Beyond the no-slip boundary condition

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Beyond the no-slip boundary condition

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This paper offers a simple macroscopic approach to the question of the slip boundary condition to be imposed upon the tangential component of the fluid velocity at a solid boundary. Plausible reasons are advanced for believing that it is the energy equation rather than the momentum equation that determines the correct fluid-mechanical boundary condition. The scheme resulting therefrom furnishes the following general, near-equilibrium linear constitutive relation for the slip velocity of mass along a relatively flat wall bounding a single-component gas or liquid: \( v_\text{slip} = -\alpha \ln \rho / \partial s \text{wall} \), where \( \alpha \) and \( \rho \) are, respectively, the fluid’s thermometric diffusivity and mass density, while the length \( \partial s \) refers to distance measured along the wall in the direction in which the slip or creep occurs. This constitutive relation is shown to agree with experimental data for gases and liquids undergoing thermal creep or pressure-driven viscous creep at solid surfaces.

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I. INTRODUCTION

The solution of fluid-mechanical problems involving contact with solid walls requires knowledge not only of the governing differential equations but also of the boundary condition imposed on the tangential component of the fluid’s velocity at the walls [1,2]. Though the empirical no-slip boundary condition codified by Stokes’ [3] at the interface between a solid surface and a liquid [4–6] or gas [7] applies in commonly occurring situations [1,2], it has been known since at least the time of Maxwell [8] that Stokes’ no-slip condition is not inviolable, especially in the case of dilute gases. Thus, slip (also called “creep” by gas kineticists) of the fluid’s mass velocity is known to occur in gases whose mean free path is large relative to the linear dimensions of the container walls confining that gas internally, or to the linear dimensions of a particle bounded externally by the gas [7]. (Moreover, there is a large body of empirical data suggesting that slip can also occur in the case of liquids moving within microfluidic and especially nanofluidic devices [4–6].) In the case of nonspherical fluids, whose temperature varies along the particle or wall surface, the resulting thermal creep [8] gives rise to the respective phenomena of thermophoresis [9–11] and thermal transpiration [12,13]. For the case of isothermal fluids (typically undergoing pressure-driven flow in a microfluidic channel) the resulting slip phenomenon is termed viscous creep.

When slip occurs, the problem becomes one of specifying its constitutive form. While equations have been proposed in attempts to quantify that slip in the case of gases [14,15], the author is unaware of any equation with a rational claim of universal applicability, namely, to both gases and liquids, as well as to whether the flow is isothermal or nonisothermal. Creep formulas that have been proposed in broadly general contexts covering both gases and liquids are invariably characterized by unknown phenomenological coefficients, such as the Navier slip length [4,5]. These coefficients generally need to be determined empirically, with their values apparently dependent upon such factors as the physicochemical natures of both the fluid and solid, the solid’s surface topology (e.g., roughness), the surface’s hydrophobicity or hydrophilicity, as well as other interfacial attributes. Given these features, definitive progress in quantifying slip phenomena is currently far from satisfactory.

This paper proposes a more-or-less general slip boundary condition at solid surfaces focused on the issue of slip in a broader, more general, context than currently exists, with emphasis placed on the fluid’s volume velocity \( v_v \) [16–19] rather than its mass velocity \( v_m \). The issue of the fluid’s volume velocity at a solid boundary arises in regard to its role in the constitutive expression \( \mathbf{P} \cdot \mathbf{v}_v \), governing the rate per unit area at which thermodynamic work is being performed at such a surface, in which \( \mathbf{P} \) is the pressure tensor.

II. VOLUME VELOCITY

In the absence of body forces such as gravity, the basic equation governing energy transport in fluids, continua or otherwise (e.g., rarefied gases), takes the form [1,2,20–23]

\[
\rho \frac{D\hat{e}}{Dt} = -\nabla \cdot (\hat{j}_m + \mathbf{P} \cdot \mathbf{v}_v),
\]

where \( \rho \) is the mass density, \( \hat{e} \) the specific energy, \( \hat{j}_m \) the flux of internal energy [24], \( \mathbf{P} \) the pressure tensor, and \( \mathbf{v}_v \) a velocity, here arbitrarily termed the fluid’s “volume velocity.” For reasons discussed in detail elsewhere [16–19], the choice of the prefix “volume” with respect to the velocity multiplying \( \mathbf{P} \) derives, in part, from an analogy between the areal rate-of-working term \( \mathbf{P} \cdot \mathbf{v}_v \), appearing in Eq. (1) and its equilibrium thermodynamic counterpart \( p \, dV \) [20], in which \( p \) is the pressure and \( V \) the volume.

Appearing in the above is the material derivative

\[
\frac{D}{Dt} = \frac{\partial}{\partial t} + v_m \cdot \nabla,
\]

in which \( v_m \) is the fluid’s mass velocity, defined as usual in terms of the mass flux \( \mathbf{n}_m \) by the relation \( v_m := \mathbf{n}_m / \rho \). It is this velocity that appears in the continuity equation

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v_m) = 0.
\]
Until recently [16–19] it was always assumed [21–23] that the velocity \( v_r \), defined by its role in the constitutive equation of the rate-of-working term in the energy equation (1), was synonymous with \( v_m \), such that
\[
    v_r = v_m. \tag{4}
\]

That is, the neutrally named and unsubscripted velocity symbol \( v \) appearing in the areal rate-of-working term \( P \cdot v \) in Eq. (1) was implicitly assumed to be congruent with the symbol \( v_m \), with the latter already defined not by its appearance in the energy equation but rather by its appearance in the continuity equation (3). The plausibility of Eq. (4) as a generality is, however, questionable, since the volume velocity is not simply a variant of the mass velocity. Rather, it is, operationally, a fundamentally different quantity. Thus, whereas no constitutive equation is required for \( v_m \), which is already defined physically by its role in the continuity equation, the volume velocity necessitates a constitutive equation, one necessarily derived from its definition in Eq. (1) [with that equation formulated in terms of the set of variables \((v_m, p, T)\), \( T \) being the temperature]. Explicitly, as a consequence of its definition, \( v_r \) necessarily depends upon the nature of its companion constitutive equation governing \( P \), with the latter already defined by its appearance in the linear momentum equation [21]. But since \( P \) itself requires constitutive formulation, the same requirement must necessarily hold true for \( v_r \), too, since it is only their product \( P \cdot v_r \) that can, in principle, be implicit rather than explicit in the first law of thermodynamics at each point of the fluid.

The preceding rationale dictating the definition of the velocity symbol \( v_r \) as the multiplier of the pressure tensor in the energy equation appears to have been overlooked until recently [16–19]. Consequently, the assumption throughout the fluid-mechanics literature that Eq. (4) holds \textit{a priori} is, in general, without a rational foundation. It thus behooves one to establish the operational protocol by means of which \( v_r \) can, in principle, be constitutively established, explicitly or implicitly, at each point of the fluid and at each instant of time, in terms of the independent variables \((v_m, p, T)\). Logically, this can only be accomplished from prior knowledge of the functional constitutive dependence of \( P \) upon these same variables (or, alternatively, by establishing both \( v_r \) and \( P \) simultaneously in terms of these variables as is, in fact, effected in earlier papers [16–19]).

Were one to define a quantity \( j_v \) by the expression
\[
    j_v := v_r - v_m, \tag{5}
\]
belief in the equality (4) would then be tantamount to supposing that \( j_v = 0 \). We refer to \( j_v \), in what follows as the diffuse flux of volume. Much of what follows below will be seen to focus ultimately, via Eq. (5), upon \( j_v \) rather than \( v_r \).

A. Velocity boundary condition at a fluid-solid interface

Consider a closed, rigid container of volume \( V \) possessing solid, immobile, impermeable walls \( \partial V \). The container as a whole is supposed held rigidly at rest (with respect to an inertial reference frame). It is completely filled with a viscous single-component fluid undergoing some generally nonisothermal transient heat-transfer process involving movement \( v_m \) of the fluid’s mass. Gravity is supposed absent.

At a given instant of time the amount of energy \( E \) present within the fluid confined in the container is [21]
\[
    E = \int_V \rho \dot{e} \, dV, \tag{6}
\]
where the specific energy \( \dot{e} \) consists of both internal and kinetic energies (potential energy being absent in single-component fluids owing to the assumed absence of gravity). The temporal rate of change in the amount of this energy is given by the expression [21]
\[
    \dot{E} = \int_V \rho \frac{D \dot{e}}{Dt} \, dV. \tag{7}
\]

Use of Eq. (1) in the above jointly with the divergence theorem gives
\[
    \dot{E} = \dot{Q} + \dot{W}, \tag{8}
\]
in which
\[
    \dot{Q} = -\int_{\partial V} dS \cdot j_v, \tag{9}
\]
and
\[
    \dot{W} = -\int_{\partial V} dS \cdot \mathbf{P} \cdot v_v. \tag{10}
\]

are, respectively, the rate of heat flow into the fluid from the surroundings and the rate at which work is being done by the surroundings on the fluid as a whole. Furthermore, \( dS = \hat{n} \, dS \) is a directed element of surface area at a point lying on \( \partial V \), at which point \( \hat{n} \) denotes the outwardly directed unit normal to the fluid domain \( V \).

Given the rigidity, immobility, and impermeability of the container walls, it is not possible for the surroundings to perform work on the fluid. This requires that \( W = 0 \), whence
\[
    \int_{\partial V} \hat{n} \cdot \mathbf{P} \cdot v_v \, dS = 0. \tag{11}
\]

Furthermore, the impermeability of the container walls to mass flow requires that
\[
    \hat{n} \cdot v_m = 0 \quad \text{on} \quad \partial V. \tag{12}
\]

Without loss of generality the functional dependence of the dependent velocity field \( v_v \) upon the independent fields \((v_m, p, T)\) [25] may, in principle, be implicit rather than explicit in the subsequent development. Moreover, this dependence may be nonlocal in nature, such that the constitutive equation for \( v_v \), at a given point of the fluid and at a given instant of time depends, functionally, upon the values of the fields \((v_m, p, T)\) at points distant from the immediate neighborhood of that point, not even necessarily even at the same time \( t \). That is, at this stage we leave open the possibility that the dependence of \( v_v \) upon this set of independent variables may take the form of an integral distribution, one dependent upon the “history” of these fields. In this context circumstances may be imagined wherein the container is so large that a disturbance originating in one portion of the (generally compressible) fluid may require a finite amount of time before manifesting some effect deriving therefrom in distant portions of the fluid. Despite
such time lags, the integral condition (11) is nevertheless required to hold at every instant of time. Moreover, it has to hold independently of the initial conditions imposed upon the differential equations governing the fluid’s motion in the closed container. The possibility must also be considered that the flow taking place is turbulent rather than laminar, or that the fluid may be rheologically non-Newtonian [21] rather than Newtonian. Other scenarios may also impact on the detailed analysis required in applications.

The point of citing all of the above possibilities, however unlikely some may be in commonly encountered applications, is to focus on the fact that Eq. (11) must be satisfied for the case of solid, immobile, and impermeable walls, independently of all details, including the form taken by the constitutive equation governing the pressure tensor. This is necessary to assure global satisfaction of the first law of thermodynamics.

B. No slip of the volume velocity

The global condition (11) will obviously be satisfied if, at each point on the bounding surface and at all times, one has that

\[ \mathbf{v}_e = 0 \text{ on } \partial V \quad (\forall t \geq 0). \]  (13)

The latter, together with Eq. (12), is sufficient in present circumstances to assure satisfaction of the first law [26]. Our goal in what follows is to demonstrate that the boundary condition posed by Eq. (13) is supported by several classes of experiments, and to thus suggest, based on that agreement, the general applicability of this local boundary condition at solid surfaces.

Equation (13) is to be regarded as a working hypothesis, one that is consistent (or at least not inconsistent) with thermodynamic principles. In particular, we do not claim to have offered a proof of the pointwise relation (13) based upon the global condition (11).

As a consequence of Eq. (5), the boundary condition (13) requires that

\[ \mathbf{v}_m = -\mathbf{j}_e \text{ on } \partial V. \]  (14)

In terms of the latter’s normal and tangential components we have that

\[ \mathbf{n} \cdot \mathbf{v}_m = -\mathbf{n} \cdot \mathbf{j}_e \text{ on } \partial V \]  (15)

and

\[ (\mathbf{I} - \mathbf{n} \mathbf{n}) \cdot \mathbf{v}_m = -(\mathbf{I} - \mathbf{n} \mathbf{n}) \cdot \mathbf{j}_e \text{ on } \partial V, \]  (16)

in which \( \mathbf{I} \) is the idemfactor. The preceding equations show that the slip velocity of the fluid relative to the bounding surface of the solid is given by the expression

\[ (\mathbf{v}_m)_{\text{slip}} = -(\mathbf{I} - \mathbf{n} \mathbf{n}) \cdot \mathbf{j}_e \text{ on } \partial V. \]  (17)

Furthermore, based upon Eq. (15), condition (12) requiring that the surface be impenetrable by mass becomes

\[ \mathbf{n} \cdot \mathbf{j}_e = 0 \text{ on } \partial V. \]  (18)

III. DIFFUSE VOLUME FLUX

As shown in earlier papers [16–19] devoted to the diffuse transport of volume it follows, inter alia, from the principles of linear irreversible thermodynamics (LIT) [22,23] that the constitutive equation for \( \mathbf{j}_e \) (in situations where body forces such as gravity are absent) is given by the expression

\[ \mathbf{j}_e = -L_{21} \nabla \ln T + L_{22} \nabla p. \]  (19)

Entropy production requirements require that \( L_{22} \geq 0 \), together with other constraints imposed upon \( L_{21} \). The phenomenological \( L \) coefficients are, according to the principles of LIT, functionally dependent only upon \( p \) and \( T \), while being independent of \( v_m \).

A. Phenomenological coefficients

Several theoretical macroscopic and molecular models quantifying the diffuse transport of volume through fluids lead, independently, to the conclusion that in near-equilibrium circumstances, and for circumstances where body forces are absent, \( \mathbf{j}_e \) is given for both liquids and gases by the linear constitutive relation

\[ \mathbf{j}_e = D_v \nabla \ln \rho, \]  (20)

in which the diffusion coefficient \( D_v \geq 0 \) (possessing the usual units of a diffusivity) denotes the fluid’s volume diffusivity. The several independent models leading from (19) to Eq. (20) include the following: (i) equidiffuse transport theory [18,19]; (ii) Burnett’s solution of the Boltzmann equation for dilute gases [27,28]; (iii) Dadzie et al.’s [29–31] extension of the Boltzmann equation so as to now include internal molecular transport processes occurring in so-called “volume space,” above and beyond the usual “velocity-space” processes; (iv) Durst et al.’s semitheoretical model [32–38] of transport processes in compressible gases; and (v) Woods’ [19,39] generic near-equilibrium constitutive hypothesis applied to the diffuse transport of volume.

It has also been argued on theoretical grounds [17,18] that in Eq. (20),

\[ D_v = \alpha, \]  (21)

where

\[ \alpha = \frac{k}{\rho \bar{c}_p} \]  (22)

is the fluid’s thermometric diffusivity [21], wherein \( k \) is the thermal conductivity and \( \bar{c}_p \) the isobaric specific heat. Equation (21) is broadly supported in the case of gases by Burnett’s constitutive equations [27,28] for the stress tensor and the heat flux, as documented in Refs. [16–19]. When applied to Eq. (19) the model posed by Eqs. (20)–(22) corresponds to the following phenomenological coefficient values:

\[ L_{21} = \alpha \beta T \]  (23a)

and

\[ L_{22} = \alpha \kappa, \]  (23b)

where

\[ \beta = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_p \]  (24a)

and

\[ \kappa = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial p} \right)_T \]  (24b)
are, respectively, the fluid’s coefficients of thermal expansion and compressibility.

IV. SLIP VELOCITY

Equations (20) and (21), jointly with (17) and (12), lead to the following pair of constitutive expressions:

\[ (v_m)_{\text{slip}} = -\alpha \left. \frac{\partial \ln \rho}{\partial s} \right|_{\text{wall}} \]

and

\[ (v_m)_{\text{normal}} = -\alpha \left. \frac{\partial \ln \rho}{\partial n} \right|_{\text{wall}} = 0, \]

where \( \delta s > 0 \) and \( \delta n > 0 \) respectively denote elements of arc length along and perpendicular to the wall in the directions of increasing \( s \) and \( n \). The algebraically signed scalar slip velocity appearing in (25), referring to the fluid’s mass velocity relative to the wall, is defined as

\[ (v_m)_{\text{slip}} = \hat{s} \cdot v_m|_{\text{wall}}, \]

where \( \hat{s} \) is a unit tangent vector along the surface \( \partial V \) drawn along a path line, and pointing in the same direction as that for which the length parameter \( s \) is increasing in magnitude. Similarly,

\[ (v_m)_{\text{normal}} = \hat{n} \cdot v_m|_{\text{wall}}, \]

where, as before, \( \hat{n} \) is a unit normal vector perpendicular the surface, pointing in the same direction as that for which the length parameter \( n \) is increasing in magnitude.

A. Slip at smooth surfaces

With \( N_{\text{wall}} \) a characteristic distance measured in proximity to, and normal to, the wall, it follows from (26) that the normal component of velocity at the wall is of order \( (v_m)_{\text{normal}} = O(\alpha / N_{\text{wall}}) \). Given the strictly local, near-wall applicability of this formula, an obvious choice for the characteristic length is \( N_{\text{wall}} = O(R) \), where \( R \) is the local radius of curvature of the wall at the point along the wall where the normal velocity is to be calculated. Hence, for the case of a relatively flat wall, one devoid of asperities, it follows that \( (v_m)_{\text{normal}} \approx 0 \). In that case it follows from (28) that

\[ \hat{n} \cdot v_m|_{\text{wall}} = 0, \]

thereby assuring satisfaction of Eq. (12). The consequent restriction of the slip formula (25) to relatively smooth surfaces is counterpart to the comparable limitations of molecularly based creep formulas [8,14,15,40] to one-dimensional transport processes [7,35].

Einzell, Panzer, and Liu [41] discuss corrections to one-dimensional-slip velocity formulas arising from curvature of the surface. In this context they presented the following formula for the variation in Navier slip length \( \lambda \) [see Eq. (38)] with the surface’s radius of curvature \( R \):

\[ \lambda = \frac{1}{\lambda_0 - 1/R} \]

where \( \lambda_0 \) refers to the limiting value for a flat surface. Their result is confirmed by Tibbs et al. [42].

B. Comparison of the slip velocity formula (25) with data: Preview

The viability of the volume-velocity boundary condition (13) can only be ascertained by examining pertinent experimental evidence bearing thereon, with the outcome reflecting on the correctness or lack thereof of this hypothesized boundary condition. This empirical attitude is analogous to that originally adopted by Stokes [3] and followed ever since with respect to the conventional no-slip fluid-mechanical mass-velocity boundary condition \( v_m = 0 \) [1,2] at solid surfaces. There, the credibility of Stokes’ hypothesis has been tested in the context of elementary, well-defined situations. The latter were sufficient in number, variety, and simplicity of interpretation, such as to render Stokes’ no-slip hypothesis credible as a general rule without, however, necessarily supposing it to be inviolable. In what follows we adapt the same empirical verification scheme to the present volume velocity case, arguing that Eq. (13) overrides Stokes’ no-slip condition in situations where fluid compressibility is sensible.

Experimental confirmation of the viability of the slip-velocity formula (25) would, concomitantly, serve to confirm (or, at least, not deny) the correctness of diffuse volume transport theory (earlier referred to as “bivelocity” theory [16,17]), as embodied in Eqs. (20) and (21), since these constitutive equations are independent of those bearing on the proposed boundary condition (13). That is, since \( v_m = v_n - j_\nu \), and since it is only \( v_m \) that is experimentally accessible independently of any constitutive hypothesis, any test of the validity of the boundary condition \( v_n = 0 \) on \( \partial V \) necessitates having explicit constitutive knowledge of \( j_\nu \). On the other hand, the converse is not true. That is, failure to confirm (25) does not necessarily indicate the failure of diffuse volume flux theory [16–19] since the source of the failure may simply lie in the invalidity of the slip hypothesis (13) rather than in the validity of the models underlying the constitutive relations (20) and (21).

The theoretical predictions of Eq. (25) for various types of gaseous and liquid-phase flows are compared below with experimental data bearing thereon.

V. COMPARISON WITH SLIP VELOCITY DATA

A. Incompressible fluids do not slip

For those fluids whose density is effectively uniform throughout, such that \( \rho = \text{const.} \), Eq. (25) yields

\[ (v_m)_{\text{slip}} = 0 \text{ on } \partial V. \]

This no-slip prediction is, of course, supported by numerous experiments performed on both liquids and “incompressible” gases [4–7]. However, prior analyses supporting Stokes’ imposition of the no-slip condition on \( v_m \) have not explicitly identified the fluid’s incompressibility as constituting a necessary (although insufficient) condition for its applicability, as is implied in the present work.

1. Real liquids are compressible and, hence, slip

While it is true that no slip occurs when \( \rho = \text{const.} \), the thermodynamic stability of fluids, liquids, as well as gases, requires that the coefficient of compressibility defined in
Eq. (24b) satisfy the inequality \( \kappa > 0 \) [43]. As such, whenever pressure gradients exist (in isothermal fluids)—which is always the case when fluid motion occurs—it is impossible for the density to be uniform throughout the fluid. In that case, in place of Eq. (30), one has either from (25) or from (19) and (23b) that

\[
(v_m)_{\text{slip}} = -\alpha \kappa \frac{\partial p}{\partial s}\bigg|_{\text{wall}}. \tag{31}
\]

Since \( \alpha \) and \( \kappa \) are each positive definite, in isothermal flows the slip must always occur in the direction in which the pressure along the walls is decreasing. For example, this direction of slip accords with all known isothermal experiments involving single-component pressure-driven Poiseuille-like flows in microchannels [4,5]. Given that \( \kappa \) is small for liquids, the slip velocity will surely be small for such fluids, except possibly for very large pressure gradients. Reviews of the literature [4,5] for this class of flows confirms the existence of some small degree of slip for virtually all liquids. As such, all liquids slip to some extent despite their relative incompressibility.

**B. Gases**

Equation (25) indicates that compressible gases fail to obey the conventional no-slip condition. This conclusion is implicitly supported, *inter alia*, by experimental data for gases as reviewed by Gad-el-Hak [7]. In what follows we compare the predictions of Eq. (25) with experimental results for both nonisothermal and isothermal gaseous flows.

1. **Nonisothermal gases: Thermal creep**

It has long been known theoretically, ever since the classic work by Maxwell [8], that the mass velocity \( v_m \) slips at a solid surface along which a temperature gradient exists, at least in the case of dilute gases. This phenomenon, termed thermal creep, has been confirmed experimentally on many occasions (see the review by Brenner [44]) as well as theoretically by molecular dynamic simulations [45,46]. The extent of such slip was shown by Maxwell [8] to be given constitutively by his thermal creep tangential-velocity boundary condition

\[
(v_m)_{\text{slip}} = C_S \frac{\nu}{T} \frac{\partial T}{\partial s}\bigg|_{\text{wall}}. \tag{32}
\]

Here, \( \nu \) is the gas’s kinematic viscosity, while \( C_S \) is a nondimensional \( O(1) \) numerical coefficient whose value Maxwell estimated to be \( 3/4 \) based on the assumption of specular reflection of the gas molecules from the surface. Theoretically established creep coefficient values for other types of reflection, intermediate between specular and diffuse, are provided in the extensive review paper by Sharipov and Seleznev [14] (and more recently by Sharipov and Kalempa [15]). Those tabulations cover the entire range of reflectivities, varying from \( C_S = 3/4 \) to \( C_S = 1.15 \) [47].

Considerable experimental evidence also exists in support of the functional form of Maxwell’s slip velocity formula (32), although not necessarily his estimate of \( 3/4 \) for the value of the thermal creep coefficient. The experimental results do, however, support the general view that \( C_S = O(1) \) [44], in accord with the tabulation of Sharipov and Seleznev [14]. These experimental data derive, more or less exclusively, from thermophoretic [9] and thermal transpiration [12] experiments. In addition to experimental support, theoretical support also exists for the correctness of Maxwell’s [8] nonisothermal creep model [14,15,46–48].

For purposes of comparing Maxwell’s molecularly derived Eq. (32) with our macroscopically derived expression (25) for the slip velocity in nonisothermal gases, consider the case where the contribution of the pressure gradient to the slip velocity is small compared with that arising from the temperature gradient. In that case Eq. (25) becomes

\[
(v_m)_{\text{slip}} = \alpha \beta \frac{\partial T}{\partial s}\bigg|_{\text{wall}}. \tag{33}
\]

For dilute gases \( \beta = 1/T \), whence the latter becomes

\[
(v_m)_{\text{slip}} = \frac{1}{\Pr} \frac{\nu}{T} \frac{\partial T}{\partial s}\bigg|_{\text{wall}}, \tag{34}
\]

in which we have noted that, by definition,

\[
\alpha = \frac{\nu}{\Pr}, \tag{35}
\]

where \( \Pr = \nu/\alpha \) is the Prandtl number. For gases \( \Pr = O(1) \) [21], with values thereof generally lying in the approximate range [49]

\[
2/3 < \Pr < 3/4, \tag{36}
\]

depending upon whether the gas is mono-, di-, or polyatomic.

Within the limits of uncertainty existing in the values of the respective parameters \( C_S \) and \( \Pr^{-1} \), Eqs. (32) and (34) are seen to be indistinguishable from one another. The previously cited theoretical and experimental vales of \( C_S \) thus enable one to conclude that our macroscopic slip-velocity formula is synonymous with that originally proposed by Maxwell [8] on the basis of his molecular model [48], which focused on the tangential transport of momentum in proximity to the walls. Given the wide acceptance in the literature of Maxwell’s thermal creep formula, this agreement contributes to confidence in the viability of our general slip-velocity model (25).

2. **Viscous creep: Isothermal, pressure-driven gaseous flows in narrow channels**

For the case of both gases and liquids, it follows from Eq. (25), together with (35), that

\[
(v_m)_{\text{slip}} = -\frac{1}{\Pr} \nu \frac{\partial \ln \rho}{\partial s}\bigg|_{\text{wall}}. \tag{37}
\]

As such, the fluid slips along the wall in the direction of diminishing density and, hence, for the case of isothermal flows, in the direction of decreasing pressure. This is also the direction in which the net flow of mass occurs through the channel under the influence of externally imposed pressure gradients.

Durst and his collaborators [33–38] have successfully interpreted experimental data pertaining to the pressure-driven isothermal flows of dilute compressible gases through
microchannels by using their empirical slip-velocity formula, namely,

\[ (v_m)_{\text{slip}} = -v \frac{\partial \ln \rho}{\partial s} \bigg|_{\text{wall}} . \]  

(38)

Use of the above boundary condition to solve the pertinent fluid-mechanical equations was found by Durst et al. to furnish results in accord with experimental data extending over substantial ranges of Knudsen numbers. Given the Prandtl number range for gases in Eq. (36), and considering the range of uncertainties existing in both the accuracy of the constitutive formula (20) relative to the model-free Eq. (19), and the value of the volume diffusivity \( D_v \), appearing the former, it is reasonable to declare our theoretical slip formula (37) to be well supported by experimental data.

According to Durst et al. [33–38] their boundary condition (38) fitted the data more closely than did Maxwell’s velocity-creep boundary condition [7,8], namely,

\[ (v_m)_{\text{slip}} = \frac{2 - \sigma}{\sigma} \lambda \frac{\partial v_m}{\partial n} \bigg|_{\text{wall}} . \]  

(39)

where \( \sigma = O(1) \) is the momentum accommodation coefficient and \( \lambda \) is the mean free path. Also noted by Durst et al. [33–38] is the generally good agreement of their theory based upon Eq. (38) with direct simulation Monte Carlo (DSMC) simulations.

Dongari, Dadzie, and Reese [31] have confirmed that the boundary condition posed by Eq. (38) leads to results for isothermal gases flowing through microchannels that agree well with experimental data.

As reviewed in Refs. [4] and [5], schemes other than pressure-driven flows in microchannels possess the potential for accurate experimental measurements of the slip velocity in both gases and liquids. Prominent among these techniques is atomic force microscopy (AFM). See, for example, Maali et al., who used AFM to measure slip velocities in both gases [50] and liquids [51].

C. Liquids

1. Isothermal liquids

According to Eq. (25), which is applicable to both gases and liquids, the slip velocity can be reexpressed in the form

\[ (v_m)_{\text{slip}} = \alpha \frac{\partial T}{\partial s} \bigg|_{\text{wall}} - \alpha \kappa \frac{\partial p}{\partial s} \bigg|_{\text{wall}} . \]  

(40)

In the case of isothermal flows, the latter reduces to Eq. (31). As discussed in connection with that equation, liquids are largely incompressible, whence \( \kappa \approx 0 \). In the idealized case where \( \kappa = 0 \) identically, no slip would occur.

2. Nonisothermal liquids

In view of the preceding comments, unequivocal quantitative confirmation of our slip velocity model appears remote for case of isothermal liquids owing to the smallness of the effect. However, the same is not true for nonisothermal liquid flows. In that case, one has from (40) that

\[ (v_m)_{\text{slip}} = \alpha \beta \frac{\partial T}{\partial s} \bigg|_{\text{wall}} . \]  

(41)
VI. SUMMARY AND CONCLUSIONS

This paper proposed a rational constitutive equation for the slip-velocity suffered by a simple fluid, whether gas or liquid, at its boundaries with a solid wall. Slip was shown to arise as a consequence of gradients in the fluid’s mass density along the wall. Experimental data derived from nonisothermal phenomena in both gases and liquids were shown to support the proposed slip velocity formula (25), although the available liquid-phase data were scanty, leaving less conclusive the support for liquids. Data encompassing isothermal pressure-driven gaseous flows in micro- and nanofluidic devices offered further evidence in support of the proposed slip model. This concordance of experiment with theory served, concomitantly, to offer indirect support for our general theory of diffuse volume transport [16–19].

Prior to the present paper, theories pertaining to the subject of slip at solid surfaces were largely limited to gases [7,14,15]. Moreover, these theories were molecular in nature, requiring, for closure, empirical knowledge of the balance between specular and diffuse reflections at the boundary, as quantified by empirical accommodation or creep coefficients. In contrast, the slip model derived herein was strictly macroscopic, requiring no empirical parameters. Despite their very different origins, our paper indicated a surprising level of compatibility between the two models.

Yet to be addressed is the task of identifying, quantitatively, the proposed slip model’s realm of applicability in regard to the Knudsen number.
[45] K. Shida and W. G. Hoover, J. Phys. Soc. Jpn. 67, 2277 (1998); To quote the authors: “Only a rough explanation of thermal creep was available to Maxwell. Our present understanding is not much better, and remains only semiquantitative.”