

## **Microscopic Theory of the Liquid–Wall Boundary Conditions; Thermophoresis**

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A microscopic theory of the boundary conditions (BC) obeyed by the hydrodynamic equations at a smooth wall is presented. The BC thus obtained contain several new features. Special attention is given to the role of surface tension. A purely hydrodynamic theory of thermophoresis is worked out based upon the new BC.

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**KEY WORDS:** Boundary conditions; generalized hydrodynamics; thermophoresis.

### **1. INTRODUCTION**

A very large amount of effort has been expended in deriving hydrodynamic equations from the microscopic equations of motion. These derivations have been mainly carried out, however, with no explicit treatment of the boundaries enclosing the system, and so have not provided a microscopic theory of the boundary conditions (BC) obeyed by the hydrodynamic equations. Recently, attention has shifted<sup>(1)</sup> to construction of a microscopic theory of BC.

To derive BC, one must, somehow, write down equations which explicitly include the interaction of the system with its walls. The BC are determined by the behavior of the equations near and at the walls. Of course, a major difficulty is that the equations may differ drastically from their usual forms near the walls, over and above any explicit (external force) wall contributions.

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In general, little is known about hydrodynamic equations near walls. One important ingredient of these equations is, however, fairly well studied—the pressure tensor, which,<sup>2</sup> near a wall, contains a part involving the surface tension. It thus behooves us to incorporate everything we know about surface tension into the hydrodynamic equations. For now, we must be content to treat other wall features of the equations, such as new transport coefficients, formally.

In this paper, we consider a smooth flat wall, and use the general approach<sup>(1a)</sup> of Ronis and Oppenheim. Our main goals are twofold. First, we wish to obtain, microscopically, even if only formally, the complete BC, that is, we include, in principle, all possible contributions of the wall. Secondly, we wish to incorporate the surface tension as simply as is possible. The microscopic equations give the coefficients of the hydrodynamic equations as equilibrium (with wall) averages. So far, surface tension has entered the theories via<sup>(1b,1c,1d)</sup> identification of some averages which also appear in an equilibrium theory<sup>(2)</sup> of surface tension. We will show how to avoid this procedure.

Our new BC differ significantly from those in common usage. Of course, we do find that the BC are zero normal velocity, zero tangential stress, and zero normal heat flux; anything else would be unphysical. Our actual expressions for the stress and heat flux, however, are not those which hold far from the wall, and this is the reason that our BC are not the usual ones. As a demonstration of the consequent implication, we give, in the last section, a calculation of the thermophoretic force. This force vanishes in a hydrodynamic approximation based upon the usual BC.

## 2. EQUATIONS

The hydrodynamic equations describe the time evolution of the non-equilibrium averages (denoted  $\bar{\quad}$ ) of the conserved densities, the number density,

$$n(\mathbf{r}, t) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \quad (1a)$$

the momentum density,

$$\mathbf{g}(\mathbf{r}, t) = \sum_i \mathbf{p}_i(t) \delta(\mathbf{r} - \mathbf{r}_i(t)) \quad (1b)$$

<sup>2</sup> For a review see Ref. 2.

and the energy density,

$$e(\mathbf{r}, t) = \sum_i \frac{p_i^2(t)}{2m} + \frac{1}{2} \sum_{j \neq i} \phi(\mathbf{r}_i(t) - \mathbf{r}_j(t)) \delta(\mathbf{r} - \mathbf{r}_i(t)) \quad (1c)$$

$\mathbf{r}_i(t)$  and  $\mathbf{p}_i(t)$  denote the position and momentum of particle  $i$  at time  $t$ , respectively,  $m$  is the mass, and  $\phi$  the intermolecular pair potential. No angular degrees of freedom will be considered here, and we further ignore memory effects.

The standard projection operator<sup>(3)</sup> or response theory methods may then be extended, as shown<sup>(1e)</sup> by Ronis and Oppenheim, to obtain equations valid for small deviations from equilibrium in the presence of the wall,

$$\frac{\partial}{\partial t} \bar{n}(\mathbf{r}, t) = \nabla \cdot (n_0 \mathbf{v}) \quad (2a)$$

$$\begin{aligned} \frac{\partial}{\partial t} \bar{\mathbf{g}}(\mathbf{r}, t) = & -\nabla \cdot \mathbf{P}(\mathbf{r}, t) + \int_0^\infty ds \int d\mathbf{r}' \nabla \cdot \langle \mathcal{T}_D(\mathbf{r}, s) \mathcal{T}_D(\mathbf{r}', 0) \rangle : \nabla' \mathbf{v}(\mathbf{r}', t) \\ & + \int_0^\infty ds \int d\mathbf{r}' \nabla \cdot \langle \mathcal{T}_D(\mathbf{r}, s) \mathbf{j}_D(\mathbf{r}') \rangle \cdot \nabla' T(\mathbf{r}', t) \\ & + \mathbf{F}_w \end{aligned} \quad (2b)$$

$$\begin{aligned} \frac{\partial}{\partial t} \bar{e}(\mathbf{r}, t) = & \int ds \int d\mathbf{r}' \nabla \cdot \langle \mathbf{j}_D(\mathbf{r}, s) \mathbf{j}_D(\mathbf{r}', 0) \rangle \cdot \nabla' T(\mathbf{r}', t) \\ & + \int ds \int d\mathbf{r}' \nabla \cdot \langle \mathbf{j}_D(\mathbf{r}, s) \mathcal{T}_D(\mathbf{r}', 0) \rangle : \nabla' v(\mathbf{r}', t) \end{aligned} \quad (2c)$$

The conjugate forces to the conserved densities are the velocity field,  $\mathbf{v}$ , and the temperature,  $T$ , and are understood to denote deviations from equilibrium, while  $\mathcal{T}_D$  and  $\mathbf{j}_D$  denote the dissipative stress tensor and heat flux, respectively;  $n_0$  is the equilibrium density,  $\mathbf{P}$  the nonequilibrium pressure tensor,  $\mathbf{F}_w$  the force directly exerted by the wall, and  $\langle \rangle$  denotes an equilibrium average in the presence of the wall. The details of the derivation of Eqs. (2) may be found in Ref. 1e.

Equation (2a), of course, is just the linearized continuity equation. We have kept the spatially nonlocal forms of Eqs. (2b, c), so they contain, in principle, derivatives of all orders. To reduce them to finite-order equations, we expand<sup>(1a)</sup> the quantities to the right of the correlation functions in a power series about  $\mathbf{r}' = \mathbf{r}$ ; the usual second-order equations result from keeping only a single term in the series. We are trying to find BC on the ordinary hydrodynamic equations, so, by construction, keeping a single term will be valid far from the wall, that is, the conjugate forces must be

sufficiently slowly varying. The only reason that we keep the nonlocal equations is to treat the region very close to the wall.

The correlation functions simplify according to the symmetry of the system. In a spatially homogeneous and isotropic system as far from the wall in the anisotropic wall system, they are functions of  $\mathbf{r} - \mathbf{r}'$  only, and

$$\int ds \int d\mathbf{r}' \langle \mathcal{F}_D^{xy}(\mathbf{r}', s) \mathcal{F}_D^{xy}(\mathbf{r}, 0) \rangle \equiv (\mathcal{F}^{xy}, \mathcal{F}^{xy}) = \eta \quad (3a)$$

$$(\mathcal{F}^{xx}, \mathcal{F}^{xx}) = \frac{4}{3}\eta + \eta^B \quad (3b)$$

and

$$(\mathcal{F}^{xx}, \mathcal{F}^{yy}) = \eta^B - \frac{2}{3}\eta \quad (3c)$$

where  $\eta$  and  $\eta^B$  are the shear and bulk viscosities. All other types of stress tensor autocorrelation function vanish, as do all the stress–heat flux correlation functions; the ordinary Navier–Stokes equation then results from Eq. (1b).

For an inhomogeneous system with one preferred direction, the second-order equations become more complicated. Let the term containing the velocity field on the right-hand side of Eq. (2b) be denoted  $\nabla \cdot \boldsymbol{\sigma}$ . Then it is not hard to determine that

$$\begin{aligned} \boldsymbol{\sigma}(\mathbf{r}) = & F(\mathbf{r})\mathbf{S}(\mathbf{r}, \mathbf{v}) + [A(\mathbf{r}) - 2C(\mathbf{r})]\nabla \cdot \mathbf{v} \\ & + [C(\mathbf{r}) - F(\mathbf{r})](\mathbf{1} - \hat{n}\hat{n}) \cdot \mathbf{S}(\mathbf{r}, \mathbf{v}) \cdot (\mathbf{1} - \hat{n}\hat{n}) \\ & + \left[ \frac{D(\mathbf{r}) - E(\mathbf{r})}{2} - F(\mathbf{r}) \right] \hat{n}\hat{n} \cdot \mathbf{S}(\mathbf{r}, \mathbf{v}) \cdot \hat{n}\hat{n} \\ & + [E(\mathbf{r}) - A(\mathbf{r}) + 2C(\mathbf{r})]\hat{n}\hat{n} \nabla \cdot \mathbf{v} \end{aligned} \quad (4)$$

where  $\hat{n}$  is the unique direction,

$$S_{\alpha\beta} = \left( \frac{\partial v_\alpha}{\partial r_\beta} + \frac{\partial v_\beta}{\partial r_\alpha} \right) \quad (5)$$

and

$$A = (\mathcal{F}^{xx}, \mathcal{F}^{xx}) \quad (6a)$$

$$C = (\mathcal{F}^{xy}, \mathcal{F}^{xy}) \quad (6b)$$

$$D = (\mathcal{F}^{zz}, \mathcal{F}^{zz}) \quad (6c)$$

$$E = (\mathcal{F}^{xx}, \mathcal{F}^{zz}) \quad (6d)$$

$$F = (\mathcal{F}^{xz}, \mathcal{F}^{xz}) \quad (6e)$$

in Eqs. (6), we have let  $\hat{n} = \hat{z}$ , with  $x$  and  $y$  equivalent. If the wall is at

$z = 0$ ,  $\sigma$  will take on its homogeneous, isotropic form for large enough  $z$ , since

$$\left. \begin{aligned} A &= D \\ C &= F \\ E &= A - 2C \end{aligned} \right\} \text{large } z \tag{7}$$

and these quantities also become  $r$  independent. Consequently, only the first two terms in Eq. (4) survive far from the wall. The remaining combinations of  $A-F$  are confined to the “boundary layer,” while  $F$  and  $(A - 2C)$  can be divided into bulk and boundary layer parts. Of course, all coefficients vanish inside the wall.

In principle, the nonlocal equations could become even more complicated tensorially than those based on Eq. (4). However, we will assume that any such effects are negligible, and just use a nonlocal version of Eq. (4); we follow this approach for the rest of the transport terms in Eqs. (2b, c) as well.

The coupling to  $T$  on the right-hand side of Eq. (2b) vanishes in the usual equations. For the wall, we find, denoting the term by  $\nabla \cdot \sigma^T$

$$\begin{aligned} \sigma^T &= Q(\mathbf{r})(\hat{n}\nabla T + \nabla T\hat{n}) + [R(\mathbf{r}) - 2Q(\mathbf{r}) - O(\mathbf{r})]\hat{n}\hat{n} \\ &\quad \times \hat{n} \cdot \nabla T + O(\mathbf{r})\hat{n} \cdot \nabla T \end{aligned} \tag{8}$$

where

$$Q = (\mathcal{J}^{zx}, \mathbf{j}^x) \tag{9a}$$

$$R = (\mathcal{J}^{zz}, \mathbf{j}^z) \tag{9b}$$

$$O = (\mathcal{J}^{xx}, \mathbf{j}^x) \tag{9c}$$

All these quantities are confined to the boundary layer.

Turning to the energy equation, of course, for the homogeneous isotropic case,

$$(\mathbf{j}^\alpha, \mathbf{j}^\alpha) = \kappa \tag{10}$$

where  $\kappa$  is the thermal conductivity. The coupling to  $\mathbf{v}$  vanishes, giving rise to Fourier’s law. In the presence of the wall, writing  $\nabla \cdot \mathbf{J}$  for the first term on the right-hand side of Eq. (2c), we have

$$J = V(\mathbf{r})\nabla T + \hat{n}[V(\mathbf{r}) - U(\mathbf{r})]\hat{n} \cdot \nabla T \tag{11}$$

with

$$U = (\mathbf{j}^x, \mathbf{j}^x) \tag{12a}$$

and

$$V = (\mathbf{j}^z, \mathbf{j}^z) \tag{12b}$$

Finally, we write the energy–velocity coupling as  $\nabla \cdot \mathbf{J}^v$ , and

$$-\mathbf{J}^v = Q(\mathbf{r})\mathbf{S} \cdot \hat{\mathbf{n}} + [R(\mathbf{r}) - 2Q(\mathbf{r}) - O(\mathbf{r})]\hat{\mathbf{n}}\hat{\mathbf{n}} \cdot \nabla \mathbf{v} \cdot \hat{\mathbf{n}} + O(\mathbf{r})\hat{\mathbf{n}}\nabla \cdot \mathbf{v} \quad (13)$$

The hydrodynamic equations have now been given in their most general local form, and we next will derive BC from nonlocal equations with the same tensorial structure. The pressure tensor will be discussed later on.

### 3. SURFACE MULTIPOLE MOMENTS

#### 3.1. Dissipative Terms

We now use the method of Ronis and Oppenheim<sup>(1a)</sup> to obtain the BC. In schematic notation, the full nonlocal equations are

$$\dot{x} = my \quad (14)$$

which, far from the wall, simplify to the usual equations,

$$\dot{x}^+ = m^+y^+ \quad (15)$$

Although  $x^+, y^+$  is not a solution near the wall, we obtain BC by setting  $x = x^+\theta^+, y = y^+\theta^+$ , where  $\theta^+$  is the unit step function, and forming the quantity

$$\dot{x} - \theta^+\dot{x}^+ = m\theta^+y^+ - \theta^+m^+y^+ \equiv Z \quad (16)$$

which is confined to the boundary layer. The surface multipole moments of  $Z$  are<sup>(1a)</sup>

$$Z^j = \int_{-\infty}^{\infty} dz z^j Z \quad (17)$$

and BC result when the correct number of  $Z^j$ , starting at  $j = 0$ , are equated to zero; the number of  $Z^j$  is just that which will give the right number of BC.

In our case, the bulk equations ( $m^+$ ) are the usual hydrodynamic equations, as just discussed, plus Eq. (2a) far from the wall, which is just, again as usual,  $\nabla \cdot \mathbf{v}^+ = 0$ . To solve these equations, we need four BC at the wall. Less empirically, the idea is that, for a system described in bulk by hydrodynamics, the boundary layer is in some sense thin, and the thinness associates a small parameter with each  $j$ ; higher moments may then be considered automatically satisfied. This argument still needs to be made more rigorous, but, for now, we do confine ourselves to  $j = 0$ . Further support for the approach comes from the fact that it reproduces the standard BC in the absence of the new features discussed here. Of course, retaining  $j = 0$  provides five BC, one for each vector component of the

combined three equations. Rather than a difficulty, this turns out to be fortuitous.

The goal of the Ronis–Oppenheim method is to obtain BC on the far fields,  $x^+$ ,  $y^+$ . If the details of  $y$  in the boundary layer are important for determination of the surface multipoles, then the BC are found from complicated equations which contain the boundary layer behavior of the  $y$ 's. Unless simplifying approximations can be used here, the basic method becomes so complicated as to be useless.

Now, the normal surface moment of the Navier–Stokes equation cannot be obtained without complete knowledge of the density in the boundary layer.  $F_w$  is just  $n\nabla\phi$ , and  $\nabla\phi$ , the gradient of the wall–molecule potential, is extremely rapidly varying near the wall; thus,  $n$  must be known in complete detail to evaluate this term. On the other hand, the remaining four moments can be gotten to a very good approximation by just writing  $y \simeq y^+$ .

Only four BC are required on the ordinary hydrodynamic equations, which hold far from the wall. It seems reasonable, then, to take them from the four moments which are easy to evaluate. This does not mean that we do not satisfy the fifth moment. Given five BC where four are needed, one must be redundant. So, unless the entire approach is faulty, use of any four moments should give the same answer, and nothing is wrong with choosing the four which are tractable. This choice is in accord with the usual practice in hydrodynamics, where BC on the normal stress are not needed. Basically this same argument was used in Ref. 1e. We would, of course, like to have a better understanding of why, by apparent coincidence, the number of BC required equals the number of *tractable* moments, not the number of moments; this is surely a fascinating coincidence.

Since we start with nonlocal equations, even the  $j = 0$  multipoles will contain derivatives of all orders, which will be generated via the expansion (“localization”) of  $y(\mathbf{r}')$  about  $y(\mathbf{r})$  in the  $\mathbf{r}'$  integrals. Since the  $y^+$  are by construction (hydrodynamic limit) slowly varying, we will only keep one term in this expansion. In addition, we will keep no derivatives higher than first order.

We now work our  $Z^j$  for the dissipative, transport coefficient parts of the equations. Since the procedure is straightforward we will carry it out in detail for one term, and then just state the final results.

Consider the shear viscosity term in the momentum density equation. The multipoles are

$$Z_\beta^j = \int dz z^j \left[ \nabla_\alpha \int d\mathbf{r}' F(\mathbf{r}, \mathbf{r}') (\nabla'_\beta v_\alpha^+ \theta^+ + \nabla'_\alpha v_\beta^+ \theta^+) - \theta^+ \nabla_\alpha \int d\mathbf{r}' F^+(\mathbf{r}, \mathbf{r}') (\nabla'_\beta v_\alpha^+ - \nabla'_\alpha v_\beta^+) \right] \quad (18)$$

When  $\alpha = z$ , we perform a partial integration. The surface terms vanish because  $F \rightarrow F^+$  as  $z \rightarrow \infty$  and  $F = 0$  at  $z = -\infty$  (inside the wall). Thus,

$$\begin{aligned} Z_{\beta; \alpha=z}^j = & -j \int dz z^{j-1} \left[ \int d\mathbf{r}' F(\mathbf{r}, \mathbf{r}') (\nabla'_{\beta} v_z^+ \theta^+ + \nabla'_z v_{\beta}^+ \theta^+) \right. \\ & \left. - \theta^+ \int d\mathbf{r}' F^+(\mathbf{r}, \mathbf{r}') (\nabla'_{\beta} v_z^+ + \nabla'_z v_{\beta}^+) \right] \\ & + \int dz z^j \delta(z) \int d\mathbf{r}' F^+(\mathbf{r}, \mathbf{r}') (\nabla'_{\beta} v_z^+ + \nabla'_z v_{\beta}^+) \end{aligned} \quad (19)$$

the third term arises when  $\nabla_z$  acts on  $\theta^+$  in the partial integration of the  $F^+$  contribution.

Two types of functions sit on the right of  $F$  and  $F^+$ ,  $v^+$ , or  $\nabla v^+$ , which is slowly varying by construction, and  $\delta(z) (\nabla_z \theta^+)$ , which, of course, is not slowly varying. Slowly varying functions are "localized," expanded about  $\mathbf{r}' = \mathbf{r}$ , as discussed earlier. With these ideas in mind, it is easy to obtain

$$\begin{aligned} Z_{\beta; d=z}^j = & \left( \delta_{j,0} \eta - j \left\{ \int dz z^{j-1} \int d\mathbf{r}' [F(\mathbf{r}, \mathbf{r}') \theta^+(z') - \theta^+(z) F^+(\mathbf{r}, \mathbf{r}')] \right\} \right) \\ & + (\nabla \mathbf{v}^+ + \mathbf{v}^+ \nabla)_{\beta z}(x, y, z=0) \\ & - j \left\{ \left[ \int dz z^{j-1} \int dx' dy' F(xyz, x'y'0) \right] (v_{\beta}^+ + v_z^+ \delta_{\beta z})(x, y, z=0) \right. \\ & \left. + \dots \right\} \end{aligned} \quad (20)$$

The  $\delta_{j,0} \eta$  comes from the third term in Eq. (20) via use of Eq. (3a) and localization. The first integral on the right-hand side is the "surface excess" of  $F$ , which would vanish if  $F$  maintained its bulk form in the boundary layer ( $F$  will vanish for  $z$  or  $z' < 0$ ). The second integral springs from the  $\delta$  function,  $\nabla_z \theta^+$ . The " $\dots$ " represents the contribution of  $(\mathbf{r}' - \mathbf{r}) \cdot \nabla \mathbf{v}$  in the expansion of  $\mathbf{v}(\mathbf{r}')$  about  $\mathbf{v}(\mathbf{r})$ .

For  $\alpha = x, y$ , we remove the  $\nabla_{\alpha}$  from under the integral, and

$$\begin{aligned} Z_{\beta; \alpha=x}^j = & \nabla_x \int dz z^j \int d\mathbf{r}' [F(\mathbf{r}, \mathbf{r}') \theta^+ - \theta^+ F(\mathbf{r}, \mathbf{r}')] \\ & \times (\nabla'_{\beta} v_x^+ + \nabla'_x v_{\beta}^+) + \nabla_x \int dz z^j \int dx' dy' F(\mathbf{r}, x'y'0) v_x^+(x'y'0) \delta_{\beta z} \\ \xrightarrow{\text{loc}} & F^j \nabla_x (\nabla v^+ + v^+ \nabla)_{x\beta}^{(xy0)} + F_s^j \nabla_x v_x^+(xy0) \delta_{\beta z} \end{aligned} \quad (21)$$

where  $F^j$  is the surface multipole of  $F$ , and

$$F_s^j = \int dz z^j \int dx' dy' F(xyz, x'y'0) \quad (22)$$



The above manipulations illustrate the treatment of a term which is nonzero in bulk. For coefficients confined to the boundary layer, the integrand of  $Z^j$  has no subtraction  $\theta^+ m^+$ , since  $m^+ = 0$ , and  $F^j$  is defined accordingly, but otherwise no new ideas are needed to evaluate the multi-poles. We eventually find

$$\begin{aligned}
 & \int z^j \nabla \cdot \sigma \\
 &= \delta_{j,0} \eta \mathbf{S}^+ \cdot \hat{n} + (A - 2C)_s^j (1 - \hat{n}\hat{n}) \cdot \nabla(\mathbf{v}^+ \cdot \hat{n}) + F_s^j \hat{n} \nabla \cdot (1 - \hat{n}\hat{n}) \cdot \mathbf{v}^+ \\
 & \quad - j \left[ F_s^{j-1} (1 + \hat{n}\hat{n}) \cdot \mathbf{v}^+ + (A - 2C)_s^{j-1} \hat{n}\hat{n} \cdot \mathbf{v}^+ + \dots \right] - j F^{j-1} \mathbf{S}^+ \cdot \hat{n} \\
 & \quad - j \hat{n} \left[ \left( \frac{D-E}{2} - F \right)^{j-1} \hat{n} \cdot \mathbf{S}^+ \cdot \hat{n} + 2 \left( \frac{D-E}{2} - F \right)_s^{j-1} \hat{n} \cdot \mathbf{v}^+ + \dots \right] \\
 & \quad - j \hat{n} \left[ (E - A - 2C)_s^{j-1} \hat{n} \cdot \mathbf{v}^+ + \dots \right] \tag{23}
 \end{aligned}$$

In obtaining Eq. (23), we have noted that, far from the wall, Eq. (2a) is, as usual  $\nabla \cdot \mathbf{v}^+ = 0$ , so we have discarded all  $\nabla \cdot \mathbf{v}^+$  from the BC. Proceeding similarly, we evaluate the coupling of  $\mathbf{g}$  to the temperature, with the result

$$\begin{aligned}
 \int z^j \nabla \cdot \sigma^T &= O_s^j (1 - \hat{n}\hat{n}) \cdot \nabla T^+ - j \hat{n} \left[ R^{j-1} \hat{n} \cdot \nabla T^+ + R_s^{j-1} T^+ + \dots \right] \\
 & \quad - j Q^{j-1} (1 - \hat{n}\hat{n}) \cdot \nabla T^+ \tag{24}
 \end{aligned}$$

Turning to the energy equation,

$$\int dz z^j \nabla \cdot \mathbf{J} = \delta_{j,0} \kappa \hat{n} \cdot \nabla T^+ - j \left[ U^{j-1} \hat{n} \cdot \nabla T^+ + U_s^{j-1} T^+ + \dots \right] \tag{25}$$

and

$$\begin{aligned}
 \int dz z^j \nabla \cdot \mathbf{J}^v &= Q_s^j \nabla \cdot (1 - \hat{n}\hat{n}) \cdot \mathbf{v}^+ \\
 & \quad - j \left[ S^{j-1} \sum_{\alpha \neq z} \nabla_\alpha (\hat{n} \cdot \mathbf{v}^+) \right. \\
 & \quad \left. + R^{j-1} \hat{n} \cdot \nabla \mathbf{v}^+ \cdot \hat{n} + R_s^{j-1} \hat{n} \cdot \mathbf{v}^+ + \dots \right] \tag{26}
 \end{aligned}$$

### 3.2. Euler Terms; Pressure Tensor

Let us now turn to the reversible ‘‘Euler’’ terms in the equations. The moments of  $\mathbf{F}_w$  cannot be evaluated but, as mentioned at the beginning of

this section, are not needed. Equation (2a) is easy; we require

$$\begin{aligned} Z^j &= \int z^j (\nabla \cdot n \theta^+ v^+ - n^\infty \theta^+ \nabla \cdot v^+) = \int z^j v_z^+ \frac{\partial n_0}{\partial z} \\ &= v_z^+ \int z^j \frac{\partial n_0}{\partial z} + \frac{\partial v_z^+}{\partial z} \int z^{j+1} \frac{\partial n_0}{\partial z} + \dots \end{aligned} \quad (27)$$

where we have used  $\nabla \cdot v^+ = 0$  and  $\theta^+ n_0 = n_0$ ; we keep  $\partial n_0 / \partial z$  as an entity, since it is conveniently confined to the boundary layer.

Setting  $j = 0$ , we would obtain a mixed BC for the normal velocity,

$$\hat{n} \cdot \mathbf{v} + \frac{(\partial n_0 / \partial z)^1}{(\partial n_0 / \partial z)^0} \hat{n} \cdot \nabla \mathbf{v} \cdot \hat{n} = 0 \quad (28)$$

if we were to keep the second term on the right-hand side of Eq. (28). We do not wish to do this, as it is inconsistent with our general approach, and the  $\nabla v$  term should be small for our problem. Nevertheless, we do want to point out that the microscopic theory does not have to give the macroscopic BC,  $\hat{n} \cdot \mathbf{v} = 0$ , depending on the situation. This possibility has been discussed in the different context of self-diffusion by a small particle by Hynes,<sup>(4)</sup> and perhaps that represents such a case.

We finally turn to the pressure tensor, which must be expressed in terms of the fluid variables. If we choose to employ the conjugate forces, then<sup>(1e)</sup>

$$P^{\alpha\beta}(\mathbf{r}) = \int d\mathbf{r}' [\langle \mathcal{T}^{\alpha\beta}(\mathbf{r}) n(\mathbf{r}') \rangle \mu(\mathbf{r}') + \langle \mathcal{T}^{\alpha\beta}(\mathbf{r}) e(\mathbf{r}') \rangle T(\mathbf{r}')] \quad (29)$$

where the chemical potential,  $\mu$ , makes its initial appearance,  $n$  and  $e$  really mean  $n - \langle n \rangle$ , etc, and  $\mathcal{T}$  is the full (not dissipative) stress tensor. It might seem that  $\mu$ , which does not appear in the ordinary hydrodynamic equations, should be eliminated in terms of its conjugate,  $n$ . We now show, however, that a treatment of  $\mathbf{P}$  in the boundary layer is simplified by retention of  $\mu$  as a variable.

In bulk systems,<sup>(5)</sup> the averages in Eq. (29) may be attacked in two ways. First,<sup>(5a)</sup> they may be written down microscopically, and the resulting microscopic expression can be related to the corresponding expression for a known quantity, in particular, a thermodynamic derivative. Of course, it is of first importance to substitute known quantities, as the thermodynamic derivatives, for the formal averages which appear in microscopic dynamical theories. But, this can also be done<sup>(5b)</sup> in a very simple way. Averages like  $\langle \mathcal{T}^{\alpha\beta}(\mathbf{r}) x(\mathbf{r}') \rangle$  are rigorously equal to the functional derivative,  $\delta P^{\alpha\beta}(\mathbf{r}) / \delta y(\mathbf{r}')$ , where  $y$  is conjugate to  $x$ . Given a knowledge of  $\delta y / \delta x$ ,  $\delta P / \delta x$  can also be considered. In the absence of walls, starting from

equilibrium, a spatially uniform  $\delta y$  or  $\delta x$  simply generates a new equilibrium system, and, thus

$$\left(\frac{\partial p}{\partial y}\right)_l = \int d\mathbf{r}' \frac{\delta P(\mathbf{r}')}{\delta y(\mathbf{r}')} \quad (30a)$$

$$\left(\frac{\partial p}{\partial x}\right)_l = \int d\mathbf{r}' d\mathbf{r}'' \frac{\delta P(\mathbf{r}')}{\delta y(\mathbf{r}'')} \frac{\delta y(\mathbf{r}'')}{\delta x(\mathbf{r}')} \quad (30b)$$

where the quantities on the left are ordinary thermodynamic derivatives, with the remaining independent variables held constant, and we have noted that, in an equilibrium bulk system,  $P(r) \rightarrow pl$ ,  $p$  being the usual pressure.

The integrals on the right of Eqs. (30) are, of course, what appear when Eq. (29) is "localized," so the thermodynamic derivatives may be introduced into the dynamical theory immediately, with no need for a microscopic theory of the derivatives. For bulk systems, all this may be done using either  $x$  or  $y$ . In the presence of a wall, however, use of  $y$  is required. Near the wall,  $x$  is not uniform, addition of a uniform  $\delta x$  does not create a new equilibrium system, and  $\int(\delta P/\delta x)$  is not a thermodynamic derivative. The conjugate  $y$ 's are constant even near the wall in equilibrium, however, so

$$\int \frac{\delta P(\mathbf{r}')}{\delta y(\mathbf{r}')} d\mathbf{r}' = \frac{\partial \langle P(\mathbf{r}) \rangle}{\partial \langle y \rangle} \quad (31)$$

$\partial \langle P(\mathbf{r}) \rangle / \partial \langle y \rangle$  is an equilibrium thermodynamic derivative in a nonuniform system, characterized by a position-dependent pressure tensor but constant  $\langle y \rangle$ . We suggest that use of Eq. (31) provides the easiest way to incorporate known equilibrium properties of nonuniform systems into the problem at hand.

Thus, Eq. (29) is localized:

$$P(\mathbf{r}) = \left[ \int d\mathbf{r}' \frac{\delta P(\mathbf{r}')}{\delta y(\mathbf{r}')} \theta^+(\mathbf{r}') \right] y^+(\mathbf{r}) + \left[ \int d\mathbf{r}' \frac{\delta P(\mathbf{r}')}{\delta y(\mathbf{r}')} \theta^+(\mathbf{r}') (\mathbf{r}' - \mathbf{r}) \right] \cdot \nabla y^+(\mathbf{r}) + \dots \quad (32)$$

The quantity in the first bracket is just the thermodynamic derivative of Eq. (31), since the functional derivative is just an average in the presence of the wall and must vanish for  $z$  or  $z' < 0$  due to the Boltzmann factor, so  $\theta^+$  cannot have any effect on the integral.

The pressure tensor has been much studied<sup>(2)</sup> for nonuniform systems, and for our case we have

$$\langle \mathbf{P}(r) \rangle = p\theta^+ \mathbf{I} + \sigma(1 - \hat{n}\hat{n})\delta(z) \quad (33)$$

where  $\sigma$  is the surface tension. It follows that

$$\mathbf{P}(\mathbf{r}) = \left( \frac{\partial p}{\partial y} \right) y^+ \theta^+ \mathbf{I} + \left( \frac{\partial \sigma}{\partial y} \right) y^+ (1 - \hat{n}\hat{n})\delta(z) + \dots \quad (34)$$

surface multipoles are now easy to write down:

$$\int z^j (\nabla \cdot \mathbf{P} - \theta^+ \nabla \cdot \mathbf{P}^+) = \delta_{j,0} \hat{n} \left( \frac{\partial p}{\partial y} \right) y^+ + \delta_{j,0} (1 - \hat{n}\hat{n}) \left( \frac{\partial \sigma}{\partial y} \right) \cdot \nabla y^+ \quad (35)$$

Of course, by  $\partial/\partial y$  we mean  $\partial/\partial \mu)_T$  and  $\partial/\partial T)_\mu$ , and so forth, and  $\mathbf{P}^+$  is  $p\mathbf{I}$ .

Note that  $\sigma$  is the surface tension for the solid (wall)–fluid interface, and is indeed a function of two independent variables,  $\mu$  and  $T$ . The extra complications present<sup>(1b–1d)</sup> for the two-phase, one-component system, where only one variable is independent, do not exist for our problem.

#### 4. THE BOUNDARY CONDITIONS

We may now collect all the  $\mathbf{Z}^j$  and obtain the BC keeping only the leading contributions to each. We already have, with this convention,

$$\hat{n} \cdot \mathbf{v}^+ = 0 \quad (36)$$

The normal components of the  $\mathbf{Z}^j$  from Eq. (2b) are to be discarded, and the tangential components give two BC,

$$\left[ \eta + \frac{1}{2} (A - 2C)_s^0 \right] \hat{t} \cdot \mathbf{S}^+ \cdot \hat{n} + \left[ O_s^0 - \left( \frac{\partial \sigma}{\partial T} \right)_\mu \right] \hat{t} \cdot \nabla T^+ - \left( \frac{\partial \sigma}{\partial \mu} \right)_T \hat{t} \cdot \nabla \mu^+ = 0 \quad (37)$$

where  $\hat{t}$  is a tangential unit vector. The remaining BC comes from the energy equation multipoles,

$$\kappa \hat{n} \cdot \nabla T^+ + Q_s^0 \nabla \cdot (1 - \hat{n}\hat{n}) \cdot \mathbf{v}^+ = 0 \quad (38)$$

Eqs. (36)–(38) constitute our microscopically derived BC on the ordinary hydrodynamic equations. To obtain them, we have discarded multipoles of  $j \geq 1$ . A sufficient condition for this to be valid is for the boundary layer to be thin. More empirically, keeping more multipoles would over-determine the problem, so our approach must be legitimate if the hydrodynamic equations are to make any sense. We have also neglected all but the first term arising in the “localization” procedure. This will be correct if  $y^+$

is slowly varying, which is also a prerequisite for use of the hydrodynamic equations.

Equation (36) is as expected. If only the term proportional to  $\eta$  in Eq. (37) were kept, we would obtain the zero tangential stress or “slip” BC generally employed at a smooth wall. The extra terms result because the stress tensor far from the wall,  $\eta \mathbf{S}^+$ , cannot give the true tangential stress at the wall. This point is clearly discussed<sup>(6)</sup> by Landau and Lifschitz, with regard to the extra  $(\partial\sigma/\partial T)_\mu \hat{t} \cdot \nabla T^+$  tangential stress. The remainder of the equation is given here for the first time.

Similarly, in Eq. (38), neglecting the surface transport coefficients in  $Q_s^0$  would give the condition of zero normal heat flux, as calculated by use of the bulk form of the flux,  $\kappa \nabla T$ . The extra coupling to  $\mathbf{v}$  in the BC is the consequence of  $\mathbf{v}$  entering the heat flux near the surface via surface transport coefficients. So, our results are consistent with zero tangential stress and zero normal heat flux at the wall, but these quantities may not be calculated using expressions valid far from the wall.

According to Eqs. (37) and (38), the solutions to the hydrodynamic equations are coupled both through the equations and through the BC. The presence of  $\mu^+$ , which appears in no equations, might be disturbing, but it actually creates no difficulty. We emphasize that the bulk equations are the usual equations. The coupled Navier–Stokes plus Fourier equations will have a solution with our BC in which  $\hat{t} \cdot \nabla \mu^+$  may be initially regarded as a parameter. Calculation of  $p$  from  $\mathbf{v}$  via the Navier–Stokes equation then allows evaluation of  $\hat{t} \cdot \nabla \mu^+$  from the relation

$$\left(\frac{\partial p}{\partial \mu}\right)_T \mu^+(z=0) = p(z=0; \hat{t} \cdot \nabla \mu^+) - \left(\frac{\partial p}{\partial T}\right)_\mu T^+(z=0; \hat{t} \cdot \nabla \mu^+) \tag{39}$$

### 5. THERMOPHORESIS

We now calculate the thermophoretic force on a sphere due to surface tension, that is, we ignore surface transport. The first goal of this exercise is to illustrate how to use the new BC, and the second is to establish the importance of surface tension for thermophoresis in liquids. We are not trying to construct a complete theory of thermophoresis in liquids.

There exists no good theory for thermophoresis in liquids, although various ideas have been tried; this is discussed by several authors.<sup>(7)</sup> A hydrodynamic calculation based upon the usual BC gives<sup>(6)</sup> zero force. Surface tension has been considered for objects, such as droplets, which may be characterized by an internal viscosity. It has been more or less

ignored, however, for rigid objects. We will show that the surface-tension-induced force can be comparable to that found in experiments, and, possibly, could be dominant for very large particles. Thus, although this force may not be a good approximation to the total force under most circumstances, it cannot be ignored in a complete theory.

Let the temperature far from the structureless hard sphere of radius  $a$  centered at the origin of coordinates be  $T_0 + \Delta z$ , i.e., constant  $T$  gradient  $\Delta$  in the  $z$  direction. We must calculate the force on the sphere in steady state. The energy equation is then just  $\nabla^2 T = 0$ , and the BC is  $\hat{r} \cdot \nabla T = 0$  at  $r = a$ , if we ignore the surface transport part of the BC. The solution to this elementary problem is

$$T^+ = T_0 + \Delta z + \frac{\Delta a^3}{2} \frac{\hat{r} \cdot \hat{z}}{r^2} \quad (40)$$

with

$$\nabla T^+ = \Delta \hat{z} + \frac{\Delta}{2} \frac{a^3}{r^3} (1 - 3\hat{r}\hat{r}) \cdot \hat{z} \quad (41)$$

Thus, the BC for the Navier–Stokes equation reads

$$\eta \hat{t} \cdot \mathbf{S}^+ \cdot \hat{n} + \left( \frac{\partial \sigma}{\partial T} \right)_\mu \frac{3}{2} \Delta \hat{t} \cdot \hat{z} + \left( \frac{\partial \sigma}{\partial \mu} \right)_T \hat{t} \cdot \nabla \mu^+ = 0, \quad r = a \quad (42)$$

We try a solution to the Navier–Stokes equation with the same form as that in<sup>(6)</sup> the Stokes problem except that  $\mathbf{v} \rightarrow 0$  as  $\mathbf{r} \rightarrow \infty$ ,

$$\mathbf{v}^+ = (A/r)(1 + \hat{r}\hat{r}) \cdot \hat{z} + (B/r^3)(3\hat{r}\hat{r} - 1) \cdot \hat{z} \quad (43)$$

and  $A$  and  $B$  to be found from the BC; the normal velocity BC immediately gives

$$B = -a^2 A \quad (44)$$

We next evaluate  $\mathbf{S}^+$  from Eq. (43), with the result

$$\mathbf{S}^+ = \frac{2A}{r^2} \left\{ (\hat{r} \cdot \hat{z})(1 - 3\hat{r}\hat{r}) - \frac{3a^2}{r^2} [(\hat{z}\hat{r} + \hat{r}\hat{z}) + (\hat{r} \cdot \hat{z})(1 - 5\hat{r}\hat{r})] \right\} \quad (45)$$

substitution of Eq. (45) into Eq. (42) yields

$$\frac{6A\eta}{a^2} \hat{t} \cdot \hat{z} = \frac{3}{2} \Delta \left( \frac{\partial \sigma}{\partial T} \right)_\mu \hat{t} \cdot \hat{z} + \left( \frac{\partial \sigma}{\partial \mu} \right)_T \hat{t} \cdot \nabla \mu^+, \quad r = a \quad (46)$$

At this point,  $A$  would be determined if we knew  $\hat{t} \cdot \nabla \mu^+$ . To find this quantity, we note, as discussed at the end of the last section, that the steady state Navier–Stokes equation is just  $\eta \nabla^2 \mathbf{v}^+ - \nabla p^+ = 0$ , and  $\mathbf{v}^+$  determines

$p^+$ . In fact,

$$p^+ - p_0 = \frac{2A\eta}{r^2} \hat{z} \cdot \hat{r} \quad (47)$$

where  $p_0$  is the pressure at infinity. And, we have

$$(p^+ - p_0) - \left( \frac{\partial p}{\partial T} \right)_\mu (T^+ - T_0) = \left( \frac{\partial p}{\partial \mu} \right)_T (\mu^+ - \mu_0) \quad (48)$$

or

$$\hat{t} \cdot \nabla p^+ - \left( \frac{\partial p}{\partial T} \right)_\mu \hat{t} \cdot \nabla T^+ = \left( \frac{\partial p}{\partial \mu} \right)_T \hat{t} \cdot \nabla \mu^+ \quad (49)$$

The left-hand side of this equation is now available from Eqs. (41) and (47); thus

$$2A\eta a^{-3} \hat{t} \cdot \hat{z} - \left( \frac{\partial p}{\partial T} \right)_\mu \frac{3}{2} \Delta(\hat{t} \cdot \hat{z}) = \left( \frac{\partial p}{\partial \mu} \right)_T \hat{t} \cdot \nabla \mu^+ \quad (50)$$

Upon substitution of this expression for  $\hat{t} \cdot \nabla \mu^+$  into Eq. (46) we finally obtain  $A$ :

$$A = \frac{a^2 \Delta}{4\eta} \left[ \frac{(\partial \sigma / \partial T)_\mu + (\partial \sigma / \partial \mu)_T (\partial \mu / \partial T)_p}{1 + (1/3) a^{-1} (\partial \sigma / \partial \mu)_T (\partial p / \partial \mu)_T^{-1}} \right] \quad (51)$$

where we have noted that

$$\left( \frac{\partial p}{\partial T} \right)_\mu \left( \frac{\partial p}{\partial \mu} \right)_T = - \left( \frac{\partial \mu}{\partial T} \right)_p \quad (52)$$

and the final fields are all known.

The last step is to calculate the force. In view of our emphasis upon the complicated form of the stress tensor very near the wall, and our explicit treatment of the microscopic wall force,  $\mathbf{F}_w$ , it might be thought that this would be more difficult here than in more macroscopic theories, but such is not the case. The generalized steady state Navier-Stokes equation may be written

$$\nabla \cdot \boldsymbol{\sigma}_{\text{tot}} + \mathbf{F}_w = 0 \quad (53)$$

where  $\boldsymbol{\sigma}_{\text{tot}}$  is the total stress,

$$\boldsymbol{\sigma} = \boldsymbol{\sigma} + \boldsymbol{\sigma}^T - \mathbf{P} \quad (54)$$

and, at the microscopic level, the force on the sphere,  $\mathbf{F}$ , is

$$\mathbf{F} = - \int d\mathbf{r} \mathbf{F}_w \quad (55)$$

The integral is over all space, but, of course, only receives contributions from  $r \sim a$ , and thus may be confined to any sphere with radius  $d$  greater than  $a$  plus the range of  $F_w$ . So, combining Eqs. (55) and (53) using the divergence theorem we have

$$\mathbf{F} = \int d\hat{r} \cdot \boldsymbol{\sigma}(\hat{r}, r = d) \quad (56)$$

If  $d$  exceeds  $a$  by more than the range of the boundary layer,  $\boldsymbol{\sigma}$  may be replaced by its bulk form. Consequently,  $\mathbf{F}$  is calculated in the usual way on any "outer" sphere. But, the answer cannot depend on  $d$ , and therefore may be evaluated on the real sphere of radius  $a$ . In sum, the macroscopic expressions for  $\mathbf{F}$  still hold, even though, from our perspective, they do not employ the true stress tensor. The force is now easy to evaluate:

$$\mathbf{F} = -2\pi a^2 \Delta \frac{(\partial\sigma/\partial T)_\mu + (\partial\sigma/\partial\mu)_T (\partial\mu/\partial T)_p}{1 + (1/3)a^{-1}(\partial\sigma/\partial\mu)_T (\partial p/\partial\mu)_T^{-1}} \hat{z} \quad (57)$$

Equation (57) is based upon ordinary hydrodynamics, plus BC which incorporate surface thermodynamics; surface transport, or dissipation, has been ignored. It represents the simplest extension of a hydrodynamic theory ignoring all surface phenomena, which predicts zero force, and is physically sensible. The numerator in the bracket gives the total change in  $\sigma$  with a change in  $T$  at constant pressure, including the potentially compensatory role of the necessary change in  $\mu$ . As Landau and Lifschitz<sup>(6)</sup> point out, a tangential force will then arise in the direction of the gradient, which is what we find. Landau and Lifschitz, however, write the change in  $\sigma$  terms of  $(\partial\sigma/\partial T)$  only, that is, they do not include the effect of the change in  $\mu$  needed to maintain constant pressure. This effect is important for thermophoresis; for example, one could obtain a net force due to pressure alone (with constant pressure at infinity) if only  $(\partial p/\partial T)_\mu$  were included in the calculation.

The denominator of the bracket is not so easy to interpret. Since it reduces to unity as  $a \rightarrow \infty$ , one might ask if we had left out other effect of curvature by applying flat wall BC to a sphere. However, at least in the absence of surface transport, it is easy to show that nothing has been neglected.

Let us now discuss Eq. (57), and relate it, to the extent possible, to experiment. We hasten to point out that our theory, including only surface tension effects, is *not expected* to reproduce the results of experiments. It is necessary to realize, however, that no good theory of thermophoresis exists for liquids; even order-of-magnitude estimates are unavailable. Thus, it will be valuable if we can find out whether surface tension alone causes a force even roughly comparable to that observed experimentally. We will then



have at least shown that no theory purporting to be a complete one can ignore surface tension, as is now done routinely. Obviously, given such limited goals, we will not be concerned with such considerations as that macromolecules should probably be modeled as rough, rather than smooth, surfaces. Also, in the comparison to follow, we will assume that the force on a polystyrene latex sphere is not too different from that on a Teflon sphere; this is because we have been unable to find needed data for the former case. To repeat, what we are about to do will be qualitative in the extreme, but we hope that the reader will be eventually convinced that we have actually established some points unambiguously.

In perhaps the most careful experiments on liquids, McNab and Meisen<sup>(6)</sup> (MM) found that, as in the case of gases,  $\mathbf{F}$  points toward the low-temperature direction. That, and the form of existing theories for liquids, led them to define the dimensionless coefficient,  $\alpha$ , in terms of the steady state thermophoretic particle velocity,

$$V_T = -\alpha \frac{\eta}{\rho} \frac{1}{T} \nabla T \quad (58)$$

where the existing theories have  $\alpha \sim 1$ . Converting our expression for  $\mathbf{F}$  into a velocity with Stokes' law for slip BC appropriate for a smooth wall, we find

$$\alpha = \frac{\rho a (\partial \sigma / \partial T) T}{2\eta^2} \quad (59)$$

where  $(\partial \sigma / \partial T)$  denotes the sum in the numerator of Eq. (57).

A difficult problem arises in trying to calculate  $\alpha$  from Eq. (59)—almost nothing is known about  $\sigma$  for solid-liquid interfaces. Of course, for many liquid-gas interfaces,  $(\partial \sigma / \partial T)$  is well established. Probably, we can do no better than to use the approximate relation,<sup>(9)</sup>

$$\sigma_{SL} = \sigma_S + \sigma_L - 2(\sigma_S \sigma_L)^{1/2} \quad (60)$$

which yields

$$\frac{\partial \sigma}{\partial T} SL = \left( \frac{\partial \sigma_L}{\partial T} \right) \left[ 1 - \left( \frac{\sigma_S}{\sigma_L} \right)^{1/2} \right] + \left( \frac{\partial \sigma_S}{\partial T} \right) \left[ 1 - \left( \frac{\sigma_L}{\sigma_S} \right)^{1/2} \right] \quad (61)$$

Both  $\partial \sigma_L / \partial T$  and  $\partial \sigma_S / \partial T$  are negative, and one of the quantities in parentheses will be negative with the other positive, so  $\partial \sigma_{SL} / \partial T$  will be a sum of a negative and positive term, either of which could dominate. Thus, it appears that the surface tension  $\alpha$  coefficient can be positive or negative, depending on the system. Of course, we must assume that use of standard "Handbook"  $\sigma$ 's in these relations will give the correct combination of partial derivatives which goes in Eq. (59). This seems plausible, but we will

not pursue the point, since the goal of this section is to make rough estimates only.

MM studied latex polystyrene spheres with radii of 1.01 and  $0.79 \times 10^{-4}$  cm in water and hexane; they reported  $\alpha = 0.1148$  and  $0.0874$ , respectively, on the order of 10–20 times smaller than predicted by existing theories. At room temperature, Eq. (59) gives, for  $10^{-4}$ -cm particles,

$$\alpha = \begin{array}{l} 2.03 \times 10^2 \left( \frac{\partial \sigma}{\partial T} \right) \quad (\text{water}) \\ 1.09 \times 10^3 \left( \frac{\partial \sigma}{\partial T} \right) \quad (\text{hexane}) \end{array} \quad (62)$$

Turning to Eq. (61) for  $(\partial \sigma_{SL}/\partial T)$ , we note that the solid–gas  $\sigma_S$ , also an elusive quantity, is required. If Eq. (60) is to be believed,  $\sigma_S$  may be obtained from measurements of contact angles for two different liquids, with known  $\sigma_L$ , in contact with the solid of interest. The two Young's equations, Eq. (60), and the two  $\sigma_L$ , and contact angles, allow a calculation of  $\sigma_S$ . We have not found the data to enable this approach for polystyrene, but Adamson's book<sup>(9)</sup> tabulates some data for *n*-octane and *n*-decane in contact with Teflon, and we obtain (CGS units)

$$\begin{aligned} \sigma_{\text{Teflon}} &= 19.2 \\ \left( \frac{\partial \sigma}{\partial T} \right) &= -0.11 \end{aligned} \quad (63)$$

In contrast to the highly questionable nature of Eq. (63), the liquid–gas numbers are well established.<sup>(10)</sup>

$$\sigma = \begin{array}{l} 72.88 \\ 18.46 \end{array} \begin{array}{l} \text{water} \\ \text{hexane} \end{array} \quad \left( \begin{array}{l} -0.16 \\ -0.11 \end{array} = \left( \frac{\partial \sigma}{\partial T} \right) \right) \quad (64)$$

and the resulting estimates are

$$\frac{\partial \sigma_{\text{Tef/liqu}}}{\partial T} = \begin{array}{l} +0.03 \\ 4.25 \times 10^{-5} \end{array} \begin{array}{l} \text{water} \\ \text{hexane} \end{array} \quad (65)$$

$$\alpha = \begin{array}{l} 6.09 \\ 0.05 \end{array} \begin{array}{l} \text{water} \\ \text{hexane} \end{array} \quad (66)$$

It is impossible to evaluate the validity of our attempts to obtain  $(\partial \sigma_{SL}/\partial T)$ . The remarkably good agreement of theory and experiment for hexane could easily be a fluke, as could be the too-large theoretical prediction for water. More complicated versions of Eq. (60) have<sup>(9)</sup> been suggested, which would give different  $(\partial \sigma_{SL}/\partial T)$ . Rather than speculate further along these lines, however, we would like to suggest that some qualitative points have actually been established, namely, the following.

(i) In the two calculations tried,  $(\partial \sigma_{SL}/\partial T)$  turned out to be positive. Thus, the surface tension force *need not* point in the opposite direction to

the true force. Also, it seems that

$$\left| \left( \frac{\partial \sigma_{SL}}{\partial T} \right) \right| \ll \left| \left( \frac{\partial \sigma_L}{\partial T} \right) \right|, \left| \left( \frac{\partial \sigma_S}{\partial T} \right) \right|$$

(ii) Whatever else may be important for thermophoresis of large solid particles in liquids, the magnitude of the surface tension force is very roughly comparable to the experimental force, and thus cannot be ignored in any complete theory.

Turning to the less numerical aspects of the expression for  $\alpha$ , Eq. (59), note that  $\alpha$  was originally defined to be more or less independent of the important parameters  $\eta$ ,  $a$ , etc., MM concluded that  $\alpha$  was in fact independent of these parameters. This contrasts with the  $a/\eta^2$  dependence of Eq. (59), which arises from the unusual  $a^2\eta^0$  dependence of the surface tension force. The  $a$  dependence is especially striking. All theories in current usage<sup>(7)</sup> predict that the force varies as  $a^2$  in gases and as  $a$  in liquids. In liquids, the radius-squared surface tension force must become larger than the forces calculated by other means for sufficiently large particles. The most obvious conclusion is that the surface tension force is *dominant* for very large particles. Of course, the forces calculated separately need not add. The fact remains that the surface tension force, which makes perfect physical sense, varies as  $a^2$ . Any theory which purports to be valid for large particles, and which predicts  $Faa$ , must confront this point.

How might a complete theory be constructed? Within our approach, the next step is to incorporate surface transport. This will, of course, involve unknown coefficients, which is one reason why we have not done so herein. Perhaps, however, the surface transport coefficients can be related to quantities in other theories.

Another question is that of the role of “nonhydrodynamic” effects. We have tried to obtain the complete BC on the hydrodynamic equations. Thus, we should be able to obtain solutions of fluid flow problems, as the thermophoretic problem, very accurately. Small errors will exist, nevertheless, due to the truncation of the gradient and multipole expansions. Such errors are negligible in, e.g., Stokes’ problem. Suppose, however, that the thermophoretic force is, in some sense, “small.” The errors may then contribute to  $\mathbf{F}$ , constituting the “nonhydrodynamic” force. These ideas should be more precisely formulated, but, in any event, the results of a full hydrodynamic calculation will be interesting.

## 6. SUMMARY AND DISCUSSION

We have given the BC at a flat wall based upon the method of Ronis and Oppenheim. The most fundamental statement of these BC is just the

usual one—zero normal velocity, zero tangential stress, and zero normal heat flux. However, the usual relations between the stress and heat flux, and the fluid fields, are modified by inclusion of surface transport coefficients and surface thermodynamics. The transport terms can only be given formally, which nevertheless seems, at least for the sake of completeness, worthwhile. The contribution of surface thermodynamics to the BC can, on the other hand, be expressed in terms of thermodynamic derivatives of the wall-liquid surface tension.

The new BC allow a nontrivial hydrodynamic calculation of the thermophoretic force. For the resulting expression, Eq. (57), to be valid, the fluid should indeed act as a continuum, that is, a liquid is indicated. We have made an attempt to estimate  $\partial\sigma_{\text{SL}}/\partial T$  and compare theory and experiment. No quantitative conclusions can be drawn, but, clearly, surface tension cannot be ignored in any complete theory of thermophoresis in liquids. For what it is worth, the calculated force is in fair agreement with MM's experiment on hexane.

## REFERENCES

- 1a. D. Ronis, D. Bedeaux, and I. Oppenheim, *Physica* **90A**:487 (1978).
- 1b. D. Ronis and I. Oppenheim, preprints.
- 1c. M. Jhon, R. Desai, and J. Dahler, *J. Chem. Phys.* **68**:5615 (1978); **70**:1544 (1979); *Advances in Chemical Physics*, Vol. XLVI, 279 (1981).
- 1d. M. Baus and C. Tejero, *Chem. Phys. Lett.* **84**:222 (1981).
- 1e. D. Ronis, J. Kovac, and I. Oppenheim, *Physica* **88A**:215 (1977); D. Ronis and I. Oppenheim, *Physica* **86A**:475 (1977).
2. J. Percus, in *The Liquid State of Matter*, E. Montroll and J. Lebowitz, eds. (North-Holland, Amsterdam, 1982).
3. H. Mori, *Prog. Theor. Phys.* **33**:423 (1965).
4. J. Hynes, R. Kapral, and M. Weinberg, *J. Chem. Phys.* **67**:3256 (1978).
- 5a. B. Felderhof and I. Oppenheim, *Physica* **31**:1441 (1965).
- 5b. J. Weare and I. Oppenheim, *Physica* **72**:20 (1974).
6. L. Landau and E. M. Lifschitz, *Fluid Mechanics* (Addison-Wesley, Reading, Massachusetts, 1959).
- 7a. I. Goldhirsch and D. Ronis, preprints.
- 7b. L. Waldmann, *Z. Naturforschung* **14A**:589 (1959); E. Mason and S. Chapman, *J. Chem. Phys.* **36**:627 (1962).
- 7c. P. Epstein, *Z. Phys.* **54**:437 (1929); J. Brock, *J. Coll. Sci.* **17**:768 (1962).
8. G. McNab and A. Meisen, *J. Coll. Int. Sci.* **44**:339 (1973).
9. A. Adamson, *Physical Chemistry of Surfaces*, 3rd ed. (Wiley, New York, 1976).
10. N. Vargafsik, *Tables on the Thermophysical Properties of Liquids and Gases* (Hemisphere, Washington, D.C., 1975).