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Long-Range Boundary Effects in Simple Fluids

J. C. Nieuwoudt,[1] T. R. Kirkpatrick,[2] and J. R. Dorfman[2]

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We discuss long-range boundary effects in simple two- or three-dimensional fluids. These boundary effects are due to the existence of long-range correlations in nonequilibrium fluids and can be computed either by means of kinetic theory or phenomenological mode-coupling theories. In particular, we use kinetic theory to compute the stress tensor and heat flux vector for a fluid in a nonequilibrium steady state in a finite geometry and show that both the effective shear viscosity and effective heat conductivity have contributions due to the walls of the container that influence the behavior of the system far into the fluid. We also show that the mechanocaloric effect is present in the bulk of a three-dimensional fluid and that there are normal stresses in a fluid whenever the temperature gradient is nonzero.

KEY WORDS: Kinetic theory; mode coupling theory; long-range correlations; boundary effects.

1. INTRODUCTION

In 1974 Wolynes[(1)] used nonlinear fluctuating hydrodynamic equations to discuss long-range boundary effects in a simple three-dimensional fluid subject to a steady shear, i.e., planar Couette flow. He found that due to mode-coupling effects the influence of the walls of the system are felt far into the bulk of the fluid. In fact, he found that in three dimensions (3d) the effects of the walls decay only as the inverse square root of the distance from the walls. Further, he showed that the coefficient of this long-range effect is very small.

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[1] Department of Chemistry, University of Rochester, Rochester, New York 14627.
[2] Institute for Physical Science and Technology, and Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742.

In this paper we use the kinetic theory of moderately dense gases to discuss similar long-range boundary effects. We will rederive the results of Wolynes from this microscopic approach and also extend his work in a number of interesting directions. We consider a moderately dense gas in either two or three dimensions confined between two parallel plates, of infinite extent, located at $y = 0$ and $y = D$. In this system we will impose a steady shear and temperature gradient by moving one of the plates relative to the other and also heating one of the plates relative to the other (cf. Fig. 1). For this system we will compute both the stress tensor and heat flux in d dimensions and show that the effective shear viscosity and heat conductivity have contributions due to the walls which extend far into the bulk of the fluid. The transport coefficients then can be expressed as the sum of two terms, a bulk contribution, η and λ, and a contribution due to the walls, η_w and λ_w. In three dimensions the contributions η_w and λ_w decay as the inverse square root of the distance from the walls. In two dimensions η_w and λ_w grow logarithmically as one moves into the bulk of the fluid, so that for sufficiently large distances these logarithmic terms begin to dominate what are usually called the bulk values of the transport coefficients. For these distances our calculations are no longer valid and must be extended. In this paper we will also show that in three dimensions a mechanocaloric effect[2] exists far into the fluid. That is, a heat flow exists even in the absence of a temperature gradient when there is a velocity gradient in the fluid. Such an effect is known to occur in kinetic boundary layers,[2] but we believe that this is the first time that the mechanocaloric effect has been shown to exist deep into the bulk of a fluid. Further, we will show that even

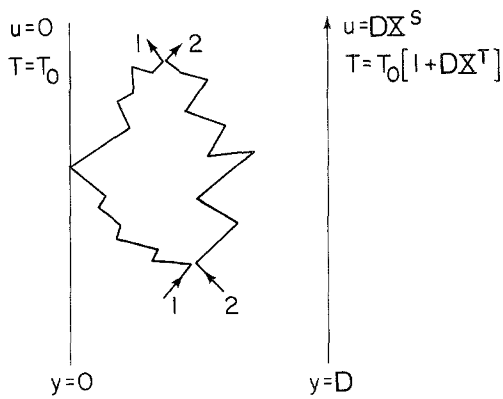

Fig. 1. Parallel plate geometry with a velocity, **u**, and temperature, T, gradient. A typical ring collision event between particles 1 and 2 is also illustrated.

when the velocity gradients are zero there can be normal stresses in a fluid due to a temperature gradient.

The long-range boundary effects discussed above are due to the fact that the nonequilibrium pair correlation function is of long range.[3,4] These long-range correlations are caused by mode-coupling contributions and have been discussed elsewhere[3–5,7] in several different contexts. Here we discuss these long-range correlations in fluids of finite extent.

It should be remarked that although we will present our calculations for a moderately dense gas, all of our final results will be quoted for general fluid densities since we have also derived them using a hydrodynamic mode-coupling theory.[6] For liquid densities we shall find that the effects we calculate are not small for two-dimensional fluids and that they may be of relevance in experiments.

The plan of this paper is as follows. In Section 2 we give the kinetic equations needed to describe a moderately dense gas in a nonequilibrium steady state in the presence of walls. In Section 3 we formally define the macroscopic functions of interest in terms of the single-particle distribution function, f_1, and in terms of the nonequilibrium pair correlation function, G_2. In Section 4 we discuss the equilibrium hydrodynamic modes of the linearized inhomogenous Boltzmann operator for finite geometries. These modes are needed to evaluate G_2 and calculate the long-range boundary effects. In Section 5 the boundary effects are calculated using the results of Section 4. The main results of this paper can be found in this section. In Section 6 we discuss the effects of the long-range boundary effects on the hydrodynamic state of the fluid. Finally, in Section 7 we make some concluding remarks and discuss the relation between the mode-coupling effects calculated here and those previously calculated. In this section we also comment on the experimental relevance of our results.

2. THE KINETIC EQUATIONS

In this section we present the basic kinetic equations needed to describe a moderately dense gas in a nonequilibrium steady state in the presence of walls.

We begin by considering a classical system of N identical particles each of mass m contained in a two- or three-dimensional volume Ω. We first define the microscopic one- and two-particle densities

$$f(1) = \sum_{i=1}^{N} \delta(1 - x_i) \tag{2.1a}$$

$$f(12) = \sum_{i \neq j}^{N} \delta(1 - x_i)\delta(2 - x_j) \tag{2.1b}$$

In Eq. (2.1) $1 \equiv (\mathbf{R}_1, \mathbf{V}_1)$ is a particular point in μ space, $x_i = (\mathbf{r}_i, \mathbf{v}_i)$ is the phase of particle i, and the sum is over the number of particles N, in a volume Ω.

In the course of our calculations, we will consider fluids that are of finite extent in only one of the spatial directions (cf. Fig. 1). For this case the limit $N, \Omega \to \infty$, $N/\Omega = n$ is to be used. All the physical quantities of interest can be related to the one- and two-particle distribution functions defined by

$$\begin{aligned} f_1(1) &= \left\langle \sum_{i=1}^{N} \delta(1 - x_i) \right\rangle_{\text{ss}} \\ f_2(12) &= \left\langle \sum_{i \neq j}^{N} \delta(1 - x_i)\delta(2 - x_j) \right\rangle_{\text{ss}} \end{aligned} \tag{2.2}$$

where $\langle \ \rangle_{\text{ss}}$ denotes a steady state ensemble average. Of particular interest is the pair correlation function defined by

$$G_2(12) \equiv f_2(12) - f_1(1) f_1(2) \tag{2.3}$$

On the basis of the methods developed by Ernst and Dorfman,[7] Krommes and Oberman,[8] Ernst *et al.*,[5] Ernst and Cohen,[9] and Dorfmand and van Beijeren[10] kinetic equations for $f_1(1)$ and $G_2(12)$ of a moderately dense gas in a nonequilibrium steady state in the presence of walls can be derived without difficulty.[11] The one-particle distribution function satisfies the equation

$$\mathbf{V}_1 \cdot \frac{\partial}{\partial \mathbf{R}_1} f_1(1) = \int d2\, \hat{T}(12)\left[f_1(1) f_1(2) + G_2(12) \right] + \bar{T}_w(1) f_1(1) \tag{2.4a}$$

For a moderately dense gas, $G_2(12)$ satisfies the equation

$$\left[\bar{L}_{\text{ss}}(1) + \bar{L}_{\text{ss}}(2) \right] G_2(12) = \hat{T}(12) f_1(1) f_1(2) \tag{2.4b}$$

In Eq. (2.4b) $\bar{L}_{\text{ss}}(1)$ is a linear kinetic operator defined by

$$\bar{L}_{\text{ss}}(1) = \mathbf{V}_1 \cdot \frac{\partial}{\partial \mathbf{R}_1} - \int d3\, \hat{T}(13)(1 + P_{13}) f_1(3) - \bar{T}_w(1) \tag{2.5a}$$

with $\hat{T}(13)$ the point binary collision operator:[7]

$$\begin{aligned} \hat{T}(13) &= \delta(\mathbf{R}_1 - \mathbf{R}_3) T_0(13) \\ &= \delta(\mathbf{R}_1 - \mathbf{R}_3) \int_0^{2\pi} d\epsilon \int_0^a db\, b |\mathbf{V}_1 - \mathbf{V}_3| (b_\sigma - 1) \end{aligned} \tag{2.5b}$$

where (b, ϵ) are, respectively, the impact parameter and azimuthal angle of the binary collision between two particles with velocities $\mathbf{V}_1, , \mathbf{V}_3$, a is the range of the interparticle forces, and b_σ is an operator that replaces the velocities $\mathbf{V}_1$ and $\mathbf{V}_3$ by the velocities of restituting collisions, $\mathbf{V}_1'$ and $\mathbf{V}_3'$.

Further, P_{13} in Eq. (2.5a) is a permutation operator that permutes the indices 1 and 3. $\bar{T}_w(1)$ in Eqs. (2.4a) and (2.5a) is a wall–particle collision operator that takes into account the change in the distribution functions due to collisions of the particles with the walls. Under quite general conditions it has been shown[10] that when $\bar{T}_w(1)$ acts on a function $h(1)$ the result is given by

$$\begin{aligned}\bar{T}_w(1)h(1) = \int d\mathbf{w}\, \delta(\mathbf{R}_1 - \mathbf{R}_w) \\ \times \Big\{ \theta(\mathbf{V}_1 \cdot \hat{\mathbf{n}}) \int d\mathbf{V}_1'\, \theta(-\mathbf{V}_1' \cdot \hat{\mathbf{n}}) |\mathbf{V}_1 \cdot \hat{\mathbf{n}}| K(\mathbf{V}_1, \mathbf{V}_1') h(\mathbf{R}_1, \mathbf{V}_1') \\ - \theta(-\mathbf{V}_1 \cdot \hat{\mathbf{n}}) |\mathbf{V}_1 \cdot \hat{\mathbf{n}}| h(1) \Big\} \end{aligned} \tag{2.5c}$$

where $\mathbf{R}_w$ denotes the position of a point on the walls, $\int d\mathbf{w}$ indicates an integral over the wall surfaces, $\theta(x) = 1$ for $x > 0$ and is zero otherwise, $\hat{\mathbf{n}}$ is a unit vector normal to the wall pointing into the fluid, and $K(\mathbf{V}_1, \mathbf{V}_1')$ is a scattering kernel which specifies the interaction mechanism between the walls and the gas particles. Explicit examples of $K(\mathbf{V}_1, \mathbf{V}_1')$ will be given further on.

The structure of the kinetic equations given by Eqs. (2.4) and (2.5) is relatively easy to understand. We have used the BBGKY hierarchy equations for the distribution functions in the presence of walls and neglected the three-particle correlation function.[3] In doing this we have obtained not only the Boltzmann equation, obtained by neglecting $G_2(12)$ in Eq. (2.4a), but corrections to it also. Although the corrections that arise from the $G_2(12)$ in Eq. (2.4a) are of higher order in the density, they are important since they lead to the long-range boundary effects discussed in Section 1. The dynamical events that are taken into account by the approximation given by Eq. (2.4b) for $G_2(12)$ are the so-called ring collision events.[12] An example of a ring collision is given in Fig. 1 where two particles, say 1 and 2, collide and then undergo a number of other collisions with other particles, or the walls, before colliding again.

3. FORMAL SOLUTIONS TO THE KINETIC EQUATIONS

In this section we construct formal solutions to our kinetic equations to first order in the macroscopic gradients and relate the stress tensor and heat flux to simple velocity moments of the one-particle distribution function. In the following two sections of this paper we will explicitly evaluate these formal expressions.

[3] We have also neglected a class of dynamical events known as the repeated ring events. As discussed elsewhere[7,12] this is consistent to the order of density considered here.

It should be remarked that although many of the formal manipulations used here are valid for fluids close to local equilibrium, our eventual calculation of the long-range boundary effects will be restricted to fluids close to thermal equilibrium (see Section 7(2) for a discussion). That is, our explicit results will be valid only to first order in the deviations from total equilibrium.

To solve Eqs. (2.4) we shall use a generalized Chapman–Enskog solution method. Since $f_1(1)$ and $G_2(12)$ vanish outside the fluid volume, we write[10]

$$\begin{aligned} f_1(1) &= W(\mathbf{R}_1)\tilde{f}_1(1) \\ G_2(12) &= W(\mathbf{R}_1)W(\mathbf{R}_2)\tilde{G}_2(12) \end{aligned} \tag{3.1a}$$

Here $W(\mathbf{R}_1)$ is a characteristic function that vanishes when $\mathbf{R}_1$ is outside the fluid volume Ω:

$$\begin{aligned} W(\mathbf{R}_1) &= 1 \qquad \text{if} \quad \mathbf{R}_1 \in \Omega \\ &= 0 \end{aligned} \tag{3.1b}$$

Inserting the Eqs. (3.1a) into Eq. (2.4a) and assuming that $\tilde{f}_1(1)$ and $\tilde{G}_2(12)$ are continuous at the walls we obtain a single equation which contains terms that are continuous at the walls and those that are not. It then follows that the continuous and discontinuous terms must vanish separately. Physically this is equivalent to requiring that there be no sources or sinks of particles at the walls.[10] The resulting two equations are

$$\mathbf{V}_1 \cdot \frac{\partial}{\partial \mathbf{R}_1} \tilde{f}(1) = \int d2\, \hat{T}(12)[\tilde{f}_1(1)\tilde{f}_1(2) + \tilde{G}_2(12)] \tag{3.2a}$$

and

$$\begin{aligned} &T_w(1)\tilde{f}_1(1) \\ &\quad \equiv \int d\mathbf{w}\, \theta(\mathbf{V}_1 \cdot \hat{\mathbf{n}})\delta(\mathbf{R}_1 - \mathbf{R}_w) \\ &\qquad \times \left\{ \int d\mathbf{V}_1'\, \theta(-\mathbf{V}_1' \cdot \hat{\mathbf{n}})|\mathbf{V}_1 \cdot \hat{\mathbf{n}}| K(\mathbf{V}_1, \mathbf{V}_1')\tilde{f}_1(\mathbf{R}_1, \mathbf{V}_1') - |\mathbf{V}_1 \cdot \hat{\mathbf{n}}|\tilde{f}_1(1) \right\} \\ &\quad = 0 \end{aligned} \tag{3.2b}$$

The Eq. (3.2b) can be used to determine boundary conditions on $\tilde{f}_1(1)$.[10]

A similar procedure with Eqs. (2.4b) and (3.1a) yields

$$[L_{ss}(1) + L_{ss}(2)]\tilde{G}_2(12) = \hat{T}(12)\tilde{f}_1(1)\tilde{f}_1(2) \tag{3.3a}$$

and

$$T_w(1)\tilde{G}_2(12) = 0 = T_w(2)\tilde{G}_2(12) \tag{3.3b}$$

In Eq. (3.3a) $L_{ss}(1)$ is given by

$$L_{ss}(1) = \mathbf{V}_1 \cdot \frac{\partial}{\partial \mathbf{R}_1} - \int d3\, \hat{T}(13)(1 + P_{13})\tilde{f}_1(3) \tag{3.3c}$$

We are interested in the behavior of the functions $\tilde{f}_1(1)$ and $\tilde{G}_2(12)$ for systems where there are small gradients in the local variables—the number density n, the temperature $T = (k_B\beta)^{-1}$, where k_B is Boltzmann's constant, and local velocity $\mathbf{u}$. The lowest-order approximation for $\tilde{f}_1(1)$ is the local Maxwellian:

$$f_l(1) = n(\mathbf{R}_1)\left[\frac{\beta(\mathbf{R}_1)m}{2\pi}\right]^{d/2} \exp\left\{-\frac{\beta(\mathbf{R}_1)m}{2}\left[\mathbf{V}_1 - \mathbf{u}(\mathbf{R}_1)\right]^2\right\} \quad (3.4)$$

while $\tilde{G}_2(12)$ vanishes to lowest order in the gradient. The vanishing of $\tilde{G}_2(12)$ to lowest order follows since $\hat{T}(12)f_l(1)f_l(2) = 0$ [cf. Eq. (3.3a)].[4]

Using that we are interested in $\tilde{f}_1(1)$ for small gradients and that $\tilde{G}_2(12)$ in Eq. (3.2a) leads to terms that are one higher order in the density than the Boltzmann equation contribution, we write $\tilde{f}_1(1)$ as

$$\tilde{f}_1(1) = f_l(1) + f_{\nabla_1}^{(B)}(1) + \delta f_{\nabla_1}(1) + \cdots \quad (3.5)$$

Here $f_{\nabla_1}^{(B)}(1)$ is the first gradient correction to $f_l(1)$ that follows from the Boltzmann equation, obtained by neglecting $\tilde{G}_2(12)$ in Eq. (3.2a), and $\delta f_{\nabla_1}(1)$ is the first gradient correction to $\tilde{f}_1(1)$ from $\tilde{G}_2(12)$. Using the Chapman–Enskog solution method and Eqs. (3.2a), (3.4), and (3.5) we obtain[10]

$$f_{\nabla_1}^{(B)}(1) = \frac{1}{\Lambda_l(1)} f_l(1)\beta m\left[C_{1\alpha}C_{1\beta} - \frac{\delta_{\alpha\beta}C_1^2}{d}\right]\frac{\partial u_\alpha}{\partial R_{1\beta}}$$
$$+ \frac{1}{\Lambda_l(1)} f_l(1)\left[\frac{\beta m C_1^2}{2} - \frac{d+2}{2}\right]C_{1\alpha}\frac{\partial \log T}{\partial R_{1\alpha}} \quad (3.6a)$$

and

$$\Lambda_l(1)\delta f_{\nabla_1}(1) = -\int d2\,\hat{T}(12)\tilde{G}_2(12) \quad (3.6b)$$

In the Eq. (3.6a), $\mathbf{C}_1(\mathbf{R}_1) = \mathbf{V}_1 - \mathbf{u}(\mathbf{R}_1)$ and $\Lambda_l(1)$ is a local linear collision operator defined by

$$\Lambda_l(1) = \int d3\,\hat{T}(13)(1 + P_{13})f_l(3) \quad (3.6c)$$

The dissipative contributions to the stress tensor, $\mathbf{P}$, and heat flux, $\mathbf{Q}$, are given in terms of $\tilde{f}_1(1)$ by[10]

$$P_{\alpha\beta}(\mathbf{B}_1) = m\int d\mathbf{V}_1\left(C_{1\alpha}C_{1\beta} - \frac{\delta_{\alpha\beta}C_1^2}{d}\right)\left[f_{\nabla_1}^{(B)}(1) + \delta f_{\nabla_1}(1)\right]$$
$$\equiv P_{\alpha\beta}^{(B)}(\mathbf{R}_1) + \delta P_{\alpha\beta}(\mathbf{R}_1) \quad (3.7a)$$

[4] The use of point $\hat{T}(12)$ operators is consistent to the orders of density considered here.[5]

and

$$Q_\alpha(\mathbf{R}_1) = \int d\mathbf{V}_1 \, C_{1\alpha}\left(\frac{mC_1^2}{2} - \frac{d+2}{2\beta}\right)\left[f_{\mathbf{V}_1}^{(B)}(1) + \delta f_{\mathbf{V}_1}(1)\right]$$

$$\equiv Q_\alpha^{(B)}(\mathbf{R}_1) + \delta Q_\alpha(\mathbf{R}_1) \tag{3.7b}$$

The Boltzmann contributions to the stress tensor and heat flux can be written as[10]

$$P_{\alpha\beta}^{(B)}(\mathbf{R}_1) = -\eta_B\left[T(\mathbf{R}_1)\right]\Delta_{\alpha\beta,\gamma\nu}\frac{\partial u_\gamma}{\partial R_{1_\nu}} \tag{3.8a}$$

and

$$Q_\alpha^{(B)}(\mathbf{R}_1) = -\lambda_B\left[T(\mathbf{R}_1)\right]\frac{\partial T}{\partial R_{1\alpha}} \tag{3.8b}$$

where $\Delta_{\alpha\beta,\gamma\nu} \equiv [\delta_{\alpha\gamma}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\gamma} - (2/d)\delta_{\alpha\beta}\delta_{\gamma\nu}]$ and η_B, λ_B are the low density, Boltzmann, value of the shear viscosity and heat conductivity[10] and the summation convention has been used in Eq. (3.8).

Using Eqs. (3.6b) and (3.7) the contributions from $\tilde{G}_2(12)$ to $P_{\alpha\beta}$ and Q_α are

$$\delta P_{\alpha\beta}(\mathbf{R}_1) = -m\int d\mathbf{V}_1 \int d2\left(C_{1\alpha}C_{1\beta} - \frac{\delta_{\alpha\beta}C_1^2}{d}\right)\frac{1}{\Lambda_l(1)}\hat{T}(12)\tilde{G}_2(12) \tag{3.9a}$$

and

$$\delta Q_\alpha(\mathbf{R}_1) = -\int d\mathbf{V}_1 \int d2 \, C_{1\alpha}\left(\frac{mC_1^2}{2} - \frac{d+2}{2\beta}\right)\frac{1}{\Lambda_l(1)}\hat{T}(12)\tilde{G}_2(12) \tag{3.9b}$$

From the Eqs. (3.3a), (3.4), (3.5), and (3.6a) and the fact that we are interested in $\delta P_{\alpha\beta}$ and δQ_α to first order in the deviations from total equilibrium and in $\tilde{G}_2(12)$ it follows that a consistent $\tilde{G}_2(12)$ is given by

$$\begin{aligned}\tilde{G}_2(12) = {} & \left[L_{\text{eq}}(1) + L_{\text{eq}}(2)\right]^{-1}\hat{T}(12)(1 + P_{12})f_{\text{eq}}(2) \\ & \times\left\{\frac{1}{\Lambda_{\text{eq}}(1)}f_{\text{eq}}(1)\beta m\left[V_{1\alpha}V_{1\beta} - \frac{\delta_{\alpha\beta}V_1^2}{d}\right]\frac{\partial u_\alpha}{\partial R_{1\beta}}\right. \\ & \left. + \frac{1}{\Lambda_{\text{eq}}(1)}f_{\text{eq}}(1)\left[\frac{\beta m V_1^2}{2} - \frac{d+2}{2}\right]V_{1\alpha}\frac{\partial \log T}{\partial R_{1\alpha}}\right\}\end{aligned} \tag{3.10a}$$

where we have consistently replaced $C_{1\alpha}$ by $V_{1\alpha}$ and $f_l(1)$ by the total equilibrium Maxwellian,

$$f_{\text{eq}}(1) = n\left(\frac{\beta m}{2\pi}\right)^{d/2}\exp -\left[\frac{\beta m V_1^2}{2}\right] \tag{3.10b}$$

In Eq. (3.10a), $L_{eq}(1)$ is the inhomogenous Boltzmann operator,

$$L_{eq}(1) = \mathbf{V}_1 \cdot \frac{\partial}{\partial \mathbf{R}_1} - \Lambda_{eq}(1) \tag{3.10c}$$

with $\Lambda_{eq}(1)$ the linearized Boltzmann operator given by

$$\Lambda_{eq}(1) = \int d3\, \hat{T}(13)(1 + P_{13}) f_{eq}(3) \tag{3.10d}$$

Further, in Eqs. (3.9) we should consistently replace $C_{1\alpha}$ by $V_{1\alpha}$ and $\Lambda_l(1)$ by $\Lambda_{eq}(1)$.

It should be remarked that the only position dependence in the transport coefficients in Eqs. (3.8) is through the temperature field and that this position dependence can be neglected to first order in the deviations from total equilibrium. In Section 5 we shall show that $\delta P_{\alpha\beta}$ and δQ_α have an additional, explicit, position dependence due to the presence of the walls of the system.

4. HYDRODYNAMIC MODES OF THE INHOMOGENOUS BOLTZMANN OPERATOR

4.1. Formulation of the Problem

In order to explicitly evaluate Eq. (3.10a), supplemented by the boundary conditions given by Eq. (3.3b), we need to solve the eigenvalue problem,

$$\left[L_{eq}(1) - \bar{T}_w(1) \right] f_{eq}(1) \Theta_j^R = \omega_j f_{eq}(1) \Theta_j^R(1) \tag{4.1a}$$

Here Θ_j^R is the right eigenfunction, there is a left or adjoint eigenvalue problem also, ω_j is the eigenvalue, j is a general eigenfunction index that can represent both discrete and continuous indices, and the factor $f_{eq}(1)$ has been inserted for convenience. By explicitly using the wall operator, $\bar{T}_w(1)$, in Eq. (4.1) the boundary conditions given by Eq. (3.3b) will be automatically satisfied if we write

$$\Theta_j^R(1) = W(\mathbf{R}_1) \tilde{\Theta}_j^R(1) \tag{4.1b}$$

and require $\tilde{\Theta}_j^R(1)$ to be continuous at the walls. Before defining the adjoint or left eigenvalue problem, we discuss how to calculate Θ_j^R and ω_j.

Physically it is reasonable to assume that the long-range boundary effects in $\tilde{G}_2(12)$ are due to the long wavelength or hydrodynamic modes of Eq. (4.1a). These hydrodynamic modes are characterized by the fact that for long wavelengths their eigenvalues vanish. In the course of our calculations we show that the vanishing of these hydrodynamic eigenvalues is the mechanism responsible for the long-range boundary effects. From this it follows that the nonhydrodynamic modes can be neglected here.

Recently Kirkpatrick and Cohen[4] showed how to calculate the hydrodynamic modes of Eqs. (4.1), and here we will only state their main results. The eigenfunction $\tilde{\Theta}_j^R(1)$ can be written

$$\tilde{\Theta}_j^R(1) = \frac{\hat{\rho}_j}{m}(\mathbf{R}_1) + \beta m V_{1\nu}\hat{p}_{j\nu}(\mathbf{R}_1) + \frac{n}{T}\left(\frac{\beta m}{2}V_1^2 - \frac{3}{2}\right)\hat{T}_j(\mathbf{R}_1) + O(l/L) \tag{4.2}$$

where l is the mean free path of the particles in the gas and L is the characteristic distance over which $\tilde{\Theta}_j^R(1)$ varies. This implies that Eq. (4.2) is a valid representation of $\tilde{\Theta}_j^R$ as long as $l/L \ll 1$. The position dependent expansion parameters, $\hat{\rho}_j(\mathbf{R}_1)$, $\hat{p}_{j\nu}(\mathbf{R}_1)$ and $\hat{T}_j(\mathbf{R}_1)$, in Eq. (4.2) satisfy the linearized hydrodynamic equations for the set of time-dependent variables of the form $e^{-\omega_j t}\{\hat{\rho}_j, \hat{p}_{j\nu}, \hat{T}_j\}$. These are

$$-\omega_j\hat{\rho}_j(\mathbf{R}_1) = \frac{\partial}{\partial R_{1\nu}}\hat{p}_{j\nu}(\mathbf{R}_1) \tag{4.3a}$$

$$-\omega_j\hat{p}_{j\alpha}(\mathbf{R}_1) = -\frac{\partial}{\partial R_{1\alpha}}\left\{nK_B\hat{T}_j(\mathbf{R}_1) + \frac{K_B T}{m}\hat{\rho}_j(\mathbf{R}_1)\right\} + \nu_B\frac{\partial^2}{\partial R_{1\beta}\partial R_{1\gamma}}\Delta_{\alpha\beta,\gamma\nu}\hat{p}_{j\nu}(\mathbf{R}_1) \tag{4.3b}$$

$$-\omega_j\frac{d}{2}nk_B\hat{T}_j(\mathbf{R}_1) = -\frac{k_B T}{m}\frac{\partial}{\partial R_{1\nu}}\hat{p}_{j\nu}(\mathbf{R}_1) + \lambda_B\frac{\partial^2}{\partial R_{1\alpha}\partial R_{1\alpha}}\hat{T}_j(\mathbf{R}_1) \tag{4.3c}$$

where $\nu_B = \eta_B/mn$ is the kinematic viscosity.

The hydrodynamic equations given by Eqs. (4.3c) must be supplemented by boundary conditions that can be explicitly determined by specifying the scattering kernel $K(\mathbf{V}_1, \mathbf{V}_1')$ in Eq. (2.5c).[4] In this paper we consider only two possible forms of $K(\mathbf{V}_1, \mathbf{V}_1')$[10]; (i) specular reflection model where the gas particles are elastically reflected by the walls so that

$$K(\mathbf{V}_1, \mathbf{V}_1') = \delta(\mathbf{V}_1' - \mathbf{V}_1 + 2\hat{\mathbf{n}}(\hat{\mathbf{n}}\cdot\mathbf{V}_1')) \tag{4.4a}$$

(ii) Diffusive reflection model where the particles are absorbed by the walls and then reemitted with a velocity determined by a Maxwell distribution with a temperature $T_w = (k_B\beta_w)^{-1}$ of the wall,

$$K(\mathbf{V}_1, \mathbf{V}_1') = |\mathbf{V}_1'\cdot\hat{\mathbf{n}}|(2\pi m\beta_w)^{1/2}\left(\frac{m\beta_w}{2\pi}\right)^{d/2}\exp\left\{-m\frac{[\mathbf{V}_1 - \mathbf{u}(\mathbf{R}_w)]^2}{2K_B T_w}\right\} \tag{4.4b}$$

where $\mathbf{u}(\mathbf{R}_w)$ is the velocity of the wall. The boundary conditions that follow from these scattering kernels for the specular reflection model for the geometry given in Fig. (1) are

$$\hat{P}_{jy}(R_w) = 0$$

$$\frac{\partial \hat{T}_j}{\partial y_1}(\mathbf{R}_1)\bigg|_{\mathbf{R}_1=\mathbf{R}_w} = 0 \tag{4.5a}$$

$$\frac{\partial \hat{p}_{jz}}{\partial y_1}(\mathbf{R}_1)\bigg|_{\mathbf{R}_1=\mathbf{R}_w} = 0 = \frac{\partial \hat{p}_{jx}}{\partial y_1}(\mathbf{R}_1)\bigg|_{\mathbf{R}_1=\mathbf{R}_w}$$

with $\mathbf{R}_w = (x_1, 0, z_1)$ and (x_1, D, z_1). For the diffusive reflection model one obtains

$$\hat{p}_{j\nu}(\mathbf{R}_w) = 0$$
$$\hat{T}_j(\mathbf{R}_w) = 0 \tag{4.5b}$$

Similarly, the left eigenvalue problem can be defined and reexpressed in terms of the solution to hydrodynamic eigenvalue problem. Kirkpatrick and Cohen[10] show that the left eigenfunction, $\Theta_j^L(1)$, can be written

$$\Theta_j^L(1) = \frac{\hat{\rho}_j^+}{m}(\mathbf{R}_1) + \beta V_{1\nu}\hat{p}_{j\nu}^+(R_1) + n\frac{\hat{T}_j^+}{T}(\mathbf{R}_1)\left(\frac{\beta m}{2}V_1^2 - \frac{3}{2}\right) + O(l/L) \tag{4.6}$$

The expansion coefficients, $\hat{\rho}_j^+$, $\hat{p}_{j\nu}^+$ and $\hat{T}_j^+$ satisfy the Eqs. (4.3) and (4.5) except that $\partial/\partial\mathbf{R}_1$ should be replaced by $-\partial/\partial\mathbf{R}_1$. Further, the hydrodynamic modes satisfy the completeness and orthogonality conditions:

$$1 = \sum_j |\tilde{\Theta}_j^R(1))_{\text{eq}}(\Theta_j^L(1)| \tag{4.7a}$$

$$\left(\Theta_K^L(1) \mid \Theta_j^R(1)\right)_{\text{eq}} \equiv \int_\Omega d\mathbf{R}_1 \int d\mathbf{V}_1\, \Theta_K^L(1)\tilde{\Theta}_j^R(1)\phi_{\text{eq}}(1) = \delta_{jK} \tag{4.7b}$$

where $\phi_{\text{eq}}(1) = f_{\text{eq}}(1)/n$ and $\int_\Omega d\mathbf{R}_1$ indicates an integral over the volume of the fluid.

For infinite space the hydrodynamic modes that can be derived from Eqs. (4.1a), (4.2), (4.3), and (4.6) are well known.[12] There are $(d+2)$ of these modes: a heat mode (H), two sound modes $(\sigma = \pm 1)$, and $(d-1)$ viscous or shear modes (ν_i). Here we compute these modes for a fluid of finite extent.

4.2. The Hydrodynamic Modes for Slip Boundary Conditions

Although the diffusive or stick boundary conditions given by Eq. (4.5b) are the most realistic boundary conditions to use to solve the right and left eigenvalue problems, the slip boundary conditions given by Eq.

(4.5a) will be used in this paper. Elsewhere[11] it is shown that the long-range boundary effects computed here are insensitive to whether stick or slip boundary conditions are used in solving Eqs. (4.1). In three dimensions this follows because the long-range boundary effects are due to the sound modes and, outside a thin hydrodynamic viscous and thermal boundary layer $\sim d_\nu \equiv (\nu L/c)^{1/2}$, $d_T \equiv (D_T L/c)^{1/2} \sim 10^{-4}$–$10^{-5}$ cm,[5] the sound modes for slip and stick boundary conditions are identical.[6,11,13] Since we are interested in distances much greater than d_ν, d_T it is not surprising that the slip and stick boundary conditions give the same results for the long-range boundary effects. In two dimensions similar arguments lead to the same conclusions.

In d dimensions there are $(d+2)$ hydrodynamic modes and for slip boundary conditions they can be easily constructed. There are $d-1$ normalized viscous modes given by

$$\begin{aligned}\tilde{\Theta}^R_{\nu_1}(\mathbf{k}, 1) &= \left[\Theta^L_{\nu_1}(\mathbf{k}, 1)\right]^* \\ &= (2\pi)^{(1-d)/2}\left(\frac{2\beta m}{Dk_\parallel^2}\right)^{1/2} \exp\left(i\mathbf{k}_\parallel \cdot \mathbf{R}_{1_\parallel}\right) \\ &\quad \times \left\{ i\hat{k}_\parallel^2 V_{1y} \sin k_y y_1 - \hat{k}_y \hat{k}_\parallel \cdot \mathbf{V}_1 \cos k_y y_1 \right\} + O(kl) \end{aligned} \tag{4.8a}$$

and

$$\begin{aligned}\tilde{\Theta}^R_{\nu_2}(\mathbf{k}, 1) = \left[\Theta^L_{\nu_2}(\mathbf{k}, 1)\right]^* &= (2\pi)^{(1-d)/2}\left(\frac{2\beta m}{D\hat{k}_\parallel^2}\right)^{1/2} \exp\left[i\mathbf{k}_\parallel \cdot \mathbf{R}_{1_\parallel}\right]\hat{\mathbf{y}} \\ &\quad \times (\hat{\mathbf{k}}_\parallel \times \mathbf{V}_1)\cos k_y y_1 + O(kl)\end{aligned} \tag{4.8b}$$

with eigenvalues

$$\omega_{\nu_{1,2}} = \nu_B\left(k_\parallel^2 + k_y^2\right) \equiv \nu_B k^2 \tag{4.8c}$$

In Eqs. (4.8) for $d=3$ $(d=2)$, $\mathbf{k} = (k_x, k_y, k_z)$ $(\mathbf{k} = k_x, k_y)$, $\mathbf{k}_\parallel = (k_x, k_z)$ number, $(\mathbf{k}_\parallel = k_x\hat{\mathbf{x}})$, $\mathbf{R}_{1_\parallel} = (x_1, z_1)$ $(\mathbf{R}_{1\parallel} = x_1\hat{\mathbf{x}})$, $\hat{\mathbf{k}} = \mathbf{k}/k$, k_x and k_z (k_x) are

[5] From Eqs. (4.9) we see that the length scale $L \sim 1/k$ where k is the wave number of the hydrodynamic modes. Further, from the Eq. (5.5) we see that the important k values in determining the long range boundary effects is $k \sim \sqrt{c/\Gamma_{sy}}$. Using that $\nu, D_T, \Gamma_s \sim .1$ cm^2/sec for air at S.P.T. and $\nu \sim \Gamma_s \sim 10^{-2}$ cm^2/sec and $D_T \sim 10^{-3}$ cm^2/sec for water at 20°C we find $d_\nu, d_T \sim 10^{-4}$–10^{-5} cm.

continuous wave numbers $-\infty < k_x, k_z(k_x) < \infty$, and k_y is a discrete wave $k_y = n\pi/D$ ($n = 0, 1, 2, \ldots$). There are two sound modes given by ($\sigma = \pm 1$):

$$\begin{aligned}\tilde{\Theta}_\sigma^R(\mathbf{k}, 1) &= \left[\Theta_\sigma^L(\mathbf{k}, 1)\right]^* \\ &= (2\pi)^{(1-d)/2}\left[\frac{d}{D(d+2)}\right]^{1/2} \\ &\quad\times\left(\frac{\beta m}{d}V_1^2 + \hat{\mathbf{k}}_\parallel \cdot \mathbf{V}_{1_\parallel}\sigma\beta mc\cos k_y y_1 + \hat{k}_y V_{1y}\sigma\beta mci\sin k_y y_1\right) \\ &\quad + O(kl)\end{aligned} \tag{4.9a}$$

with eigenvalues given by

$$\omega_\sigma = i\sigma ck + \frac{\Gamma_{sB}}{2}k^2 \tag{4.9b}$$

where

$$\Gamma_{sB} = \frac{2(d-1)\nu_B}{d} + (\gamma - 1)D_{TB} \tag{4.9c}$$

In Eq. (4.9c) $D_{TB} = \lambda_B/\rho Cp$, $\rho = mn$, and $\gamma = C_p/C_v$ is the ratio of specific heats. Finally, there is a heat mode (H) given by

$$\begin{aligned}\tilde{\Theta}_H^R(\mathbf{k}, 1) &= \left[\Theta_H^L(\mathbf{k}, 1)\right]^* \\ &= (2\pi)^{(1-d)/2}\left[\frac{4}{D(d+2)}\right]^{1/2}\exp\left[i\mathbf{k}_\parallel \cdot \mathbf{R}_{1_\parallel}\right] \\ &\quad\times\left(\frac{\beta m}{2}V_1^2 - \frac{d+2}{2}\right)\cos k_y y_1 + O(kl)\end{aligned} \tag{4.10a}$$

with an eigenvalue

$$\omega_H = D_{TB}k^2 \tag{4.10b}$$

Further, an approximate completeness relation exist for these modes given by [cf. Eq. (4.7a)]

$$1 \simeq \sum_{j=\nu,H,\sigma}\sum_{k_y=n\pi/D}{}' \int' dk_\parallel \,|\tilde{\Theta}_j^R(\mathbf{k}, 1))_{\text{eq}}(\Theta_j^L(\mathbf{k}, 1)| \tag{4.11a}$$

and these modes satisfy the orthogonality condition

$$\left(\Theta_j^L(\mathbf{k}, 1)\,|\,\Theta_l^R(\mathbf{k}', 1)\right)_{\text{eq}} = \delta_{jl}\delta_{k_y,k_y'}\delta(\mathbf{k}_\parallel - \mathbf{k}_\parallel') \tag{4.11b}$$

In the Eq. (4.11a) the primes on the k_y sum and $\mathbf{k}_\parallel$ integral denote an ultraviolet cutoff, k_0, on the order of l^{-1} which is present due to the fact that we have used a hydrodynamic approximation in calculating the $\Theta_j^{R,L}$.

In the next section Eqs. (4.8), (4.9), (4.10), and (4.11) will be used to evaluate $\delta P_{\alpha\beta}$ and δQ_α given by Eqs. (3.4) and (3.10).

5. EVALUATION OF $\delta P_{\alpha\beta}$ AND δQ_α

To evaluate $\delta P_{\alpha\beta}$ and δQ_α given by Eq. (3.9) the pair correlation function $G_2(12)$ given by Eq. (3.10) is needed. Using Eq. (4.11a) in Eq. (3.10) yields $G_2(12)$. From this result and Eq. (3.9a), retaining terms to first order in the deviations from equilibrium only, we obtain

$$\delta P_{\alpha\beta}(y_1) = -m \sum_{j,l=\nu,N,\sigma} \sum_{k_y,k_y'}' \int' d\mathbf{k}_\parallel \int' d\mathbf{k}_\parallel' \int d\mathbf{V}_1 \int d2 \Bigg(V_{1\alpha}V_{1\beta} - \frac{\delta_{\alpha\beta}V_1^2}{d} \Bigg)$$
$$\times \frac{1}{\Lambda_{\text{eq}}(1)} \hat{T}(12) | |\tilde{\Theta}_j^R(\mathbf{k},1)\tilde{\Theta}_l^R(\mathbf{k}',2))_{\text{eq}} \frac{1}{[\omega_j(k)+\omega_l(k')]}$$
$$\times (\Theta_j^L(\mathbf{k},1)\Theta_l^L(\mathbf{k}',2) | |\hat{T}(12)(1+P_{12}) f_{\text{eq}}(2) \frac{1}{\Lambda_{\text{eq}}(1)} f_{\text{eq}}(1)$$
$$\times \Bigg[\beta m V_{1x} V_{1y} X^s + \Bigg(\frac{\beta m V_1^2}{2} - \frac{d+2}{2} \Bigg) V_{1y} X^T \Bigg] \Bigg) \Bigg) \qquad (5.1)$$

In giving Eq. (5.1) we have used (cf. Fig. 1) $\mathbf{u} = u_x(y_1)\hat{\mathbf{x}}$, $T = T(y_1)$ and denoted $\partial u_x/\partial y_1$ by X^s and $\partial \log T/\partial y_1$ by X^T. From identities like,[7]

$$\int d\mathbf{V}_1 \int d\mathbf{V}_2\, \Theta_j^L(\mathbf{k},1)\Theta_l^L(\mathbf{k}',2)\hat{T}(12)(1+P_{12}) f_{\text{eq}}(2) h(1)$$
$$= -\delta(\mathbf{R}_1 - \mathbf{R}_2) n \langle \Theta_j^L(\mathbf{k},1)\Theta_l^L(\mathbf{k}',1) \,|\, \Lambda_{\text{eq}}(1) h(1) \rangle_{\text{eq}}$$
$$+ O(kl, k'l) \qquad (5.2a)$$

where $h(1)$ is an arbitrary function and

$$\langle g(1) \,|\, h(1) \rangle_{\text{eq}} \equiv \int d\mathbf{V}_1\, g(1) h(1) \phi_{\text{eq}}(V_1) \qquad (5.2b)$$

we can write the Eq. (5.1) as

$$\delta P_{\alpha\beta}(y_1) = -\frac{m}{2} \sum_{j,l=\nu,H,\sigma} \sum_{k_y,k_y'} \int' d\mathbf{k}_\parallel \int' d\mathbf{k}_\parallel'$$
$$\times \Bigg\langle V_{1\alpha}V_{1\beta} - \delta_{\alpha\beta}\frac{V_1^2}{d} \Bigg| \tilde{\Theta}_j^R(\mathbf{k},1)\tilde{\Theta}_l^R(\mathbf{k}',1) \Bigg\rangle_{\text{eq}} [\omega_j(k)+\omega_l(k')]^{-1}$$
$$\times \int_\Omega d\mathbf{R}_1 \Bigg\langle \Theta_j^L(\mathbf{k},1)\Theta_l^L(\mathbf{k}',1) \,|$$
$$\times \Bigg[\beta m V_{1x} V_{1y} X^s + \Bigg(\frac{\beta m V_1^2}{2} - \frac{d+2}{2} \Bigg) V_{1y} X^T \Bigg] \Bigg\rangle_{\text{eq}} \qquad (5.3)$$

It should be remarked that the corrections to Eq. (5.2a) of $O(kl, k'l)$ can be neglected when computing the long-range boundary effects since they can be shown to lead to terms that decay faster than those retained as one moves away from the walls.

A similar expression for $\delta Q_\alpha(y_1)$ follows in an identical manner and it can be obtained from Eq. (5.3) by replacing $m(V_{1\alpha}V_{1\beta} - \delta_{\alpha\beta}V_{1/d}^2)$ in Eq. (5.3) by

$$V_{1\alpha}\left(\frac{mV_1^2}{2} - \frac{d+2}{2\beta}\right)$$

To proceed further we explicitly use that we are interested in boundary effects that exist far into the bulk of the fluid. That is, we fix the parallel plate at $y = 0$ in Fig. 1, let the separation, D, between the two plates tend to infinity, and examine the behavior of $\delta P_{\alpha\beta}(y_1)$ and $\delta Q_\alpha(y_1)$ for large y_1. With these approximations we can use the replacement

$$\frac{2}{D}\sum_{k_y} \rightarrow \frac{2}{\pi}\int_0^\infty dk_y \tag{5.4}$$

and evaluate Eq. (5.3) with the aid of Eqs. (4.8), (4.9), (4.10), and (5.4).

For three-dimensional fluids the crucial point in the evaluation of Eq. (5.3) for $\delta P_{\alpha\beta}(y_1)$, and the corresponding expression for $\delta Q_\alpha(y_1)$, when compared with the similar calculation in infinite space,[12] is that due to the presence of the wall at $y = 0$ the wave numbers $\mathbf{k}$ and $\mathbf{k}'$ in Eq. (5.3) no longer satisfy the spatial homogeneity condition $\mathbf{k}' = -\mathbf{k}$. That is, due to the wall at $y = 0$ one has instead $\mathbf{k}'_\parallel = -\mathbf{k}_\parallel$ and $k'_y = -k_y + O(1/y)$. Because of this feature the evaluation of the $(\sigma, -\sigma)$ sound-mode contribution in Eq. (5.3) will involve a wave number integral of the form

$$\begin{aligned}
&\int_0' dk\, k^{d-1} \frac{1}{i\sigma c(k-k') + \Gamma_s k^2 + \Gamma_s k(k-k')} \\
&\quad \cong \int_0' dk\, k^{d-1} \frac{1}{\Gamma_s k^2 + i\sigma c/y} \\
&\quad \cong O(1) + O(1/y^{1/2}) + \cdots \qquad \text{in 3d} \\
&\quad \cong O(\log y) \qquad \text{in 2d}
\end{aligned} \tag{5.5}$$

This incomplete cancellation of the propagating parts of the sound modes in the mode-coupling integrals in the Eq. (5.3) leads to the long-range boundary effects discussed in the introduction. Using similar ideas it follows that for three dimensions the remaining hydrodynamic mode combinations lead to less dominant long-range boundary effects.

In two-dimensional fluids the long-range boundary effects arise from contributions in Eq. (5.3) whose sums of eigenvalues $[\omega_j(k) + \omega_l(k')]$ is of $O(k^2)$ if $\mathbf{k}' = -\mathbf{k}$. That is, for the combinations $(\sigma, -\sigma)$, (ν, ν), (ν, D_T),

(D_T, ν) and (D_T, D_T). To see this one can use integral estimates in two dimensions like Eq. (5.5) for $k_x = -k'_x$, $k_y + k'_y \sim O(1/y)$.

The explicit evaluation of Eq. (5.3) for $\delta P_{\alpha\beta}(y_1)$ and the corresponding expression for $\delta Q_\alpha(y_1)$ is straightforward. For three-dimensional fluids we obtain

$$\begin{aligned}\delta P'_{xy}(y_1) &= \delta P_{xy}(y_1) - \delta P_{xy}(y_1 \to \infty)\\ &= \frac{X^s k_B T}{77\pi}\left(\frac{c}{\Gamma_s^3 \pi y_1}\right)^{1/2} + O\left(\frac{\log y_1}{y_1}\right)\end{aligned} \tag{5.6a}$$

and

$$\begin{aligned}\delta P_{yy}(y_1) - \delta P_{xx}(y_1) &= \delta P_{yy}(y_1) - \delta P_{zz}(y_1)\\ &= X^T \frac{k_B T}{30\pi}\left(\frac{c^3}{\Gamma_s^3 \pi y_1}\right)^{1/2} + O\left(\frac{\log y_1}{y_1}\right)\end{aligned} \tag{5.6b}$$

and

$$\delta Q_x(y_1) = \frac{X^s k_B T}{45\pi}\left(\frac{c^3}{\Gamma_s^3 \pi y_1}\right)^{1/2} + O\left(\frac{\log y_1}{y_1}\right) \tag{5.6c}$$

and

$$\begin{aligned}\delta Q'_y(y_1) &= \delta Q_y(y_1) - \delta Q_y(y_1 \to \infty)\\ &= \frac{X^T k_B T c}{14\pi}\left(\frac{c^3}{\Gamma_s^3 \pi y_1}\right)^{1/2} + O\left(\frac{\log y_1}{y_1}\right)\end{aligned} \tag{5.6d}$$

with all other $\delta P_{\alpha\beta}$ and δQ_α equal to zero. In giving these results we have subtracted the bulk contributions which are finite as $y_1 \to \infty$. These contributions yield finite renormalizations to the transport coefficients in Eq. (3.8).[12] Further, we have given only the differences in the normal stresses since they are the quantities of physical interest.

In the two-dimensional case we obtain

$$\delta P_{xy}(y_1) = -\frac{k_B T}{32\pi}\left(\frac{1}{\nu} + \frac{1}{\Gamma_s}\right) X^s \log(y_1/l) + O(y_1^0) \tag{5.7a}$$

$$\delta Q_y(y_1) = -\frac{k_B}{8\pi}\left(\frac{T C_p}{(\nu + D_T)} + \frac{c^2}{\Gamma_s}\right) X^T \log(y_1/l) + O(y_1^0) \tag{5.7b}$$

with all other $\delta P_{\alpha\beta}$ and δQ_α equal to zero to $O(\log y_1)$.

In Eqs. (5.6) and (5.7), $c = [(\partial p/\partial \rho)_s]^{1/2}$ is the speed of the sound with p the pressure and s the entropy density, $\Gamma_s = [2(d-1)/d]\nu + \zeta/\rho + (\gamma - 1)D_T$ is the sound damping constant with $\nu = \eta/\rho$ the kinematic viscosity, η the shear viscosity ζ the bulk viscosity, $\gamma = C_p/C_v$ the ratio of specific heats, and $D_T = \lambda/\rho C_p$ is the thermal diffusivity with λ the heat conductivity. As mentioned in Section 1, we have written Eqs. (5.6) and (5.7) in a form valid for all densities, as obtained from a hydrodynamic mode-coupling theory rather than the kinetic theory presented here. The kinetic theory result is obtained if the low-density limits of Eqs. (5.6) and (5.7) are taken, i.e., c^2 is replaced by $(d+2)/d\beta m$, Γ_s by Γ_{sB}, ν by ν_B, and C_p by $(d+2)k_B/2m$. In the next section of this paper we discuss the effects of the explicit position, y_1, dependences in Eqs. (5.6) and (5.7) on the hydrodynamic fields in the fluid.

6. THE MODIFICATION OF THE HYDRODYNAMIC FIELDS DUE TO THE WALLS

In the linear approximation of the hydrodynamic equations that follow from Eqs. (2.4a), (3.8), and (3.9) are

$$\frac{\partial u_\alpha(\mathbf{R})}{\partial R_\alpha} = 0 \tag{6.1a}$$

$$-\eta_B \frac{\partial^2}{\partial R_\beta \partial R_\beta} u_\alpha(\mathbf{R}) + \frac{\partial}{\partial R_\alpha} p(\mathbf{R}) + \frac{\partial}{\partial R_\beta} \delta P_{\alpha\beta}(\mathbf{R}) = 0 \tag{6.1b}$$

$$-\lambda_B \frac{\partial^2}{\partial R_\alpha \partial R_\alpha} T(\mathbf{R}) + \frac{\partial}{\partial R_\alpha} \delta Q_\alpha(\mathbf{R}) = 0 \tag{6.1c}$$

where p is the pressure ($= nk_BT$ for a dilute gas). The structure of these equations is that of linearized Navier–Stokes equations in a steady state appended by terms involving the long-range boundary effects, $\delta P_{\alpha\beta}$ and δQ_α, computed in Section 5. If we neglect the terms $\delta P_{\alpha\beta}$ and δQ_α in Eqs. (6.1), i.e., neglect the long-range boundary effects, and use the boundary conditions (cf. Fig. 1)[6]

$$\begin{aligned} \mathbf{u}(\mathbf{R}_\parallel, 0) &= 0 \\ T(\mathbf{R}_\parallel, 0) &= T_0 \end{aligned} \tag{6.1d}$$

then to linear order we obtain

$$\begin{aligned} \mathbf{u}_B(y) &= yX^s\hat{x} \\ T_B(y) &= T_0[1 + yX^T] \\ n_B(y) &= n_0(1 - yX^T) \end{aligned} \tag{6.2}$$

[6] Since we have already taken the limit $D \to \infty$ only the boundary conditions at $y = 0$ are given.

In Eqs. (6.2) the subscript B denotes the hydrodynamic fields that follow from the Boltzmann equation.

Owing to the contributions $\delta P_{\alpha\beta}$ and δQ_α in Eqs. (6.1) there are additional, explicit, y dependences in the hydrodynamic equations which when taken into account modify the form of the hydrodynamic fields. Since we are treating $\delta P_{\alpha\beta}$ and δQ_α as small quantities we can solve Eqs. (6.1) iteratively by using Eqs. (6.2) as our zeroth-order solutions. Writing

$$\begin{aligned} \mathbf{u}(y) &= \mathbf{u}_B(y) + \delta\mathbf{u}(y) + \cdots \\ T(y) &= T_B(y) + \delta T(y) + \cdots \\ n(y) &= n_B(y) + \delta n(y) + \cdots \end{aligned} \tag{6.3}$$

and using Eqs. (5.6), (5.7), (6.1), (6.2), and (6.3) we can solve for $\delta\mathbf{u}$, δT, and δn.

For general densities in three dimensions we obtain

$$\mathbf{u}(\mathbf{y}) = yX^s\left[1 + \frac{2k_BT}{77\pi\eta}\left(\frac{c}{\Gamma_s^3\pi y}\right)^{1/2}\right]\hat{\mathbf{x}} \tag{6.4a}$$

$$T(y) = T_0\left\{1 + yX^T\left[1 + \frac{k_Bc}{7\pi\lambda}\left(\frac{c^3}{\Gamma_s^3\pi y}\right)^{1/2}\right]\right\} + O(y^{-1/2}) \tag{6.4b}$$

$$n(y) = n_0\left\{1 - \alpha_T TyX^T\left[1 + \frac{k_Bc}{7\pi\lambda}\left(\frac{c^3}{\Gamma_s^3\pi y}\right)^{1/2}\right]\right\} + O(y^{-1/2}) \tag{6.4c}$$

In two dimensions the results are

$$\mathbf{u}(y) = yX^s\left[1 - \frac{k_BT}{32\pi\eta}\left(\frac{1}{\nu} + \frac{1}{\Gamma_s}\right)\log(y/l)\right]\hat{\mathbf{x}} \tag{6.5a}$$

$$T(y) = T_0\left\{1 + yX^T\left[1 - \frac{k_B}{8\pi\lambda}\left(\frac{Tc_p}{(\nu + D_T)} + \frac{c^2}{\Gamma_s}\right)\log(y/l)\right]\right\} \tag{6.5b}$$

$$n(y) = n_0\left\{1 - \alpha_T TyX^T\left[1 - \frac{k_B}{8\pi\lambda}\left(\frac{Tc_p}{(\nu + D_T)} + \frac{c^2}{\Gamma_s}\right)\log(y/l)\right]\right\} \tag{6.5c}$$

In Eqs. (6.4) and (6.5) $\alpha_T = -(\partial\rho/\partial T)_{p/\rho}$ is the thermal expansion coefficient. Further, $l \sim k_0^{-1}$ in Eqs. (6.5) is on the order of the mean free path for gas densities and on the order of a molecular diameter for liquid densities. For moderately dense gases the long range boundary corrections in Eqs. (6.4) [Eqs. (6.5)] are of $O[(na^3)^2(\rho/y)^{1/2}]$ ($O(na^2)$) for three (two) dimensional systems.

In two dimensions Eqs. (6.5) imply that for large enough y the perturbed hydrodynamic fields are larger than the unperturbed fields so that the iterative solution procedure used above is no longer valid. The restrictions that this imposes on the theory are discussed in the following section.

7. DISCUSSION

Here we discuss in more detail some of the results obtained in this paper.

(1) We have used the kinetic theory for a moderately dense gas to compute long-range boundary effects in simple two- and three-dimensional fluids. Physically these long-range boundary effects arise because in non-equilibrium in the pair correlation function $G_2(12)$ is of long range due to mode-coupling effects.[3,4]

In three dimensions it is the contribution from two parallel propagating sound modes to $G_2(12)$ that leads to the dominant long-range boundary effect. This follows since sound modes propagate and thus the influence of the walls on the behavior of the bulk of the fluid is most effectively mediated by sound waves.

(2) One of the central approximations in this work is the restriction of our calculations to the case where there are only small deviations of the system from a total equilibrium state. That is, we have considered velocity gradients X^s, temperature gradients X^T, and distances from the wall, y, such that $X^s y \ll c$, and $X^T y \ll T$, where c is the velocity of sound and T is the equilibrium temperature. This restriction was introduced in Section 3, so that we could use the hydrodynamic modes of the Boltzmann collision operator, linearized about total equilibrium, in our analysis of the mode-coupling contributions to the pressure tensor and heat flux vector. In order to extend our results to larger gradients or distances, we would have to construct the hydrodynamic modes of the Boltzmann collision operator linearized about a spatially inhomogenous local equilibrium state. As this would involve mathematical problems of considerable complexity, e.g., solution of equations similar to the Orr–Sommerfeld equation,[11] we have elected not to treat this case here.

(3) In Section 5 we stressed that the mathematical mechanism for the long-range boundary effects in three dimensions was due to an incomplete cancellation of the propagating parts of two sound mode eigenvalues. This incomplete cancellation mechanism is also responsible for other mode-coupling effects that have been discussed previously in the literature. For example, this mechanism is responsible for the dominant boundary effects in nonequilibrium light scattering[3] and for the mode-coupling contributions to the hydrodynamic dispersion relations.[7,14]

(4) In three dimensions, the long-range boundary effects have small numerical coefficients. For example, for a three-dimensional gas, say air at

20°C and one atmosphere, Eqs. (6.4) give

$$\delta\mathbf{u}(y) \cong (1.1 \times 10^{-9}\ \mathrm{cm}^{1/2}) y^{1/2} X^s \tag{7.1a}$$

$$\delta T(y) \cong (2.27 \times 10^{-6}\ \mathrm{cm}^{1/2}) y^{1/2} X^T \tag{7.1b}$$

where we have used that for air at STP,

$$\eta = 2 \times 10^{-4}\ \mathrm{g/cm\,sec}, \qquad c = 3.3 \times 10^4\ \mathrm{cm/sec},$$

$$\Gamma_s = 0.29\ \mathrm{cm}^2/\mathrm{sec}, \qquad \lambda = 5.83 \times 10^2\ \mathrm{g/{}^\circ K\,sec}^3$$

For liquid densities, say argon at 110°K and a pressure of 60 atm, we obtain

$$\delta\mathbf{u}(y) = (3.4 \times 10^{-8}\ \mathrm{cm}^{1/2}) y^{1/2} X^s \tag{7.2a}$$

$$\delta T(y) = (1.42 \times 10^{-4}\ \mathrm{cm}^{1/2}) y^{1/2} X^T \tag{7.2b}$$

where we have used $\eta = 1.55 \times 10^{-3}$ g/cm sec, $c = 7.12 \times 10^4$ cm/sec, $\Gamma_s = 5.07 \times 10^{-3}$ cm^2/sec, and $\lambda = 1.03 \times 10^4$ g/°K sec^3.

For two-dimensional fluids the effects are larger, and to estimate them we use Eqs. (6.5) and consider a two-dimensional gas of hard disks at the density $na^2 = 0.3$, where[5,15] $l \cong a$, $\eta = (1.3)mn\nu_0$, $\nu_0 = [2\pi^{1/2}(\beta m)^{1/2} na]^{-1}$, $\Gamma_s = 3\nu_0$, $\lambda = 2nk_B\nu_0$, $c^2 = 6.2/\beta m$, $C_p = (1.75)k_B/m$, and $D_T = \lambda/mnC_p$. From Eq. (6.5) we obtain

$$\delta\mathbf{u}(y) \cong -(0.03) y X^s \log(y/l) \tag{7.3a}$$

$$\delta T(y) \cong -(0.2) y T_0 X^T \log(y/l) \tag{7.3b}$$

The Eqs. (7.1), (7.2), and (7.3) imply that the long-range boundary effects are most important for the temperature field, and the heat flux, and that for two-dimensional fluids the long-range boundary effects are not small.

(5) In two-dimensional systems the contributions δP_{xy} and δQ_y given by Eqs. (5.7) actually dominate the Boltzmann values $P_{xy}^{(B)}$ and $Q_y^{(B)}$ given by Eqs. (3.8) for large y. Thus the theory presented here breaks down at large enough y. To remedy this a more complete theory is needed such as in the kinetic theory in which more complicated collision sequences are taken into account, e.g., rings within rings. This approach as well as a self-consistent mode-coupling theory[16] suggest that for large y the $\log y$ terms in δP_{xy} and δQ_y are to be replaced by $(\log y)^{1/2}$ terms.

(6) Two interesting results of our three-dimensional calculations are that the normal stresses P_{ii} are nonzero even when X^s is zero if $X^T \neq 0$ and there is a heat flux, $Q_x \neq 0$, when $X^T = 0$ if $X^s \neq 0$. Physically the normal stresses that occur when $X^s = 0$ and $X^T \neq 0$ are due to the fact that sound waves originating in the hot region will transport heat and carry more energy than those from the cold region, and thus normal stresses will occur in the fluid.

The appearance of a heat flux in the absence of a temperature gradient is similar to the mechanocaloric effect found in kinetic boundary layers[2] and superfluids.[17]

(7) In Section 5 we showed that in three dimensions the leading corrections to the bulk stress tensor and heat flux are of $O(y_1^{-1/2})$. In analogy with the hydrodynamic dispersion relations in simple fluids[14] we expect that there are an infinite sequence of contributions between $y_1^{-1/2}$ and y_1^{-1} of the form $y_1^{-(1-2^{-n})}$ $(n = 2, 3, 4, \ldots)$.

(8) As mentioned in Section 1 Wolynes[1] has also calculated δP_{xy} for a three-dimensional fluid with $X^s \neq 0$ and $X^T = 0$. Our results for δP_{xy} are qualitatively the same as his. However, a precise comparison of the numerical coefficient is not possible due to some simplifications Wolynes used in his calculations.

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