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THE STATISTICAL MECHANICAL DERIVATION OF THE HYDRODYNAMIC
EQUATIONS FOR A SYSTEM OF SPHERICAL MOLECULES

by

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I. INTRODUCTION

The derivation of the hydrodynamic equations, the general conservation laws of macroscopic physics, from the principles of molecular mechanics has always been a central problem in statistical mechanics. One of the earliest approaches to this problem starts with the Boltzmann transport equation¹ which arises in the study of dilute gases. Although this approach yielded the correct kinetic contributions to the equations of hydrodynamics, the role played by intermolecular forces was not generally understood until about twenty years ago. At that time Irving and Kirkwood developed their general distribution function formalism² to obtain explicit expressions for the stress tensor and heat flux in terms of microscopic quantities. Since then their results have been widely used as the starting point of more detailed investigations³.

In order to obtain expressions for the stress tensor and heat flux, Irving and Kirkwood arbitrarily expanded a pair distribution function occurring in the general conservation expressions in a Taylor series. The underlying assumption for performing this expansion is that the pair distribution function is a slowly varying function of the center of mass of the two molecules over distances comparable to the "range" of the intermolecular forces. Similar expansions appear frequently in the literature^{4,5,6,7} and may be characterized as "long wavelength" expansions. Irving and Kirkwood, as well as Green, Mori, Zwanzig and Frohlich, assume that for most situations the convergence of the expansion is sufficiently rapid to justify disregarding all but the first nonvanishing term.

Unfortunately, as shown in section XIV of this paper, the long wavelength expansions for the stress tensor and heat flux do not converge unless the intermolecular pair potential vanishes faster than any positive power of $(\frac{1}{r})$ in the limit of large r (r is the internuclear distance). This is a requirement no realistic potential can meet and poses the problem of obtaining a satisfactory derivation of the hydrodynamic equations. It is our intention to supply solutions for these problems under the limitations of classical statistical mechanics.

We rigorously derive the equations of hydrodynamics for a single component system of spherical molecules, and obtain exact expressions for the stress tensor and heat flux. We consider not only molecules exhibiting continuous, differentiable potentials, but also a system of rigid spheres. The effects of finite wavelength on the intermolecular contribution to the stress tensor, as opposed to the kinetic contribution, are then considered in an elementary example. Any external forces on the systems considered are assumed to be conservative, and functions of position only.

Although the results for a system with a continuous intermolecular potential were obtained by Choh⁸ from the BBGKY hierarchy,⁹ he immediately employs the long wavelength expansion of Irving and Kirkwood. It should be noted that the derivation presented here has two distinct advantages: It gives the physical origin of all terms appearing in the transport equations and is independent of the equations governing the evolution in time of the required distribution functions.

Transport equations for a system of perfectly rigid spheres were obtained by Enskog¹⁰ for moderately dense, as well as dilute systems. All of his results depend on approximation methods of limited applicability and are incorrect for highly dense systems.

II. DISTRIBUTION FUNCTIONS

Let $g^{(N)}(\underline{x}_1, \underline{p}_1; \dots; \underline{x}_N, \underline{p}_N; t)$ be the canonical distribution function, normalized to unity, of the entire system, where \underline{x}_i is the position and \underline{p}_i the momentum of the i^{th} molecule, and N is the total number of molecules in the system. The two particle distribution function in configuration and momentum space is defined by

$$g^{(2)}(\underline{x}_1, \underline{p}_1; \underline{x}_2, \underline{p}_2) = \frac{N(N-1) \int d\underline{x}_3 \dots d\underline{x}_N d\underline{p}_3 \dots d\underline{p}_N g^{(N)}}{6(N-2)\text{dim.}} \quad (\text{II.1})$$

and the one particle distribution function in configuration and momentum space is given by

$$g^{(1)}(\underline{x}_1, \underline{p}_1) = \frac{N \int d\underline{x}_2 \dots d\underline{x}_N d\underline{p}_2 \dots d\underline{p}_N g^{(N)}}{6(N-1)\text{dim.}} \quad (\text{II.2})$$

The two and one particle distribution functions in configuration space are, respectively,

$$f^{(2)}(\underline{x}_1, \underline{x}_2) = \int d\underline{p}_1 \int d\underline{p}_2 g^{(2)}(\underline{x}_1, \underline{p}_1; \underline{x}_2, \underline{p}_2) \quad (\text{II.3})$$

$$f^{(1)}(\underline{x}_1) = \int d\underline{p}_1 g^{(1)}(\underline{x}_1, \underline{p}_1). \quad (\text{II.4})$$

For convenience we have suppressed the dependence of these functions on the time, t , but it is assumed that there may be explicit dependence on t in any or all of them.

(II-2)

It will be convenient to introduce the vectors \underline{w} , \underline{p} , \underline{r} , \underline{x} where

$$\begin{aligned}\underline{w} &= \underline{p}_2 - \underline{p}_1 & \underline{p} &= \frac{1}{2}(\underline{p}_2 + \underline{p}_1) \\ \underline{r} &= \underline{x}_2 - \underline{x}_1 & \underline{x} &= \frac{1}{2}(\underline{x}_2 + \underline{x}_1)\end{aligned}\tag{II.5}$$

and the functions Γ and γ defined by

$$\begin{aligned}\Gamma(\underline{w}, \underline{r}; \underline{p}, \underline{x}) &= g^{(2)}(\underline{x}_1, \underline{p}_1; \underline{x}_2, \underline{p}_2) \\ \gamma(\underline{r}, \underline{x}) &= f^{(2)}(\underline{x}_1, \underline{x}_2).\end{aligned}\tag{II.6}$$

Because the molecules are identical, $g^{(2)}$ and $f^{(2)}$ are such that

$$\begin{aligned}g^{(2)}(\underline{x}_1, \underline{p}_1; \underline{x}_2, \underline{p}_2) &= g^{(2)}(\underline{x}_2, \underline{p}_2; \underline{x}_1, \underline{p}_1) \\ f^{(2)}(\underline{x}_1, \underline{x}_2) &= f^{(2)}(\underline{x}_2, \underline{x}_1),\end{aligned}\tag{II.7}$$

so that

$$\begin{aligned}\Gamma(\underline{w}, \underline{r}; \underline{p}, \underline{x}) &= \Gamma(-\underline{w}, -\underline{r}; \underline{p}, \underline{x}) \\ \gamma(\underline{r}, \underline{x}) &= \gamma(-\underline{r}, \underline{x}).\end{aligned}\tag{II.8}$$

We mention that in hydrodynamics the mass density, ρ , is frequently employed in place of $f^{(1)}$. If m is the mass of one molecule, then ρ is defined by

$$\rho(\underline{x}_1) = mf^{(1)}(\underline{x}_1).\tag{II.9}$$

Having defined all of the distribution functions we shall require, we may now proceed to derive the statistical transport equations.

III. TRANSPORT OF MASS

Throughout the following work we shall be concerned with the rate of change of some property (mass, momentum, etc.) of a simply connected region, R , in configuration space. The velocity of a boundary point of R is defined to be the average velocity, \underline{v}_0 , of a molecule at that point:

$$\underline{v}_0(\underline{x}_1) = \frac{1}{m} \int d\underline{p}_1 \frac{g^{(1)}(\underline{x}_1, \underline{p}_1)}{f^{(1)}(\underline{x}_1)} \underline{p}_1 = \frac{1}{m} \underline{p}_0(\underline{x}_1) \quad (\text{III.1})$$

where \underline{p}_0 is the average momentum of a molecule at \underline{x}_1 .

The mass contained in the region R , M_R , is given by

$$M_R = \int_R d\underline{x}_1 \rho(\underline{x}_1) \quad (\text{III.2})$$

so that, from the definition of R , the rate of change of M_R is

$$\frac{dM_R}{dt} = \int_R d\underline{x}_1 \frac{\partial \rho}{\partial t} + \oint_R da \hat{n} \cdot \underline{v}_0 \rho \quad (\text{III.3})$$

where da is an element of the boundary surface of R , and \hat{n} is the unit vector normal to the boundary surface and directed outward. Applying Gauss' Thm. to the second term on the right of Eq. (III.3) we find

$$\frac{dM_R}{dt} = \int_R d\underline{x}_1 \left(\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \underline{x}_1} \cdot \rho \underline{v}_0 \right). \quad (\text{III.4})$$

Now, the only way in which M_R may change is by the flow of molecules across the boundary surface of R . Consider a molecule with position \underline{x}_1 and momentum

\underline{p}_1 such that \underline{x}_1 is in the region $\frac{1}{m}(\underline{p}_1 - \underline{p}_0) \cdot \hat{\underline{n}} da \delta t$ just inside the surface and $(\underline{p}_1 - \underline{p}_0) \cdot \hat{\underline{n}} > 0$ for some surface element da : Clearly, if δt is positive but very small, the molecule shall leave R in the time δt . Thus, the number of molecules with $\underline{p}_1 \in d\underline{p}_1$ and $\underline{x}_1 \in \frac{1}{m}(\underline{p}_1 - \underline{p}_0) \cdot \hat{\underline{n}} da \delta t$ leaving R in the time δt is

$$\frac{1}{m}(\underline{p}_1 - \underline{p}_0) \cdot \hat{\underline{n}} g^{(1)}(\underline{x}_1, \underline{p}_1) H[(\underline{p}_1 - \underline{p}_0) \cdot \hat{\underline{n}}] d\underline{p}_1 da \delta t$$

where $H(x) = 1$ if $x > 0$ and $H(x) = 0$ if $x < 0$. Similarly, the number entering in δt from just outside da and with $\underline{p}_1 \in d\underline{p}_1$ is

$$- \frac{1}{m}(\underline{p}_1 - \underline{p}_0) \cdot \hat{\underline{n}} g^{(1)}(\underline{x}_1, \underline{p}_1) H[(\underline{p}_0 - \underline{p}_1) \cdot \hat{\underline{n}}] d\underline{p}_1 da \delta t$$

so that, as each molecule carries with it the mass m ,

$$\frac{dM_R}{dt} = - \oint_R da \int d\underline{p}_1 \hat{\underline{n}} \cdot (\underline{p}_1 - \underline{p}_0) g^{(1)}(\underline{x}_1, \underline{p}_1) = 0 \quad (\text{III.5})$$

by Eqs. (III.1) and (II.4). As this is true for any R in the system, we find from Eq. (III.4) that

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \underline{x}_1} \cdot \rho \underline{v}_0 = 0, \quad (\text{III.6})$$

which is the familiar equation of continuity in hydrodynamics.

From the foregoing analysis it should be clear that if $x(\underline{x}_1, \underline{p}_1)$ is some property associated with a molecule located at \underline{x}_1 with momentum \underline{p}_1 , then the rate of change of X_R , the quantity of x contained in R , due to the flow of molecules across the boundary of R is given by

(III-3)

$$\begin{aligned} \left(\frac{dX_p}{dt} \right)_{\text{flow}} &= - \frac{1}{m} \oint_R da \int dp_1 (p_1 - p_0) \cdot \hat{n} x_g^{(1)} & \text{(III.7)} \\ &= - \frac{1}{m} \int_R dx_1 \frac{\partial}{\partial x_1} \cdot \int dp_1 (p_1 - p_0) x_g^{(1)} \end{aligned}$$

where we have used Gauss' Thm. in the above. We shall make frequent use of Eq. (III.7) in what follows. Moreover, it should be noted that Eq. (III.7) applies regardless of whether the property x is a scalar, vector, or tensor quantity.

IV. TRANSPORT OF MOMENTUM

The momentum contained in the region R at the time t , \underline{P}_R , is given

by

$$\underline{P}_R = \int_R d\underline{x}_1 \int d\underline{p}_1 \underline{p}_1 g^{(1)}(\underline{x}_1, \underline{p}_1) = \int_R d\underline{x}_1 \rho \underline{v}_0 \quad (\text{IV.1})$$

by Eq. (III.1), so that the rate of change of \underline{P}_R is

$$\begin{aligned} \frac{d\underline{P}_R}{dt} &= \int_R d\underline{x}_1 \frac{\partial}{\partial t} \rho \underline{v}_0 + \oint_R d\underline{a} \hat{\underline{n}} \cdot \underline{v}_0 \rho \underline{v}_0 \\ &= \int_R d\underline{x}_1 \left(\frac{\partial}{\partial t} \rho \underline{v}_0 + \frac{\partial}{\partial \underline{x}_1} \cdot \underline{v}_0 \rho \underline{v}_0 \right) \\ &= \int_R d\underline{x}_1 \rho \left(\frac{\partial}{\partial t} + \underline{v}_0 \cdot \frac{\partial}{\partial \underline{x}_1} \right) \underline{v}_0 \end{aligned} \quad (\text{IV.2})$$

where, in the above, we first applied Gauss' Theorem and then the continuity equation, Eq. (III.6), to obtain the result.

The contribution to the rate of change of \underline{P}_R due to the flow of molecules across the boundary of R is, from Eq. (III.7),

(IV-2)

$$\left(\frac{dP_R}{dt}\right)_{\text{flow}} = -\frac{1}{m} \int_R d\mathbf{x}_1 \frac{\partial}{\partial \mathbf{x}_1} \cdot \int d\mathbf{p}_1 (p_{1x} - p_{0x})(p_{1y} - p_{0y}) g^{(1)} \quad (\text{IV.3})$$

as $\int d\mathbf{p}_1 (p_{1x} - p_{0x}) g^{(1)} = 0$.

If $F(\mathbf{x}_1)$ is the external force per unit mass acting on the molecules in R , then F contributes

$$\left(\frac{dP_R}{dt}\right)_{\text{ext}} = \int_R d\mathbf{x}_1 \int d\mathbf{p}_1 m F g^{(1)} = \int_R d\mathbf{x}_1 \rho F \quad (\text{IV.4})$$

to the rate of change of P_R .

The force exerted on a molecule at \mathbf{x}_1 due to the presence of another molecule at \mathbf{x}_2 is

$$-\frac{\partial \phi(|\mathbf{x}_2 - \mathbf{x}_1|)}{\partial \mathbf{x}_1} = -\frac{\partial \phi(|\mathbf{r}|)}{\partial \mathbf{x}_1} = \frac{\mathbf{r}}{r} \frac{d\phi(r)}{dr} = \hat{\mathbf{r}} \phi'(r)$$

where $\phi(r)$ is the intermolecular potential. Now, given a molecule at \mathbf{x}_1 , the probability that there is another molecule located in $d\mathbf{x}_2$ is

$$\frac{f^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{f^{(1)}(\mathbf{x}_1)} d\mathbf{x}_2.$$

Thus, the rate of change of P_R due to intermolecular forces is

$$\begin{aligned} \left(\frac{dP_R}{dt}\right)_{\text{int}} &= \int_R d\mathbf{x}_1 \int d\mathbf{r} \hat{\mathbf{r}} \phi'(r) f^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \mathbf{r}) \\ &= \int_R d\mathbf{x}_1 \int d\mathbf{r} \hat{\mathbf{r}} \phi'(r) \gamma(\mathbf{r}, \mathbf{x}_1 + \frac{1}{2}\mathbf{r}). \end{aligned} \quad (\text{IV.5})$$

We shall now express the integrand as the divergence of a tensor quantity. We note that

$$\begin{aligned} \left(\frac{dP}{dt} \right)_{\text{int}} &= - \int_R dx_1 \int dr \hat{r} \phi'(r) \gamma(-r, x_1 - \frac{1}{2}r) \\ &= \frac{1}{2} \int_R dx_1 \int dr \hat{r} \phi'(r) [\gamma(r, x_1 + \frac{1}{2}r) - \gamma(r, x_1 - \frac{1}{2}r)] \end{aligned} \quad (\text{IV.6})$$

where, in the above, we first let $r \rightarrow -r$ (without altering the limits) and then used Eq. (II.8). Now, as γ is a continuous function of the components of x ,

$$\begin{aligned} \gamma(r, x_1 + \frac{1}{2}r) - \gamma(r, x_1 - \frac{1}{2}r) &= \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \frac{\partial}{\partial \eta} \gamma(r, x_1 + \eta r) \\ &= \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \frac{\partial}{\partial \eta} \gamma(r, y) \\ &= \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \frac{\partial \gamma}{\partial y_i} \frac{\partial y_i}{\partial \eta} \\ &= \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta r_i \frac{\partial \gamma}{\partial y_i} \end{aligned} \quad (\text{IV.7})$$

where $y = x_1 + \eta r$, the y_i and r_i are the Cartesian components of y and r , and repeated indices are summed over. But,

$$\frac{\partial \gamma}{\partial x_1} = \frac{\partial \gamma}{\partial y_j} \frac{\partial y_j}{\partial x_1} = \frac{\partial \gamma}{\partial y_1} .$$

(IV-4)

Hence

$$\begin{aligned}
\gamma(\underline{r}, \underline{x}_1 + \frac{1}{2}\underline{r}) - \gamma(\underline{r}, \underline{x}_1 - \frac{1}{2}\underline{r}) &= \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \underline{r} \frac{\partial \gamma}{\partial \underline{x}_1} \\
&= \underline{r} \cdot \frac{\partial}{\partial \underline{x}_1} \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \gamma(\underline{r}, \underline{x}_1 + \eta \underline{r}) \\
&= \underline{r} \cdot \frac{\partial}{\partial \underline{x}_1} \bar{\gamma}(\underline{r}, \underline{x}_1),
\end{aligned} \tag{IV.8}$$

where we have defined $\bar{\gamma}$ by

$$\bar{\gamma}(\underline{r}, \underline{x}_1) = \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \gamma(\underline{r}, \underline{x}_1 + \eta \underline{r}). \tag{IV.9}$$

The intermolecular contribution to the rate of change of $P_{\underline{R}}$ may now be written as

$$\left(\frac{dP_{\underline{R}}}{dt} \right)_{int} = \int_{\underline{R}} d\underline{x}_1 \frac{\partial}{\partial \underline{x}_1} \cdot \frac{1}{2} \int d\underline{r} \hat{\underline{r}} \underline{r} \phi'(\underline{r}) \bar{\gamma}(\underline{r}, \underline{x}_1). \tag{IV.10}$$

Adding up all of the contributions and using the fact that R is arbitrary, we obtain the balance equation for the transport of momentum:

$$\begin{aligned}
\rho \left(\frac{\partial}{\partial t} + \underline{v}_o \cdot \frac{\partial}{\partial \underline{x}_1} \right) \underline{v}_o &= \rho \underline{F} \\
&+ \frac{\partial}{\partial \underline{x}_1} \cdot \left\{ -\frac{1}{m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_o) (\underline{p}_1 - \underline{p}_o) \underline{g}^{(1)} \right. \\
&\quad \left. + \frac{1}{2} \int d\underline{r} \hat{\underline{r}} \underline{r} \phi' \bar{\gamma} \right\}.
\end{aligned} \tag{IV.11}$$

V. TRANSPORT OF ANGULAR MOMENTUM

Because we have assumed that the molecules of our system have no internal angular momentum, a molecule with position \underline{x}_1 and momentum \underline{p}_1 possesses solely its orbital angular momentum, $\underline{x}_1 \times \underline{p}_1$. We shall see later that such a system must have a symmetric stress tensor. Here, however, we shall simply find the balance equation for the transport of orbital angular momentum.

The angular momentum contained in R is

$$\begin{aligned} \underline{L}_R &= \int_R d\underline{x}_1 \int d\underline{p}_1 (\underline{x}_1 \times \underline{p}_1) g^{(1)} = \int_R d\underline{x}_1 \underline{x}_1 \times \int d\underline{p}_1 \underline{p}_1 g^{(1)} \\ &= \int_R d\underline{x}_1 \underline{x}_1 \times \rho \underline{v}_0, \end{aligned} \quad (V.1)$$

so that the rate of change of \underline{L}_R is found in the usual way to be

$$\begin{aligned} \frac{d\underline{L}_R}{dt} &= \int_R d\underline{x}_1 \underline{x}_1 \times \frac{\partial}{\partial t} \rho \underline{v}_0 + \oint_R da \hat{n} \cdot \underline{v}_0 (\underline{x}_1 \times \rho \underline{v}_0) \\ &= \int_R d\underline{x}_1 \rho \left(\frac{\partial}{\partial t} + \underline{v}_0 \cdot \frac{\partial}{\partial \underline{x}_1} \right) (\underline{x}_1 \times \underline{v}_0) \end{aligned} \quad (V.2)$$

where we have used the arguments leading to Eq. (IV.2) to obtain Eq. (V.2).

The rate of flow of angular momentum into R is, from Eq. (III.7),

$$\begin{aligned} \left(\frac{d\underline{L}_R}{dt} \right)_{\text{flow}} &= - \frac{1}{m} \int_R d\underline{x}_1 \frac{\partial}{\partial \underline{x}_1} \cdot \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_0) (\underline{x}_1 \times \underline{p}_1) g^{(1)} \\ &= \frac{1}{m} \int_R d\underline{x}_1 \frac{\partial}{\partial \underline{x}_1} \cdot \left\{ \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_0) (\underline{p}_1 - \underline{p}_0) g^{(1)} \times \underline{x}_1 \right\}. \end{aligned} \quad (V.3)$$

(V-2)

We define the symmetric tensor \underline{A} by

$$\underline{A} = \frac{1}{m} \int dp_{\underline{1}} (p_{\underline{1}} - p_{\underline{0}}) (p_{\underline{1}} - p_{\underline{0}}) g^{(1)} \quad (V.4)$$

so that

$$\begin{aligned} \left(\frac{dL}{dt} \right)_{\text{flow}} &= \int_R dx_{\underline{1}} \frac{\partial}{\partial x_{\underline{1}}} \cdot (\underline{A} \times x_{\underline{1}}) \\ &= \int_R dx_{\underline{1}} \frac{\partial}{\partial x_{\underline{1}}} (A_{\underline{1}j} x_{\underline{k}} \hat{e}_{\underline{j}} \times \hat{e}_{\underline{k}}) \\ &= - \int_R dx_{\underline{1}} x_{\underline{1}} \times \frac{\partial}{\partial x_{\underline{1}}} \cdot \underline{A} + \int_R dx_{\underline{1}} A_{\underline{1}j} \hat{e}_{\underline{j}} \times \hat{e}_{\underline{1}} \end{aligned} \quad (V.5)$$

where the $\hat{e}_{\underline{i}}$ are the Cartesian unit vectors, the $x_{\underline{i}}$ are the components of $x_{\underline{1}}$, the $A_{\underline{1}j}$ are the elements of \underline{A} , and we have employed the convention of summing over repeated indices. Now, since \underline{A} is symmetric,

$$A_{\underline{1}j} \hat{e}_{\underline{j}} \times \hat{e}_{\underline{1}} = 0, \quad (V.6)$$

and the contribution due to flow may be written as

$$\begin{aligned} \left(\frac{dL}{dt} \right)_{\text{flow}} &= \frac{1}{m} \int_R dx_{\underline{1}} \frac{\partial}{\partial x_{\underline{1}}} \cdot \left\{ \left[\int dp_{\underline{1}} (p_{\underline{1}} - p_{\underline{0}}) (p_{\underline{1}} - p_{\underline{0}}) g^{(1)} \right] \times x_{\underline{1}} \right\} \\ &= - \frac{1}{m} \int_R dx_{\underline{1}} x_{\underline{1}} \times \frac{\partial}{\partial x_{\underline{1}}} \cdot \int dp_{\underline{1}} (p_{\underline{1}} - p_{\underline{0}}) (p_{\underline{1}} - p_{\underline{0}}) g^{(1)}. \end{aligned} \quad (V.7)$$

(V-3)

As the external forces are functions of position only, the contribution they make is simply

$$\left(\frac{dL_R}{dt}\right)_{\text{ext}} = \int_R d\mathbf{x}_1 \mathbf{x}_1 \times \rho \mathbf{F}. \quad (\text{V.8})$$

In the previous section we demonstrated that the average force on a molecule at \mathbf{x}_1 due to the presence of all the other molecules is

$$\int d\mathbf{r} \hat{\mathbf{r}} \phi'(\mathbf{r}) \frac{f^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \mathbf{r})}{f^{(1)}(\mathbf{x}_1)}.$$

Hence, the intermolecular forces contribute

$$\int_R d\mathbf{x}_1 \mathbf{x}_1 \times \int d\mathbf{r} \hat{\mathbf{r}} \phi' f^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \mathbf{r})$$

to the torque acting on the molecules in R. Applying Eqs. (IV.5) through (IV.9) to the above, we obtain

$$\left(\frac{dL_R}{dt}\right)_{\text{int}} = \int_R d\mathbf{x}_1 \mathbf{x}_1 \times \left(\frac{\partial}{\partial \mathbf{x}_1} \cdot \frac{1}{2} \int d\mathbf{r} \hat{\mathbf{r}} \phi' \overline{\gamma}\right). \quad (\text{V.9})$$

Now, the tensor

$$\int d\mathbf{r} \hat{\mathbf{r}} \phi' \overline{\gamma}$$

is obviously symmetric so that the arguments used on A in Eqs. (V.5) through (V.7) also apply here, and Eq. (V.9) may be alternatively expressed by

(V-4)

$$\left(\frac{dL_R}{dt}\right)_{\text{int}} = - \int_R d\mathbf{x}_1 \frac{\partial}{\partial \mathbf{x}_1} \cdot \left(\frac{1}{2} \int d\mathbf{r} \hat{\mathbf{r}} \mathbf{r} \phi' \bar{\gamma} \times \mathbf{x}_1\right). \quad (\text{V.10})$$

Adding the contributions due to flow, external forces, and intermolecular forces, equating the sum to the right hand side of Eq. (V.2), and using the fact that R is arbitrary, we obtain the balance equation for the transport of angular momentum:

$$\begin{aligned} \rho \left(\frac{\partial}{\partial t} + \mathbf{v}_0 \cdot \frac{\partial}{\partial \mathbf{x}_1} \right) (\mathbf{x}_1 \times \mathbf{v}_0) &= \mathbf{x}_1 \times \rho \mathbf{F} \\ &- \frac{\partial}{\partial \mathbf{x}_1} \cdot \left\{ \left[-\frac{1}{m} \int d\mathbf{p}_1 (\mathbf{p}_1 - \mathbf{p}_0) (\mathbf{p}_1 - \mathbf{p}_0) g^{(1)} + \frac{1}{2} \int d\mathbf{r} \hat{\mathbf{r}} \mathbf{r} \phi' \bar{\gamma} \right] \times \mathbf{x}_1 \right\} \\ &= \mathbf{x}_1 \times \left\{ \rho \mathbf{F} + \frac{\partial}{\partial \mathbf{x}_1} \cdot \left[-\frac{1}{m} \int d\mathbf{p}_1 (\mathbf{p}_1 - \mathbf{p}_0) (\mathbf{p}_1 - \mathbf{p}_0) g^{(1)} + \frac{1}{2} \int d\mathbf{r} \hat{\mathbf{r}} \mathbf{r} \phi' \bar{\gamma} \right] \right\}. \end{aligned} \quad (\text{V.11})$$

The motivation for expressing this balance equation in two alternative forms will be made apparent when we discuss the stress tensor.

VI. TRANSPORT OF ENERGY

We ascribe to each molecule in a given pair the potential energy $\frac{1}{2}\phi$, and we write $m\phi(\underline{x}_1)$ as the scalar potential due to the external forces of a molecule at \underline{x}_1 , so that

$$\underline{F} = - \frac{\partial}{\partial \underline{x}_1} \phi . \quad (\text{VI.1})$$

With these definitions, the average energy of a molecule at \underline{x}_1 with momentum \underline{p}_1 is

$$e(\underline{x}_1, \underline{p}_1) = \frac{1}{2m} |\underline{p}_1|^2 + m\phi + \frac{1}{2} \int d\underline{r} \int d\underline{p}_2 \phi \frac{g^{(2)}(\underline{x}_1, \underline{p}_1; \underline{x}_1 + \underline{r}, \underline{p}_2)}{g^{(1)}(\underline{x}_1, \underline{p}_1)} \quad (\text{VI.2})$$

while the average energy of a molecule located at \underline{x}_1 is

$$\bar{e}(\underline{x}_1) = m\phi + \frac{1}{f^{(1)}} \left[\frac{1}{2m} \int d\underline{p}_1 |\underline{p}_1|^2 g^{(1)} + \frac{1}{2} \int d\underline{r} f^{(2)}(\underline{x}_1, \underline{x}_1 + \underline{r}) \phi \right]. \quad (\text{VI.3})$$

The total energy contained in the region R, E_R , is then

$$E_R = \int_R d\underline{x}_1 f^{(1)} \bar{e} = \int_R d\underline{x}_1 \rho \epsilon \quad (\text{VI.4})$$

where ϵ is the energy per unit mass:

$$\epsilon = \frac{1}{m} \bar{e}. \quad (\text{VI.5})$$

(VI-2)

In the usual manner we find that the rate of change of E_R is given by

$$\frac{dE_R}{dt} = \int_{\mathbb{R}} dx_1 \rho \left(\frac{\partial}{\partial t} + \underline{v}_0 \cdot \frac{\partial}{\partial \underline{x}_1} \right) \epsilon. \quad (\text{VI.6})$$

The contribution due to flow is simply

$$\left(\frac{dE_R}{dt} \right)_{\text{flow}} = - \frac{1}{m} \int_{\mathbb{R}} dx_1 \frac{\partial}{\partial \underline{x}_1} \cdot \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_0) g^{(1)} e \quad (\text{VI.7})$$

and it should be noted that, as ϕ depends solely on \underline{x}_1 , the external forces make no contribution to the flow term.

The average increase in the kinetic energy of a molecule at \underline{x}_1 with momentum \underline{p}_1 in the time δt is

$$\left\{ \underline{F} \cdot \underline{p}_1 + \frac{1}{mg^{(1)}} \underline{p}_1 \cdot \int d\underline{r} \int d\underline{p}_2 \hat{r} \phi' g^{(2)}(\underline{x}_1, \underline{p}_1; \underline{x}_1 + \underline{r}, \underline{p}_2) \right\} \delta t$$

and the average increase of the potential energy of such a molecule in δt is

$$\left\{ \underline{p}_1 \cdot \frac{\partial \phi}{\partial \underline{x}_1} + \frac{1}{2mg^{(1)}} \int d\underline{r} \int d\underline{p}_2 (\underline{p}_2 - \underline{p}_1) \cdot \hat{r} \phi' g^{(2)}(\underline{x}_1, \underline{p}_1; \underline{x}_1 + \underline{r}, \underline{p}_2) \right\} \delta t$$

where, in the above, we have expanded ϕ and ϕ' through first order in δt to obtain the result. Multiplying the last two expressions by $g^{(1)}$, integrating over all \underline{p}_1 and over $\underline{x}_1 \in \mathbb{R}$, dividing by δt , and adding on the flow contribution we find

(VI-3)

$$\begin{aligned} \frac{dE_R}{dt} &= - \int_R dx_1 \frac{\partial}{\partial x_1} \cdot \frac{1}{m} \int dp_1 (p_1 - p_0) e g^{(1)} \\ &+ \int_R dx_1 \int dr \int dp_1 \int dp_2 \frac{1}{2m} (p_1 + p_2) \hat{\alpha} \phi' g^{(2)}(x_1, p_1; x_1 + r, p_2) \end{aligned} \quad (VI.8)$$

where we have used Eq. (VI.1) in the above.

We shall now proceed in a manner similar to that of section IV to express the second term on the right of Eq. (VI.8), the intermolecular term, as the integral over $x_1 \in R$ of the divergence of a vector quantity. Transforming to w , r , and p coordinates, the intermolecular term may be written as

$$\int_R dx_1 \int dr \phi' \hat{r} \cdot \int dw \int dp \frac{1}{m} p \Gamma(w, r; p, x_1 + \frac{1}{2}r).$$

Defining $b(r, x)$ by

$$b(r, x) = \int dw \int dp p \Gamma(w, r; p, x) \quad (VI.9)$$

we have

$$\begin{aligned} b(-r, x) &= \int dw \int dp p \Gamma(w, -r; p, x) \\ &= \int dw \int dp p \Gamma(-w, r; p, x) \\ &= \int dw \int dp p \Gamma(w, r; p, x) \\ &= b(r, x) \end{aligned} \quad (VI.10)$$

where, in the above, we first used Eq. (II.8) and then let $w \rightarrow -w$ without altering the limits. We may now write the intermolecular term as

(VI-4)

$$\begin{aligned}
& \frac{1}{m} \int_R dx_1 \int dr \phi' \hat{r} \cdot b(r, x_1 + \frac{1}{2}r) \\
&= -\frac{1}{m} \int_R dx_1 \int dr \phi' \hat{r} \cdot b(-r, x_1 - \frac{1}{2}r) \\
&= \frac{1}{2m} \int_R dx_1 \int dr \phi' \hat{r} \cdot [b(r, x_1 + \frac{1}{2}r) - b(r, x_1 - \frac{1}{2}r)] \\
&= \frac{1}{2m} \int_R dx_1 \int dr \phi' \hat{r} \cdot \int dw \int dp p [\Gamma(w, r; p, x_1 + \frac{1}{2}r) - \Gamma(w, r; p, x_1 - \frac{1}{2}r)].
\end{aligned}$$

But, applying the arguments used in Eqs. (IV.7) through (IV.9), we find that

$$\Gamma(w, r; p, x_1 + \frac{1}{2}r) - \Gamma(w, r; p, x_1 - \frac{1}{2}r) = r \cdot \frac{\partial}{\partial x_1} \bar{\Gamma} \quad (\text{VI.11})$$

where $\bar{\Gamma}$ is given by

$$\bar{\Gamma}(w, p; r, x_1) = \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \Gamma(w, r; p, x_1 + \eta r). \quad (\text{VI.12})$$

Finally, the intermolecular contribution may be expressed as

$$\frac{1}{2m} \int_R dx_1 \frac{\partial}{\partial x_1} \cdot \int dr \hat{r} \phi' r \cdot \int dw \int dp p \bar{\Gamma}.$$

Adding up the contributions and using the fact that R is arbitrary, we find that the balance equation for the transport of energy may be written as

$$\begin{aligned}
\rho \left(\frac{\partial}{\partial t} + v_o \cdot \frac{\partial}{\partial x_1} \right) \epsilon = \\
\frac{\partial}{\partial x_1} \cdot \left\{ -\frac{1}{m} \int dp_1 (p_1 - p_o) g^{(1)} e + \frac{1}{2m} \int dr \hat{r} \phi' r \cdot \int dw \int dp p \bar{\Gamma} \right\}. \quad (\text{VI.13})
\end{aligned}$$

(VI-5)

While the term in curly brackets may be interpreted as the total energy flux, in order to find the heat flux we shall first need to determine the stress tensor.

VII. THE STRESS TENSOR

In hydrodynamics and the theory of continuous media it is assumed that the rate of change of $P_{\underline{R}}$ is due to forces acting on the surface of R (stresses) and external forces (or body forces). If da is an element of the boundary surface of R , and if T is the stress tensor, then the force acting on da is $\hat{n} \cdot T da$, where \hat{n} is the outward directed unit vector normal to da . Thus, if T exists,

$$\begin{aligned} \frac{dP_{\underline{R}}}{dt} &= \oint_R da \hat{n} \cdot T + \int_R dx_1 \rho F \\ &= \int_R dx_1 (\rho F + \frac{\partial}{\partial x_1} \cdot T) \end{aligned} \quad (VII.1)$$

so that the momentum balance equation of hydrodynamics is, from Eq. (IV.2),

$$\rho \left(\frac{\partial}{\partial t} + \underline{v}_0 \cdot \frac{\partial}{\partial \underline{x}_1} \right) \underline{v}_0 = \frac{\partial}{\partial \underline{x}_1} \cdot T + \rho F. \quad (VII.2)$$

The rate of change of $L_{\underline{R}}$ in hydrodynamics is

$$\begin{aligned} \frac{dL_{\underline{R}}}{dt} &= \oint_R da \underline{x}_1 \times \hat{n} \cdot T + \int_R dx_1 \underline{x}_1 \times \rho F \\ &= \int_R dx_1 [\underline{x}_1 \times \rho F - \frac{\partial}{\partial \underline{x}_1} \cdot (T \times \underline{x}_1)] \end{aligned} \quad (VII.3)$$

giving us, with Eq. (V.2), the balance equation

(VII-2)

$$\rho \left(\frac{\partial}{\partial t} + \underline{v}_0 \cdot \frac{\partial}{\partial \underline{x}_1} \right) (\underline{x}_1 \times \underline{v}_0) = \underline{x}_1 \times \rho \underline{F} - \frac{\partial}{\partial \underline{x}_1} \cdot (\underline{T} \times \underline{x}_1). \quad (\text{VII.4})$$

Now, it is easy to verify that

$$\left(\frac{\partial}{\partial t} + \underline{v}_0 \cdot \frac{\partial}{\partial \underline{x}_1} \right) (\underline{x}_1 \times \underline{v}_0) = \underline{x}_1 \times \left(\frac{\partial}{\partial t} + \underline{v}_0 \cdot \frac{\partial}{\partial \underline{x}_1} \right) \underline{v}_0 \quad (\text{VII.5})$$

which may be combined with Eqs. (VII.2) and (VII.4) to give us the further condition on \underline{T} :

$$\underline{x}_1 \times \left(\frac{\partial}{\partial \underline{x}_1} \cdot \underline{T} \right) + \frac{\partial}{\partial \underline{x}_1} \cdot (\underline{T} \times \underline{x}_1) = 0. \quad (\text{VII.6})$$

This condition is satisfied if and only if \underline{T} is symmetric.

Hence, the conditions that any candidate for the stress tensor must satisfy are, first of all, that it satisfy the momentum and angular momentum balance equations, secondly, that it be symmetric, and thirdly, that it reduce to the familiar result obtained from the virial theorem for a system in thermal and mechanical equilibrium. Thus, from Eqs. (IV.10) and (V.11), and from the fact that, in equilibrium, γ depends only on \underline{r} , the stress tensor is given by

$$\underline{T} = - \frac{1}{m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_0) (\underline{p}_1 - \underline{p}_0) g^{(1)} + \frac{1}{2} \int d\underline{r} \hat{r} r \phi' \bar{\gamma}. \quad (\text{VII.7})$$

VIII. THE HEAT FLUX

In hydrodynamics the rate of change of E_R is ascribed to the work done by the surface forces and the flow of heat across the boundary surface of R . Thus,

$$\begin{aligned} \frac{dE_R}{dt} &= \oint_R da \hat{n} \cdot \underline{T} \cdot \underline{v}_o - \oint_R da \hat{n} \cdot \underline{q} \\ &= \int_R dx_1 \frac{\partial}{\partial x_1} \cdot (\underline{T} \cdot \underline{v}_o - \underline{q}) \end{aligned} \quad (\text{VIII.1})$$

where \underline{q} is defined as the heat flux, or conductive heat current. The balance equation for the transport of energy is, from Eq. (VI.6),

$$\rho \left(\frac{\partial}{\partial t} + \underline{v}_o \cdot \frac{\partial}{\partial \underline{x}_1} \right) \epsilon = \frac{\partial}{\partial \underline{x}_1} \cdot (\underline{T} \cdot \underline{v}_o - \underline{q}) \quad (\text{VIII.2})$$

so that, from Eq. (VI.13),

$$\underline{q} = \underline{T} \cdot \underline{v}_o + \frac{1}{m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_o) g^{(1)} e - \frac{1}{2m} \int d\underline{r} \hat{r} \phi'_{\underline{r}} \int d\underline{w} \int d\underline{p} \underline{p} \bar{\Gamma}. \quad (\text{VIII.3})$$

Inserting the right hand side of Eq. (VII.7) in the above, and noting that

$$\bar{\gamma}(\underline{r}, \underline{x}_1) = \int d\underline{w} \int d\underline{p} \bar{\Gamma} \quad (\text{VIII.4})$$

we find, with a little rearrangement,

(VIII-2)

$$\begin{aligned} \underline{q} = & \frac{1}{2m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_o) |\underline{p}_1 - \underline{p}_o|^2 g^{(1)} \\ & + \frac{1}{2m} \int d\underline{p}_1 \int d\underline{p}_2 \int d\underline{r} (\underline{p}_1 - \underline{p}_o) \phi g^{(2)}(\underline{x}_1, \underline{p}_1; \underline{x}_1 + \underline{r}, \underline{p}_2) \\ & - \frac{1}{2m} \int d\underline{r} \hat{\underline{r}} \phi' \underline{r} \cdot \int d\underline{p} \int d\underline{w} (\underline{p} - \underline{p}_o) \bar{\Gamma}. \end{aligned} \tag{VIII.5}$$

Any candidate for the heat flux not only must satisfy Eq. (VIII.2), but must also vanish for a system in thermal and mechanical equilibrium. By inserting the Maxwellian form of the momentum distribution functions on the right hand side of Eq. (VIII.5) it is easily verified that our expression for \underline{q} vanishes in equilibrium, and hence is the correct choice.

IX. TRANSPORT OF INTERNAL ENERGY

The internal energy of a molecule located at \underline{x}_1 is defined as the sum of its average intermolecular potential energy and the difference between its average kinetic energy and $\frac{1}{2m} |\underline{p}_o|^2$. The appropriate transport equation is obtained easily from the balance equations for momentum and energy transport.

We observe that

$$\begin{aligned} \frac{\partial}{\partial \underline{x}_1} \cdot (\underline{T} \cdot \underline{v}_o) &= \underline{v}_o \cdot \left(\frac{\partial}{\partial \underline{x}_1} \cdot \underline{T} \right) + \underline{T} : \frac{\partial \underline{v}_o}{\partial \underline{x}_1} \\ &= \rho \left(\frac{\partial}{\partial t} + \underline{v}_o \cdot \frac{\partial}{\partial \underline{x}_1} \right) \frac{1}{2} |\underline{v}_o|^2 + \underline{T} : \frac{\partial}{\partial \underline{x}_1} - \rho \underline{F} \end{aligned} \quad (\text{IX.1})$$

where, in the above, we first asserted the symmetry of \underline{T} and then Eq. (VII.2).

Inserting this result into Eq. (VIII.2) we obtain

$$\begin{aligned} \rho \left(\frac{\partial}{\partial t} + \underline{v}_o \cdot \frac{\partial}{\partial \underline{x}_1} \right) \left[\frac{1}{2m} \int d\underline{p}_1 (|\underline{p}_1|^2 - |\underline{p}_o|^2) \frac{g^{(1)}}{f^{(1)}} \right. \\ \left. + \frac{1}{2m} \int d\underline{r} \phi \frac{f^{(2)}(\underline{x}_1, \underline{x}_1 + \underline{r})}{f^{(1)}} \right] &= \underline{T} : \frac{\partial \underline{v}_o}{\partial \underline{x}_1} - \frac{\partial}{\partial \underline{x}_1} \cdot \underline{q} \end{aligned} \quad (\text{IX.2})$$

where the term in square brackets is the internal energy per unit mass. Now, the kinetic temperature, θ , is defined by

$$\begin{aligned} \theta(\underline{x}_1) &= \frac{1}{3m} \int d\underline{p}_1 |\underline{p}_1 - \underline{p}_o|^2 \frac{g^{(1)}}{f^{(1)}} \\ &= \frac{1}{3m} \int d\underline{p}_1 (|\underline{p}_1|^2 - |\underline{p}_o|^2) \frac{g^{(1)}}{f^{(1)}} \end{aligned} \quad (\text{IX.3})$$

(IX-2)

and we define the internal potential energy, u , by

$$u = \frac{1}{2} \int d\vec{r} \phi \frac{f^{(2)}(\vec{x}_1, \vec{x}_1 + \vec{r})}{f^{(1)}} \quad (\text{IX.4})$$

so that u is the average potential energy of a molecule at \vec{x}_1 . Inserting these definitions into Eq. (IX.2) we obtain

$$\frac{1}{m} \rho \left(\frac{\partial}{\partial t} + \vec{v}_0 \cdot \frac{\partial}{\partial \vec{x}_1} \right) \left(\frac{3}{2} \theta + u \right) = T: \frac{\partial \vec{v}_0}{\partial \vec{x}_1} - \frac{\partial}{\partial \vec{x}_1} \cdot \vec{q}, \quad (\text{IX.5})$$

the balance equation for the transport of internal energy.

X. PROPERTIES OF A SYSTEM OF RIGID SPHERES

In the previous sections we have shown that well defined representations for the stress tensor and heat flux may be found for systems with a continuous intermolecular potential ϕ . We shall now demonstrate that this is also true for a system consisting of perfectly rigid spheres of mass m and radius σ .

Before we start, we need to consider two more characteristics of the distribution functions Γ and γ for a system consisting specifically of rigid spheres (the definitions and some of the general properties of these functions are in section II). First of all, as two rigid spheres cannot overlap, we note that Γ and γ must vanish if $r < 2\sigma$; clearly there is a discontinuity at $r = 2\sigma$. In this work we shall define $\Gamma(\underline{w}, \hat{2\sigma\underline{r}}; \underline{p}, \underline{x})$ and $\gamma(\hat{2\sigma\underline{r}}, \underline{x})$ by

$$\begin{aligned} \Gamma(\underline{w}, \hat{2\sigma\underline{r}}; \underline{p}, \underline{x}) &= \lim_{\epsilon \rightarrow +0} \Gamma(\underline{w}, (1 + \epsilon)\hat{2\sigma\underline{r}}; \underline{p}, \underline{x}) \\ \gamma(\hat{2\sigma\underline{r}}, \underline{x}) &= \lim_{\epsilon \rightarrow +0} \gamma((1 + \epsilon)\hat{2\sigma\underline{r}}, \underline{x}), \end{aligned} \tag{X.1}$$

that is, as the limit $r \rightarrow 2\sigma$ taken from above. These quantities are perfectly well defined and have a definite physical interpretation.

In order to develop the second property, we consider the collision of two rigid spheres at the time t . Suppose that, at the time $t - 0$, their momenta are

$$\underline{p}_1 = \underline{p}_{1\perp} + \underline{p}_1 \cdot \hat{\underline{r}} \hat{\underline{r}} \quad \text{and} \quad \underline{p}_2 = \underline{p}_{2\perp} + \underline{p}_2 \cdot \hat{\underline{r}} \hat{\underline{r}},$$

where $\underline{p}_{1\perp}$ and $\underline{p}_{2\perp}$ are the projections of \underline{p}_1 and \underline{p}_2 in a plane perpendicular to $\hat{\underline{r}}$,

(X-2)

so that after the collision, at the time $t + 0$, their momenta are

$$\underline{p}_1' = \underline{p}_{1\perp} + \underline{p}_2 \cdot \hat{r}\hat{r} \quad \text{and} \quad \underline{p}_2' = \underline{p}_{2\perp} + \underline{p}_1 \cdot \hat{r}\hat{r}.$$

We observe that the collision has duration zero, so that no simultaneous triple, or higher multiplicity, collisions occur. Thus, if two molecules are approaching each other at the time $t - 0$ with separation $2\sigma + 0$, the outcome of the collision is completely determined. The probability that two molecules are approaching each other at $t - 0$ with momenta \underline{p}_1 and \underline{p}_2 must be equal to the probability that they are moving apart at $t + 0$ with momenta \underline{p}_1' and \underline{p}_2' , so that Γ must have the property

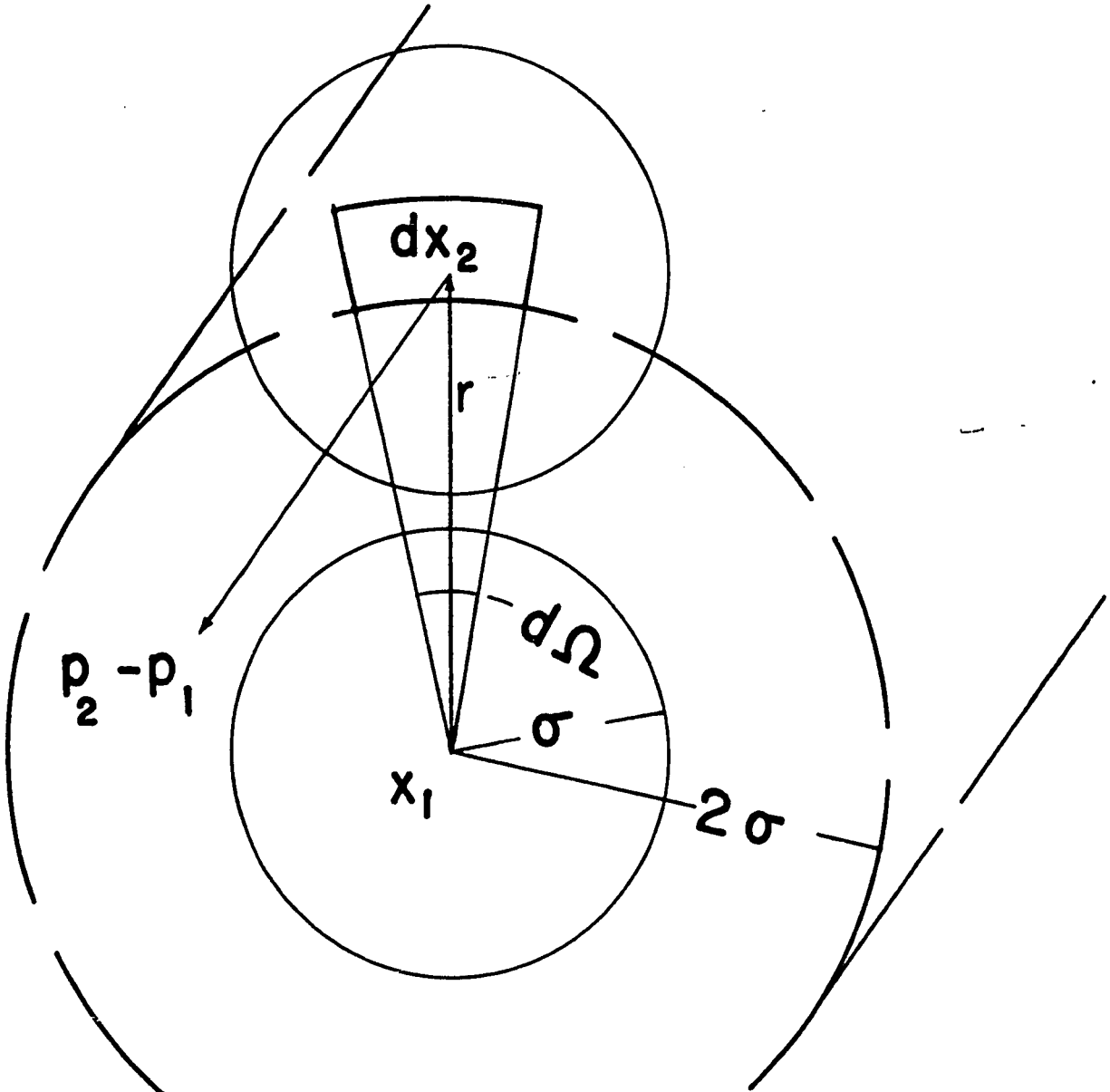
$$\Gamma(\underline{w}_{\perp} + \underline{w} \cdot \hat{r}\hat{r}, 2\sigma\hat{r}; \underline{p}, \underline{x}) = \Gamma(\underline{w}_{\perp} - \underline{w} \cdot \hat{r}\hat{r}, 2\sigma\hat{r}; \underline{p}, \underline{x}) \quad (\text{X.2})$$

for a system consisting specifically of rigid spheres.

CAPTIONS

Figure 1. The collision of two rigid spheres.

COLLISION
CYLINDER



COLLISION
SPHERE

XI. COLLISIONAL CONTRIBUTIONS TO THE EQUATIONS OF TRANSPORT

The differences in the equations of transport between a system of rigid spheres and a system with a continuous intermolecular potential arise only in the intermolecular contributions. Rather than repeat all of the formalism of the first nine sections, our prescription will be first to calculate the collisional, or intermolecular, contributions of a system of rigid spheres to the various transport processes, and then to modify the previous results accordingly. We shall be concerned with the average increase of some property of a hard sphere molecule located at \underline{x}_1 with momentum \underline{p}_1 due to collisions with other molecules in the time δt . Hence, we need to know the probability that such a collision occurs in the time δt .

Suppose we are given a molecule at \underline{x}_1 with momentum \underline{p}_1 ; the probability that it has a collision with another molecule having \underline{p}_2 and \underline{x}_2 in the time δt is

$$\frac{g^{(2)}(\underline{x}_1, \underline{p}_1; \underline{x}_1 + 2\sigma\hat{\underline{r}}, \underline{p}_2)}{g^{(1)}(\underline{x}_1, \underline{p}_1)} (2\sigma)^2 \frac{1}{m} |\underline{w} \cdot \hat{\underline{r}}| H(-\underline{w} \cdot \hat{\underline{r}}) d\Omega dp_2 \delta t \quad (\text{XI.1})$$

where $d\Omega$ is the solid angle subtended by $d\underline{x}_2$ at \underline{x}_1 (see Fig. 1), 2σ is the radius of the collision sphere, and the requirement $\underline{w} \cdot \hat{\underline{r}} < 0$ ($H(x)$ is defined in Section III) insures that the molecules will collide in the limit $\delta t \rightarrow 0$. Thus, if $\Delta\chi$ is the increase in the property χ of the molecule at \underline{x}_1 with momentum \underline{p}_1 due to a collision with a molecule at $\underline{x}_1 + 2\sigma\hat{\underline{r}}$ with momentum \underline{p}_2 , then the rate of change of X_R due to collisions is

(XI-2)

$$\begin{aligned}
\left(\frac{dX_R}{dt}\right)_{\text{col}} &= \int_R dx_1 \int dp_1 \int dp_2 \int d\Omega \frac{(2\sigma)^2}{m} \Delta x |\underline{w} \cdot \hat{r}| H(-\underline{w} \cdot \hat{r}) g^{(2)}(\underline{x}_1, \underline{p}_1; \underline{x}_1 + 2\sigma \hat{r}, \underline{p}_2) \\
&= - \int_R dx_1 \int dp \int dw \int d\Omega \frac{(2\sigma)^2}{m} \Delta x \underline{w} \cdot \hat{r} H(-\underline{w} \cdot \hat{r}) \Gamma(\underline{w}, 2\sigma \hat{r}; \underline{p}, \underline{x}_1 + \sigma \hat{r}),
\end{aligned}$$

(XI.2)

where X_R is the amount of x contained in the region R .

The momentum increase of the molecule at \underline{x}_1 due to the collision is $\underline{w} \cdot \hat{r}$ so that

$$\left(\frac{dP_R}{dt}\right)_{\text{col}} = - \int_R dx_1 \int dp \int dw \int d\Omega \frac{(2\sigma)^2}{m} (\underline{w} \cdot \hat{r})^2 H(-\underline{w} \cdot \hat{r}) \Gamma; \quad \text{(XI.3)}$$

the increase in angular momentum is $\underline{x}_1 \times (\Delta p_1)$ giving us

$$\left(\frac{dL_R}{dt}\right)_{\text{col}} = - \int_R dx_1 \underline{x}_1 \times \int dp \int dw \int d\Omega \frac{(2\sigma)^2}{m} (\underline{w} \cdot \hat{r})^2 H(-\underline{w} \cdot \hat{r}) \Gamma; \quad \text{(XI.4)}$$

and, as the increase in energy of the molecule at \underline{x}_1 due to the collision is $\frac{1}{m}(\underline{w} \cdot \hat{r})(\underline{p} \cdot \hat{r})$,

$$\left(\frac{dE_R}{dt}\right)_{\text{col}} = - \int_R dx_1 \int dp \int dw \int d\Omega \frac{(2\sigma)^2}{m} (\underline{w} \cdot \hat{r})^2 \underline{p} \cdot \hat{r} H(-\underline{w} \cdot \hat{r}) \Gamma. \quad \text{(XI.5)}$$

The integrands in Eqs. (XI.3) through (XI.5) depend on $\underline{w} \cdot \hat{r}$ precisely in the same manner; namely, through the function $(\underline{w} \cdot \hat{r})^2 H(-\underline{w} \cdot \hat{r}) \Gamma$. But, from Eq. (X.2), we see that Γ is an even function of $\underline{w} \cdot \hat{r}$. Hence, if we integrate over \underline{w} before

we integrate over Ω , and if we break up the integration over \underline{w} into an integration over $\underline{w} \cdot \underline{\hat{r}}$ (where $\underline{\hat{r}}$ is fixed) and then an integration over \underline{w}_\perp , we may replace $H(-\underline{w} \cdot \underline{\hat{r}})$ by $\frac{1}{2}$ in the integrand without altering the result. As the order of integration is arbitrary, we shall assume in what follows that this substitution has been executed.

XII. THE BALANCE EQUATIONS, STRESS TENSOR, AND HEAT FLUX

FOR A SYSTEM OF RIGID SPHERES

Equations (XI.3) through (XI.5) are the collisional contributions to the transport of momentum, angular momentum, and energy for a system of rigid spheres. Each shall replace the appropriate intermolecular contribution (with subscript int) in the earlier work for a system with a continuous intermolecular potential. As in the earlier work, we shall express each contribution as an integral over $\underline{x}_1 \in R$ of the divergence of a tensor, or vector, quantity. This is quickly accomplished by observing that each collisional contribution contains

$$\begin{aligned}
 & \int d\Omega \int d\underline{w} \hat{\underline{r}}(\underline{w} \cdot \hat{\underline{r}})^2 \Gamma(\underline{w}, 2\sigma\hat{\underline{r}}; \underline{p}, \underline{x}_1 + \sigma\hat{\underline{r}}) \\
 &= - \int d\Omega \int d\underline{w} \hat{\underline{r}}(\underline{w} \cdot \hat{\underline{r}})^2 \Gamma(\underline{w}, -2\sigma\hat{\underline{r}}; \underline{p}, \underline{x}_1 - \sigma\hat{\underline{r}}) \\
 &= - \int d\Omega \int d\underline{w} \hat{\underline{r}}(\underline{w} \cdot \hat{\underline{r}})^2 \Gamma(-\underline{w}, 2\sigma\hat{\underline{r}}; \underline{p}, \underline{x}_1 - \sigma\hat{\underline{r}}) \\
 &= - \int d\Omega \int d\underline{w} \hat{\underline{r}}(\underline{w} \cdot \hat{\underline{r}})^2 \Gamma(\underline{w}, 2\sigma\hat{\underline{r}}; \underline{p}, \underline{x}_1 - \sigma\hat{\underline{r}}) \\
 &= \frac{1}{2} \int d\Omega \int d\underline{w} \hat{\underline{r}}(\underline{w} \cdot \hat{\underline{r}})^2 [\Gamma(\underline{w}, 2\sigma\hat{\underline{r}}; \underline{p}, \underline{x}_1 + \sigma\hat{\underline{r}}) - \Gamma(\underline{w}, 2\sigma\hat{\underline{r}}; \underline{p}, \underline{x}_1 - \sigma\hat{\underline{r}})] \\
 &= \sigma \int d\Omega \int d\underline{w} \hat{\underline{r}}(\underline{w} \cdot \hat{\underline{r}})^2 \cdot \frac{\partial}{\partial \underline{x}_1} \bar{\Gamma}(\underline{w}, \underline{p}; 2\sigma\hat{\underline{r}}, \underline{x}_1) \tag{XII.1}
 \end{aligned}$$

(XII-2)

where, in the first step we let $\underline{r} \rightarrow -\underline{r}$ without changing the limits on Ω , in the second step we used Eq. (II.8), in the third step we let $\underline{w} \rightarrow -\underline{w}$ without changing the limits, and in the last step we used Eq. (VI.11). Inserting this result into Eqs. (XI.3) through (XI.5) we obtain

$$\left(\frac{dP_{\underline{R}}}{dt}\right)_{\text{col}} = -\int_{\underline{R}} d\underline{x}_1 \frac{\partial}{\partial \underline{x}_1} \cdot \frac{2\sigma^3}{m} \int d\underline{p} \int d\underline{w} \int d\Omega \hat{\underline{r}} \hat{\underline{r}} (\underline{w} \cdot \hat{\underline{r}})^2 \overline{\Gamma}, \quad (\text{XII.2})$$

$$\left(\frac{dL_{\underline{R}}}{dt}\right)_{\text{col}} = -\int_{\underline{R}} d\underline{x}_1 \underline{x}_1 \times \frac{\partial}{\partial \underline{x}_1} \cdot \frac{2\sigma^3}{m} \int d\underline{p} \int d\underline{w} \int d\Omega \hat{\underline{r}} \hat{\underline{r}} (\underline{w} \cdot \hat{\underline{r}})^2 \overline{\Gamma}, \quad (\text{XII.3})$$

and

$$\left(\frac{dE_{\underline{R}}}{dt}\right)_{\text{col}} = -\int_{\underline{R}} d\underline{x}_1 \frac{\partial}{\partial \underline{x}_1} \cdot \frac{2\sigma^3}{m} \int d\underline{p} \int d\underline{w} \int d\Omega \hat{\underline{r}} (\underline{p} \cdot \hat{\underline{r}}) (\underline{w} \cdot \hat{\underline{r}})^2 \overline{\Gamma}. \quad (\text{XII.4})$$

It is now a straightforward matter to obtain the balance equations of transport for a system of rigid spheres; we simply perform the aforementioned substitution of each collisional contribution for the appropriate intermolecular contribution in the balance equations obtained for a system with a continuous intermolecular potential (Eqs. (IV.11), (V.11) and (VI.13)). We must also delete the terms containing ϕ (as opposed to ϕ') in the energy per unit mass and in the flow contribution in the earlier energy balance equation, Eq. (VI.13), as there is no long range intermolecular potential in our hard sphere system. Performing these operations we find that, for a system of rigid spheres, the momentum balance equation is

(XII-3)

$$\rho \left(\frac{\partial}{\partial t} + \underline{v}_o \cdot \frac{\partial}{\partial \underline{x}_1} \right) \underline{v}_o = \rho \underline{F} - \frac{\partial}{\partial \underline{x}_1} \cdot \left\{ \frac{1}{m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_o) (\underline{p}_1 - \underline{p}_o) g^{(1)} \right. \\ \left. + \frac{2\sigma^3}{m} \int d\underline{p} \int d\underline{w} \int d\Omega \hat{\underline{r}} \hat{\underline{r}} (\underline{w} \cdot \hat{\underline{r}})^2 \overline{\Gamma} \right\}, \quad (\text{XII.5})$$

the angular momentum equation is

$$\rho \left(\frac{\partial}{\partial t} + \underline{v}_o \cdot \frac{\partial}{\partial \underline{x}_1} \right) (\underline{x}_1 \times \underline{v}_o) = \underline{x}_1 \times \rho \underline{F} - \underline{x}_1 \times \frac{\partial}{\partial \underline{x}_1} \cdot \left\{ \frac{1}{m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_o) (\underline{p}_1 - \underline{p}_o) g^{(1)} \right. \\ \left. + \frac{2\sigma^3}{m} \int d\underline{p} \int d\underline{w} \int d\Omega \hat{\underline{r}} \hat{\underline{r}} (\underline{w} \cdot \hat{\underline{r}})^2 \overline{\Gamma} \right\}, \quad (\text{XII.6})$$

and the energy balance equation is

$$\rho \left(\frac{\partial}{\partial t} + \underline{v}_o \cdot \frac{\partial}{\partial \underline{x}_1} \right) \varepsilon = - \frac{\partial}{\partial \underline{x}_1} \cdot \left\{ \frac{1}{2m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_o) |\underline{p}_1|^2 g^{(1)} \right. \\ \left. + \frac{2\sigma^3}{m} \int d\underline{p} \int d\underline{w} \int d\Omega \hat{\underline{r}} (\underline{p} \cdot \hat{\underline{r}}) (\underline{w} \cdot \hat{\underline{r}})^2 \overline{\Gamma} \right\}. \quad (\text{XII.7})$$

From the above, and the discussion of hydrodynamics in sections VII through IX, it is clear that the stress tensor \underline{T} is given by

$$\underline{T} = - \frac{1}{m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_o) (\underline{p}_1 - \underline{p}_o) g^{(1)} - \frac{2\sigma^3}{m} \int d\underline{p} \int d\underline{w} \int d\Omega \hat{\underline{r}} \hat{\underline{r}} (\underline{w} \cdot \hat{\underline{r}})^2 \overline{\Gamma} \quad (\text{XII.8})$$

for a system of rigid spheres. Inserting the equilibrium form of the distribution functions one quickly obtains agreement with the virial theorem for a system in thermal and mechanical equilibrium.

(XII-4)

The heat flux, \underline{q} , is found as before by setting the term in curly brackets in Eq. (XII.7) equal to $\underline{q} - T \cdot \underline{v}_0$ to obtain

$$\begin{aligned} \underline{q} = & \frac{1}{2m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_0) (\underline{p}_1 - \underline{p}_0) g \quad (1) \\ & + \frac{2\sigma^3}{m} \int d\underline{p} \int d\underline{w} \int d\Omega \hat{\underline{r}} (\underline{p}_1 - \underline{p}_0) \cdot \hat{\underline{r}} (\underline{w} \cdot \hat{\underline{r}})^2 \overline{\Gamma}. \end{aligned} \quad (\text{XII.9})$$

As a hard sphere molecule possesses no intermolecular potential energy, the transport equation for the internal energy is simply

$$\rho \left(\frac{\partial}{\partial t} + \underline{v}_0 \cdot \frac{\partial}{\partial \underline{x}_1} \right) \frac{3}{2m} \theta = T : \frac{\partial \underline{v}_0}{\partial \underline{x}_1} - \frac{\partial}{\partial \underline{x}_1} \cdot \underline{q}. \quad (\text{XII.10})$$

XIII. SUMMARY OF RESULTS

We have shown that a single component system of spherical molecules possessing either a continuous intermolecular potential $\phi(r)$, or a hard core interaction of radius σ , obeys the general hydrodynamic equations of motion:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \underline{x}_1} \cdot (\rho \underline{v}_0) = 0 \quad \text{mass transport} \quad (\text{XIII.1})$$

$$\rho \left(\frac{\partial}{\partial t} + \underline{v}_0 \cdot \frac{\partial}{\partial \underline{x}_1} \right) \underline{v}_0 = \rho \underline{F} + \frac{\partial}{\partial \underline{x}_1} \cdot \underline{T} \quad \text{momentum transport} \quad (\text{XIII.2})$$

$$\rho \left(\frac{\partial}{\partial t} + \underline{v}_0 \cdot \frac{\partial}{\partial \underline{x}_1} \right) (\underline{x}_1 \times \underline{v}_0) = \underline{x}_1 \times \rho \underline{F} - \frac{\partial}{\partial \underline{x}_1} \cdot (\underline{T} \times \underline{x}_1) \quad \text{angular momentum transport} \quad (\text{XIII.3})$$

$$\rho \left(\frac{\partial}{\partial t} + \underline{v}_0 \cdot \frac{\partial}{\partial \underline{x}_1} \right) \epsilon = \frac{\partial}{\partial \underline{x}_1} \cdot (\underline{T} \cdot \underline{v}_0 - \underline{q}) \quad \text{energy transport} \quad (\text{XIII.4})$$

$$\rho \left(\frac{\partial}{\partial t} + \underline{v}_0 \cdot \frac{\partial}{\partial \underline{x}_1} \right) \left(\frac{3}{2m} \theta + \frac{1}{m} u \right) = \underline{T} : \frac{\partial \underline{v}_0}{\partial \underline{x}_1} - \frac{\partial}{\partial \underline{x}_1} \cdot \underline{q} \quad \text{internal energy transport} \quad (\text{XIII.5})$$

where, in the above,

m = mass of one molecule

ρ = mass density

\underline{v}_0 = macroscopic velocity ($= \frac{1}{m} \underline{p}_0$)

(XIII-2)

\underline{F} = external force per unit mass

\underline{T} = stress tensor

ϵ = energy per unit mass

\underline{q} = heat flux

θ = kinetic temperature

u = average intermolecular potential energy of a molecule at \underline{x}_1 .

For a system having a continuous intermolecular potential ϕ , we have found that the stress tensor and heat flux are given by

$$\underline{T} = -\frac{1}{m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_0)(\underline{p}_1 - \underline{p}_0) g^{(1)} + \frac{1}{2} \int d\underline{r} \hat{\underline{r}} \underline{r} \phi' \bar{\gamma} \quad (\text{XIII.6})$$

and

$$\begin{aligned} \underline{q} = & \frac{1}{2m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_0) |\underline{p}_1 - \underline{p}_0|^2 g^{(1)} \\ & + \frac{1}{2m} \int d\underline{p}_1 \int d\underline{p}_2 \int d\underline{r} (\underline{p}_1 - \underline{p}_0) \phi g^{(2)}(\underline{x}_1, \underline{p}_1; \underline{x}_1 + \underline{r}, \underline{p}_2) \\ & - \frac{1}{2m} \int d\underline{r} \hat{\underline{r}} \phi' \underline{r} \cdot \int d\underline{w} \int d\underline{p} (\underline{p} - \underline{p}_0) \bar{\Gamma}. \end{aligned} \quad (\text{XIII.7})$$

For a system consisting of rigid spheres of radius σ we have found that

$$\begin{aligned} \underline{T} = & -\frac{1}{m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_0)(\underline{p}_1 - \underline{p}_0) g^{(1)} \\ & - \frac{2\sigma^3}{m} \int d\underline{p} \int d\underline{w} \int d\Omega \hat{\underline{r}} \hat{\underline{r}} (\underline{w} \cdot \hat{\underline{r}})^2 \bar{\Gamma}(\underline{w}, \underline{p}; 2\sigma \hat{\underline{r}}, \underline{x}_1) \end{aligned} \quad (\text{XIII.8})$$

and

$$\begin{aligned}
q &= \frac{1}{2m} \int d\underline{p}_1 (\underline{p}_1 - \underline{p}_0) |\underline{p}_1 - \underline{p}_0|^2 g^{(1)} \\
&+ \frac{2\sigma^3}{m} \int d\underline{p} \int d\underline{w} \int d\Omega \hat{r}(\underline{p} - \underline{p}_0) \cdot \hat{r}(\underline{w} \cdot \hat{r})^2 \bar{\Gamma}(\underline{w}, \underline{p}; 2\sigma\hat{r}, \underline{x}_1). \quad (\text{XIII.9})
\end{aligned}$$

In the last four equations we have used the notation

$$\begin{aligned}
\bar{\gamma}(\underline{r}, \underline{x}_1) &= \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \gamma(\underline{r}, \underline{x}_1 + \eta\underline{r}) \\
\bar{\Gamma}(\underline{w}, \underline{p}; \underline{r}, \underline{x}_1) &= \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \Gamma(\underline{w}, \underline{r}; \underline{p}, \underline{x}_1 + \eta\underline{r}). \quad (\text{XIII.10})
\end{aligned}$$

In obtaining these results we have assumed that the interactions between molecules may be described by classical statistical mechanics, that the external forces are conservative and depend only on position, and that the interactions of molecules far from the system boundary with molecules in the boundary material are negligible.

XIV. DISCUSSION

The stress tensor and the heat flux may each be considered as the sum of two parts which we label a local and a nonlocal contribution. The local part depends only on the distribution function $g^{(1)}$, whereas the nonlocal contribution depends on $f^{(2)}$ ($=\gamma$), or $g^{(2)}$ ($=\Gamma$). The local contribution is a familiar result of the kinetic theory of gases and is discussed in great detail elsewhere.¹¹ It is the nonlocal contribution that interests us here. We call any contribution depending on $f^{(2)}$ or $g^{(2)}$ nonlocal because it depends not simply on what is happening to the system at \underline{x}_1 , but also at points near \underline{x}_1 . Thus, we would expect that the nonlocal contribution would be highly sensitive to the distribution of molecules in the substance making up the boundary wall (we have ignored this contribution here) when \underline{x}_1 is near the system boundary.

The functions $\bar{\gamma}$ and $\bar{\Gamma}$ play an important role in our theory. They appear in the stress tensor and heat flux in the terms due to the force exerted, and work done, by molecules outside of the region R on the molecules inside R. They are obtained by averaging γ and Γ in their center of mass dependence over the straight line connecting $\underline{x}_1 - \frac{1}{2}\underline{r}$ to $\underline{x}_1 + \frac{1}{2}\underline{r}$. To understand the importance of this averaging process, consider the case when the system is perturbed by a plane wave of such short wavelength that any significant variation of ϕ or ϕ' occurs over many wavelengths. In the limit of such short wavelength phenomena, it can be expected that the dependence of $\bar{\gamma}$ and $\bar{\Gamma}$ on \underline{r} will become insensitive to the disturbance. We shall see that this is so for the elementary example considered in the next section.

(XIV-2)

In order to understand the difficulties encountered with the Taylor expansion obtained by Irving and Kirkwood, we shall now examine the trace of the nonlocal part of the stress tensor, $\Delta p \underline{T}_{int}$, for a system with a continuous intermolecular potential. From Eq. (XIII.6) we find

$$\begin{aligned} \Delta p \underline{T}_{int} &= \frac{1}{2} \int d\mathbf{r} \mathbf{r} \phi' \bar{\gamma} \\ &= \frac{1}{2} \int d\Omega \int_0^\infty dr r^3 \phi' \bar{\gamma}. \end{aligned} \quad (\text{XIV.1})$$

We quickly obtain their result by expanding $\bar{\gamma}$ about $\gamma(\mathbf{r}, \mathbf{x}_1)$:

$$\begin{aligned} \bar{\gamma}(\mathbf{r}, \mathbf{x}_1) &= \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \gamma(\mathbf{r}, \mathbf{x}_1 + \eta \mathbf{r}) \\ &= \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \sum_0^\infty \frac{1}{n!} (\eta \mathbf{r} \cdot \frac{\partial}{\partial \mathbf{x}_1})^n \gamma(\mathbf{r}, \mathbf{x}_1) \\ &= \sum_0^\infty \frac{1}{n!} r^n \left(\int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \eta^n \right) (\hat{\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{x}_1})^n \gamma(\mathbf{r}, \mathbf{x}_1) \\ &= \sum_0^\infty \frac{1}{(2n+1)!} r^{2n} \left(\frac{1}{2} \hat{\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{x}_1} \right)^{2n} \gamma(\mathbf{r}, \mathbf{x}_1) \end{aligned} \quad (\text{XIV.2})$$

giving us

$$\Delta p \underline{T}_{int} = \frac{1}{2} \sum_0^\infty \frac{1}{(2n+1)!} \int d\Omega \left(\frac{1}{2} \hat{\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{x}_1} \right)^{2n} \int_0^\infty dr r^{2n+3} \phi'(r) \gamma(\mathbf{r}, \mathbf{x}_1).$$

(XIV-3)

Let's examine the integrand of

$$\int_0^{\infty} dr r^{2n+3} \phi'(r) \gamma(\underline{r}, \underline{x}_1)$$

in the limit of large r . As γ becomes the product of the number densities,

$$\lim_{r \rightarrow \infty} \gamma(\underline{r}, \underline{x}_1) = f^{(1)}(\underline{x}_1 - \frac{1}{2}\underline{r}) f^{(1)}(\underline{x}_1 + \frac{1}{2}\underline{r}), \quad (\text{XIV.3})$$

it does not vanish for large r . Thus, either ϕ' goes to zero faster than $(\frac{1}{r})^{2n+3}$ or the integral blows up and the n^{th} term in the expansion is not defined. Hence, for a square well potential or a Yukawa potential the Irving and Kirkwood expansion produces meaningful results, but for a Leonard Jones potential the expansion is useless. The reader may easily verify that the same difficulties are encountered with the heat flux. It is a straightforward matter, however, to avoid this pitfall. If one wants to determine T , one must know, or assume some form for, $\gamma(\underline{r}, \underline{x})$. But, if one knows γ , it is just as easy to integrate over η to obtain $\bar{\gamma}$ and then perform the integration over \underline{r} as to perform an expansion under the integral. Any long wavelength expansion can then be made on the expression for T obtained in closed form.

XV. AN ELEMENTARY EXAMPLE

Suppose our system is a fluid which is slightly perturbed by a density wave of angular frequency ω and wave vector \underline{k} . We shall assume that the amplitude of the wave is small and that it may be considered a constant over distances of many wavelengths. For such a disturbance the density is given by

$$f^{(1)}(\underline{x}_1) = n[1 + \epsilon \cos(\underline{k} \cdot \underline{x}_1 - \omega t)] \quad (\text{XV.1})$$

where n is the number density in equilibrium. We shall also assume that in the perturbed state the two particle distribution function is of the form

$$f^{(2)}(\underline{x}_1, \underline{x}_2) = f^{(1)}(\underline{x}_1)f^{(1)}(\underline{x}_2)h(r) \quad (\text{XV.2})$$

where we require

$$\lim_{r \rightarrow \infty} h(r) = 1 \quad (\text{XV.3})$$

in order that $f^{(2)}$ have the proper asymptotic behavior.

With these conditions we find

$$\gamma(\underline{r}, \underline{x}) = n^2 h(r) [1 + 2\epsilon \cos(\underline{k} \cdot \underline{x} - \omega t) \cos \frac{1}{2} \underline{k} \cdot \underline{r}] + \text{order } \epsilon^2, \quad (\text{XV.4})$$

where we shall ignore all terms in ϵ^2 , so that

(XV-2)

$$\begin{aligned} \bar{\gamma}(\underline{r}, \underline{x}_1) &= \int_{-\frac{1}{2}}^{\frac{1}{2}} d\eta \gamma(\underline{r}, \underline{x}_1 + \eta \underline{r}) \\ &= n^2 h(r) [1 + 2 \epsilon \cos(\underline{k} \cdot \underline{x}_1 - \omega t) \frac{\sin \underline{k} \cdot \underline{r}}{\underline{k} \cdot \underline{r}}]. \end{aligned} \quad (\text{XV.5})$$

The intermolecular contribution to the stress tensor for a system with a continuous potential is, from Eq. (XIII.6),

$$\underline{T}_{\text{int}} = \frac{1}{2} \int d\underline{r} \hat{\underline{r}} \underline{r} \phi'(r) \bar{\gamma}(\underline{r}, \underline{x}_1) \quad (\text{XV.6})$$

so that, for our example,

$$\begin{aligned} \underline{T}_{\text{int}} &= \frac{1}{2} n^2 \int d\underline{r} \hat{\underline{r}} \underline{r} \phi'(r) h(r) \\ &+ \epsilon \cos(\underline{k} \cdot \underline{x}_1 - \omega t) n^2 \int d\underline{r} \hat{\underline{r}} \underline{r} \phi'(r) h(r) \frac{\sin \underline{k} \cdot \underline{r}}{\underline{k} \cdot \underline{r}}. \end{aligned} \quad (\text{XV.7})$$

Now, the first term on the right of Eq. (XV.7) is not to be confused with the intermolecular contribution to the equilibrium pressure, as we have not assumed that $h(r)$ is the equilibrium radial distribution function.

The Irving and Kirkwood expansion is obtained by expanding $\frac{\sin \underline{k} \cdot \underline{r}}{\underline{k} \cdot \underline{r}}$ in a power series in $(\underline{k} \cdot \underline{r})$ in Eq. (XV.7). We see immediately that unless ϕ' goes to zero in the limit of large r faster than any positive power of $(\frac{1}{r})$ we encounter the previous difficulty in that the contributions of most of the terms are not defined. The long wavelength limit is found by setting $\frac{\sin \underline{k} \cdot \underline{r}}{\underline{k} \cdot \underline{r}} = 1$ giving us

$$(\underline{T}_{\text{int}})_{\ell_w} = [(1 + 2 \epsilon \cos(\underline{k} \cdot \underline{x}_1 - \omega t)) \frac{2\pi}{3} n^2 \int_0^{\infty} dr r^3 \phi'(r) h(r)] \underline{I} \quad (\text{XV.8})$$

where $\underline{\underline{I}}$ is the unit tensor. Hence, in the long wavelength limit $\underline{\underline{T}}_{int}$ is spherical and there are no shears present unless the kinetic contribution is nonspherical.

In order to determine $\underline{\underline{T}}_{int}$ in the general case we shall assume that \underline{k} is in the \hat{e}_3 direction. Performing the integration over angles in Eq. (XV.7) we find

$$\begin{aligned} \left(\underline{\underline{T}}_{int} \right)_{3,3} &= \frac{2\pi}{3} n^2 \int_0^\infty dr r^3 \phi' h \\ &+ 4\pi \epsilon \cos(\underline{k} \cdot \underline{x}_1 - \omega t) n^2 \int_0^\infty dr r^3 \phi' h \left(\frac{1}{kr} \right)^3 (\sin kr - kr \cos kr) \end{aligned} \quad (XV.9)$$

and

$$\begin{aligned} \left(\underline{\underline{T}}_{int} \right)_{1,1} &= \left(\underline{\underline{T}}_{int} \right)_{2,2} = \frac{2\pi}{3} n^2 \int_0^\infty dr r^3 \phi' h \\ &+ 2\pi \epsilon \cos(\underline{k} \cdot \underline{x}_1 - \omega t) n^2 \int_0^\infty dr r^3 \phi' h \left[\frac{1}{kr} \text{Si}(kr) - \left(\frac{1}{kr} \right)^3 (\sin kr - kr \cos kr) \right] \end{aligned} \quad (XV.10)$$

where, in the above,¹²

$$\text{Si}(x) = \int_0^x dy \frac{\sin y}{y} . \quad (XV.11)$$

All of the off diagonal elements vanish, but the stress quadric is now an ellipsoid of revolution so that the fluid is undergoing shear.

It is interesting to note that, in the short wavelength limit ($k \rightarrow \infty$), $\text{Si}(kr) \rightarrow \frac{\pi}{2}$ so that

$$\left(\begin{array}{c} T_{int} \\ z \end{array} \right)_{3,3} \rightarrow \frac{2\pi}{3} n^2 \int_0^{\infty} dr r^3 \phi' h + \text{order } \left(\frac{1}{k}\right)^2 \quad (\text{XV.12})$$

and

$$\begin{aligned} \left(\begin{array}{c} T_{int} \\ z \end{array} \right)_{1,1} &= \left(\begin{array}{c} T_{int} \\ z \end{array} \right)_{2,2} \rightarrow \frac{2\pi}{3} n^2 \int_0^{\infty} dr r^3 \phi' h \\ &+ \frac{\pi}{k} \cos(k \cdot \tilde{x}_1 - \omega t) n^2 \int_0^{\infty} dr r^2 \phi' h + \text{order } \left(\frac{1}{k}\right)^2. \end{aligned} \quad (\text{XV.13})$$

Hence, in the limit of short wavelength the stress tensor returns to its spherical form. Moreover, if in this limit $h(r)$ approaches the equilibrium radial distribution function then T_{int} is unaffected by the disturbance and the perturbed part of T_{int} in the \hat{k} "direction" vanishes more quickly than the perturbed part of T_{int} in the \hat{e}_1 and \hat{e}_2 "directions".

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FOOTNOTES

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