly polar molecules. For example, the dispersion, orientation and induction forces are in the ratios 4:20:1 for water but for non-polar CO, the ratios in the same unit are 7:0.0003:0.006 (42).

In this study, rejection forces due to overlapping of electronic clouds will not be discussed as these forces only occur at very short distances of the order of interatomic distances.

The force between macroscopic bodies can then be computed by assuming the additivity of the pair-interactions between molecules. Such computations were done extensively in the 1930's. The resulting equations are written as the product of a geometrical term, which depends on the shape, size and disposition of the bodies, times a term which depends on the nature of the media considered,

\[
F = f(\text{dielectric properties}) \times g(\text{geometry})
\]  

(3.24)
The most frequently used expressions are due to Hamaker, and the term, $f$, in Equation (3.24) is referred to as the Hamaker constant, $A_{12}$. It is related to London's constant by the relation

$$A_{12} = \pi^2 N_1 N_2 C_{12} \quad (3.25)$$

where $N_i$ is the number of molecules per unit volume in material $i$. In the case of retarded forces, the force between macroscopic bodies can again be written in the form of Equation (3.24) and the retarded Hamaker constant, $B_{12}$, is related to the retarded London constant, $K_{12}$, by:

$$B_{12} = \pi N_1 N_2 K_{12} \quad (3.26)$$

As an example of the form taken by Equation (3.24), the force between a sphere (material 1), of radius $R$, and a half plane (material 2) is:

$$F = -A_{12} \cdot \frac{R}{6h_o^2} \quad \text{for small separations} \quad (3.27)$$

$$F = -B_{12} \cdot \frac{2\pi R}{3h_o^3} \quad \text{for large separations} \quad (3.28)$$

where $h_o$ is the distance sphere-half space measured along the axis of symmetry. For two half spaces, at a distance $h_o$ from one another the force per unit area is:

$$\Pi = -A_{12} \cdot \frac{1}{6\pi h_o^3} \quad \text{for small separations} \quad (3.29)$$

$$\Pi = -B_{12} \cdot \frac{1}{h_o^4} \quad \text{for large separations} \quad (3.30)$$

Results for other simple geometries are given in Table 7-1.

In these computations of the force between macroscopic bodies, only dispersion forces have been considered, since orientation or induction forces are not amenable to a simple pair-interaction additivity treatment.
Since the orientation and induction intermolecular forces have the same distance dependence \( (\text{in } 1/d^6) \) as the dispersion forces, neglecting them might lead to a large error. The electric field strength acting on an atom is, however, the vectorial sum of the separate field strength generated by each of the other atoms. The total interaction energy due to orientation or induction is not therefore equal to the sum of the separate interaction energies but will be much smaller and will decrease very rapidly with increasing distance \((63)\).

When the two interacting bodies 1 and 2 are separated by a medium 3, other than vacuum, the Hamaker constant \(A_{132}\) can be approximated by various formulae. Among these are:

\[
A_{132}^2 \approx A_{131} A_{232} \quad (3.31)
\]

The values of \(A_{132}\) computed in this way are too large but according to Israelachvili \((42)\) the error is often only a few percent or less.

\[
A_{132} \approx A_{12} + A_{33} - A_{13} - A_{23} \quad (3.32)
\]

Several modifications of Equation \((3.32)\) have also been proposed \(\text{see, e.g., Ref. 59}\). Combining Equations \((3.31)\) and \((3.32)\), it is possible to estimate the Hamaker constant \(A_{132}\) from single component Hamaker constants, \(A_{ii}\):\[
A_{132} \approx (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (3.33)
\]

When media 1 and 2 are identical, the London constant \(C_{11} [\text{Equation } (3.21)]\) is equal to \(C_{11} = \frac{3}{4} \pi \cdot \omega \cdot \alpha^2\) and is positive. The Hamaker constant \(A_{12} [\text{Equation } (3.25)]\) is also positive and the van der Waals force between two bodies of the same material is always attractive. Equation \((3.33)\) illustrates how the interaction force between bodies 1 and 2 can be repulsive. This occurs if \(A_{11} < A_{33} < A_{22}\) or \(A_{22} < A_{33} < A_{11}\). As will be shown
further in this chapter, these inequalities will be satisfied if the "static" dielectric constant of the liquid has a value intermediate between that of the solid and of the particle.

Another useful formula is:

$$A_{121} = A_{131} + A_{232} - 2A_{132} = (\sqrt{A_{131}} - \sqrt{A_{232}})^2$$

(3.34)

The negative sign must be used when $A_{132} > 0$, i.e., when bodies 1 and 2 attract one another, and the positive sign when $A_{132} < 0$. This equation gives a lower limit for $A_{121}$ in the former case and an upper limit in the latter case.

The case of multilayered bodies has been reviewed by Nir (62). The force between a multilayered sphere ($N$ layers) and a multilayered plane ($N'$ layers) separated by a medium, 0, is (Figure 3-1).

$$F = -\frac{1}{12} \sum_{i=1}^{N'} \sum_{j=1}^{N} A(i,j) \cdot \frac{R_j^3}{d_{ij}^2 (d_{ij} + R_j)^2}$$

(3.35)

if $d_{ij}$ is the distance between plane $i$ and sphere $j$ measured along the axis of symmetry and $R_j$ is the radius of the sphere limited by layer $j$.

$$A(i,j) = A_{ij} - A_i, j-1 - A_{i-1, j} + A_{i-1, j-1}$$

(3.36)

Two criticisms can be raised against this simple additive treatment of pair interactions which neglects the influence of neighboring atoms on the interaction of any pair of atoms. First, the atomic polarizability, determined for isolated atoms, will be modified by the overlapping of the electron clouds. Therefore this treatment will be acceptable for molecular crystals, and may be sufficient for ionic crystals; but it will certainly be wrong for metals. Second, multiple interaction occurs: when the inter-
FIGURE 3-1 MULTILAYERED SYSTEM
action between atoms 1 and 2 is studied, if a 3rd atom is present, the second atom will be affected not only by the field of atom 1 but also by the field created by atom 1 in atom 3. A further drawback of this treatment is that orientation forces are neglected.

The first problem has been solved by using a modified microscopic approach in which the polarizabilities and characteristic frequencies are not computed from first principles but are derived from macroscopic optical properties of the media through a Lorenz-Lorentz relationship; the problem of distance of the orbital is therefore implicitly taken into account. The second problem of multiple interactions has been treated by several authors. The derivations are exact but extremely complex and the results become comparable to those obtained by the macroscopic approach.

By using the macroscopic approach that will now be discussed, these two problems are avoided and the orientation interactions are taken into account. Furthermore, the equations giving the van der Waals forces can be treated with fewer approximation and therefore should give more exact values.

3.3.2. Macroscopic Approach

3.3.2.1. Molecular Forces

The macroscopic treatment of van der Waals forces introduced by Lifshitz in 1955 (64) takes into account both many-body and retardation effects. The media are treated as continua. Within all media, the electrons are in continuous motion, and this motion gives rise to a fluctuating electromagnetic field. The interaction of the media occurs via this fluctuating electromagnetic field. The interaction energy $U$ and force $F$ are
derived by solving Maxwell's equations for this fluctuating electromagnetic field (random field) with the proper boundary conditions. Lifshitz's initial derivation treated only the interaction between two half spaces separated by a vacuum. The results have been extended to the case of half-spaces 1 and 2 separated by a medium 3 (65). The equations have also been derived by other macroscopic approaches (66, 69), and also by modified microscopic treatments (70, 71). These new derivations have allowed the computation of the force between spheres (72, 73) and for multilayered systems.

The general expression of the molecular force per unit area, $II_m$, between two half spaces 1 and 2 separated by a layer of thickness $h$ of medium 3 is:

$$II_m(h) = \frac{kT}{\pi c^3} \int_{n=0}^{\infty} \xi_n^3 \left( \int_1^{\infty} \frac{dp}{\Delta_1 \Delta_2 \exp(q)-1} + \frac{1}{\Delta_1 \Delta_2 \exp(q)-1} \right)$$

where $\Delta_1 = \frac{S_1 - p}{S_1 + p}$, $\Delta_i = \frac{S_i \varepsilon_3 - p \varepsilon_i}{S_i \varepsilon_3 + p \varepsilon_i}$,

$$\varepsilon_i = \frac{\sqrt{\varepsilon_i} - 1 + p^2}{\varepsilon_3}$$

$$q = \frac{2p\xi_n h}{c}$$

$$\xi_n = \frac{2\pi nkT}{h}$$

$\varepsilon_j = \varepsilon_j(i\xi_n)$ = permittivity of medium $j$, taken along the imaginary axis; $c$ is the speed of light; $h$ is the distance between the two half-planes; and $p$ is a dummy variable.

The summation is carried out over integer values of $n$ and the prime on the summation sign means that the first term, ($n=0$) should be multiplied by
1/2. Since the media are treated as continua, Lifshitz's derivation is only valid if the distance between media, h, is larger than a few inter-atomic distances. A positive value of $\Pi_m$ corresponds to a repulsion between bodies 1 and 2. This expression is quite complex but a closer examination of Equation (3.37) shows that $\Pi_m$ is a function only of the dielectric properties, and this information is available from spectroscopic measurements; the force $\Pi_m$ can therefore be computed by numerical integration of Equation (3.37). The difficulty, however, is that the dielectric properties must be known over the whole range of frequencies (zero to infinity). The frequencies used in Equation (3.37) are given in Table 3-2 as a function of n for a temperature of 450°K. The first term (n=0) is often referred to as the temperature dependent term or microwave contribution. This name is not immediately clear since in Equation (3.37), each term is multiplied by a factor kT. However, if the first few terms of the summation over n are omitted, the summation over n can be replaced by an integration, with $dn = \frac{\Omega}{2\pi kT} \, d\xi$; and in this form Equation (3.37) becomes independent of temperature (except for the dependence of the dielectric constants on temperature). Contrary to the Hamaker equations, distances and dielectric properties are not separable and Equation (3.37) cannot be written in the simplified form of Equation (3.20).

To gain a better understanding of Equation (3.37), and to simplify the numerical computations several limiting cases have been considered.

a. **Short Distances** – For short distances, h, between the two half spaces, it has been shown that the first few terms of the sum are negligible and the summation can be replaced by an integration. After a few simplifications Dzyaloshinskii et al. (65) showed that:
<table>
<thead>
<tr>
<th>n</th>
<th>$\xi_n \times 10^{-14}$ rad/sec</th>
<th>Wavelength $\lambda_n$ nm</th>
<th>Spectroscopic region</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td></td>
<td>microwave</td>
</tr>
<tr>
<td>1</td>
<td>3.70</td>
<td>5090</td>
<td>infrared</td>
</tr>
<tr>
<td>2</td>
<td>7.41</td>
<td>2540</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>22.23</td>
<td>850</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>25.93</td>
<td>730</td>
<td>visible</td>
</tr>
<tr>
<td>12</td>
<td>44.46</td>
<td>424</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>48.16</td>
<td>391</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>190</td>
<td>704</td>
<td>26.8</td>
<td>X-ray</td>
</tr>
</tbody>
</table>

Table 3-2. Values of the frequency $\xi_n$ used in Equation 3.31 and the corresponding wavelength, $\lambda_n$, at $T = 450^\circ$K
\[ \Pi_m = -\frac{\kappa}{8\pi^2 h^3} \left( \int_0^\infty \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \cdot \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \, d\xi + \frac{1}{8} \int_0^\infty \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \cdot \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \, d\xi + \ldots \right) \] (3.38)

Since \( \left| \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right| < 1 \), the second term of Equation (3.38) is at most 1/8 of the first, the third term would be at most 1/27 of the first \ldots; in most cases, the expression can be limited to the first term. This Equation (3.38) has the form of a non retarded Hamaker equation, i.e., a product of a Hamaker constant and of a geometrical term; and if media 1 and 2 are identical, the Hamaker constant is equal to:

\[ A_{131} = \frac{3\kappa}{4\pi} \left( \int_0^\infty \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \, d\xi + \ldots \right) \] (3.39)

and

\[ \Pi_m (\hbar) = -A_{131} / 6\pi h^3 \] (3.40)

This equation however is symmetrical in 1 and 3; i.e., the force between two half plane of medium 1 separated by a layer of 3 is the same as the force between two half planes of 3 separated by a layer of 1. This symmetry, which does not exist in the initial Equation (3.37), has been criticized as physically unrealistic [the same criticism was made of the Hamaker Equations (3.32) or (3.33)]. Nir et al. (74), avoiding one simplification used in deriving Equation (3.36) showed that:

\[ \Pi_m = -\frac{\kappa}{8\pi^2 h^3} \left( \int_0^\infty \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \cdot \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \cdot \exp(-x) \cdot \left[ 1 + x + \frac{x^2}{2} \right] \, d\xi \right) \] (3.41)

with \( x = \frac{2\hbar \varepsilon \sqrt{\varepsilon_3}}{c} \).

The forces computed by this equation are very similar to those computed with Equation (3.38), but show the expected dissymmetry. Equation (3.38) can therefore be used in most cases to compute the interaction forces if the separation \( h \) is small. By small it is meant:
where \( \lambda_0 \) is the principal wavelength of the absorption peaks of the interacting bodies. If the bodies have their strongest absorption peaks in the near ultra-violet, \( \lambda_0 \) will be of the order of 200 nm and Equation (3.38) will be applicable for distances of about 10 nm or less.

Equation (3.39) has been used by Krupp and co-workers (59, 75), who were mainly interested in the problem of adhesion, to compute the Hamaker constant for many systems. They showed that at such short distances, the main contribution to the interaction energy is due to ultra-violet and far ultra-violet absorptions. One can therefore neglect microwave and infrared absorptions, except in the case of strongly polar materials (76, 77, 79).

b. **Large Distances**

By large distances, it is meant, \( h \gg \lambda_0 \) but less than 1 \( \mu \)m or so. (The range of distances is therefore small if \( \lambda_0 \) is of the order of 0.1 \( \mu \)m. Equation (3.37) can then be simplified to:

\[
\Pi_m = \frac{3\pi c}{16\pi^2 \sqrt{\varepsilon_{30}}} \cdot \frac{1}{h} \int \frac{1}{\hbar} \left( \Delta_{10} \Delta_{20} + \Delta_{10} \Delta_{20} \right) \frac{dp}{p^2} \tag{3.43}
\]

where in the expression for \( \Delta_{11} \) and \( \Delta_{11} \), the permitivities, \( \varepsilon_j (i\pi_n) \) are replaced by the "static" dielectric constants \( \varepsilon_j (0) \), noted \( \varepsilon_{j0} \). Equation (3.43) has the form of a retarded Hamaker equation with

\[
B_{12} = \frac{\pi^2 c}{240 \sqrt{\varepsilon_{30}}} \cdot \frac{\varepsilon_{10-\varepsilon_{30}}}{\varepsilon_{10+\varepsilon_{30}}} \cdot \frac{\varepsilon_{20-\varepsilon_{30}}}{\varepsilon_{10+\varepsilon_{30}}} \phi (\varepsilon_{10}, \varepsilon_{20}, \varepsilon_{30}) \tag{3.45}
\]

where \( \phi \) is a function varying between 0.35 and 1.
The previous derivation is not valid for metal-metal interactions. For a liquid metal film on a metal, Equation $(3.43)$ must be replaced by:

$$
\Pi_m = -\frac{3k_0^2}{32\pi^2 \sigma_3^2} \cdot \frac{1}{h^5} \cdot \frac{\sigma_1 - \sigma_3}{\sigma_1 + \sigma_3}
$$

(3.46)

where $\sigma_j$ is the electric conductivity of metal $j$.

The main problem with Equation $(3.43)$ is to decide what is denoted by the "static" dielectric constant. Lifshitz (65) suggests that for bodies which absorb not only in the ultra violet but also in the infrared (e.g., quartz or water), values of $\varepsilon_j = n_j^2$ (i.e., the square of the index of refraction in the visible) should be used instead of the true static dielectric constant $\varepsilon_{jo}$, since $\varepsilon_{jo}$ contains contributions from dipole orientation. The difference in some cases is important. For water, $\varepsilon_o = 87.0$ but $n^2 = 1.78$. Churaev (78) compared experimental values of the interaction forces with values computed using either $\varepsilon_o$ or $n^2$. The scatter in the experimental data is very large and makes any judgement difficult. He concludes, however, that the use of $n^2$ gives a better fit than the use of $\varepsilon$.

Equation $(3.45)$ illustrates that the force between bodies can be repulsive or attractive, depending on the relative value of $\varepsilon_{10}$, $\varepsilon_{20}$ and $\varepsilon_{30}$. The force will be repulsive if $\varepsilon_{10} < \varepsilon_{30} < \varepsilon_{20}$ or $\varepsilon_{10} < \varepsilon_{30} < \varepsilon_{20}$. In general, at the melting point, a solid is denser than its melt and the index of refraction of the solid, $n_1$, will be larger than that of the melt, $n_3$, i.e. $\varepsilon_{10} > \varepsilon_{30}$. This relation shows, therefore, that, first a solid is wetted by its melt and that second, a particle will be repelled at large distance if its index of refraction is lower than that of the melt.
c. **Intermediate Distances** - At intermediate distances, the forces are neither non-retarder nor retarded and Equation (3.37) cannot be simplified to take the form of a Hamaker equation. Churaev (80) showed, however, that if the three media have similar dielectric properties, and for \( h > 10 \text{ nm} \), Equation (3.37) can be simplified to take the form proposed by Nir (74) for short distances [Equation (3.41)].

\[ \Pi_{m,0} = \frac{-kT}{8\pi h^3} \sum_{n=1}^{\infty} \frac{\varepsilon_{10} - \varepsilon_{30}}{\varepsilon_{10} + \varepsilon_{30}} \frac{\varepsilon_{20} - \varepsilon_{30}}{\varepsilon_{20} + \varepsilon_{30}}^n \]

Contrary to the initial assumption (65) that this term is only important for very large separations, Parsegian and Ninham (77) showed that, in the case of highly polar materials, it could not be neglected even at short distances. This result was confirmed by Nir (62) who showed that for the system water-benzene-water, \( \Pi_{m,0} \) (the orientation and induction contribution) accounts for more than 60% of the total interaction force when \( h = 5 \text{ nm} \). Such a large contribution will be encountered if the materials considered have very similar properties at the u.v. frequencies so that the u.v. contributions tend to cancel one another. In general, however, this orientation term is only a small fraction of the total interaction force at short distances and becomes important only at large distances.
e. **Discussion of the Approximate Formulae** - The distinction between retarded and non-retarded forces is often not clear. First, there is a region of transition between retarded and non-retarded forces. In this region, the use of a Hamaker constant notation can be misleading, since a different value of $A_{132}$ will be obtained depending on whether the energy equation ($U = \frac{-A_F}{12\pi h^2}$) or the force equation ($F = \frac{\partial U}{\partial h}$) is used (recall that $A_u$ is a function of $h$). Donners et al. (81) have shown that for hydrocarbon-water films, the forces are neither non-retarded nor retarded for thicknesses varying between 5 and 150 nm. Second, the i.r. peaks may give a non-retarded contribution ($h << \lambda_{i.r.}$) whereas the u.v. peaks will give a retarded contribution ($h >> \lambda_{u.v.}$). This fact explains why as the separation $h$, increases, the longer wavelength contribution becomes more and more important. In fact, for water and for distances larger than 50 nm, the i.r. and u.v. contributions may be in some cases negligible and the magnitude of the interaction is essentially determined by the "static" properties. This result has been discussed at length by Ninham and Parsegian (76) and Smith et al. (73).

f. **Layered Systems** - The effect of an adsorbed or oxidized layer of thickness $t$ at the surface of the materials will dominate the interaction between two solids if the separation, $h$, between the solids is smaller than the thickness of the layers. If, on the contrary, $h > t$, the interaction will be mainly determined by the bulk properties of the materials. The equations for multilayered systems have been derived by Langbein (70, 72) and Parsegian and Ninham (87). With the notation,

$$
\delta_{jk} = \frac{\varepsilon_j(i\xi) - \varepsilon_k(i\xi)}{\varepsilon_j(i\xi) + \varepsilon_k(i\xi)} \quad (3.49)
$$
the force between two bodies 1' and 1 coated by a layer 2 and 2' of
thickness t and t' and separated by a layer of material 3 of thickness h,
is
\[
\Pi_m = -\frac{\hbar}{8\pi^2} \int_0^\infty \left[ \frac{\delta_{23} \delta_{2'3'}}{h^3} + \frac{\delta_{2'3} \delta_{12}}{(h+t)^3} + \frac{\delta_{23} \delta_{1'2'}}{(h+t')^3} + \frac{\delta_{12} \delta_{1'2'}}{(h+t+t')^3} \right] d\xi 
\] (3.50)

3.3.2.2. Determination of \( \varepsilon(i\xi) \)

a. Exact Formulae – To compute the van der Waals forces with
Equation (3.37) one must know the dielectric constant, estimated along the
imaginary axis, \( \varepsilon(i\xi) \), for each medium. This quantity cannot be measured
directly but is related to the imaginary part or loss factor \( \varepsilon'' \), of
the complex dielectric constant by a relation derived from the Kramers-
Kronig relations between real and imaginary parts of \( \varepsilon \):

\[
\text{if } \varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \\
\varepsilon(i\xi) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \varepsilon''(\omega) d\omega}{\omega^2 + \xi^2} 
\] (3.51) (3.52)

This relation is exact, in a mathematical sense, if the complex function
\( \varepsilon \) is regular, but is always approximate, in a physical sense since the
integration must be performed between zero and infinity. For more details
on the Kramers-Kronig equation, see for example Ref. 82. \( \varepsilon'(\omega) \) and
\( \varepsilon''(\omega) \) can be measured by dielectric methods from static values up to
frequencies of about \( 10^{11} \) rad/sec, and for larger frequencies \( \varepsilon''(\omega) \) must
be derived from optical measurements. The complex index of refraction,
\( n^* \) and the complex dielectric constant \( \varepsilon \) are related by the relation

\[
\varepsilon = n^{*2} 
\] (3.53)

if

\[
n^* = n + il 
\]
where $n$ is the refractive index and $k$ the absorption index.

Therefore,

$$
\varepsilon''(\omega) = 2n(\omega) \cdot k(\omega)
$$

(3.55)

In general, only the absorption coefficient (or the reflectivity) is measured and it is related to the index of refraction by a Kramers-Kronig relation:

$$
n(\omega_0) = 1 + \frac{2}{\pi} \text{P} \int_0^\infty \frac{\omega k(\omega)}{\omega^2 - \omega_0^2} d\omega
$$

(3.56)

where $\text{P}$ denotes a principal value in the Cauchy sense (to avoid the point of indetermination $\omega=\omega_0$). The reflectivity is also related to the index of refraction by a similar relation.

Hence a knowledge of the absorption coefficient or the reflectivity of the various materials over a wide range of frequency is sufficient to compute $n(\omega)$, [Equation (3.56)], $\varepsilon''(\omega)$, [Equation (3.55)], $\varepsilon'(i\xi)$, [Equation (3.52)] and finally the van der Waals forces [Equation (3.37)].

This succession of operations is fairly long and cumbersome, but three considerations help check the validity of the successive computations:

- $n$ and $k$ have been in some cases measured simultaneously or, $n$ can be measured, at least in the optical range. The range over which Equation (3.54) must be used is therefore reduced.

- $n$ must satisfy the relation:

$$
\int_0^\infty [n(\omega)-1] d\omega = 0
$$

(3.57)

- $\varepsilon''$ must satisfy the relation:

$$
\int_0^\infty \omega \varepsilon''(\omega) d\omega = \frac{\pi}{2} \omega^2 p
$$

(3.58)
where \( \omega_p \) is the plasma frequency as defined by Equation (3.61). The usefulness of Equations (3.57) and (3.58) in checking the computed values of \( n \) and \( \varepsilon^" \) is, however, limited since the integration must be carried between zero and infinity.

The quantities entering in Equation (3.52) have been determined for several materials (62, 73). A very interesting new source of data is from synchrotron measurements (85, 86) where data can be gathered from the far infra-red to the X-ray region. The published data are, however, limited for the moment to only a few materials.

b. **Approximate Formulae** - Because of the lack of extensive knowledge of the dielectric properties of most materials and of the difficulty of such determinations, several approximate formulae have been suggested. First, from dispersion theory, the dielectric constant \( \varepsilon(\omega) \) can be represented by a sum of relaxation peaks:

\[
\varepsilon(\omega) = \sum_{j=1}^{R} C_j \frac{1}{1 - i \frac{\omega}{\omega_j}} + \sum_{k=1}^{V} C_k \frac{\omega - \omega_k}{1 - (\frac{\omega}{\omega_k})^2 + i \gamma_k (\frac{\omega}{\omega_k})} + 1
\]  

(3.59)

The first sum corresponds to simple Debye rotational relaxations and the second sum represents Lorentz-harmonic oscillation dispersion. The constants \( C_j \) and \( C_k \) and the characteristic frequencies \( \omega_j \) and \( \omega_k \) can be obtained from tables of dielectric data. The \( \gamma_k \) are damping coefficients.

For very high frequencies, in the far ultra-violet and soft X-ray region, \( \varepsilon \) can be represented by the plasma regime equation:

\[
\varepsilon(\omega) = 1 - \left( \frac{\omega_p}{\omega} \right)^2
\]  

(3.60)

Here \( \omega_p \) is the plasma frequency:
\[ \omega_p^2 = \frac{4\pi N e^2}{m} \]  

(3.61)

where \( N \) is the electronic density and \( m \) and \( e \) are the effective mass and charge of the electron. Ninham and Parsegian (83) considered that the various relaxation phenomena could be lumped into three peaks: a Debye peak at microwave frequencies, a vibrational peak in the i.r. and an electronic absorption peak in the u.v. Furthermore, they considered that the damping coefficients, equal to the widths of the absorption peaks, are negligible on the imaginary axis (this is not the case if \( \omega \) is real since \( \varepsilon(\omega) \) would then go to infinity at the characteristic frequencies).

Equation (3.59) simplifies to:

\[ \varepsilon(\imath \xi) = \frac{C_{\text{rot}}}{1 + \frac{\omega}{\omega_{\text{rot}}}} + \frac{C_{\text{vib}}}{1 + \left(\frac{\omega}{\omega_{\text{vib}}}\right)^2} + \frac{C_{\text{el}}}{1 + \left(\frac{\omega}{\omega_{\text{el}}}\right)^2} + 1 \]  

(3.62)

For non-polar materials, the first term is zero. If either the atoms are very weakly bound (e.g., liquid helium) or if the dipole moments are very weak (e.g., diamond and saturated hydrocarbons), the second term can often be neglected. To a good approximation, the frequency corresponding to the first ionization potential can be used for \( \omega_{\text{el}} \).

To bridge the gap between Equation (3.62) or (3.59), valid for frequencies up to the first ionization potential (\( \sim 10^{16} \) rad/sec) and the plasma equation [Equation (3.60)] in the X-ray region (\( \omega > 10^{17} \) rad/sec), Ninham and Parsegian used a logarithmic extrapolation formula (i.e., \( \varepsilon \) varies linearly with \( \log \omega \)). This approximation is partly justified by the fact that, on the imaginary axis, \( \varepsilon \) is a monotonic decreasing function of frequency. Since all the dielectric susceptibilities approach the limiting form [Equation (3.60)] as \( \omega \to \infty \) and since in the Lifshitz equation [Equation (3.33)]
the integrand is a function of the differences of the dielectric constants only; they argued that if the media do not have greatly different densities, the far u.v. and X-ray contribution will be small and the computed interactive force will be fairly insensitive to the extrapolation technique used. This was checked for the case of water: changing the interpolation range from \( \log \omega = 16.2-16.9 \) to \( 16.5-17.1 \) decreased the van der Waals force by less than 20%. For the case of very short interaction distances, Donners et al (81) have shown that the interpolation procedure used will be critical; and they recommend that data computed in this fashion be used with caution for \( h<10 \) nm.

In subsequent work (73), it was shown that Equation (3.62) may give erroneous results in the case of three media with different densities, and that Equation (3.59) should be used instead with as many peaks as necessary. This latter work (73) confirmed, however, that the omission of band width has very little effect.

A similar technique has been used by Nir (62, 84) to compute the dielectric constants.

For many materials, the dielectric constant can be estimated from a limited number of experimental data since it follows, over a broad range of frequencies, the simple empirical relation (60):

\[
\frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+1} = a \exp(-b\omega) \tag{3.63}
\]

where \( a \) and \( b \) are empirical constants and materials of the same type often have the same coefficient \( b \).

For metals, at low frequency, the dielectric constant goes to infinity
and the previous formulae are not applicable; instead the dielectric constant is approximately equal to (see for example, ref. 84):

\[
\varepsilon'(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + g_1^2}; \quad \omega \varepsilon''(\omega) = \frac{g_1 \omega_p^2}{\omega^2 + g_1^2}
\]

(3.65)

where \(\omega_p\) is the plasma frequency with \(N_i\) equal to the effective number of electrons per unit volume and \(1/g_1\) is the relaxation time of the changes.

c. **Range of Frequencies where an Accurate Knowledge of \(\varepsilon(i\omega)\) is Required**

Some controversy exists in the literature as to which data (microwave, i.r., u.v.) are more important. The general opinion (59) is that only u.v. and far u.v. data are necessary; but Ninham and Parnebian (76) have shown that microwave and i.r. data may have a dominant role in some cases. The answers seems to depend on the systems: (1) at short distances and for interaction across a vacuum, the u.v. peaks are the most important; (2) at short distances but when the third medium is not a vacuum, there is no general conclusion; (3) at larger distances, the u.v. contributions becomes retarded and i.r. and microwave contributions become dominant until for very large distances (>500 nm) the forces are only determined by static dielectric properties.

3.3.3. **Comparison of Microscopic and Macroscopic Approaches**

Several reports on the comparison of macroscopic and microscopic approaches have been published (60, 62, 73). The concensus is that in many cases, if modified microscopic formulae are used and if the permittivities of the materials are not too different, then the forces between bodies computed by the microscopic and macroscopic approaches do not differ by more than 10 to 15% when the separation between the bodies is small.
In other cases, however, for long distances or if the materials are very different, the error introduced in using the microscopic approach may be large. The less sophisticated addition formulae in the microscopic approach [Equations (3.31) to (3.34)] can be totally misleading (88) since even the sign of the predicted force may be wrong.

In conclusion, the macroscopic approach should be preferentially used. In the case of solid, liquid and a particle, it is not clear which region of the spectrum is most important and only further computations can provide insight.
CHAPTER 4

LITERATURE REVIEW - THEORETICAL TREATMENTS

The various theoretical treatments of the problem of particle rejection and of the prediction of critical velocities will be reviewed in this chapter.

The first theoretical study of the subject is that of Khaimov-Mal'kov (1). He studied crystallization pressure, i.e. the maximum pressure that can be exerted on a crystal growing from a solution and resting on a solid, without stopping crystal growth (Figure 2-7). Through a thermodynamic argument, he showed that crystallization pressure increases with the supercooling. However, since his argument is based on the assumption that the total volume (liquid plus crystal) is constant, his other results may not be applicable to the more frequent case, in practice, of isobaric systems.

The specific problem of particle pushing has been treated in several studies. The nature of the forces tending to favor entrapment of the particles by the growing crystal has been recognized in most of the theoretical studies. They are: first, the gravitational forces in a vertical geometry apparatus or the frictional forces in an horizontal geometry; second, the drag force (due to the flow of liquid around the particle); and third, the force (pressure or chemical potential gradient) necessary to diffuse fresh liquid behind the particle in the region where the liquid film is very thin. This last force may or may not be included in the drag force.
The major differences between the various studies are: first, the assumptions about the nature of the repulsive force between front and particle; and second, the approximations used. In all these studies, the thermal properties of matrix and particles were assumed to be identical, to simplify the mathematical treatment of the problem (see Chapter 9 for a discussion of this approximation).

4.1. Hoekstra and Miller

Hoekstra and Miller (8) studied the migration of solid particles in an ice matrix placed in a temperature gradient. They observed that the particles (glass beads) migrated toward higher temperatures and they developed a theory to explain the phenomenon. They generalized their results to the pushing of particles by an ice-front, considering that the driving force for migration (or rejection) was the existence of a temperature gradient, i.e. the change with temperature of the thickness of the transition layer existing on the ice surface associated in turn with the temperature dependence of the surface energy. They obtained the following relation between the growth rate, \( V \), and the particle-front distance, along the center-line, \( h_0 \):

\[
V = \frac{2D \Delta S_m}{kT \rho_s \Delta V} \cdot \frac{h_0}{R} C \tag{4.1}
\]

where

\( D \) = diffusion coefficient in the liquid \( = 10^{-9} \text{ m}^2/\text{s} \) for water

\( \Delta S_m \) = molecular entropy of fusion \( = 3.67 \times 10^{-23} \text{ J/}^\circ\text{K} \) for water

\( k \) = Boltzmann's constant \( = 1.38 \times 10^{-23} \text{ J/}^\circ\text{K} \)

\( \Delta V \) = difference between specific volumes of solid and liquid

\( = 9.07 \times 10^{-5} \text{ m}^3/\text{kg} \) for ice and water
\( \rho_s = \text{density of solid} = 0.9167 \times 10^3 \text{ kg/m}^3 \) for ice

\( R = \text{radius of the particle} \)

\( G = dT/dz = \text{temperature gradient at the solidification front} \)

For a temperature gradient of 20 °C/cm and a particle of radius 100 \( \mu \text{m} \) in the water-ice system, Equation (4.1) becomes

\[ V = 0.0047 \ h_o \]

They observed that the critical velocity, \( V_c \), for particles of radius 100 \( \mu \text{m} \) was 0.065 \( \mu \text{m/s} \) (Figure 2-4). The distance \( h_{oc} \) should therefore have been approximately 14 \( \mu \text{m} \) and should have been easily observable; but this was not the case. Conversely, since the liquid film between particle and front has never been observed, a more realistic value for \( h_o \) would be: \( h_o < 0.5 \mu \text{m} \); and the computed corresponding growth rate is then less than \( 2.3 \times 10^{-3} \mu \text{m/s} \)--i.e. at least an order of magnitude too low. Further, if Equation (4.1) were applied to materials with a low entropy of fusion, the computed steady state pushing rate would be even lower.

This quick numerical computation shows that the existence of a transition layer at the surface of ice, the thickness of which decreases with decreasing temperature cannot account for the observed rates of particle rejection.

4.2. Uhlmann, Chalmers and Jackson

A thermodynamic argument involving the different surface energies, particle-liquid-solid, had been used in the 1940's to explain the stability of liquid films (50). It was extended and applied to the present problem (see Chapter 3) by Uhlmann, Chalmers and Jackson (12,13)
(referred subsequently as U.C.J.). As discussed previously, U.C.J. considered that the surface free energy of the thin liquid film existing between particle and solid varied with the thickness of the film [Equations (3.3) and (3.5)]:

\[ \Delta \sigma = \Delta \sigma_\infty \times \left( \frac{h}{h_0} \right)^n \]

In a first approximation, they determined the shape of the interface by solving the diffusion equation in the region where particle and solid are very close to one another. The chemical potential (driving force) for diffusion was assumed to be due only to the variation in surface energy with distance [Equation (3.4)] and they first neglected the contribution of curvature (Gibbs-Thompson effect) and of temperature gradient. The resulting expression for the shape of the front was:

\[ h(r) = h_0 \left( \frac{r^2}{r_0^2} \right)^{1/n} \]  

(4.2)

where \( r \) is the radial distance; \( h(r) \) is the thickness of the film; \( h_0 = h(0) \); and \( r_0 \) is the radius of the zone beyond which the interaction particle-solid can be assumed to be negligible = radius of the zone of strong interaction; \( n \) is a constant equal to 2 or 3 (see Chapter 3).

The critical velocity was then obtained by writing the equilibrium condition between solid and liquid at the interface introducing the effect of curvature. Since the shape of the front had been already determined, to avoid over-defining the problem (i.e. having more equations that unknowns), the equilibrium condition was only written for the point on the axis of symmetry (point A on Figure 4-1). Furthermore, the difference in temperature between points A and B was neglected (i.e. the
FIGURE 4-1 GEOMETRY OF THE PARTICLE FRONT SYSTEM
front was assumed to be only very slightly curved). This equilibrium
equation can be written: \( V = f(h_0, R, \Delta \sigma_\infty) \); and a closer examination of
this expression shows that for a given system (i.e. constant \( R \) and \( \Delta \sigma_\infty \)),
the velocity, \( V \), goes through a maximum, \( V_c \), the critical velocity, for
a distance \( h_0 = h_{oc} \).

The existence of such a critical velocity can be physically explained
since the equilibrium equation contains only two terms: the variations
of chemical potential with the curvature of the front and with the
distance \( h_0 \). At low growth rate, the distance \( h_0 \) is large and the front
is practically flat. As the growth rate increases, the front curves
around the particle. To compensate for this increase in curvature, the
distance \( h_0 \) decreases, increasing the rejection term. At the critical
velocity, \( V_c \), the front becomes unstable: a further increase in
curvature cannot be compensated by a decrease in \( h_0 \), and entrapment occurs.

The expression for the critical velocity is:

\[
V_c = \frac{(n+1) K a_0 D}{kT} \cdot \frac{L \Omega}{R^2} \tag{4.3}
\]

where \( K \) is a constant defined by Equation (3.12). \( K = 1/4 \) to 1 (U.C.J.
used \( K = 1/2 \)); \( \Omega \), the molecular volume \( = \text{Molecular weight}/(N_o \times \rho) \)
density) if \( N_o \) is Avogadro's number; \( D \) is the diffusion coefficient;
\( L \) is the latent heat of fusion per unit volume; and \( a_0 \), the molecular
diameter \( = \Omega^{1/3} \).

Using the Stokes-Einstein equation,

\[
D = \frac{kT}{3\pi \eta a_0} \tag{4.4}
\]

where \( \eta \) is the viscosity of the liquid in the thin film, Equations (4.3)
becomes:

\[ V_c = \frac{(n+1)K}{3\pi} \cdot \frac{L\Omega}{nR^2} \]  \hspace{1cm} (4.5)

Surprisingly, the critical velocity is independent of the driving force, \( \Delta \sigma_\infty \)-- i.e., in first approximation, geometrically identical particles should have the same critical velocity in a given matrix. This maximum velocity occurs for a minimum distance particle-front, \( h_{oc} \) equal to:

\[ h_{oc} = h_\circ \left( \frac{R}{n+1} \cdot \frac{2\Delta \sigma_\infty R}{L a_\circ h_\circ} \right) \]  \hspace{1cm} (4.6)

where \( h_\circ \) = minimum separation between solid and particle = \( a_\circ \). The minimum distance, \( h_{oc} \), increases with increasing particle size and for \( n=2 \),

\[ h_{oc} \propto R^{1/3} \]  \hspace{1cm} (4.7)

At the critical velocity, the radius, \( r_{oc} \), of the zone of close interaction between particle and solid is:

\[ r_{oc} = \frac{2}{\sqrt{n}} \left[ \frac{n}{n+1} \cdot \frac{2\Delta \sigma_\infty R^{n+2}}{L a_\circ h_\circ^2} \right] ^{1/(2(n+1))} = 2 \left( \frac{R h_{oc}}{n} \right) \]  \hspace{1cm} (4.8)

The expressions for \( h_{oc} \) and \( r_{oc} \) are slightly different from what would be found by using directly U.C.J.'s derivation since in the expression for the chemical potential of the thin film (Equation 4 in Ref. 13) a factor \( n/n+1 \) was omitted. [From Equation (3.5), the surface energy of the thin liquid film is:

\[ \sigma = (\sigma_{SL} + \sigma_{LP}) + \Delta \sigma_\infty \left( \frac{h}{h_\circ} \right)^n \]  \hspace{1cm} (4.9)

The area, \( A_M \), per mole in the liquid film is equal to \( \Omega/h \) and the gradient in chemical potential in the film is

\[ d\mu = -A_M d\sigma \]  \hspace{1cm} (4.10)
Therefore
\[ \frac{d\mu}{dh} = \frac{\Omega}{h} \cdot n \Delta \sigma_\infty \frac{h^n}{h^{n+1}} \]  
(4.11)

and the chemical potential in the thin film is

\[ \mu = -\left(\frac{n}{n+1}\right) \frac{\Omega \Delta \sigma_\infty h^n}{h^{n+1}} \]  
(4.12)

The omission of this factor \( n/(n+1) \) does not change however in any way U.C.J.'s results since it is simply equivalent to a change in \( \Delta \sigma_\infty \). This is pointed out here so that the formalism used by U.C.J. and the Hamaker constant formalism used subsequently by Chernov et al. (31) be exactly equivalent.

In a second approximation, the drag force due to fluid flow around the particle was considered. U.C.J. showed that the drag force on a particle moving at a velocity, \( V \), in a liquid is much larger than that predicted by Stoke's law, if the particle is at a short distance, \( h_s \), from a flat liquid sink (the solidification front). The expression for the drag force in this case was derived by Carrier (12):

\[ F_D = 6\pi \eta V \frac{R^2}{h_s} \]  
(4.13)

For further discussion of the subject, see Chapter 7. The corresponding free energy was introduced as a correction factor in the equation of equilibrium between solid and melt, at the interface. U.C.J. showed that the drag force was only important in the case of large particles. The previous derivation should therefore be valid for small particles.

The case of rough particles, with irregularities of radius \( R_i \), was also introduced. This refinement is extremely important since very few particles are smooth. The resulting critical velocity is slightly more complex; using the Stokes-Einstein relation [Equation (4.4)] it can be
\[ V_c = \frac{\frac{K_a L}{3nR} \cdot \frac{h_o h_{(R-H)}}{R_1^2}}{\left(1 + \frac{2n(n+1)R_o}{\pi a_o} \cdot \frac{1}{h_s h_{o(R-H)}} \right)^{1/2} - 1} \]  

(4.14)

where: \( H \) is the distance in the z direction between the center of the particle and the undisturbed front; and \( (R-H) \) is the depth of the indentation made by the particle in the solid (see Figure 4-2).

The distance, \( h_s \), used in the computation of the drag force is not clearly defined since on one hand the particle is rough and \( h_s \) might be slightly larger than \( h_o \), but on the other hand the front is curved and therefore the real drag force should be larger than that computed by Equation (4.13)—i.e., the distance \( h_s \) used should be slightly smaller than \( h_o \).

The critical velocity, \( V_c \), is now a function of the driving force for rejection, \( \Delta g_\infty \), through \( h_{oc} \)—i.e., particles geometrically identical will have different critical velocity depending on their nature. Making reasonable estimates of \( h_s \) and \( R_1 \), U.C.J. computed critical velocities of the same order of magnitude as the measured ones. U.C.J.'s results are summarized in Table 4-5.

The following comments can be made of U.C.J.'s treatment:

a. To be able to solve the problem they treated it by a method of successive approximations, introducing in succession the effect of diffusion, curvature and drag force.

b. They neglected the temperature gradient in the matrix.

c. Since the drag force was computed as the force necessary to drive liquid behind the particle, to avoid redundancy between diffusion and
FIGURE 4.2 (a) GEOMETRY IN THE CASE OF A ROUGH SURFACE
(b) MAGNIFIED VIEW OF THE REGION OF CLOSE CONTACT
fluid flow, the expression for the drag force should be modified (or the
distance $h_s$ should be skillfully chosen).

d. The final expression [Equation (4.14)] is a function of several
interrelated unknown parameters: $h_s$, $h_o$ and (R-H).

In spite of these remarks, U.C.J.'s work is most useful since it was
the first one to present a derivation of the critical velocity and to
predict values in agreement with experiments. The assumptions made are
acceptable if the front remains practically flat while particles are
pushed. As will be shown later, this is the case either for small
particles or for crystals with high entropy of fusion growing in a prismatic
fashion (the case to which the analyses was originally applied).

4.3. **Bolling and Cisse**

Bolling and Cisse modified Bolling's initial treatment of the
subject (90) after the publication of U.C.J.'s work. Their present
treatment (9) contains therefore many references to U.C.J.'s work and
cannot be read without a detailed knowledge of it.

a. Their first contribution was to compute more accurately the
shape of the interface behind a particle. Instead of using a chemical
potential argument, they used an equivalent argument based on the tem-
perature of the interface, $T_i(r)$. It was computed by taking into account
the kinetic undercooling and the shift in melting point due to the
curvature of the front and to the pressure exerted on the solid. The
shape of the front was then obtained by matching the temperature $T_i(r)$
with the temperatures in the matrix, assumed to vary linearly with
distance. After simplifications and integration, the shape of the front
was obtained as a sum of Bessel functions, with one adjustable parameter,
the radius of the zone of strong interaction. The Bessel functions were expressed as function of the dimensionless parameter \( x = r \sqrt{\frac{\text{GAS}}{\sigma_{\text{SL}}}} \), where \( \sigma_{\text{SL}} \) is the free energy of the solid-liquid interface and \( \text{G} \) is the temperature gradient \( dT/dz \). Since the entropy of fusion \( \Delta S \) and the surface energy \( \sigma_{\text{SL}} \) are related by Equation (3.12), the parameter \( x \) is only a function of \( \sqrt{G} \). Their equation shows that the front becomes flatter if the temperature gradient \( G \) decreases.

In this derivation, however, they considered that the drag force, \( F_D \), was uniformly supported by the solid over a region of radius \( r_o \) (region where particle and solid are very close to one another). Each point of the solid in this region was therefore assumed to withstand a pressure

\[
 p_s = \frac{F_D}{\pi r_o^2} 
\]

(4.15)

This is not the case since the rejection force—i.e., the force acting on the solid—varies with the separation solid-particle [Equation (3.5)].

The expression for the shape of the front close to the particle was not used in subsequent computations; instead, the front was assumed to be spherical with radius of curvature \( R/\alpha \).

b. B.C. derived an expression for the drag force in the case of a curved solidification front (radius of curvature \( R/\alpha \)); and they showed that if the front is only slightly curved, the drag force is obtained by multiplying the drag force for a flat front [Equation (4.13)] by a factor \( 1/(1-\alpha)^2 \). This derivation is discussed in more detail in Chapter 7.

c. B.C. also considered in some detail the problem of transport of liquid in the region of strong interaction \( r < r_o \) since fresh liquid
can either flow or diffuse in this region; and they tried to estimate the
magnitude of the contribution of this region to the total drag force. In
their treatment of the diffusion case, instead of considering that a
gradient in chemical potential must exist to drive the diffusion process,
they assumed a random walk model and computed the value of $r_0$ in this case.
In subsequent computations, they used this value as an upper bound for
$r_0$ where, in fact, it is a lower bound. They concluded that the resulting
drag force is smaller than that computed using an hydrostatic approach.
This result should not be surprising since in the random walk process, no
driving force, i.e., no pressure gradient is assumed to exist.

d. The nature of the rejection force used in B.C.'s derivation was
not discussed; it is not clear if they accepted U.C.J.'s idea that the
variation in surface free energy of the thin liquid film is the driving
force or if they considered that it was the increase in free energy due
to curvature.

As in U.C.J.'s derivation, the critical velocity was obtained by
writing the equilibrium condition between solid and melt at the point of
the front on the axis of symmetry. They also used the assumption that the
temperature gradient was negligible. The equilibrium equation expresses
simply that the undercooling due to curvature is compensated by the under-
cooling due to pressure. As discussed before, for the pressure term they
used an average value [Equation (4.15)]. Since, in fact, a pressure
gradient exists from the periphery to the center of the liquid film,
the pressure at the axis of symmetry was underestimated. This error was
partially compensated by underestimating the size of the zone of strong
interaction, i.e. overestimating the average pressure. The equilibrium
condition can be written: \( V = f(h_o, r_o, \alpha) \) for a given particle and matrix. Since \( V \) is a function of 3 interrelated variables, it cannot be differentiated readily to find whether it goes through a maximum, \( V_c \). To eliminate two of the three variables, the radius \( r_o \) was assumed to have the value computed in the random walk model; and the distance, \( h_o \), and the curvature term, were assumed to be related by:

\[
h_o = a_o (\beta - \ln \alpha) \quad (4.16)
\]

where \( \beta \) is "some characteristic only of the fluid for inert particles."

This Equation (4.16) expresses that the distance \( h_o \) is an increasing function of the radius of curvature, and that for a flat interface (\( \alpha = 0 \)) the distance \( h_o \) is very large. The velocity can now be written as

\( V = f(\alpha, \beta) \) where \( \beta \) is a constant for a given system and the critical velocity can be computed by solving the equation \( dV/d\alpha = 0 \). The resulting critical velocity is

\[
V_c = \frac{2}{3} \sqrt{\frac{\psi(\beta) kT a_o}{\pi}} \cdot \frac{\sigma}{\eta R^{1.5}} \quad (4.17)
\]

where \( \psi(\beta) \) is a function of \( \beta \). If the surface free energy is replaced by its expression as a function of the latent heat of fusion [Equation (3.12)], Equation (4.17) becomes:

\[
V_c = \frac{2a_o}{3} \sqrt{\frac{\psi(\beta) kT}{\pi}} \cdot \frac{L^{0.5}}{\eta R^{1.5}} \quad (4.18)
\]

In subsequent derivations, \( \beta \) was assumed to be equal to unity i.e. the distance

\[
h_{oc} = a_o (1-\ln \alpha) \quad (4.19)
\]

and \( h_{oc} \) is equal to a few molecular diameters if the front is moderately curved.
e. They observed that particles were pushed at higher critical velocities at grain-boundaries and at even higher rates at triple points. This result was explained by the fact that since near contact occurs now in 2 or 3 points, the area of the zone of strong interaction, $\pi r_o^2$, at each point could be reduced to create a total rejection force equal to that existing when there is only one zone of contact. Therefore the drag force was reduced and the particle could be pushed at higher rate. They computed that the critical velocities at a grain edge, grain boundary and triple point were in the ratio $1 : \sqrt{2} : \sqrt{3}$.

f. In a second approximation, they considered the effect of gravity in a verticle setup. It was introduced as a correction factor to the force $F_D$ exerted on the solid. For very small particles, the effect of gravity is negligible and the critical velocity is given by Equation (4.18).

In the same derivation, they also considered the case of rough particles. For very large particles, the resulting critical velocity is

$$V_c = \frac{2kT}{\pi g \Delta \rho} \cdot \alpha N \cdot \frac{c_{SL}}{\eta R_i R_f^2}.$$  \hspace{1cm} (4.20)

where: $N$ is the number of "bumps" of radius $R_1$ in contact with the front; $g$ is the acceleration of gravity; and $\Delta \rho$ is the difference in density between particle and liquid.

For particles of medium size the critical velocity is a solution to an equation of the second degree.

In these derivations, they assumed that for rough particles, the drag force was the sum of a Carrier type drag force [Equation (4.13)] for the small surface irregularities and a standard Stoke's drag force for the bulk of the particle. This last assumption seems poorly
justified in the case of particles with small surface irregularities. Their results are summarized in Table 4-5. They found a good agreement between the critical velocities measured on smooth tungsten particles in water and the values computed with Equation (4.17). This data could be better fitted by an equation of the type $V \propto \frac{1}{R^{1.1}}$ rather than $V \propto \frac{1}{R^{1.5}}$ but considering the inaccuracy of any critical velocity measurement, it may be difficult to distinguish between the two. This agreement is somewhat surprising considering the numerous approximations used.

Since, in fact, $\beta$ is an adjustable parameter (chosen "reasonably" as 1) it is interesting to look at the dependence of the computed critical velocities on $\beta$. The results are given in Table 4-1. The choice of $\beta=1$ is not supported by U.C.J.'s and Chernov's results (see Table 4-4). The last workers found that for a particle of radius 10$\mu$m, in a camphor matrix, $h_o = 9.3 \mu$m and to compute such a value, $\beta$ must be chosen equal to 13.4.

The computed critical velocities are not a rapidly varying function of $\beta$: increasing $\beta$ from 1 to 13.4 would only increase the computed critical velocity by a factor of 2.6. The difference is such, however, that the "perfect" agreement between theory and experiment found by Bolling and Cissé may simply be due to a proper choice of $\beta$.

In conclusion, B.C. tried to improve on some of the shortcomings of U.C.J.'s derivation. They computed more rigorously the shape of the front behind a particle and extended U.C.J.'s expression for drag force to a spherical interface. Their derivation of critical velocity is however subject to many criticisms presented in the course of the discussion (assumed spherical front, $r_o$ determined from a random walk
<table>
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<th>$\beta$</th>
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<th>$h_{oc \ nm}$</th>
<th>$\sqrt{\psi}$</th>
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<td>1.3</td>
<td>.32</td>
</tr>
<tr>
<td>.229</td>
<td>1</td>
<td>2.46</td>
<td>1.6</td>
<td>.58</td>
</tr>
<tr>
<td>.3</td>
<td>5.8</td>
<td>7</td>
<td>4.5</td>
<td>1.01</td>
</tr>
<tr>
<td>.318</td>
<td>13.4</td>
<td>14.5</td>
<td>9.3</td>
<td>1.48</td>
</tr>
</tbody>
</table>

Note: $a_o = .64 \ \text{nm}$ (value for camphor)

$\beta = \ln \alpha + (1-\alpha)/(1-3\alpha) \ \text{at} \ V = V_c$

$h_{oc} = a_o \cdot (1-\alpha)/(1-3\alpha)$

$\psi = \alpha(1-\alpha)^3/(1-3\alpha)$

Table 4-1: Dependence of the function $\psi$ on the radius of curvature $R/\alpha$. (From Bolling and Cissé's derivation, Reference 9)
diffuse model, introduction of a poorly defined parameter \( \beta \), similar
assumption to that used by U.C.J.). Their final expression for the
critical velocity should therefore be only used with great circumsppection.

4.4. Chernov, Temkin and Mel'nikova

This recent work (31) by Chernov, Temkin and Mel'nikova (referred to
as C.T.M.) gives the most complete treatment of the problem for smooth
particles. They considered that rejection was due to the existence of a
"disjoining pressure" of van der Waals origin. They only treated the case
of non retarded forces and instead of using the Hamaker constant \( A_{132} \) used
a constant \( B_3 = -A_{132}/6\pi \). It was shown in Chapter 3 that this approach
is equivalent to the surface energy approach used by U.C.J., since \( \Delta \sigma_\infty \)
can be deduced from the Hamaker constant, \( A_{132} \).

To determine the critical velocity, they wrote the condition of
equilibrium between solid and liquid at the interface. This equation is
written in a chemical potential form; it is similar to that used by B.C.
but C.T.M. neglected the kinetic undercooling term, and for the effect of
pressure used an expression depending on the thickness of the liquid film
(expression similar to that used by U.C.J.) and not an average pressure.
The equilibrium equation was therefore written as the sum of a curvature,
a pressure and a temperature term

\[
\Delta G_{\text{curv}} + \Delta G_p + \Delta G_T = 0 \tag{4.21}
\]

where
\[
\Delta G_{\text{curv}} = \Omega \sigma \frac{z' z''}{r} \left( \frac{z'}{r} + \frac{z''}{l+z'^2} \right) \frac{1}{\sqrt{1+z'^2}} 
\tag{4.22}
\]

\[
\Delta G_p = \frac{-\Omega B_3}{h} \tag{4.23}
\]

\[
\Delta G_T = \Delta S_M G (z-H) \tag{4.24}
\]
if \( \Omega \) is the molecular volume; \( r \) and \( z(r) \) are the coordinates of a point on the solidification front; \( \Delta S \) is the molecular heat of fusion; and \( H \) is defined in Figure 4-2.

They showed that for small particles only the first two terms of Equation (4.21) are important. Equation (4.21) becomes then identical to that used by U.C.J. One would therefore expect that for small particles U.C.J.'s and C.T.M.'s approaches should give very similar results. In the case of very large particles, the curvature term becomes negligible and only the last two terms of Equation (4.21) need to be considered.

As B.C., C.T.M. chose \( \alpha \) priori the shape of the front. They considered that it was flat (ordinate equal to \(-H\)) for radii larger than \( r_o \) and that it was parabolic for radii smaller than \( r_o \). The parabolic part of the front was defined by the minimum distance front-particle, \( h_o \), and by the radius of curvature at this point, \( R/\alpha \). This approach is identical in practice to that used by B.C. since B.C. used a spherical front but used a parabolic approximation for small radii.

The growth rate \( V \) is introduced by writing that, at steady state, the drag force is equal to the disjoining force. This equation can be written

\[
V = f(h_o, \alpha, r_o, H)
\]

(4.25)

The problem is now to determine the various relationship existing between the parameters to be able to express \( V \) as a function of a single variable. Geometrical considerations give a relation between \( r_o \) and \( H \). A second relation is found by writing the equilibrium Equation (4.21) on the axis of symmetry. As in the previous two studies, since the shape of
the front is arbitrarily chosen or determined from an incomplete set of
relations, the equilibrium equation, (4.21) cannot be satisfied at each
point of the front.

The velocity can now be expressed as a function of two parameters
only. For example, \( V = f(H, h_o) \). C.T.M. use two different approaches to
eliminate the last parameter. In a first approach, they consider that
\( r_o = \infty \). This approximation is justified by the fact that in the compu-
tation of drag and disjoining forces, only the region where particle and
front are very close is important. The final result should therefore
be insensitive to the shape of the front in the regions where the liquid
film is thick. Equation (4.25) can now be written \( V = f(h_o) \) and the
initial velocity is obtained by looking for the maximum value of \( V \)
(i.e. \( dV/dh_o = 0 \)).

Their second approach is more elaborate but gives results practically
identical to that found with the first approach (the expressions of the
critical velocity differ by a constant). In this second approach, they
noticed that the equilibrium equation (4.21) was approximately the Euler-
Lagrange equation for a function

\[
G = \int_0^\infty f(r,z,z') r \, dr
\]  

(4.26)

[The Euler-Lagrange equation of \( G \) is missing a term \( \frac{z'}{r/v^{1+z^2}} \) which appears
in Equation (4.21)]; i.e., the equilibrium equation is the differential
equation that \( f' \) must satisfy so that \( G \) be minimum (see e.g., Ref.91).
Integrating Equation (4.26) and looking for a minimum value of \( G \) gives
the extra relation between \( r_o, h_o, \alpha \) and \( H \).
Using this more elaborate derivation, the critical velocity for small particles \((R \leq 500 \mu m)\) is

\[
V_c = \frac{0.14 B_3^{2/3} \sigma_{SL}^{1/3}}{\eta R^{4/3}}
\]  
(4.27)

or replacing \(\sigma_{SL}\) by its expression as a function of the latent heat of fusion \(L\), [Equation (3.12)]

\[
V_c = 0.14(Ka_o)^{1/3} \cdot \frac{B_3^{2/3} L^{1/3}}{\eta R^{4/3}}
\]  
(4.28)

They also found that the radius of curvature is equal to \(R/0.35\) and the distance \(r_{oc}\) and \(h_{oc}\) are equal to:

\[
h_{oc} = \frac{B_3 R}{0.7Ka_o L}^{1/3}
\]  
(4.29)

\[
r_{oc} = 2\left[\frac{B_3^4}{0.7Ka_o L}\right]^{1/6} = 2 \sqrt{\frac{R}{h_{oc}}}
\]  
(4.30)

The expression for the critical velocity is somewhat different from that found by U.C.J. [Equation (4.5)], but the expression for \(h_{oc}\) and \(r_{oc}\) are very similar. For large particles \((R > 500 \mu m)\)

\[
V_c = \frac{0.15}{T^{1/4}} \cdot \frac{B_3^{3/4}(LG)^{1/4}}{\eta R}
\]  
(4.31)

In this case the distance \(h_o\) was found to be independent of the particle size

\[
h_o = \frac{B_3 \Omega}{\Delta S_M G}^{1/4}
\]  
(4.32)

Using the data for camphor (Table 4-3) and a temperature gradient of \(10^4 \degree C/m\), \(h_o = 35 \text{ nm}\). The results on critical velocity are summarized in Table 4-5.

In conclusion, C.T.M.'s derivation for small particles is similar in many respects to that of U.C.J., but as B.C. they assumed à priori a
front shape. The expressions for the radius of the zone of strong interaction, $r_{oc}$, and the minimum distance particle-front, $h_0$, are very similar to that derived by U.C.J. The expressions for critical velocities are quite different from these derived by U.C.J. and B.C.

4.5. Chen

Chen (20) considered that the repulsive interaction between particle and solid was due to the existence of a disjoining pressure. This approach is identical to that used independently by C.T.M. (Chen's and C.T.M.'s studies were published the same year). The shape of the front behind the particle was determined using a diffusion model similar to that used by U.C.J. With the proper changes of variables (replacing mobility by $D/kT$, and Hamaker constant by $A_{oo}, a_o^2$) the equation obtained by Chen for the shape of the front is identical to that derived by U.C.J. [Equation (4.2)]. He justified the use of a diffusion model by computing the Reynold's number for the flow of liquid in the thin liquid film between particle and solid. By assuming that the thickness of the liquid film, $h(r)$ was equal to $r/10$, he found that the Reynold's jumber was much less than unity ($5 \times 10^{-3}$) and that, therefore, transport must occur by creeping flow. Checking this result, a posteriori, using the computed shape of the front, one finds again a very small Reynold's number.

Chen considered, as in the previous studies, that most of the interaction particle-liquid and solid occurred in a small region of radius $r_o$. He derived a relation between $h_o$, $r_o$ and velocity by writing that the sum of the forces on the particle is zero or: Drag force + Body force (due
to external fields or friction) = Disjoining force.

In this derivation, however, he considered that

\[
\frac{dp_f}{dr} = - \frac{d\Pi(h)}{dr}
\]  

(4.33)

where \( p_f \) = pressure in the liquid film; and \( \Pi \) is the disjoining pressure \( = -A/6 h^3 \); and furthermore he neglected curvature effects and temperature gradient effects. He obtained finally the growth rate as a function of \( h_0 \) and \( r_0 \), but did not try to derive a relation between the two.

In a numerical computation of the growth rate for various values of \( h_0 \), he found growth rates too small by five orders of magnitude. This result is not surprising since in these computations he used for the radius, \( r_0 \), the radius of the particle instead of a much smaller value (see Table 4-4). He justified this choice by considering that when the particle is entrapped, the front wraps around the particle. This is true; but when the particle is pushed, if the differences in thermal properties between particle and matrix are neglected, the front remains practically flat behind the particle.

4.6. Conclusion

From the various derivations, the following conclusions can be drawn:

a. In practice, in all the studies where a rejection force was explicitly taken into account, the same expression was used: it was shown in Chapter 3 that the surface energy argument used by U.C.J. is equivalent to the disjoining force argument used by C.T.M. and Chen. The various derivations of \( V_c \) differ mainly in the approximations used to solve the
differential equation that the solidification front must satisfy.

b. U.C.J. determined the shape of the front by solving the diffusion equation behind the particle whereas B.C. and U.C.J. assumed, a priori, a parabolic shape. The resulting equations are very different [Equation (4.2) and a paraboloid respectively]; however a numerical computation using the physical constants of camphor (Table 4-2) and assuming a Hamaker constant $A = -2 \times 10^{-20} \text{J}$ (or $\Delta G_\infty = 3.9 \text{ mJ/m}^2$) shows that for distances up to $0.7 r_0$, the shapes used by C.T.M. or U.C.J. are practically identical (Table 4-3). This similarity is partially due to the very small value of $r_0$.

c. In every derivation, a zone of strong interaction particle-solid was introduced. The radius of this zone, $r_0$, was determined from a random walk model by B.C. The expressions derived by U.C.J. and C.T.M. for $r_0$ and the minimum distance particle-front, $h_0$, at $V_c$ are very similar. The results of numerical computations, using again the data for camphor and a Hamaker constant $A = -2 \times 10^{-20} \text{J}$, are given in Table 4-4. The choice of $A$ is not critical to the present discussion since $r_{oc}$ and $h_{oc}$ are slowly varying functions of $A$. The values computed using U.C.J. and C.T.M. expressions are very close. In both cases, the radius of the zone of strong interaction is a small fraction of the radius of the particle (for $R = 1$ to $100 \text{ m}, r_0 = 0.13$ to $0.02 R$); therefore, the front remains practically flat behind the particle, and no visible cusping should occur. This result justifies, a posteriori, the assumption used by U.C.J. and B.C. of neglecting the difference in temperature between the points A and B in Figure 4-1. The minimum distance front-particle, $h_{oc}$, computed using either a diffusion approach (U.C.J.) or a flow approach
Melting point \[ T_m = 453^\circ K \]
Density \[ \rho = 0.941 \text{ g/cm}^3 \]
Molecular diameter \[ a_o = 6.41 \times 10^{-10} \text{ m} \]
Molecular volume \[ \Omega = 2.63 \times 10^{-28} \text{ m}^3 \]
Molecular entropy of fusion \[ \Delta S_M = 1.4 \text{ k} \]
Latent heat of fusion \[ L = 23.3 \times 10^6 \text{ J/m}^3 \]
Surface tension \[ \sigma_{SL} = 0.86 \times a_o \text{ L} = 12.8 \text{ mJ/m}^2 \]
Viscosity \[ \eta = 0.005 \text{ poise} = 5 \times 10^{-4} \text{ S.I.u.} \]

Table 4-2: Physical properties of camphor
<table>
<thead>
<tr>
<th>Radial distance (in $\mu$m)</th>
<th>h(r) in nm</th>
<th>h(r) - h(o) in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U.C.J.</td>
<td>C.T.N.</td>
</tr>
<tr>
<td>0</td>
<td>24.3</td>
<td>20.1</td>
</tr>
<tr>
<td>0.4</td>
<td>24.7</td>
<td>20.6</td>
</tr>
<tr>
<td>0.8</td>
<td>26.1</td>
<td>22.2</td>
</tr>
<tr>
<td>1.2</td>
<td>29.0</td>
<td>24.8</td>
</tr>
<tr>
<td>1.6</td>
<td>35.4</td>
<td>28.4</td>
</tr>
<tr>
<td>2</td>
<td>58.3</td>
<td>33.1</td>
</tr>
<tr>
<td>2.2</td>
<td>$\infty$</td>
<td>35.8</td>
</tr>
<tr>
<td>2.8</td>
<td></td>
<td>45.6</td>
</tr>
</tbody>
</table>

Table 4-3: Thickness $h$ of the liquid film behind a 100 $\mu$m radius particle
<table>
<thead>
<tr>
<th>R (µm)</th>
<th>h_{oc} nm</th>
<th>r_{oc}/R</th>
<th>V_c µm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.2</td>
<td>1.6</td>
<td>4.3</td>
</tr>
<tr>
<td>10</td>
<td>11.3</td>
<td>1.6</td>
<td>9.3</td>
</tr>
<tr>
<td>100</td>
<td>24.3</td>
<td>1.6</td>
<td>20.1</td>
</tr>
</tbody>
</table>

Table 4-4: Variation of h_{oc}, r_{oc} and V with particle size
(camphor, A = 2 x 10^{-20} J)
(C.T.M.) for the transport of liquid behind the particle, is small but at least equal to 10 molecular diameters (if \( R \geq 1 \mu m \)). The transport of liquid should, therefore, be better described by a flow mechanism rather than a diffusion mechanism.

d. The equilibrium equations between solid and its melt used by U.C.J. and C.T.M. are identical; but due to the different approximations used, the expressions for critical velocity are very different.

e. The various expressions obtained for the critical velocity are summarized in Table 4-5. They can be written in the form:

\[
V_c = \frac{\lambda}{\eta R^m}
\]  \hspace{1cm} (4.34)

where \( \lambda \) is a proportionality factor and \( m \) varies between 1.3 and 2 for small particles and 1 and 2 for large particles. The rejection force (Hamaker constant or \( \Delta \sigma \)) appears only in the expression derived by C.T.M. The results of numerical computations using again the values for camphor are given in Table 4-4. The values of \( V_c \) computed with U.C.J.'s equation (4.5) seem low considering the high Hamaker constant and low viscosity used (10 \( \mu m \) zinc particles were observed to be pushed at a few \( \mu m/s \)). The critical velocities computed with either B.C.'s or C.T.M.'s equations (4.17 and 4.28) are surprisingly similar and closer to experimentally measured values.

The expression for \( V_c \) derived by C.T.M. seems, therefore, to be the most reliable since it gives a better agreement with experimental data than U.C.J.'s derivation and is more rigorous than B.C.'s derivation. C.T.M. did not treat, however, the very important case of rough particles.
Authors
Reference
U.C.J. (13)
B.C. (9)
C.T.M. (31)

Small particles
\( K_1 \cdot \frac{L}{\eta R^2} \)
\( K_3 \cdot \frac{L^{0.5}}{\eta R^{1.5}} \)
\( K_5 \cdot \frac{B^{0.66} L^{0.33}}{\eta R^{1.33}} \)

Large particles
\( K_1 \cdot \frac{L^{0.5}}{\eta R^{1.5}} \)
\( K_3 \cdot \frac{L^{0.5}}{\eta R^{1.5}} \)
\( K_6 \cdot \frac{B^{0.75} \eta^{0.25}}{\eta R} \)

Large and rough particles
\( K_2 \cdot \frac{B^{0.33} N^{0.5}}{\eta R R_i^{0.66}} \)
\( K_4 \cdot \frac{N^{0.5}}{\eta R^{1.5}} \)

Note: The \( K_i \) are proportionality constants.

Table 4-5: Comparison of various expressions for the critical velocity in the absence of a field
CHAPTER 5

EXPERIMENTAL WORK

As discussed in Chapter 2, a few general rules can be drawn from existing experimental data, but these published results do not always agree. It was therefore necessary to conduct more measurements of critical velocities. Since one purpose of the present study is to relate optical and dielectric measurements to critical velocities, it was felt that new measurements must be done with particles of well defined materials, sizes and surface properties to obtain a consistent set of data. To resolve the discrepancy between measurements done with various growth geometries, it was decided to conduct some experiments in a microgravity environment. In this way, the drawbacks of both horizontal and vertical growth geometries could be avoided. This experiment would also permit us to check Chen's conclusion that the critical velocity increases with increasing load. Finally, experiments were run to familiarize ourselves with the physical aspect of the phenomenon.

5.1. Materials

5.1.1. Matrices

In the present study, critical velocities were measured for several types of particles in organic matrices. Organic matrix materials were used instead of metals for two reasons. First, most organics are transparent in samples of moderate thickness, and particles could be observed while they were pushed or entrapped by the growing organic crystal. As will be discussed later, this condition was essential to obtaining accurate data, and it made it possible to see the shape of the front behind a particle that was pushed. The second reasons for using organics
is that they have a low melting point. The equipment could therefore remain simple and observation with a microscope was possible without complex and expensive devices.

Among the large number of commercially available organic materials, about 40 organics were chosen for possible study. The criteria for this selection were that the materials be non toxic or at least not too dangerous to handle, be available in high purity grade and have a melting point between 20 and 220°C. With these constraints, the organics were chosen to provide a variety of molecular structures and inter-molecular interactions, from straight chains, to complex cyclic compounds, with both polar and non polar molecular interactions. A quick screening test was then run to observe crystallization morphology and to measure the critical velocity of small glass and zinc particles. Partial results of this test are given in Table 5-2. The major problem encountered was that of the purity of the organic materials. Even "high purity" grade organic materials may contain enough impurities to give a cellular or needle growth; and purification is often difficult due to thermal decomposition and/or presence of impurities with melting point and chemical properties very close to that of the organic. Following this screening test, five organics were chosen for more extensive studies: two low entropy of fusion materials, carbon tetrabromide and d-camphor, and three high entropy of fusion organics, naphthalene, durene and thymol, this last being a glass former in bulk.

a. **Carbon Tetrabromide and Camphor:**

These two organics have a low entropy of fusion \( \Delta S < 2k \), where \( k \) is Boltzmann's constant). The very interesting properties of low entropy
of fusion organic materials, often called plastic or globular crystals, were recognized by Timmermans (92, 93) and Van de Vloed (94). The name globular crystal is due to the shape of the molecules: they are either symmetrical around their center (CBr₄) or give a sphere by rotation around an axis (camphor). These compounds have a melting point higher than compounds chemically similar but non-globular. With this high melting point is associated a high vapor pressure and a narrow range of liquid state stability (some of the globular crystals sublime rather than melt at atmospheric pressure). They have one or more solid-state transitions at temperatures below the melting point. The high temperature form is most often cubic, or in some cases hexagonal; the low temperature form has lower symmetry. The solid-state transformation occurs with a sizable entropy and volume change (at 47°C for CBr₄; at -32°C for d-camphor with a second transformation at 87°C). Due to the high symmetry of the globular crystals and the freedom of the molecules to rotate in the solid state, high temperature form, the low frequency dielectric properties of globular crystals are practically identical to those of their melt. Upon solidification, the static dielectric constant drops only by an amount corresponding to the volume change and continues to increase, as in the liquid state, upon cooling. When the crystal transforms to a lower symmetry form, the dielectric constant drops by a large amount and decreases with decreasing temperature as in most solids (93, 95). In their high temperature form, globular crystals flow easily (hence the name plastic crystals). This is a consequence of the weak intermolecular forces combined with a high crystal symmetry leading to a large number of favorable crystalline slip systems. Upon solidification, plastic or
globular crystals grow from the melt with an atomically rough interface and therefore a macroscopically smooth interface (96, 97, 98); and the kinetic undercooling is very small.

Globular crystals have therefore properties in many respects similar to those of metals: they have a low entropy of fusion, melt with a small volume change, crystallize in the cubic or hexagonal system, can be deformed plastically and grow with a macroscopically smooth interface and with a very small kinetic undercooling.

These similarities to metals make therefore the study of carbon tetrabromide and camphor particularly interesting; furthermore materials with small entropies of fusion have not been studied in previous investigations of particle rejection. Both organics were purified before rejection experiments by repeated sublimation (2 to 5 times) at low temperatures (T<100°C) under low gas pressures.

b. Durene, Naphthalene and Thymol:

These compounds, like the majority of organic materials, have a high entropy of fusion (ΔS>4k). The choice of high entropy of fusion materials was, however, limited by the nature of the solid-liquid interface. As discussed by Jackson (97), a high entropy of fusion is associated with a microscopically smooth interface, and the crystal will grow by successive nucleation of new atomic planes or by growth on dislocations, giving a macroscopically faceted front. Many organic compounds had to be eliminated due to middle-like growth rendering any measurement of critical velocity questionable.
Wilcox (99) showed that the macroscopic appearance of the front is also influenced by the temperature gradient existing in the material and the growth rate. At sufficiently low growth rates and high temperature gradients, some high entropy of fusion materials can be grown with a macroscopically flat (non-faceted) interface. The shape of the front is strongly determined by the anisotropy of the surface energy and of the growth kinetics. In a temperature gradient of about 50°C/cm, durene and naphthalene grow with a flat interface for growth rates up to 8 to 12 μm/s in the case of durene and up to at least 40 μm/s in the case of naphthalene.

Thymol was included in this study since it is a glass former in bulk, and the viscosity of its melt is larger than that of the previous materials.

5.1.2. **Particles**

A large variety of particles was tested: glass spheres, fused silica, metallic particles (Au, Cu, Fe, Ni, Zn, W), oxides (CuO, MgO, Al₂O₃, Fe₂O₃), graphite, mica, germanium and lucite. The particles ranged in size between a few tenths of a micron to several hundred microns. The list of the particles finally used is given, with their size and origin, in Table 5-1. In the case of glass and copper particles, where the original supply covered a broad range of sizes, the particles were separated into narrower size ranges. The shape and surface finish of the particles were studied by optical microscopy and by transmission electron microscopy (Siemens Elmiskop 101). The reason for the choice of these particles were:
<table>
<thead>
<tr>
<th>Particle</th>
<th>Origin</th>
<th>Size in µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass spheres</td>
<td>Potters Industries Inc., N.J.</td>
<td>1 - 120</td>
</tr>
<tr>
<td>Au lumps</td>
<td>Ventron-Alfa Products</td>
<td>large agglomerates (&lt;150 µm) of 2-10 µm particles</td>
</tr>
<tr>
<td>Cu spheres</td>
<td>J. T. Baker</td>
<td>2 - 140</td>
</tr>
<tr>
<td>Cu (coated with CuO) spheres, agglomerates</td>
<td>Ventron-Alfa Products</td>
<td>&lt;10</td>
</tr>
<tr>
<td>&quot;5 µm&quot; Ni spheres</td>
<td>Ventron-Alfa Products</td>
<td>2 - 30</td>
</tr>
<tr>
<td>Zn (coated with ZnO) spheres</td>
<td>Mallinckrodt Chemical works</td>
<td>2 - 25</td>
</tr>
<tr>
<td>Ge powder</td>
<td>Eagle Picher Ind.</td>
<td>agglomerates of 2 to 25 µm particles</td>
</tr>
<tr>
<td>Mica</td>
<td>crushed mica sheet</td>
<td>20 - 200 µm flakes</td>
</tr>
</tbody>
</table>

Table 5-1: Particles used for critical velocity measurements
a. The glass particles were nearly spherical, had a smooth surface (Figure 5-1) and were available in a wide range of sizes. The irregularities on the surface of the sphere were less than 10 nm high. The size dependence of critical velocity could therefore be tested unequivocally for these particles.

b. Metallic, oxide and semi-conductor particles have widely different optical properties; and a comparison of the measured critical velocities could allow testing the influence of van der Waals forces. Gold and to a lesser extent copper are specially interesting since their surfaces can be kept oxide free for long periods of time.

The gold particles consisted of agglomerated smaller particles. The particles were not spherical but their surfaces were oxide free and smooth (Figure 5-2). The majority of the copper particles were nearly spherical with surface irregularities less than 0.2 μm high (Figure 5-3). Often a few small particles (μm or sub μm size) were attached to a large one. Some particles were more irregular and/or consisted of several spheres. For the particle shown in Figure 5-3b, the radius of curvature varied between 1.4 and 4.2 μm. A few particle were partially coated by a thin oxide film (Figure 5-4). This example of the copper particles illustrates how even for the nearly spherical particles, the nature of the surface and the radii of curvature can change from point to point on a given particle. Some copper particles were coated with a layer of black oxide (CuO), and were used to test the influence of an oxide layer. These particles were very irregular and rough (Figure 5-5). Since no special care was used in storing the zinc particles, they were coated with a thick zinc oxide layer. The particles had to be observed in the electron
Figure 5-1: Glass particles - Transmission Electron Micrographs - 100 kV
Figure 5-2: Gold particles, T.E.M. 100 kV
Figure 5-3: Copper particles T.E.M. - 100 kV

(a) particles of radius 1, 2 and 21 μm

(b) particles of radius 3.4 and 4.2 μm
Figure 5-4: Copper particle, T.E.M. 100 kV
Particle of radius 1 \mu m
Figure 5-5: Copper particles coated with CuO - T.E.M. 100 kV
microscope with a low intensity beam to avoid vaporization of the zinc and, in some cases, explosion of the particles. The particles were not spherical (Figure 5-6) and their surface was irregular with irregularities of various sizes (2 or 3 to 100 nm). The size of the irregularities did not appear to be a function of the size of the particle. The nickel particles were in their majority nearly spherical and had a smooth surface (Figure 5-7). The germanium particles consist of agglomerates of small (2 to 20 \( \mu \text{m} \)) particles (Figures 5-8, 5-9).

5.2. Apparatus

5.2.1. Horizontal Growth

A schematic drawing of the horizontal growth device is given in Figure 5-10. In this set-up, the sample was translated at a controlled rate through a fixed temperature gradient. When the pushing rate was changed, after a few minutes, the front stabilized to a new position in the fixture and growth occurred at a speed equal to the pushing speed. As a consequence, the front was seen at a fixed plane under the microscope. This geometry was convenient for observing the front and taking pictures of the phenomena. The temperature profile was fixed by aluminum blocks either heated electrically or water cooled. The vertical shape of the front was adjusted by controlling the top and bottom temperatures of the hot zone and the distance between cold zone and sample. To obtain a smooth and uniform motion of the sample in the temperature gradient, the sample glided on teflon supports. The sample was simply pushed through the temperature gradient. This set-up only allowed movement in one direction but eliminated the problem of alignment inherent to
Figure 5-6: Zinc particle, T.E.M. 100 kV

Figure 5-7: Nickel particles, T.E.M. 100 kV (Radius 1.2 and 4.5 μm)
Figure 5-8: Germanium particle - Optical microscopy

Figure 5-9: Germanium particle, T.E.M. 100 kV
FIGURE 5-10 HORIZONTAL SET-UP
any system where the sample is mechanically linked to the displacement device. The push-rod was guided by a bored teflon block and driven by a variable speed motor. Through the use of a reductor, the range of speed available was 0.03 to 35 μm/s. The rheostat of the variable speed motor had been calibrated in growth rates; but this calibration was subject to variations of up to ±10%. Therefore, for accurate measurements and/or measurements where the growth rate was different from the pushing rate, the growth rate was constantly measured by microscopic observation, using the particles dispersed either in the solid or the liquid as references.

The cell was made of two thin microscope cover slides fused together on three sides. The problem of evaporation of the sample was therefore eliminated. The cells were 50 to 500 μm thick. The cells were filled by capillarity by placing them in a large test tube containing a small amount of liquid organic. These cells were then taped on a microscope slide and placed in the jig (Figure 5-10).

The jig was insulated by a lucite cover and glass wool; and all the apertures were covered with glass tape to eliminate drafts and limit convection on the sample. The sample was observed with a microscope under magnifications ranging from 30 to 220X. The higher magnification objectives were long working distance objectives. The microscope was equipped with a camera and a movie camera and several movies of the most interesting features of the phenomenon were taken.

Most of the measurements reported in this chapter were done in this jig.
5.2.2. Microgravity or Vertical Cell

This cell was designed for the study of particle rejection in a microgravity environment and could be used in any position. The cell was fixed between two aluminum blocks, the temperatures of which were controlled very accurately. The temperature gradient and growth rate were adjusted by controlling the temperatures and cooling rates of "top" and "bottom" heaters (Figure 5-11). This function was performed electronically, the temperatures being measured by thermistors. The temperature and cooling rates were adjusted by simply setting variable resistors. The cell was a flat quartz bottle 1 cm wide, 4 cm tall and about 200 μm thick internally. This very thin geometry was chosen to allow a fast response to temperature changes and give a solidification front as flat as possible. To allow for thermal expansion of the organic material, the cell was closed by a thin teflon gasket. The cell was sealed with a teflon O-ring. Teflon was used in spite of its poor mechanical properties since it was the only existing O-ring that would not swell or degrade in the presence of the chosen organics. This equipment was for the major part designed and built at the C. S. Draper Laboratories by F. Sirraco and his groups.

5.2.3. Horizontal vs. Vertical Growth Geometry

Critical velocities have been mainly measured in the horizontal growth geometry, in either of the two cells. The disadvantage of the horizontal geometry was that the particles glided or rolled on the bottom or top glass plates (top plate in the case of light particles in a dense liquid e.g., glass in CBr₄), introducing an unknown friction
FIGURE 5-11 SCHEMATIC DIAGRAM OF THE "VERTICAL" CELL ASSEMBLY
factor; whereas in the vertical geometry, the particles were subjected
to the known gravitational forces. This disadvantage was, however,
compensated by the possibility of observing pushing even in the case of
prismatic or needle growth since the particles did not fall between grains
or needles where they would have been readily entrapped.

5.3. Results

5.3.1. Description of the Phenomenon

To illustrate the phenomenon of particle pushing, let us consider the
case of a durene matrix containing glass particles. Figures 5-12(a), (b)
and (c) have been taken with the horizontal set-up. The thin layer of
durene was a few hundred microns thick and the glass particles ranged
in size from 1 to 50 μm. The black spheres visible on some glass particles
are air bubbles. The glass particles were initially randomly distributed
in the matrix. The pictures were taken with polarized light to facilitate
the observation of the interface between solid (multicolored) and liquid
(gray). At high growth rate (11 μm/s, Figure 5-12a) the glass particles
were readily entrapped with little or no displacement when the front
reached them. When the growth rate was decreased (5 μm/s, Figure 5-12b)
some particles were pushed for long distances and pile-ups were formed,
while other particles of apparently the same size were entrapped. At
lower speeds (2.0 μm/s, Figure 5-12c), large pile-ups were pushed and a
few particles were entrapped. Upon pushing, the front appeared to remain
flat. To measure critical velocities, the experiment must be run with
a much smaller density of particles to avoid formation of large pile-ups.

From a more careful examination, several observations could be made:
Figure 5-12 (a) and (b): Durene matrix with glass particles.
Growth rate 11 \( \mu m/s \) and 5 \( \mu m/s \).
Figure 5-12 (c); Durene matrix with glass particles.
Growth rate 2 μm/s
a. When a particle was pushed at a speed close to its critical velocity, often the crystal growing behind the particle contained defects (visible in polarized light) and/or bubbles. The foreign particles may therefore be a source of defects in the crystal even when they are not entrapped (Figure 5-13).

b. If the matrix had not been previously degassed, after entrapment of a particle, in some cases, small bubbles were seen to migrate from the particle toward the front (e.g., Figure 9-3h)---i.e., the melt close to the particle was enriched in soluble gases. This observation confirms Temkin et al.'s(46) computations that indicated that the film of melt behind a particle becomes enriched in impurities.

c. Often, pile-ups were entrapped a few layers of particles at a time with the remaining particles of the pile-up continuing to be pushed. This partial entrapment occurred either when the pile-up became too large and/or when a fluctuation in growth rate occurred. This resulted in a banded structure outlining the previous positions of the front.

5.3.2. Uncertainties Associated with the Measurement of Critical Velocity

Measurements of critical velocities were subject to many errors and ambiguities. Several of the many potential causes of error were under the control of the experimentalist, or at least, erroneous data could be detected by visual observation of the particles while they were pushed or entrapped. At least five such causes of error can be listed.

a. Small particle pushing a large one, or agglomerate pushed by a few particles. As discussed in Chapter 2, small particles have a higher
Figure 5-13: Defects behind a particle (Thymol - Copper particle)

Figure 5-14: Layered structure observed after entrapment of pile-ups (5 μm Nickel spheres in thymol)
critical velocity than larger ones. If a small particle was trapped between a large particle and the solidification front (Figure 5-15) the large particle appeared to have a large critical velocity when, in fact, the velocity measured was only slightly lower than that of the small particle, responsible for pushing. At the limit, the phenomenon is similar to that of particles with a rough surface.

b. Slanted or curved front. In the case of materials growing with a smooth (non-faceted) front, the interface follows the isotherms and will therefore often be curved. When the front was convex (Figure 5-16a), particles were often readily entrapped at the wedge formed between the glass plate and the growing crystal; and the measured critical velocity was much smaller than for a straight front. Hence, measurements were only taken when the front was straight or slightly concave (Figure 5-16b). The same remark is valid in the case of prismatic growth and measurements were only taken when the front was straight or slanted as shown on Figure 5-16c. A geometry often encountered in prismatic growth was that of Figure 5-16d. In this case, large particles were pushed at the tip of the crystal and the measured critical velocity was larger than for a flat front since the drag force was lower. On the other hand, smaller particles could fit in the wedge formed by the growing crystal and the glass plate and were entrapped. When the front was too slanted as shown in Figure 5-16c, small particles could climb up the solidification front to the top of the cell where they were finally entrapped. With such a slanted front, the friction force exerted on large particles might be reduced since the particle tended to be pushed upward.
FIGURE 5-15 LARGE PARTICLE OR AGGLOMERATE PUSHED BY A FEW SMALL PARTICLES.
FIGURE 5.16 SHAPE OF THE SOLIDIFICATION FRONT
c. **Grain boundaries.** Particles were either preferentially entrapped or pushed at grain boundaries, depending on the size of the particles and the shape of the grain boundaries. In the case of prismatic growth, most often the angle between grains at the grain boundary was small and particles were readily entrapped there (wedge effect, Figure 5-17a). This was even more so the case for impure materials, since the grain boundary, enriched in impurities, had a lower melting point and formed a deep trough (Figure 5-17b). This preferential entrapment at grain boundaries is illustrated for the case of a pure matrix, in Figure 5-18. In this case, a durene crystal pushed a pile-up of glass and zinc particles, and the grain boundary was decorated by a trail of small particles (the picture was taken after remelting the crystal for a short distance).

Particles can also be preferentially pushed at grain boundaries. This result had been previously reported by Bolling and Cissé in the ice-water system (10). In the present study, in the case of prismatic growth, this was only observed for particles that were larger than the opening of the liquid wedge or trough (Figure 5-17b); in the case of low entropy of fusion materials (camphor), on the other hand, particles were generally preferentially pushed at grain boundaries. The critical velocity was found to be larger by a factor of 1.2 to 1.6 at a grain boundary that at a grain face. This result is in good agreement with the value of $\sqrt{2}$ suggested by Bolling and Cissé (9). At fast growth rates, most of the small particles that were pushed moved laterally on the growing front until they reached a grain-boundary where they continued to be pushed, further lateral motion being hindered.
FIGURE 5-17 ENTRAPMENT AT GRAIN BOUNDARIES
Figure 5-18: Preferential entrapment at grain boundary.
Glass and zinc particles in durene
d. Bubbles. If the matrix had not been carefully degassed prior to the experiment, bubbles were formed upon crystallization since the solubility of the gas is lower in the solid than in the liquid. The particles were observed to interact with these bubbles in two ways. First, most often the particles were electrostatically repelled by the bubbles; and second, the particles swirled in front of the bubbles as illustrated in Figure 5-19. Therefore, a large particle could be "pushed" for long distances without ever coming in close proximity to the front. The liquid flow around the bubble can be explained by the variation in surface tension with temperature. The surface tension of the liquid-gas interface decreases with increasing temperature; and the bubble tends therefore to grow in the hotter region, rejecting liquid toward the colder region. This problem was avoided by degassing the matrix prior to measuring the critical velocity. Degassing was done either by growing the crystal under a low gas pressure or by growing and melting the organic materials several times in the experimental cell to reject gases to one end of the cell.

e. Uneven growth rate. It was observed that at high growth rates, prismatic fronts grew in a discontinuous fashion. The average growth rate remained constant but some grains would grow more slowly and then be overtaken by grains growing, for a moment, much faster than the average growth rate. It was therefore necessary, in this case, to measure rapidly the growth rate of each grain studied.

At the other extreme, it appeared very difficult to obtain uniform growth rates at speeds below 0.1 or 0.2 µm/s. Small variations in convection currents above the sample, ... were sufficient to induce, especially
Figure 5-19: Swirling motion of particles near a bubble
in the case of small temperature gradients, uneven growth. The true
growth rate for entrapment was therefore larger than the measured dis-
placement rate of the sample.

Critical velocities were measured with these five possible sources of
error in mind and data that might have been influenced by any one were
rejected. This rejection of "bad" data was possible since the samples were
observed under a microscope during measurements. In spite of these
precautions, however, even in the case of glass particles that were nearly
spherical and free of large surface irregularities, the uncertainty in the
measured critical velocities was large. In many cases, particles were
pushed for some distance before being entrapped, and three different cases
had to be considered. At high growth rates, the particles were readily
entrapped. At low growth rates, the particles were pushed indefinitely.
But in an intermediate range of growth rates, particles were pushed for
some distance and then entrapped. Arbitrarily, particles that were
pushed for distances larger than 5 to 20 diameters (in the case of large
particles diameter >25 μm) or 300 to 400 μm (in the case of small particles),
were considered pushed—i.e., considered to have a critical velocity
larger than the growth rate. In the same experiment, particles that
looked identical had different critical velocities or the same particle
was entrapped at different growth rates in successive experiment.

The large uncertainty associated with critical velocity measurements
has been reported in previous studies. Uhlmann et al. (13) reporting
on critical velocity of magnesia particles in thymol showed that partial
entrainment occurred for velocities between \( V_c \) and 1.75 \( V_c \). Similarly
Omenyi (16) through a careful experimental study reported that for a
given particle size, the range of velocity for partial entrapment was in some cases several hundred percent of the critical velocity and this range was especially large for large particles. This uncertainty is not limited to the horizontal growth geometry since Bolling and Cissé (11) mentioned also a range of partial entrapment.

These variations in critical velocity may be due to:

a. Unnoticed defects on the particles and/or non spherical particles—i.e. various sides of the particles having different critical velocities (e.g. Figure 5-3b or Figure 5-6). Since particles were often observed to rotate during pushing, these irregularities can also explain why particles were pushed for some distance. Also, these small defects or irregularities may give rise to changes in friction coefficient and the particles may roll or glide freely on the glass plate and then be blocked by a small irregularity.

b. Difference in surface chemistry either from particle to particle or for different regions of the same particle. This non uniformity of the surface of the particle was clearly observed in the case of the copper particles where an oxide film was only visible on portions of some particles.

c. The time necessary to reach thermal equilibrium. As discussed in Chapter 9, the solidification front often curves behind a particle and the equilibrium front shape will only be attained after a short time. Hence, the particle may be pushed for a short distance until the front curves sufficiently, for thermal reasons, and entraps the particle.

d. The effect of the crystalline orientation of the front. Since surface tension is in general anisotropic one would expect the critical
velocity to be a function of the orientation of the solidification front. This might have been the case in Figure 5-12b, where at one grain a pile-up of particles is pushed whereas at another grain, particles of the same size or smaller are entrapped. No special care was taken to assure reproducible orientation of the grains or to record the crystalline orientation of the front.

5.3.3. Measured Critical Velocity

The critical velocities of small glass and zinc particles in many organic materials are given in Table 5-2. A careful examination of these results does not reveal any general pattern for the influence of molecular structure (polarity, molecule size) on critical velocity. Organics with a high viscosity (vanillin, thymol) have a low critical velocity. The results of a more extensive study on a few of these organics are presented in Table 5-3. Generally the highest critical velocities were observed in naphthalene, followed by, in order of decreasing $V_c$, durene, d-camphor and finally thymol and CBr$_4$. It was expected that the critical velocities in low entropy of fusion materials would be very low since their interfacial energy solid-melt is very low and therefore the front must be nearly "invisible" energetically. Our first measurements on succinonitrile and carbon tetrabromide confirmed this point. However, more careful measurements showed that the critical velocities in CBr$_4$ were not as low as initially measured. This discrepancy in measured $V_c$ may be due to the shape of the front: in the first set of measurements, the front might have been slanted or convex (Figure 5-16a); and since the front is difficult to see in CBr$_4$, such an error would have been extremely difficult to notice. The critical velocities in camphor and CBr$_4$ were, however, found
1. Low Entropy of Fusion Organics

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Melting point in °C</th>
<th>Growth Morphology</th>
<th>Critical Velocity (μm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Observed pure organic</td>
<td></td>
<td>Zn (2-8 μm)</td>
</tr>
<tr>
<td>Camphene</td>
<td>C_{10}H_{16}</td>
<td>40-45</td>
<td>51</td>
<td>dendritic</td>
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<td>Succinonitrile</td>
<td>CN-CH_{2}-CH_{2}-CN</td>
<td>53-55</td>
<td>54.5</td>
<td>flat front</td>
</tr>
<tr>
<td>Carbon tetrabromide</td>
<td>CBr_{4}</td>
<td>90-92</td>
<td>90.1</td>
<td>flat front</td>
</tr>
<tr>
<td>d-camphor</td>
<td>C_{10}H_{16}O</td>
<td>178-180</td>
<td>179.8</td>
<td>flat front</td>
</tr>
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</table>

2. High Entropy of Fusion Organics

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Melting point in °C</th>
<th>Growth Morphology</th>
<th>Critical Velocity (μm/s)</th>
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<td>Observed</td>
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<td>Zn (2-8 μm)</td>
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<tr>
<td>Eicosane</td>
<td>CH_{3}-(CH_{2})<em>{18}-CH</em>{3}</td>
<td>35.5-37.5</td>
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<td>prismatic</td>
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<tr>
<td>Thymol</td>
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<td>50-52</td>
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<td>flat front below 2μm/s</td>
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<td>Bibenzyl</td>
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<td>Chalcone</td>
<td>C_{6}H_{5}-CH-CH-CO-C_{6}H_{5}</td>
<td>55-57</td>
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<td>prismatic sluggish growth (glass former)</td>
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<td>o-Terphenyl</td>
<td>C_{6}H_{5}-C_{6}H_{4}-C_{6}H_{5}</td>
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<td>Cyclododecane</td>
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<td>61-63</td>
<td>flat below 2.2 μm/s needles above</td>
<td>1.3-2.1</td>
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<td>3-4 Dimethyl phenol</td>
<td>(CH_{3})<em>{2}C</em>{6}H_{3}OH</td>
<td>64.5-66.5</td>
<td>66</td>
<td>prismatic</td>
</tr>
<tr>
<td>3-5 Dimethyl phenol</td>
<td>(CH_{3})<em>{2}C</em>{6}H_{3}OH</td>
<td>64 - 65</td>
<td>68</td>
<td>needles</td>
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### 2. High Entropy of Fusion Organics

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<tr>
<th>Name</th>
<th>Formula</th>
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<th>Critical Velocity (µm/s)</th>
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<td>Hexatriacontane</td>
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<td>-</td>
<td>No?</td>
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<td>Phenanthrene</td>
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2. High Entropy of Fusion Organics

<table>
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<tr>
<th>Name</th>
<th>Formula</th>
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<th>Growth Morphology</th>
<th>Critical Velocity (µm/s)</th>
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<td>pure organic</td>
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<td>Zn (2–8 µm)</td>
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<td>Pyrocatechol</td>
<td>1,2(OH)₂C₆H₄</td>
<td>105</td>
<td>prismatic</td>
<td>10</td>
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<td>2-Naphtyl</td>
<td>C₆H₅COOC₁₀H₇</td>
<td>107-108</td>
<td>glass former</td>
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<td>benzoate</td>
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<td>107</td>
<td>spherulitic growth</td>
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<td>Resorcinol</td>
<td>C₆H₄·1,3(OH)₂</td>
<td>109-110</td>
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<td>~.4</td>
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<td>Iodoform</td>
<td>CHI₃</td>
<td>116-121</td>
<td>needles</td>
<td>&lt;.2</td>
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<tr>
<td>Cholesteryl</td>
<td>(liquid crystal)</td>
<td>123</td>
<td>needles</td>
<td>~.2</td>
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<tr>
<td>Acetate</td>
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Table 5-2: Critical velocities of zinc and glass particles in various organics (screening test), (other organic studied: anthrone, cyclohexanol, D+ galactose, hydroquinone, 2-methyl-1,4 naphtoquinone, p-tert-pentylphenol, pentacrythritol).
<table>
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<tr>
<th>Particles</th>
<th>size in μm</th>
<th>Durene</th>
<th>Naphthalene</th>
<th>Thymol</th>
<th>D-Camphor</th>
<th>CBr₄</th>
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<td></td>
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<tr>
<td>Glass</td>
<td>10</td>
<td>5-9</td>
<td>9-13</td>
<td>3.5</td>
<td>4-5</td>
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<td>2-3</td>
<td>1-1.3</td>
<td>.8-1</td>
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<td></td>
<td>90</td>
<td>0.6-1.2</td>
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<td>&lt;.2</td>
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<td>Zn(ZnO)</td>
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<td>30-40</td>
<td>8-14</td>
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<td>8</td>
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<td>1-2</td>
<td>&lt;.4</td>
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<td>pile-up</td>
<td>5-10</td>
<td>6-8</td>
<td>4-6</td>
<td>1.1.5</td>
<td></td>
</tr>
<tr>
<td>Cu(CuO)</td>
<td>2.5-4</td>
<td>&gt;33</td>
<td>&gt;40.5</td>
<td>19-25</td>
<td>30-40</td>
<td>5-9</td>
</tr>
<tr>
<td>Cu</td>
<td>4</td>
<td>13-18</td>
<td>&gt;38</td>
<td>10-12</td>
<td>25-30</td>
<td>3-5</td>
</tr>
<tr>
<td></td>
<td>30-40</td>
<td>2</td>
<td>(15μ) 10-12</td>
<td>2</td>
<td>&lt;.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0-6-0.7</td>
<td>.15</td>
<td>&lt;.2</td>
<td></td>
<td></td>
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<tr>
<td>Ni</td>
<td>4-5</td>
<td>19</td>
<td>&gt;39</td>
<td>5.5-6</td>
<td>12-20</td>
<td>5-10</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>6-7</td>
<td>16-20</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>3-4</td>
<td>8-9</td>
<td>1-3</td>
<td>&lt;.4</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>50</td>
<td>5-10</td>
<td>3-5</td>
<td>0.2-0.8</td>
<td>&lt;.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>3</td>
<td></td>
<td>1.6</td>
<td>0.1-0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>5-7</td>
<td>&gt;36</td>
<td>30-40</td>
<td>3-4</td>
<td>14-20</td>
<td>8-13</td>
</tr>
<tr>
<td>Mica</td>
<td>40</td>
<td></td>
<td></td>
<td>12</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>90</td>
<td></td>
<td></td>
<td>2-3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5-3: Critical velocities in μm/s of various particles
to be lower than in durene and naphthalene, these organics having approximately the same viscosity.

Among the high entropy of fusion materials, thymol (which has a much higher viscosity) had critical velocities much lower than durene or naphthalene.

The variation of $V_c$ with size is shown in Table 5-3 and Figure 5-20. $V_c$ varies as $R^{-n}$, with $n$ approximately equal to 1. In the case of smooth glass particles or copper particles (curve Cu (1)), $V_c$ drops faster, for large radii, than $1/R$. The uncertainty associated with these measurement is large, specially for the irregular zinc particles.

For small radii, the critical velocity curves were not observed to flatten as reported in other studies (i.e., that $V_c$ became independent of size for small enough particles). Such a flattening may occur but for sizes smaller than a few microns.

Metallic particles (Cu, Ni) have similar critical velocities higher than those for glass particles. The higher critical velocities observed with oxide coated particles (CuO, ZnO) are most likely due to the very rough surface of these particles. The germanium particles were observed to have a high $V_c$. In the horizontal set-up, mica flakes were pushed on their edge and since this edge was very rough, no valuable information could be gained from these measurements.

Results in camphor in the vertical and horizontal set-ups show that the critical velocities were lower in the vertical set-up (Table 5-4) even for the small particles. This result is somewhat surprising in the case of small particle since the frictional forces in this case should be
FIGURE 5-20 CRITICAL VELOCITIES OF Cu, Ni, Zn AND GLASS PARTICLES IN DURENE
<table>
<thead>
<tr>
<th>Particle</th>
<th>Vertical growth</th>
<th>Horizontal growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>glass 10 μm</td>
<td>1.4</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.8 - 1</td>
</tr>
<tr>
<td>Ni 4-5 μm</td>
<td>4-8</td>
<td>12 - 20</td>
</tr>
</tbody>
</table>

Table 5-4: Comparison of critical velocities for horizontal and vertical growth geometries in camphor
about equal to the gravitational forces. The lower $V_c$ measured in the vertical set-up may be due to preferential entrapment at the walls of the cell.

To test Chen's suggestion that an increase in body forces increases the critical velocity, a simpler and more reliable experiment was used. The critical velocity of large copper particles was measured in the horizontal set-up. Since the particles were large (200 μm) and slightly rough, the frictional forces were much lower than the gravitational forces (100). The jig was then tilted by plus or minus 2 to 5 degrees. This small change in angle was sufficient to change considerably the critical velocity. When the pressure exerted by the particles on the front was decreased by tilting the stage minus 3°, the large copper particles were pushed at about 1.2 μm/s. When the stage was horizontal or tilted +3° to increase the pressure exerted by the particle on the front, the particles were not pushed at 0.1 μm/s. On Figure 5-20, curve Cu-1 corresponds to the stage in an horizontal position whereas curve Cu-2 corresponds to a stage slightly tilted to decrease the frictional forces. This result was confirmed by similar experiments on 90 μm copper particles and by observation of particles pushed on the solidification front: in naphthalene, 20 μm glass particles were observed to be pushed up to 3 or 4 μm/s when they were rolling or gliding on the bottom glass plate but were pushed up to 11 μm/s when the particles were partly up the solidification front and were therefore not subjected to frictional forces. It was hoped that these results could be confirmed by an experiment in a microgravity environment; however, due to malfunctioning of the equipment, no result could be obtained from this experiment.
5.3.4. **Electrostatic Effect**

It was noted by Uhlmann et al. (13) that particles of various electrical charges and even charges of different sign had about the same critical velocity—i.e., rejection is not of electrostatic origin. This result was confirmed in the case of chalcone and camphor where many of the nickel, copper, germanium or glass particles were observed to be attracted by the front upon melting and were subsequently repelled up to about the same critical velocity as particles that had not been attracted by the front upon melting.

5.3.5. **Shape of the Front**

A complete description of the shape of the front behind a particle is deferred to Chapter 9. The front was observed to remain flat behind the particles in the case of prismatic growth (i.e., no visible cusping at a magnification of 200 X). At growth rates close to $V_c$, however, defects were often observed to form behind the particles (Figure 5-13). The front was observed to curve markedly behind the particles in the case of materials growing with a macroscopically smooth front.

5.3.6. **Conclusion**

In conclusion, the measurements of critical velocity, $V_c$, are subject to many uncertainties and errors. The following conclusions can, however, be drawn:

a. $V_c$ is a decreasing function of the matrix viscosity and for a given viscosity is lower for organic materials with a low entropy of fusion ($\Delta S<2k$) than for those with a high entropy of fusion ($\Delta S>7k$).

b. $V_c$ decreases with increasing particle size as $1/R$, but for large glass particle, this decrease is faster than $1/R$. For particles of
diameter as small as few microns, $V_c$ was observed to increase with decreasing particle size and no levelling off of $V_c$ was observed.

c. When the pressure expected by a particle on the solidification front is increased, $V_c$ decreases.
In Chapter 4, various methods of computing the disjoining forces of van der Waals origin were presented. The most reliable method is the macroscopic approach where the dispersion forces can be computed if the loss term of the dielectric constant, ε", is known over a broad range of frequencies. In this chapter, the determination of ε" and the computation of the Hamaker constant will be discussed. Due to equipment limitations, the optical properties of the various organics materials were only measured between $10^2$ and $10^{16}$ rad/s. Ninham and Parsegian showed, however, that in some cases most of the interaction forces between bodies are due to the i.r and near u.v. regions (76, 77) and therefore this limited frequency range may be sufficient.

6.1. Absorption Index

The absorbances, Y, of solid and liquid films of several organics have been measured by the present author between 185 nm and 25 μm. The absorption index, k, is equal to:

$$k = \frac{\lambda Y}{2\pi t} \quad (6.1)$$

and

$$Y = -\log_{10} \frac{I}{I_o} \quad (6.2)$$

where λ is the wavelength at which the absorbance is measured, t is the thickness of the sample, and I_o and I are the incident and transmitted luminous intensities.
6.1.1. **Infra-red**

In the range 2.5 - 25 \( \mu m \) the absorbances were measured on a Digilab "Computerized Fourier Transform Spectrophotometer". The organic samples were prepared in the molten state by pressing some liquid organic between two KBr disks (25 mm x 4 mm). The disks were mounted in an electrically heated brass jig. Leakage was prevented by two silicone rubber, ethylene-propylene or teflon O-rings. The thickness of the film of organic liquid was controlled by a ring of gold or aluminum foil and varied between 0.05 and 0.2 mm. The thickness of the sample was determined by difference, measuring the overall thickness of the two KBr disks with and without the organic film. The solid sample was prepared by slow cooling of the jig. The center of the disk was cooled faster-than the edges so that crystallization would start there. In this way, the number of defects appearing upon solidification was small. The sample was observed visually and an area free of bubbles or cracks was chosen for measurement of absorbance. The spectra of the liquid and solid were slightly different. For naphthalene the major differences were: the peaks occurring between 5 and 6.25 \( \mu m \) were broader and occurred at slightly higher wavelength in the liquid (shift of .03 to .05 \( \mu m \)); a large absorption peak at 12.74 \( \mu m \) was also broader and shifted by 0.15 \( \mu m \) in the liquid; two peaks at 7.19 and 7.35 \( \mu m \) in the solid were replaced by two peaks of different magnitude at 7.02 and 7.17 \( \mu m \) in the liquid; finally the relative height of the peaks were somewhat different between solid and liquid. In spite of these differences the overall spectra were very similar.

The absorbances of the organics were measured between 2 \( \mu \text{m} \) and 185 nm on a Carey 14 spectrophotometer. Due to the existence of high absorption peaks in the u.v., the samples had to be as thin as possible and, at the same time, continuous. The liquid sample was therefore pressed between two thick u.v. grade quartz disks (25 mm x 4 mm) polished to better than 2 wavelengths/inch. The sample was mounted in the same jig as for the i.r. measurements and the same precautions were taken to prepare the solid sample. The thinner samples prepared in this fashion were about 0.9 \( \mu \text{m} \) thick. The thickness of the sample was determined by weighing the quartz plates with and without the organic film. Measurements were done on a balance accurate to \( \pm 0.05 \) mg. For organics with a density of 1 g/cm\(^3\) the thickness of the film was therefore determined to \( \pm 0.1 \) \( \mu \text{m} \). In practice, the accuracy was not as high due to evaporation of the film at the edges and adsorption of water on the quartz plates. It was initially hoped that the thickness of the sample could be measured more accurately from the interference pattern due to reflection on the walls of the cell; the thickness, \( t \), of the film being deduced from the number \( N_F \) of fringes existing between two wavelengths \( \lambda_1 \) and \( \lambda_2 \) by the relation:

\[
t = \frac{N_F \lambda_1 \lambda_2}{2(\lambda_2 - \lambda_1)}
\]  

(6.3)

However, the fringes were clearly visible with an empty cell but were generally too weak when the cell was filled. This was due to the fact that the organics studied had an index of refraction close to that of quartz. The thickness of the solid samples was also determined by visual
observation of the coloured fringes.

Minute cracks or defects can reduce considerably the measured absorbance in regions of high absorbance. This result is best demonstrated by a numerical example. Let us consider a sample of thickness \( t \) and absorbance \( Y = 5 \). If 1% of the sample has a thickness \( 1/10 \) that of the rest of the sample, the measured absorbance will only be:

\[
Y' = - \log \left( \frac{10^{-0.5} + 99 \times 10^{-5}}{100} \right) = 2.50
\]

and more generally, for high absorbance peaks, if a fraction \( a \% \) has a thickness \( 1/b \) that of the rest of the sample, the measured absorbance \( Y' \) is:

\[
Y' = \frac{Y}{b} - \log \left( \frac{a}{100} \right)
\]  \hspace{1cm} (6.4)

if \( Y \) is the true absorbance.

The measured absorption curves were always lower for the solid than for the liquid. This difference may be due to the existence of micro-cracks not detected by visual observation. To check this result, the absorbance of solid naphthalene was also measured on flakes (\( \sim 60 \mu m \) thick) and thin films prepared by evaporation of a solution. But these samples always contained many defects and the measured absorbance at the largest peaks was always lower than that measured for a film between two quartz plates.

The maximum absorbance that could be measured was about 5. All the organics studied had a strong absorption peak between 190 and 220 nm; and the height of this peak could not be measured accurately. For example, in the case of naphthalene, if the data for solutions are extrapolated to
pure naphthalene, an absorbance of about 80 would be predicted at about 210 nm for a 1 μm thick specimen. To be able to measure such a peak by transmission, the sample must be only 0.05 μm thick (or thinner). Spectra for solids and liquids were quite different from the published spectra of these organics in solution. The absorbance curves for naphthalene are given in Figure 6-1. The spectrum of naphthalene in solution was shifted to lower wavelengths (with the exception of the peak at 210 nm) compared to the spectrum of the liquid or solid.

6.2. Computation and measurement of ε''

As discussed in Chapter 3, the refractive index, n, was computed from the absorption index k, by a Kramers-Kröning relation [Equation (3.56)]. This relation was lightly modified to normalize the data with the known refractive index at the sodium frequency, \( n_{Na} \).

\[
n(\xi) = n(n_{Na}) + P \int_1^{\omega_{2-\xi}^2} \frac{\omega_{Na}^2 - \omega_{Na}^2}{(\omega_{2-\xi}^2)(\omega^2-\omega_{Na}^2)} \cdot \omega k(\omega) \, d\omega \quad (6.5)
\]

When data were not available, the index of refraction of the liquid organics was measured with a simple V block refractometer (116, 117). The cell was mounted in a small tube furnace to control the temperature. This simple technique gave results with an accuracy of better than three significant figures.

This method of normalizing n was preferred to the frequently used technique of adding a large tail to the absorption curve in the far u.v., the size of this addition being chosen to compute the proper visible or i.r. indices of refraction. A large absorption peak must exist for all the organic studied beyond 6.6 eV (185 nm) since the index of refraction,
Figure 6-1: Absorbance of solid and liquid naphthalene. Sample thickness = 1.1 µm
computed directly from Equation (3.56) were much too low in the visible. Equivalently, if \( n \) was computed with Equation (6.5) the index for large energies did not tend toward unity.

The dielectric constants \( \varepsilon_1 \) and \( \varepsilon_2 \) were also directly measured between \( 10^2 \) and \( 1.5 \times 10^{11} \) rad/s at the Laboratory for Insulation at MIT. The measurements were done between static and \( 2 \times 10^8 \) rad/s on a modified Schering bridge, between \( 9.5 \times 10^8 \) and \( 3.1 \times 10^{10} \) rad/s by a standing wave technique in a coaxial line and above by a hollow wave-guide technique (134).

6.3. Computation of \( \varepsilon(i\xi) \)

6.3.1. Organic Materials

From the \( \varepsilon''(\omega) \) data, (known between \( \omega = 10^2 \) and \( \omega = 10^{16} \) rad/s—i.e., \( 6.6 \times 10^{-14} \) to \( 6.6 \) eV), \( \varepsilon(i\xi) \) was computed with Equation (3.52). The computation of \( \varepsilon(i\xi) \) proved, however, to be much more difficult than anticipated. In the Kramers-Kröning equation, to compute for example \( \varepsilon'(\omega_0) \), the integration is over a term in \( \omega \varepsilon''(\omega)/(\omega^2-\omega_0^2) \) and the value of \( \varepsilon'(\omega_0) \) depends mainly on the value of \( \varepsilon''(\omega) \) in the vicinity of \( \omega_0 \), the value of \( \varepsilon'' \) far from \( \omega_0 \) being negligible. To compute \( \varepsilon(i\xi) \) on the other hand, the integration is over a term in \( \omega \varepsilon''(\omega)/(\omega^2+\omega^2) \) and now the whole spectrum is important in computing \( \varepsilon(i\xi) \)—i.e., neglect of the high energy spectrum can give an erroneous result. For example, in the case of water where the spectrum is known over a very broad range of frequencies, if only the value of \( \varepsilon'' \) between 0 and 6 eV was used to compute \( \varepsilon(i\xi) \), at 0.1 eV, it was only equal to 1.5 instead of the value of
2.20 computed by using the whole spectrum. A tail can be added to the \( \varepsilon'' \) curve, the size of which is adjusted so that \( \varepsilon(0) \) is the static dielectric constant or that in the visible, far from large u.v. and i.r. peaks, \( \varepsilon(i\xi) \propto n^2 \). These techniques were tried; but since the quantity of interest to compute the disjoining force is the difference in the dielectric value for solid and liquid, a small change in extrapolation procedure was sufficient to change the magnitude and even the sign of the computed disjoining force.

A different approach used previously by Parsegian et al. (118), was also tried. In this case the complex dielectric constant was determined by fitting the known \( \varepsilon' \) and \( \varepsilon'' \) curves by a function:

\[
\varepsilon(\omega) = \varepsilon' + i\varepsilon'' = 1 + \frac{f_D}{\gamma_D - i\omega} + \sum \frac{f_r}{\omega_r^2 - \omega^2 - i\gamma_r\omega}
\]  

(6.6)

where the \( f_D, \gamma_D, f_r, \gamma_r, \omega_r \) are adjustable parameter. The function \( \varepsilon(i\xi) \) was then simply obtained by replacing \( \omega \) by \( i\xi \). The far u.v. peaks were replaced by a peak of amplitude\([\varepsilon(\hbar\omega=6 \text{ e.V.})-1] \) located at the first ionization potential (8.1 e.V.). But again the error associated with the introduction of this far u.v. peak was such as to render any computation of disjoining force meaningless.

6.3.2. **Particles**

\( \varepsilon(i\xi) \) was computed with Equation (3.52) for several materials, using the published dielectric spectra. In the case of metals, the \( \varepsilon'' \) curve was completed at low frequencies by a free electron model [Equation (3.65)]. The parameters \( \omega_p \) and \( g_i \) used in this equation were adjusted so that
the $\varepsilon'$ curve computed from $\varepsilon''$ through a Kramer-Krönig relation matched as close as possible the published curve; for copper, $\omega_p = 8.82$ e.V. and $1/g_i = 2.5 \times 10^{-14}$ s. At high frequencies ($\hbar \omega > 50$ to 80 e.V.) the dielectric constant was represented by a plasma equation [Equations (3.60) and (3.61)]. Between the upper limit of the known data (10 to 30 e.V.) and the plasma range, $\varepsilon$ was extrapolated by a log curve:

$$\varepsilon = -\alpha \ln(\hbar \omega) + \beta \quad (6.7)$$

The values of the various parameters used and the origin of the dielectric data are given in Table 6-1.

For gold, polystyrene and teflon, $\varepsilon(i\xi)$ was represented by Equation (6.6) using the parameters determined by Parsegian et al. (118).

6.4. **Disjoining forces**

6.4.1. **Water-Ice System**

To determine the order of magnitude of the disjoining forces of van der Waals origin, it was decided to study the system water-ice since the dielectric constants of these materials are known over a broad range of frequencies. $\varepsilon(i\xi)$ was represented by a sum of peaks [Equation (6.6)]. The data for water are those of Parsegian et al. (118) derived from the optical data of Heller et al. (131). The parameters for ice were computed using the optical data of refs. (131), (132) and (133) and are given in Table 6-2.

The range of log interpolation and the plasma frequencies are given in Table 6-1. The plasma frequency of ice was simply deduced from $\omega_p$ of water by correcting for the change in density.
<table>
<thead>
<tr>
<th>Material</th>
<th>Ref. for dielectric data</th>
<th>$\varepsilon_0$ (static)</th>
<th>$n^2$ (visible)</th>
<th>range of log. extrapolation in e.V.</th>
<th>$\omega_\rho$ in e.V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>(118)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Cu</td>
<td>(119)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>(120), (121)</td>
<td>16.0</td>
<td>17.8-80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>(123), (124)</td>
<td>11.75</td>
<td>4.76</td>
<td>22.2-70</td>
<td>32.2</td>
</tr>
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<td>MgO</td>
<td>(125), (126)</td>
<td>9.8</td>
<td>2.95</td>
<td>22.2-60</td>
<td>21.0</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>(130)</td>
<td>2.53</td>
<td>2.53</td>
<td>9-65</td>
<td>15.0</td>
</tr>
<tr>
<td>fused silica</td>
<td>(127), (128)</td>
<td>3.78</td>
<td>2.13</td>
<td>25-60</td>
<td>19.1</td>
</tr>
<tr>
<td>Teflon</td>
<td>(130)</td>
<td>2.0</td>
<td>1.96</td>
<td>20-70* or 12-70**</td>
<td>21.0</td>
</tr>
<tr>
<td>water</td>
<td>(118), (131)</td>
<td>87.0</td>
<td>1.78</td>
<td>25-80</td>
<td>21.4</td>
</tr>
<tr>
<td>ice</td>
<td>(131), (132)</td>
<td>3.2</td>
<td>1.72</td>
<td>25-70</td>
<td>20.5</td>
</tr>
</tbody>
</table>

Table 6-1: Parameters used in computing $\varepsilon(i\xi)$
<table>
<thead>
<tr>
<th>$\omega_r$ (eV)</th>
<th>$f_r$</th>
<th>$\gamma_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.24 \times 10^{-2}$</td>
<td>$4.97 \times 10^{-4}$</td>
<td>0</td>
</tr>
<tr>
<td>.102</td>
<td>$4.79 \times 10^{-3}$</td>
<td>0</td>
</tr>
<tr>
<td>.394</td>
<td>$4.66 \times 10^{-3}$</td>
<td>0</td>
</tr>
<tr>
<td>8.61</td>
<td>4.5</td>
<td>1.0</td>
</tr>
<tr>
<td>15.0</td>
<td>150.8</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Table 6-2: Parameters for ice used in Equation (6.6)
The computed $\epsilon(i\xi)$ are given in Figure 6-2. The disjoining forces for short interaction distances were then computed with Equation (3.38). The resulting Hamaker constants are given in Table 6-3. For oxide and metal particles, the Hamaker constants were of the order of $0.15$ to $1 \times 10^{-20}$ J. The range of variation was therefore relatively small. Metallic particles had a higher Hamaker constant than oxide particles. The Hamaker constant of Teflon was computed using two different extrapolation ranges: 20 to 70 e.V.* and 12 to 70 e.V.** In both cases, the Hamaker constant was quite small.

In Table 6-3 and in the following discussion, the subscripts 1, 2 and 3 will be used to design the particle, ice and water respectively. For most of the particles the constants $A_{11}$ and $A_{131}$ had been previously computed (61, 75); the agreement with the present computation is good.

Closer examination of the computation of $A$ shows that the region contributing most (90%) to the Hamaker constant is between 1 and 25 e.V. for the systems particle, water–ice $(A_{132})$ and 1 to 50 e.V. for the other computations. This result may seem surprising in view of the very large differences in $\epsilon(i\xi)$ in the low energy region. Below .01 e.V. for metallic particles $\epsilon_1 >> \epsilon_3 >> \epsilon_2$ and the integrand in Equation (3.39): $(\epsilon_1 - \epsilon_3)(\beta_1 + \epsilon_3) x (\epsilon_2 - \epsilon_3)(\beta_2 + \epsilon_3)$ is approximately equal to -1; and the contribution of the region below .01 e.V. to $A_{132}$ is approximately $(-3\hbar/4\pi) x 0.01 = -.04 \times 10^{-20}$ J—i.e., much smaller than the computed $A_{132}$.

In the visible, far from u.v. and i.r. peaks $\epsilon(i\xi)$ is approximately equal to the square of the index of refraction, $n^2$. Since $\epsilon(i\xi)$ tends toward unity at high energy (and is smaller than 1.35 at 50 e.V. for all
<table>
<thead>
<tr>
<th>Medium (1)</th>
<th>$A_{102}$</th>
<th>$A_{103}$</th>
<th>$A_{101}$</th>
<th>$A_{131}$</th>
<th>$A_{132}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>3.75</td>
<td>-</td>
<td>4.11</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>ice</td>
<td>-</td>
<td>3.75</td>
<td>3.43</td>
<td>.0489</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>11.32</td>
<td>12.42</td>
<td>37.90</td>
<td>24.33</td>
<td>-.92 ± 1.09</td>
</tr>
<tr>
<td>Cu</td>
<td>10.48</td>
<td>11.48</td>
<td>32.67</td>
<td>20.72</td>
<td>-.80 ± 1.01</td>
</tr>
<tr>
<td>Ge</td>
<td>9.69</td>
<td>10.63</td>
<td>28.66</td>
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<td>-.71 ± .90</td>
</tr>
<tr>
<td>N$_2$O</td>
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<td>10.26</td>
<td>25.91</td>
<td>11.52</td>
<td>-.61 ± .75</td>
</tr>
<tr>
<td>MgO</td>
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<td>7.13</td>
<td>12.54</td>
<td>2.87</td>
<td>-.32 ± .37</td>
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<tr>
<td>Polystyrene</td>
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<td>5.88</td>
<td>8.76</td>
<td>1.26</td>
<td>-.18 ± .25</td>
</tr>
<tr>
<td>fused silica</td>
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<td>5.55</td>
<td>7.60</td>
<td>.68</td>
<td>-.15 ± .18</td>
</tr>
<tr>
<td>Teflon</td>
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<td>4.45</td>
<td>4.88</td>
<td>.10</td>
<td>-.022 ± .071</td>
</tr>
<tr>
<td>**4.42</td>
<td>4.82</td>
<td>5.75</td>
<td>.23</td>
<td></td>
<td>-.048 ± .106</td>
</tr>
</tbody>
</table>

Table 6-3: Hamaker constants computed from the macroscopic theory [Equation (3.39)] for various particles (1) in the ice (2) water (3) system. $A_{132}$ computed from (a) optical data, (b) Equation (3.31), (c) Equation (3.32), (d) Equation (3.33). $A$ in 10$^{-20}$ J.

*, **, see Table 6-1.
the materials considered in this study), the amplitude of the dielectric curve between 1 and 50 e.V. will be strongly influenced by its value in the visible (1.5 to 3.1 e.V.) i.e. by \( n^2 \). \( A_{132} \) should therefore vary as:

\[
X = \frac{n_1^2 - n_3^2}{n_2^2 + n_3^2} \cdot \frac{n_2^2 - n_3^2}{n_2^2 + n_3^2}
\]

(6.8)

This ratio decreases in the order \( N_1, MgO, \) polystyrene, fused silica and teflon \((10^3X = -7.81, -4.24, -2.98, -1.53, -.82 \) respectively) which is the order of decreasing Hamaker constant \( A_{132} \). Hence, for the water-ice system, the Hamaker constant for short interaction distances can be estimated from the values of the index of refraction in the visible.

This result cannot be generalized to other systems since the relative position of the \( \varepsilon(\omega) \) curves for solid and liquid will be different. In general \( \varepsilon_2 < \varepsilon_3 \) at low energies (2 referring to the solid and 3 to the liquid); \( \varepsilon_2 > \varepsilon_3 \) in the visible (but the proximity of i.r. or u.v. peaks may change this inequality); \( \varepsilon_2 > \varepsilon_3 \) in the far u.v. if the only differences in the plasma frequency of solid and liquid are assumed to be due to changes in density. It is therefore difficult to predict à priori the value of the Hamaker constant and the region influencing most its value.

The Hamaker constants were also computed using the approximate macroscopic formulae [Equations (3.31), (3.32) and (3.33)--column (b), (c) and (d) respectively in Table 6-3]. These values are close to those computed with the macroscopic theory, with Equation (3.31) giving, as expected, an upper limit. Computations with slightly different expressions for \( \varepsilon(\omega) \) of water and ice did not, however, always give such a good agreement; Equation (3.32) in some cases predicted a positive Hamaker
constant whereas the macroscopic computations gave a negative value.

At large distances, the Hamaker constant is given by Equation (3.45). For a metallic particle, since the static dielectric constant, $\varepsilon_{10}$, is very large, the Hamaker constant is proportional to $(\varepsilon_{20} - \varepsilon_{30})^2 \sqrt{\varepsilon_{20} + \varepsilon_{30}}$; (the indices 2 and 3 refer to the solid and liquid respectively).

For high entropy of fusion organics, the static dielectric constant of the liquid is much larger than that of the solid and Equation (3.45) would therefore predict a large negative Hamaker constant. For low entropy of fusion organics, for which the static dielectric constant of the solid is only very slightly less than that of the liquid (the difference is only due to the change in density), the Hamaker should be negative but very small. If, on the other hand, by "static" is meant the values in the visible range, the answer is not so clear. In general, solids are denser than their liquids, and therefore $\varepsilon_{20} > \varepsilon_{30}$. Equation (3.45) would therefore predict that metallic particles would be attracted at large distances by the solidification front. For naphthalene the index of refraction is anisotropic. For some orientation $\varepsilon_{20} > \varepsilon_{30}$, whereas for others $\varepsilon_{20} < \varepsilon_{30}$. Particles should therefore be attracted by some faces and rejected by other.

6.4.2. Metallic systems

The Hamaker constant was computed for metallic systems using the published optical data for solid and melt (135). These data do not extend to vacuum u.v. and the plasma frequency at high energies is not given. Various extrapolation procedures have been used between 5 and 50 e.V., using for plasma frequency the values for the solid corrected for density.
Computation in the copper-silica system gave values of $+0.5 \times 10^{-20}$ J to $-0.3 \times 10^{-20}$ J, depending on the extrapolation procedure. The optical properties in the vacuum u.v. must therefore be known before the Hamaker constants can be computed.

6.5. Conclusion

In conclusion, the Hamaker constant of a system crystal-melt-particle can only be computed if the optical or dielectric properties of liquid and crystal are known over a very broad range of frequencies. Since several of the organics studied have a high vapor pressure, measurements in the vacuum u.v. by reflection are very cumbersome and the above requirement is difficult to satisfy. For the ice-water-particle system, the Hamaker constants were of the order of $-0.1$ to $-1 \times 10^{-20}$ J. The Hamaker constant was larger for metals than for oxides; and teflon has a very low Hamaker constant.
CHAPTER 7

ESTIMATION OF DISJOINING, DRAG, AND GRAVITATIONAL FORCES

In the previous chapters, the nature of the disjoining forces and the computation of the Hamaker constant have been discussed in detail. In this chapter, drag and disjoining forces will be computed for a few simple geometries to see how the balance of these two forces is affected by the shape of the solidification front and to gain a better understanding of the phenomenon of particle rejection. If the particle is subjected to no other external force, steady state rejection will occur when the ratio of drag and disjoining forces is equal to unity. The drag forces will also be compared with gravitational forces in a vertical solidification geometry to determine when the weight of the particles is an important factor.

7.1. Disjoining Force

To compute the disjoining force for various geometries, it is assumed that the dispersion forces are additive in terms of pairwise interactions—i.e., that the dispersion force between two macroscopic bodies can be computed by summing the interaction forces between all pairs of atoms. The results for some simple geometries (42) are given in Table 7-1 along with the definition of the London and Hamaker constants. The computations in the case of more complex geometries (rods, many layers bodies) and the general formulae for the simple cases shown in Table 7-1 have been reviewed by Nir (62). The limitations of this macroscopic approach have been discussed in Chapter 3. It is a useful approximation in many applications since an exact derivation by the macroscopic theories is
Table 7-1: Non-retarded and retarded forces between macroscopic bodies in vacuum, calculated by assuming pairwise additivity.
very difficult for shapes other than flat infinite layers or spheres. Even
the formulae for planes or spheres (70, 71, 72, 101) contain infinite
series and integrations to infinity and are very complex; contrarily to
the Hamaker formulae, geometrical and dielectric terms are intermixed. The
dependence of van der Waals force on geometry is therefore a function not
only of the dimensions and geometry of the bodies but also of the relative
value of these dimensions compared with the wavelength of the frequency
regime considered (62, 73). For short or long distances, however, the
macroscopic expression can be simplified to a Hamaker type equation where
the geometrical factor is independent of the dielectric properties and
is the same as that derived in the microscopic approach. One can therefore
hope that for more complex geometries and over limited ranges of distances,
the same will be approximately true, and that the ratio of the forces for
two different geometries will be the same when the forces are computed
with this simplified microscopic treatment and when the macroscopic theory
is used.

7.1.1. Force Between a Sphere and a Tubular Element

The force between a sphere and a tubular element, having a common
axis of symmetry (Figure 7-1-a) is derived in Appendix B and is equal to:

\[ \frac{dF}{dis} = -\frac{1}{3} \frac{A \, dr}{\ell^3 (1 + \frac{\ell}{2R})^3} \quad \text{if } \ell \ll R \]  (7.1)

where \( A \) is the Hamaker constant, \( r \) the radius of the tube of thickness
\( dr \), \( \ell \) the distance cylinder-sphere and \( R \) the radius of the sphere.
This expression will be used in most of the subsequent derivations.
FIGURE 7-1 FORCES BETWEEN A HALF SPACE AND (a) A SPHERE AND (b) A PORTION OF SPHERE.
7.1.2. **Sphere - Flat Front**

In the case of a flat front at a distance \( h_0 \) from a sphere (Figure 7-1a) the force is simply:

\[
F_{\text{dis}} = - \int_{h_0}^{\infty} \frac{1}{3} \frac{A(R+\ell)}{\ell^3 (1 + \frac{\ell}{2R})^3} d\ell
\]  

(7.2)

since \( r \, dr = (R+\ell)d\ell \), and after integration,

\[
F_{\text{dis}} = - \frac{AR}{6h_0^2} \cdot \frac{1}{(1 + \frac{h_0}{2R})^2}
\]  

(7.3)

If \( h_0 << R \)

\[
F_{\text{dis}} \approx - \frac{AR}{6h_0^2}
\]  

(7.4)

which is the expression previously given in Table 7-1. In the rest of this chapter, the disjoining force between a sphere and a half-space [Equation (7.4)] will be referred to as \( F_{\text{dis}}^o \). It is interesting at this point to compute the force between a portion of sphere and a half-space (Figure 7-1b). The force is obtained by integrating the force between an atom and a half-space (Table 7-1) over the volume of the portion of sphere. With the assumption that the distance \( h_0 \) is much smaller than the radius of the particle, this force is approximately given by:

\[
F_{\text{dis}} = - \frac{AR}{6h_0^2} \cdot \frac{H}{H+h_0} \cdot \left[ \frac{H(H+3h_0)}{(H+h_0)^2} - \frac{3h_0}{R} \right]
\]  

(7.5)

where \( H \) is the thickness of the particle. If \( H = h_0 \), the force is already equal to half of the force \( F_{\text{dis}}^o \) between a half-space and a whole sphere; and if \( H = 10h_0 \), \( F_{\text{dis}} = 0.98 \, (F_{\text{dis}}^o) \). Since \( h_0 << R \), a very small fraction
of the sphere accounts for the computed disjoining force.

7.1.3. Spherical Front Concentric to the Sphere

Here again, the integration of Equation (7.1) is straightforward
(see Figure 7-2-a)

\[ F_{\text{dis}} = -\frac{A}{3} \cdot \int_{h_0}^{\infty} \frac{r_o}{h_o(1 + \frac{h_o}{2R})^3} \, r_o \, dr - \frac{A}{3} \int_{h_o}^{\infty} \frac{(R + \xi) d\xi}{\xi^3(1 + \frac{\xi}{2R})^3} \]  

(7.6)

The second term is exactly the force between a sphere and a flat front at
a distance \( h_o \). If \( h_o \ll R \),

\[ F_{\text{dis}} = -\frac{AR}{6h_o} \left( \frac{r_o}{Rh_o} + 1 \right) \]  

(7.7)

or

\[ F_{\text{dis}} = (F_{\text{dis}})_o \cdot \left( \frac{r_o}{Rh_o} + 1 \right) \]  

(7.8)

If the front is hemispherical, i.e., \( r_o = R + h_o \), the force of interaction
is equal to \( -\frac{AR^2}{6h_o^3} \) and is \( \frac{R}{h_o} \) times larger than for a flat front. In all
the cases studied experimentally, \( R \) is at least of the order of a few
microns and \( h_o \) is generally of the order of a few nanometers. This ratio
is therefore at least equal to \( 10^3 \).

7.1.4. Spherical Front non-Concentric to the Sphere

Consider a solidification front with a radius of curvature of \( R/\alpha \),
not concentric to the sphere (Figure 7-2-b). The force between the
sphere and front is:

\[ F_{\text{dis}} = -\frac{A}{3} \int_{0}^{r_o} \frac{rdr}{\xi^3(1 + \frac{\xi}{2R})^3} - \frac{AR}{6\xi^2} \left( \frac{1}{(1 + \frac{\xi}{2R})^2} \right) \]  

(7.9)
FIGURE 7.2 FORCE BETWEEN A SPHERE AND A SOLID WITH A SPHERICAL INTERFACE (a) CONCENTRIC TO THE SPHERE, OR (b) NON CONCENTRIC
From the geometry:

\[(R+l)^2 = r^2 + \left( R + h_0 - \frac{R}{\alpha} + \sqrt{\frac{R^2}{\alpha^2} - r^2} \right)^2 \tag{7.10}\]

After integration and some simplifications, as \(h_0\) and \(l \ll R\),

\[F_{\text{dis}} = -\frac{AR}{6h_0} \left\{ \frac{1-h_0/l}{1} \left[ \frac{1}{\alpha - 1} - \frac{h_0}{R} \right] - 2 \frac{h_0}{R} + \left( \frac{h_0}{R} \right)^2 \right\} \tag{7.11}\]

Equation (7.11) reduces to Equation (7.3) in the cases of a flat interface \((\alpha = 0)\) and to Equation (7.7) in the case of a front concentric to the particle \((R/R_0 = R+h_0)\). For a slightly curved interface \((R/R_0 > R)\) close to the particle \((h_0 \ll R)\) Equation (7.11) simplifies to:

\[F_{\text{dis}} \approx (F_{\text{dis}})_0 \cdot \frac{h_0^2}{1 - \alpha} \tag{7.12}\]

7.1.5. **Rough Particle**

An exact mathematical treatment for the case of a rough particle is extremely difficult. This problem can, however, be satisfactorily treated if the radius of the irregularities is less than a few microns. In this case, when the particle is pushed, the solidification front will not follow each irregularity since the increase in surface energy would be too large (this point is well documented in Chapter 9 where the shape of the solidification front in a complex temperature profile is discussed); and the shape of the front is more like curve 1 in Figure 7-3 than like curve 2. Since the radius of curvature of the front is much larger than the radius \(R_1\) of the small irregularities, in the computation of the disjoining force between irregularities and solid, the solidification
FIGURE 7-3 SHAPE OF THE FRONT BEHIND A ROUGH PARTICLE
front can be assumed to be flat; and the disjoining force for each asperity of radius, \( r_i \), and height, \( H_i \), is given by Equation (7.14). The number, \( N \), of asperities in contact with the front can be computed by dividing the area of the particle in contact with the front by the area occupied by each asperity.

Only the component of the force in the \( z \) direction should be taken into account in summing the individual forces; this is equivalent to using a corrected number of asperities, \( N' \), obtained by dividing the projection of the zone of contact on a plane normal to the \( z \) direction by the area occupied by each irregularity. The area occupied by each irregularity is (see Figure 7-3-a).

\[
S_i = 2 \sqrt{3} \ r_i^2
\]  
(7.13)

assuming a close packing of the asperities, or since

\[
r_i = \sqrt{2H_iR_i} \sqrt{1 - \frac{H_i}{2R_i}}
\]  
(7.14)

\[
S_i = 4 \sqrt{3} H_i R_i \left(1 - \frac{H_i}{2R_i}\right)
\]  
(7.15)

The area of the projection of the zone of contact is:

\[
S = \pi(R^2 - H^2)
\]  
(7.16)

and the corrected number of asperities, \( N' \), is equal to

\[
N' = \frac{\pi(R^2 - H^2)}{2\sqrt{3} H_i (2R_i - H_i)}
\]  
(7.17)

If the solidification front is only slightly curved, Equation (7.16) should be replaced by \( S = \pi r_o^2 \) where \( r_o \) is the radius of the zone of near contact.
The contribution of the irregularities to the disjoining force is therefore:

\[
(F_{\text{dis}})_i = -N' \cdot \frac{AR_i}{6h_o^2} \frac{H_i}{H_1 + h_o} \left[ \frac{H_i(H_i + 3h_o)}{(H_i + h_o)^2} - \frac{3h_o}{R_i} \right] 
\]  
(7.18)

The contribution of the smooth particle is given by the formulae previously derived, using a minimum distance front-particle equal to \((H_i + h_o)\). For example, in the case of an hemispherical front concentric to the particle [Equation (7.7)], the disjoining force is:

\[
F_{\text{dis}} = (F_{\text{dis}})_i - \frac{AR_i^2}{6(h_o + H_i)^3} 
\]  
(7.19)

and replacing \((F_{\text{dis}})_i\) by its value with the further assumptions that \(h_o \ll R_i\) and \(h_o \ll H_i\)

\[
F_{\text{dis}} = -\frac{AR_i^2}{6} \left[ \frac{\pi R_i}{2\sqrt{3} H_i(2R_i - H_i)h_o} + \frac{1}{H_i^3} \right] 
\]  
(7.20)

If the distance \(H_i\) is larger than 2 or 3 \(h_o\), the contribution of the smooth sphere is negligible and the disjoining force is simply the sum of the forces on the irregularities. On the other hand, if the ratio \(H_i/R_i\) is small and if \(H_i\) is smaller than \(h_o\), for computation purposes, the particle can be considered to be smooth, the minimum distance front-particle being equal to \(h_o\).

Even very small irregularities are sufficient to change considerably the disjoining force. To illustrate this point, let us consider the case of a large particle \((R = 100 \, \mu m)\) and a slightly curved front \((\alpha = \frac{1}{3}; r_0 = 3 \, \mu m; h_o = 20 \, nm)\). These values were chosen according to Chernov's results for a smooth particle. See Table 4-4). If the particle has
irregularities \( R_i = 1 \, \mu m; H_i = 50 \, nm, h_o = 4.3 \, nm \) the number of irregularities in contact with the front is \( N = 82 \) and the contribution of these irregularities to the disjoining force is [(Equation (7.18))]:

\[
(F_{\text{dis},i}) = 15.5 \times 10^{10} \left( - \frac{A}{6} \right) \quad N.
\]

The disjoining force due to the smooth particle is [Equation (7.11)]

\[
(F_{\text{dis},\text{part}}) = 2.59 \times 10^{10} \left( - \frac{A}{6} \right) \quad N.
\]

The total disjoining force is therefore

\[
18.1 \times 10^{10} \left( - \frac{A}{6} \right) \quad N.
\]

compared to a force of

\[
36.2 \times 10^{10} \left( - \frac{A}{6} \right) \quad N.
\]

on a smooth particle at a distance \( h_o \) from the front. The force on the rough particle is therefore only about 1/2 of the force on the smooth particle, and the irregularities account for 85% of the total disjoining force. Therefore for small distances \( h_o \), most generally the disjoining force may be considered to be only due to the irregularities.

7.1.6. Large Distances Front-Particle

For large interaction distances \( h_o > 50 \, nm \) the disjoining force should be computed by using the retarded form of the pair-interaction force (Table 7-1). The derivations are similar to the one presented for non retarded forces. The results will not be presented, however, since the distances of interest in particle pushing are small.
7.2. Drag Force

When a particle is pushed by a solidification front, fresh liquid must constantly flow behind the particle to maintain a liquid film. A pressure gradient must therefore exist behind the particle; and this pressure gradient induces a drag force on the particle, pressing it against the front. For a spherical particle moving with a velocity \( V \) in a liquid of viscosity \( \eta \), the drag force is expressed by Stoke's law:

\[
F_D = K \cdot \eta V
\]  
(7.21)

where

\[
K = 6 \pi R
\]  
(7.22)

For non spherical particles, Equation (7.21) is still valid if a different geometrical factor \( K \), is used. For example, in the case of a disk of radius \( R \), \( K \) is equal to \( 16R \) (102). This expression is not however valid when the particle is very close to a solidification front, since the flow of liquid is perturbed by the front. Carrier (12) showed that for a spherical particle at a distance \( h_o \) from a flat solidification front, the force is very much larger and is equal to:

\[
F_{D_o} = 6\pi \eta \frac{\rho_s}{\rho_l} \frac{R^2}{h_o} \cdot V
\]  
(7.23)

The term \( \rho_s/\rho_l \) where \( \rho_s \) and \( \rho_l \) are the densities of the solid and liquid respectively was neglected by Carrier and is introduced here for completeness. In the rest of this chapter, this drag force will be referred to as \( F_{D_o} \). For a spherical interface with radius of curvature \( R/\alpha \), Bolling and Cisse (9) showed that if the dimpled region is small
The method used to compute the drag force is best illustrated by considering the case of a disk at a distance \( h_0 \), from a flat solidification front (Figure 7-4).

7.2.1. Disk

For all the growth rates studied in practice, the Reynold's number is low and the flow behind the particle is laminar. The radial velocity, \( u_r \), of the fluid is zero at the front and along the disk and if the gap thickness is small in an hydrodynamic sense (i.e., less than 0.5 mm or so), the velocity distribution can be approximated by a parabolic distribution:

\[
\begin{align*}
    u_r &= C(r) \cdot z \left( h_0 - z \right) \\
    \end{align*}
\]

The term \( C(r) \) is determined from a mass balance equation: considering a liquid cylinder of radius \( r \) behind the disk, the mass of liquid entering the cylinder is equal to the mass of material necessary to grow the solid at a rate \( V \):

\[
\begin{align*}
    - 2 \pi r \rho_1 \int_{0}^{h_0} u_r (r,z) \, dz &= \rho_s V \cdot \pi r^2 \\
    \end{align*}
\]

Solving this equation, the radial velocity can be written:

\[
\begin{align*}
    u_r (r,z) &= - \frac{3V}{h_0^3} \cdot \frac{\rho_s}{\rho_1} \cdot \frac{r}{z} \cdot (h_0 - z) \\
    \end{align*}
\]

The pressure gradients in the fluid are given by the Navier-Stokes equations. For an incompressible fluid with a constant viscosity and for steady state conditions, these equations can be written in cylindrical coordinates, neglecting the effect of gravity:
FIGURE 7-4 DRAG FORCE ON A DISK

FIGURE 7-5 DRAG FOR A SPHERE (CONCENTRIC INTERFACE)
\[
\frac{\partial P}{\partial r} = \eta \left( \nabla^2 u_r - \frac{u_r}{r^2} - \frac{2}{r^2} \frac{\partial u_\theta}{\partial \theta} \right) \\
\frac{1}{r} \cdot \frac{\partial P}{\partial \theta} = \eta \left( \nabla^2 u_\theta - \frac{u_\theta}{r^2} + \frac{2}{r^2} \cdot \frac{\partial u_r}{\partial \theta} \right) \\
\frac{\partial P}{\partial z} = \eta \nabla^2 u_z
\]

(7.28)

where \( P \) is the liquid pressure and \( \nabla^2 \) the Laplacian. It is assumed that
the flow is radial, i.e., \( u_\theta = u_z = 0 \) and that the pressure varies
appreciably only in the radial direction; hence, the Navier-Stokes
equations simplify to:

\[
\frac{dP}{dr} = \eta \left( \nabla^2 u_r - \frac{u_r}{r^2} \right) 
\]

(7.29)

Replacing \( u_r \) by its value [Equation (7.27)] the pressure gradient
becomes:

\[
\frac{dP}{dr} = 6\eta \frac{\rho_s}{\rho_1} \frac{V}{h_o} \frac{r}{r^3} 
\]

(7.30)

and the pressure at a distance \( r \) is obtained by integration:

\[
P(r) = P(R) - 3 \eta \frac{\rho_s}{\rho_1} \frac{V}{h_o} \frac{r^2}{R^2} (R^2 - r^2)
\]

(7.31)

The drag force acting on the disk is:

\[
F_D = \int_0^R 2\pi r \left[ P_o - P(r) \right] dr
\]

(7.32)

if \( P_o \) is the hydrostatic pressure in the liquid. Assuming that at a
distance \( R \), the pressure is practically equal to the hydrostatic pressure
i.e., \( P(R) = P_o \), the drag force becomes:

\[
F_D = \frac{3}{2} \pi \frac{\rho_s}{\rho_1} \eta \frac{V}{h_o} \frac{R^4}{3}
\]

(7.33)
Comparing this result to the drag force on a sphere of radius \( R \) [Equation (7.23)] one sees that the drag force on a disk is larger by a factor
\[
\left( \frac{R}{2h_0} \right)^2
\]
than that on a sphere:
\[
F_D = F_{D_0} \times \left( \frac{R}{2h_0} \right)^2
\]  \( \text{(7.34)} \)

In this computation, the drag force due to the interruption of the flow of liquid, moving a velocity \( V \), by the top of the particle should also be considered. This "top" drag force is however very much smaller than the "bottom" drag force due to the flow of liquid between particle and solidification front and can be neglected.

To gain a better understanding of the phenomenon, it is interesting to compute the pressure gradient that must exist in the liquid film to drive the flow of fresh liquid [Equation (7.31)]. Assuming a viscosity \( \eta = 0.5 \) cpoise \( (5 \times 10^{-4} \) S.I. u.), \( \frac{\rho_s}{\rho_l} = 1 \) and a velocity \( V = 1 \) \( \mu \text{m/s} \), for a disk of radius 10 \( \mu \text{m} \), the pressure difference between center and edge of the disk is \( \Delta P = 1.5 \times 10^{-19} / h_0^3 \) Pascals. The pressure gradient is computed in Table 7-2. The pressure gradient necessary to induce flow behind the particle is very large for small \( h_0 \), and becomes of the order of the cavitation pressure, \( \Delta P_{\text{cav}} \), if \( h_0 \) is less than a few nm. For camphor, \( \Delta P_{\text{cav}} \) is of the order of 40 atm. (103).

7.2.2. \underline{Front Concentric to the Sphere}

In this case (Figure 7-5), the tangential velocity, \( u_\phi \), can be assumed to follow a parabolic distribution:
\[
U_\phi = C(\phi) \cdot (\rho - R) (R + h_0 - \rho)
\]  \( \text{(7.35)} \)
<table>
<thead>
<tr>
<th>$h_o$ (nm)</th>
<th>$\Delta P$ (Pascals)</th>
<th>$\Delta P$ (atm)</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>$1.5 \times 10^8$</td>
<td>1480</td>
</tr>
<tr>
<td>5</td>
<td>$1.2 \times 10^6$</td>
<td>12</td>
</tr>
<tr>
<td>10</td>
<td>$1.5 \times 10^5$</td>
<td>1.5</td>
</tr>
<tr>
<td>20</td>
<td>$1.9 \times 10^4$</td>
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<td>$2.3 \times 10^{-2}$</td>
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<tr>
<td>80</td>
<td>$2.9 \times 10^2$</td>
<td>$2.9 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

**Table 7-2:** Pressure gradient behind a disk of radius 10 μm
where \( \rho \) is the radial distance; and the constant \( C(\phi) \) is again determined from a mass balance:

\[
\begin{align*}
\phi = - \frac{3VR}{h_o} \cdot \frac{\rho}{\rho_1} \sin \phi \cdot (\rho - R + h_o - \rho)
\end{align*}
\]  

(7.36)

If the radial and cylindrical velocities are considered to be zero, the Navier-Stokes in spherical coordinates take the form:

\[
\begin{align*}
\frac{\partial P}{\partial \rho} &= - \frac{2n}{\rho^2} \left( \frac{\partial u}{\partial \phi} + u \cot \phi \right) \\
\frac{\partial P}{\rho \partial \phi} &= \eta \left[ \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left( \frac{3}{2} \right) \frac{\partial (\rho^2 u)}{\partial \rho} + \frac{1}{\rho^2 \sin \phi} \frac{\partial}{\partial \phi} \left( \sin \phi \frac{\partial u}{\partial \phi} \right) - \frac{u}{\rho \sin \phi} \right]
\end{align*}
\]  

(7.37)

After replacing \( u \) by the expression previously found [Equation (7.36)], the second equation becomes:

\[
\begin{align*}
\frac{\partial P}{\partial \phi} &= - 6 \frac{\rho}{\rho_1} \eta \frac{V}{h_o} \frac{R}{3} \left[ -2\rho + \frac{R(R+h_o)}{\rho} \right] \sin \phi
\end{align*}
\]  

(7.38)

and after integration,

\[
P(\phi, r) = 6 \frac{\rho}{\rho_1} \eta \frac{V}{h_o} \frac{R}{3} \left[ -2\rho + \frac{R(R+h_o)}{\rho} \right] \cos \phi + f(\rho)
\]  

(7.39)

where \( f(\rho) \) is a function of \( \rho \) defined by the first differential equation.

Since the gap thickness, \( h_o \) is very small, \( f(\rho) \) can be considered to be constant and \( \rho \) is to a good approximation equal to \( R \); therefore,

\[
P(\phi) = P(\phi) - 6 \frac{\rho}{\rho_1} \eta \frac{V}{h_o} \frac{R}{3} \left( \cos \phi - \cos \phi_M \right)
\]  

(7.40)

The drag force is:

\[
P_D = \int_{\phi_o}^{\phi_M} \left[ P_0 - P(\phi) \right] 2\pi R^2 \sin \phi \cos \phi \, d\phi
\]  

(7.41)
Assuming again that the pressure at $\phi = \phi_M$ is the static hydrostatic pressure, i.e., $P_o = P(\phi_M)$, the drag force becomes:

$$F_D = \frac{1}{3} \left( \frac{R}{h_o} \right)^2 \left( \cos^3 \phi_M + 2 - 3\cos \phi_M \right) F_{D_o} \quad (7.42)$$

If the front is hemispherical,

$$F_D = \frac{2}{3} \left( \frac{R}{h_o} \right)^2 \cdot F_{D_o} \quad (7.43)$$

For a particle of radius 1 $\mu$m, located at a distance $h_o = 5$ nm from a solidification front, the drag force for a hemispherical interface is $2.7 \times 10^4$ times larger than for a flat interface. When $\phi_M = 90^\circ$, $\Delta P$ becomes of the order of the cavitation pressure if $h_o$ is less than 4 nm (.65 nm if $\phi_M = 5^\circ$).

7.2.3. Spherical Front non Concentric to the Particle

For this case, (Figure 7-6) as for the case of a flat interface, the problem should be treated in bispherical coordinates. In this way, the velocities tangential to the particle or solidification front, $u_{\psi}$, are directly defined, and the boundary condition can be exactly written. As for the previous cases, the velocity (now $u_{\psi}$) can be approximated by a parabolic distribution. But the Navier-Stokes equations are more complex, and the mass balance equation used to determine the constant of proportionality in the expression for the velocity, $u_{\psi}$, is not exactly solvable. This problem will therefore be treated by using similar approximation to the ones used for a flat front:

a. The radial velocity, $u_r(z)$ follows a parabolic distribution at a given $r$, and $u_z$, the vertical component of the velocity is equal to
FIGURE 7.6 SPHERICAL INTERFACE
\[ u_r(r, z) = -\frac{3rV}{h^3} \cdot \frac{\rho_s}{\rho_1} (h + S - z)(z - s) \]  

(7.44)

where the gap thickness

\[ h = h_o + \frac{r^2}{2R} (1-\alpha) \]  

(7.45)

and \( S(r) \) is defined in Figure 7-6.

\[ S(r) = \frac{r^2 \alpha}{2R} = \frac{(h-h_o)\alpha}{1-\alpha} \]  

(7.46)

This approximation for \( u_r \) is only valid close to the axis of symmetry and will be very poor if the radius, \( r \), is larger than 0.2 or 0.3R. The pressure distribution in the radial direction is obtained by solving the Navier-Stokes equations; but when the radial velocity is explicitly used [Equation (7.44)] these equations become very cumbersome and a second approximation is used.

b. The gap thickness is considered to vary slowly enough with \( r \) to neglect its variations with \( r \) and the Navier-Stokes equations can be simplified:

\[ \frac{dP}{dr} = \frac{6Vr}{h^3} \cdot \frac{\rho_s}{\rho_1} \cdot \eta \]  

(7.47)

as in the case of a disk where the thickness \( h \) is constant.

These very crude approximations are sufficient, since most of the drag force is due to the flow of liquid in the small region behind the particle where the solidification front and particle are nearly in contact. This fact was checked in the numerical computation of the drag force for various shapes of the front (Chapter 9).
The differential equation (7.47) can now be integrated.

\[
\text{for } r < r_o, \quad \Delta P = P(r) - P(R) = \frac{6\rho_s}{\rho_1} \nu \eta \left( -\frac{h_2}{2h_1} + \frac{1}{h_1} - \frac{1}{2h_2} - \frac{R}{2(1-\alpha)} \left( \frac{1}{h_2} - \frac{1}{h_1} \right) \right)
\]

(7.48)

and if the zone of close approach is small,

\[
h_1 = h_o + \frac{r_o^2(1-\alpha)}{2R}
\]

(7.49)

and

\[
\Delta P = -\frac{6\rho_s}{\rho_1} \nu \eta \cdot \frac{R}{2(1-\alpha)} \left( \frac{1}{h_2} - \frac{\alpha}{h_1} \right)
\]

(7.50)

For example, using the values found by Chernov et al. (31) for a smooth particle pushed at the critical velocity (\(R=10 \text{ } \mu m\), \(r_o=0.6 \text{ } \mu m\), \(h_o=9.3 \text{ } \text{nm}\), \(\alpha=0.35\), \(\rho_s/\rho_1=1\), \(V_c=3.2 \text{ } \mu m/s\), \(\eta = 5 \times 10^{-4} \text{ S.I.}\)), \(\Delta P=780\) Pascals or \(7.7 \times 10^{-3}\) atm. A similar computation, using the values found by Bolling and Cissé (9) (\(R=10 \text{ } \mu m\), \(\alpha=.229\), \(r_o=1.31 \text{ } \mu m\), \(h_o=1.6 \text{ } \text{nm}\), \(V_c=3.1 \text{ } \mu m/s\)) gives a pressure gradient \(\Delta P=0.24\) atm. This high value is due to the very small value of \(h_o\).

Summing Equation (7.48) over the zone of strong interaction, the resulting drag force is, after simplifications:

\[
F_D = F_{D_o} \left[ \frac{h_1-h_o}{(1-\alpha)h_1} + \frac{h_o(h_1-h_o)h_2}{(1-\alpha)h_1 R} + \frac{h_h^2}{h_1R^2} \right]
\]

(7.51)

For small \(r_o\), this expression can be simplified to

\[
F_D = F_{D_o} \times \frac{1}{(1-\alpha)^2}
\]

which is the expression found by Bolling and Cissé (9).
7.2.4. General Case

When the front is neither flat nor spherical, the drag force can be estimated by using the same approximations as previously. After integration, the Navier-Stokes equations become:

\[ P(R) - P(r) = 6 \frac{\rho_s}{\rho_1} \nu \eta \int_r^R \frac{x dx}{h^3(x)} \]  \hspace{1cm} (7.52)

where \( h \) is the thickness of the liquid layer. If the pressure \( P(R) \) is assumed to be the unperturbed hydrostatic pressure at the level of the particle, the drag force is approximately:

\[ F_D = \int_0^R [P(R) - P(r)] \cdot 2\pi r \, dr \]  \hspace{1cm} (7.53)

Such approximations will be poor if the front wraps around the particle, but will be adequate for the general use where the front is nearly flat. These formulae, (7.52) and (7.53) will be used in Chapter 9 to compute the drag force when the shape of the front is known numerically.

7.2.5. Rough Particle

An exact computation of the drag force on a rough particle is mathematically too complex. Simplifying assumptions must therefore be used. As a limiting case, let us consider the case of a large particle pushed by a few small ones (Figure 5-15). The drag force in this case is simply the sum of the drag forces on the \( N \) small particles and on the large one, and for a flat front:

\[ F_D = 6\pi \eta V \left( \frac{R_1^2}{h_o} + \frac{R^2}{R_1 + h_o} \right) \]  \hspace{1cm} (7.54)
where $R$ and $R_i$ are the radii of large and small particles and $h_o$ the minimum distance small particle-front. If $R=50 \ \mu m$, $R_i=1 \ \mu m$, $N=3$, $h_o=4 \ \text{nm}$, $F_D = 6\pi \eta V(.75 \times 10^{-4} + 25 \times 10^{-4})$. Most of the drag force is due in this case to the large particle, but it is much smaller than if there were no small particle present to increase the thickness of the liquid film.

For the more general case of small irregularities, the drag force can also be considered to be the sum of the drag force on the $N'$ irregularities close to the front and of the drag force on the large particles. At the scale of the irregularities, the front can be considered flat and since most of the drag force on an irregularity is due to a small zone where front and irregularity are nearly in contact, the overall shape of the irregularity is irrelevant. The drag force on each irregularity is therefore given by Equation (7.23) for a sphere close to a flat front. The contribution of the large particle to the drag force is more difficult to compute since the thickness of the liquid film is variable. However, for a good approximation for irregularities of radius $R_i$ much larger than the minimum distance irregularity-front, $h_o$ (Figure 7-3) the film can be considered to be of constant thickness equal to $\frac{3}{4} \cdot (h_o + H_i)$ where $H_i$ is the height of the irregularities (see Appendix C).

For example in the case of a slightly curved front of radius of curvature $R/\alpha$ and a rough particle of radius $R$ covered with irregularities of radius $R_i$ and height $H_i$

$$F_D = 6\pi \eta \rho S \left[ \frac{R_i^2}{h_o} + \frac{4R^2}{3(1-\alpha)^2(h_o+H_i)} \right]$$

(7.55)
For $R = 100 \mu m$, $a = 0.35$, $R_1 = 1 \mu m$, $H_1 = R_1/2$, if the radius of the zone of near contact is $3 \mu m$ (See Table 4-4), $N_1 = 11$ [Equation (7.15)], and $h_o = 4$ nm,

$$F_D = 6\pi \eta \frac{\rho_s}{\rho_1} 10^{-6}(2750 + 62615)$$

i.e. most of the drag force is due to the large particle and an increase in $h_o$ would further decrease the contribution of the irregularities.

### 7.3. Comparison of Drag Force and Disjoining Force

#### 7.3.1. Smooth Particle

When a particle is pushed by a solidification front, the disjoining force must balance exactly the drag force if the gravitational forces are neglected. It is therefore very instructive to know how the ratio, $q$, of the drag force to the disjoining force varies when the minimum distance $h_o$ varies or when the shape of the front is changed. This ratio is given for various geometries in Table 7-3. In this table,

$$\gamma = -36\pi \frac{\rho_s}{\rho_1} \frac{\eta}{A}$$

(7.56)

and as an order of magnitude, using as previously the values for camphor, $\rho_s/\rho_1 = 1.05$, $\eta = 0.5$ cpoise, $A = -2 \times 10^{-20}$ Joules and $\gamma = 3 \times 10^{+18}$ S.I.u.

If a sphere of radius $60 \mu m$ is at a distance $h_o = 12$ nm from a flat front, the ratio, $q$, equals 1—i.e., the drag force equals the disjoining force— if $V = 0.56 \mu m/sec$. Rephrasing the same result, a sphere of radius $50 \mu m$ will be at a distance $h_o$ equal to $12$ nm from the solidification front when pushed at $0.56 \mu m/sec$ (assuming that the front remains flat). If the growth rate is increased by a factor 2, to maintain the equality of drag and disjoining forces, (i.e. $q = 1$) the distance $h_o$ must decrease by a factor 2. Further increases in growth rate will result in further
Geometry

Sphere-flat interface
\[ \gamma VRh_o \]

Disk-flat interface (Figure 7-4)
\[ \gamma VR^2/4 \]

Sphere-concentric interface (Figure 7-5)
\[ \gamma VR^2 \times \frac{2-\cos \phi_M - \cos^3 \phi_M}{3(1 + \cos \phi_M)} \]

Sphere-slightly curved interface (Figure 7-6)
\[ \frac{\gamma VRh_o}{1 - \alpha} \]

Table 7-3: Ratio, q, of the drag force to the disjoining force for various geometries: \( q = \frac{F_D}{F_{dis}} \)
decreases in \( h_0 \); and since \( h_0 \) cannot be less than 0.3 to 1 nm, depending on the size of the liquid molecules, the particle will finally be entrapped. This minimum value for \( h_0 \), will be referred to as \( h_0^\circ \). A computation of the critical velocity simply based on this argument that \( h_0 \) cannot be less than a minimum distance \( h_0^\circ \), equal to one molecular diameter, would therefore predict, in the case of a sphere and a flat solidification front, a critical velocity varying as \( 1/R \):

\[
V_c = \frac{1}{36\pi} \cdot \frac{\rho_1}{\rho_s} \cdot \frac{\eta}{h_0^\circ} \cdot \frac{1}{R}
\]  

(7.57)

When the solidification front approaches a particle, it does not, however remain flat but curves slightly; the ratio \( q \) is increased by a factor \( 1/1-\alpha \) and for the particle to continue to be pushed at the same velocity, the distance \( h_0 \) must be decreased by a factor \( (1-\alpha) \). For example, if \( \alpha = 1/3 \), i.e. if the radius of curvature of the front is 3R, the distance \( h_0 \) is 1/3 of that for a flat front. Equation (7.57) should be therefore replaced by:

\[
V_c = \frac{1-\alpha}{\eta h_0^\circ R}
\]  

(7.58)

where \( R/\alpha \) is the curvature of the front when \( h_0 \) has its minimum value \( h_0^\circ \). This equation (7.58) shows that the more the front bends around the particle, the lower is the critical velocity.

This discussion can be approached slightly differently, using the argument that the pressure drop, \( \Delta P \), behind the particle cannot be more than the cavitation pressure, \( \Delta P_{\text{cav}} \). For a slightly curved front, \( h_0 \) cannot therefore be less than [from Equation (7.50)]:

\[
h_0 = \left[ 3 \frac{\rho_s}{\rho_1} \frac{V \eta R}{(1-\alpha)\Delta P_{\text{cav}}} \right]^{1/2}
\]  

(7.59)
The expression for the critical velocity obtained by combining Equation (7.59) with the condition \( q = 1 \) is similar to Equation (7.58) if now, the minimum distance \( h_0 \) is not a few molecular diameters but

\[
h_0 = \left( \frac{-A}{12\Delta P_{\text{cav}}} \right)^{1/3}
\]  

(7.60)

The cases of the disk and of the concentric interface are interesting because as a first approximation, the ratio \( q \) is independent of \( h_0 \). This result is, however, misleading since to avoid the existence of a large pressure gradient behind the particle, it was shown that the distance \( h_0 \) must be larger than 20 or 30 nm. The retarded faces should therefore be considered in the computation of the disjoining force and the ratio \( q \) becomes proportional to \( h_0 \):

\[
q = -\frac{3}{2} \frac{p_S}{\eta} \cdot \frac{R^2 h_0}{\rho_0} \tag{7.61}
\]

where \( B \) is the retarded Hamaker constant; and the critical velocity is:

\[
v_c \leq \frac{2}{3} \frac{\rho_1}{\rho_S} \cdot \frac{(-B)}{\eta} \cdot \frac{1}{h_0 R^2} \tag{7.62}
\]

For the system ice, water, mica, computing \( B \) with Equation (3.45) using the dielectric constants in the visible range, \( B = -10^{-29} \text{ Jm} \) and corresponds to a repulsion; \( \eta = 1.79 \text{ cp} \), \( \rho_S / \rho_1 = 0.917 \), \( h_0 = 0.5 \text{ nm} \). If \( R = 10 \mu m \), \( v_c \leq 0.067 \mu m/s \). This value is much smaller than the value reported by Corte (7) (100 \( \mu m \) flakes pushed at about 1 \( \mu m/s \)). This discrepancy is due to first the presence of irregularities on the large flakes and second to the fact that the major contribution to disjoining force in the water-mica-system is not due to dispersion forces but to structural forces that can be several orders of magnitude larger (33).
If the solidification front is concentric to the interface, for a 10 μm particle to be pushed at 1 μm/s, the radius \( r_0 \) of the zone of close approach must be less than 1 μm (again using \( \gamma = 3 \times 10^{18} \) S.I.u).

These results show that with the range of critical velocities observed experimentally (a few μm/s for particles of radius a few tens of microns) the front must be nearly flat, i.e. the curved zone where particle and solidification front are nearly in contact must be very small (less than 1/10 to 1/20 the radius of the particle. In this computation, an estimated value was used for \( \gamma = 3 \times 10^{18} \) S.I.u. \( \gamma \) cannot be much smaller (i.e. the viscosity of the liquid cannot be much smaller than 0.5 cpoise and the Hamaker constant cannot be much larger than 2 × 10^{-20} \) S.I.u.). If \( \gamma \) were smaller by a factor of ten, the radius of the zone of contact would be increased by a factor of 3. Conversely, if \( \gamma \) were larger by a factor of one hundred, the radius of the zone of contact would be decreased by a factor of 10. Therefore, in any case, the zone of near contact must be very small. This result has been confirmed experimentally by observation at magnifications up to 200X; in the case of solid growing in a prismatic morphology, no dimpling was noticeable behind the particles that were pushed.

7.3.2. Rough Particle

Let us first consider the simpler case of a smooth particle of radius \( R \) pushed by a few (\( N = 2 \) or 3) small particles of radius \( R \). For a slightly curved interface and if \( h_0 << R_1 \)

\[
q = \gamma V \frac{R^2}{N \frac{R_1^2}{h_0} + \frac{R^2}{2R_1(1-\alpha)^2}}
\]

(7.63)
Numerical computation with \( R=100 \ \mu m, \ R_i=1 \) or 0.1 \( \mu m \), show that the small particles contribution to drag force is negligible and that if \( h_o \) is approximately the value computed by C.T.M. or D.R.U. (Table 4-4) at the critical velocity for the small particles, the large particle contribution to disjoining force is negligible. Equation (7.63) can then be simplified to

\[
q = \gamma V \frac{R^2 h_o^2}{2NR_i^2 (1-\alpha)^2} \quad (7.64)
\]

The critical velocity of a smooth particle of radius 100 \( \mu m \) is 0.108 \( \mu m/s \) (computed from Equation (7.58) with \( \alpha=0.35 \) and \( h_o=20 \) nm). The presence of 3 small particles of radius 1 \( \mu m \) increases this velocity by a factor 24 [Equation (7.63) with \( \alpha=.35 \) and \( h_o=4 \) nm]. A few smaller particles would increase the critical velocity by a smaller amount. A similar computation for an hemispherical solidification front shows that the critical velocity of a 100 \( \mu m \) particle is increased by a factor 1300 by the presence of 3 small particles of radius 2 \( \mu m \).

For a rough particle the expression for \( q \) is more cumbersome:

\[
q = \gamma V \left( H_i + h_o \right)^2 \frac{R_i^2}{h_o} + \frac{4}{3} \frac{R^2}{(H_i+h_o)(1-\alpha)^2} \quad (7.65)
\]

Here again, numerical computations with \( R=100 \ \mu m, \ R_i=1 \) or 0.1 \( \mu m, \ H_i=R_i \) or \( R_i/10 \) show that Equation (7.65) can be simplified to:

\[
q = \gamma V \frac{R^2 h_o^2}{N'R_i h_i (1-\alpha)^2} \cdot \frac{4}{3} \frac{(H_i+h_o)^2}{H_i (H_i+3h_o)} \quad (7.66)
\]
The results of numerical computations of \( V_c \) for a rough particle and a slightly curved front (\( \alpha = 0.35 \)) are given in Table 7-4. C.T.M.'s values for \( h_0 \) and \( r_0 \) have been used in this computation. Irregularities of radius 1 \( \mu m \) on a 100 \( \mu m \) particle increase \( V_c \) by a factor of 30 to 50. The smaller increase is obtained when the height of the irregularities is small (0.1 \( \mu m \)). Smaller hemispherical irregularities (\( R_i = H_i = 0.1 \mu m \)) increase \( V_c \) by a factor 74. In these computations, the distance (\( H_i + h_0 \)) must always be about equal to or larger than the minimum distance \( h_0 \) for a smooth large particle. Obviously if the radius of the irregularities and/or their height become very small, the particle can be considered to be smooth. At the other extreme, if the size of the irregularity is large (\( R = 10 \mu m \), \( R_i = 1 \mu m \), \( V_c \) is simply \( V_c \) of the irregularity and Equation (7.65) does not apply when \( N' \) is too small. The increase in critical velocity is most noticeable for the largest particles.

In conclusion, these simple computations have shown that roughness can increase the critical velocity of particles of radius 10 to 100 \( \mu m \) by one or two orders of magnitude.

7.4. Comparison of Gravitational Forces and Drag Forces

In the previous discussion, the gravitational forces were neglected. To estimate when this neglect is reasonable in the case of a vertical geometry, the drag force \( F_D \) for a flat interface is compared to the weight \( W \), of the particle:

\[
F_D = 6\pi \eta \frac{\rho}{\rho_1} \frac{S}{h_0} \frac{VR^2}{h_0} \quad (7.67)
\]

\[
W = \frac{4}{3} \rho R^3 \Delta \rho \ g \quad (7.68)
\]
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Table 7-4: Critical velocity for rough particles (all distances are in $\mu$m)
\[ \frac{W}{F_D} = \frac{2}{9} \cdot g \cdot \frac{\Delta \rho \cdot R \cdot h}{\eta \cdot V} \]  \hspace{1cm} (7.69)

where \( \Delta \rho \) is the difference in density between particle and liquid, and \( g \) is the acceleration of gravity.

The ratio \( W/F_D \) has been computed in Table 7-5 for glass and zinc particles of various sizes in an organic liquid of density 1 \( \text{g/cm}^3 \) and viscosity 0.5 c.poise. This table shows that the gravitational forces are important in the case of large particles and/or very small growth rates. For a growth rate of 0.1 \( \mu \text{m/s} \) the gravitational forces cannot be neglected; they can be several times (\( n \) times) larger than the drag forces and the critical velocity previously computed must be reduced by a similar factor (\( n+1 \)). On the other hand, for a growth rate of 10 \( \mu \text{m/sec} \), the gravitational forces can almost always be neglected. The same conclusions could be drawn for the frictional forces since for small particle and smooth surfaces the frictional and gravitational forces are of the same order of magnitude.
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<th>GLASS</th>
<th>ZINC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \rho$ in g/cm³</td>
<td>2</td>
<td>6.14</td>
</tr>
<tr>
<td>V µm/sec</td>
<td>R µm</td>
<td>h µm</td>
</tr>
<tr>
<td>0.1</td>
<td>1</td>
<td>$8.7 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>$4.4 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>11</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>$8.7 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>$4.4 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>1.1</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>$8.7 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>$4.4 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>$1.1 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

Table 7-5: Ratio of weight over drag force, $W/F_D$, for various growth condition
CHAPTER 8

SHAPE OF THE SOLIDIFICATION FRONT - CRITICAL VELOCITY

In Chapter 7, the ratio of drag force to disjoining force was computed for various shapes of the solidification front. These computations demonstrated the existence of a maximum growth rate at which pushing occurred for a given shape of the front. This maximum velocity is due to limitations on the distance particle-solid, \( h_o \); \( h_o > h_o' \), where \( h_o' \) is a few molecular diameters, or to limitations on the maximum hydrostatic depression that can exist behind the particle. This derivation did not allow, however, a determination of the shape of the front behind a particle pushed at a given velocity. The complete differential equation which the front must satisfy will now be derived, and expressions will be deduced for the critical velocities of smooth and rough particles.

8.1. Differential Equation of the Front Behind a Particle.

The temperature of the interface, \( T_i \), is a function of the kinetics of crystallization, of the pressure and of the curvature of the front.

\[
T_i(r,z) = T_i = T_m - \Delta T_{\text{kin}} - \Delta T_{\text{pres}} - \Delta T_{\text{curv}}. \tag{8.1}
\]

where \( T_m \) is the equilibrium melting point for a flat front under 1 atm.

a. The kinetic undercooling, \( \Delta T_{\text{kin}} \), is the undercooling necessary to grow the front at a normal velocity, \( V_n \):

\[
\Delta T_{\text{kin}} = T_m(V=0) - T_i(V=V_n) \tag{8.2}
\]
For an atomically rough interface of the type expected for materials with low entropies of fusion (98):

$$V_n = \mu \Delta T_{\text{kin}}$$  \hspace{1cm} (8.3)

where $\mu$ is the kinetic coefficient for growth from the melt. In cylindrical coordinates $(r, z)$, the growth rate in the $z$ direction, $V$ is equal to:

$$V = V_n \cdot \sqrt{1 + z'^2}$$

and

$$\Delta T_{\text{kin}} = \frac{V}{\mu \sqrt{1 + z'^2}}$$  \hspace{1cm} (8.4)

For an atomically smooth interface, as observed with materials having a high entropy of fusion, the growth rate is proportional to the square of the undercooling and the undercooling may be large (98). In this case, however, the front remains practically flat behind the particle (even when for thermal reasons a large cusping would be expected, no deformation of the front was observed -- see Chapter 9). Since only the variations in kinetic undercooling with direction of growth enter in the final differential equation, this term can be neglected for materials growing with a prismatic morphology.

b. The pressure undercooling, $\Delta T_{\text{pres}}$, is due to two factors. The general expression for $\Delta T_{\text{pres}}$ is:

$$\Delta T_{\text{pres}} = T_m(h_o) - T_m(P) = \frac{1}{\Delta S_M} (\Omega_S \Delta P_S - \Omega_l \Delta P_l)$$  \hspace{1cm} (8.5)

where $\Delta S_M$ is the molar entropy of fusion (>0); $\Omega_S$ and $\Omega_l$ are the molar volumes of solid and liquid, and $\Delta P_l$ is the pressure change supported by phase $l$. Since liquid flows from the bulk to behind the particle,
a pressure (or chemical potential) gradient must exist. This pressure gradient was shown to be [Equation (7.52)]:

\[ \Delta P_h = P(r) - P(R) = 6 \frac{\rho_s}{\rho_1} V \eta \int_R^r \frac{x dx}{h^3(x)} \]

Since the hydrostatic pressure is supported by the solid as well as the liquid and since \( P(R) \) can be considered to be equal to the undisturbed hydrostatic pressure, the change in pressure, \( \Delta P_h \), induces a temperature shift:

\[ \Delta T_{\text{pres.}} = - \frac{\Delta \Omega_f}{\Delta S_M} \cdot \Delta P_h \quad (8.6) \]

where \( \Delta \Omega_f \), the molar volume change upon fusion = \( \Omega_1 - \Omega_S \), is in general positive (except for water, bismuth, some silicates). This hydrostatic pressure contribution will therefore, in general, lower the melting point and will tend to dimple the front behind the particle.

The solids are also supporting the disjoining pressure \( \Pi \). For short distances, \( \Pi = -A/6\pi h^3 \) and for large distance, \( \Pi = -B/h^4 \) where \( A \) and \( B \), the non-retarded and retarded Hamaker constant respectively are negative if the front repels the particle. The resulting melting point shift is:

\[ \Delta T_{\text{pres.}} = \frac{\Omega}{\Delta S_M} \cdot \Pi \quad (8.7) \]

If the particle is repelled by the front, the disjoining pressure will lower the melting point and will tend to dimple the front.

c. The curvature undercooling or Gibbs-Thompson effect is equal to:
\[
\Delta T_{\text{curv.}} = T_m(R_1 = \infty) - T_m(R_1) = - \frac{\sigma_{\text{SL}} \Omega}{\Delta S} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)
\]  
(8.8)

where \( \sigma_{\text{SL}} \) is the interfacial free energy solid-melt and the \( R_i \) are the principal radii of curvature. In cylindrical coordinates,

\[
\Delta T_{\text{curv.}} = - \frac{\sigma_{\text{SL}} \Omega}{\Delta S} \left( \frac{z'}{r} + \frac{z''}{1 + z'} \right) \frac{1}{\sqrt{1 + z'^2}}
\]  
(8.9)

The curvature undercooling tends to straighten the front.

Assuming that liquid and particle have identical thermal properties (see Chapter 9) and neglecting the difference in conductivity between solid and liquid, the temperature distribution in the matrix varies linearly in the \( z \) direction:

\[
T(z) = G(z+H) + (T_m - \frac{V}{\mu})
\]  
(8.10)

where \( (T_m - \frac{V}{\mu}) \) is the temperature at the interface growing with a velocity \( V \); \( G \) is the temperature gradient in the \( z \) direction and \( H \) is the distance between the center of the particle and the undisturbed front (Figure 4-2).

Consideration of the difference in thermal conductivity between solid and liquid would introduce a small factor tending to straighten the front. Combining Equations (8.1) and (8.10), the interface must satisfy the following differential equation:

\[
- G(z+H) + \frac{V}{\mu} \left( 1 - \frac{1}{\sqrt{1 + z'^2}} \right) + \frac{\Delta \rho f}{\Omega \Delta S} \cdot 6 \frac{\rho s}{\rho_1} V \eta \int_R^r \frac{xdx}{h^3(x)} + \frac{1}{\Delta S} \frac{A}{6\pi h^3}
\]

\[
+ \frac{\sigma_{\text{SL}}}{\Delta S} \left( \frac{z'}{r} + \frac{z''}{1 + z'} \right) \frac{1}{\sqrt{1 + z'^2}} = 0
\]  
(8.11)

where \( \Delta S = \Delta S_m / \Omega \) is the entropy of fusion per unit volume. The third
and fourth terms equal zero where \( r > R \). The existence of a critical velocity can be rationalized by considering that the dimpling effect due to pressure can be compensated in some limits by the Gibbs-Thompson effect; but if the pressure term becomes too large (\( V \) increases, \( h_o \) decreases), since the front cannot bend more than the particle radius, equilibrium cannot be reached and the particle will be entrapped. Mathematically, the critical velocity is the maximum growth for which Equation (8.11) has a stable solution; the existence of such a limit is demonstrated by experimental observations.

Furthermore, the front must be such that under steady-state growth conditions the total force exerted on the particle is zero:

\[
F_D + W = F_{\text{dis}}. \tag{8.12}
\]

where \( W \) is either the weight of the particle (vertical growth geometry) or the frictional resistance to displacement (horizontal growth geometry):

\[
W = \frac{4}{3} \pi R^3 (\rho_{\text{part.}} - \rho_{\text{liq.}}) f \cdot g \tag{8.13}
\]

Here \( f \) is the coefficient of friction for an horizontal setup and is equal to unity for a vertical setup; \( g \) is the acceleration of gravity and \( \rho_{\text{part.}} \) and \( \rho_{\text{liq.}} \) are the densities of particle and liquid respectively. Since even at growth rates slightly larger than \( V_c \) particles are pushed for short distances before being entrapped, the dynamic coefficient of friction should be used in Equation (8.13). In the case of a sufficiently small particle, as discussed in Chapter 7, \( W \) can be neglected and Equation (8.12) simplifies to \( q = F_D/F_{\text{dis}} = 1 \). This last relation has been discussed in detail in Chapter 7.
The shape of the front must therefore be such that Equations (8.11) and (8.12) be satisfied simultaneously. To simplify the writing of these equations, the following symbols have been introduced:

\[
\tau = \frac{1}{\mu G} \quad (8.14)
\]

\[
\delta = 6 \frac{\rho}{\rho_1} \eta \frac{\Delta \omega f}{\Omega G \Delta S} \quad (8.15)
\]

\[
\lambda^4 = -\frac{A}{6\pi G \Delta S} \quad (8.16)
\]

\[
\lambda^2 = \frac{\sigma_{SL}}{G \Delta S} \quad (8.17)
\]

\[
\gamma = \frac{36\pi}{-A} \eta \frac{\rho}{\rho_1} \quad (8.18)
\]

\[
W_o = 12\pi \quad g f \frac{\Delta \rho}{-A} \quad (8.19)
\]

Using the physical constants of camphor (Table 4-2), a temperature gradient \( G = 100^\circ C/cm \), a Hamaker constant \( A = -2 \times 10^{-20} \) J and \( f.\Delta P = 6 \) g/cm\(^3\), the parameters are equal to:

\[
\tau = 10^{-2} \; s; \quad \delta = 2.09 \times 10^{-13} \; m.s; \quad \lambda = 3.44 \times 10^{-8} \; m
\]

\[
\lambda = 4.12 \times 10^{-6} \; m; \quad \gamma = 3 \times 10^{18} \; s/m^3; \quad W_o = 1.11 \times 10^{26} \; m^{-4}
\]

Equation (8.11) can now be written:

\[
-(z+H) + \tau V(1 - \frac{1}{\sqrt{1 + z'^2}}) + \delta V \int_R^T \frac{x dx}{h^3(x)} - \frac{z'^4}{h^3} + \frac{\lambda^2}{\sqrt{1 + z'^2}} \left(\frac{z'}{r} + \frac{z''}{1 + z'^2}\right) = 0
\]

\[
(8.20)
\]

The parameter \( H \), the distance in the \( z \) direction between the front far from the particle and the center of the particle, can be eliminated by writing Equation (8.20) for two points on the front and subtracting
these two equations; or equivalently, \( H \) can be eliminated by differentiating Equation (8.20):

\[
-z' + \tau V \frac{z'z''}{(1+z'^2)^{3/2}} + \delta V \frac{x}{h^3} + \frac{3 \lambda^4}{h^4} h' + \frac{\lambda^2}{(1+z'^2)^{3/2}} \left( \frac{z'z''(1+z'^2)}{r^2} \right) + z'' \frac{3z'z''}{1+z'^2} = 0 \tag{8.21}
\]

On the axis of symmetry \( (r=0) \) since the slope of the front must be continuous, \( h'=z'=z''=0 \). Equation (8.21) is therefore always satisfied on the axis of symmetry - i.e., any function \( z \) that is a solution of Equation (8.20) on the axis of symmetry will also be a solution in a small region close to the axis of symmetry. This result justifies, a posteriori, U.C.J.'s and C.T.M.'s approaches, where a simplified version of Equation (8.20) was written only for a point on the axis of symmetry.

To obtain a non trivial equation and eliminate \( H \), one must use the second derivative of Equation (8.20). This equation is more complex; but on the axis of symmetry, \( r=0 \), it simplifies to:

\[
-z'' + \tau V z''^2 + \delta V \frac{z''}{h_o^3} + 3 h_o^4 \frac{z''}{h_o^4} + 4 \lambda^2 \frac{z''^3}{3 h_o^3} = 0 \tag{8.22}
\]

The force balance equation (8.12) can be written for a slightly curved front:

\[
\frac{\gamma h RV}{1-\alpha} + \frac{2}{3} W_o (1-\alpha) h_o^2 R^2 = 1 \tag{8.23}
\]

8.2. Solutions

Equation (8.11) is too complex to be solved exactly. The order of magnitude of each term will therefore be computed to determine their relative importance.
a. The temperature gradient term is less than 0.010°C if \( \Delta z \) is less than 1 \( \mu \)m and \( G = 100°C/cm \).

b. The kinetic undercooling term is inversely proportional to a factor \( \mu \) [Equation (8.3)] for low entropy of fusion materials. For CBr\(_4\) and camphor, \( \mu \) is of the order of 1 cm/s\(^0\)K and for the growth rates used in the present experiments (less than 40 \( \mu \)m/s) the undercooling \( \Delta T_{kin} \) is less than 0.007°C. Only the variations in undercooling with growth direction (i.e. with \( z' \)) appear in Equation (8.11). For small particles, since the front is only slightly curved behind a particle (\( z' << 1 \)) and since the kinetic undercooling is not very large, this term can be neglected. For materials growing with a prismatic morphology, this term can also be neglected since the front remains practically flat behind a particle. For high entropy of fusion materials growing with a macroscopically smooth interface, however, the kinetic undercooling is 4 or 5 times larger than for low entropy of fusion materials, and this term may have to be considered.

c. Pressure undercooling. If the hydrostatic depression is equal to 0.5 atmosphere, the resulting undercooling [Equation (8.6)] is equal to 0.012°C in naphthalene, 0.035°C in camphor and 0.0035°C in lead. In these computations, the following values were used: \( \Delta S_M = 6.7 \) k and 0.99 k, \( \Delta \Omega f/\Omega = 10\% \) and 3.1\% for naphthalene and lead respectively. This undercooling can become large if the depression \( \Delta P \) is large. The disjoining contribution [Equation (8.7)] is a function of the thickness of the liquid film, \( h \). For a Hamaker constant \( A = -2 \times 10^{-20} \) J, \( T \) is given in Table 8-1 as a function of \( h \).
<table>
<thead>
<tr>
<th>$h_{nm}$</th>
<th>camphor</th>
<th>$\Delta T$ in °C</th>
<th>lead</th>
<th>naphthalene</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.226</td>
<td>0.037</td>
<td>0.040</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.020</td>
<td>0.0032</td>
<td>0.0035</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.002</td>
<td>0.0003</td>
<td>0.0003</td>
<td></td>
</tr>
</tbody>
</table>

Table 8-1: Disjoining undercooling

For values of $h$ of the order of a few nm, this contribution is large but becomes very small for large distances $h$.

d. Curvature undercooling [Equation (8.8)]. The surface energies were computed with Equation (3.12). The undercooling corresponding to various radii of curvature is given in Table 8-2.

<table>
<thead>
<tr>
<th>$R_{\mu m}$</th>
<th>camphor</th>
<th>$\Delta T$ in °C</th>
<th>lead</th>
<th>naphthalene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.174</td>
<td>0.161</td>
<td>0.146</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.017</td>
<td>0.016</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.0017</td>
<td>0.0016</td>
<td>0.0015</td>
<td></td>
</tr>
</tbody>
</table>

Table 8-2: Curvature undercooling

These computations show that if the front curves only very slightly behind a particle (high entropy of fusion materials and/or small particles) the temperature gradient term and the kinetic undercooling term may be neglected.

For large particles and non-prismatic growth the temperature gradient term can be large and must be taken into consideration, the kinetic term
may be neglected since the growth rates are very small and the curvature term is also very small.

Let us now consider more specifically various particles.

8.2.1. Disk Shaped Particles

In Chapter 7, it was shown that if the front remained flat behind the particle and if the distance particle-front $h_o$ was not too large, the critical velocity was:

$$ V_c = \frac{4}{\gamma} R^2 $$

and for larger distances $h_o$, an upper limit was derived for $V_c$ [Equation (7.62)].

The exact shape of the front is defined by Equation (8.20). Since the front cannot be very curved behind the particle, in first approximation only the temperature gradient and pressure terms need to be considered. By differentiating this equation twice, the radius of curvature of the front on the axis of symmetry is found to be positive and small. A numerical construction by small increments of the front close to the axis of symmetry shows that the curvature changes sign repeatedly; these ripples would, however, disappear if the surface energy term was introduced. The radius of curvature of the smoothed front is large but these numerical computations were not accurate enough to give unambiguously its sign. Let us consider that the front is a paraboloid with radius of curvature on the axis of symmetry equal to $R/a$; or using as parameters the distance particle-front on the axis of symmetry, $h_o$, and at $r=R$, $h_R$, the radius of curvature is equal to $R^2/2(h_o-h_R)$. For such a parabolic front, the drag and disjoining forces
are respectively:

\[ F_D = \frac{6}{4} \pi \frac{\rho_s}{\rho_1} \eta \frac{R^4}{h^2_o h^2_R} V \]  \hspace{1cm} (8.25)

\[ F_{\text{dis.}} = -\frac{AR^2(h_o + h_R)}{12h^2_o h^2_R} \]  \hspace{1cm} (8.26)

and the equilibrium condition, \( F_D = F_{\text{dis.}} \), becomes

\[ h_R = \left( \frac{\gamma R^2 V}{2} - 1 \right) h_o \]  \hspace{1cm} (8.27)

By writing Equation (8.20) for \( r=0 \) and \( r=R \), and subtracting these two equations, one obtains an expression in \( h_o, h_R \) and \( V \). \( h_R \) can be eliminated through Equation (8.27) to give:

\[ h_o^4 = \left[ \frac{\delta x^2 (x-1)}{\gamma} - \ell^4 (2-x)(x^2 - x + 1) \right] / (x-1)^3 (2-x) \]  \hspace{1cm} (8.28)

where \( x = \frac{\gamma R^2 V}{2} \).

Numerical computations using for \( \delta, \gamma \) and \( \ell \) the values given at the beginning of this chapter, show that a solution only exists when \( x \) is nearly equal but slightly less than 2; i.e., \( h_R \approx h_o \). The front is therefore practically flat behind the particle (very slightly concave) and the critical velocity is given by Equation (8.24) (equivalent to the condition \( x=2 \)), or by Equation (7.62). In this approximation, the weight of the particle was neglected. This derivation is therefore limited, in the case of a vertical setup, to thin and/or small particles.

8.2.2. Spherical Particles

For a spherical particle, the thickness \( h \) of the liquid film is equal to:
\[ h = - \sqrt{r^2 - R^2} - z(r) \]  \hspace{1cm} (8.29)

where \( z(r) \) is the ordinate of the points of the front at \( r \), and when \( r/R < 0.3 \)

\[ h = - R + \frac{r^2}{2R} - z(r) \]  \hspace{1cm} (8.30)

Even if this approximated form is used for \( h \), Equation (8.20) is difficult to solve; at best, using approximations similar to those used by Bolling and Cissé (9), the equation of the front is given by a sum of Bessel functions which is difficult to handle. However, it was shown in Chapter 4 that two very different approaches (diffusion, flow and parabolic front) yielded similar front shapes; this similarity was due to the very small size of the zone of strong interaction and to the fact that the various curves used must have the same first and second derivative on the axis of symmetry. Therefore the equation used to represent the shape of the front is not critical to our discussion and can be chosen à priori. Let us therefore consider, à priori, that the gap thickness, \( h \), follows an exponential relation:

\[ h = h_0 \exp \left( \frac{ar^2}{2} \right) \]  \hspace{1cm} (8.31)

where \( a \) is an adjustable parameter. This form is suggested by a derivation similar to that used by U.C.J. (13) to determine the shape of the front but considering a flow mechanism rather than a diffusion mechanism. This choice of a flow process rather than a diffusion process is justified since U.C.J. using a diffusion mechanism found the minimum thickness \( h_0 \) to be larger than 10 molecular diameters for particles
larger than 1 μm (see Chapter 4). For such a shape [Equation (8.31)],
the drag and disjoining forces are respectively:

\[ F_D = \frac{4\pi \rho_s s \eta V}{3 \rho_1 a^2 h_o} \]  

(8.32)

\[ F_{dis} = -\frac{A}{9ah_o} \]  

(8.33)

and the equilibrium equation (8.12) becomes:

\[ \omega_o h_o^3 R^3 a^2 - a + \frac{\gamma V}{3} = 0 \]  

(8.34)

At \( r = 0 \), the differential equation (8.20) and its second derivative
(8.22) can be written:

\[ (R + h_o - H) - (1 + \frac{\delta V}{3a\lambda^4}) \frac{\rho^4}{h_o^3} + 2\lambda^2 \left( \frac{1}{R} - a h_o \right) = 0 \]  

(8.35)

\[ -\frac{1}{R} + ah_o + \gamma V(\frac{1}{R} - ah_o)^2 + (1 + \frac{\delta V}{3a\lambda^4}) \frac{3a\lambda^4}{h_o^3} - 4\lambda^2 \left[ a^2 h_o + (\frac{1}{R} - ah_o)^3 \right] = 0 \]  

(8.36)

8.2.2.1. Weight much smaller than Drag Force

This case corresponds either to small particles or to experiments
in microgravity. Equation (8.34) simplifies to

\[ a = \frac{\delta V}{3} \]  

(8.37)

and the term \( \delta V/3a\lambda^4 = \Delta \Omega f/\Omega \). Since the relative change of volume upon
fusion \( \Delta \Omega f/\Omega \), is of the order of -8 to +10%, this term can be
neglected relative to unity.
a. Slightly Dimpled Front. This case corresponds either to small particles or to prismatic growth. In this case the temperature gradient term can be neglected in Equation (8.35) (i.e., \( R + h_o - H = 0 \)) and Equation (8.35) simplifies to:

\[
V = \frac{3}{\gamma h_o} \left( \frac{1}{R} - \frac{\xi^4}{2\lambda^2 h_o^3} \right) \tag{8.38}
\]

This velocity goes through a maximum (critical velocity) for \( h_o \) equal to:

\[
h_{oc} = \left( \frac{\lambda^2}{\xi^4} \right)^{1/3} R = -\frac{AR}{3\pi\sigma_{SL}} \tag{8.39}
\]

and the corresponding critical velocity is:

\[
V_c = \frac{9}{4\gamma} \left( \frac{\lambda^2}{\xi^4} \right)^{1/3} \frac{1}{R^{4/3}} = 4.20 \times 10^{-2} \frac{\sigma_{SL}^{1/3}}{\rho_s} \frac{\xi^4}{\eta R^{4/3}} \tag{8.40}
\]

These expressions for \( h_{oc} \) and \( V_c \) are practically identical to those derived by C.T.M. using a parabolic front [Equations (4.28) and (4.29)]. Equation (8.38) gives a value 1.12 time larger than Equation (4.29) and the critical velocity is 2.13 times larger than with Equation (4.28). These results confirm the lack of sentivity of these derivations to the analytical form used to describe the front.

b. Large Particles. In this case the curvature term in Equation (8.35) can be neglected and the equation becomes:

\[
R - H = \frac{\xi^4}{h_o^3} - h_o \tag{8.41}
\]

It is interesting to see how \((R-H)\) varies with \( h_o \). For a particle of radius 100 \( \mu \)m, when \( h_o \geq 100 \) nm, \((R-H)\) is equal to \(-h_o\), i.e., the front
remains flat, when \( h_o = 10 \text{ nm} \), the front is slightly cusped; but when \( h_o \leq 2.4 \text{ nm} \), the particle is entrapped (H<0). The velocity is directly given as a function of \( h_o \) by Equation (8.36):

\[
V = \frac{3h_o^3}{RY(h_o^4 + 3\ell^4)} \tag{8.42}
\]

This velocity goes through a maximum for \( h_o \) equal to

\[
h_{oc} = \sqrt{3} \ell \tag{8.43}
\]

and the corresponding critical velocity is:

\[
V_c = \frac{3\sqrt{3}}{4} \frac{1}{\gamma \ell R} \tag{8.44}
\]

Again, these expressions are similar to those derived by C.T.M. The critical velocity computed with Equation (8.44) is larger than that computed with C.T.M.'s Equation (4.32) by a factor 1.44 and the minimum distance \( h_{oc} \) [Equation (8.43)] is larger than that computed with Equation (4.32) by a factor \( \sqrt{3} \). The distance \( H \) is equal to \( R + 8/9 h_o \) -- i.e., the front is nearly flat. The radius of curvature on the axis of symmetry is equal to \( 4R \) for small as well as large particles.

8.2.2.2. Weight of the same order of magnitude or larger than the drag force.

In this case, Equation (8.34) cannot be simplified; however, an upper limit for \( V \) is found by writing that this equation must have a solution in "a":

\[
V \leq \frac{3}{4W_o \gamma h_o^3 R^3} \tag{8.45}
\]
Let us again consider separately the case of small and large particles.

a. Small Particles: Neglecting the temperature gradient term in Equation (8.35) (1st term), this equation yields a value of $a$:

$$a = \frac{1}{h_o} \left( \frac{1}{R} - \frac{k^4}{2\lambda^2 h_o^3} \right)$$  \quad (8.46)

and replacing $a$ by this value, Equation (8.34) becomes:

$$V = \frac{3}{\gamma R h_o} \left\{ \frac{3}{\gamma R h_o} [1 - \frac{R}{\lambda h_o} + \frac{R^2 / \lambda^4}{4 \lambda h_o^6}] + [1 + \frac{R^4 / \lambda^4}{2 \lambda^2 h_o^3}] \right\}$$  \quad (8.47)

If

$$W_0 R^2 h_o^2 << 1$$  \quad (8.48)

the correction for gravitational forces is negligible and Equation (8.47) simplifies to the previously derived Equation (8.39). As will be shown later [Equations (8.50) and (8.51)], the effect of gravity is to decrease $h_{oc}$; therefore $h_{oc}$ will be smaller than the value computed in the absence of an external field [Equation (8.39)] and the condition (8.48) takes the form:

$$R^4 << \frac{1}{W_0} \frac{1}{1.5} \left( \frac{\lambda^2}{2\ell^2} \right)$$  \quad (8.49)

For the numerical values previously used, this condition corresponds to $R << 8.5 \mu m$—i.e., $R$ of the order of one micron or less.

For slightly larger particles, the distance $h_{oc}$ will not differ very much from the expression computed in the absence of a field and it can be written:

$$h_{oc} \approx \left( \frac{2\ell^4 R}{\lambda^2} \right)^{1/3} (1-Y); \quad |Y| << 1$$  \quad (8.50)
where $Y$ is a dimensionless parameter. Substituting this expression in the equation defining the critical velocity ($dV/dh_o = 0$), one finds:

$$Y = \frac{1.5}{\frac{8}{3W_o R^2} \left( \frac{\lambda^2}{2\ell_4 R} \right)^{2/3} - 1} > 0$$  \hspace{1cm} (8.51)

and therefore, the critical velocity [Equation (8.47)] is:

$$V_c \approx \frac{9}{4^4 R} \left( \frac{\lambda^2}{2\ell_4 R} \right)^{1/3} \left( \frac{27}{16\gamma} \frac{W_o R}{\lambda^2} \left( \frac{\ell_4 R}{\lambda^2} \right)^{1/3} \right) (1 - 2Y)$$  \hspace{1cm} (8.52)

These results confirm that for small particles (1 to 8 $\mu$m with the values previously used) the effect of gravity is to decrease slightly the critical distance $h_{oc}$ and to reduce the critical velocity [Equation (8.52) versus Equation (8.40)].

For still larger particles:

$$R^4 >> \frac{1}{W_o} \frac{1.5}{\left( \frac{\lambda^2}{2\ell_4 R} \right)}$$  \hspace{1cm} (8.53)

but $R < 500$ $\mu$m (so that the temperature gradient can still be neglected versus the curvature term), the gravitational terms become dominant in Equation (8.47). If only the terms in $W_c$ are kept in Equation (8.47), $h_{oc}$ (the value of $h_o$ for which $dV/dh_o = 0$) is found to be equal to $(R\ell_4/2\lambda^2)^{1/3}$. Therefore to a good approximation $h_{oc}$ can be written:

$$h_{oc} = \left( \frac{\ell_4 R}{2\lambda^2} \right)^{1/3} (1 + Y); \hspace{1cm} |Y| \ll 1$$  \hspace{1cm} (8.54)

where $Y$ is again a dimensionless parameter, and substituting this expression in the equation defining the critical velocity, $Y$ is found to be:
\[
Y = \frac{1}{6} \cdot \frac{1}{1 + \frac{w_o R^2 \left( \frac{4}{2} \right)^{2/3}}{2 \lambda^2}} = \frac{1}{6w_o R^2} \left( \frac{2\lambda^2}{\ell^4 R} \right)^{2/3} \quad (8.55)
\]

and the critical velocity is:

\[
V_c = \frac{9}{\gamma R} \left( \frac{2\lambda^2}{\ell^4 R} \right)^{1/3} \quad \text{Y.} = \frac{3}{\gamma w_o} \frac{\lambda^2}{\ell^4 R^4} \quad (8.56)
\]

The critical velocity is now a very quickly decreasing function of particle size \( V_c \propto R^{-4} \). The radius of curvature of the front on the axis of symmetry is nearly equal to \( R \)--i.e., the front is practically concentric to the particle.

For particle sizes intermediate between these extreme cases [Equations (8.49) and (8.53)] the critical distance \( h_{oc} \) can again be defined by a development in \( Y \) [Equation (8.50) or (8.54)] but keeping terms in \( Y^2 \) or even \( Y^3 \). The resulting expression for \( V_c \) is in \( R^{-n} \) with \( \frac{4}{3} < n < 4 \).

b. Large Particles. Using a derivation similar to that used in the absence of an external field--i.e., neglecting the curvature effect--Equation (8.36) yields:

\[
a = \frac{h_o^3}{R(h_o^4 + 3\ell^4)} \quad (8.57)
\]

and Equation (8.34) becomes:

\[
V = \frac{3}{\gamma R} \frac{h_o^3}{h_o^4 + 3\ell^4} \left[ 1 - \frac{w_o h_o^6 R^2}{h_o^4 + 3\ell^4} \right] \quad (8.58)
\]

The velocity \( V \) is maximum \( (dV/dh_o = 0, d^2V/dh_o^2 < 0) \) for

\[
h_{oc} = \left( \frac{\ell^4}{w_o R^2} \right)^{1/6} \quad (8.59)
\]
and
\[ V_c = \frac{2}{3 \gamma l^2 \sqrt{W_0} R^2} \] (8.60)

For \( R \geq 500 \mu m \), \( V_c < 10^{-10} \mu m/s \)--i.e., in practice it would not be possible to observe such a large particle being pushed.

8.2.3. Irregular Particles

8.2.3.1. Weight much smaller than Drag Force

This case was discussed in some detail in Chapter 7. It was shown that the presence of a few irregularities or small particles at the surface of a large one can increase the critical velocity by one or two orders of magnitude; it was also shown that generally the contribution of the small particles or irregularities to drag force is negligible and that most of the disjoining force is due to the interaction of the small particles with the front.

To quantify this relation, it was shown by writing the balance between drag and disjoining force [Equation (7.66)] that the critical velocity \( V_{c_i} \) for a particle of radius \( R \) covered with hemispherical irregularities of radius \( R_i \) was:
\[ V_{c_i} = \frac{3}{4} \frac{N'R_i^2}{\gamma R^2 h_{oi}^2} \] (8.61)

where \( N' \) is the number of irregularities interacting with the front and \( h_{oi} \) is the minimum distance irregularities-front when the particle is pushed at \( V_{c_i} \). For a smooth particle the critical velocity was:
\[ V_c = \frac{1}{\gamma R h_{oc}} \] (8.62)
Assuming a close packing of the irregularities at the surface of the particle, the number of irregularities \( N' \) in contact with the front is:

\[
N' = \frac{r^2}{2\sqrt{3} R_i^2 R_{oc}^2}
\] (8.63)

where \( R_{oc} \) is the radius of the zone of strong interaction between particle and front. C.T.M. showed (Chapter 4) that this radius is equal to \( 2\sqrt{R/h_{oc}} \) [Equation (4.30)]. Therefore combining Equations (8.61) to (8.63)

\[
\frac{V_{ci}}{V_c} = \frac{\pi \sqrt{3}}{2} \left( \frac{h_{oc}}{h_{oi}} \right)^2
\] (8.64)

\( h_{oc} \) and \( V_c \) have been previously computed [Equations (8.39) and (8.40)].

If the radius of the irregularities is smaller than 0.01 \( \mu m \), \( h_{oi} \) is independent of \( R_i \) and is about equal to 1 nm. If the irregularities are larger than 0.01 \( \mu m \), the minimum distance \( h_{oi} \) is again given by Equation (8.39) and Equation (8.64) becomes:

\[
\frac{V_{ci}}{V} = \frac{\pi \sqrt{3}}{2} \left( \frac{R}{R_i} \right)^{2/3}
\] (8.65)

or

\[
V_{ci} = \frac{9\pi \sqrt{3}}{8} \left( \frac{\lambda^2}{2l^4} \right)^{1/3} \left( \frac{1}{R_i R} \right)^{2/3}
\] (8.66)

8.2.3.2. Weight of the same Order of Magnitude or larger than Drag Force

Let us consider a particle of radius \( R \) with \( N' \) asperities (or attached small particles) of radius \( R_i \) in close contact with the front. For the size of interest, \( R > 10 \mu m \), gravitational forces are of the same order of magnitude or larger than the drag forces (this is even more so
the case for a rough particle since it was shown in Chapter 7 that the presence of irregularities reduces the drag force); the critical velocity can therefore be determined by computing the critical velocity of a small irregularity of radius \( R_i \) considered to have a weight \( W = W_o R_i^3/N' \)--i.e., distributing the total weight of the large particle over the \( N' \) small irregularities. This problem has already been treated: Equation (8.47) becomes

\[
v = \frac{3}{\gamma h_0 R_i} \left[ -\frac{W_o R_i^3 h_0}{N' R_i} \right] \left[ 1 - \frac{1}{\lambda^2 h_0^3} + \frac{R_i \ell^4}{4 \lambda h_0^6} \right] + 1 - \frac{R_i \ell^4}{2 \lambda h_0^3} \tag{8.67}
\]

and since the term \( W_o R_i^3 h_0^2/N' R_i \) is large, Equation (8.54) is applicable. Differentiating Equation (8.67) to find the maximum velocity, gives:

\[
y = \frac{1}{6} \frac{N' R_i}{W_o R_i^3} \left( \frac{2 \lambda^2}{\ell^4 R_i^3} \right)^{2/3} \tag{8.68}
\]

and

\[
V_{ci} = \frac{2 \lambda^2 N'}{\gamma W_o \ell^4 R_i R_i^3} \tag{8.69}
\]

This should be compared with the critical velocity given by Equation (8.56) for particles of radius 30 to 5.0 \( \mu m \). The presence of the small irregularities increases the critical velocity by a factor \( 2/3 N'/R_i \).

For example, for a particle of radius 100 \( \mu m \) with 10 irregularities of radius 0.5 \( \mu m \) in contact with the front, the critical velocity is increased by a factor of 1300. Assuming that the irregularities are close packed, \( N' \) is given by Equation (8.63) and \( h_{oc} \) by Equation (8.54). The presence of the irregularities increases therefore the critical velocity by a
factor:

\[ \frac{2\pi}{\sqrt{3}} \cdot \left( \frac{2R}{2\lambda} \right)^{1/3} \cdot \frac{1}{R} \left( \frac{R}{R_1} \right)^3 \]

and again \( V_{ci} \) varies as \( R^{-2/3} \). This increase is in general larger than that computed in the absence of a field [Equation (8.65)]. This last result was expected since when a field is present, \( V_c \) decreases faster with increasing particle size than in the absence of a field.

8.3. Discussion

The results for spherical particles are summarized in Table 8-3. \( h_{oc} \) and \( V_c \) have been computed using the same parameters as previously (Table 4-2, \( A = -2 \times 10^{20} J \)) and are plotted in Figures 8-1 and 8-2. In the absence of an external field, \( h_{oc} \) is an increasing function of particle size. At very small particle sizes, \( h_o \) cannot be less than a molecular diameter \( (h_{oc} > h_o) \) and at very large particle sizes \( h_{oc} \) tends toward an upper limit. For a given particle size, \( h_{oc} \) increases if the absolute value of the Hamaker constant increases or if the surface tension crystal-melt decreases. In the range of particle sizes of interest in this study (1-100 \( \mu m \)), \( h_{oc} \) varies between 5 and 24 nm. Application of an external field (gravity, friction) decreases \( h_{oc} \) and \( h_{oc} \) goes now through a maximum.

In the absence of an external field, the critical velocity decreases with particle size as \( R^{-4/3} \) for small particles and \( R^{-1} \) for large ones. Application of a field decreases substantially the critical velocity for particles of radius larger than:
FIGURE 8.1 SPHERICAL PARTICLE; VALUE OF $h_{oc}$ AS A FUNCTION OF PARTICLE SIZE
FIGURE 8-2 SPHERICAL PARTICLE: CRITICAL VELOCITY AS A FUNCTION OF PARTICLE SIZE
\[ R = \frac{1}{W_0^{3/8}} \left( \frac{\lambda^2}{2L^4} \right)^{1/4} = \left[ -\frac{AgS_L^2}{3\pi} \cdot \frac{1}{\left(4gf\Delta\rho\right)^3} \right]^{1/8} \] (8.70)

For large particle sizes, the velocity decreases as \( R^{-4} \).

In all the cases the critical velocity is inversely proportional to the viscosity. The critical velocity increases if either the absolute value of the Hamaker constant or the surface tension solid-melt increases.

These results agree with the experimental observation reported in Chapter 5. For small particles of Ni, Zn, Cu and glass, the critical velocity was observed to decrease a \( R^{-1} \). Considering the uncertainty on critical velocity measurements, it seems difficult to differentiate between a relation in \( R^{-1} \) and in \( R^{-4/3} \). For glass particles, using a value of \( \Delta\rho f = 750 \text{ kg/m}^3 \), the radius above which friction should begin to reduce the critical velocity is equal to about 20 \( \mu \text{m} \) [Equation (8.64)], and experimentally the critical velocity curve was observed to deviate from a relationship in \( 1/R \) for radii larger than 15 to 25 \( \mu \text{m} \). Assuming a Hamaker constant of \( -2 \times 10^{-20} \text{ J} \), the computed critical velocity for glass particle of radius 15 \( \mu \text{m} \) is 3.7 \( \mu \text{m/s} \) compare to a measured 2 \( \mu \text{m/s} \) [Equation (8.40)].

As discussed in Chapter 5, the uncertainty associated with the determination of critical velocity as a function of particle size was particularly large in the case of zinc particles; this uncertainty was explained by the fact that the zinc particles were very rough. The presence of irregularities on the zinc particles explains also the positive curvature of the curve \( \log V_c \) v.s. \( \log R \) since according to Section 8.2.3.2 the critical velocity varies as \( R^{-2/3} \) for rough particles instead of \( R^{-4/3} \).
The flattening of the critical velocity curve observed with copper particles of large dimension is explained by the facts that first the stage was very slightly tilted (1 to 3°) to reduce the frictional forces and that second, as shown on the micrographs in Chapter 5, the surface of the particles was irregular, and in some cases sub-micron particles were present.

The present derivation confirms the importance of viscosity. Naphthalene, durene and thymol have a high entropy of fusion but thymol is 5 to 10 times more viscous than naphthalene or durene; and it was observed (Chapter 5) that all the particles tested had a much lower critical velocity in thymol than in durene or naphthalene.

The critical velocity is proportional to \((-A)^{2/3}\) or \((-A)\). It was shown in Chapter 6 that for the water-ice system, the Hamaker constant of all the particles considered was negative (i.e. rejection) and that its absolute value decreased in the order Au, Cu, Ge, NiO, MgO, polystyrene, fused silica, teflon. The value of teflon was about 20 times smaller than for copper or gold. This order agrees with the present observations that in general, for particles of comparable size, copper, nickel, gold and germanium had critical velocities larger than zinc oxide or glass; and it was reported (15) that teflon particles were not pushed in naphthalene. Therefore, even though the Hamaker constants could not be computed for the organic materials of interest, the trend indicated by the results on water seem to apply to these organic materials.

Experiment and theory are therefore in very good agreement. This derivation cannot however explain the observation of Subko et al. (17) that metallic particles of radius 1 or 2 mm were pushed in a vertical
setup at velocities larger than $14 \mu m/s$; whereas the present computation would predict critical velocities of less than $10^{-10} \mu m/s$. This discrepancy will be explained by considering thermal effects in Chapter 9.

The previous discussion is quite general and can be extended to include the action of other external fields (magnetic, electric). The gravitational force term, $4/3 \pi R^3 \Delta \rho$ needs simply be replaced by the proper force term.

Down to particle sizes of a few $\mu m$, the critical velocity has been observed to vary as $R^{-1}$. This curve is expected however to flatten for very small particle sizes for several reasons.

a. When $R$ decreases, the minimum distance particle-front decreases, but $h_o \geq 0$ cannot be less than one or two molecular diameters ($h_o > h_o$). If $h_o$ is constant Equation (8.40) now becomes: $V_c \propto R^{-1}$.

b. When $h_o$ becomes of the order of a few molecular diameters, the viscosity of the liquid in the film may become much larger than the bulk viscosity (115). Such an increase should be most pronounced with polar liquids and surfaces. Furthermore, for such thin films, the transport of liquid behind the particle must occur by a diffusion process instead of the faster flow process considered in this derivation (13).
CHAPTER 9

SHAPE OF THE INTERFACE - THERMAL EFFECTS

9.1. Position of the Problem

In most previous theoretical studies of the phenomenon of rejection of second-phase particles, it was assumed, for reasons of simplicity, that solid, liquid and particle had the same thermal conductivity. However, most experiments have been done with metallic, oxide or glass particles in an organic matrix or in water; and in these cases, the thermal conductivity of the particles is at least one order of magnitude larger than that of the matrix (Table 9-1). As a consequence, the isotherms will not remain flat in the vicinity of a particle but will curve around the particle; and for materials growing with a non-faceted morphology—i.e. either materials with a low entropy of fusion or some materials with a high entropy of fusion at slow growth rates (97,99). The solidification front follows the isotherms, and the front will bend around the particle (e.g. Figure 9-28). This phenomenon must not be ignored, since a deep cusping of the solidification front around the particle can increase the drag force by several orders of magnitude (see Chapter 7).

The importance of a difference in thermal conductivity between liquid and particle was noted by Bolling and Cissé (9) but they limited their remarks to a schematic drawing of the isotherms around a particle, and to the conclusion that if the particle has a much larger thermal conductivity than the matrix, it should be entrapped more readily. This idea was further developed by Zubko et al. (17), who studied mainly large metallic particles (2-3 mm diameter) in a metallic matrix. All the particles with larger thermal conductivity than the matrix were entrapped,
<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature range °C</th>
<th>$k$ Watt/cm. °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag, Cu, Au, Al, W</td>
<td>100 - 200</td>
<td>4.2 to 1.6</td>
<td>(104)</td>
</tr>
<tr>
<td>Zn, Ni, Pt, Pb</td>
<td>100 - 200</td>
<td>1.1 to 0.34</td>
<td>(104)</td>
</tr>
<tr>
<td>SiC (single crystal)</td>
<td>100 - 150</td>
<td>0.86</td>
<td>(104)</td>
</tr>
<tr>
<td>MgO</td>
<td>100 - 150</td>
<td>0.30</td>
<td>(104)</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>100 - 200</td>
<td>0.13</td>
<td>(104)</td>
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<tr>
<td>MgSiO$_4$</td>
<td></td>
<td>0.05</td>
<td>(104)</td>
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<tr>
<td>Fused silica</td>
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<td>(104)</td>
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<tr>
<td>Soda-lime glass</td>
<td>100</td>
<td>0.0095 to 0.0115</td>
<td>(104)</td>
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<td>Shale</td>
<td>100 - 200</td>
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<td>(105)</td>
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<td></td>
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<td>0.0056-0.0060</td>
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<td>Naphthalene</td>
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<td>(106)</td>
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<td></td>
<td>liquid</td>
<td>0.0013; 0.0015</td>
<td>(107)</td>
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<tr>
<td>Diphenyl</td>
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<td>0.0030; 0.0024</td>
<td>(105); (107)</td>
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<td></td>
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<td>0.0014; 0.0013</td>
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<td>0.0030</td>
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<tr>
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<td>0.0034</td>
<td>(107)</td>
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<tr>
<td>Organic liquids</td>
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<td>0.0009-0.0030</td>
<td>(104)</td>
</tr>
</tbody>
</table>

Table 9-1: Thermal conductivity of various matrix materials and particles
and all particles with a lower thermal conductivity than the matrix were pushed (Table 2-2).

Another thermal factor influencing the critical velocity is the temperature gradient in the liquid. In a recent study, Chernov, Temkin and Mel'nikova (31) introduced the temperature gradient, $G$, in the expression for the critical velocity of large particles. In this expression, the critical velocity varies as $G^{1/4}$. This result is in contradiction with the experimental results of Cissé and Bolling (10) for copper particles in water (Table 9-2), who concluded however that the temperature gradient had little influence on critical velocity.

<table>
<thead>
<tr>
<th>Radius of particle in $\mu$m</th>
<th>$10^5$C/cm</th>
<th>1°C/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.7</td>
<td>2.4</td>
</tr>
<tr>
<td>32.5</td>
<td>0.47</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 9-2: Critical velocities (in $\mu$m/s) for copper particles in water as a function of temperature gradient (Ref. 10)

Cusping behind large particles with a larger thermal conductivity than the matrix can frequently be seen at fairly low magnification, but it is difficult to know if the particle is touching the front or if a liquid film still exists between particle and front. This effect is seen much more clearly by looking at a pile-up of Zn particles pushed by a solidification front of durene, at a few micrometers per second. The front is clearly depressed behind the particles (Figure 9-1). Simple heat flow computations (see Appendix D) show that for a small pile-up in a large cell, the front is depressed by an amount $\Delta z$ equal to:
Figure 9-1: Pile up of zinc particles pushed by a crystal of durene: 4 \( \mu m/s \) – horizontal set-up (Liquid on top)
\[ \Delta z = \frac{e}{2} \left(1 - \frac{k_1}{k_{p.u.}}\right) \]  

(9.1)

if \( e \) is the thickness of the pile-up in the direction of growth and \( k_1 \) and \( k_{p.u.} \) are the thermal conductivities of liquid and pile-up respectively. In the case of metallic particles in an organic liquid,

\[ k_{p.u.} \gg k_1 \]

and

\[ \Delta z = \frac{e}{2} \]  

(9.2)

To determine the shape of the front behind a particle, one must know the temperature profile around the particle. Such a computation is straightforward in the case of a large flat particle, where edge effects can be neglected, but it is much more complex in the case of a spherical particle. Chernov and Mel'nikova have studied the problem of the growth of a crystal with a spherical particle at a fixed distance from the front (i.e. stationary condition). They considered both cases of growth from a supersaturated solution (110) and growth from the melt (111). In these derivations, they introduced the influence of latent heat of solidification, thermal diffusivity, and a kinetic crystallization coefficient characteristic of the growth process. The system of differential equations was solved by using bispherical coordinates to make the boundary conditions manageable. In the case of growth from a solution, they showed that if the relative distance \( \varepsilon = H/R \) (Figure 9-2) is less than a critical distance \( \varepsilon_c \), channels will develop in the growing crystal behind the particle. This distance \( \varepsilon_c \) is a function of the radius \( R \) of the particle and of the growth rate \( V \)

\[ \varepsilon_c \propto R^{1/2} V^{1/4} \]  

(9.3)
FIGURE 9-2 SOLIDIFICATION FRONT BEHIND A PARTICLE
They did not, however, attempt to determine from a force balance the equilibrium distance \( \varepsilon \) and its dependence on \( R, V \) and the characteristics of the materials.

Mathematically, their solution is quite elegant; but it has two restrictions that limit its utility. First, it is limited to small perturbations, as the front is initially assumed to be flat; and second, the particle must be in front of the unperturbed solidification front (i.e. \( H>R \)). These restrictions limit their results, in the case of a high conductivity particle in a low conductivity matrix, to the determination of the shape of a solidification front located at a large distance from the particle.

9.2. Numerical Determination of the Temperature Profile near a Particle

Since it is not possible to solve analytically the system of differential equations describing the temperature distribution when a particle is very close to the solidification front, an approximate numerical method was used.

The heat conduction equations were solved by a finite element method; i.e., space was divided in small cells and between each pair of cells, the differential equation was approximated by the method of finite differences. To illustrate this method, the case of two dimensional Cartesian coordinates is presented in Appendix E.

For the present problem of a spherical particle in a column of matrix material, a slightly more complex grid was used. To obtain as much detail as possible for the temperature distribution in the vicinity of the sphere, spherical coordinates were used for the sphere and its
immediate proximity (up to 1.1 particle radius). Cylindrical coordinates were used for the rest of the matrix material. The grid used, containing 658 nodes, is shown in Figures 9-3 and 9-4. To make the figure clearer, only the nodes have been marked. The figure has symmetry of revolution around a verticle axis (to simplify the terminology, the particle is assumed to be in a vertical temperature gradient). The planes marked top and bottom in Figure 9-4, located 5.3 particle radii above and below the particle, were assumed isotherms. Horizontally, the temperatures were assumed constant at distances larger than 5 particle radii from the particle, i.e. the particle did not influence temperature profiles at distances larger than 5 radii from the particle.

The latent heat of fusion was introduced as a change in heat capacity for temperatures very close to the melting point (Figure 9-5). A compromise had to be found for the extent $2\delta T$ of the temperature region around the melting point with increased heat capacity. If $\delta T$ is too small, most of the nodes when changing temperature will skip this change in heat capacity; and this is equivalent to neglecting the latent heat of fusion. Further, since the heat capacity will then have a very high value at the melting point, the mathematical solution may oscillate. In contrast, a large $\delta T$ is equivalent to using a very impure material which melts over a broad range of temperature. In most cases, a $\delta T$ of 0.03°C was used.

In the present study, the cases of a camphor matrix (melting point 180°C) with various particles was considered. Three different particle materials were used: copper, glass and an hypothetical material (referred as H.M.) with a thermal conductivity 1/3 that of camphor. In practice,
FIGURE 9-3  GRID USED CLOSE TO THE PARTICLE FOR HEAT FLOW ANALYSIS
FIGURE 9-4 GRID USED FOR NUMERICAL ANALYSIS OF HEAT FLOW
FIGURE 9-5 INTRODUCTION OF THE LATENT HEAT OF FUSION $\Delta H_m$ AS A CHANGE IN HEAT CAPACITY.
no dense material has such a low thermal conductivity and a melting or softening point higher than 180°C; but this last material was introduced to illustrate the case of particles which are less conductive than the matrix. It would correspond, for example, to particles of plexiglass in water. The properties of the materials used in the computations are given in Table 9-3.

To test the validity of the model, since a fairly complex set of nodes was used, the program was run with a camphor particle in a camphor matrix. This test was successful; i.e., the isotherms were horizontal and no discontinuity was observed in the region of transition between cylindrical and spherical coordinates. The procedure used to determine the temperature profile was the following: The temperatures of the top and bottom isotherm planes were fixed and a steady state temperature distribution computed. The top and bottom isotherm planes were then cooled at, for example, 0.01°C/second and the temperature distribution was computed every 0.2 or 0.5 second. Typically, it took between 300 and 600 iterations to compute a steady state and 200 iterations for each time step. All these computations were done on a computer Amdahl 470 V/6 at the C.S. Draper Laboratories; 100 iterations took about 25 seconds of C.P.U. time.

It was found that for the low entropy of fusion matrix, at growth rates below 10 μm/sec, the temperature distribution was very close to a steady state distribution. For higher growth rates or for materials with high entropy of fusion, growing in a non faceted form, the temperature gradient in the solid becomes different from the steady state temperature profile due to the larger release of heat at the interface.
<table>
<thead>
<tr>
<th>Material</th>
<th>Density g/cm³</th>
<th>Heat capacity J/g. °K</th>
<th>Thermal Conductivity W/cm. °K</th>
<th>Melting point °C</th>
<th>Heat of fusion J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camphor - solid</td>
<td>0.94 (113)</td>
<td>2.259 (b)</td>
<td>0.0019 (c)</td>
<td>180.0 (113)</td>
<td>35.56 (113)</td>
</tr>
<tr>
<td>- liquid</td>
<td>0.89 (a)</td>
<td>2.008 (b)</td>
<td>0.0015 (c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper at 170°C</td>
<td>8.85 (104)</td>
<td>0.4000 (105)</td>
<td>3.90 (104)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>190°C</td>
<td>8.85 (104)</td>
<td>0.4019 (105)</td>
<td>3.89 (104)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass at 160°C</td>
<td>2.5 (104)</td>
<td>0.936 (105)</td>
<td>0.0120 (105)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200°C</td>
<td>2.5 (104)</td>
<td>1.004 (105)</td>
<td>0.0120 (105)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H.M. at 160°C</td>
<td>2.5</td>
<td>1.0</td>
<td>0.0005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200°C</td>
<td>2.5</td>
<td>1.0</td>
<td>0.0005</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note:  
(a) Estimated values  
(b) Measured  
(c) Estimated value (Ref. 114)

Table 9-3: Properties of matrix and particles used in the numerical computations
The shapes of the isotherms near the particle are given in Figures 9-6, 9-7 and 9-8, for the condition where the solidification front nearly touches the particle. The temperature profiles along the axis of the cell and far from the particle (at the edge of the cell), are given in Figure 9-9 for the case of a glass particle in camphor (respectively curves #1 and #2). The temperature distribution was also computed when the particle of radius R is replaced by a slab of glass of thickness 2R (curve #3). The temperature profile along the axis of the cell lies, as expected, between the curve for a slab of glass and the curve for pure camphor. Far from the particle, the curve tends towards the temperature distribution at the edges corresponding to pure camphor; and close to the particle, it tends towards the temperature distribution with a slab of second-phase material. The temperature gradient in the vicinity of the particle is much larger than the average temperature gradient in liquid or solid. Reasoning with the average temperature gradient may therefore be somewhat misleading as the region of interest for particle pushing or entrapment is the region very close to the particle. The similar curves for the case of a particle with a smaller conductivity than the melt are given in Figure 9-10. In this case, the temperature gradients close to the particle are slightly smaller than in the rest of the liquid or solid.

The isotherm plots show that, in the case of a copper particle, the particle is nearly isothermal. The difference in temperature between the top and bottom of a particle of radius 10 μm in a temperature gradient of 110°C/cm is only 0.00026 °C (computations for a slab gives a ΔT of 0.00011 °C) or a temperature gradient in the particle of 0.12 °C/cm. The solidification front should therefore wrap around the particle, entrapping
FIGURE 9-6 ISOThERM FOR A COPPER PARTICLE IN A CAMPHOR MATRIX
FIGURE 9-7 ISONTERM FOR A GLASS PARTICLE IN A CAMPHOR MATRIX
FIGURE 9-8 ISOTHERM FOR A PARTICLE OF $k_p = \frac{1}{3} k_L$
IN A CAMPHOR MATRIX
FIGURE 9-9 TEMPERATURE PROFILES FOR A GLASS PARTICLE OF RADIUS R.
IN CAMPHOR. (1) ALONG THE AXIS OF THE CELL (- - - - -),
(2) AT THE EDGE OF THE CELL (---) AND (3) WHEN THE
PARTICLE IS REPLACED BY A SLAB OF THICKNESS 2R (-----).

DISTANCE IN R UNITS

TEMPERATURE IN °C
FIGURE 9-10 TEMPERATURE PROFILES FOR A PARTICLE CONDUCTING LESS THAN CAMPHOR, $k_p/k_L = 1/3$, (1) ALONG THE AXIS OF THE CELL (---), (2) AT THE EDGE OF THE CELL (---) AND (3) WHEN THE PARTICLE IS REPLACED BY A SLAB OF THICKNESS $2R$ (-----).
it readily. In the reverse case of a particle with lower thermal conductivity than the matrix, the particle rests on top of a "hill" of solid, and fresh liquid can flow more easily behind the particle. Hence the particle should be more easily pushed; or perhaps the configuration may be unstable and the particle will move laterally on the front, constantly falling from the "thermal hill".

These conclusions show in detail what was suggested in previous studies and emphasize the possible importance of thermal properties in affecting solidification behavior, but they are not sufficient for our purposes since the solidification front does not follow exactly the isotherm lines.

9.3. Numerical Determination of the Shape of the Front

As seen in Chapter 8, the temperature of the interface, $T_i$, is a function of the kinetics of crystallization, of the pressure and of the curvature of the front:

$$T_i = T_m - \Delta T_{kin} - \Delta T_{pres} - \Delta T_{curv}. \quad (9.4)$$

where $T_m$ is the equilibrium melting point for a flat front under normal pressure. It was shown that the kinetic undercooling term, $\Delta T_{kin}$, could be neglected in the case of small entropy of fusion materials since it is small and since only variations in undercooling affect the shape of the front. The pressure and curvature terms, $\Delta T_{pres}$ and $\Delta T_{curv}$, can both be large (up to a few tenths of degree). An exact solution of the problem would require introducing the temperature profile, $T(z,r)$ in Equation (9.4) and solving this differential equation for various growth rates. The critical velocity would be the maximum growth rate for which a stable
solution exists. However, as discussed in Chapter 8, no exact solution exists even when the temperature profile is assumed to vary linearly and to be independent of \( r \). The influence of a complex temperature profile will therefore be treated as a correction to the previous computation.

First, the shape of the front will be determined when the distance particle-solid, \( h_o \), is larger than 50 to 100 nm, i.e. when the pressure undercooling, due to drag and disjoining force, is negligible. This undisturbed (except for the thermal effect) shape corresponds to the flat front assumed to exist in the previous treatment. Drag and disjoining forces can then be computed for various distances, \( h_o \), (even smaller than 50 nm) and compared with the corresponding values computed for a flat front, to quantify the effect of thermal distortion of the front. Since in the previous derivation for materials with identical properties, it was shown that the front is only very slightly disturbed behind a pushed particle, one can assume that the previous computations are still valid as long as the changes in drag and disjoining forces are considered to occur to a curved front instead of a flat front.

Hence one must first compute the shape of the front when kinetic and pressure effects are neglected. The curvature undercooling, \( \Delta T_{\text{curv.}} \), or Gibbs-Thompson effect is described by the relation

\[
\Delta T_{\text{curv.}} = \frac{\sigma_{\text{SL}}}{\Delta S} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)
\]

(9.5)

where \( R_1 \) and \( R_2 \) are the principal radii of curvature, and \( \sigma_{\text{SL}} \) the surface energy between solid and its melt. The temperature profile around a particle is only known numerically; hence the shape of the front can only be determined by a numerical method. For a given temperature profile,
the position of the front has been computed by a trial and error process, constructing each time the front step by step.

A point of coordinates \((r=0, z=z_0)\), assumed to be on the solidification front was arbitrarily chosen on the axis of symmetry. The coordinates of a point on the solidification front, a short distance away \((r, z(r_1))\) were computed from an expansion in a Taylor series, since first and second derivatives \([z'(o)\text{ and } z''(o)]\) could be determined at the starting point. The procedure was then repeated; at the new point of coordinates \([r, z(r_1)]\) the first and second derivatives \([z'(r_1)\text{ and } z''(r_1)]\) were computed and the coordinates of the next point \([r_2, z(r_2)]\) were determined from a Taylor series.

The first and second derivatives were determined in the following way: at the starting point \((r=0, z_0)\), by reason of symmetry, the tangent to the front is horizontal, \(z'(o) = 0\). Since the temperature is known at this point, the curvature of the front, \(\frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)\) can be known from the Gibbs-Thompson Equation (9.5). The front having symmetry of revolution, the curvature is equal to:

\[
\frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{1}{2} \left( \frac{z'}{r} + \frac{z''}{1+z'^2} \right) \frac{1}{\sqrt{1+z'^2}} \tag{9.6}
\]

and from this equation, \(z''(o)\) can be computed.

The ordinate, \(z(r_1)\) of the front, at a distance \(\Delta r\) from \(r_0\) and the tangent at this point, \(z'(r_1)\), can be approximated by the first terms of a Taylor series:

\[
\begin{align*}
  r_1 &= r_0 + \Delta r \\
  z(r_1) &= z(r_0) + \Delta r \cdot z'(r_0) + \frac{\Delta r^2}{2} \cdot z''(r_0) \\
  z'(r_1) &= z'(r_0) + \Delta r \cdot z''(r_0)
\end{align*} \tag{9.7}
\]
The temperature at the point \([r_1, z(r_1)]\), is known and the second derivative \(z''(r_1)\) can again be computed from Equations [(9.5) and (9.6)]. This computation process can be repeated at \(r_2 = r_1 + \Delta r\), \(r_3 = r_2 + \Delta r\) ... until the shape of the front is completely known.

If the initial position \((o, z_o)\) was too low, the front would curve down (Figure 9-11) and never tend toward the isotherm corresponding to the melting point. If on the contrary, the initial position was too high, the front would curve up, if the initial position was correct would the front tend, at large distances from the particle, toward the melting point isotherm.

For the computation of the thermal profile around a particle, it was assumed that the liquid solidifies at exactly 180.0°C. Obviously, this assumption is not valid in detail [see Equation (9.2)]; and some points that were assumed, according to their temperature, to be solid should have been considered liquid, and vice versa (shaded areas in Figure 9-11). The thermal program was therefore rerun to compute a temperature profile when the nature of each node (solid or liquid) was fixed. From this new temperature distribution, a second approximation of the position of the front was computed. As expected in most cases, the first and second approximation of the shape of the front were practically identical.

All these iterative computations of the shape of the front were done on a computer. The increment \(\Delta r\) used was 0.005 radius of the particle close to the axis of the particle and 0.025 radius further away. The shape of the solidification front when it nearly touches the particle
FIGURE 9-11 COMPUTATION BY A TRIAL AND ERROR PROCESS OF THE SHAPE OF THE SOLIDIFICATION FRONT

--- (1) - ISOTHERM T = MELTING JOINT

----- (2) - SOLIDIFICATION FRONT - STARTING POINT TOO LOW

----- (3) - SOLIDIFICATION FRONT - STARTING POINT TOO HIGH

----- (4) - TRUE SOLIDIFICATION FRONT
(distance between particle and front on the axis of symmetry, \( h_0 \), equal to a few nm) has been determined by this method and is shown in Figures 9-12 to 9-20 for copper, glass and H.M. particles of radius 10 and 100 \( \mu m \) and for different temperature gradients in the liquid phase.

The front behind a 10 \( \mu m \) copper particle (Figure 9-12) is practically flat at small temperature gradients; it dimples for larger temperature gradients (Figure 9-13), but is far from following an isotherm.

For a larger particle (\( R = 100 \ \mu m \)), the same trend is observed when the temperature gradient increases (Figure 9-14, 9-15, 9-16): the steeper the temperature gradient, the more curved is the front. But now, as the correction for curvature is small, the front practically follows an isotherm; and is the case of large temperature gradients, the front is nearly hemispherical.

Similar results are observed with glass particles; but the front is not so curved as with copper particles (Figures 9-17, 9-18). These plots show very clearly that the effect of thermal conductivity is negligible for small particles, but becomes the dominating factor for large particles; and, for example, one would not expect that a 100 \( \mu m \) copper particle could be pushed if the temperature gradient is larger than 30 or 40 \( ^\circ C/cm \).

Finally, the results for a H.M. particle are given in Figures 9-19 and 9-20. Here again, the higher the temperature gradient, the more curved is the front; but greater curvatures imply now more effective pushing of the particles. The radius of curvature of the front behind the particle on the axis of symmetry is not limited by the radius of curvature of the particle, and in fact for large particles and large temperature
FIGURE 9-12  COPPER PARTICLE OF RADIUS $10\mu m$ IN A CAMPHOR MATRIX
TEMPERATURE GRADIENT IN THE LIQUID $\sim 11^\circ C/cm$
(---) SOLIDIFICATION FRONT; (---) 180$^\circ C$ ISOTHERM
FIGURE 9-13 COPPER PARTICLE OF RADIUS 10 μm IN A CAMPHOR MATRIX TEMPERATURE GRADIENT IN THE LIQUID ~ 110°C/cm (——) SOLIDIFICATION FRONT; (-----) 180°C ISOTHERM
FIGURE 9-14 COPPER PARTICLE OF RADIUS 100 $\mu$m IN A CAMPHOR MATRIX
TEMPERATURE GRADIENT IN THE LIQUID $\sim 1.1 ^\circ C/cm$
(—) SOLIDIFICATION FRONT; (—-) 180°C ISOTHERM
FIGURE 9-15 COPPER PARTICLE OF RADIUS 100\(\mu\)m IN A CAMPHOR MATRIX TEMPERATURE GRADIENT IN THE LIQUID \(\sim 11^\circ\text{C/cm}\) (---) SOLIDIFICATION FRONT; (——) 180°C ISOTHERM
FIGURE 9-16 COPPER PARTICLE OF RADIUS 100 μm IN A CAMPHOR MATRIX. TEMPERATURE GRADIENT IN THE LIQUID ~ 110°C/cm. (——) SOLIDIFICATION FRONT; (—–) 180°C ISOTHERM
FIGURE 9-17  GLASS PARTICLE OF RADIUS 10\,\mu m IN A CAMPHOR MATRIX. SHAPE OF THE SOLIDIFICATION FRONT FOR VARIOUS TEMPERATURE GRADIENTS
Figure 9.18 Glass particle of radius 100μm in a camphor matrix. Shape of the solidification front for various temperature gradients.
FIGURE 9-19 PARTICLE WITH A LOWER THERMAL CONDUCTIVITY THAN THE CAMPHOR MATRIX \( \frac{\kappa_L}{\kappa_P} = 3 \) AND RADIUS 10 \( \mu \)m. SHAPE OF THE SOLIDIFICATION FRONT FOR VARIOUS TEMPERATURE GRADIENTS.
FIGURE 9-20 PARTICLE WITH A LOWER THERMAL CONDUCTIVITY THAN THE CAMPHOR MATRIX ($k_L/k_P = 3$) AND RADIUS 100 $\mu$m. SHAPE OF THE SOLIDIFICATION FRONT FOR VARIOUS TEMPERATURE GRADIENTS.
gradients, the radius of curvature of the front is about half the radius of the particle.

9.4. Drag and Disjoining Forces

To quantify these observations, the drag force, $F_D$, was computed for the various shapes of the solidification front. The formula used to compute the drag force has been discussed in Chapter 7.

$$ F_D = \int^\infty_R 2\pi r \cdot \Delta P(r) \cdot dr $$

(9.8)

$$ \Delta P(r) = \frac{QV}{\pi} \cdot \int^r_R \frac{x dx}{h^3(x)} $$

(9.9)

$$ Q = 6 \pi \frac{\rho_s}{\rho_L} \eta $$

(9.10)

where $P(r)$ is the difference in pressure between a point in the liquid at $r$, and a point at the same height in the liquid far from the particle; $h(r)$ is the height of the liquid film; and $V$ the growth rate. For a viscosity, $\eta$, of 0.5 c.poise, and a ratio of the densities of solid and liquid, $\rho_s/\rho_L = 0.94/0.89$, the constant $Q$ is equal to 0.02 S.I.u.

This derivation of the drag force is only valid for a slowly varying gap thickness and will therefore be inadequate in the case of hemispherical fronts. The value computed in this fashion will, however, be an underestimate of the real drag force and is sufficient for purpose of comparison. In the graphs previously shown, the minimum distance between solid and particle, $h_0$, was arbitrarily fixed at 10 nm for the 100 $\mu$m particles and 1 nm for the 10 $\mu$m particles. This choice was considered reasonable as it has been shown in the previous chapters that the minimum distance $h_0$ is of the order of 1 to 20 nm and increases with particle size.
It was also observed during numerical computations that the shape of the front changed very little when $h_0$ decreased from 20 nm to 1 nm. These computations are therefore sufficient to determine the effect of changes in the shape of the front on drag force for a given particle size but cannot be used to compare the drag forces on particle of different sizes. For the computation of drag force, the growth rate was fixed at 5 μm/sec. The gap thickness, h, and the drag forces are given for the 10 and 100 μm particles in Tables 9-4 and 9-5. The shift in the melting point is also given for the point of the front on the axis of symmetry. With the values for camphor, the undercooling corresponding to the radius of curvature of the particle is 0.005°C and 0.050°C for respectively 100 μm and 10 μm particles.

For small particles (Table 9-4) and small temperature gradients, the drag force for copper or glass particles is only slightly larger than that for a flat front. The approximation of neglecting the differences in thermal conductivity is therefore acceptable in this case. But even for small particles, if the temperature gradient increases to 110°C/cm, the drag force behind a glass particle becomes 5 times larger than that for a flat front, and behind a copper particle nearly 200 times larger than for a flat front.

For large particles (R = 100 μm) and temperature gradients of at least 10°C/cm, the drag force behind a glass particle is more than 40 times that for a flat front, and behind a copper particle, the drag force becomes more than 5 orders of magnitude larger than for a flat front. In these cases, the effect of thermal conductivity clearly cannot be neglected. The results for 100 μm particles in a temperature gradient
<table>
<thead>
<tr>
<th>Particle</th>
<th>Copper</th>
<th>Glass</th>
<th>H.M.</th>
<th>Flat Front</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔT/Δz in °C/cm</td>
<td>11</td>
<td>110</td>
<td>11</td>
<td>110</td>
</tr>
<tr>
<td>z in μm</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>11.5</td>
<td>3.9</td>
<td>12</td>
</tr>
<tr>
<td>0.5</td>
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<tr>
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<td>2.5</td>
<td>393</td>
<td>117</td>
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<td>219</td>
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<td>3.0</td>
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<td>414</td>
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<td>964</td>
<td>544</td>
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<td>1160</td>
<td>405</td>
<td>1211</td>
<td>700</td>
</tr>
<tr>
<td>5.0</td>
<td>T(x=0) - T&lt;sub&gt;m&lt;/sub&gt; in °C</td>
<td>0.0077</td>
<td>0.0377</td>
<td>0.0055</td>
</tr>
<tr>
<td>Drag force x10&lt;sup&gt;9&lt;/sup&gt; in N</td>
<td>7.4</td>
<td>933</td>
<td>6.5</td>
<td>27.2</td>
</tr>
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</table>

Table 9-4: Thickness of the gap (in nm) between a copper, glass or H.M. particle and a camphor solidification front and resulting drag force for various temperature gradients (Radius of particle = 10 μm)
<table>
<thead>
<tr>
<th>z in μm</th>
<th>ΔT/Δz in °C/cm</th>
<th>Copper</th>
<th>Glass</th>
<th>Hyp. Mat.</th>
<th>Flat Front</th>
</tr>
</thead>
<tbody>
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<td>10</td>
<td>10</td>
<td>10</td>
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<tr>
<td>5</td>
<td>39</td>
<td>9.3</td>
<td>67</td>
<td>30</td>
<td>34</td>
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<tr>
<td>10</td>
<td>128</td>
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<td>1502</td>
<td>534</td>
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<td>1930</td>
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</tr>
<tr>
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<td>7040</td>
<td>2550</td>
<td>16100</td>
</tr>
</tbody>
</table>

\[ T(x=0) - T_m \] in °C

| Drag force x10^6 N | 1.45 | >9000 | >300 | 0.036 | 0.015 | 0.004 | 0.05 |

Table 9-5: Thickness of the gap (in nm) between a copper, glass or H.M. particle and a camphor solidification front for various temperature gradients. Radius of particle = 100 μm
of $110^\circ C/cm$ are incomplete as it was not possible to determine the shape of the front beyond 0.3 to 0.4 radius. This difficulty is due to small uncertainties in the temperature calculations—since the particle is very close to the front and the temperature gradient is very steep, a small error in temperature is sufficient to force the front against the particle or away from it.

In these computations, the minimum distance $h_o$ was chosen arbitrarily within reasonable limits. The next question that must therefore be answered is how the shape of the front and the resulting drag force vary when $h_o$ varies.

We saw previously that for a flat interface, the drag force $(F_D)_F$ is inversely proportional to $h_o$:

$$ (F_D)_F = 6\pi \eta V \cdot \frac{R^2}{h_o} $$  \hspace{1cm} (9.11)

The drag force, $F_D$, has been computed for a particle of radius 60 $\mu m$ in a temperature gradient of $10^\circ C/cm$ and $50^\circ C/cm$, as a function of $h_o$; $F_D$ has been normalized by dividing it by the drag force, $(F_D)_F$ for a flat interface, located at the same distance $h_o$. These relative or normalized drag forces are plotted in Figure 9-21 for copper, glass and H.M. particles. Even for the small temperature gradient, in the case of a copper particle, the drag force is increased by more than three orders of magnitudes by the bending of the front. As the front approaches a copper or glass particle, it curves more and more around the particle, and as a result the drag force increases faster than if the front were flat. This variation is large for a copper particle in a large temperature gradient but much smaller for a glass particle. This difference
FIGURE 9-21 RATIO OF THE DRAG FORCE FOR A CURVED INTERFACE TO THAT FOR A FLAT INTERFACE (RESPECTIVELY $F_D$ AND $(F_D)_F$) AS A FUNCTION OF $h_0$, THE MINIMUM DISTANCE PARTICLE FRONT. RADIUS OF PARTICLES = 60 $\mu$m TEMPERATURE GRADIENT = 10°C/cm AND 50°C/cm
Figure 9-21-b
is due to the fact that in the case of a copper particle, the front is very close to the particle over a large area of the particle and a small deformation of the front is sufficient to increase drastically the drag force.

For distances varying between 50 and 1 nm, the relative drag force is almost constant for glass and H.M. particles since the shape of the front varies only slightly when $h_o$ varies (the range of distances covered is less than $0.1\%$ of the radius). Therefore in these cases, the thermal bending of the front can be taken into account even if the minimum distance $h_o$ is not accurately known.

The relative drag force was also computed for particles of radius 10 μm in a temperature gradient of 10 and 50°C/cm. The front remains much flatter in this case, and the drag force is not very different from the drag force for a flat front (i.e. relative drag force close to unity). The relative drag force remains practically constant when $h_o$ varies between 0.5 and 25 nm. The results are given in Table 9-6.

Considering drag force alone may, however, be misleading. If the front curves around the particle, the disjoining force will also increase; and one must study the ratio of drag force over disjoining force. The growth rate, $V$, at which a particle is pushed for a given geometry can be obtained by taking this ratio as equal to unity (assuming that no other force acts on the particle). For a flat interface, this ratio is equal to $-6QVRh_o/A$ and the velocity at which a particle is pushed is

$$V_F = \frac{-A}{6QVRh_o}$$  \hspace{1cm} (9.12)
<table>
<thead>
<tr>
<th>Particle</th>
<th>Temperature gradient °C/cm</th>
<th>$F_D/(F_D)_F$</th>
<th>$V/V_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>50</td>
<td>4.69 - 4.25</td>
<td>0.485 - 0.520</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.45 - 1.41</td>
<td>0.855</td>
</tr>
<tr>
<td>Glass</td>
<td>50</td>
<td>2.45</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.28</td>
<td>0.89</td>
</tr>
<tr>
<td>H.M.</td>
<td>50</td>
<td>.75</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>.935</td>
<td>1.035</td>
</tr>
</tbody>
</table>

Table 9-6: Relative draft forces ($F_D/(F_D)_F$) and relative velocities ($V/V_F$). $R = 10 \mu m$; $h_o = 0.5$ to $25 \text{ nm}$
Hence if a particle is pushed at increasing velocities, the minimum distance \( h_o \) decreases as \( 1/V \). The notion of critical velocity can be introduced in this derivation by simply considering that the distance \( h_o \) cannot be less than a few molecular diameters. This derivation for a "flat front" is also somewhat unrealistic as even if particle and melt have exactly the same thermal conductivity the front does not remain flat, but curves slightly around the particle. This notion of a flat front was, however, introduced to normalize the subsequent results and illustrate the effect of the thermal properties.

In the computation of the disjoining force, \( F_{\text{dis.}} \) [Equation (9.13)] the retarded forces have been neglected. This approximation is very good however since the minimum distances \( h_o \) considered are small (less than 50 nm) and since the disjoining forces decrease very rapidly with increasing distances:

\[
F_{\text{dis.}} = -\frac{A}{3} \int_0^R \frac{r^2 dr}{1^3(r)}
\]  

(9.13)

(see Chapter 7 for the derivation of this formula and Figure 9-2 for the definition of 1). \( A \) is the Hamaker constant.

The disjoining force was computed for the same 60 μm particles in a 10°C/cm an 50°C/cm temperature gradient; and the steady state growth rate, i.e. the growth rate for which the drag force equals the disjoining force, was deduced. The results, normalized by dividing this growth rate \( V \) by the growth rate for a flat interface, \( V_F \) [Equation (9.12)] are plotted as a function of \( h_o \) in Figure 9-22. Curving of the interface around the particle decreases the growth rate by a factor of about 5 in
FIGURE 9-22 RATIO OF THE STEADY STATE PUSHING RATES FOR A CURVED INTERFACE TO THAT FOR A FLAT INTERFACE (V AND V_F RESPECTIVELY) AS A FUNCTION OF THE MINIMUM DISTANCE PARTICLE-FRONT, h_0. RADIUS OF PARTICLE, 60 μm TEMPERATURE GRADIENT: 10 AND 50°C/cm
the case of glass particles and by a factor of 20 to 30 for copper particles in a 10°C/cm temperature gradient. The normalized growth rate varies only slowly with $h_0$. The distance $h_{cr}$ corresponding to the critical velocity must be within the range of values covered in this study (1 to 50 nm). Therefore even for a small temperature gradient of 10°C/cm, in the case of a 60 μm particle, the influence of thermal properties is very large. The results of similar computations for 10 μm particles in 10 and 50°C/cm temperature gradients are given in Table 9–6. The effect of thermal bending of the front is in this case very small.

To complete this study, the shape of the front, drag force and disjoining force were computed for various particles of radius 5 to 150 μm in temperature gradients of 10 and 50°C/cm. To obtain a consistent set of values, the minimum distance particle-front, $h_0$ was considered to be a function of R: The relation derived by Chernov et al. (31) was used; they found that for particles with radius much smaller than $R_M = 500$ μm, the distance $h_0$ varies as $R^{1/3}$. The minimum distance, computed according to their equation, for a 10 μm particle in camphor, is, $h_0 = 7.1$ nm. (The limiting radius $R_M$ computed using the data for camphor is even larger than 500 μm.) One may note that this relation between $h_0$ and R is different from the one Chernov et al. (110) derived in the case of a particle pushed by a crystal growing from a supersaturated solution [Equation (9.3)]: $h_0 \propto R^{1/2}$. In the case of growth from a supersaturated solution, the critical distance $h_0$ is the distance below which defects are formed in the crystal behind the particle and entrapment of the particle finally occurs. The parameter of interest in this case is not the temperature distribution around the particle but the concentration
of solute. It is therefore difficult to compare these two derivations. Furthermore, using a relation in $R^{1/2}$ instead of $R^{1/3}$ would not change appreciably the present results.

The resulting normalized drag forces and normalized equilibrium growth rates are plotted in Figures 9-23 and 9-24. As was previously shown, the effect of thermal conductivity is more important for large particles and large temperature gradients. In the case of copper particles, the very rapid change in normalized drag force when the particle size varies from 20 to 60 $\mu$m is illustrated in Figure 9-25.

The normalized growth rate varies rapidly with $R$ for radii larger than 5 or 10 $\mu$m; and for a limited range of radii, the change in growth rate can be approximated by an exponential form:

$$\frac{V}{V_F} \propto \exp(-\beta R)$$  \hspace{1cm} (9.14)

In all previous studies where particle and matrix were assumed to have the same thermal conductivity, it was found that for smooth particles, the critical velocity varied as $1/R^n$ with $n$ between 1 and 2; and for the most common case of rough particles since the size of the irregularities is often independent of the particle size, the critical velocity is predicted to decrease even more slowly with increasing particle size. This dependence is true for $V_F$, but the real velocity $V$ varies much faster:

$$V \propto \frac{1}{R^n} \exp(-\beta R)$$  \hspace{1cm} (9.15)

Experimentally, the critical velocities for copper and glass particles of radius 5 $\mu$m were measured as 8 and 3 $\mu$m/sec respectively. The
FIGURE 9-23 NORMALIZED DRAG FORCES FOR VARIOUS PARTICLES AND TEMPERATURE GRADIENTS AS A FUNCTION OF PARTICLE SIZE. NORMALIZATION IS DONE BY DIVIDING THE DRAG FORCE FOR A CURVED INTERFACE, $F_D$, BY THAT FOR A FLAT INTERFACE $(F_D)_F$ LOCATED AT THE SAME MINIMUM DISTANCE, $h_0$, FROM THE PARTICLE.
FIGURE 9-24 NORMALIZED EQUILIBRIUM PUSHING RATES FOR VARIOUS PARTICLES AND TEMPERATURE GRADIENTS AS A FUNCTION OF PARTICLE SIZE. THE PUSHING RATE IS NORMALIZED BY DIVIDING IT BY THAT FOR A FLAT INTERFACE LOCATED AT THE SAME MINIMUM DISTANCE, $h_0$, FROM THE PARTICLE.
Figure 9-25: Copper particle in a temperature gradient of 10°C/cm. Variation of normalized drag force as a function of particle size.
critical velocity for an H.M. particle of radius 5 μm was arbitrarily assumed to be 3 μm/sec. For radii of 5 μm or less, the thermal correction is small (Figure 9-24); these experimental data can therefore be used as a scaling factor to compute the dependence of critical velocity on particle size. This dependence was obtained by considering that n=1 and correcting the curve with the results of Figure 9-24. The resulting curves (Figures 9-26 and 9-27) show a sharp drop in critical velocity for copper or glass particles as the size increases. Experimentally, velocities of less than 5 x 10⁻² μm/sec are extremely difficult to observe (as the front tends to move unevenly) and the critical velocity may be assumed to be zero. The shape of these curves is very similar to the curves observed experimentally (Figure 2-4). The difference in thermal conductivity between particle and liquid explains therefore the very rapid decrease of the critical velocity for large particles and why, in some works, the existence of critical size beyond which particles are never pushed has been assumed.

These computations explain also the success of Zubko et al's experiment. If the thermal effect is neglected, one would predict that these very large particles (radius of the order of a few mm) should have been readily entrapped at the large growth rates used (> 14 μm/sec). But if the particles are less conductive than the matrix, for these very large particles, the thermal effect becomes dominant (corresponding to the hypothetical case treated in this chapter, k_p/k_1 < 1) and the particles are pushed.

In conclusion, for large particles and/or large temperature gradients, the difference in thermal conductivity between particle and liquid is a
FIGURE 9-26 DEPENDENCE OF CRITICAL VELOCITY ON PARTICLE SIZE COPPER PARTICLES IN 50 AND 10°C/cm TEMPERATURE GRADIENTS
major factor in determining the critical velocity for low entropy of fusion materials and for some high entropy of fusion materials at low growth rates. It has also been shown that the influence of this "thermal effect" on critical velocity can be estimated quantitatively.

9.5. Shape of the Front—Experimental Results

As discussed previously in Chapter 5, the shape of the front is not only a function of the entropy of fusion of the materials but also of the temperature gradient and growth rate. It was therefore possible to observe the solidification front bending behind a particle i.e. following isothermal lines not only with low entropy of fusion materials like camphor or carbon tetrabromide but also with some high entropy of fusion materials like naphthalene or durene, at low growth rates.

9.5.1. Non Prismatic Front:

When the solidification front follows the isotherms (but for the effect of curvature and pressure) the theory developed in this chapter should be directly applicable. The bending of the front observed behind a pile-up of material with a higher thermal conductivity than the matrix was discussed in the first part of this chapter (Figure 9-1). As expected, in the case of metallic particles with much higher conductivity than the matrix, the front is depressed behind the pile-up by about half the thickness of the pile-up.

In the case of large particles (diameter >50 μm) having a higher thermal conductivity than the matrix, the previous computation predict that the front should bend and be practically hemispherical. This case is illustrated by a succession of photographs (Figure 9-28) showing the
Figure 9-28 (a) to (h) (from top to bottom, left to right)

Copper particle of diameter 210 μm in a durene matrix (Liquid on top)

Growth rate 1.2 μm/s
shape of a front of durene as it encounters a large copper particle (diameter 210 \( \mu \)m). The temperature gradient was about 50°C/cm and the growth rate 1.2 \( \mu \)m/s. In these pictures, the solid is at the bottom with two visible grain boundaries and the liquid is at the top. These pictures were taken by focusing the camera at the level of the largest cross section of the particle. When the front approaches the particle, it dimples behind the particle and then, after entrapment, bulges ahead of the particle. More important is the fact that at lower growth rates, large particles were observed to be pushed when the front had a shape like that shown in the photographs (c) and (d) of Figure 9-28. Up to photograph (d), included, the particle is separated from the solid by a liquid film. To obtain a three-dimensional representation of the phenomenon, a picture of copper particles close to a slanted front was taken (Figure 9-29). The sample was illuminated with polarized light so that lines of equal elevation appeared as isochromatic lines. The curvature of the front is hence made clearly visible, even when the particle is some distance away.

The shape of the front behind a particle with lower thermal conductivity than the matrix was observed with an air bubble. In general, the air bubbles are attracted by the front and partially entrapped (Figure 5-20); but in some cases (Figure 9-30) it was possible to observe the bubble before entrapment. The front in this case is raised behind the particle.

In these two cases of large particles, the shape of the front observed is in accord with the previous computations.

The case of small particles with higher thermal conductivity than
Figure 9-29: Durene matrix with copper particles. The diameter of the largest particle is about 150 µm. (Liquid on top)
Figure 9-30: Durene matrix. Air bubble pushed at the solidification front (Liquid on top)
Figure 9-31: Small copper particles (10-20 μm) in durene.
(Liquid to the right)
Figure 9-32: Nickel particles (2-5 μm) in thymol

Figure 9-33: Copper particles (2-45 μm) in thymol
(Liquid on top)
the matrix is illustrated in Figure 7-31a (10 μm copper particles in duroene). The front in this case is not as bent as for larger particles. The particle had been pushed for several minutes at about 2 μm/sec when the picture was taken.

It was also observed in many cases that pile-ups of particles were pushed while single particles were entrapped. This phenomenon can be due either to the presence of small particles forming a layer between front and larger particles (Figure 5-15) or to the smoothing of the thermal dimples. This last point is clearly seen in Figure 9-31b where the front is nearly flat behind the group of copper particles whereas it is very dimpled behind a single particle.

9.5.2. Prismatic Growth

In this case, the previous computations do not apply since the front follows well defined crystallographic planes and is insensitive to small variations in thermal profile. The front does not bend behind pile-ups of materials as shown in Figure 9-32 (Ni particles in Thymol); the front also remains flat behind small or large single particles (Figure 9-33), Thymol, Cu particles).

9.5.3. Conclusion

From this analysis one can draw the following conclusion: In the case of materials growing with a non faceted morphology, large particles should be entrapped more readily than predicted from the derivation in Chapter 8, and small pile-ups pushed more readily than single particles; and simply for thermal reasons, the critical velocity of a given particle should be higher in a high entropy of fusion matrix than in a low entropy of fusion matrix.
CHAPTER 10

SUMMARY AND CONCLUSION

The problem of the interaction of second phase particles with a solidification front has been experimentally and theoretically studied. In the first part of this study the existing literature related to this problem was reviewed. The results of existing experimental studies were often found to be in poor agreement. This discrepancy must be due to differences in the morphology and the chemical nature of the surface of the particles used. When a particle is pushed by a solidification front, a thin liquid film must always exist between particle and front. The problem of particle rejection is, therefore, directly related to that of the stability of thin liquid film. The latter problem has been extensively studied by Deryagin and his group who introduced the notion of disjoining pressure. For non-polar pure liquid this disjoining pressure or rejection force is mainly of van der Waals origin.

It had been initially shown by Uhlmann et al. that the rejection force was not of electrostatic origin. This result was confirmed in the present work: particles that were electrostatically attracted by the front were subsequently rejected by the same growing front. The rejection forces between two solids separated by a liquid have seldom been directly measured but in the cases where data exist a fair agreement was found with values computed from the molecular force theory. The rejection force can be considered to be due either to the variation in surface free energy of the liquid film with its thickness (Uhlmann's et al.'s approach) or to be due to the change in bulk free energy of the system (molecular forces) with film thickness (Chernov et al.'s approach). It was shown how
both approaches were, in fact, identical. The major difficulty associated with the surface energy approach was the determination of the interfacial free energy solid-particle. It was shown that Neuman's computations predict interfacial energies solid-melt too small by one or two orders of magnitude. Extension of his results to the solid particle interface was, therefore, meaningless. The molecular forces can be computed either by summing all the molecular pair interactions (microscopic approach) or by treating the media as continuum. This latter approach is the more rigorous for separation distances larger than a few molecular distances. Lifshitz, who developed this treatment showed that the dispersion forces could be computed if the complex part, $\varepsilon''$, of the dielectric constant was known at all frequencies. The value of the rejection force could, therefore, be deduced from optical and dielectric measurements.

The theoretical derivation of critical velocity has been treated in several studies. These treatments differ mainly in the approximations used. Uhlmann et al. were the first to present a derivation of critical velocity in agreement with experimental data and were also the first to realize the importance of surface irregularities on critical velocity. The most complete treatment for smooth particles is that of Chernov et al.'s. In all these derivations, particle and matrix were assumed to have identical thermal properties.

In the present study the critical velocity was measured in an horizontal set-up for various particles (Au, Cu, Zn, Ni, glass, Ge) in low and high entropy of fusion organics. The low entropy of fusion organics (camphor, carbon tetrabromide) have properties in many respect
similar to that of metals. Measurements of critical velocities are subject to many errors and uncertainties. The possible causes of error have been discussed. Visual observation of the particles while they are pushed or entrapped allowed to eliminate some of these errors (curved or slanted front, particle pushed by a bubble or by smaller particle, pushing or entrapment at grain boundaries), but in spite of these precautions it was observed that a range of growth rates existed for which particles were pushed for some distance before being entrapped. This behavior was partially due to non-sphericity of the particles, to irregularities on the surface of the particles, and to local changes in the chemical nature of the surfaces. The following conclusions could be drawn: The critical velocity decreased when the viscosity of the melt increased; it was lower in low entropy of fusion organics than in high entropy of fusion organics having the same viscosity; it decreased with increasing particle size as $R^{-n}$ where $n$ was equal to unity for small spherical particles (1 μm<$R<$30 μm) and increased with increasing particle sizes. Contrarily to what was observed by Chen, an increase in the force exerted by a particle on the front was not observed to increase the critical velocity but on the contrary to reduce it.

An attempt was made to compute the disjoining force from optical properties. It was shown that the present measurements limited to wavelength longer than 185 nm were not sufficient to determine with precision the dielectric constant $\varepsilon(i\omega)$ needed to compute the dispersion forces. A knowledge of the optical constant in the vacuum u.v. and far u.v. were necessary but these measurements are very difficult for liquids with
a high vapor pressure and absorbing strongly in this frequency range. The Hamaker constants were computed for the water-ice system for which the optical data are known over a broad range of frequencies (0 to 30 eV). These computations showed that the Hamaker constant for short distances of interaction varied between -0.1 and $-1 \times 10^{-20} \text{ J}$ for several metals and oxides and was negative but very small for teflon. These computations also showed that the approximate formulae used to estimate the rejection force may be misleading since in some cases the sign of the Hamaker constant was wrong.

The forces acting on a particle were computed for various geometries of the solidification front. It was shown that cusping of the front behind a particle increased drastically the drag force and reduced the critical velocity. The differential equation that the solid-liquid interface must satisfy was derived. The critical velocity is the maximum velocity for which a stable solution exists. Physically, the existence of a critical velocity is due to the balance between drag and disjoining force. When the growth rate is increased, the distance particle-front decreases, increasing the rejection force more than the drag force but at the same time the front curves behind the particle increasing the drag force more than the disjoining force. At low growth rates, the first effect is the largest whereas at growth rates higher than the critical velocity the second effect dominates. The differential equation of the shape of the interface could not be solved exactly but it was shown that an exact knowledge of the shape of the front was not necessary to compute the critical velocity. The thickness of the liquid film behind a particle was larger than about 10 molecular
diameters. The transport of liquid in this film was, therefore, assumed
to occur by a flow mechanism. The computed critical velocity was found
to be proportional to the Hamaker constant to a power 2/3 or 1, inversely
proportional to the viscosity of the melt and to vary with particle size
as $R^{-n}$. In the absence of an external field the coefficient $n$ varied
between 4/3 and 1. Introduction of a field drastically reduced the
critical velocity for particles larger than 10 or 20 $\mu$m, and $n$
increased with particle size from 4/3 to 4. The presence of irregularities
at the surface of the particles increased the critical velocity by
several orders of magnitude and decreased $n$ ($n = 2/3$). The computed
critical velocities (assuming a Hamaker constant of $10^{-20}$ J) and the
computed particle size for which the effect of an external field became
important were in good agreement with experimental data.

Finally, it was shown that for a macroscopically smooth front--
i.e. a front following the isotherms-- , the approximation of neglecting
the differences in thermal properties between particles and matrix
could be very poor especially for large particles. The temperature
profile in the vicinity of a particle was determined by a finite
element analysis and the solidification front was constructed
numerically. These computations showed that if the particles had a
higher thermal conductivity than the matrix, the front dimpled behind
the particle. As a result the critical velocity was reduced by
several orders of magnitude, and the coefficient $n$ was increased. This
effect was estimated quantitatively. The larger the particle the more
pronounced was the dimpling, and the larger was the reduction in
critical velocity. This thermal dimpling has been well documented
experimentally and the reduction in critical velocity with particle size explained the observation that beyond a certain particle size the critical velocity decreased very quickly. Some authors even introduced the notion of a critical size above which no pushing occurred. Conversely, if the particles had a lower thermal conductivity than the matrix, the front was raised behind the particle and the critical velocity was increased.

In conclusion, critical velocities were measured for various systems and analytical expressions in qualitative and quantitative agreement with these experimental data were derived. The importance of differences in thermal properties was demonstrated. An exact computation of the critical velocity would require a knowledge of the optical properties of the solid and liquid matrix over a broader range than presently available.
APPENDIX A

LIST OF SYMBOLS

\( A \)  
non retarded Hamaker constant

\( A_{132} \)  
A between bodies 1 and 2 separated by a medium 3. If 3 vacuum, this subscript is omitted

\( A_m \)  
area occupied/mole

\( a_0 \)  
molecular diameter

\( B \)  
retarded Hamaker constant

\( B_3 \)  
\(-A/6\pi\)

\( C_{ij} \)  
London constant (non retarded)

\( C_i \)  
adjustable parameter [Equations (3.59) and (3.62)]

\( c \)  
speed of light = \( 2.998 \times 10^8 \) m/s

\( D \)  
diffusion coefficient

\( d \)  
distance

\( e \)  
charge of the electron = \( 4.803 \times 10^{-10} \) e.s.u.

\( F \)  
force

\( F_D \)  
drag force (\( >0 \) if attraction)

\( F_{D_0} \)  
drag force on sphere close to a flat front

\( F_{\text{dis.}} \)  
disjoining force (\( >0 \) if repulsion)

\( (F_{\text{dis.}})_o \)  
force between a sphere and a flat front

\( G \)  
temperature gradient in the z direction

\( G_i \)  
chemical potential

\( g \)  
acceleration of gravity = \( 9.81 \text{ m/s}^2 \)

\( H \)  
distance in the z direction between the center of a particle and the undisturbed front
$H_1$ hight of irregularities on a particle

$h$ separation particle-front in the $z$ direction

$h_0$ $h$ on the axis of symmetry

$h_{oc}$ $h_0$ when $V = V_c$

$h_\phi$ minimum value of $h_0$

$h_1, h_2$ $h$ at $r = r_o$ and $r = R$

$h$ Plank's constant/2$\pi = 1.054 \times 10^{-34}$ J.s

$I$ ionization potential

$K$ constant in Equation (3.12) (= .25 to .86)

$K_{ij}$ London's constant (retarded)

$k$ Boltzmann's constant = $1.321 \times 10^{-23}$ J/°K

absorption index (Chapters 3, 6)

thermal conductivity (Chapter 9)

$L$ latent heat of fusion/unit volume

$L$ radial distance particle-front

$L_1$ $L$ at $r = r_o$

$m$ rest mass of the electron = $0.911 \times 10^{-27}$ g

$N, N'$ number and effective number of irregularities in contact with the front

$N_1$ number of molecule/unit volume

$n^*$ complex index of refraction

$n$ index of refraction

$n_s$ number density of molecules in the surface

$P$ pressure

$P_e$ external pressure

$P_f$ pressure of the liquid in a film
\( \Delta p_{cav} \)
- negative pressure necessary to induce cavitation

\( q \)
- \( F/F_{\text{dis.}} \)

\( R, R_i \)
- radius of particle and irregularities

\( r \)
- radial distance in cylindrical coordinates

\( r_0 \)
- radius of the zone of strong interaction

\( S, S_i \)
- area of the projection of the zone of contact and of the zone occupied by each irregularity

\( \Delta S_M, \Delta S \)
- entropy of fusion per mole and per unit volume

\( T \)
- absolute temperature

\( t \)
- thickness of surface layers

\( U \)
- interaction energy

\( u \)
- velocity

\( V, V_n \)
- velocity, normal velocity

\( V_c \)
- critical velocity

\( V_F \)
- velocity of a spherical particle pushed by a flat front

\( W \)
- apparent weight of a particle

\( Y \)
- absorbance (Chapter 6) or dummy variable

\( z \)
- direction of growth in cylindrical coordinates

\( \alpha \)
- polarizability

\( R/\alpha \)
- radius of curvature of a solidification front

\( \gamma \)
- Equation (7.56)

\( \varepsilon \)
- dielectric constant = \( \varepsilon' + i\varepsilon'' \)

\( \varepsilon_0 \)
- dielectric constant of vacuum

\( \varepsilon_{ij} \)
- molecular pair interaction energies
\( \eta \) viscosity
\( \lambda, \lambda_0 \) wavelength, and characteristic wavelength
\( \mu \) permanent dipole moment
\( \xi \) chemical potential
\( \omega \) circular frequency
\( \Pi \) disjoining pressure (>0 if repulsion)
\( \rho \) radial distance in spherical coordinates
\( \rho_i \) density (i = s, l, part for solid, liquid or particle)
\( \Delta \rho \) \( \rho \) _part \(-\rho \) _l
\( \sigma_{ij} \) surface tension (i,j = S, L or P for solid, liquid and particle)
\( \sigma_d \) dispersion force component of the surface tension
\( \sigma_i \) surface charge density (Chapter 3)
\( \phi \) electrical conductivity
\( \phi \) interaction parameter (Garifalco)

Lifshitz's function used for computing retarded forces
\( \Omega \) molecular volume = \( a^3 \)
\( \omega \) circular frequency
\( \omega_p \) plasma frequency
APPENDIX B

Disjoining Force Between a Sphere and a Tubular Element

First let us compute the disjoining force between a sphere and an atom. Let us consider an atom of material (2) at a distance, \( \ell \), from a sphere of material (1) and radius \( R \) (Figure B-1). The non-retarded force between two atoms is

\[
F_{\text{dis.}} = -\frac{6\pi}{r^7} \quad \text{(see Table 7-1)}
\]

where \( C \) is the London constant. The force between a ring of material and an atom at a distance \( r \) from the atom \( (r, r + dr, \beta, \beta + d\beta) \) is therefore:

\[
d^2 F_{\text{dis.}} = -(2\pi \sin \beta \, d\beta \, r^2 \, dr) \cdot N_1 \cdot \frac{6\pi}{r^7} \cos \beta
\]

where \( N_1 \) is the number of polarizable atoms of material 1 per unit volume. Integrating over the whole portion of the sphere at distance \( r \) from the atom,

\[
d F_{\text{dis.}} = -\frac{6\pi N_1 C \, dr}{r^5} \left(1 - \cos^2 \beta_1\right)
\]

with

\[
\cos \beta_1 = \frac{(R+\ell)^2 + r^2 - R^2}{2r(R+\ell)}
\]

Summing over the whole sphere,

\[
F_{\text{dis.}} = -6\pi N_1 C \int_\ell^{\ell+2R} \left\{\frac{1 - \left[\frac{(R+\ell)^2 + r^2 - R^2}{2r(R+\ell)}\right]^2}{r^5} \, dr\right\}
\]

and after integration, the force between an atom on a sphere is:

\[
F_{\text{dis.}} = -\frac{8\pi N_1 C R^3 (R+\ell)}{\ell^4 (2R+\ell)^4}
\]

The force between a sphere of material (1) and a ring of material (2) (Figure B-1b) can now be computed by integration of Equation (B.5)
FIGURE B-1 FORCE BETWEEN A SPHERE AND (a) AN ATOM, AND (b) A TUBE
\[ d^2F_{\text{dis.}} = -2\pi r \, dr \, d\lambda \, \frac{8\pi N_1 cR^3(R+\lambda)}{1^4(2R+\lambda)^4} \cdot \cos \alpha \]  \hspace{1cm} (B.6) \\

and

\[ d\lambda = \cos \alpha \, dz \]  \hspace{1cm} (B.7)

Summing over the whole tube of material (2) and introducing the Hamaker constant \( A = N_1 N_2 \pi^2 \), the force is:

\[ dF_{\text{dis.}} = -\frac{16A \, r \, dr}{R^3} \int_0^\infty \frac{(1 + \frac{\lambda}{R})}{(2+\frac{\lambda}{R}) \cdot \left( \frac{\lambda}{R} \right)^4} \, d\left( \frac{\lambda}{R} \right) \]  \hspace{1cm} (B.8)

\[ dF_{\text{dis.}} = -\frac{1}{3} \frac{Ar \, dr}{\lambda^3 \left( 1 + \frac{\lambda}{2R} \right)^3} \]  \hspace{1cm} (B.9)

In the limit of \( \lambda \ll R \), Equation (B-9) of the force between a sphere and a tube simplifies to:

\[ dF_{\text{dis.}} = \frac{1}{3} \frac{Ar \, dr}{\lambda^3} \left( 1 - \frac{3}{2} \frac{\lambda \lambda_0}{R} \right) \]  \hspace{1cm} (B.10)

This relation can be used to compute the force between a sphere and a solid with a solidification front of any shape.
APPENDIX C

Average Film Thickness for Flow

In the case of a conduit of constant height, \( h \), in the \( z \) direction and of unidimensional flow in the \( x \) direction, the liquid velocity \( u \) follows a parabolic law:

\[
u(z) = cz(h-z) \tag{C.1}\]

and the average velocity \( \bar{u} \) is:

\[
\bar{u} = \frac{1}{h} \int_0^h u(y) \, dy = \frac{ch^2}{6} \tag{C.2}
\]

The constant \( c \) is determined by the Navier-Stokes equation for incompressible flow:

\[
c = -\frac{1}{2\eta} \frac{\Delta P}{\Delta x} \tag{C.3}
\]

if \( \Delta P/\Delta x \) is the pressure gradient in the \( x \) direction.

As an illustration of Equation (C.2) if the height of the conduit is decreased by a factor 2, the pressure gradient must be increased by a factor 4 to maintain the same flow.

If the height of the conduit is not constant in a direction normal to the flow, the average flow velocity through the conduit is

\[
\bar{u} = \frac{1}{A} \int_0^y \bar{u}(y) \cdot h(y) \, dy \tag{C.4}
\]

where \( A \) is the area of the cross-section of the conduit; and combining Equations (C.2) and (C.4), the average height, \( \bar{h} \), of the conduit is such that

\[
\bar{h}^2 = \frac{1}{A} \int_0^y h^3(y) \, dy \tag{C.5}
\]
For example for a trapezoidal cross-section of hight $h_1$ at one end and $h_2$ at the other, the average hight $\bar{h}$ is such that:

$$\bar{h}^2 = \frac{h_1^2 + h_2^2}{2} \quad (C.6)$$

In the case of interest for the derivation of drag force, the conduit hight varies in the x and y directions: the liquid flows between an approximately flat crystalline solid and spherical asperities. (See Figure 7-3). An exact mathematical treatment of the liquid flow is too complex but to a good approximation, the average hight of the liquid film is such that

$$\bar{h}^2 = \frac{1}{V_1} \int_A h^3 \, dA \quad (C.7)$$

where $V_1$ is the volume of liquid below one asperity; and $dA$ is the area where the film has a hight $h$ (Figure C-1). Integrating Equation (C.7) with the assumption that the irregularities are close-packed on the surface of the large sphere and that $h \ll R_i$, $\bar{h}^2$ is equal to:

$$\bar{h}^2 = 0.5852 \cdot \frac{h_0 + H_i}{R_i} \cdot \frac{h_0 + H_i}{R_i} \times \left( \frac{h_0 + H_i}{R_i} \right)^2 \quad (C.8)$$

When the ratio $(h_0 + H_i)/R_i$ varies between 0 and 1, the relative distance $\bar{h}/(H_0 + H_i)$ varies between 0.765 and 0.682; therefore to a good approximation, $\bar{h}/(H_0 + H_i)$ can be considered constant and equal to $3/4$. 
FIGURE C-1 FLOW UNDERNEATH AN ASPERITY
APPENDIX D

Shape of the Interface behind a Disk-Shaped Particle

To simplify the problem of the influence of a particle, with thermal conductivity different from that of the matrix, on the shape of the interface, only the case of a disk-shaped particle will be treated and the edge effects will be neglected. In spite of these simplifications, this treatment should be sufficient to illustrate the effect of a particle and to treat the problem of large pile-ups of particles.

The bottom and top temperatures, $T_o$ and $T_4$, of the solidification cell are fixed (Figure D-1). The position of the solidification front, far from the disk, $x_1$, is such that

$$k_s \cdot \frac{T_m - T_o}{x_1 - x_o} = k_1 \frac{T_4 - T_m}{x_4 - x_1} \quad (D.1)$$

where $k_s$ and $k_1$ are the thermal conductivities of solid and liquid matrix and $T_m$ is the melting point.

Equation (D.1) can be written:

$$x_1 - x_o = \frac{x_4 - x_o}{\frac{1}{k_1} \cdot \frac{T_4 - T_m}{x_4 - x_1} + \frac{1}{k_s} \cdot \frac{T_m - T_o}{x_1 - x_o}} \quad (D.2)$$

Similarly, in the region of the particle, the heat flow equations are:

$$k_s \cdot \frac{T_m - T_o}{x_1^r - x_o} = k_1 \frac{T_2 - T_m}{x_2^r - x_1^r} = k_p \frac{T_3 - T_2}{x_3 - x_2} = k_1 \frac{T_4 - T_3}{x_4 - x_3} \quad (D.3)$$

where $k_p$ is the thermal conductivity of the particle and $(x_3 - x_2)$ is the thickness of the disk. Rearranging these equations,
FIGURE D-1  INFLUENCE OF A DISK-SHAPED PARTICLE ON THE SHAPE OF THE SOLIDIFICATION FRONT. PARTICLE MORE CONDUCTIVE THAN THE MATRIX.
\[ x'_{1 - x} = \frac{x_4 - x_0}{k \frac{T_m - T_o}{T_m - T_0}} \cdot \left[1 - \frac{e^{-\frac{k_p \cdot k_1}{k}}}{x_4 - x_0} \cdot \frac{k_p - k_1}{k_p} \right] \]  \hspace{1cm} (D.4)

Combining Equations (D.2) and (D.3), the depression of the front behind the particle is:

\[ x_{1 - x'} = \frac{e^{-\frac{k_p \cdot k_1}{k_p}}}{1 + \frac{k_1}{k} \frac{T_m - T_0}{k_s T_m - T_0}} \]  \hspace{1cm} (D.5)

or

\[ x_{1 - x'} = (1 - \frac{k_1}{k_p}) \cdot \frac{x_{1 - x}}{x_4 - x_0} \cdot e \]  \hspace{1cm} (D.6)

Considering that the front is approximately in the middle of the cell, Equation (D.6) can be simplified to:

\[ x_{1 - x'} = (1 - \frac{k_1}{k_p}) \cdot \frac{e}{2} \]  \hspace{1cm} (D.7)

In the case of a particle of high thermal conductivity in a matrix of low conductivity \((k_p >> k_1)\), as for example a copper particle in an organic matrix, the depression of the front is equal to:

\[ x_{1 - x'} = \frac{e}{2} \]

Conversely, if the liquid has a much higher thermal conductivity than the particle, the front will be higher behind the particle and

\[ x_{1 - x'} = -\frac{e}{2} \]

It is interesting to note that the thermal conductivity of the solid does not appear in the final equation since only the problem of a static solidification front was treated. This would not, however, be the case
for a growing solid as the latent heat of solidification must be removed through the solid. The equations in this case are much more cumbersome.

Equation (D.7) can also be used to determine the shape of the front after a particle has been entrapped, by interverting the roles of solid and liquid. In this new form, the equation shows that when a copper particle is entrapped, the front will bulge above the particle by half the thickness of the particle.
APPENDIX E

Numerical Solution of Heat Flow Equations

The heat conduction equations can be solved numerically, in the case of complex shapes, by a finite difference method. To illustrate this method, the case of two-dimensional Cartesian coordinates will be presented in this appendix. One must first choose a grid of nodes at which the temperatures will be determined. Each node represents a small volume or cell and the temperature is supposed to be uniform for such an elementary volume. In the present example nodes arranged in Cartesian coordinates are used (Figure E-1). The basic thermal differential equation is:

$$\rho c \frac{\partial T}{\partial t} = k \cdot \nabla^2 T$$  \hspace{1cm} (E.1)

where \(\rho\) is the density, \(c\) the heat capacity, \(k\) the thermal conductivity, \(T\) the absolute temperature and \(t\) the time. It becomes for node \((i,j)\), after replacing the differentials by divided differences:

$$\rho c \left( \frac{\Delta X_{i+1,i} + \Delta X_{i,i-1}}{2} \right) \cdot \left( \frac{\Delta Y_{j+1,j} + \Delta Y_{j,j-1}}{2} \right) \cdot \frac{\Delta T}{\Delta t} =$$

$$\Sigma \left( T_{i+1,j} - T_{i,j} \right) \cdot \left( \frac{k}{\Delta X_{i+1,i}} \cdot \frac{\Delta Y_{j+1,j} + \Delta Y_{j,j-1}}{2} \right) \hspace{1cm} (E.2)$$

where the summation, \(\Sigma\), is over all the surrounding nodes, \((i+1, j)\), \((i-1, j)\), \((i, j+1)\), \((i, j-1)\); and \(T_{i,j}\) is the temperature of node \((i,j)\).

Using physically more meaningful parameters, the equation can also be written:
FIGURE E-1 CARTESIAN GRID OF NODES USED TO MAP A TWO DIMENSIONAL SURFACE.
\[ \rho c V_{ij} \frac{\Delta T_{ij}}{\Delta t} = \sum K_{(i+1,j)(i,j)} \cdot (T_{i+1,j} - T_{i,j}) \quad (E.3) \]

where \( V_{ij} \) is the volume associated with node \((i,j)\). The boundary between nodes is the plane normal to the line joining the nodes, halfway between the nodes. \( K_{1,2} \) is the conductance between nodes 1 and 2:

\[ K_{1,2} = k \frac{A_{1,2}}{d_{1,2}} \quad (E.4) \]

where \( A_{1,2} \) is the area of contact between nodes 1 and 2 and \( d_{1,2} \) the distance between these two nodes.

For each node, one must write an equation such as Equation (E.3). For steady state, \( \Delta T_{ij}/\Delta t = 0 \) and the equations contain only the conductances \( K \). If there are, \( N \) nodes, the \( N \) temperatures are computed by solving the system of \( N \) equations (E.3) with \( N \) unknowns. Although such a system can theoretically be solved rigourously, in practice an approximate iterative technique is used since \( N \) is often equal to several hundreds. For unsteady state, the temperatures \( T_{i,j} \) are determined at time intervals \( t \):

\[ T_{i,j}(t+\Delta t) = T_{i,j}(t) + \Delta T_{i,j} \quad (E.5) \]

Equation (E.3) can be approximated in two ways by considering that the temperatures in the r.h.s. are either the temperatures at time \( t \) (explicit form) or the temperatures at time \( t + \Delta t \) (implicit form). In practice, the best results are obtained by using both forms simultaneously. The system of equations (E.3) can again be solved for each time \( t \) by successive approximations. For more details on this technique, see for example Reference (112).
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