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Relaxation Phenomena in Glass-Forming Liquids and Long Range Correlations in Nonequilibrium Steady States.

by

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Abstract

This thesis is comprised of two parts. In the first part, fluctuating hydrodynamics is used to calculate the equal time temperature correlations in a heat conducting fluid maintained under a constant temperature gradient. Of particular interest is the influence of boundaries on the fluctuations within the bulk of the fluid. By coupling the thermal modes of the walls and the enclosed fluid, we investigate the conditions under which the boundary condition for a perfectly conducting wall becomes applicable. The second part of the thesis is devoted to the study of complex relaxation phenomena in strongly supercooled glass-forming liquids. An expression for the longitudinal viscosity of a simple liquid is derived in the spirit of the extended mode-coupling theory for the glass transition, and it is shown that the previously suggested initial time cutoff in the hopping kernel is invalid. Instead, a wavevector cutoff for the hopping kernel is proposed through an alternative nonperturbative approach. Lastly, we investigate deviations from the Stokes-Einstein relation for the diffusion constant of probes immersed in deeply supercooled fluids. We offer a phenomenological model and a molecular treatment as theoretical explanations for this phenomenon.

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Part I

NONEQUILIBRIUM FLUID SYSTEMS
Fluctuations about nonequilibrium steady states of a fluid may differ markedly from equilibrium fluctuations. Nonequilibrium effects are manifested in the breaking of time-reversal symmetry and in the existence of long range order that decays as $1/r$ in physical space. An extension of fluctuating hydrodynamics to the nonequilibrium regime is available where one considers fluctuations linearized about the steady state and stochastic random forces that satisfy local fluctuation-dissipation relations.

The problem of a fluid in a stationary temperature gradient is a prototypical model of a steady state system that has been extensively studied from both experimental and theoretical perspectives. In most cases, finite-size effects arising from interactions with boundaries are neglected by assuming that the separation length between the two parallel walls is significantly larger than the characteristic length scale of the confined liquid.

In this part of the thesis, we study the influence of boundaries on the equal time thermal correlations in a three dimensional fluid maintained under a constant temperature gradient. Within the confines of the model for an idealized fluid bounded by two infinite, parallel walls, we show that it is crucial to retain the unbounded spacial components in the problem so that the solutions approach meaningful results as we move the walls infinitely far apart. In addition, we consider a composite system by including the dynamics of the walls, and we investigate the conditions for the relevant physical parameters under which the details of wall dynamics may be neglected by employing the simple boundary condition $\delta T = 0$. 
Chapter 1

Spatial correlations in bounded nonequilibrium fluid systems

The contents of this chapter is based on the work found in

1.1 INTRODUCTION

The study of fluctuations in nonequilibrium stationary states of fluid systems has received considerable attention in the literature [1, 2, 3, 4, 5, 6, 7, 8]. Prior studies of systems in the steady state range from phenomenological [7] to microscopic treatments based on kinetic theory or mode-coupling theory [4, 5, 6]. Despite the numerous theoretical approaches employed, the different techniques generally yielded similar results. In addition to the breaking of time-reversal symmetry, one obtains nonlocal long-ranged correlations of the hydrodynamic variables in a noncritical state. These predictions have in fact been confirmed by recent experiments performed by Law, Sengers et al. [9, 10, 11, 12]

Most of the previous studies have considered hydrodynamic steady states in the limit of a large system where boundary effects may be neglected. Recently, there has been a renewed interest in the problem of nonequilibrium fluctuations in finite systems bounded by solid walls [13, 14, 15, 16, 17, 18, 19, 20, 21, 22]. Using the fluctuating
hydrodynamics formalism, several papers have addressed the spatial correlations of the various conserved densities (number, momentum, and energy) of bounded fluids subject to nonequilibrium constraints.

We shall focus in this chapter on the static temperature autocorrelation function for a fluid maintained under a constant temperature gradient. In previous work, the temperature-temperature correlation function has been predicted to be long-ranged and encompassing the entire system [15, 17, 18]. The absence of an intrinsic characteristic correlation length persisted even in the limit of a large system of size $L$. Our results for this problem are different.

This chapter is organized as follows: A brief review of the results of Rubí et al.[15] and Garcia et al.[18] is presented in section 1.2. Using the fluctuating hydrodynamics formalism, we obtain the temperature correlator for a three-dimensional fluid in section 1.3 and show that it reduces to the infinite domain solution as $L \to \infty$. Unlike the previous researchers, we retain the unbounded spatial dimensions in the derivation. In section 1.4, we study the dynamics of a composite system by coupling the thermal modes of the walls to system variables. We show the conditions under which the problem can be simplified with the simple boundary condition used in the derivation of section 1.3. In section 1.5, we present our conclusions.

1.2 REVIEW OF THE PROBLEM

In this section we present a brief summary of the results of Rubí et al.[15] and Garcia et al.[18] for completeness. The fluid is bounded by two parallel plates at $z= 0,L$ and is infinite in the $x,y$ directions. The boundaries are rigid, impermeable, and held in contact with heat reservoirs at $T_0$ and $T_L$ respectively, where $T_L > T_0$. The two plates are assumed to be perfectly heat conducting; thus, the temperature of the fluid at $z= 0,L$ is equal to the temperature of the reservoirs. Following previous researchers, one imposes the restriction that the thermal expansion coefficient vanishes. This condition decouples the energy equation from the density and velocity equations, thereby vastly simplifying the analysis. Furthermore, the transport and thermodynamic coefficients
of the model fluid are taken to be constants.

The stationary solution to the heat diffusion equation

$$\frac{\partial}{\partial t} T(r, t) = \alpha_T \nabla^2 T(r, t)$$  \hspace{1cm} (1.1)

is

$$T(r) = T(z) = T_0 + r \cdot \nabla T,$$  \hspace{1cm} (1.2)

where $\alpha_T$ is the thermal diffusivity and $\nabla T = \hat{e}_z [(T_L - T_0)/L]$. The equation of motion for fluctuations about the steady state has an additional contribution to the heat flux modeled by a stochastic source

$$\frac{\partial}{\partial t} \delta T(r, t) = \alpha_T \nabla^2 \delta T(r, t) - \frac{1}{\rho C_p} \nabla . J(r, t),$$  \hspace{1cm} (1.3)

where $\rho$ is the mass density and $C_p$ is the heat capacity per unit mass at constant pressure. The random part of the heat flux is assumed to be a gaussian white noise whose correlation function is given by

$$\langle J(r, t) J(r', t') \rangle = 2k_B T^2(r) \delta(r - r') \delta(t - t') I,$$  \hspace{1cm} (1.4)

where $k_B$ is Boltzmann's constant, $\lambda$ is the thermal conductivity of the fluid, $I$ is the identity matrix, and $\langle ... \rangle$ denotes a steady state average.

The model is further simplified by taking the parallel spatial Fourier transform in the $x,y$ plane. Then the fluctuating hydrodynamic variable $\delta T$ is reduced to

$$\delta T(z; k_\parallel, t) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy e^{-i(k_x x + k_y y)} \delta T(r, t),$$  \hspace{1cm} (1.5)

where $k_\parallel^2 = k_x^2 + k_y^2$.

Defining

$$C(z, z') = \frac{\langle \delta T(z; k_\parallel = 0, t) \delta T(z'; k_\parallel = 0, t) \rangle}{(2\pi)^2 \delta(k_\parallel + k_\parallel')},$$  \hspace{1cm} (1.6)
one gets for the static correlation function [15, 18]:

$$C(z, z') = k_B(\rho C_p)^{-1}T^2(z)\delta(z - z') + f(z, z'),$$

(1.7)

where the first term is simply the local equilibrium contribution, and the second term is the nonequilibrium contribution given by (see Fig.1-1)

$$f(z, z') = k_B(\rho C_p)^{-1}\frac{\left| \nabla T \right|^2}{L} [\theta(z' - z)L - z') + \theta(z - z')z'(L - z)],$$

(1.8)

where \(\theta\) is the unit step function. The boundary condition used corresponds to \(\delta T = 0\) at the boundaries (perfectly conducting plates). As a result, the delta function contribution to the temperature-temperature correlation is expandable in a Fourier sine series,

$$\delta(z - z') = \frac{2}{L} \sum_{n=0}^{\infty} \sin\left(\frac{n\pi z}{L}\right)\sin\left(\frac{n\pi z'}{L}\right).$$

(1.9)

We note in passing that the procedure described in this section inappropriately reduces the description to a one dimensional system.
1.3 REANALYSIS OF THE PROBLEM: (PART I)

The nonequilibrium contribution to the static correlation function predicted in references [15, 18] is long-ranged and encompasses the entire system. The result would therefore suggest that the thermal fluctuations at any two given points is always positively correlated regardless of the size of the system. For large $L$ and $|\nabla T|$ constant, however, we should expect that the solution would exhibit an intrinsic length scale and decay as in an infinite system.

We shall attempt to resolve this paradox in two ways. First, we rederive the static temperature correlator in a three-dimensional system and show that the solution behaves properly in the limit of a large system. Second, in the next section, we justify the simple boundary condition $\delta T = 0$ at $z = 0, L$ by considering a composite system consisting of reservoirs plus the system of interest. By analyzing the thermal fluctuations in the composite system, we arrive at a sequence of characteristic relaxation times which allows us to predict a bound on the size of the system where boundary effects are important.

By combining the equations of motion for $\delta T(r, t)$ and $\delta T(r', t)$ and using relations (1.4) and

\[
< \delta T(r, t)J(r', t) > = \frac{k_B \lambda}{\rho C_p} \nabla_r [T^2(r)\delta(r - r')]I
\]

it is easy to show that [17, 18]

\[
\frac{\partial}{\partial t} < \delta T(r, t)\delta T(r', t) > = \alpha_T (\nabla_r^2 + \nabla_r'^2) < \delta T(r, t)\delta T(r', t) > + 2\frac{k_B \lambda}{(\rho C_p)^2} \nabla_r \cdot \nabla_r' [T^2(r)\delta(r - r')].
\]
Using $T(r) = T_0 + r \cdot \nabla T = T(z)$, one obtains for the correlator at steady state:

$$\left( \nabla^2 + \nabla^2 \right) \langle \delta T(r, t) \delta T(r', t) \rangle + 2 \frac{|\nabla T|^2 k_B}{\rho C_p} \delta(r - r') = 0,$$  \hspace{1cm} (1.12)

where

$$\langle \delta T(r, t) \delta T(r', t) \rangle \equiv \langle \delta T(r, t) \delta T(r', t) \rangle - \frac{k_B T^2(r)}{\rho C_p} \delta(r - r').$$ \hspace{1cm} (1.13)

We shall omit the time dependence of the correlator since we are dealing with the steady state. Examination of Eqn(1.12) reveals that it is essentially the same as the Poisson equation for the electric field generated by a point charge. Thus, the temperature-temperature correlator defined by (1.13) may be interpreted as the potential at $r$ corresponding to a source $(|\nabla T|^2 k_B)/\rho C_p$ at $r'$. For the case of an infinite system, the potential is a function of $|r - r'|$ only,

$$\langle \delta T(r) \delta T(r') \rangle = \frac{|\nabla T|^2 k_B}{\rho C_p} \left( \frac{1}{4\pi|r - r'|} \right).$$ \hspace{1cm} (1.14)

This long range behavior decaying as $|r - r'|^{-1}$ has also been predicted for the density-momentum correlation in an infinite fluid subject to a temperature gradient [7].

Using the boundary condition $\delta T = 0$ for $z = 0, L$, it is straightforward to show that the correlation function for the bounded fluid is given by [23]

$$\langle \delta T(r) \delta T(r') \rangle = \frac{|\nabla T|^2 k_B}{\rho C_p} \left( \frac{1}{4\pi|r - r'|} + \sum_{n=-\infty}^{\{n\neq0\}} \frac{1}{4\pi|r - r_n|} - \sum_{n=-\infty}^{\infty} \frac{1}{4\pi|r - r_n''|} \right),$$ \hspace{1cm} (1.15)

where $r_n' = \hat{e}_x x' + \hat{e}_y y' + \hat{e}_z (2nL + z')$ and $r_n'' = \hat{e}_x x' + \hat{e}_y y' + \hat{e}_z (2nL - z')$. Note that in Eqn(1.15) we have explicitly separated the term corresponding to the infinite dimension solution from the first summation. To be specific, we shall consider the case where $z' = L/2$. The infinite series given in Eqn(1.15) does not converge rapidly unless we have the condition:

$$|r - r'| \ll L$$ \hspace{1cm} (1.16)
When this condition is satisfied, the temperature correlation function is given by the infinite domain solution plus a small correction term. Thus, the influence of the boundaries on the fluctuations in the bulk of the fluid vanishes as the plates move infinitely far apart, which is the behavior we expect from physical intuition. A similar result was obtained by Spohn [22] for the nonequilibrium correlations of a stochastic lattice gas.

1.4 REANALYSIS OF THE PROBLEM: (PART II)

In this section we shall motivate the simplified boundary condition $\delta T = 0$ by including the dynamics of the heat-bath in our model. Following Procaccia et al.[1], we shall consider an isolated composite system with three compartments, two of which are the reservoirs separated by the system of interest. The boundaries of the system of interest are located at $-L$ and $L$. Again, we shall consider only the thermal modes of each compartment. Thus, the corresponding heat diffusion equation is expressed as

$$\frac{\partial}{\partial t} T(r, t) = \alpha_T(r) \nabla^2 T(r, t), \quad (1.17)$$

where the thermal diffusivity $\alpha_T(r) = \alpha_T(z)$ is given by

$$\alpha_T(r) = \begin{cases} 
\alpha_T^R & \text{for } -L_B \leq z \leq -L \\
\alpha_T^L & \text{for } -L \leq z \leq L \\
\alpha_T^R & \text{for } L \leq z \leq L_B.
\end{cases}$$

The boundaries between the compartments are rigid and impermeable but heat conducting. By imposing the boundary conditions that $T(r, t)$ and the energy flux
are continuous and the initial condition

\[ T(r, 0) = T(z, 0) = \begin{cases} 
T_{-L} & \text{for } -L_B \leq z \leq -L \\
T_S & \text{for } -L \leq z \leq L \\
T_L & \text{for } L \leq z \leq L_B,
\end{cases} \]

it can be shown that for an intermediate time scale the temperature is well approximated by (see Fig.1-2)[1]

\[ T(r, t) = T(z, t) = \begin{cases} 
T_{-L} & \text{for } -L_B \leq z \leq -L \\
T_{-L} + \left( \frac{T_L - T_{-L}}{2L} \right) (z + L) & \text{for } -L \leq z \leq L \\
T_L & \text{for } L \leq z \leq L_B.
\end{cases} \]

Specifically, for the time interval

\[ \frac{L^2}{\alpha_L^2} < t < \frac{(L_B - L)^2}{\alpha_L^2}, \quad (1.18) \]

and the condition

Figure 1-2: Steady state temperature profile of the composite system within the time interval specified by Eqn(1.18)
\[
\frac{\alpha_T^B}{\alpha_T^S} \to \infty, \quad (1.19)
\]
the middle compartment has the usual steady-state temperature distribution. Thus, in order to maintain this quasi-nonequilibrium steady state for a long time, we choose highly conducting reservoirs of large extent so that the conditions \((L_B - L)^2/\alpha_T^B \to \infty\) are satisfied.

Within the time interval \((1.18)\) where a steady state is maintained, we will in the following analyze the corresponding thermal fluctuations. The equation of motion for \(\delta T(\mathbf{r}, t)\) is given by

\[
\frac{\partial}{\partial t} \delta T(\mathbf{r}, t) = \alpha_T(\mathbf{r}) \nabla^2 \delta T(\mathbf{r}, t) - \alpha_T(\mathbf{r}) \lambda^{-1}(\mathbf{r}) \nabla \cdot \mathbf{J}(\mathbf{r}, t), \quad (1.20)
\]
where \(\alpha_T(\mathbf{r})\) was given previously in this section and \(\alpha_T\lambda^{-1} = (\rho C_p)^{-1}\) is \(\alpha_T^B\lambda_B^{-1}\) for the bath and \(\alpha_T^S\lambda_S^{-1}\) for the system. Using the relation

\[
A(z; k, w) = \int_{-\infty}^{\infty} d\mathbf{r} \int_{-\infty}^{\infty} d\mathbf{r} A(\mathbf{r}, t) e^{i\omega t - ik \cdot \mathbf{r}}, \quad (1.21)
\]
where \(A\) is an arbitrary dynamical variable, Eqn(1.20) is reduced to an ordinary differential equation in the variable \(z\):

\[
(i\tilde{w} + \alpha_T(z) \frac{\partial^2}{\partial z^2}) \tilde{T}(z; k, w) = \alpha_T(z) \lambda^{-1}(z) \left( \frac{\partial}{\partial z} \tilde{J}_z + i k \cdot \tilde{J}_z \right), \quad (1.22)
\]
with \(\tilde{w} = w + i \alpha_T(z) k^2\). Whenever confusion can arise, we will denote \(\tilde{w}_B\) as \(w + i \alpha_T^B k^2\) and \(\tilde{w}_S\) as \(w + i \alpha_T^S k^2\). The solution to the preceding equation can be expressed in terms of a Green’s function

\[
\delta \tilde{T}(z; k, w) = \alpha_T(z) \lambda^{-1}(z) \int_{-L_B}^{L_B} dz' G(z', z; k, w) \left( \frac{\partial}{\partial z'} \tilde{J}_{z'} + i k \cdot \tilde{J}_{z'} \right), \quad (1.23)
\]
where the Green’s function satisfies the equation:

\[
(i\tilde{w} + \alpha_T(z) \frac{\partial^2}{\partial z^2}) G(z, z'; k, w) = \delta(z - z'), \quad (1.24)
\]
and is subject to the homogeneous boundary conditions corresponding to [24]

\[ \lambda_B \frac{\partial}{\partial z} G(z, z'; k_{||}, w)|_{z=\pm L_B} = 0 \]  
(1.25)

\[ G(-L - 0, z'; k_{||}, w) = G(-L + 0, z'; k_{||}, w) \]  
(1.26)

\[ \lambda_B \frac{\partial}{\partial z} G(z, z'; k_{||}, w)|_{z=-L-0} = \lambda_S \frac{\partial}{\partial z} G(z, z'; k_{||}, w)|_{z=-L+0} \]  
(1.27)

\[ G(L - 0, z'; k_{||}, w) = G(L + 0, z'; k_{||}, w) \]  
(1.28)

\[ \lambda_S \frac{\partial}{\partial z} G(z, z'; k_{||}, w)|_{z=L-0} = \lambda_B \frac{\partial}{\partial z} G(z, z'; k_{||}, w)|_{z=L+0} \]  
(1.29)

Since we are interested in fluctuations in the middle compartment only, we shall quote the explicit form for the Green's function \( G(z, z'; k_{||}, w) \) for \( z, z' \in (-L, +L) \):

\[ G(z, z'; k_{||}, w) = \frac{-\gamma_S}{\alpha_T} \frac{\sinh \left( \frac{L+z_\gamma}{\gamma_S} \right) + \frac{\lambda_S}{\gamma_S} \cosh \left( \frac{L+z_\gamma}{\gamma_S} \right) \sinh \left( \frac{L-z_\gamma}{\gamma_S} \right) + \frac{\lambda_S}{\gamma_S} \cosh \left( \frac{L-z_\gamma}{\gamma_S} \right)}{\sinh \left( \frac{2L}{\gamma_S} \right) + \frac{\lambda_S}{\gamma_S} \cosh \left( \frac{2L}{\gamma_S} \right) + \frac{\lambda_S}{\gamma_S} \sinh \left( \frac{2L}{\gamma_S} \right)} \]  
(1.30)

where \( z_\gamma = \min(z, z') \), \( z_\geq = \max(z, z') \), \( \gamma_S = \left( \frac{i\omega_S}{\omega_{\text{ph}}} \right)^{1/2} \), \( \gamma_B = \left( \frac{i\omega_B}{\omega_{\text{ph}}} \right)^{1/2} \), and \( \delta = \frac{\lambda_B}{\gamma_B} \tanh \left( \frac{L-L_B}{\gamma_B} \right) \). Note that alternatively \( G \) in Eqn (1.30) satisfies the effective boundary condition

\[ \lambda_S \frac{\partial}{\partial z} G(z, z'; k_{||}, w) \pm \delta G(z, z'; k_{||}, w) = 0 \text{ for } z = \pm L \text{ and } z' \in (-L, +L), \]  
(1.31)

where \( \delta \) is a frequency dependent temperature-slip coefficient of the boundary [25]. In effect, we have included all the dynamics of the heat bath into a single surface transport coefficient. We remark that Eqn(1.30) for the Green's function with a constant \( \delta \) coefficient has been obtained previously by Pagonabarraga et al.[16]

Using standard manipulations with Green's functions, it is straightforward to show that the expression for the temperature correlation function between two points within the middle compartment is given by

\[ \frac{\langle \delta T(z; k_{||}, w) \delta T(z'; k_{||}', w) \rangle}{2k_B(\alpha_S \lambda_S^{-1})^2 \delta(w + w') \delta(k_{||} + k_{||}')} = \frac{1}{2} \left\{ -\frac{1}{\alpha_S \lambda_S^{-1}} (G(z', z)T^2(z') + G^*(z, z')T^2(z)) \right\} \]
As VT 2

\[ +i \frac{\lambda_S |\nabla T|^2}{w} (G(z', z) - G^*(z, z')) \]

\[ -\lambda_S (G(z_1, z) G^*(z_1, z') \frac{\partial}{\partial z_1} T^2(z_1)|_{z_1=\pm L} \]

\[ -i \frac{\lambda_S |\nabla T|^2 \alpha_S}{w} (G(z_1, z) \frac{\partial}{\partial z_1} G^*(z_1, z')) \]

\[ -G^*(z_1, z') \frac{\partial}{\partial z_1} G(z_1, z)|_{z_1=\pm L} \right) , \quad (1.32) \]

where we have suppressed the \( w \) and \( k_{\parallel} \) dependence in \( G(z, z') \) for notational simplicity, \( * \) denotes replacing \( w \) by \( -w \), and \( |\nabla T| = (T_L - T_{-L})/2L \). The preceding expression can be simplified since we will consider the limits \((L_B - L)^2/\alpha_T^B \rightarrow \infty \) and \( \alpha_T^B/\alpha_T^S \rightarrow \infty \). Under these constraints, the combination \( \lambda_S/\gamma_S \delta \) that appears in the Green’s function in Eqn(1.30) becomes

\[ \frac{\lambda_S}{\gamma_S \delta} = \left( \frac{\lambda_S}{\lambda_B} \right) \frac{\gamma_B}{\gamma_S} \coth \left( \frac{L_B - L}{\gamma_B} \right) \rightarrow 0. \quad (1.33) \]

When condition (1.33) is satisfied, the boundary condition for \( G \) (Eqn(1.31)) reduces to

\[ G(\pm L, z'; k_{\parallel}, w) = 0, \quad (1.34) \]

or equivalently \( \delta T = 0 \) at the boundaries. The previous conclusion is perhaps not surprising since, intuitively, we expect a perfectly conducting bath to dissipate thermal fluctuations infinitely fast at the boundaries. We may thus neglect the last two terms in Eqn(1.32) and insert for \( G \)

\[ G(z, z'; k_{\parallel}, w) = G(z, z', \bar{w}_S) = -\frac{\gamma_S \sinh \left( \frac{L+z}{\gamma_S} \right) \sinh \left( \frac{L-z}{\gamma_S} \right)}{\alpha_T^S \sinh \left( \frac{2k}{\gamma_S} \right)}. \quad (1.35) \]

By examining Eqn(1.35), we can infer two time scales \((L+z_\leq)^2/\alpha_T^S\) and \((L-z_\geq)^2/\alpha_T^S\) corresponding to the time it takes for a thermal fluctuation generated at \( z_\leq \) (or \( z_\geq \)) to reach \(-L\) (or \( L\)). Physically, we expect that if this thermal diffusion time is much longer than the typical hydrodynamic relaxation time, we may neglect the boundary effects. Indeed, if we take the limit \( L^2/\alpha_T^S \rightarrow \infty \) (but \( \frac{L^2}{(L_B-L)^2} \alpha_T^B \ll 1 \)) and with \( z \)
and $z'$ not at the boundaries, $G$ in Eqn(1.35) reduces to the Green's function for an infinite system.

For a finite system, we expand Eqn(1.35) in a Fourier series

$$G(z, z', \tilde{w}_S) = \sum_{n=\infty}^{\infty} G_n(z', \tilde{w}_S)e^{i\frac{2\pi n z}{L}}.$$  \hspace{1cm} (1.36)

In order to calculate the equal time averages for the temperature correlator, we must perform an integration over $w$ and $w'$ of Eqn(1.32). It is easy to show using the series expansion for $G$ that the first term in Eqn(1.32) will generate the local equilibrium contribution proportional to $T^2(z)\delta(z - z')$. The remaining non-local contribution is given by the expression

$$\frac{\lambda_S}{\alpha_T} \frac{\left| \nabla T \right|^2 k_B}{(2\pi)^3} \int_{-\infty}^{\infty} dk || \int_{-\infty}^{\infty} dw e^{ik|| (r|| - r'||)} \sum_{n=\infty}^{\infty} \left\{ \frac{G_n(z', \tilde{w}_S) - G_n^*(z', \tilde{w}_S)}{w} \right\} e^{i\frac{2\pi n z}{L}}.$$  \hspace{1cm} (1.37)

This result is formally equivalent to Eqn(1.15) except for the change in the boundaries of the system from $0, L$ to $-L, L$. In the limit of large $L$, suffice it to say that the Fourier series converts to an integral with $n\pi/L = k_z$, yielding as a result the three dimensional Fourier transform of $1/k^2$ which is proportional to $|r - r'|^{-1}$ as expected.

1.5 CONCLUSIONS

In this chapter we have examined the influence of boundaries on the thermal correlations of a three dimensional fluid system. We have restricted our analysis to an idealized system in which the thermal modes are uncoupled from the other conserved densities. Furthermore, the assumption that the thermodynamic and transport coefficients of the fluid are constants restricts the length scale for which we probe the system to be smaller than a characteristic macroscopic length. We emphasize that for this particular model it is important to retain the parallel (i.e. unbounded) spacial
components in the problem so that the temperature correlator behaves properly as we let the boundaries move infinitely far apart.

Ultimately, the influence of boundaries on bulk dynamics depends on the length and time scales for which we probe the physical system. As mentioned previously in section 1.4, one can roughly estimate the importance of boundaries by comparing the thermal diffusion time, $L^2/\alpha_T$, to the characteristic relaxation time one is probing, say $\tau_{\text{probe}}$. For the case $L^2/\alpha_T \gg \tau_{\text{probe}}$, one should be able to neglect the boundaries for correlations within the fluid system. For concreteness, we can choose parameters corresponding to a typical light scattering experiment on water at 283K, which has a thermal diffusivity of $1.38 \times 10^{-3} cm^2 s^{-1}$. For this system, if the characteristic time scale one is probing is of the order of $10^{-7}s$, the previous argument would suggest that boundary effects can be neglected for thermal bulk dynamics if $L$ is greater than $10^{-5} cm$.

Our present results differ markedly from those obtained in references [15, 17, 18]. We have considered a three dimensional system and have properly treated the spatial components parallel to the walls across which heat is transferred. Even though there is a temperature gradient in the $z$ direction only, this is not a one dimensional system which the previous results effectively describe.
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Part II

SUPERCOOLED LIQUIDS
Upon cooling from high temperatures, a liquid normally undergoes a first-order phase transition and crystallizes at the melting temperature $T_m$. If the cooling rate is sufficiently rapid, the process of crystallization can be circumvented to obtain a supercooled liquid. Eventually at low enough temperatures, one obtains an amorphous solid which can be effectively regarded as a frozen liquid on the time scale of experimental observation. A supercooled liquid is said to form a glass at the glass transition temperature $T_g$, which is defined as the temperature where there is a jump in the specific heat measurement or, more recently, as the temperature where the macroscopic shear viscosity reaches $10^{13}$ Poise. Whereas a supercooled liquid is referred to as existing in a metastable state, a glass is really a thermodynamically unstable form of matter that is continually relaxing, albeit at a rate that may be too slow to measure. The nonequilibrium effects of the glassy state, which are commonly referred to as “annealing” or “aging” processes, manifest themselves in time-dependent thermodynamic and dynamical properties of the system. These features are fascinating in their own right but are beyond the scope of this thesis.

The classification scheme which assigns glass-forming liquids as either “fragile” or “strong” is based on the success of fitting the temperature dependence of the macroscopic viscosity to an Arrhenius law

$$\tilde{\nu}_t \propto e^{\frac{T_g}{T_A}}$$

where $\tilde{\nu}_t$ is the shear viscosity and $T_A$ is a temperature-independent constant which is proportional to the effective activation barrier energy. In fact, supercooled liquids which form covalent- or hydrogen-bonded network structures (e.g., $SiO_2$ and $B_2O_3$) display a nearly Arrhenius behavior and are classified as strong glass-formers. On the other hand, fragile liquids (e.g., o-terphenyl ($OTP$), salol, and $Ca_0.4K_0.6(NO_3)_{1.4}$ ($CKN$)) exhibit strongly non-Arrhenius relaxation properties and are characterized by non-directional interactions among the constituent molecules. The temperature dependence of the viscosity for liquids belonging to the latter category is often well
described by the Vogel-Tammann-Fulcher equation

\[ \tilde{\nu}_t \propto e^{\frac{T_\infty}{T - T_\infty}}, \]

with \( T_\infty \) as a material specific constant. For the remainder of this thesis, we will deal exclusively with fragile liquids, since they exhibit more fluid-like behavior and can be better described by the theoretical machinery developed for simple liquids.

It is important to realize that the formation of a glass at \( T_g \) observed in the laboratory is not any kind of a phase transition but merely a kinetic event that occurs as a result of the system falling out of equilibrium. The early theories for the glass transition postulated the existence of a true phase transition at a temperature below \( T_g \) where the structural relaxation time would diverge. The fact that the relaxation times become enormous far above this purported transition temperature presents a tremendous obstacle for any convincing experimental verification of such theories.

With the advent of mode-coupling theory for the supercooled liquids in 1984, attention has shifted to a high temperature critical point located at \( T_c \), where \( T_g < T_c < T_m \). The original version of the work, now known in the literature as the idealized mode-coupling theory, envisioned a purely dynamical transition arising from a nonlinear feedback mechanism of density fluctuations and a divergent relaxation time at \( T_c \). Later revisions of the theory claimed to extend the validity of the mode-coupling approach to lower temperatures by including couplings to current fluctuations that model thermally activated hopping transport and, thereby, removing the unphysical divergences at \( T_c \).

In addition to the fact that the relevant temperatures lie within the experimentally accessible regime, mode-coupling theory has enjoyed tremendous support because of its detailed and experimentally testable predictions, much of which have been confirmed in experiments and computer simulations for supercooled systems above \( T_c \). At and below \( T_c \) where hopping transport dominates structural relaxation, the success of mode-coupling theory has been the subject of considerable debate.

This part of the thesis is devoted to the study of structural relaxation and molec-
ular transport in deeply supercooled liquids below the mode-coupling critical temperature. Within the context of a general mode-coupling theory previously developed for the description of equilibrium fluctuations in simple classical fluids, we derive in chapter 2 an expression for the effective longitudinal viscosity including couplings to currents so that certain key assumptions inherent in previous work on the glass transition can be analyzed critically. We show that the hopping kernels arise from an approximate resummation of the dominant class of diagrams resulting from bilinear modes. Although the resummed expression for the viscosity obtained here is very similar to the result previously obtained from a kinetic theory approach, there are important differences, most notably in the form of the vertices connecting the hopping kernels and the lack of subtractions in the kernels representing the cage effect and activated hopping transport. Using the formalism developed here, we show that the introduction of an initial cutoff time in the hopping kernel to obtain a strong temperature dependence for the viscosity amounts to neglecting a class of processes that may be of comparable if not greater importance than the terms explicitly kept in previous work.

Next, under the assumption that structural relaxation is dominated by the decay of clusters of particles, we develop in chapter 3 a microscopic theory for transport in a strongly supercooled liquid. By introducing a local order parameter that describes the geometry of particle aggregates in addition to the number density and momentum density, we obtain an expression for the effective longitudinal viscosity in which a hopping term emerges nonperturbatively. We find that the hopping kernel obtained via this route arises from couplings to bilinear density-momentum modes in agreement with previous mode-coupling treatments. However, the magnitude of the hopping kernel is suppressed through a wavevector cutoff instead of the previously suggested initial time cutoff.

Finally in the last two chapters, we investigate the translational motion of a probe immersed in a supercooled liquid below $T_c$. We propose both a phenomenological treatment and a molecular theory to explain the deviations from the Stokes-Einstein relation for the diffusion constant. Within the confines of the phenomeno-
logical model, we study the diffusion in a dynamically disordered continuum in which small, compact regions of greater diffusivity appear and disappear in time, and we show that a systematic increase in the ratio of the diffusivity of the fluidized domains to the background diffusivity appears to be the single most important factor in explaining the anomalous diffusion. Using a standard mode-coupling formalism, we offer a microscopic justification for the phenomenological model suggested to explain the phenomenon.
Chapter 2

Re-examination of the mode-coupling scheme for the glass transition

The contents of this chapter is based on the work found in

2.1 INTRODUCTION

Structural relaxation in glass forming liquids has been the focus of considerable attention in the literature over the years. Despite both recent theoretical [1] and experimental [2] efforts, there is still no consensus as to the nature of the liquid-glass transition. For instance, controversies remain as to whether the transition is purely dynamic in origin or if there is some underlying thermodynamic transition governed by a growing length scale [3, 4]. Moreover, although many key features of the relaxational properties of glassy substances appear to be material sensitive, recent scaling of the dielectric susceptibility [5] and viscosity [6] data for a wide variety of both fragile and strong glass forming liquids (according to Angell’s classification scheme [7]) suggests an apparent universality.

Perhaps the most widely accepted theoretical approach involves the mode-coupling
theory (MCT) for the glass transition pioneered by Leutheusser [8] and Bengtzelius et al. [9]. The original idealized version of MCT predicts an ergodic to nonergodic dynamical transition and a viscosity divergence at a crossover temperature $T_c$. In addition, the theory makes specific statements about the sequence of relaxation behavior of the dynamic structure factor that have been verified with remarkable success in dense colloidal suspensions [10, 11, 12]. Nevertheless, since the absolute structural arrest predicted by the ideal MCT is not observed for molecular glass systems, extended versions of the MCT including couplings to current fluctuations were introduced [13, 14, 15, 16]. Such additional couplings are intended to model thermally activated "hopping" processes that restore ergodicity and smear out the bifurcation singularities of the original version of MCT. The success of fitting experimental data for molecular glasses such as CKN or salol with the extended MCT has been less clear cut. In one instance, the hopping parameter was assumed to follow an Arrhenius dependence with respect to the temperature, and the adjustable parameters were chosen to optimize the fits [17]. Theoretical derivation of the activated behavior based on kinetic theory relies on the introduction of an initial cutoff time in the hopping kernel and the so called von Schweidler relaxation of the density correlation function [18].

It is the purpose of this chapter to develop a general MCT for the glass transition in a systematic fashion so that certain key assumptions in previous work can be analyzed critically. We will be almost exclusively concerned with the extended MCT based on the kinetic theory of liquids [1, 14, 19] since it bears the closest resemblance to our formalism. Suffice it to say that other mode-coupling models for the glass transition rely on the one-loop approximation even though higher order terms are presumably of comparable magnitude.

The success of MCT in explaining critical phenomena and the long time dynamics of moderately dense liquids away from the critical point stems from the fact that the long wavelength fluctuations dominate the problem. For dense fluids undergoing the glass transition, one is primarily concerned with a more local behavior in which dynamics occurs with a characteristic length scale of a few tens of Angstroms or less. Whether a mode-coupling description remains valid is difficult to assess and we do
not claim to find a resolution here.

The chapter is organized as follows: In Section 2.2, we briefly review the formal mode-coupling hierarchy developed by Schofield, Lim, and Oppenheim [20, 21]. The MCT presently used allows for a systematic perturbation series in terms of a mode-coupling parameter, and a diagrammatic representation can be constructed to aid visualization and calculation of individual terms of the series. By keeping only the dominant 1-loop renormalizations from bilinear modes in Section 2.3, we reproduce the result for the longitudinal viscosity previously obtained by the idealized MCT. In Section 2.4, we show that the hopping kernel arises naturally when one includes the dominant contributions from bilinear modes at all loop orders. By approximately resumming a whole class of diagrams, we obtain an expression for the viscosity similar to that reported previously. We discuss the validity of introducing the cutoff time in the hopping kernel in Section 2.5. Sjögren [18] claimed that the short and intermediate time contribution should not be included in the hopping kernel since it was already contained in the bare viscosity and the density relaxation kernel that drives the ideal glass transition. We reorganize the mode-coupling series with propagators in which the short time contributions are subtracted, and we show that the coupling vertices are in fact renormalized by the early time contributions. More importantly, if the microscopic time region does indeed give a significant contribution to the hopping term as previously suggested [22, 23, 24, 25], we show that the kinetic theory result for the viscosity arises from neglecting contributions of comparable if not greater magnitude. In Section 2.6, we present our conclusions.

2.2 MODE-COUPLING FORMALISM

In this section, we review the MCT of equilibrium fluctuations in simple liquids [21]. We consider a classical system of $N$ identical particles of mass $m$ interacting via an isotropic and short ranged potential $u(|r_{ij}|)$. The microscopic state of the system is completely specified by the phase point $X(t) \equiv \{r^N(t), p^N(t)\}$, whose evolution in
time is governed by the Hamiltonian

\[ H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} u(|r_{ij}|) = \sum_{i=1}^{N} e_i. \] (2.1)

The long time behavior of equilibrium correlation functions is determined by the slow modes of the system. The slow linear dynamical variables are the hydrodynamic variables, i.e. number, energy, and momentum densities:

\[
\begin{align*}
N(r, X(t)) &= \sum_{i=1}^{N} \delta (r - r_i(t)), \\
E(r, X(t)) &= \sum_{i=1}^{N} e_i(t) \delta (r - r_i(t)), \\
P(r, X(t)) &= \sum_{i=1}^{N} p_i(t) \delta (r - r_i(t)).
\end{align*}
\] (2.2)

Assuming that products of the linear variables comprise the remaining slow modes of the system, one can define a column vector \( A(r, t) \) composed of the densities \( N(r, t), \) \( E(r, t), \) and \( P(r, t) \) and an infinite column vector \( Q \) with the following components:

\[
\begin{align*}
Q_0 &= 1, \\
Q_1(r) &= A(r) - \langle A(r) \rangle \equiv \dot{A}(r), \\
Q_2(r, r') &= Q_1(r)Q_1(r') - \langle Q_1(r)Q_1(r') \rangle \\
&\quad - \langle Q_1(r)Q_1(r')Q_1(r_1) \rangle K_{11}^{-1}(r_1; r_2) \cdot Q_1(r_2), \\
Q_3(r, r', r'') &= Q_1(r)Q_1(r')Q_1(r'') - \langle Q_1(r)Q_1(r')Q_1(r'') \rangle \\
&\quad - \langle Q_1(r)Q_1(r')Q_1(r'')Q_1(r_1) \rangle K_{11}^{-1}(r_1; r_2) \cdot Q_1(r_2) \\
&\quad - \langle Q_1(r)Q_1(r')Q_1(r'')Q_2(r_1, r_2) \rangle K_{22}^{-1}(r_1, r_2; r_3, r_4) \cdot Q_2(r_3, r_4), \\
&\vdots
\end{align*}
\] (2.3)

where the angular brackets \( \langle \ldots \rangle \) denote an equilibrium ensemble average,

\[
K_{ii}(r_1, \ldots, r_i; r'_1, \ldots, r'_i) = \langle Q_i(r_1, \ldots, r_i)Q_i(r'_1, \ldots, r'_i) \rangle, \] (2.4)
and the \( \cdot \) notation denotes an integration of repeated spatial arguments over the volume of the system, a sum over hydrodynamic labels (\( N, E, \) and \( P \)), and a sum over mode order when dealing with the different elements of \( Q \). The subtractions at each mode order are required to insure that the components of \( Q \) are orthogonal to each other, i.e.

\[
\langle Q_i Q_j \rangle = K_{ii} \delta_{ij}.
\] (2.5)

Using the definition of the two projection operators,

\[
\hat{P} B = \langle B \dot{A} \rangle \cdot (\dot{A} \dot{A})^{-1} \cdot \dot{A},
\]

\[
P B = \langle B Q \rangle \cdot K^{-1} \cdot Q,
\] (2.6)

where \( B \) is an arbitrary dynamical variable, we obtain the generalized Langevin equations:

\[
\dot{A}(t) = \int_0^t \tilde{M}(\tau) \cdot \dot{A}(t - \tau) d\tau + f(t),
\]

\[
\dot{Q}(t) = \int_0^t M(\tau) \cdot Q(t - \tau) d\tau + \phi(t),
\] (2.7)

where

\[
\tilde{M}(\tau) = \{2(\dot{A} \dot{A}) \delta(\tau) - \langle f(\tau) f \rangle \} \cdot (\dot{A} \dot{A})^{-1},
\]

\[
M(\tau) = \{2(\dot{Q} Q) \delta(\tau) - \langle \phi(\tau) \phi \rangle \} \cdot K^{-1},
\] (2.8)

and

\[
f(t) = e^{(1 - \hat{P}) iLt} (1 - \hat{P}) \dot{A},
\]

\[
\phi(t) = e^{(1 - \hat{P}) iLt} (1 - \hat{P}) \dot{Q},
\] (2.9)

with \( L \) being the Liouvillian. By construction, \( f(t) \) is a fluctuating force orthogonal to \( A \) only, while \( \phi(t) \) is a fluctuating force orthogonal to all \( Q \). Under the assumption that the elements of the vector \( Q \) comprise all the slow variables of the system, \( \phi(t) \) is
strictly a fast variable in the sense that \( \langle \dot{\phi}(t)\dot{\phi} \rangle \) decays on a microscopic timescale. On the other hand, \( f(t) \) still contains slow behavior because it has projections onto \( Q_2, Q_3, \) etc..., and hence \( \langle f(t)f \rangle \) still decays slowly. The matrices \( \bar{M} \) and \( M \) are referred to as the dressed and bare hydrodynamic matrix, respectively. In Eqn(2.8), the instantaneous term is referred to as the Euler part of the hydrodynamic matrix, and the second term containing correlation functions of the fluctuating forces is referred to as the dissipative or Navier-Stokes part.

Using the orthogonality properties of \( f(t) \) and \( \phi(t) \) and transforming to Laplace space \( s \), it can be shown that

\[
\langle \hat{A}(s)\hat{A} \rangle = (sI - \bar{M}(s))^{-1} \cdot \langle \hat{A}\hat{A} \rangle, \tag{2.10}
\]

and

\[
\langle Q(s)Q \rangle = (sI - M(s))^{-1} \cdot \langle QQ \rangle, \tag{2.11}
\]

where \( I \) is the identity matrix. With the aid of Eqns(2.10) and (2.11) and \( Q_1 = \hat{A} \), it follows that

\[
(sI - \bar{M}(s))^{-1} = (sI - M(s))^{-1}_{11}, \tag{2.12}
\]

where \((sI - M(s))^{-1}_{11}\) is the one-one sub-block (in mode-order) of an infinite dimensional matrix. Following previous arguments, we expect a much stronger \( s \)-dependence for the dressed hydrodynamic matrix than the bare matrix at small \( s \) or for long times.

Due to the translational invariance of the system, we will find it convenient to work in Fourier space. In addition, we employ the \( N \) ordering scheme [26] to order terms using the inverse system size as an implicit expansion parameter.

Deferring details to the original work, we present the result obtained after several resummations [21]:

\[
\bar{M}(a(k); b(k), s) = M_{11}(a(k); b(k), s) + \sum_{i=2}^{\infty} \theta^i_{11}(a(k); b(k), s), \tag{2.13}
\]

where \( a \) and \( b \) refer to the hydrodynamic labels. Using the short hand notation
\( \theta_{11}^i(a(k); b(k), s) = \theta_{ab}^i(k, s) \), the explicit forms of the \( \theta^i \)'s are

\[
\begin{align*}
\theta_{ab}^1(k, s) &= \sum_{|\gamma|=2}^{\infty} X_{a\gamma} \cdot G_{\gamma\gamma'} \cdot X_{\gamma'b}, \\
\theta_{ab}^2(k, s) &= \sum_{|\gamma|=2}^{\infty} \sum_{|\delta|=2}^{\infty} X_{a\gamma} \cdot G_{\gamma\gamma'} \cdot X_{\gamma\delta} \cdot G_{\delta\delta'} \cdot X_{\delta'b}, \\
\:
\end{align*}
\]

where the \( \cdot \) notation denotes a summation over repeated hydrodynamic labels and internal wavevectors (if applicable), the greek letter \( \gamma \), for instance, denotes a multilinear mode of order \( |\gamma| \) and associated with a set of hydrodynamic indices and wavevectors, and \( \gamma \) and \( \gamma' \) are modes of the same order and with the same set of wavevectors but possibly differing in the hydrodynamic labels. Also, the coupling vertices, \( X \), are given explicitly by

\[
X_{\gamma\delta} = \begin{cases}
\hat{M}_{\gamma\delta}^{(od)} & \text{if } |\gamma| \neq |\delta| \\
\hat{M}_{\gamma\delta}^{(od)} - s(O.D^{-1})_{\gamma\delta} & \text{if } |\gamma| = |\delta|,
\end{cases}
\]

where \( O \) and \( D \) are, respectively, the off-diagonal and diagonal in wavevector components of the matrix \( K \), \( \hat{M} \) is related to \( M \) in Eqn(2.8) with \( K^{-1} \) replaced by \( D^{-1} \), and \( \hat{M}^{(od)} \) is the off-diagonal part of \( \hat{M} \) in wavevector space. The dressed propagators \( G \) can be expressed as the Laplace transforms of products of correlation functions. For instance,

\[
G_{22}(a_1(k - q), a_2(q); b_1(k - q)b_2(q), s)
= \mathcal{L}\left\{ \mathcal{L}^{-1}[sI - \hat{M}(k - q, s)]_{(a_1, b_1)}\mathcal{L}^{-1}[sI - \hat{M}(q, s)]_{(a_2, b_2)}^{(od)} \right\},
\]

\[
= \mathcal{L}\{ (a_1(k - q, t)a_j(k - q)\gamma) \cdot K_{11}^{-1}(a_j(k - q)b_1(k - q)) \\
\quad \times (a_2(q, t)a_i(q)\gamma) \cdot K_{11}^{-1}(a_i(q)b_2(q)) \},
\]

\[
= \mathcal{L}\{ \phi_{a_1b_1}(|k - q|, t)\phi_{a_2b_2}(q, t) \}, \tag{2.15}
\]
where
\[ \phi_{ab}(k, s) = \langle a(k, s)c_i(k)^* \rangle \cdot K_{11}^{-1}(c_t(k)b(k)) \].

(2.16)

We note in passing that the explicit s-dependent term in \( \chi_{\gamma\delta} \) arises from corrections to the factorization approximation for static correlation functions.

For liquids under normal conditions, the mode-coupling result in Eqn(2.13) may be interpreted as a systematic perturbation series in terms of a small mode coupling parameter \( \mathcal{M}/N \). Using the \( N \)-ordering scheme, it is easy to show that the \( N \) order of the hydrodynamic matrix \( \tilde{M}_{\alpha\beta}^{(od)} \) (\( = \chi_{\alpha\beta} \) for small \( s \)) is given by

\[ \tilde{M}_{\alpha\beta}^{(od)} \leq N^{1-|\beta|}. \]

(2.17)

Each summation over wavevector \( q \) introduces a factor of

\[ \mathcal{M} = \sum_{q=0}^{K_c} = \frac{4\pi V K_c^3}{3(2\pi)^3}, \]

(2.18)

where \( V \) is the volume and \( K_c \) is a large wavevector cutoff. At high temperatures when \( K_c \approx 10^7 \text{ cm}^{-1} \), the mode-coupling parameter is indeed quite small (\( \approx 10^{-5} \)).

### 2.3 APPLICATION TO THE GLASS TRANSITION - 1-loop diagrams

In the following, we will apply the general MCT formalism discussed in Section 2.2 to study fluctuations in dense, supercooled liquids. Since MCT was originally intended to describe the long time behavior of correlation functions as determined by long wavelength hydrodynamic modes, generalizing the theory to include structural relaxation on a molecular scale is not without its difficulties. In particular, inclusion of wavenumbers \( k \) near the peak of the static structure factor implies that the mode-coupling parameter \( \mathcal{M}/N \) is of the order 1. We emphasize that the lack of a small parameter to carry systematic expansions for dense liquids is a common shortcoming of all MCT proposed to study the glass transition.
In order to make the calculations more tractable, we will adopt two commonly used approximations. First, we will neglect the energy density since it is not expected to play a significant role in the renormalizations discussed below. Second, we will include only linear and bilinear modes in our multilinear hierarchy. This is a particularly tricky point, and we will defer comments to the conclusions section.

With the two simplifications discussed above in mind, we have for the column vector $\hat{A}(k)$:

$$
\begin{pmatrix}
\hat{N}(k) \\
\hat{k}.P(k) \\
\hat{k}_{\perp 1}.P(k) \\
\hat{k}_{\perp 2}.P(k)
\end{pmatrix},
$$

where $\hat{k}(k_{\perp})$ is a unit vector parallel(perpendicular) to $k$. The dressed hydrodynamic matrix $\tilde{M}(k,s)$ for the set $\hat{A}(k)$ is explicitly given by

$$
\tilde{M}(k,s) = 
\begin{pmatrix}
0 & \frac{ik}{m} & 0 & 0 \\
\frac{ik\frac{k_BT}{S(k)}}{S(k)} & -\tilde{\Gamma}(k,s) & 0 & 0 \\
0 & 0 & -\tilde{\Gamma}(k,s) & 0 \\
0 & 0 & 0 & -\tilde{\Gamma}(k,s)
\end{pmatrix},
$$

where $S(k)$ is the static structure factor defined by $S(k) \equiv \langle \hat{N}(k)\hat{N}(k)^* \rangle_N$ and $\tilde{\Gamma}_{L,T}(k,s)$ are, respectively, the longitudinal and transverse current relaxation kernels, which are related to the generalized viscosities by the relation $\tilde{\Gamma}_{L,T}(k,s) = (k^2/nm)\tilde{\nu}_{L,T}(k,s)$ with $n = N/V$. From Eqn(2.10), we obtain for the density autocorrelation function

$$
\phi_{NN}(k,s) = \frac{\langle \hat{N}(k,s)\hat{N}(k)^* \rangle}{\langle \hat{N}(k)\hat{N}(k)^* \rangle} = \frac{1}{s + \frac{\Omega_k^2}{s + \tilde{\Gamma}_L(k,s)}},
$$

(2.19)

where $\Omega_k^2 = k^2\frac{k_BT}{mS(k)}$ is a characteristic microscopic frequency of the fluid. Appealing to Eqn(2.13), we can express $\tilde{\Gamma}_L(k,s)$ as the sum of two terms: a bare part representing contributions from the fast modes of the system and a renormalized part.
arising from the slowly decaying multilinear hydrodynamic modes. Since only bilinear renormalizations are included, the sums over mode order in Eqn(2.14) for the \( \theta \)'s are truncated after the first term. The mode-coupling series for the renormalized part of the longitudinal viscosity may be represented diagrammatically as shown in Fig.2-1. The endpoints on the left(right) are the \( X_{12}(X_{21}) \) vertices, the points within the diagrams are the \( X_{22} \) vertices, and the pairs of lines represent the \( G_{22} \) full propagators.

In this section, we include renormalizations from the one-loop diagrams only (of the order \( \mathcal{M}/N = 1 \)) in order to make contact with the idealized MCT for the glass transition. The relevant one-loop diagrams contributing to the effective viscosity are given in Fig.2-2. Since the slowly decaying density fluctuations drive the kinetic slowing down of the liquid, the dominant contribution at first order in the mode-coupling parameter to the viscosity is due to the first diagram in Fig.2-2.

\[
-\tilde{\Gamma}_L(k, s) = -\Gamma^0_L(k, s) + \frac{1}{2} \sum_q X_{12}(\hat{k}.P(k); \hat{N}(k - q)\hat{N}(q), s) \\
\mathcal{L}[\phi_{NN}(|k - q|, t)\phi_{NN}(q, t)]X_{21}(\hat{N}(k - q)\hat{N}(q); \hat{k}.P(k), s).
\] (2.20)

The factor of 1/2 in Eqn(2.20) is to prevent overcounting, and the contributions from the other diagrams have been absorbed into the bare viscosity, \( \Gamma^0_L \). Note that since \((1-P)Q^2(N(k-q)N(q)) = 0\), only the Euler term in the coupling vertices contribute, and these are given by (see Appendix A)

\[
\hat{M}^F_{12}(\hat{k}.P(k); \hat{N}(k - q)\hat{N}(q)) = \langle (\hat{k}.P(k))Q_2(\hat{N}(k-q)\hat{N}(q)) \rangle^* \\
\times K^{-1}_{11}(\hat{N}(k - q)\hat{N}(k - q)) \times K^{-1}_{11}(\hat{N}(q)\hat{N}(q)),
\]

\[
\hat{M}^F_{21}(\hat{N}(k - q)\hat{N}(q); \hat{k}.P(k)) = \langle Q_2(\hat{N}(k - q)\hat{N}(q))(\hat{k}.P(k)) \rangle^* \\
\times K^{-1}_{11}(\hat{k}.P(k); \hat{k}.P(k)).
\] (2.21)

After some straightforward calculations, we obtain

\[
\tilde{\Gamma}_L(k, s) = \Gamma^0_L(k, s) + \frac{1}{2} \sum_q V(k, q)\mathcal{L}[\phi_{NN}(|k - q|, t)\phi_{NN}(q, t)],
\] (2.22)
Figure 2-1: Diagrammatic representation of the mode-coupling series for the renormalized part of the longitudinal viscosity. Note that the diagram with n-loops is of the order $(\mathcal{M}/N)^n$.

where the vertex $V(k, q)$ is given by

$$V(k, q) = \frac{k_BT}{m} \frac{1}{N} \{ S(|k - q|) S(q) [\hat{k}.(k - q)(1 - \frac{1}{S(|k - q|)}) + \hat{k}.q(1 - \frac{1}{S(q)})$$

$$+ \hat{k}.k \left( \frac{t(k - q, q, k)}{S(|k - q|) S(q) S(k)} - 1 \right)^2 \},$$

(2.23)

where $t(k - q, q, k)$ is a three-point correlation function defined by $t(k - q, q, k) \equiv \langle \tilde{N}(k-q)\tilde{N}(q)\tilde{N}(k) \rangle$. If the convolution approximation is applied to $t(k - q, q, k)$, the last term in $V(k, q)$ vanishes, and we obtain the same coupling vertex as previous researchers [1]. Substitution of Eqn(2.22) into the equation of motion for the density correlator constitutes the self-consistent idealized MCT for the glass transition.
2.4 APPLICATION TO THE GLASS TRANSITION - higher loop diagrams

The two and higher loop diagrams in Fig.2-1 that are neglected in the ideal MCT represent relaxation sequences of increasing complexity. In simple liquids under normal conditions, the relative importance of these decay processes may be gauged by examining their $M/N$ order. However, a proper description of the glass transition requires inclusion of phenomena occurring at small or intermediate length scales, and, while the mode-coupling expansion in Eqn(2.13) is systematic, it is in terms of a parameter which is no longer small. Instead of simply ignoring the higher order processes as is commonly done, we attempt instead an approximate resummation of a whole class of diagrams that contain the most physically relevant processes. We note in passing that a similar resummation appears to be implicit in the work of Götze et al. [14], but the procedure described below is considerably more systematic, and the approximations incurred at each stage of the derivation are more obvious.

Naively following the criteria for deciding the dominant contribution at 1-loop order, one would expect that the most important higher order processes are those involving solely density fluctuations; namely, diagrams such as shown in Fig.2-3.
However, all such processes give no contribution to the long time renormalization of the longitudinal viscosity. Specifically, for frequencies \( s \) small enough where the term \( s O.D^{-1} \) in the coupling vertices is negligible, we have

\[
X_{22}(\tilde{N}(k - q)\tilde{N}(q); \tilde{N}(k - q')\tilde{N}(q'), s) = \tilde{M}_{22}^{E}(\tilde{N}(k - q)\tilde{N}(q); \tilde{N}(k - q')\tilde{N}(q')) = 0
\]

by symmetry considerations. As before, the dissipative coupling of the \( X_{22} \) vertex above vanishes since \((1-P)\tilde{Q}_2(\tilde{N}(k-q)\tilde{N}(q)) = 0\). Thus, for small \( z \), bilinear density-density modes will couple only to density-momentum modes. Thus, \( G_{22} \) propagators containing solely density modes must be mediated by propagators containing a pair of density modes and a pair of momentum modes. It is exactly these mediating propagators that represent hopping transport in the extended MCT. Diagrammatically, the infinite set of diagrams that we will include is illustrated in Fig.2-4. A few comments are appropriate at this point. In Fig.2-4, we have shown explicit renormalizations from diagrams containing the most \( G_{22}(\tilde{N}(k - q)\tilde{N}(q); \tilde{N}(k - q)\tilde{N}(q), s) \)

---

**Figure 2-3:** Higher loop diagrams containing solely density fluctuations which do not contribute to the small frequency renormalization of \( \tilde{\Gamma}(k, z) \).
propagators at each loop order. All other contributions have been included in the

Figure 2-4: Dominant class of diagrams renormalizing the bare longitudinal viscosity. Here $\delta_h$ refers to the hopping terms given by diagrams (d) and (e) of Figure 2-2.

bare viscosity. The magnitude of $G_{22}$ propagators containing at least one momentum mode in their argument is taken to decrease significantly as the liquid is supercooled since the large viscosities cause rapid exchange of momentum. Thus, we have omitted explicit renormalizations from even-looped diagrams containing the most $G_{22}(\tilde{N}(k-q)\tilde{N}(q); \tilde{N}(k-q)\tilde{N}(q), s)$ propagators since they are essentially the diagrams in Fig.2-4 multiplied by a kernel of small magnitude.

The mode-coupling series in Fig.2-4 is in the form of a geometric series. However, a straightforward resummation to obtain a Dyson-like equation for $\tilde{\Gamma}_L$ cannot be performed due to the complicated nature of the $X_{22}$ coupling vertices. Since we are interested in the small frequency anomalies of the longitudinal viscosity, we may neglect the explicit $s$-dependent term of $X_{22}$. The remaining Euler term is off-diagonal in its wavevector argument; thus, no simple factorization approximation can be performed. The different loops of a single diagram are therefore intimately coupled via
complicated three-point correlation functions given by (see Appendix A)

\[ X_{22}(P(k - q), \hat{N}(q); \hat{N}(k - q'), \hat{N}(q')) = \langle \hat{Q}_2(P(k - q), \hat{N}(q)Q_2(\hat{N}(k - q'), \hat{N}(q'))^* \]
\[ \times K^{-1}_{11}(\hat{N}(k - q'), \hat{N}(q)) \]
\[ \times K^{-1}_{11}(\hat{N}(q') \hat{N}(q)). \] (2.25)

Nevertheless, we may resort to an approximate resummation by effectively decoupling the higher loop diagrams at the \( X_{22}(P(k - q), \hat{N}(q); \hat{N}(k - q'), \hat{N}(q')) \) vertex.

The mode-coupling series for the renormalized part of the longitudinal current relaxation kernel in

\[ \hat{\Gamma}_L(k, s) = \Gamma^o_L(k, s) + \Gamma^R_L(k, s), \] (2.26)

may be written as

\[-\Gamma^R_L(k, s) = X_{12} \cdot G^{NN,NN}_{22} X_{21} \]
\[+ X_{12} \cdot G^{NN,NN}_{22} X_{22} \cdot \delta^8_{22} X_{22} \cdot G^{NN,NN}_{22} X_{21} \]
\[+ X_{12} \cdot G^{NN,NN}_{22} X_{22} \cdot \delta^8_{22} X_{22} \cdot G^{NN,NN}_{22} X_{22} \]
\[\cdot \delta^8_{22} X_{22} \cdot G^{NN,NN}_{22} X_{21} + \ldots \]
\[= X_{12} \cdot G^{NN,NN}_{22} X_{21} \]
\[+ X_{12} \cdot G^{NN,NN}_{22} X_{22} \cdot \delta^8_{22} \{ X_{22} \cdot G^{NN,NN}_{22} X_{21} \}
\[+ X_{22} \cdot G^{NN,NN}_{22} X_{22} \cdot \delta^8_{22} X_{22} \cdot G^{NN,NN}_{22} X_{21} + \ldots \}, \] (2.27)

where we have omitted the explicit wavevector, frequency, and hydrodynamic index labelings of the vertices and propagators unless confusion can arise, and we have used the conventions:

\[ G^{ab,cd}_{22}(k, q, s) = G_{22}(a(k - q)b(q); c(k - q)d(q), s), \] (2.28)
\[ X_{22} \cdot \delta^h_{22} X_{22} = \]
\[ \cdots \{ X_{22}(\hat{N}(k-q)\hat{N}(q); P(k-q')\hat{N}(q')) \cdot G_{22}^{NN,NN}(k, q', s) \]
\[ + X_{22}(P(k-q')\hat{N}(q'); \hat{N}(k-q'')\hat{N}(q'')) \cdots \{ X_{22}(P(k-q')\hat{N}(q'); \hat{N}(k-q'')\hat{N}(q'')) \} \cdots \]
\[ (2.29) \]

Here, the \( \cdot \) notation denotes a summation over repeated momentum modes and internal wavevectors.

The terms in the curly brackets of Eqn(2.27) comprise a renormalized vertex, \( X_{21}^R(P_i(k-q)\hat{N}(q); \hat{k}.P(k), s) \). We thus have for \( \Gamma_L^R(k, s) \)
\[ -\Gamma_L^R(k, s) = X_{12} \cdot G_{22}^{NN,NN} X_{21} + \]
\[ + X_{12} \cdot G_{22}^{NN,NN} X_{22} \cdot \delta^h_{22} X_{21}^R. \]
\[ (2.30) \]

In order to obtain a closed expression for \( \Gamma_L^R(k, s) \), we employ the following approximation:
\[ X_{21}^R(P_i(k-q)\hat{N}(q); \hat{k}.P(k), s) = -f_i(k, q, s)\Gamma_L^R(k, s) \]
\[ \approx -f_i(k, q)\Gamma_L^R(k, s). \]
\[ (2.31) \]

In ignoring the \( s \)-dependence of the matching function \( f_i \), we have assumed that the time dependence of the renormalized vertex \( X_{21}^R \) is completely determined by \( \Gamma_L^R \).

Notice also that Eqn(2.31) implies that the \( q \)- and \( s \)-dependences of \( X_{21}^R \) factorize.

We may examine the merit of Eqn(2.31) by writing the exact expression for \( f_i(k, q, s) \):
\[ f(k, q, s) = \frac{[X_{22} \cdot G_{22}^{NN,NN} X_{21} + X_{22} \cdot G_{22}^{NN,NN} X_{22} \cdot \delta^h_{22} X_{22} \cdot G_{22}^{NN,NN} X_{21} + \cdots]}{X_{12} \cdot G_{22}^{NN,NN} X_{21} + X_{12} \cdot G_{22}^{NN,NN} X_{22} \cdot \delta^h_{22} X_{22} \cdot G_{22}^{NN,NN} X_{21} + \cdots}. \]
\[ (2.32) \]
We see from Eqn(2.32) that the only difference between the series in the numerator and denominator is the first vertex of each term, $X_{22}(P_{i}(k - q), \hat{N}(q); \hat{N}(k - q')\hat{N}(q'))$ versus $X_{12}(\hat{k}.P(k); \hat{N}(k - q')\hat{N}(q'))$, both of which have only instantaneous Euler terms for small $s$. Therefore, for small frequencies where the terms $sO.D^{-1}$ of the coupling vertices can be neglected, we believe that it is a reasonable approximation to assume that $f(k, q, s)$ has negligible $s$-dependence. A similar approach is used to obtain the kinetic theory result [14, 19], but the matching function is derived from initial value arguments. In the present context, we cannot approximate $f$ as

$$f(k, q) = \frac{X_{22}^{R}(P(k - q), \hat{N}(q); \hat{k}.P(k), t = 0)}{-\Gamma_{L}^{R}(k, t = 0)}, \quad (2.33)$$

since $X_{22}^{R}(k, q, s)$ and $\Gamma_{L}^{R}(k, s)$ actually have significantly different $s$-dependence for large $s$'s because of the $sO.D^{-1}$ terms. Although the expression for $f$ given in Eqn(2.32) is considerably more complicated than the analogous kinetic theory result, we believe that Eqn(2.32) is the correct procedure for determining the matching function. In practical situations, one may estimate $f$ by taking the leading term in the numerator and denominator of Eqn(2.32). We remark that the kinetic theory result, which is analogous to using Eqn(2.33) instead of Eqn(2.32), arises from an ansatz that has not been justified rigorously [14, 19], and while it gives the correct $t = 0$ expression for the renormalized vertex, it does not necessarily give the correct behavior at long times.

By inserting the approximate expression for $X_{21}^{R}$ into Eqn(2.30), we obtain the result:

$$\tilde{\Gamma}_{L}(k, s) = \Gamma_{L}^{o}(k, s) - \frac{X_{12} \cdot G_{22}^{N,N;NN} X_{21}}{1 - X_{12} \cdot G_{22}^{N,N;NN} X_{22} \cdot \delta_{22}^{b}} f, \quad (2.34)$$

where, explicitly,

$$-X_{12} \cdot G_{22}^{N,N;NN} X_{21} =$$

$$\frac{1}{2} \sum_{q} \{X_{12}(\hat{k}.P(k); \hat{N}(k - q)\hat{N}(q)) \times L[\phi_{NN}(|k - q|, t)\phi_{NN}(q, t)]$$

$$\times X_{21}(\hat{N}(k - q)\hat{N}(q); \hat{k}.P(k))\},$$
\[ V(k, q) = \frac{1}{2} \sum_{q} V(k, q) \mathcal{L}[\phi_{NN}(|k - q|, t)\phi_{NN}(q, t)]. \]  

(2.35)

with \( V(k, q) \) given previously in Section 2.3 and

\[
X_{12} \cdot G_{22}^{NN:NN} X_{22} \cdot \delta_{22} f =
\frac{1}{2} \sum_{q} \sum_{q'} \sum_{i} X_{12} \{ \hat{k} \cdot P(k) ; \hat{N}(k - q)\hat{N}(q) \} \mathcal{L}[\phi_{NN}(|k - q|, t)\phi_{NN}(q, t)]
\times \{ X_{22} \{ \hat{N}(k - q)\hat{N}(q) ; P_i(k - q')\hat{N}(q') \} \mathcal{L}[\phi_{NN}(|k - q'|, t)\phi_{NN}(q', t)]
\times f_i(k, q'), \]

(2.36)

where \( \{ P_i(q) \} = \{ q \cdot P(q), q \cdot P(q), q \cdot P(q) \} \) and "long" denotes the longitudinal component of the momentum mode. Again, the factors of 1/2 are to prevent over-counting when summing over intermediate wavevectors.

### 2.5 COMPARISON WITH PREVIOUS WORK

Eqn(2.34) for the dressed longitudinal viscosity has essentially the same form as the expression proposed in the extended MCT of Götzte et al. [14]. However, there are differences in the placement of the bare viscosity, the form of the coupling vertices, and the lack of subtractions in the density and hopping kernels in the present result. Since the explicit mode-coupling terms provide the dominant contribution at small \( s \), the particular placement of the bare viscosity will be important only when one is concerned about the short time behavior of the relevant correlation functions. Also, differences in the coupling vertices (in particular, those associated with the hopping kernel) arise from the different approximations used to obtain a closed expression for the longitudinal viscosity. Within the kinetic theory approach, the hopping vertices originate from an initial value matching of a particular \( T \) matrix [19]. As mentioned previously, we believe that our approach is considerably more systematic, and we have shown how the hopping terms arise naturally without resorting to a successive
approximation scheme [14].

Instead, we will focus on the subtractions in the nontrivial kernels of the viscosity obtained in previous work. In the kinetic theory scheme [14, 18, 19], the splitting of the viscosity into a bare and a renormalized part is done such that all the short time behavior (of the order of a binary collision time) is contained in the bare viscosity. Thus, the mode-coupling kernels contain subtractions to remove the short time contributions already included in the bare transport coefficient. For instance, the kernel $m$ representing the cage effect is given by [14]

$$m(k, t) = \frac{1}{2} \sum_{q} V(k, q) \{\phi_{NN}(|k - q|, t)\phi_{NN}(q, t) - \phi_{NN}^{R}(|k - q|, t)\phi_{NN}^{R}(q, t)\}, \tag{2.37}$$

where the superscript $B$ indicates that the time evolution is governed by a binary collision operator [19], which is valid only for short times, instead of the full Liouvillian. For the hopping kernel, Sjögren [18] argued that the subtractions should not only remove the short time contributions contained in the bare viscosity but also the intermediate $\beta$-relaxation processes already contained in the kernel $m(k, t)$. These deletions, which amount to including an initial cutoff time in the Laplace transform, are essential in the derivation of the strong temperature dependence of the hopping terms. Numerical evaluation of the equation of motion for the density correlator has shown that the hopping terms do not decrease as dramatically as predicted if the initial cutoff is not introduced [22, 23, 24, 25]. For a schematic model where the wavevector dependences of the vertices are ignored, Götze et al. [23] and Kim [22] have shown that the magnitude of the hopping parameter can be significantly reduced in the presence of a cutoff time. However, since the short time behavior gave the main contribution, the size of the hopping kernel was a strong function of the cutoff time.

In order to verify the validity of introducing the initial cutoffs, we will rewrite the mode-coupling series in Eqn(2.27) so as to remove all short time contributions from the renormalized term. For the hopping kernels, we will subtract only the microscopic time regime, which presumably gives a greater contribution than the intermediate
time behavior [22, 23]. Defining

\[
\Delta_{22}^{NN,NN} = G_{22}^{NN,NN} - G_{22}^{B,NN,NN},
\]
\[
\Delta_{22}^h = \delta_{22}^h - \delta_{22}^B h,
\]  

(2.38)

it is straightforward to show that

\[
\tilde{\Gamma}_L(k, s) = \Gamma_1^o(k, s) + \Gamma_2^R(k, s),
\]  

(2.39)

where the new bare viscosity \(\Gamma_1^o(k, s)\) is given by

\[
-\Gamma_1^o(k, s) = -\Gamma_2^o(k, s) + X_{12} \cdot G_{22}^{B,NN,NN} X_{21} + X_{12} \cdot G_{22}^{B,NN,NN} X_{22} \cdot \delta_{22}^h + X_{12} \cdot G_{22}^{B,NN,NN} X_{21} + \ldots,
\]  

(2.40)

and the new renormalized viscosity \(\Gamma_2^R(k, s)\) is given by

\[
-\Gamma_2^R(k, s) = \{X_{12} + X_{12} \cdot G_{22}^{B,NN,NN} X_{22} \cdot \delta_{22}^h X_{22} + \ldots\} \cdot \Delta_{22}^{B,NN,NN} \{X_{21} + \ldots\} + \{X_{12} \cdot G_{22}^{B,NN,NN} X_{22} + \ldots\} \cdot \Delta_{22}^h
\]
\[
\{X_{22} \cdot G_{22}^{B,NN,NN} X_{21} + X_{22} \cdot G_{22}^{B,NN,NN} X_{22} \cdot \delta_{22}^h X_{22} + \ldots\} \cdot \Delta_{22}^{NN,NN} \{X_{21} + \ldots\} + \ldots
\]  

(2.41)

or equivalently,

\[
-\Gamma_2^R(k, s) = X_{12} \cdot \Delta_{22}^{NN,NN} X_{21} + X_{12} \cdot \Delta_{22}^h X_{21} + X_{12} \cdot \Delta_{22}^{NN,NN} X_{22} \cdot \Delta_{22}^h X_{22} + \ldots
\]  

(2.42)

Again, we have omitted the hydrodynamic and wavevector labeling of the propagators.
and vertices for notational simplicity.

As a result of introducing the subtractions in Eqn(2.38), we have renormalized the bare viscosity and all the coupling vertices by the short time propagators, \( G_{22}^{NN;NN} \) and \( \delta_{2h}^B \). In particular, the dominant one-loop contribution still arises from solely density fluctuations with \( X_{12}(\hat{k}.P(\hat{k}); \hat{N}(k-q)\hat{N}(q)) \) (and \( X_{21} \)) replaced by \( X'_{12}(\hat{k}.P(\hat{k}); \hat{N}(k-q)\hat{N}(q), s) \) (and \( X'_{21} \)) and with the propagator \( G_{22}(\hat{N}(k-q)\hat{N}(q), s) \) replaced by \( \Delta_{22}(\hat{N}(k-q)\hat{N}(q); \hat{N}(k-q)\hat{N}(q), s) \). Since the density modes decay extremely slowly in supercooled liquids, the difference between \( G_{22}^{NN;NN} \) and \( \Delta_{22}^{NN;NN} \) for small \( s \) is expected to be negligible. However, the coupling of the longitudinal momentum to the bilinear density modes represented by \( X_{12}(\hat{k}.P(\hat{k}); \hat{N}(k-q)\hat{N}(q)) \) is no longer instantaneous since \( X'_{12}(\hat{k}.P(\hat{k}); \hat{N}(k-q)\hat{N}(q), s) \) will have \( s \)-dependence from the short time renormalizations. This \( s \)-dependence is in fact neglected in previous work. More importantly, if the short time behavior of the hopping kernels is significant, the neglect of the class of terms given by

\[
X'_{12} \cdot \Delta_{22}^{NN;NN} X'_{22} \cdot \Delta_{22}^{NN;NN} X'_{21} + X'_{12} \cdot \Delta_{22}^{NN;NN} X'_{22} \cdot \Delta_{22}^{NN;NN} X'_{21} + \ldots \tag{2.43}
\]

cannot be justified. We remark that while the terms in Eqn(2.43) are included in the resummed expression for the viscosity kernel of the present work, they are in fact neglected in the kinetic theory result [14].

### 2.6 CONCLUSIONS

In this chapter we have attempted a systematic derivation of the expression for the longitudinal viscosity that was previously obtained via an extended MCT treatment. Our main motivation in developing the present mode-coupling scheme is to understand how the so-called hopping processes, which restore ergodicity via couplings to current relaxations, may enter the problem in a more natural and rigorous manner.
We have shown that hopping kernels arise inevitably if the dominant relaxation processes at each loop order are to be included. Since there is no small parameter to carry systematic expansions, we believe that it is essential to resum the most physically relevant subseries of diagrams, at least up to bilinear modes in the multilinear hierarchy. Due to the complicated nature of the vertices coupling the different loops of a multiloop diagram, we have resorted to an approximate decoupling scheme in order to obtain a Dyson-like equation for the renormalized viscosity. We emphasize that a similar approximation is used in the kinetic theory analysis in order to obtain a closed expression for the viscosity kernel [14, 19].

While our resummed expression for the longitudinal viscosity has essentially the same form as the kinetic theory result, it differs in one crucial respect: the kernels describing the cage effect and hopping transport in the present treatment lack the subtractions to remove the initial time dependence. The influence of the subtractions in the kernel containing a pair of density fluctuations is negligible for small \( z \). However, the subtractions in the hopping kernel may play a crucial role in determining its temperature dependence (and hence the temperature dependence of the viscosity itself) if, in fact, the short time regime gives the main contribution as suggested by previous work [22, 23, 24, 25]. In the spirit of the kinetic theory argument, we reorganized our mode-coupling series by removing all short time contributions from the mode-coupling kernels and absorbing these in the bare viscosity. We find that not only do the short time propagators renormalize the bare viscosity but they also renormalize the coupling vertices and, thus, generate new couplings among the bilinear modes. For instance, bilinear density modes may now couple through intervening short time propagators contained in the renormalized vertex \( X'_{22}(\hat{N}(k - q)\hat{N}(q); \hat{N}(k - q')\hat{N}(q'), s) \). This effect appears to be neglected in the kinetic theory result. Consequently, we find the claim that the subtracted terms in the viscosity kernel represent processes already included in the bare viscosity to be misleading. Only relaxation sequences where all propagators are short time propagators strictly renormalize the bare viscosity. While the additional contributions generated by the new coupling vertices can in principle be absorbed in the bare viscosity, the class of terms shown in Eqn(2.43) may actually
be of greater importance than the processes explicitly retained in the kinetic theory result.

If the initial cutoff time is not introduced for the hopping kernel, the extended MCT still predicts a considerable slowing down of transport without a discontinuous ergodic-nonergodic transition at $T_c$. However, the slowing down of structural relaxation is not nearly as pronounced as observed for experimental glass systems [22, 23, 24, 25]. In fact, if the magnitude of the hopping kernel does not decrease dramatically upon supercooling, much of the dynamical behavior predicted by the original MCT may be masked, and the meaning of the special temperature $T_c$ may come into question. The present work suggests that MCT in its present state is unable to generate self-consistently the strong temperature dependence for the viscosity without the arbitrary introduction of a cutoff time [18] or a phenomenological transport parameter that is assumed to be anomalously small [22, 27].

Lastly, we would like to comment upon the truncation of the multilinear hierarchy at bilinear order used in this chapter. Although small wavenumber renormalizations from higher order modes have been considered for tagged particle correlation functions [28, 29], to our knowledge, finite wavenumber renormalizations from trilinear and higher order modes have never been explicitly included in the MCT of dense liquids, primarily due to the increasing complexity of the vertices. For instance, it is straightforward to show that the vertex in the one-loop diagram resulting from trilinear density modes contains two-, three-, four-, and even five-point static correlation functions. To date, no justification for the neglect of higher order modes has been given except for the a posteriori success of this approximation in various applications.

2.7 APPENDIX A

In this Appendix, we give the explicit forms for all relevant coupling vertices $X_{\gamma \delta}$ discussed in the text. We will consider only the small $s$ limit of $X_{\gamma \delta}$ so that the $s(O.D^{-1})_{\gamma \delta}$ term can be dropped. The remaining term is easily evaluated with the definitions of the multilinear hierarchy in Eqn(2.3) and the bare hydrodynamic matrix in
Eqn(2.8). Defining \( S(k) \equiv \frac{\langle N(k), N(k)^* \rangle}{N} \) and \( t(q_1, q_2, q_3) \equiv \delta_{q_1+q_2, q_3} \frac{\langle N(q_1), N(q_2), N(q_3)^* \rangle}{N} \), the results are as follows:

\[
\hat{M}_{12}^E(\hat{k}.\hat{p}(k); \hat{N}(k-q)\hat{N}(q)) = \frac{ik_BT}{N}[\hat{k}.(k-q)(1 - \frac{1}{S(|k-q|)})
+ \hat{k}.q(1 - \frac{1}{S(q)}) + \hat{k}.k(\frac{t(k-q, q, k)}{S(|k-q|)S(q)S(k)} - 1)],
\]

(A - 1)

\[
\hat{M}_{21}^E(\hat{N}(k-q)\hat{N}(q); \hat{k}.\hat{p}(k)) = \frac{i}{m} S(|k-q|)S(q)[\hat{k}.(k-q)(1 - \frac{1}{S(|k-q|)})
+ \hat{k}.q(1 - \frac{1}{S(q)}) + \hat{k}.k(\frac{t(k-q, q, k)}{S(|k-q|)S(q)S(k)} - 1)],
\]

(A - 2)

\[
\hat{M}_{22}^E(P_j(k-q)\hat{N}(q); \hat{N}(k-q')\hat{N}(q')) =
\frac{ik_BT}{N}S(q)[(k-q')_j(1 - \frac{1}{S(|k-q'|)}) + (q')_j(1 - \frac{1}{S(q')})
+ (k-q')_j(\frac{t(q-q', q, q')}{S(|k-q'|)S(q)S(q') - 1}) + (q')_j(\frac{t(k-q-q', q, k-q')}{S(|k-q'|)S(q)S(q') - 1})],
\]

(A - 3)

\[
\hat{M}_{22}^E(\hat{N}(k-q)\hat{N}(q); P_j(k-q')\hat{N}(q')) = \frac{i}{Nm} S(|k-q|)S(q)[(k-q)_j(1 - \frac{1}{S(|k-q|)}) + (q)_j(1 - \frac{1}{S(q)})
+ (k-q)_j(\frac{t(q-q', q', q)}{S(|k-q|)S(q)S(q') - 1}) + (q)_j(\frac{t(k-q-q', q', k-q)}{S(|k-q|)S(q)S(q') - 1})],
\]

(A - 4)

where the subscript \( j \) in A-3 (or A-4) denotes the projections upon the unit vectors \( (\widetilde{k} - \widetilde{q}) \) and \( (\widetilde{k} - \widetilde{q})_{\perp 1,2} \) (or \( (\widetilde{k} - \widetilde{q}') \) and \( (\widetilde{k} - \widetilde{q}')_{\perp 1,2} \)). Note also that the vertex \( \hat{M}_{22}^E(\hat{N}(k-q)\hat{N}(q); \hat{N}(k-q')P_j(q')) \) is obtained from Eqn(A-4) by substituting \( k-q' \) for \( q' \).
Bibliography


Chapter 3

Microscopic theory for hopping transport in glass-forming liquids

The contents of this chapter is based on the work found in
C. Z.-W. Liu and I. Oppenheim, submitted to Physica A

3.1 INTRODUCTION

Our understanding of the dynamical behavior of supercooled liquids has been tremendously enhanced by the application of mode-coupling theory (MCT) to the glass transition [1, 2]. In essence, MCT involves an analysis of the self-consistent solutions to a set of nonlinear integro-differential equations for space- and time-dependent correlation functions that describe fluctuations in a fluid system. MCT makes several nontrivial predictions for the glass transition including a critical temperature $T_c$ or density $n_c$, critical decay behavior, anomalous exponents, and $\alpha$- and $\beta$-relaxation processes [1, 2]. While the MCT results have been largely verified in certain model systems [3, 4, 5] and real systems above $T_c$ [6, 7], the MCT analysis for realistic systems below $T_c$ has not been free of controversy. Later revisions of the original "idealized" MCT (known in the literature as the "extended" MCT [8, 9, 10, 11]) claim to describe real glass transitions by including couplings to currents and thus allowing activated processes to occur below the critical temperature. However, as
shown in chapter 2 of this thesis, the hopping kernel of the "extended" MCT is in fact not sufficiently small to yield the drastic slowing down of structural relaxations unless an initial time cutoff is introduced arbitrarily [11, 12, 13, 14, 15, 16]. Moreover, it is not clear what the region of validity of the standard mode-coupling formalism is since there appears to be no small parameter to carry out systematic expansions.

It is the purpose of this chapter to develop a microscopic theory for the glass transition that avoids the shortcomings of conventional MCT and properly describes structural relaxations in the highly supercooled regime. In particular, we obtain an expression for the effective longitudinal viscosity in which a hopping kernel naturally emerges without resorting to implicit or explicit resummation schemes. Moreover, we find that the hopping kernel contains a wavevector cutoff that may sufficiently suppress its magnitude to yield the slow relaxation of density fluctuations observed experimentally.

The chapter is organized as follows: We give a brief review of the MCT for the glass transition in Section 3.2. In Section 3.3, we supplement the usual set of slow linear dynamical variables (number and momentum densities) by an order parameter that describes the local arrangement of particles within long-lived clusters in the supercooled liquid. By analyzing the resulting equations of motion in Section 3.4, we identify a hopping kernel in the effective longitudinal viscosity that is related to the transport coefficient governing the decay of clusters of particles. In Section 3.5, we examine in detail the hopping kernel, and we show that it reduces to a form similar to that obtained previously in the extended MCT. However, in the present work, the magnitude of the hopping kernel is suppressed through a wavevector cutoff instead of an initial time cutoff [12]. In Section 3.6, we present our conclusions.

3.2 REVIEW OF MCT

In this section, we review the mode-coupling formalism for the glass transition discussed in the previous chapter for completeness. We restrict our attention to a classical fluid system of $N$ identical, structureless particles of mass $m$ interacting via an
isotropic and short-ranged potential \( u(|r_{ij}|) \). The Hamiltonian of the system is given by

\[
H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} u(|r_{ij}|). \tag{3.1}
\]

In the conventional MCT for the glass transition \([1, 2, 11]\), one begins by choosing a column vector \( \mathbf{A}(r, t) \) which includes the slow linear dynamical variables of the system:

\[
\hat{\mathbf{A}}(r, t) = \begin{pmatrix} \hat{N}(r, t) \\ \mathbf{P}(r, t) \end{pmatrix},
\]

where

\[
\begin{align*}
\hat{N}(r, t) &= \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t)), \\
\hat{\mathbf{P}}(r, t) &= \sum_{i=1}^{N} \mathbf{p}_i(t) \delta(\mathbf{r} - \mathbf{r}_i(t)),
\end{align*} \tag{3.2}
\]

\( \hat{B} \equiv B - \langle B \rangle \) for arbitrary \( B \), and the angular brackets \( \langle \ldots \rangle \) denote an equilibrium ensemble average. In the Fourier-Laplace space representation, the standard projection operator techniques can be used to construct the set of generalized Langevin equations corresponding to the different components of \( \hat{A} \). Specifically, one obtains for the density autocorrelation function \([1, 2, 11]\):

\[
\phi_{NN}(k, s) = \frac{\langle \hat{N}(k, s)\hat{N}(k)^* \rangle}{\langle \hat{N}(k)\hat{N}(k)^* \rangle} = \frac{1}{s + \frac{\Omega_k^2}{s + \tilde{\Gamma}_L(k, s)}}, \tag{3.3}
\]

where \( \Omega_k^2 = k^2 \langle \frac{k_B T}{mS(k)} \rangle \), \( S(k) \) is the static structure factor defined by \( S(k) \equiv \frac{\langle \hat{N}(k)\hat{N}(k)^* \rangle}{N} \), and \( \tilde{\Gamma}_L(k, s) \) is the longitudinal current relaxation kernel, which is related to the generalized longitudinal viscosity \( \tilde{\nu}_L(k, s) \) by the relation \( \tilde{\Gamma}_L(k, s) = \frac{k^2}{nm} \tilde{\nu}_L(k, s) \) with \( n = N/V \).

A perturbative scheme can be constructed expressing \( \tilde{\Gamma}_L(k, s) \) as a sum of two terms: a bare contribution arising from the fast modes of the system and a renormal-
ized contribution arising from the slowly decaying multilinear hydrodynamic modes, of which the bilinear density modes play a prominent role [1, 2, 11, 17]. In particular, if the dominant contribution at 1-loop order is included, one obtains the idealized MCT result:

\[
\dot{\Gamma}_L(k, s) = \Gamma_0^p(k, s) + \frac{1}{2} \int_0^\infty dt e^{-st} \left\{ \sum_q V(k, q) [\phi_{NN}(|k - q|, t) \phi_{NN}(q, t)] \right\}
\]

\[
= \Gamma_0^p(k, s) + m(k, s),
\]

(3.4)

where \(\Gamma_0^p(k, s)\) is the bare contribution to the relaxation kernel, and the vertex \(V(k, q)\) was given previously [1, 2, 11]. If the dominant contributions from higher order relaxation channels are included, one obtains the extended MCT result in which a hopping kernel \(\delta_{MCT}(k, s)\) emerges in addition to \(m(k, s)\) [8, 9, 10, 11]. Below \(T_c\), \(\dot{\Gamma} \approx 1/\delta_{MCT}\), where \(\delta_{MCT}\) is assumed to be small but finite.

### 3.3 LOCAL-ORDER PARAMETER

As mentioned in the introduction, there are inherent problems with the MCT approach. Since microscopic length scale fluctuations must be included for a proper treatment of the glass transition, the expansion parameter for MCT is actually not small [11], and the resulting hopping kernel is not sufficiently small to generate the dramatic temperature dependence for the viscosity [13, 14, 15, 16]. We believe that a more natural procedure is to include at least a subset of the bilinear modes at the outset instead of in a perturbative fashion as employed by MCT.

In a dense liquid, particles are temporarily trapped in "cages" formed by neighboring particles. Under normal conditions, these cages have a characteristic lifetime of a few collision times. However, as a liquid is supercooled, particle trapping becomes increasingly more effective and eventually leads to partial localization of particles within metastable clusters. It is a basic assumption of various theoretical approaches in addition to MCT that the \(\alpha\)-relaxation process, which corresponds to the longest time scale of the problem, arises from the deformation and eventual decay of such par-
We mention in particular a recent theory motivated by the concept of geometric frustration in which structural relaxation of moderately growing frustrated domains dominates the low temperature dynamics [22].

![Figure 3-1](image)

**Figure 3-1:** A central particle trapped in a cage formed by neighboring particles. Here $\lambda$ denotes the radius of the cluster of particles.

In order to account for the cluster relaxation, we introduce a dynamical variable which describes the local geometry of the center of masses within a prescribed volume corresponding to the typical domain size $\lambda$ (see Fig.3-1). Even though one expects a distribution of cluster sizes, we will utilize for simplicity a single length scale at which the rearrangement of the atoms corresponds to the $\alpha$-relaxation process observed experimentally. In this work, we postulate the existence of such clusters in a supercooled liquid, and we will assume that the size of such clusters increases in a mild and controlled manner as the temperature is lowered. Roughly, we expect the typical cluster in a mildly supercooled liquid to be comprised of a central particle
surrounded by its first coordination shell. As the temperature is lowered further, the cluster may include a second or third coordination shell. For simple liquids, it was observed that a particle and its 12 nearest neighbours prefer to adopt an icosahedral geometry [23, 24]. Naturally, for nonspherical molecules interacting via complicated potentials, one would expect more complex symmetries for the stable clusters.

We can write down a general expression for this order parameter:

\[
O(r, t) = \sum_{i=1}^{N} \sum_{j \neq i}^{N} f(r_i(t) - r_j(t))U_{\lambda}(r_i(t) - r_j(t))\delta(r - r_i(t)),
\]

(3.5)

where \( f(r) \) is an arbitrary smoothly varying function and \( U_{\lambda}(r) \) is a unit step function with the properties:

\[
U_{\lambda}(r) = \begin{cases} 
1 & |r| \leq \lambda \\
0 & |r| > \lambda.
\end{cases}
\]

A few comments are appropriate at this point. First, for different physical choices of \( f(r) \), the variable \( O(r, t) \) specifies the orientation of particles \( j \) relative to a particle \( i \) located at the center of a spherical region of radius \( \lambda \). Eqn(3.5) specifies a coarse-grained variable over a coarse-graining cell with the volume \( \frac{4}{3}\pi\lambda^3 \). Here we emphasize a basic assumption: we take the \( \alpha \)-relaxation process to occur on the length scale \( \lambda \) and thus to be insensitive to the microscopic details of the system on length scales much smaller than \( \lambda \). Such coarse-graining will have profound effects later when we compute the hopping kernel in Section 3.5. Second, it is interesting to note that by selecting a value of \( \lambda \) corresponding roughly to the typical nearest neighbor separation length, one can choose different \( f(r) \) such that \( O(r, t) \) reduces to a dynamical version of order parameters previously introduced for the study of dense liquids, namely, the moment of inertia tensor [25, 26], the bond-orientational order parameter [23], and the number of neighboring particles in the first coordination shell [27]. For the present purposes, a specific \( f(r) \) is not necessary, and we will work with the general expression given by Eqn(3.5) with a scalar function \( f(r) \) and a moderately increasingly cutoff length \( \lambda \). Third, although the idea of incorporating another slow variable in addition to the conserved set is not new [16, 28, 29, 30], previous
treatments did not employ a microscopic definition as for \( O(r, t) \) and relied on the introduction of a phenomenological relaxation coefficient which is strongly temperature dependent. Lastly, while it is natural to ask whether the local clusters in the glassy state correlate with each other to create some sort of long range order \([23, 31]\), there is no convincing evidence from experiments \([32, 33]\) or computer simulations \([34]\) to suggest the existence of a large correlation length. As a result, we will assume in this chapter that the static susceptibility of our order parameter exhibits no anomalies upon supercooling in contrast to the situation for critical phenomena.

Using the definition

\[
W(r) = f(r)U_\lambda(r) = \frac{1}{(2\pi)^3} \int dq \{ W(q)e^{-iqr} \}, \tag{3.6}
\]

it is easy to show that the Fourier transform of \( O(r, t) \) is given by

\[
O(k, t) = \frac{1}{(2\pi)^3} \int dq \left( \sum_{i=1}^{N} \sum_{j \neq i}^{N} W(q)e^{-i(q \cdot (r_i(t) - r_j(t)))} e^{i(k \cdot r_i(t))} \right) \\
= \frac{1}{(2\pi)^3} \int dq \left( \sum_{i=1}^{N} \sum_{j \neq i}^{N} W(q)e^{i(k - q) \cdot r_i(t)} e^{iqr_j(t)} \right) \\
= \frac{1}{(2\pi)^3} \int dq \{ W(q)N(k - q, t)N(q, t) \} \\
- \left( \frac{1}{(2\pi)^3} \int dq W(q) \right) N(k, t). \tag{3.7}
\]

It is extremely fortuitous that the order parameter we introduced can be expressed, at least in part, as a linear combination of bilinear density modes, since we know from MCT that these pairs dominate the renormalization of the transport coefficients \([1, 2]\). Also, we remark that the function \( W(q) \) acts as a wavevector cutoff for \( |q| \gg 1/\lambda \). For the special case where \( f(r) \) in Eqn(3.6) is a constant, we have \( W(q) \propto \frac{\sin(q\lambda) - q\lambda \cos(q\lambda)}{(q\lambda)^3} \).

In the following, we will use a modified version of Eqn(3.7) for computational
simplicity. Explicitly, we redefine the order parameter in the form:

\[
\hat{O}(k, t) = \frac{1}{(2\pi)^3} \int dq \left[ W(q) \left( \hat{N}(k - q, t) \hat{N}(q, t) - \langle \hat{N}(k - q) \hat{N}(q) \rangle \right) - \frac{\langle \hat{N}(k - q) \hat{N}(q) \hat{N}(k) \rangle}{\langle \hat{N}(k) \hat{N}(k) \rangle} \hat{N}(k, t) \right].
\] (3.8)

We have replaced the density variables in Eqn(3.7) by their hatted counterparts, and the subtractions in Eqn(3.8) are to ensure that \( \langle \hat{O}(k, t) \rangle = 0 \) and that the order parameter is orthogonal with respect to the conserved linear variables at \( t = 0 \).

### 3.4 DYNAMICAL EQUATIONS

We are interested in the relaxation dynamics of density fluctuations in the presence of direct and indirect couplings to the longitudinal momentum and the order parameter. Using the column vector

\[
\hat{A}(k) = \begin{pmatrix} \hat{N}(k) \\ \hat{O}(k) \\ \hat{1} \cdot P(k) \end{pmatrix},
\]

and the definition of the projection operator,

\[
\mathcal{P}B(k) = \langle B(k) \hat{A}(k)^* \rangle \cdot \langle \hat{A}(k) \hat{A}(k)^* \rangle^{-1} \cdot \hat{A}(k),
\] (3.9)

where \( B \) is an arbitrary dynamical variable, we obtain the generalized Langevin equations:

\[
\hat{A}(k, t) = \int_0^t M(k, \tau) \cdot \hat{A}(k, t - \tau) d\tau + f(k, t),
\] (3.10)

where

\[
M(k, \tau) = \{2\langle \hat{A}(k) \hat{A}(k)^* \rangle \delta(\tau) - \langle f(k, \tau) f(k)^* \rangle \} \cdot \langle \hat{A}(k) \hat{A}(k)^* \rangle^{-1},
\] (3.11)

and

\[
f(k, \tau) = e^{(1 - \mathcal{P}) \mathcal{L} \tau} (1 - \mathcal{P}) \hat{A}(k),
\] (3.12)
with $\mathcal{L}$ being the Liouvillian. Using the orthogonality property of $f(k, t)$ and transforming to Laplace space $s$, it can be shown that

$$\langle \dot{A}(k, s) \dot{A}(k)^* \rangle = (sI - M(k, s))^{-1} \cdot \langle \dot{A}(k) \dot{A}(k)^* \rangle,$$  \hspace{1cm} (3.13)

where $I$ is the identity matrix. The matrix $M(k, s)$ for the set $\dot{A}(k)$ is explicitly given by

$$M(k, s) = \begin{pmatrix} 0 & 0 & \frac{i k}{m} \\ 0 & -\delta_h(k, s) & i \gamma(k) - \psi(k, s) \\ \frac{i k \rho T_s}{S(k)} & i \gamma'(k) - \psi'(k, s) & -\Gamma(k, s) \end{pmatrix},$$

with the definitions:

$$\delta_h(k, s) = \frac{\langle f_o(k, s) f_o(k)^* \rangle}{\langle \dot{O}(k) \dot{O}(k)^* \rangle},$$

$$\Gamma(k, s) = \frac{\langle f_p(k, s) f_p(k)^* \rangle}{\langle [k, \dot{P}(k)] [\dot{k}, \dot{P}(k)]^* \rangle},$$

$$\psi(k, s) = \frac{\langle f_o(k, s) f_p(k)^* \rangle}{\langle \dot{O}(k) \dot{O}(k)^* \rangle},$$

$$\psi'(k, s) = \frac{\langle f_p(k, s) f_o(k)^* \rangle}{\langle \dot{O}(k) \dot{O}(k)^* \rangle},$$

$$i \gamma(k) = \frac{\langle \dot{O}(k) [\dot{k}, \dot{P}(k)]^* \rangle}{\langle [k, \dot{P}(k)] [\dot{k}, \dot{P}(k)]^* \rangle},$$

$$i \gamma'(k) = \frac{\langle [k, \dot{P}(k)] \dot{O}(k)^* \rangle}{\langle \dot{O}(k) \dot{O}(k)^* \rangle}. \hspace{1cm} (3.14)$$

Solving Eqn(3.13) for the density autocorrelation function, we obtain the result:

$$\phi_{NN}(k, s) = \frac{1}{s + \frac{k^2 \rho T_s}{m S(k)} + \frac{s \delta_h(k, s) - (-\gamma(k) + \psi(k, s))( -i \gamma'(k) + \psi'(k, s))}{s + \delta_h(k, s)}}.$$  \hspace{1cm} (3.15)
3.5 EFFECTIVE VISCOSITY AND HOPPING KERNEL

Comparing Eqn(3.15) with Eqn(3.3), we can identify the effective longitudinal viscosity in the presence of the order parameter as

\[ \tilde{\Gamma}_L(k,s) = \frac{k^2 \nu_l(k,s)}{nm} = \Gamma_L(k,s) - \frac{(-i\gamma(k) + \psi(k,s))(-i\gamma'(k) + \psi'(k,s))}{s + \delta_h(k,s)}. \] (3.16)

Here \( \Gamma_L(k,s) \) involves an autocorrelation function of the random force \( f_P \) associated with longitudinal current fluctuations. Since \( f_p \) is orthogonal to \( \hat{O} \) at all times through relation (3.12), the nontrivial kernel \( \Gamma_L(k,s) \) contains not only fast microscopic relaxation processes but also intermediate time regime structural rearrangements which are not accounted for by using a coarse grained variable \( \hat{O} \). This intermediate time regime or \( \beta \)-relaxation presumably corresponds to initial intradomain relaxation that occurs prior to the eventual cluster decay, which is represented by the second term in Eqn(3.16).

In order to analyze the kernels \( \psi(k,s), \psi'(k,s), \) and \( \delta_h(k,s) \), we investigate the random force \( f_O \) associated with order parameter fluctuations:

\[ f_O(k) = (1 - \mathcal{P}) \hat{O}(k), \] (3.17)

where

\[ \hat{O}(k) = \left( \frac{1}{(2\pi)^3} \int dq \left[ W(q) \left( \frac{i}{m} (k - q) \cdot P(k - q) \hat{N}(q) + \frac{i}{m} q \cdot P(q) \hat{N}(k - q) - \frac{\langle \hat{N}(k - q) \hat{N}(q) \hat{N}(k)^* \rangle}{\langle \hat{N}(k) \hat{N}(k)^* \rangle} \frac{i}{m} k \cdot P(k) \right] \right]. \] (3.18)

Since current fluctuations always decay to zero, we expect that there is no singular behavior for small frequencies in both \( \psi(k,s), \psi'(k,s), \) and \( \delta_h(k,s) \). Moreover, \( f_O(k,t) \) becomes a fast variable in a highly viscous fluid in the sense that any cor-
relation function involving such a random force decays rapidly to zero. This implies that the kernels $\psi(k, s)$, $\psi'(k, s)$, and $\delta_h(k, s)$ will become rather small in the highly supercooled regime. We can therefore neglect $\psi(k, s)$ and $\psi'(k, s)$ relative to the Euler coupling terms $\gamma(k)$ and $\gamma'(k)$ (see Appendix B) in Eqn(3.16) and rewrite the effective viscosity as

$$\tilde{\Gamma}_L(k, s) \approx \Gamma_L(k, s) + \frac{\gamma(k)\gamma'(k)}{s + \delta_h(k, s)},$$

(3.19)

where

$$\delta_h(k, s) = \int_0^\infty dt e^{-st} \left[ \frac{\langle (e^{(1-P)i\xi t} f_\infty(k)) f_\infty(k)^* \rangle}{\langle \hat{O}(k)\hat{O}(k)^* \rangle} \right],$$

(3.20)

or explicitly

$$\delta_h(k, s) = \frac{1}{V^2\langle \hat{O}(k)\hat{O}(k)^* \rangle} \int_0^\infty dt e^{-st} \left\{ \sum_q \sum_{q'} W(q)W(q') \times \left\{ e^{(1-P)i\xi t} (1 - P) \frac{d}{dt} \{ \hat{N}(k - q)\hat{N}(q) \} \right\} \right\}. \tag{3.21}$$

Assuming that the dominant contributions to the wavevector summations arise from the diagonal terms in Eqn(3.21) [17], we can write the hopping kernel as

$$\delta_h(k, s) = \frac{1}{V^2\langle \hat{O}(k)\hat{O}(k)^* \rangle} \int_0^\infty dt e^{-st} \left\{ \sum_q [V_h(k - q, q)R(k - q, q, t)] \right\}, \tag{3.22}$$

where

$$R(k - q, q, t) = \left\langle \left[ e^{(1-P)i\xi t} (1 - P) \frac{d}{dt} \{ \hat{N}(k - q)\hat{N}(q) \} \right] (1 - P) \frac{d}{dt} \{ \hat{N}(k - q)\hat{N}(q) \}^* \right\}, \tag{3.23}$$

and the vertex $V_h$ is given by

$$V_h(k - q, q) = [W(k - q)W(q) + W(q)W(q)]. \tag{3.24}$$

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3.6 CONCLUSIONS

In this chapter we have attempted a derivation of the longitudinal viscosity in the highly supercooled regime where a hopping-like kernel emerges nonperturbatively. Assuming that structural relaxation is dominated by the decay of clusters, we have incorporated to the usual set another slow variable which describes the local order within a volume corresponding to the mean cluster size $\lambda$. In fact, this order parameter, $\hat{O}(k,t)$, is a linear combination of bilinear density modes with a weighting function that acts to coarse-grain out length scales smaller than $\lambda$. Thus, instead of including renormalizations from bilinear density modes in a perturbative fashion as done in conventional MCT [1, 2, 11], we have chosen to include at the outset a particular subset of such modes which we believe to be associated with the $\alpha$-relaxation process. Using straightforward projection operator techniques, we have constructed the generalized Langevin equations for our slow variables and have shown that the effective longitudinal viscosity is given as a sum of two terms: a part representing contributions from fast microscopic processes and intermediate time regime structural relaxation and a part arising from the decay of particle aggregates, which is associated with a generalized transport coefficient given by Eqn(3.22).

At this point, we would like to compare our expression for the hopping kernel with that previously obtained within the context of kinetic theory [9] or nonlinear fluctuating hydrodynamics [8]. While a detailed analysis of Eqn(3.22) is complicated by the fact that the time evolution is governed by the modified propagator $e^{(1-\nu)i\mathcal{L}}$, certain qualitative features are comparable to previous results. In particular, hopping transport in all cases is associated with the decay of bilinear density-momentum modes. However, unlike previous treatments where the hopping kernel arises fortuitously in a perturbative scheme, there is no ambiguity in the interpretation of the hopping kernel in the present work. Once a physically motivated choice for the order parameter is selected, we have a clear and precise definition for Eqn(3.22) as the transport coefficient governing the decay of the order parameter. Moreover, the hopping term in previous works does not decrease sufficiently upon lowering of temperature to correlate with
experimental observations below $T_c$ [13, 14, 15, 16] and must be supplemented with an initial time cutoff without justification [11, 12]. In the present context, the vertex in Eqn(3.22) contains wavevector cutoffs which will suppress the magnitude of the hopping kernel for large enough $\lambda$. We interpret the wavevector cutoff in the following qualitative manner: a cluster of size $\lambda$ will not "see" current fluctuations unless its wavelength is comparable to or larger than the cluster itself. Note that this situation is analogous to the diffusion of a Brownian particle in a bath of smaller molecules, and a similar wavevector cutoff emerges in the mode-coupling expression for the diffusion constant [35, 36].

Lastly, we will comment on the effectiveness of the wavevector cutoff in generating a dramatic decrease in the magnitude of the hopping kernel. For concreteness, let's consider the zero wavenumber and frequency limit of the hopping kernel given by Eqn(3.22):

\[
\lim_{k \to 0} \lim_{s \to 0} \delta_h(k, z) = \frac{1}{V^2 \chi_{oo}} \sum_q [V_h(-q, q) R(-q, q, z = 0)] , \tag{3.25}
\]

where $\chi_{oo}$ is the zero wavenumber limit of the order parameter static susceptibility. The correlator $R(-q, q, t)$ involves current modes which will decay faster as the fluid gets more viscous. If we make the approximation $R(-q, q, s = 0) \propto 1/\tilde{\nu}_l(q, s = 0)$ (see Appendix C), where $\tilde{\nu}_l$ is the longitudinal viscosity, we see that the hopping kernel is given by a restricted sum over wavevectors of the inverse of the zero frequency generalized viscosity. The behavior of $\tilde{\nu}_l(q, s = 0)$ as a function of wavenumber in a dense fluid is well known [13, 37]. In the limit of zero wavenumber, $\tilde{\nu}_l(q, s = 0)$ approaches the value of the macroscopic viscosity, which increases strongly with temperature in a supercooled liquid. As the wavenumber increases to finite values, $\tilde{\nu}_l(q, s = 0)$ decreases and eventually approaches the free streaming limit for very large wavenumbers. The temperature dependence of $\tilde{\nu}_l(q, s = 0)$ at small length scales is expected to be substantially weaker than that of the macroscopic viscosity since transport over microscopic distances is less affected by supercooling. Clearly, if the wavevector cutoff in Eqn(3.25) can remove enough of the finite wavenumber contributions
of $R(-\mathbf{q}, \mathbf{q}, s = 0)$, the hopping kernel will decrease strongly with temperature because of the rapid increase of $\tilde{\nu}(q, s = 0)$ at small wavenumbers upon lowering of temperature. For a sufficiently large cutoff length scale $\lambda$, the wavevector cutoff not only removes the number of modes involved in the hopping kernel but also effectively removes the contributions from the fluctuations that are most effective in breaking up the cluster.

### 3.7 APPENDIX B

In this Appendix, we give the explicit form for the Euler couplings, $\gamma(k)$ and $\gamma'(k)$, between the order parameter and the longitudinal momentum that appear in Eqn(3.19). Defining $S(k) \equiv \frac{\langle \hat{N}(\mathbf{k}) \hat{N}(\mathbf{k})^* \rangle}{N}$ and $t(q_1, q_2, q_3) \equiv \frac{\langle \hat{N}(q_1) \hat{N}(q_2) \hat{N}(q_3)^* \rangle}{N}$, the results are as follows:

$$
\gamma(k) = \frac{1}{m(2\pi)^3} \int d\mathbf{q} \left\{ W(\mathbf{q}) S(|\mathbf{k} - \mathbf{q}|) S(\mathbf{q}) \left[ \mathbf{k} \cdot (\mathbf{k} - \mathbf{q}) \left( 1 - \frac{1}{S(|\mathbf{k} - \mathbf{q}|)} \right) \right]ight. \\
+ \hat{\mathbf{k}} \cdot \mathbf{q} \left( 1 - \frac{1}{S(\mathbf{q})} \right) + \mathbf{k} \cdot \mathbf{k} \left( \frac{t(\mathbf{k} - \mathbf{q}, \mathbf{q}, \mathbf{k})}{S(|\mathbf{k} - \mathbf{q}|) S(\mathbf{q}) S(\mathbf{k})} - 1 \right) \right\}, \quad (B - 1)
$$

$$
\gamma'(k) = \gamma(k) \frac{Nm k_B T}{\langle \hat{O}(\mathbf{k}) \hat{O}(\mathbf{k})^* \rangle}, \quad (B - 2)
$$

### 3.8 APPENDIX C

In this Appendix, we will comment on the qualitative behavior of the time-dependent correlation function that appears in the hopping kernel of Eqn(3.21). In particular, we compare the time-dependence of the term

$$
\left\langle e^{(1-P)\mathcal{L}t}(1 - \mathcal{P}) \frac{d}{dt} \{ \hat{N}(\mathbf{k} - \mathbf{q}) \hat{N}(\mathbf{q}) \} (1 - \mathcal{P}) \frac{d}{dt} \{ \hat{N}(\mathbf{k} - \mathbf{q}') \hat{N}(\mathbf{q}') \}^* \right\rangle \quad (C - 1)
$$

with the analogous form where the propagator $e^{(1-P)\mathcal{L}t}$ is replaced by the usual $e^{i\mathcal{L}t}$. To proceed further, we will consider the related, albeit considerably more simplified,
problem of comparing the time-dependence of
\[ \left\langle e^{(1-P')i\mathcal{L}t}(1-P') \frac{d}{dt} \hat{N}(k) \right\rangle (1-P') \frac{d}{dt} \hat{N}(k)^* \equiv \theta_{NN}(k, t), \quad (C - 2) \]
with
\[ \left\langle e^{i\mathcal{L}t}(1-P') \frac{d}{dt} \hat{N}(k) \right\rangle (1-P') \frac{d}{dt} \hat{N}(k)^* \equiv \theta_{NN}'(k, t), \quad (C - 3) \]
where the projection operator \( \mathcal{P}' \) is defined as
\[ \mathcal{P}' B(k) = \langle B(k) \hat{N}(k)^* \rangle - \langle \hat{N}(k) \rangle \langle \hat{N}(k)^* \rangle - \hat{N}(k). \quad (C - 4) \]
for arbitrary \( B \). First, from symmetry considerations, it is easy to see that \((1-P') \frac{d}{dt} \hat{N}(k) = \frac{d}{dt} \hat{N}(k)\). Next, we will consider a description of density fluctuations using projection operator techniques starting with two different sets of slow variables. In the first case, we employ solely the number density \( \hat{N}(k) \), and we obtain after a straightforward calculation that the density autocorrelation function is given as
\[ \phi_{NN}(k, s) = \frac{1}{s + \theta_{NN}(k, s)/\langle \hat{N}(k) \rangle \langle \hat{N}(k)^* \rangle}, \quad (C - 5) \]
with \( \theta_{NN}(k, t) \) given exactly by \((C-2)\). In the second case, we employ the usual set consisting of the number density and longitudinal momentum density, and we obtain for the density and momentum autocorrelation functions, respectively
\[ \phi_{NN}(k, s) = \frac{1}{s + \Omega_k^2 / s + \Gamma_L(k, s)}, \quad (C - 6) \]
\[ C_L(k, s) = \frac{s}{s[s + \Gamma_L(k, s)] + \Omega_k^2} = \frac{m}{k^2 N k_B T} \theta_{NN}'(k, s). \quad (C - 7) \]
Here, \( \Omega_k^2 = k^2 \frac{k_B T}{m S(k)} \) and \( \Gamma_L(k, s) \) is the longitudinal current relaxation kernel. Since the two descriptions for the density autocorrelation function must agree, we can
identify
\[ \theta_{NN}(k, s) = \frac{k^2Nk_BT}{m} \frac{1}{s + \Gamma_L(k, s)}, \] (C - 8)
as compared to the analogous expression for \( \theta'_{NN}(k, s) \)
\[ \theta'_{NN}(k, s) = \frac{k^2Nk_BT}{m} \frac{s}{s + \Gamma_L(k, s)} + \Omega_k^2. \] (C - 9)

Note that while \( \theta'_{NN}(k, s) \) vanishes in the limit of zero frequency for all wavenumbers, \( \theta_{NN}(k, s) \) has a finite value in the limit of zero frequency. The time dependence of (C-8) and (C-9) become more transparent if we replace \( \Gamma_L(k, s) \) by its hydrodynamic limit \( (k^2/\nu m)\tilde{\nu}_t \), yielding
\[ \theta_{NN}(k, t) = \frac{k^2Nk_BT}{m} e^{-\frac{k^2\tilde{\nu}_t}{\nu m} t}, \]
\[ \theta'_{NN}(k, t) = \frac{k^2Nk_BT}{m} e^{-\frac{k^2\tilde{\nu}_t}{\nu m} t} \left( \cos \Omega_o t - \frac{k^2\tilde{\nu}_t}{2\nu m \Omega_o} \sin \Omega_o t \right), \] (C - 10)
where \( \Omega_o^2 = \Omega_k^2 - \left( \frac{k^2\tilde{\nu}_t}{\nu m} \right)^2 \) is taken to be positive. We observe that \( \theta_{NN}(k, t) \), which evolves in time with the modified propagator, decays faster and does not contain the oscillatory behavior found in \( \theta'_{NN}(k, t) \). We expect an analogous effect when considering the more complicated correlator given by (C-1).

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Chapter 4

Phenomenological description of the anomalous diffusion below $T_c$

The contents of this chapter is based on the work found in

4.1 INTRODUCTION

For many liquids under normal conditions, the translational diffusion constant of a tagged particle obeys the Stokes-Einstein (SE) law relatively well [1, 2]:

$$D = \frac{k_b T}{b \eta R},$$

(4.1)

where $k_b$ is Boltzmann's constant, $T$ is the temperature, $\tilde{\eta}$ is the transverse viscosity of the fluid system, $R$ is the radius of the diffusing particle, and $b$ is either 4 or 6 depending upon the boundary conditions at the surface of the Brownian particle. From a molecular point of view, the conditions for which Eqn(4.1) ought to be valid correspond to the motion of a large, massive particle immersed in a fluid of small, light molecules. More precisely, the Stokes law should apply in the limit $(m/M) \rightarrow 0$ and $(\xi/R) \ll 1$, where $m$ and $M$ are the masses of the fluid and Brownian particle, respectively, and $\xi$ is the correlation length for fluid correlation functions in the
absence of the tagged particle [3, 4, 5]. Therefore, it is remarkable that the SE formula works reasonably well to relate the diffusion coefficient of a constituent particle or a small tracer molecule to the shear viscosity of the liquid medium.

However, recent experimental and simulation data on strongly supercooled "fragile" glass-forming liquids have shown significant deviations from the SE relation [6, 7, 8, 9, 10, 11]. Specifically, the SE law works well until a particular temperature that is identified as $T_c$ in the glass transition literature [12, 13, 14]. $T_c$ appears at about $1.3T_g$ (glass transition temperature) where the viscosity $\eta$ is 100-1000 Poise, corresponding to relaxation times in the mesoscopic regime ($10^{-11} - 10^{-9}s$). The temperature dependence of the viscosity changes from an Arrhenius to a Vogel-Fulcher-like dependence at $T_c$. Below this critical temperature, the prediction of ordinary incompressible hydrodynamics underestimates the diffusion coefficient by as much as a factor of $10^2$ near the kinetic glass transition. According to mode-coupling theories of the glass transition, this critical crossover behavior is associated with the smearing out of the ideal transition due to activated hopping processes [14]. Specifically, hopping presumably corresponds to activated, correlated jump motions of molecules which restore ergodicity via an extremely slow relaxation of the underlying metastable structure.

Molecular dynamics simulations of tagged particle motion have confirmed that diffusive behavior changes from liquid or Brownian motion-like to jump diffusion below $T_c$ [8, 9, 10]. While diffusion occurs continuously in a normal and slightly supercooled liquid, particles near $T_g$ remain trapped for hundreds of Einstein periods before hopping to neighbouring sites. Such jumps are rare events and molecules experience on average only a few jumps during the entire duration of the MD run. Deviation from normal diffusive behavior can also be seen from the density autocorrelation function, namely [8]

$$G_s(r, t) = \frac{1}{N} \sum_{i=1}^{N} <\delta(r_i(t) - r_i(0) - r)>, \quad (4.2)$$

where $r_i(t)$ denotes the position of particle $i$ at time $t$. Hopping behavior is characterized by the presence of a secondary peak in $G_s$ located at approximately the radius
of the diffusing species.

Recent investigators have proposed a "fluidized" domain model to account for the discrepancy from the SE relation [15, 16]. In brief, it is postulated that thermal fluctuations create domains that are temporarily more fluidized than the background. These domains result from the disentangling of molecules from more energetically favorable packing geometries, local fluctuation in the molecular number density, or a combination of both effects. Regardless, these structural excitations allow for greater diffusivity than the solid-like matrix in the surroundings and create the hopping transport seen in MD experiments.

4.2 JUMP-DIFFUSION MODEL

We consider a dynamical version of the "two-zone" model which closely follows Zwanzig’s treatment of percolation in a dynamically disordered continuum [17, 18]. In the following, we present a brief summary of the results of [18] for completeness. Specifically, the diffusion that occurs in an inhomogeneous medium characterized by a fluctuating diffusion coefficient $D(\mathbf{r}, t)$ is described by the equation

$$\frac{\partial}{\partial t} C(\mathbf{r}, t) = \nabla \cdot [D(\mathbf{r}, t) \nabla C(\mathbf{r}, t)],$$

(4.3)

where $C(\mathbf{r}, t)$ is the concentration of the diffusing particles. For simplicity, it is assumed that fluctuations in $D$ occur within compact spherical domains of radius $\lambda$ with the fluidized regions of diffusivity $D_1$ (as opposed to $D_2$ of the background). These regions appear and disappear in time with a relaxation time $\tau$, and, for a given $\mathbf{r}$, the time independent probability that $D$ is $D_1$ (or $D_2$) is $p_1$ (or $p_2$). Quite naturally, a more realistic model should incorporate a distribution of domain sizes and a corresponding set of relaxation times.

Using a mean-field approximation, one may focus on a spherical region of radius $\lambda$ centered at the origin. The diffusion constant within the sphere fluctuates between $D_1$ and $D_2$, while the diffusion constant outside is taken to be a constant value, $D_{eff}$.
The problem thus reduces to a coupled set of differential equations

\[ \frac{\partial}{\partial t} C^{(1)} = \nabla \cdot D^{(1)} \nabla C^{(1)} + \frac{1}{\tau} (p_1 C^{(2)} - p_2 C^{(1)}), \]  
\[ \frac{\partial}{\partial t} C^{(2)} = \nabla \cdot D^{(2)} \nabla C^{(2)} + \frac{1}{\tau} (p_2 C^{(1)} - p_2 C^{(2)}), \]

where

\[ D^{(1)}(r) = \begin{cases} 
  D_1 & \text{for } |r| \leq \lambda \\
  D_{\text{eff}} & \text{for } |r| > \lambda 
\end{cases} \]

\[ D^{(2)}(r) = \begin{cases} 
  D_2 & \text{for } |r| \leq \lambda \\
  D_{\text{eff}} & \text{for } |r| > \lambda 
\end{cases} \]

Note that Eqns\((4.4)\) and \((4.5)\) resemble the coupled master equations for a composite Markov process except for the spacial dependence of the diffusion coefficients [19].
The steady state solution of the previous equations are obtained by choosing the asymptotic solution far from the origin as

\[ C^{(1)} \rightarrow p_1 z = p_1 r \cos \theta, \]
\[ C^{(2)} \rightarrow p_2 z = p_2 r \cos \theta. \]  

(4.6)

Although the local concentrations should be chosen to be positive from a physical point of view, we remark that the preceding asymptotic conditions are utilized merely for mathematical convenience and do not affect the final result for \( D_{\text{eff}} \). It can be verified that the appropriate solutions that satisfy both the asymptotic and symmetry requirements are (for \(|r| > \lambda\))

\[ C^{(1)} = p_1 r \cos \theta + a h_1(i\alpha r) \cos \theta, \]  

(4.7)

\[ C^{(2)} = p_2 r \cos \theta - a h_2(i\alpha r) \cos \theta, \]  

(4.8)

where \( \alpha^2 = 1/(D_{\text{eff}} \tau) \) and \( h_1 \) is the spherical Hankel function of order 1 given by \( h_1(x) = (-1/x - i/x^2)e^{ix} \), and (for \(|r| \leq \lambda\))

\[ C^{(1)} = \frac{D_2}{D} \left\{ \frac{p_1}{D_2} \text{Arcos} \theta + B j_1(i\beta r) \cos \theta \right\}, \]  

(4.9)

\[ C^{(2)} = \frac{D_1}{D} \left\{ \frac{p_2}{D_1} \text{Arcos} \theta - B j_1(i\beta r) \cos \theta \right\}, \]  

(4.10)

where \( \beta^2 = \frac{D}{D_1 D_2 \tau} \), \( < D >= p_1 D_1 + p_2 D_2 \), and \( j_1(x) = \sin x/x^2 - \cos(x)/x \).

By matching the values and radial derivatives (multiplied by the appropriate diffusion coefficients) of the steady state solutions in the inner and outer regions and elimination of the constants \( a, A, \) and \( B \) after some straightforward algebra, Zwanzig [18] obtains a highly implicit expression for \( D_{\text{eff}} \):

\[ D_{\text{eff}} \left( \frac{D_{\text{eff}} - < D >}{D_1 - D_2} \right) \left( \frac{i\alpha \lambda h'_1(i\alpha \lambda)}{h_1(i\alpha \lambda)} \right) = \]
\[
p_{1}p_{2}\frac{(D_{1} - D_{2})D_{\text{eff}}}{< D >} + \frac{D_{1}D_{2}}{< D >} \left( \frac{D_{\text{eff}} - < D >}{D_{1} - D_{2}} \right) \left( \frac{i\beta \lambda j_{1}(i\beta \lambda)}{j_{1}(i\beta \lambda)} \right). \tag{4.11}
\]

4.3 RESULTS

The preceding expression can be simplified into a more manageable form by introducing the definitions of dimensionless variables:

\[
\frac{D_{1}}{D_{2}} = \gamma; \quad \frac{D_{\text{eff}}}{D_{2}} = \tilde{D}; \quad \frac{\tau_{D_{2}}}{\lambda^2} = \tilde{\tau}, \tag{4.12}
\]

yielding as a result

\[
-\tilde{D}(\tilde{D} - 1 - (\gamma - 1)p_{1})f(\alpha \lambda) = \frac{p_{1}(1-p_{1})(\gamma - 1)^2 \tilde{D}}{(1 + (\gamma - 1)p_{1})} + \frac{\gamma}{(1 + (\gamma - 1)p_{1})}(\tilde{D} - 1 - (\gamma - 1)p_{1})g(\beta \lambda), \tag{4.13}
\]

where \( \alpha \lambda = 1/(\tilde{D}\tilde{\tau})^{1/2} \), \( \beta \lambda = (1 + (\gamma - 1)p_{1})^{1/2} \), \( f(x) = \frac{2 + 2x + x^2}{1 + x} \), and \( g(x) = \frac{2x \coth x - (x^2 + 2)}{1 - x \coth x} \). It is easy to verify that the trivial conditions \( \gamma = 1 \) or \( p_{1} = 0 \) yield \( \tilde{D} = 1 \) as a solution.

Next, we choose values for the various parameters of the model guided by physical intuition gained from MD simulations. First, we take \( p_{1} \) to be small and a constant with respect to temperature, and we also propose that the size of the domain can be to a good approximation taken as a constant with \( \lambda \) somewhat larger than \( R \) (radius of diffusing particle). We believe that the probability and size of these fluctuations show only weak temperature dependences that can be neglected in our simple model.

The relaxation time of the fluctuations (which is related to Maxwell’s relaxation time \( \tau_{M} = \tilde{\nu}t/G_{\infty} \)) is expected to increase dramatically with a decrease in temperature. However, this rapid rise is tamed since \( \tau \) appears in the dimensionless combination \( \tau D_{2}/\lambda^2 \), where \( D_{2} \) decreases rapidly with the lowering of temperature. In fact, since \( D_{2} \) roughly goes as \( \tau_{M}^{-1} \) (or \( \tau^{-1} \)), \( \tilde{\tau} \) is expected to have a weak temperature dependence, and its slight variation cannot account for the significant increase of \( \tilde{D} \) below \( T_{c} \). A physical interpretation can be given for \( \tilde{\tau} \) by writing it as \( \tau / \tau_{\lambda} \), where \( \tau_{\lambda} \) is roughly the mean time the diffusing particle spends within a sphere of radius \( \lambda \) with a diffusivity.
$D_2$. We expect $\tilde{\tau} < 1$ (how small depending on the size of $\lambda$) since, on the time scale $\tau_\lambda$ of the diffusing species, the fluctuations are fast, which is the same scenario for the diffusion of a tagged particle in a liquid under normal conditions. There is of course another time scale for diffusion in the fluidized domains, which is simply $\tau_\lambda/\gamma$. We are thus led to the conclusion that the enhancement of $\tilde{D}$ below $T_c$ is most likely associated with a significant increase in $\gamma$ or $D_1/D_2$. Figures 4-2 and 4-3 show the variation of $\tilde{D}$ with $\gamma$ given plausible sets of values for $p_1$ and $\tilde{\tau}$. Note in Figure 4-3 that a ratio of the order of $10^3$ for $D_1/D_2$ gives an enhancement of the effective diffusion constant by a factor of $10^2$ that is observed near the kinetic glass transition.

For $\gamma$ not too large, an expansion of $\tilde{D}$ in terms of the small parameter $p_1$ is possible with the result

$$\tilde{D} = 1 + p_1(\gamma - 1) \left[ 1 - \frac{(\gamma - 1)}{f((\frac{1}{\tilde{\tau}})^{\frac{1}{2}}) + \gamma g((\frac{1}{\tilde{\tau}})^{\frac{1}{2}})} \right] + O(p_1^2).$$

It is also interesting to note that $D_{eff} \rightarrow <D> = p_1 D_1 + p_2 D_2$ as $\tilde{\tau} \rightarrow 0$.

### 4.4 CONCLUSIONS

Within the confines of the model, the above results should perhaps be expected. Given that the probability for the appearance of a fluidized domain is small, the effect of these regions on the effective diffusion constant is significant only if the diffusivity within the spheres is much greater than the background diffusion constant. As a liquid is supercooled below $T_c$, particle transport becomes increasingly dominated by the appearance of these fluidized regions that allow much greater mobility than the solid-like matrix of the surroundings. In a dense liquid, molecules are trapped in a "cage" of surrounding molecules temporarily. This cage effect introduces time dependent potential barriers that hinder the relaxation of the configurational degrees of freedom. Under normal conditions, these cages have a characteristic lifetime of a few collision times. However, when a liquid is supercooled, particle trapping becomes increasingly more effective and eventually yields partial localization of particles within
metastable clusters. Structural relaxation creates domains that are less constricted and allows the trapped particles to jump to adjacent sites.

Although we have considered a simple, dynamic two-zone model where the fluctuations in diffusivity are spacially and temporally uncorrelated, we emphasize that hopping transport is not a strictly local process. From a molecular perspective, jump diffusion is most likely a medium assisted process where there is a feedback mechanism between short wavelength or local disturbances and long wavelength fluctuations [14].

Recently, Stillinger and Hodgdon suggested that spontaneous fluctuations create large domains of low viscosity to account for the different behavior of the translational and rotational coefficients near the glass transition temperature [16]. The large size of the domains was proposed to account for the continued adherence of the rotational Brownian motion to the Stokes-Einstein-Debye model for a sphere rotating in a viscous continuum. However, observations from time resolved spectroscopy of molecular rotation are inconsistent with a model with large domains [20, 21]. In particular, probe rotation was found to depend significantly upon probe size, with all probes smaller than the domain size suggested. As mentioned previously, it is our view that the most relevant domain size affecting molecular motion in strongly supercooled liquids corresponds to dimensions not significantly larger than 10 times the radius of the diffusing molecule itself. Obviously, domain sizes smaller than the tagged species cannot accommodate its passage and can be neglected, while the creation of larger domains is increasingly less probable, i.e. $p_1$ is a decreasing function of the size $\lambda$. The structure of a fluid near $T_g$ appears to be essentially homogeneous on large length scales, and it is unlikely that large fluid-like domains can have a significant effect on particle transport. The model used in this chapter is not sufficiently detailed to explain differences in behavior between translational and rotational motion. While translational motion may be enhanced by local density fluctuations, rotational relaxation depends not only on density but on the symmetry of the arrangement of host molecules around the rotational probe. Unless the local density fluctuation is approximately symmetric, translation and rotation will be affected differently.
Figure 4-2: Plot of $\dot{D}^{-1}$ vs $\gamma$ for three different values of $\tau$ given $p_1 = 1/10$. The values of $\tau$ are $10^{-1}$, $10^{-3}$, and $10^{-5}$ for curves 1, 2, and 3, respectively.
Figure 4-3: Plot of $\tilde{D}^{-1}$ vs $\gamma$ for curve 3 of Fig.4-2, showing a diffusivity enhancement of the order $10^2$. 
Bibliography


Chapter 5

Translation of a tagged particle in a supercooled liquid below $T_c$

The contents of this chapter is based on the work found in C. Z.-W. Liu, F. L. H. Brown, and I. Oppenheim, in preparation

5.1 INTRODUCTION

As mentioned previously in chapter 4, the Stokes-Einstein (SE) relation provides a connection between the translational diffusion constant $D$ of a tagged particle and the macroscopic viscosity of the surrounding fluid [1, 2, 3]. Specifically, we have

$$\frac{D\nu_t}{T} = C,$$

(5.1)

where $\nu_t$ is the shear viscosity of the bath, $T$ is the temperature, and $C$ is a numerical constant that depends on the relevant molecular dimensions and the interaction between the probe and bath particles. Eqn(5.1) is rigorously applicable to describe the motion of a large, massive particle immersed in a fluid of small, light particles [4, 5, 6]. Nevertheless, the SE law has proved to be extremely robust for a variety of probes in fluids at different densities, and usually the only modification necessary is to allow for a slight temperature dependence of the numerical constant $C$ [7].
In the last decade, considerable effort has been devoted towards understanding molecular transport in supercooled "fragile" glass-forming liquids \[8\]. Significant deviations from the SE relation were observed for the translational motion of probes below \(T_c\) \[9, 10, 11, 12\], the critical temperature identified by mode-coupling theory (MCT) where the liquid would freeze into a glass if activated hopping processes did not occur \[13\]. In one study \[12\], the temperature dependence of the diffusion constants of probes of varying sizes in strongly supercooled OTP were measured, and it was observed that the SE relation works increasingly well as the probe size is increased. While this is an expected result, the large discrepancy between the translational motion of small versus large probes is particularly striking. For probes which are the same size as OTP molecules, Eqn(5.1) underestimates the magnitude of the diffusion coefficient by as much as two orders of magnitude as the temperature is lowered towards the calorimetric glass transition temperature \(T_g\). On the other hand, the temperature dependence of \(D\) follows \(T/\dot{\nu}_t\) relatively well once the probe is some 2 to 3 times larger than the surrounding OTP molecules \[12\]. This trend is not unique for OTP but appears to be a general feature of fragile glass formers \[14\].

The various phenomenological explanations for this remarkable phenomenon universally rest on the assumption of spatially heterogeneous dynamics in deeply supercooled liquids \[12, 14, 15, 16, 17, 18, 19\]. As discussed in the previous chapter, it is postulated that thermal fluctuations create domains of varying sizes and degrees of fluidity. As the temperature is lowered, the difference in mobility within the fast and slow regions becomes more pronounced, making the environment more heterogeneous. Since the translational motion of probes becomes increasingly dependent on encounters with the fluidized domains, the diffusion constant \(D\) becomes decoupled from the macroscopic viscosity and exhibits a weaker temperature dependence than \(T/\dot{\nu}_t\). In addition, since these domains have a characteristic size, a sufficiently large probe will simply sample a homogeneous environment and is expected to conform to the SE relation.

It is the purpose of this chapter to present a molecular theory for the diffusion constant of a tagged particle below \(T_c\) and to explain the breakdown of the SE relation.
that is observed for smaller probes. While the phenomenological models are elegant in their own right, it is ultimately desirable to have a microscopic theory that yields the correct qualitative and, perhaps, quantitative features of the problem. Towards this goal, we take a simplistic approach and use the existing mode-coupling formalism which has proved successful for supercooled liquids above $T_c$ and for normal liquids [4].

5.2 THE DIFFUSION CONSTANT

We will consider the motion of a single tagged particle of mass $M$ and radius $R$ immersed in a fluid of $N$ particles each with mass $m$ and radius $\sigma$. For simplicity, all the particles in our system are spherical with no internal degrees of freedom and interact via isotropic potentials. The Hamiltonian of this $N + 1$ particle system is

$$H = \frac{P_o^2}{2M} + \sum_{i=1}^{N} \phi(|r_{io}|) + \sum_{i=1}^{N} \frac{P_i^2}{2m} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} u(|r_{ij}|),$$

(5.2)

where the label "o" denotes the tagged particle, $\phi(|r_{io}|)$ is the interaction potential between the solute and solvent particle, and $u(|r_{ij}|)$ is the interaction potential between two solvent particles.

The frequency dependent diffusion coefficient for the tagged particle is defined as [4]

$$D(s) = \frac{1}{M^2} \int_0^\infty dt e^{-st}\langle P_o^z(t)P_o^z \rangle$$

$$= \frac{1}{M^2} \langle P_o^z(s)P_o^z \rangle,$$

(5.3)

where $\langle \ldots \rangle$ is a thermal average, the superscript "x" denotes a projection onto the x-axis, and the time evolution of an arbitrary dynamical variable $B$ is governed by the Liouville operator $L$ in the form $B(t) = e^{itL}B$. The diffusion constant $D$ is simply given as the zero frequency limit of Eqn(5.3).

Using the Mori hierarchy [20], the momentum correlation function in Eqn(5.3)
can be expressed as
\[
\langle P_{o}^{z} \mid P_{o}^{z} \rangle = \frac{\langle P_{o}^{z} \mid P_{o}^{z} \rangle}{s + \gamma(s)}, \quad (5.4)
\]
where the generalized friction kernel \(\gamma(s)\) is given as
\[
\gamma(s) = \frac{1}{\langle P_{o}^{z} \mid P_{o}^{z} \rangle} \int_{0}^{\infty} dt e^{-st} \langle [e^{i(1-P)Lt}][1-P]F_{o}^{z}][1-P]F_{o}^{z} \rangle
\]
\[
= \frac{1}{\langle P_{o}^{z} \mid P_{o}^{z} \rangle} \int_{0}^{\infty} dt e^{-st} \langle [e^{i(1-P)Lt}F_{o}^{z}]F_{o}^{z} \rangle. \quad (5.5)
\]

In Eqn(5.5), the projection operator \(P\) is defined as \(PB = \langle BP_{o}^{z} \mid P_{o}^{z} \rangle^{-1} P_{o}^{z}\) and \(F_{o}\) is the force acting on the tagged particle. By projecting out the variable \(F_{o}^{z}\) in addition to \(P_{o}^{z}\) when setting up the Langevin equations, the friction term \(\gamma(s)\) can be further expressed as
\[
\gamma(s) = \frac{\langle F_{o}^{z} F_{o}^{z} \rangle}{\langle P_{o}^{z} P_{o}^{z} \rangle} \frac{1}{s + \xi(s)}, \quad (5.6)
\]
where the memory function \(\xi(s)\) is given by the expression
\[
\xi(s) = \frac{1}{\langle F_{o}^{z} F_{o}^{z} \rangle} \int_{0}^{\infty} dt e^{-st} \langle [e^{i(1-P)Lt}][1-P]F_{o}^{z}][1-P]F_{o}^{z} \rangle, \quad (5.7)
\]
with \(PB' = \langle BP_{o}^{z} \rangle \cdot \langle P_{o}^{z} P_{o}^{z} \rangle^{-1} P_{o}^{z} + \langle BF_{o}^{z} \rangle \cdot \langle F_{o}^{z} F_{o}^{z} \rangle^{-1} P_{o}^{z}\). Combining Eqns(5.4) and (5.6), we obtain an alternate and formally exact expression for the generalized diffusion constant, i.e.,
\[
D(s) = \frac{1}{M^2} \frac{\langle P_{o}^{z} P_{o}^{z} \rangle}{\langle F_{o}^{z} F_{o}^{z} \rangle} \frac{1}{s + \xi(s)}. \quad (5.8)
\]
It is interesting to note that the expression given in Eqn(5.8) gives the short time behavior of \(D(t)\) correctly regardless of what approximation is employed for the kernel \(\xi(s)\) [4].

### 5.3 MODE-COUPLING APPROXIMATION

The physical situation we are considering is as follows: the motion of the tagged particle couples to the hydrodynamic modes of the fluid, which are the number density, the momentum density, and the energy density. The excitation and subsequent
relaxation of these slow variables of the bath influences the long-time decay of the single-particle correlation functions in a feedback mechanism which is accounted for by MCT. In particular, the single-particle quantities can couple to bilinear products of tagged-particle and fluid variables such as $\hat{n}_k \hat{N}_{-k}$, $\hat{n}_k \hat{P}_{-k}$, and $\hat{n}_k \hat{E}_{-k}$, where

\[
\begin{align*}
n_k &= e^{ikr_o}, \\
N_k &= \sum_{i=1}^{N} e^{ikr_i}, \\
P_k &= \sum_{i=1}^{N} \rho_i e^{ikr_i}, \\
E_k &= \sum_{i=1}^{N} \left( \frac{P^2_i}{2m} + \frac{1}{2} \sum_{j \neq i}^{N} u(|r_{ij}|) \right) e^{ikr_i},
\end{align*}
\]

and $\hat{B} \equiv B - \langle B \rangle$. It is easy to show that product modes consisting of solely tagged-particle or fluid variables give a negligible contribution for single-particle correlators [4, 5].

We expect that the primary mechanism for translational diffusion in a strongly supercooled liquid involves coupling to current modes of the solvent. Recent computer simulation studies have revealed that diffusive behavior changes from Brownian-motion like to jump diffusion below $T_c$ [21, 22, 23, 24]. Particles in the highly supercooled regime remain trapped in cages formed by neighboring particles for long periods before hopping to neighboring sites. In the extended MCT for the glass transition [25, 26, 27, 28, 29], hopping transport is accounted for in the microscopic derivation of the generalized viscosity by including couplings to current modes through the bilinear variables $\hat{N}_k \hat{P}_{-k}$. Thus, the present problem is simply the analog for single-particle motion where the dominant decay channel involves $\hat{n}_k \hat{P}_{-k}$ rather than $\hat{N}_k \hat{P}_{-k}$. It is these bilinear current modes which aid the motion of the tagged particle through a medium assisted hopping process.

Within the mode-coupling approximation, we insert the projection of $(1 - \mathcal{P}') \hat{F}_o^z$
onto the bilinear variables \( \hat{n}_k P_{-k} \) in Eqn(5.7), leading to the result

\[
\xi(s) \approx \frac{1}{\langle F_\alpha^* F_\alpha \rangle} \int_0^\infty dt e^{-st} \left\{ \sum_k \sum_{\alpha, \beta} \frac{\langle [(1 - P') \hat{F}_\alpha^*] \hat{n}_k P_\alpha^{\alpha} \rangle \langle \hat{n}_k \hat{n}_{-k} \rangle}{\langle \hat{P}_k^{\alpha} P_{-k}^{\alpha} \rangle \langle \hat{n}_k \hat{n}_{-k} \rangle \langle \hat{P}_k^{\beta} P_{-k}^{\beta} \rangle} \times \langle \hat{P}_k^{\alpha} P_{-k}^{\beta} \rangle \langle \hat{n}_k \hat{n}_{-k} \rangle \langle \hat{P}_k^{\beta} P_{-k}^{\beta} \rangle \right\}.
\] (5.10)

In writing Eqn(5.10), we have employed the factorization approximation for equal time averages and for averages of products evolving in time with the modified propagator \( e^{i(1 - P') C t} \) as products of averages each evolving in time with the usual generator \( e^{iC t} \). From symmetry considerations, it is easily checked that direct couplings of \( (1 - P') \hat{F}_\alpha^* \) to \( \hat{n}_k \hat{N}_{-k} \) and \( \hat{n}_k \hat{E}_{-k} \) analogous to that in Eqn(5.10) give a null contribution.

Previous mode-coupling descriptions for translational diffusion in normal liquids at high density [30, 31] and in supercooled liquids [13] above \( T_c \) involved an analysis of the friction kernel \( \gamma(s) \) given in Eqn(5.5), where the variable \( F_\alpha^* \) is directly coupled to the pair \( \hat{n}_k \hat{N}_{-k} \). In the same vein as the extended MCT [25, 26, 27, 28, 29], higher order contributions caused by current fluctuations can be kept to extend the theory to lower temperatures. In the regime where density fluctuations decay sufficiently slowly, one finds that the friction kernel \( \gamma(s) \) is inversely proportional to a single-particle hopping kernel of the form given in Eqn(5.10) [30, 31]. Thus, both approaches give essentially the same result below \( T_c \), and the choice of applying MCT to \( \xi(s) \) in this work is merely one of convenience, allowing direct couplings to the hopping modes.

The static correlation function that we require are easily evaluated for a particular system from a knowledge of the interaction potentials and pair distribution functions. Here, we simply list their explicit forms:

\[
\langle \hat{n}_k \hat{n}_{-k} \rangle = 1,
\]
\[
\langle P_\alpha^{\alpha} P_\alpha^{\alpha} \rangle = M k_B T,
\]
\[
\langle P_\alpha^{\alpha} P_{-k}^{\alpha} \rangle = N m k_B T,
\]
\[
\langle F_\alpha^{\alpha} F_\alpha^{\alpha} \rangle = n k_B T \int dr |r| \nabla_\alpha \nabla_\beta (|r|)
\]

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\[ (1 - \mathcal{P}') \hat{\phi} \hat{n}_k \hat{P}_\beta^{-k} = nk_B T \int d\mathbf{r} e^{i \mathbf{k} \cdot \mathbf{r}} G(|\mathbf{r}|) \nabla_\alpha \nabla_\beta \phi(|\mathbf{r}|). \]  

(5.11)

Here, \( G(|\mathbf{r}|) \) is the solute-solvent pair distribution function, \( n \) is the number density \( N/V \), and \( \Omega_\alpha^2 \) is the Einstein frequency [3] of the tagged particle. We define a dimensionless vertex function \( V_{\alpha\beta}(k) \) according to [3, 32]

\[ V_{\alpha\beta}(k) = \frac{\langle (1 - \mathcal{P}') \hat{\phi} \hat{n}_k \hat{P}_\beta^{-k} \rangle}{\langle \hat{F}_\beta \hat{F}_\alpha \rangle} \]

\[ = \hat{k}_\alpha \hat{k}_\beta V_L(|k|) + (\delta_{\alpha\beta} - \hat{k}_\alpha \hat{k}_\beta)V_T(|k|), \]  

(5.12)

where \( V_{L,T} \) are the longitudinal and transverse components of the vertex tensor. Note that the microscopic dimensions of the tagged-particle and the bath particles are explicitly accounted for in the vertex through the interaction potential \( \phi(|\mathbf{r}|) \). The normalized vertex functions \( V_{L,T} \) act as wavevector cutoffs, removing contributions from \( k(R + \sigma) \gg 1 \) and ensuring that the summation over intermediate wavevectors in Eqn(5.10) converges (see Figures 5-1 and 5-2).

Using Eqns(5.11) and (5.12) and the explicit forms for the intermediate modes

\[ \langle \hat{n}_k(t) \hat{n}_{-k} \rangle = \mathcal{F}_o(|k|, t), \]

\[ \frac{\langle \hat{F}_\alpha^o(t) \hat{F}_\beta^{-k} \rangle}{\langle \hat{F}_\alpha^o \hat{F}_\beta^{-k} \rangle} = \hat{k}_\alpha \hat{k}_\beta C_L(|k|, t) + (\delta_{\alpha\beta} - \hat{k}_\alpha \hat{k}_\beta)C_T(|k|, t), \]  

(5.13)

where \( \mathcal{F}_o \) is the tagged particle dynamic structure factor and \( C_{L,T} \) are the longitudinal and transverse components of the current correlation function tensor, one obtains the result for the diffusion constant

\[ D = \frac{k_B T}{nm \ 27 (2\pi)^{3}} \int_0^\infty dt \int d\mathbf{k} \left[ \hat{k}_x \hat{k}_x V_L^2(|k|) \mathcal{F}_o(|k|, t) C_L(|k|, t) \right. \]

\[ + \left. (1 - \hat{k}_x \hat{k}_x) V_T^2(|k|) \mathcal{F}_o(|k|, t) C_T(|k|, t) \right]. \]  

(5.14)

It is no accident that the expression for \( D \) given in Eqn(5.14), which is intended to describe single-particle motion in a strongly supercooled liquid, has also been applied
for diffusion in a normal liquid at intermediate densities [4, 5, 6, 32]. In both cases, it is the coupling to current modes which makes the dominant contribution to the diffusion coefficient, although the details of the two situations are drastically different. For a liquid at intermediate densities, couplings to the solvent's density fluctuations are unimportant because the cage effect is not fully developed. On the other hand, it is the current modes which allows the tagged-particle to hop over potential barriers created by surrounding particles of the long-lived cages in a supercooled liquid below $T_c$.

### 5.4 DIFFUSION BELOW $T_c$

Within the strongly supercooled regime, $\mathcal{F}_o(||k||, t)$ decays extremely slowly compared to the current correlators $C_{L,T}(||k||, t)$, whose Laplace transformed counterparts are given by

\begin{align}
C_L(||k||, s) &= \frac{s}{s[s + \tilde{\Gamma}_L(||k||, s)] + \Omega_k^2}, \\
C_T(||k||, s) &= \frac{1}{s + \tilde{\Gamma}_T(||k||, s)},
\end{align}

where $\Omega_k^2$ is a characteristic microscopic frequency of the bath defined by $\Omega_k^2 = k^2 \frac{k_B T}{ms(||k||)}$ and $\tilde{\Gamma}_{L,T}$ are the longitudinal and transverse current relaxation kernels. In writing Eqn(5.15), we have ignored couplings to energy fluctuations, whose inclusion, albeit straightforward, would make the exposition unnecessarily cumbersome.

To a good approximation, $\mathcal{F}_o(||k||, t)$ may be replaced by unity for the transverse contribution to the diffusion constant, and we find

\[ \int_0^\infty dt \mathcal{F}_o(||k||, t)C_T(||k||, t) \approx C_T(||k||, s = 0) = \frac{1}{\tilde{\Gamma}_T(||k||, s = 0)}. \] (5.17)

The longitudinal current correlator in Eqn(5.15) vanishes in the limit $s \to 0$ independent of the value of $k$ because of conservation of particle number. Thus, if $\mathcal{F}_o(||k||, t)$
is similarly set to unity for the longitudinal component of $D$, we would find a null result. However, because $\mathcal{F}_0(|k|, t)$ does in fact decay, this is not the case, and one finds that longitudinal currents do make an important contribution to the diffusion coefficient, at least for normal liquids [3, 32]. For the present purposes, we replace

$$\int_0^\infty dt \mathcal{F}_0(|k|, t) C_L(|k|, t) \approx \frac{1}{\tilde{\Gamma}_L(|k|, s = 0)},$$

(5.18)

in analogy with Eqn(5.17). With these approximations we find

$$D = \frac{k_B T}{6\pi^2} \frac{1}{nm} \int_0^\infty dk k^2 \left[ V_T^2(|k|) \left( \frac{1}{\tilde{\Gamma}_L(|k|, s = 0)} \right) + 2V_T^2(|k|) \left( \frac{1}{\tilde{\Gamma}_T(|k|, s = 0)} \right) \right],$$

(5.19)

where $\tilde{\nu}_{l,t}(|k|, s)$ are the generalized longitudinal and transverse viscosities of the fluid.

If we ignore the wavevector dependence of the viscosities in Eqn(5.19) and simply use the corresponding zero wavenumber and frequency values, we obtain

$$D = \frac{k_B T}{6\pi^2} \left( \frac{A}{\tilde{\nu}_t} + \frac{2B}{\tilde{\nu}_t} \right),$$

(5.20)

where $A$ and $B$ are given by wavevector integrals of the squared vertices $V_{L,T}^2(|k|)$. It is easy to manipulate Eqn(5.20) into the standard SE form given by Eqn(5.1) with $C$ exhibiting a weak temperature dependence arising from the factors $A$, $B$, and $\tilde{\nu}_t/\tilde{\nu}_t$. We remark that Eqn(5.20) is highly reminiscent of the SE relation derived by Zwanzig within the context of normal modes of liquids [33].

Actually, the manipulations leading from Eqn(5.19) to Eqn(5.20) are valid only for a large probe particle in a bath of smaller particles. Under such circumstances, $V_{L,T}^2(|k|)$ decay sufficiently rapidly with $k$ so as to remove all finite wavenumber contributions of $1/\tilde{\nu}_{l,t}(|k|, s = 0)$ in the integral of Eqn(5.19) (see Figures 5-1 and 5-2). When the probe and the bath particles are comparable in size, this is no longer the case. In fact, it is the wavenumber dependence of the generalized viscosities which reflect the spatial inhomogeneity present in dense liquids at smaller length scales and
give rise to deviations from the SE relation.

The behavior of $\tilde{\nu}_{t,t}(|k|, s = 0)$ as a function of wavenumber in dense liquids is well known [3, 34, 35]. In the zero wavenumber limit, $\tilde{\nu}_{t,t}(|k|, s = 0)$ become simply the macroscopic values for the longitudinal and transverse viscosities. As $k$ increases to finite values, $\tilde{\nu}_{t,t}(|k|, s = 0)$ decreases, approaching values obtained from short time behavior and eventually reaching the free streaming limit for very large wavenumbers where collisions can be ignored and particles move in uninterrupted straight lines [34]. In a supercooled liquid, the small wavenumber limit of the generalized viscosities increases dramatically with a lowering of temperature as structural rearrangements slow down [13]. However, the finite wavenumber values of $\tilde{\nu}_{t,t}(|k|, s = 0)$ exhibit a weaker increase as temperature decreases, since molecular transport at finite wavenumbers or microscopic length scales is less affected by supercooling.

For $R/\sigma \approx 1$ or comparable solute-solvent sizes, the vertices in the expression for the diffusion constant (Eqn(5.19)) do not decay rapidly with $k$, and finite wavevector contributions from $1/\tilde{\nu}_{t,t}(|k|, s = 0)$ can make a greater contribution than the small $k$ terms in the integral over intermediate wavevectors. Thus, $D$ is predicted to become decoupled from the macroscopic viscosities and to exhibit a weaker temperature dependence than the SE Law, as indeed is observed experimentally for fragile glass formers [9, 10, 11, 12].

## 5.5 CONCLUSIONS

The fact that $\tilde{\nu}_{t,t}(|k|, s = 0)$ at finite $k$ can become significantly smaller than the macroscopic viscosities provides a microscopic justification for the fluidized domain models [15, 16, 17, 18, 19] proposed to explain the breakdown of the SE relation. A smaller tagged-particle is able to probe finite wavenumber fluctuations associated with the generalized viscosities and experiences a greater diffusivity than a larger particle which is only effectively coupled to smaller wavenumber excitations. Stated in another way, a smaller solute particle experiences a more heterogeneous environment which, on average, provides less resistance to translation at microscopic length scales.
A quantitative verification of the scenario proposed in this work would be highly desirable not only within the context of the present problem but also to test whether MCT remains valid below $T_c$. Since MCT for supercooled liquids generally employs equilibrium averages, it is clear that nonequilibrium effects associated with "aging" of deeply supercooled systems are unaccounted for [36]. But even ignoring these subtle effects, the extended MCT for the glass transition appears to be plagued by the fact that the hopping kernel in the current relaxation memory functions does not decrease sufficiently with a lowering of temperature, and the introduction of an initial time cutoff, while effective, appears to be unjustifiable [28]. It has been recently suggested that a wavevector cutoff should be introduced instead to account for the finite size of clusters that dominate structural relaxation in a supercooled liquid [29]. We find it extremely interesting that the mode-coupling expression for $D$ obtained here, which resemble the hopping kernel of the extended MCT, naturally contains wavevector cutoffs in the vertices $V_{L,T}(|k|)$.
Figure 5-1: Plot of $V^2(k)$ vs. $k(2\sigma)$ corresponding to a typical solute-solvent interaction potential for two different solute-solvent size ratios.
Figure 5-2: *Plot of $V_2^2(k)$ vs. $k(2\sigma)$ corresponding to a typical solute-solvent interaction potential for two different solute-solvent size ratios.*
Bibliography


