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777.9 cm^{-1} . The band at 809.7 cm^{-1} has been interpreted as 2×394 , the rather large difference between calculated and observed frequency being ascribed to the proximity to the A_g fundamental. However, this band could be an upper-stage band corresponding to 819 cm^{-1} .

The interpretation of the faint sharp band at 769.4 cm^{-1} as an upper-stage band, $778 + \nu_i - \nu_i$, seems more plausible than its interpretation as the B_{3g} combination, $210 + 558 \text{ cm}^{-1}$. The faint sharp Raman band at 828.7 cm^{-1} has been interpreted as an upper-stage band, $2\times 407 + \nu_k - \nu_k$, rather than as the B_{3g} difference band $1340 - 510 \text{ cm}^{-1}$, because the corresponding sum band

has not been observed. If the preferred interpretations are correct, the group of Raman bands, 769, 778, 819, and 829 cm^{-1} , are related to each other in much the same manner as similar groups in the spectra of CO_2 and CS_2 .

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The Statistical Mechanical Theory of Transport Processes. IV. The Equations of Hydrodynamics*

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The equations of hydrodynamics—continuity equation, equation of motion, and equation of energy transport—are derived by means of the classical statistical mechanics. Thereby, expressions are obtained for the stress tensor and heat current density in terms of molecular variables. In addition to the familiar terms occurring in the kinetic theory of gases, there are terms depending upon intermolecular force. The contributions of intermolecular force to the stress tensor and heat current density are expressed, respectively, as quadratures of the density and current density in the configuration space of a pair of molecules.

INTRODUCTION

THIS paper will be concerned with a derivation of the equations of hydrodynamics from the principles of the classical statistical mechanics. In particular, the equation of continuity, the equation of motion, and the equation of energy transport will be derived. By so doing, the stress tensor and heat current density can be expressed in terms of molecular variables. The stress tensor consists of a kinetic part (which occurs in the kinetic theory of gases) and another term (dominant for a liquid) which will be expressed as a quadrature involving the potential of intermolecular force and the density of pairs of molecules. The heat current density is the sum of the familiar kinetic part and a quadrature involving the potential of intermolecular force and the density and current density in the configuration space of a pair of molecules. The results were previously stated in the first article of this series,¹ when this derivation was promised.

To obtain explicit expressions for the pair probability density and probability current density one would in principle need to solve the Liouville equation [Eq. (2.2)] for the probability distribution in Gibbs phase space and then perform repeated integrations. Since

this program is untenable for a liquid, various attempts have been made to obtain a closed equation satisfied approximately by the probability distribution function² in the phase space of a pair of molecules. One such equation has been derived by Born and Green² using a generalized "superposition" assumption. Another, a generalization of the well-known Fokker-Planck equation of stochastic theory, has been derived by Kirkwood³ by introducing the concepts of time smoothing and a friction constant. This latter equation has been applied to obtain an expression for the stress tensor linear in gradients of fluid velocity and, thereby, expressions (in terms of molecular variables) for coefficients of shear and volume viscosity.³ The same equation generalized to non-uniform temperatures, after linearizing in the temperature gradient, leads to an explicit expression for the heat current and thereby to an expression for the coefficient of thermal conductivity.⁴ We shall assume, for purposes of mathematical simplicity, a single component, single phase fluid system consisting of molecules which interact under central forces only. It is not difficult to generalize the treatment to a multiple component or multiple

² M. Born and H. S. Green, Proc. Roy. Soc. A188, 10 (1946).

³ Kirkwood, Buff, and Green, J. Chem. Phys. 17, 988 (1949).

⁴ Kirkwood, Standart, and Irving (in preparation). The numerical evaluation awaits a more precise computation of the theoretical radial distribution function.

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¹ J. G. Kirkwood, J. Chem. Phys. 14, 180 (1946).

phase system or to include molecular interaction depending upon rotational or internal degrees of freedom. Before entering upon the statistical mechanical theory, we shall first review the phenomenological theory of the hydrodynamical equations.

I. THE PHENOMENOLOGICAL THEORY

We imagine a continuous fluid consisting of a single chemical component with mass density $\rho(\mathbf{r}; t)$ and local velocity $\mathbf{u}(\mathbf{r}; t)$ at the point \mathbf{r} and at the time t . We now imagine ω to be a fixed region somewhere in the interior of the fluid. The mass of the fluid within ω is given by

$$\int_{\omega} \rho(\mathbf{r}; t) d\omega.$$

Its rate of change, since ω is fixed (not moving with the fluid), is

$$\int_{\omega} \frac{\partial}{\partial t} \rho(\mathbf{r}; t) d\omega.$$

This increase of mass must be entirely due to influx of fluid through the boundary S of ω , i.e.,

$$\int_{\omega} \frac{\partial}{\partial t} \rho d\omega = - \int_S \rho \mathbf{u} \cdot d\mathbf{S} = - \int_{\omega} \nabla \cdot [\rho \mathbf{u}] d\omega$$

where the surface integral has been converted to a volume integral by Gauss' theorem. Since ω is quite arbitrary, upon equating integrands, we get the continuity equation

$$\frac{\partial}{\partial t} \rho(\mathbf{r}; t) = - \nabla \cdot [\rho(\mathbf{r}; t) \mathbf{u}(\mathbf{r}; t)]. \quad (1.1)$$

The hydrodynamical equation of motion may be derived by equating the rate of change of momentum within ω ,

$$\int_{\omega} \frac{\partial}{\partial t} [\rho(\mathbf{r}; t) \mathbf{u}(\mathbf{r}; t)] d\omega$$

plus the rate of flow of momentum out through the surface of ω ,

$$\int_S \rho(\mathbf{r}; t) \mathbf{u}(\mathbf{r}; t) \mathbf{u}(\mathbf{r}; t) \cdot d\mathbf{S} = \int_{\omega} \nabla \cdot [\rho \mathbf{u} \mathbf{u}] d\omega$$

to the sum of the forces acting on the fluid within ω . These forces are the body force

$$\int_{\omega} \mathbf{X}(\mathbf{r}; t) d\omega,$$

where \mathbf{X} is the force per unit volume due to external sources, and the surface force.

$$\int_S \boldsymbol{\sigma}(\mathbf{r}; t) \cdot d\mathbf{S} = \int_{\omega} \nabla \cdot \boldsymbol{\sigma} d\omega,$$

where $\boldsymbol{\sigma}$ is the symmetric stress tensor.

Since ω is arbitrary, the resulting differential equation is

$$\frac{\partial}{\partial t} [\rho \mathbf{u}] + \nabla \cdot [\rho \mathbf{u} \mathbf{u}] = \mathbf{X} + \nabla \cdot \boldsymbol{\sigma}. \quad (1.2)$$

We now introduce the internal energy density, $E(\mathbf{r}; t)$, consisting of three parts—the interaction potential energy density, $E_V(\mathbf{r}; t)$, due to interactions between fluid particles; the kinetic energy density, $E_K(\mathbf{r}; t)$; and the potential energy density, $E_{\psi}(\mathbf{r}; t)$, due to external sources, assumed to be conservative.

$$E = E_V + E_K + E_{\psi}. \quad (1.3)$$

The rate of change of internal energy within ω is

$$\int_{\omega} \frac{\partial}{\partial t} E(\mathbf{r}; t) d\omega.$$

The rate of flux of energy from ω is

$$\int_S [E(\mathbf{r}; t) \mathbf{u}(\mathbf{r}; t) + \mathbf{q}(\mathbf{r}; t)] \cdot d\mathbf{S} = \int_{\omega} \nabla \cdot [E \mathbf{u} + \mathbf{q}] d\omega$$

where $E \mathbf{u}$ is the convective energy current and \mathbf{q} is the conductive heat current. The work done per unit time by the fluid within ω on the rest of the system is

$$- \int_{\omega} \mathbf{u} \cdot \boldsymbol{\sigma} \cdot d\mathbf{S} = - \int_{\omega} \nabla \cdot (\mathbf{u} \cdot \boldsymbol{\sigma}) d\omega.$$

According to the law of conservation of energy, the sum of these three rates must vanish. Since ω is arbitrary, the sum of the integrands must also vanish, giving the energy transport equation

$$(\partial/\partial t) E + \nabla \cdot [E \mathbf{u} + \mathbf{q} - \mathbf{u} \cdot \boldsymbol{\sigma}] = 0. \quad (1.4)$$

II. STATISTICAL MECHANICAL THEORY—THE DISTRIBUTION FUNCTION AND EXPECTATION VALUES

In the statistical mechanical theory we no longer consider a continuous fluid, but rather we treat a system consisting of N molecules, each having three degrees of translational freedom (but for the sake of simplicity, no other degrees of freedom). We denote the positions of these molecules by the sequence of three-vectors $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N$, and their momenta by $\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N$. According to Gibbs, the instantaneous state of the system may be represented by a point in the $6N$ -dimensional phase space representing the $3N$ coordinates and $3N$ momenta of the system. We may consider our representative system as drawn randomly from an ensemble of similar systems, the state of each being confined to that portion of phase space consistent with the macroscopic restraints imposed in the preparation of the system.†

† See reference 1 for a discussion of the process of measurement.

The probability distribution function (relative density of representative points in phase space) we denote by

$$f(\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{p}_1, \dots, \mathbf{p}_N; t),$$

satisfying the normalization condition

$$\int \cdots \int_{6N \text{ fold}} f d\mathbf{R}_1 \cdots d\mathbf{R}_N d\mathbf{p}_1 \cdots d\mathbf{p}_N = 1 \quad (2.1)$$

where $d\mathbf{R}_k$ stands for a volume element in the configuration space and $d\mathbf{p}_k$ a volume element in the momentum space of the k th molecule. f changes in time according to the well-known Liouville equation

$$\frac{\partial f}{\partial t} = \sum_{k=1}^N \left[-\frac{\mathbf{p}_k}{m_k} \cdot \nabla_{\mathbf{R}_k} f + \nabla_{\mathbf{R}_k} U \cdot \nabla_{\mathbf{p}_k} f \right] \quad (2.2)$$

where U is the potential energy of the entire system.

Any dynamical variable, $\alpha(\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{p}_1, \dots, \mathbf{p}_N)$, has an expectation value given at time t by

$$\langle \alpha; f \rangle = \int \cdots \int_{6N \text{ fold}} \alpha(\mathbf{R}_1, \dots, \mathbf{p}_1 \cdots) f(\mathbf{R}_1, \dots, \mathbf{p}_1, \dots; t) \times d\mathbf{R}_1 \cdots d\mathbf{R}_N d\mathbf{p}_1 \cdots d\mathbf{p}_N. \quad (2.3)$$

We thus denote by $\langle \alpha; f \rangle$ the expectation value of α for a distribution function f . (It is merely the inner product of α and f taken over phase space.)

Providing α does not depend on time explicitly, the rate of change of the expectation value of α is given by

$$\frac{\partial}{\partial t} \langle \alpha; f \rangle = \left\langle \alpha; \frac{\partial f}{\partial t} \right\rangle = \sum_{k=1}^N \left[\left\langle \alpha; -\frac{\mathbf{p}_k}{m_k} \cdot \nabla_{\mathbf{R}_k} f \right\rangle + \langle \alpha; \nabla_{\mathbf{R}_k} U \cdot \nabla_{\mathbf{p}_k} f \rangle \right]. \quad (2.4)$$

By Green's theorem applied in the space of \mathbf{R}_k

$$\left\langle \alpha; -\frac{\mathbf{p}_k}{m_k} \cdot \nabla_{\mathbf{R}_k} f \right\rangle = \left\langle \frac{\mathbf{p}_k}{m_k} \cdot \nabla_{\mathbf{R}_k} \alpha; f \right\rangle \quad (2.5)$$

providing the integrated part vanishes; i.e., providing the system is bounded or f falls off sufficiently rapidly as $\mathbf{R}_k \rightarrow \infty$. Likewise, since $\nabla_{\mathbf{R}_k} U$ is independent of momentum \mathbf{p}_k , and since f falls off rapidly as $\mathbf{p}_k \rightarrow \infty$, use of Green's theorem in the momentum space of \mathbf{p}_k yields

$$\langle \alpha; \nabla_{\mathbf{R}_k} U \cdot \nabla_{\mathbf{p}_k} f \rangle = -\langle \nabla_{\mathbf{R}_k} U \cdot \nabla_{\mathbf{p}_k} \alpha; f \rangle. \quad (2.6)$$

Thus, (2.4) becomes

$$\frac{\partial}{\partial t} \langle \alpha; f \rangle = \sum_{k=1}^N \left\langle \frac{\mathbf{p}_k}{m_k} \cdot \nabla_{\mathbf{R}_k} \alpha - \nabla_{\mathbf{R}_k} U \cdot \nabla_{\mathbf{p}_k} \alpha; f \right\rangle \quad (2.7)$$

giving the rate of change of the expectation value of α

as the expectation value of the dynamical variable

$$\sum_{k=1}^N \left[\frac{\mathbf{p}_k}{m_k} \cdot \nabla_{\mathbf{R}_k} \alpha - \nabla_{\mathbf{R}_k} U \cdot \nabla_{\mathbf{p}_k} \alpha \right].$$

We shall use (2.7) to derive the equations of hydrodynamics.

III. STATISTICAL MECHANICAL EXPRESSIONS FOR DENSITIES

The equations of hydrodynamics (1.1), (1.2), and (1.4) are concerned with densities in ordinary 3-space, e.g., mass density, momentum density, and energy density. We shall now express these as the expectation values of dynamical variables over an ensemble having distribution function f .

The probability per unit volume that the k th molecule be at \mathbf{R}_k is

$$\int \cdots \int_{6N-3 \text{ fold}} f(\mathbf{R}_1, \dots, \mathbf{p}_1, \dots; t) d\mathbf{R}_1 \cdots \times d\mathbf{R}_{k-1} d\mathbf{R}_{k+1} \cdots d\mathbf{R}_N d\mathbf{p}_1 \cdots d\mathbf{p}_N$$

where the integration is over all position vectors except \mathbf{R}_k and over all momenta vectors. Introducing Dirac's δ -function, the probability per unit volume that the k th molecule be at \mathbf{r} at time t is

$$\begin{aligned} &\langle \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \\ &= \int \cdots \int_{6N \text{ fold}} \delta(\mathbf{R}_k - \mathbf{r}) f(\mathbf{R}_1, \dots; \mathbf{p}_1, \dots; t) d\mathbf{R}_1 \cdots d\mathbf{p}_N. \end{aligned}$$

The total mass density at \mathbf{r} due to all molecules is thus given at time t by

$$\rho(\mathbf{r}; t) = \sum_{k=1}^N m_k \langle \delta(\mathbf{R}_k - \mathbf{r}); f \rangle. \quad (3.1)$$

The mean momentum of the k th molecule, providing it is at \mathbf{r} and the locations of the others are unspecified, is given by the ratio

$$\begin{aligned} &\frac{\int \cdots \int_{6N \text{ fold}} \mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r}) f(\mathbf{R}_1, \dots; \mathbf{p}_1, \dots; t) d\mathbf{R}_1 \cdots d\mathbf{p}_N}{\int \cdots \int_{6N \text{ fold}} \delta(\mathbf{R}_k - \mathbf{r}) f(\mathbf{R}_1, \dots; \mathbf{p}_1, \dots; t) d\mathbf{R}_1 \cdots d\mathbf{p}_N} \\ &= \frac{\langle \mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r}); f \rangle}{\langle \delta(\mathbf{R}_k - \mathbf{r}); f \rangle}. \end{aligned}$$

Consequently, $\langle \mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r}); f \rangle$ is the product of this mean momentum by the probability per unit volume that the k th molecule be at \mathbf{r} ; i.e., it is the contribution of the k th molecule to the momentum per unit volume (mass current density). The total momentum density

at \mathbf{r} is thus given at time t by

$$\rho(\mathbf{r}; t) \mathbf{u}(\mathbf{r}; t) = \sum_{k=1}^N \langle \mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r}); f \rangle, \quad (3.2)$$

where $\mathbf{u}(\mathbf{r}; t)$, thus defined, is the mean fluid velocity at \mathbf{r} .

There is no difficulty encountered in defining mass density or momentum density since the mass or momentum of any molecule may be considered as localized at that molecule. This is also true of kinetic energy density. Since the kinetic energy of the k th molecules is $\mathbf{p}_k^2/2m_k$ (where \mathbf{p}_k is the magnitude of the vector \mathbf{p}_k), its contribution to the kinetic energy density at \mathbf{r} is $\langle (\mathbf{p}_k^2/2m_k) \delta(\mathbf{R}_k - \mathbf{r}); f \rangle$, and the entire kinetic energy density at \mathbf{r} is given at the time t by

$$E_K(\mathbf{r}; t) = \sum_{k=1}^N \left\langle \frac{\mathbf{p}_k^2}{2m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle. \quad (3.3)$$

The potential energy, U , of the system we shall assume to be of the form

$$U = \sum_{k=1}^N \psi_k(\mathbf{R}_k) + \frac{1}{2} \sum_{j \neq k} V_{jk} \quad (3.4)$$

where $\psi_k(\mathbf{R}_k)$ is the potential energy of the k th molecule in an external field of force, and V_{jk} is the mutual potential between the j th and k th molecules.

The potential energy $\psi_k(\mathbf{R}_k)$ may quite naturally be considered localized at \mathbf{R}_k , the location of the k th molecule. Thus, the total potential energy density at \mathbf{r} associated with the interaction of molecules with the external field is

$$\begin{aligned} E_\psi(\mathbf{r}; t) &= \sum_{k=1}^N \langle \psi_k(\mathbf{R}_k) \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \\ &= \sum_{k=1}^N \psi_k(\mathbf{r}) \langle \delta(\mathbf{R}_k - \mathbf{r}); f \rangle. \end{aligned} \quad (3.5)$$

Similarly the force on the k th molecule due to external sources is $-\nabla_{\mathbf{R}_k} \psi_k(\mathbf{R}_k)$, and the external force (body force) per unit volume at \mathbf{r} is

$$\begin{aligned} X(\mathbf{r}; t) &= - \sum_{k=1}^N \langle [\nabla_{\mathbf{R}_k} \psi_k(\mathbf{R}_k)] \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \\ &= - \sum_{k=1}^N \langle \nabla_{\mathbf{r}} \psi_k(\mathbf{r}) \rangle \langle \delta(\mathbf{R}_k - \mathbf{r}); f \rangle. \end{aligned} \quad (3.6)$$

The potential V_{jk} , depending on the location of both the j th and the k th molecule, is not so naturally localizable; it may only be considered as localized at a point in the six-dimensional configuration space of the pair. It is necessary, however, to define interaction potential energy density in 3-space, for this concept is required to give meaning to the internal energy density of the energy transport equation. For most systems of interest the potential V_{jk} is a short-range function of the

molecular separation, R_{jk} , and consequently contributes negligibly to the potential energy unless molecules j and k are close, in which case, if the interaction potential energy be considered as distributed in any manner in the vicinity of the pair, it is sufficiently localized for macroscopic applications. This localization may be made quite precise (though arbitrary) by saying that half of the energy V_{jk} resides in each molecule of the pair. By this formal definition the total interaction potential energy residing in the k th molecule is

$$\frac{1}{2} \sum_{j=1, j \neq k}^N V_{jk}$$

and the total interaction potential energy density at \mathbf{r} is

$$E_V(\mathbf{r}; t) = \frac{1}{2} \sum_{j \neq k} \langle V_{jk} \delta(\mathbf{R}_k - \mathbf{r}); f \rangle. \quad (3.7)$$

As mentioned previously, the stress tensor and heat current density will be expressed as quadratures involving the pair density of molecules and the current density in pair space, respectively.

The pair density, $\rho^{(2)}(\mathbf{r}, \mathbf{r}'; t)$ is the probability per (unit volume)² that one molecule (any molecule) will be at \mathbf{r} and another will be at \mathbf{r}' . It is given by

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}'; t) = \sum_{j \neq k} \langle \delta(\mathbf{R}_j - \mathbf{r}) \delta(\mathbf{R}_k - \mathbf{r}'); f \rangle. \quad (3.8)$$

The pair density is a symmetric function of its two arguments, \mathbf{r} and \mathbf{r}' .

The particle current density in pair space is given by the six-component vector

$$\begin{aligned} \mathbf{j}^{(2)}(\mathbf{r}, \mathbf{r}'; t) &= \sum_{k \neq i} \left\langle \left(\frac{\mathbf{p}_k}{m_k} \oplus \frac{\mathbf{p}_i}{m_i} \right) \right. \\ &\quad \left. \times \delta(\mathbf{R}_k - \mathbf{r}) \delta(\mathbf{R}_i - \mathbf{r}'); f \right\rangle. \end{aligned} \quad (3.9)$$

In this equation $(\mathbf{p}_k/m_k) \oplus (\mathbf{p}_i/m_i)$ is also a six-component vector, the velocity in the pair space of the k th and i th molecules. It is the direct sum of \mathbf{p}_k/m_k , lying entirely in the three-dimensional subspace of the k th molecule, and \mathbf{p}_i/m_i , lying in the subspace of the i th molecule. The six components of $\mathbf{j}^{(2)}$ may be labeled as the corresponding components of $\mathbf{r} \oplus \mathbf{r}'$. The first three components, i.e., the projection of $\mathbf{j}^{(2)}$ onto the space of its first argument, \mathbf{r} , is

$$\mathbf{j}_1^{(2)}(\mathbf{r}, \mathbf{r}'; t) = \sum_{k \neq i} \left\langle \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}) \delta(\mathbf{R}_i - \mathbf{r}'); f \right\rangle. \quad (3.10)$$

It is this quantity which will arise in the expression for heat current. $\mathbf{j}_1^{(2)}(\mathbf{r}, \mathbf{r}'; t)$ may be interpreted as the particle current density at \mathbf{r} (in ordinary physical space), if another particle is at \mathbf{r}' , multiplied by the particle

density at \mathbf{r}' . In contrast to the pair density, $j_1^{(2)}(\mathbf{r}, \mathbf{r}'; t)$ is not a symmetrical function of \mathbf{r} and \mathbf{r}' .

The densities which have been defined in this section are point functions. They are all ensemble averages of dynamical variables. It should be emphasized, however, that the conventional hydrodynamics is concerned with macroscopic observables. In measuring these observables one not only takes a statistical average over the systems of an ensemble (by repeating the observations many times) but two additional averages as well. The first is a spatial average over a microscopically large though macroscopically small domain, determined by the resolving power of one's measuring instruments. The second is a time average over an interval determined by the relaxation time of one's measuring instruments. The equation of hydrodynamics are thus relations among these measured averages, found to hold empirically.

In addition to the point function densities defined above, we shall later give a point function definition for stress tensor and heat current. It is interesting that these point functions, though averaged neither over space nor time, satisfy equations that are identical in form to the equations of hydrodynamics (at least to those hydrodynamical equations for a single component, single phase system, derived in Section I). In the following sections we shall derive the hydrodynamical-like equations satisfied by these point functions. To obtain the hydrodynamical equations themselves it is merely necessary to perform the appropriate space and time averages.

It will be noted that in defining the densities, heretofore, we have made no reference to the similarity of molecules. Nor are the derivations of the statistical mechanical expressions for the time rate of change of these densities facilitated by imposing the restriction of similar molecules. It is only when we are ready to define the point function stress tensor and heat current density that we must impose this restriction; for these functions are defined so as to satisfy the hydrodynamical equations of Section I, which are only valid for a single component, single phase system.

IV. THE EQUATION OF CONTINUITY

We now apply Eq. (2.7) to the derivation of the equation of continuity. To this end we take α to be

$$\alpha = \sum_{j=1}^N m_j \delta(\mathbf{R}_j - \mathbf{r}). \quad (4.1)$$

Then, as required for (2.7),

$$\begin{aligned} \frac{\mathbf{p}_k}{m_k} \cdot \nabla \mathbf{R}_k \alpha - \nabla \mathbf{R}_k U \cdot \nabla \mathbf{p}_k \alpha &= \mathbf{p}_k \cdot \nabla \mathbf{R}_k \delta(\mathbf{R}_k - \mathbf{r}) \\ &= -\nabla \mathbf{r} \cdot [\mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r})]. \end{aligned} \quad (4.2)$$

From the definition (3.1), Eqs. (4.1), (2.7), and (4.2),

and finally the definition (3.2)

$$\begin{aligned} \frac{\partial}{\partial t} \rho(\mathbf{r}; t) &= -\langle \alpha; f \rangle = \sum_{k=1}^N \langle -\nabla \mathbf{r} \cdot [\mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r})]; f \rangle \\ &= -\nabla \mathbf{r} \cdot [\rho(\mathbf{r}; t) \mathbf{u}(\mathbf{r}; t)] \end{aligned}$$

which is the equation of continuity, (1.1).

V. THE HYDRODYNAMICAL EQUATION OF MOTION (MOMENTUM TRANSPORT)

Before deriving the hydrodynamical equation of motion we wish to alter (2.7) to give the rate of change of the expectation value of a vector α having components α_ν . According to (2.7), for $\nu = 1, 2, 3$,

$$\frac{\partial}{\partial t} \langle \alpha_\nu; f \rangle = \sum_{k=1}^N \left\langle \frac{\mathbf{p}_k}{m_k} \cdot \nabla \mathbf{R}_k \alpha_\nu - \nabla \mathbf{R}_k U \cdot \nabla \mathbf{p}_k \alpha_\nu; f \right\rangle.$$

These three equations ($\nu = 1, 2, 3$) may be written in diadic notation as

$$\frac{\partial}{\partial t} \langle \alpha; f \rangle = \sum_{k=1}^N \left\langle \left(\frac{\mathbf{p}_k}{m_k} \cdot \nabla \mathbf{R}_k \right) \alpha - (\nabla \mathbf{R}_k U \cdot \nabla \mathbf{p}_k) \alpha; f \right\rangle. \quad (5.1)$$

We now take α to be

$$\alpha = \sum_{j=1}^N \mathbf{p}_j \delta(\mathbf{R}_j - \mathbf{r}). \quad (5.2)$$

Then

$$\begin{aligned} \left(\frac{\mathbf{p}_k}{m_k} \cdot \nabla \mathbf{R}_k \right) \alpha - (\nabla \mathbf{R}_k U \cdot \nabla \mathbf{p}_k) \alpha &= \left(\frac{\mathbf{p}_k}{m_k} \cdot \nabla \mathbf{R}_k \right) \mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r}) \\ &\quad - (\nabla \mathbf{R}_k U \cdot \nabla \mathbf{p}_k) \mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r}) = -\nabla \mathbf{r} \cdot \left[\frac{\mathbf{p}_k \mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}) \right] \\ &\quad - (\nabla \mathbf{R}_k U) \delta(\mathbf{R}_k - \mathbf{r}). \end{aligned} \quad (5.3)$$

From (3.4)

$$\nabla \mathbf{R}_k U = \nabla \mathbf{R}_k \psi_k(\mathbf{R}_k) + \sum_{\substack{j=1 \\ j \neq k}}^N \nabla \mathbf{R}_k V_{jk}. \quad (5.4)$$

From (5.2) and the definition of momentum density, (3.2), we have

$$\langle \alpha; f \rangle = \rho(\mathbf{r}; t) \mathbf{u}(\mathbf{r}; t). \quad (5.5)$$

Substituting (5.5) and (5.3) into (5.1) and replacing $\nabla \mathbf{R}_k U$ by its equivalent given in (5.4), we obtain, upon introducing \mathbf{X} , the body force defined in (3.6),

$$\begin{aligned} \frac{\partial}{\partial t} [\rho(\mathbf{r}; t) \mathbf{u}(\mathbf{r}; t)] &= -\nabla \mathbf{r} \cdot \sum_{k=1}^N \left\langle \frac{\mathbf{p}_k \mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \\ &\quad + \mathbf{X}(\mathbf{r}; t) - \sum_{j \neq k} \sum \langle (\nabla \mathbf{R}_k V_{jk}) \delta(\mathbf{R}_k - \mathbf{r}); f \rangle. \end{aligned} \quad (5.6)$$

The first term on the right in Eq. (5.6) may be

modified by noting that

$$\begin{aligned} & \sum_{k=1}^N m_k \left\langle \left(\frac{\mathbf{p}_k}{m_k} - \mathbf{u} \right) \left(\frac{\mathbf{p}_k}{m_k} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \\ &= \sum_{k=1}^N \left\langle \frac{\mathbf{p}_k \mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle - \mathbf{u} \sum_{k=1}^N \langle \mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \\ & - \sum_{k=1}^N \langle \mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \mathbf{u} + \mathbf{u} \mathbf{u} \sum_{k=1}^N m_k \langle \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \\ &= \sum_{k=1}^N \left\langle \frac{\mathbf{p}_k \mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle - \rho \mathbf{u} \mathbf{u} \quad (5.7) \end{aligned}$$

where we have used (3.1) and (3.2).

The last term in (5.6) may be cast in a more convenient form by symmetrizing with respect to the dummy indices j and k .

$$\begin{aligned} & - \sum_{j \neq k} \langle (\nabla \mathbf{R}_k V_{jk}) \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \\ &= -\frac{1}{2} \sum_{j \neq k} \langle (\nabla \mathbf{R}_k V_{jk}) \delta(\mathbf{R}_k - \mathbf{r}) \\ & + (\nabla \mathbf{R}_j V_{kj}) \delta(\mathbf{R}_j - \mathbf{r}); f \rangle = -\frac{1}{2} \sum_{j \neq k} \langle (\nabla \mathbf{R}_k V_{jk}) \\ & \times [\delta(\mathbf{R}_k - \mathbf{r}) - \delta(\mathbf{R}_j - \mathbf{r})]; f \rangle. \quad (5.8) \end{aligned}$$

$$\begin{aligned} (\partial/\partial t)[\rho \mathbf{u}] + \nabla_r \cdot [\rho \mathbf{u} \mathbf{u}] &= \mathbf{X} + \nabla_r \cdot \left[- \sum_{k=1}^N m_k \left\langle \left(\frac{\mathbf{p}_k}{m_k} - \mathbf{u} \right) \left(\frac{\mathbf{p}_k}{m_k} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \right. \\ & \left. + \frac{1}{2} \sum_{j \neq k} \left\langle (\nabla \mathbf{R}_k V_{jk}) \mathbf{R}_{jk} \left\{ 1 - \frac{1}{2} \mathbf{R}_{jk} \cdot \nabla_r + \dots + \frac{1}{n!} (-\mathbf{R}_{jk} \cdot \nabla_r)^{n-1} + \dots \right\} \delta(\mathbf{R}_j - \mathbf{r}); f \right\rangle \right]. \quad (5.11) \end{aligned}$$

Equation (5.11) has been derived without referring to the restriction of a single component, single phase system. In fact, the equation holds as well when there are non-central forces depending upon rotational or other internal degrees of freedom.†

† In the event that there are other degrees of freedom ξ_i having conjugate momenta η_i , then f is a distribution function in a phase space of higher dimensions, and the expectation value of a dynamical variable α is $\langle \alpha; f \rangle$, where the brackets now indicate integration over this entire phase space. The Liouville equation, (2.2), must be amended by adding to the right

$$\sum_i \left[-\frac{\partial H}{\partial \eta_i} \frac{\partial f}{\partial \xi_i} + \frac{\partial H}{\partial \xi_i} \frac{\partial f}{\partial \eta_i} \right],$$

where H is the Hamiltonian of the system. This changes the expression for $(\partial/\partial t)\langle \alpha; f \rangle$ by

$$\sum_i \left\langle \alpha; -\frac{\partial H}{\partial \eta_i} \frac{\partial f}{\partial \xi_i} + \frac{\partial H}{\partial \xi_i} \frac{\partial f}{\partial \eta_i} \right\rangle.$$

Providing α is independent of all ξ_i and η_i , this vanishes upon integrating the first term by parts with respect to ξ_i , and the second term with respect to η_i , assuming that the integrated parts also vanish (e.g., if ξ_i is cyclic and $f \rightarrow 0$ rapidly as $\eta_i \rightarrow \pm \infty$).

Where we have used Newton's third law:

$$\nabla \mathbf{R}_j V_{kj} = -\nabla \mathbf{R}_k V_{jk}.$$

The difference of the δ -functions may be expanded formally as a Taylor's series in the vector separation, $\mathbf{R}_{jk} = \mathbf{R}_k - \mathbf{R}_j$.

$$\begin{aligned} & \delta(\mathbf{R}_k - \mathbf{r}) - \delta(\mathbf{R}_j - \mathbf{r}) \\ &= -\mathbf{R}_{jk} \cdot \nabla_r \delta(\mathbf{R}_j - \mathbf{r}) + \frac{1}{2} (\mathbf{R}_{jk} \cdot \nabla_r)^2 \delta(\mathbf{R}_j - \mathbf{r}) - \dots \\ & + \frac{1}{n!} (-\mathbf{R}_{jk} \cdot \nabla_r)^n \delta(\mathbf{R}_j - \mathbf{r}) + \dots \\ &= -\nabla_r \cdot \left[\mathbf{R}_{jk} \left\{ 1 - \frac{1}{2} \mathbf{R}_{jk} \cdot \nabla_r + \dots \right. \right. \\ & \left. \left. + \frac{1}{n!} (-\mathbf{R}_{jk} \cdot \nabla_r)^{n-1} + \dots \right\} \delta(\mathbf{R}_j - \mathbf{r}) \right]. \quad (5.9) \end{aligned}$$

Substituting (5.9) into (5.8) gives, after commuting ∇_r with the integration over phase space:

$$\begin{aligned} & - \sum_{j \neq k} \langle (\nabla \mathbf{R}_k V_{jk}) \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \\ &= \nabla_r \cdot \left[\frac{1}{2} \sum_{j \neq k} \left\langle (\nabla \mathbf{R}_k V_{jk}) \mathbf{R}_{jk} \left\{ 1 - \frac{1}{2} \mathbf{R}_{jk} \cdot \nabla_r \right. \right. \right. \\ & \left. \left. + \dots + \frac{1}{n!} (-\mathbf{R}_{jk} \cdot \nabla_r)^{n-1} + \dots \right\} \delta(\mathbf{R}_j - \mathbf{r}); f \right\rangle \right]. \quad (5.10) \end{aligned}$$

Substituting (5.7) and (5.10) into (5.6), we obtain

We now wish to compare (5.11) with (1.2), the hydrodynamical equation for a single component, single phase system. Consequently we must consider (5.11) when all particles are identical. We shall also limit the subsequent treatment to central forces depending on range only. Hence,

$$V_{jk} = V(R_{jk})$$

and

$$\nabla \mathbf{R}_k V_{jk} = \frac{\mathbf{R}_{jk}}{R_{jk}} V'(R_{jk}).$$

We are now ready to define a point function stress tensor, σ .

$$\sigma(\mathbf{r}; t) = \sigma_K(\mathbf{r}; t) + \sigma_V(\mathbf{r}; t) \quad (5.12)$$

Consequently, the expression for the rate of change of the expectation value of a dynamical variable independent of internal degrees of freedom is unchanged by the existence of these internal degrees of freedom. Thus, the derivation of (5.11) is equally valid for central or non-central forces depending upon rotational or other internal degrees of freedom.

$\sigma_K(\mathbf{r}; t)$

$$= -\sum_{k=1}^N m \left\langle \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \quad (5.13)$$

$$\sigma_V(\mathbf{r}; t) = \frac{1}{2} \sum_{j \neq k} \left\langle \frac{\mathbf{R}_{jk} \mathbf{R}_{jk}}{R_{jk}} V'(R_{jk}) \left\{ 1 - \frac{1}{2} \mathbf{R}_{jk} \cdot \nabla_{\mathbf{r}} + \dots + \frac{1}{n!} (-\mathbf{R}_{jk} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \right\} \delta(\mathbf{R}_j - \mathbf{r}); f \right\rangle. \quad (5.14)$$

With this definition Eq. (5.11) becomes identical in form to the hydrodynamical equation of motion, (1.2). It is an equation relating point function densities and the point function stress tensor. When appropriate space and time averages are taken, it becomes the hydrodynamical equation itself.

Since only the divergence of σ enters into the hydrodynamical equation of motion, σ itself is undetermined (so far as this equation goes) up to an arbitrary tensor of vanishing divergence. The stress tensor we have defined in Eqs. (5.12)–(5.14) is not only the most apparent choice to reduce (5.11) to the hydrodynamical equation of motion but also is the only choice in accord with the physical definition of the stress tensor as the force transmitted per unit area.

σ_K is the kinetic contribution to the stress tensor. $\sigma_K \cdot d\mathbf{S}$, viewed from a coordinate system moving with the local velocity \mathbf{u} , is the momentum transferred per unit time across the area $d\mathbf{S}$ due to the macroscopically imperceptible spread of the fluid velocities about the mean fluid velocity. σ_K is the familiar expression for the stress tensor which arises in the kinetic theory of gases, when the intermolecular force can be neglected. It is dominated by σ_V in liquids.

σ_V is the contribution of intermolecular forces to the stress tensor. $\sigma_V \cdot d\mathbf{S}$ represents the force acting across $d\mathbf{S}$ due to the interaction of molecules on opposite sides of $d\mathbf{S}$. This fact is demonstrated in the Appendix.

We now set out to express σ_V as a quadrature involving the pair density defined in (3.8). First we introduce into (5.14) a new δ -function, $\delta(\mathbf{R}_{jk} - \mathbf{R})$, and integration over the new variable, \mathbf{R} .

$$\sigma_V(\mathbf{r}; t) = \frac{1}{2} \sum_{j \neq k} \left\langle \int_{3 \text{ fold}} \delta(\mathbf{R}_{jk} - \mathbf{R}) \frac{\mathbf{R} \mathbf{R}}{R} V'(R) \left\{ 1 - \frac{1}{2} \mathbf{R} \cdot \nabla_{\mathbf{r}} + \dots + \frac{1}{n!} (-\mathbf{R} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \right\} \delta(\mathbf{R}_j - \mathbf{r}) d\mathbf{R}; f \right\rangle.$$

We now commute the integration over \mathbf{R} with the integration over phase and with the summation, and we factor out of the brackets and out of the sum all quantities which do not depend on the particle coordinates

nor the indices j and k .

$$\sigma_V(\mathbf{r}; t) = \frac{1}{2} \int_{3 \text{ fold}} \frac{\mathbf{R} \mathbf{R}}{R} V'(R) \times \left\{ 1 - \frac{1}{2} \mathbf{R} \cdot \nabla_{\mathbf{r}} + \dots + \frac{1}{n!} (-\mathbf{R} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \right\} \times \sum_{j \neq k} \langle \delta(\mathbf{R}_{jk} - \mathbf{R}) \delta(\mathbf{R}_j - \mathbf{r}); f \rangle d\mathbf{R}.$$

The product $\delta(\mathbf{R}_{jk} - \mathbf{R}) \delta(\mathbf{R}_j - \mathbf{r})$ is equivalent to the product $\delta(\mathbf{R}_j - \mathbf{r}) \delta(\mathbf{R}_k - \mathbf{r} - \mathbf{R})$; consequently the sum may be identified as the pair density defined in (3.8). This gives

$$\sigma_V(\mathbf{r}; t) = \frac{1}{2} \int_{3 \text{ fold}} \frac{\mathbf{R} \mathbf{R}}{R} V'(R) \left\{ 1 - \frac{1}{2} \mathbf{R} \cdot \nabla_{\mathbf{r}} + \dots + \frac{1}{n!} (-\mathbf{R} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \right\} \rho^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R}; t) d\mathbf{R}. \quad (5.15)$$

For a liquid, the pair density, $\rho^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R})$, considered as a function of the two independent coordinates \mathbf{r} and \mathbf{R} , is a slow function of \mathbf{r} , although a sensitive function of the relative coordinate, \mathbf{R} . Since the change in the pair density due to changing the independent variable \mathbf{r} by an amount \mathbf{R} , $\mathbf{R} \cdot \nabla_{\mathbf{r}} \rho^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R})$ is negligible with respect to $\rho^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R})$ for \mathbf{R} of the order of the "range" of intermolecular force [range of $V'(R)$], all terms beyond the first in the brace of (5.15) may be neglected. Only at a boundary or interface is $\rho^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R})$ also sensitive to \mathbf{r} , in which case neglecting terms beyond the first may not be justified.

For a fluid with identical particles it is convenient to express the pair density as a product of singlet particle densities, $\rho(\mathbf{r}; t)/m$ and $\rho(\mathbf{r} + \mathbf{R}; t)/m$, and a correlation function, $g^{(2)}$.

$$\rho^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R}; t) = \frac{1}{m^2} \rho(\mathbf{r}; t) \rho(\mathbf{r} + \mathbf{R}; t) g^{(2)}(\mathbf{r}; \mathbf{R}; t). \quad (5.16)$$

$g^{(2)}$ is expressed as a function of \mathbf{r} , the coordinate of the first of the pair (to which it is insensitive) and \mathbf{R} , the relative coordinate (to which it is sensitive).

When (5.16) is substituted into (5.15), neglecting all terms beyond the first in the brace and replacing the slowly varying mass density $\rho(\mathbf{r} + \mathbf{R}; t)$ by $\rho(\mathbf{r}; t)$, we obtain the approximation (very accurate for a bulk fluid phase).

$$\sigma_V(\mathbf{r}; t) = \frac{[\rho(\mathbf{r}; t)]^2}{2m^2} \int_{3 \text{ fold}} \frac{\mathbf{R} \mathbf{R}}{R} V'(R) g^{(2)}(\mathbf{r}; \mathbf{R}; t) d\mathbf{R}. \quad (5.17)$$

The intermolecular force contribution to the macroscopic stress tensor may be obtained by taking the appropriate space and time averages of (5.17). The equation is invariant under averaging except that $g^{(2)}$ must be replaced by its average.

The pressure may be obtained by taking the diagonal sum of the stress tensor

$$P = -\frac{1}{3} \text{Trace } \sigma. \quad (5.18)$$

From (5.13)

$$-\frac{1}{3} \text{Trace } \sigma_K = -\frac{2}{3} \sum_{k=1}^N \left\langle \frac{m}{2} \left| \frac{\mathbf{p}_k}{m} - \mathbf{u} \right|^2 \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \quad (5.19)$$

and from (5.17)

$$-\frac{1}{3} \text{Trace } \sigma_V = -\frac{[\rho(\mathbf{r}; t)]^2}{6m^2} \int_{\text{3 fold}} R V'(R) g^{(2)}(\mathbf{r}; \mathbf{R}; t) d\mathbf{R}. \quad (5.20)$$

The sum occurring in (5.19) is [according to (3.3)] the kinetic energy density at \mathbf{r} measured from a frame of reference moving with the mean velocity, \mathbf{u} . In equilibrium this is given by $(3/2)kT \times \rho/m$, the kinetic energy per molecule times the particle density. In an equilibrium state, $g^{(2)}$ and ρ are independent of \mathbf{r} and $g^{(2)}$ is isotropic with respect to the relative coordinate, \mathbf{R} ; i.e., $g^{(2)}$ is a function of the distance R only. Equations (5.18)–(5.20) thus give for the equilibrium pressure

$$P_{\text{eq}} = \frac{\rho}{m} kT - \frac{2\pi}{3} \left(\frac{\rho}{m} \right)^2 \int R^3 V'(R) g^{(2)}(R) dR. \quad (5.21)$$

This is the "equation of state" for a fluid which may be derived without regard to hydrodynamics by using the virial theorem.

VI. THE ENERGY TRANSPORT EQUATION

The derivation of the energy transport equation follows the lines of the preceding section. However, since the equations involved have more terms, confusion can be avoided by deriving separate expressions for the rate of change of the several parts of the energy density.

First we shall apply Eq. (2.7) taking

$$\alpha = \sum_{j=1}^N \frac{\dot{p}_j^2}{2m_j} \delta(\mathbf{R}_j - \mathbf{r}). \quad (6.1)$$

The kinetic energy density, (3.3), is

$$E_K(\mathbf{r}; t) = \langle \alpha; f \rangle. \quad (6.2)$$

As required by (2.7)

$$\begin{aligned} \frac{\mathbf{p}_k}{m_k} \cdot \nabla_{\mathbf{R}_k} \alpha - (\nabla_{\mathbf{R}_k} U) \cdot \nabla_{\mathbf{p}_k} \alpha \\ = -\frac{\dot{p}_k^2}{2m_k} \frac{\mathbf{p}_k}{m_k} \cdot \nabla_{\mathbf{r}} \delta(\mathbf{R}_k - \mathbf{r}) - (\nabla_{\mathbf{R}_k} U) \cdot \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}) \\ = -\nabla_{\mathbf{r}} \cdot \left[\frac{\dot{p}_k^2}{2m_k} \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}) \right] \\ - \left[\nabla_{\mathbf{R}_k} \psi_k(\mathbf{R}_k) + \sum_{\substack{j=1 \\ j \neq k}}^N \nabla_{\mathbf{R}_k} V_{jk} \right] \cdot \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}), \quad (6.3) \end{aligned}$$

where we have used (5.4). When (6.2) and (6.3) are substituted into (2.7), we obtain

$$\begin{aligned} \frac{\partial}{\partial t} E_K(\mathbf{r}; t) = -\nabla_{\mathbf{r}} \cdot \sum_{k=1}^N \left\langle \frac{\dot{p}_k^2}{2m_k} \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \\ - \sum_{k=1}^N [\nabla_{\mathbf{r}} \psi_k(\mathbf{r})] \cdot \left\langle \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \\ - \sum_{j \neq k} \left\langle (\nabla_{\mathbf{R}_k} V_{jk}) \cdot \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle. \quad (6.4) \end{aligned}$$

Next we apply (2.7) using

$$\alpha = \sum_{j=1}^N \psi_j(\mathbf{r}) \delta(\mathbf{R}_j - \mathbf{r}). \quad (6.5)$$

Then, according to (3.5), the energy density due to external fields is

$$E_\psi(\mathbf{r}; t) = \langle \alpha; f \rangle \quad (6.6)$$

and

$$\begin{aligned} (\mathbf{p}_k/m_k) \cdot \nabla_{\mathbf{R}_k} \alpha - (\nabla_{\mathbf{R}_k} U) \cdot \nabla_{\mathbf{p}_k} \alpha \\ = \psi_k(\mathbf{r}) (\mathbf{p}_k/m_k) \cdot \nabla_{\mathbf{R}_k} \delta(\mathbf{R}_k - \mathbf{r}) \\ = -\psi_k(\mathbf{r}) \nabla_{\mathbf{r}} \cdot [(\mathbf{p}_k/m_k) \delta(\mathbf{R}_k - \mathbf{r})]. \quad (6.7) \end{aligned}$$

Substituting (6.6) and (6.7) into (2.7) gives

$$\frac{\partial}{\partial t} E_\psi(\mathbf{r}; t) = -\sum_{k=1}^N \psi_k(\mathbf{r}) \nabla_{\mathbf{r}} \cdot \left\langle \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle. \quad (6.8)$$

Finally, we shall apply (2.7) using

$$\alpha = \frac{1}{2} \sum_{i \neq j} V_{ij} \delta(\mathbf{R}_j - \mathbf{r}). \quad (6.9)$$

The potential energy density due to molecular interaction is then, according to (3.7),

$$E_V(\mathbf{r}; t) = \langle \alpha; f \rangle \quad (6.10)$$

and

$$\begin{aligned} (\mathbf{p}_k/m_k) \cdot \nabla_{\mathbf{R}_k} \alpha - (\nabla_{\mathbf{R}_k} U) \cdot \nabla_{\mathbf{p}_k} \alpha \\ = \frac{\mathbf{p}_k}{2m_k} \cdot \left[\sum_{\substack{j=1 \\ j \neq k}}^N (\nabla_{\mathbf{R}_k} V_{kj}) \delta(\mathbf{R}_j - \mathbf{r}) + \sum_{\substack{i=1 \\ i \neq k}}^N (\nabla_{\mathbf{R}_k} V_{ik}) \delta(\mathbf{R}_k - \mathbf{r}) \right. \\ \left. + \sum_{\substack{i=1 \\ i \neq k}}^N V_{ik} \nabla_{\mathbf{R}_k} \delta(\mathbf{R}_k - \mathbf{r}) \right] \\ = \frac{\mathbf{p}_k}{2m_k} \cdot \sum_{\substack{j=1 \\ j \neq k}}^N (\nabla_{\mathbf{R}_k} V_{jk}) [\delta(\mathbf{R}_j - \mathbf{r}) + \delta(\mathbf{R}_k - \mathbf{r})] \\ - \frac{1}{2} \nabla_{\mathbf{r}} \cdot \left[\sum_{\substack{j=1 \\ j \neq k}}^N V_{jk} \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}) \right]. \quad (6.11) \end{aligned}$$

When (6.10) and (6.11) are substituted into (2.7), we obtain

$$\begin{aligned} \frac{\partial}{\partial t} E_V(\mathbf{r}; t) = & -\frac{1}{2} \sum_{j \neq k} \sum \left\langle (\nabla \mathbf{R}_k V_{jk}) \cdot \frac{\mathbf{p}_k}{m_k} [\delta(\mathbf{R}_j - \mathbf{r}) \right. \\ & \left. + \delta(\mathbf{R}_k - \mathbf{r})]; f \right\rangle \\ & - \frac{1}{2} \nabla \mathbf{r} \left[\sum_{j \neq k} \sum \left\langle V_{jk} \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \right]. \quad (6.12) \end{aligned}$$

Adding up the rates given in (6.4), (6.8), and (6.12), we obtain the rate of change of the total internal energy density.

$$\begin{aligned} \frac{\partial}{\partial t} E(\mathbf{r}; t) = & -\nabla \mathbf{r} \cdot \left[\sum_{k=1}^N \left\langle \frac{p_k^2}{2m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \right. \\ & + \sum_{k=1}^N \psi_k(\mathbf{r}) \left\langle \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \\ & + \frac{1}{2} \sum_{j \neq k} \sum \left\langle V_{jk} \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \left. \right] \\ & + \frac{1}{2} \sum_{j \neq k} \sum \left\langle (\nabla \mathbf{R}_k V_{jk}) \cdot \frac{\mathbf{p}_k}{m_k} [\delta(\mathbf{R}_j - \mathbf{r}) - \delta(\mathbf{R}_k - \mathbf{r})]; f \right\rangle. \quad (6.13) \end{aligned}$$

From the definitions of the several parts of the energy density

$$\begin{aligned} \nabla \mathbf{r} \cdot (E \mathbf{u}) = & \nabla \mathbf{r} \cdot \left[\sum_{k=1}^N \left\langle \frac{p_k^2}{2m_k} \mathbf{u} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \right. \\ & + \sum_{k=1}^N \psi_k(\mathbf{r}) \langle \mathbf{u} \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \\ & + \frac{1}{2} \sum_{j \neq k} \sum \langle V_{jk} \mathbf{u} \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \left. \right]. \quad (6.14) \end{aligned}$$

Adding (6.14) to (6.13), we obtain

$$\begin{aligned} \frac{\partial}{\partial t} E(\mathbf{r}; t) + \nabla \mathbf{r} \cdot (E \mathbf{u}) = & -\nabla \mathbf{r} \cdot \left[\sum_{k=1}^N \left\langle \frac{p_k^2}{2m_k} \left(\frac{\mathbf{p}_k}{m_k} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \right. \\ & + \sum_{k=1}^N \psi_k(\mathbf{r}) \left\langle \left(\frac{\mathbf{p}_k}{m_k} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \\ & + \frac{1}{2} \sum_{j \neq k} \sum \left\langle V_{jk} \left(\frac{\mathbf{p}_k}{m_k} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \left. \right] \\ & + \frac{1}{2} \sum_{j \neq k} \sum \left\langle (\nabla \mathbf{R}_k V_{jk}) \cdot \frac{\mathbf{p}_k}{m_k} [\delta(\mathbf{R}_j - \mathbf{r}) \right. \\ & \left. - \delta(\mathbf{R}_k - \mathbf{r})]; f \right\rangle. \quad (6.15) \end{aligned}$$

Equation (6.15) has been derived without any reference to the assumption of a single component, single phase system. The derivation is equally valid for central or non-central forces depending upon rotational or other internal degrees of freedom.

In order to reduce (6.15) to the point function counterpart of the hydrodynamical equation of energy transport for a single component, single phase system, (1.4), we must assume all molecules identical. We shall further impose the restriction that the intermolecular force shall be central, depending upon range only.

Under the assumption of identical molecules, the second term on the right of (6.15) vanishes, for it becomes

$$\frac{\psi(\mathbf{r})}{m} \left[\sum_{k=1}^N \langle \mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r}); f \rangle - \mathbf{u} \sum_{k=1}^N m \langle \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \right] = 0$$

by the definition (3.1) and (3.2).

To reduce (6.15) to the form of (1.4) it is necessary to define a point function heat current density, $\mathbf{q}(\mathbf{r}; t)$, satisfying the equation:

$$\begin{aligned} \nabla \mathbf{r} \cdot (\mathbf{q} - \mathbf{u} \cdot \boldsymbol{\sigma}) = & \nabla \mathbf{r} \cdot \left[\sum_{k=1}^N \left\langle \frac{p_k^2}{2m} \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \right. \\ & + \frac{1}{2} \sum_{j \neq k} \sum \left\langle V(R_{kj}) \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \left. \right] \\ & + \frac{1}{2} \sum_{j \neq k} \sum \left\langle \frac{V'(R_{kj})}{R_{kj}} \mathbf{R}_{kj} \cdot \frac{\mathbf{p}_k}{m} [\delta(\mathbf{R}_j - \mathbf{r}) - \delta(\mathbf{R}_k - \mathbf{r})]; f \right\rangle \quad (6.16) \end{aligned}$$

where $\boldsymbol{\sigma}$ is the point function stress tensor defined in (5.12). We have used the relations:

$$V_{jk} = V(R_{kj})$$

$$\nabla \mathbf{R}_k V_{jk} = \frac{\mathbf{R}_{jk}}{R_{jk}} V'(R_{jk}) = -\frac{\mathbf{R}_{kj}}{R_{kj}} V'(R_{kj}).$$

Equation (6.16) merely specifies the divergence of the heat current, and leaves \mathbf{q} itself undetermined up to the curl of an arbitrary vector field. We shall now find a particular solution of (6.16), and then we shall demonstrate that this solution agrees with the physical definition of the heat current density.

The last term of (6.16) may be converted into a divergence by replacing the difference of the δ -functions by the Taylor's series expansion given in (5.9), inter-

changing the roles of j and k .

$$\begin{aligned} & \frac{1}{2} \sum_{j \neq k} \left\langle \frac{V'(R_{kj})}{R_{kj}} \mathbf{R}_{kj} \cdot \frac{\mathbf{p}_k}{m} [\delta(\mathbf{R}_j - \mathbf{r}) - \delta(\mathbf{R}_k - \mathbf{r})]; f \right\rangle \\ &= -\nabla_{\mathbf{r}} \cdot \left[\frac{1}{2} \sum_{j \neq k} \left\langle \frac{V'(R_{kj})}{R_{kj}} \mathbf{R}_{kj} \mathbf{R}_{kj} \cdot \frac{\mathbf{p}_k}{m} \left\{ 1 - \frac{1}{2} \mathbf{R}_{kj} \cdot \nabla_{\mathbf{r}} \right. \right. \right. \\ & \quad \left. \left. \left. + \dots + \frac{1}{n!} (-\mathbf{R}_{kj} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \right\} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \right]. \quad (6.17) \end{aligned}$$

From the definition of σ_k in (5.13),

$$\begin{aligned} & \nabla_{\mathbf{r}} \cdot (\mathbf{u} \cdot \sigma_K) \\ &= \nabla_{\mathbf{r}} \cdot \left[\sum_{k=1}^N \left\langle \frac{m}{2} \left(-2 \frac{\mathbf{p}_k}{m} \cdot \mathbf{u} + 2u^2 \right) \right. \right. \\ & \quad \left. \left. \times \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \right] \\ &= \nabla_{\mathbf{r}} \cdot \left[\sum_{k=1}^N \left\langle \frac{m}{2} \left(-2 \frac{\mathbf{p}_k}{m} \cdot \mathbf{u} + u^2 \right) \right. \right. \\ & \quad \left. \left. \times \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \right] \quad (6.18) \end{aligned}$$

since

$$\begin{aligned} & \sum_{k=1}^N \left\langle \frac{m}{2} u^2 \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \\ &= \frac{u^2}{2} \left[\sum_{k=1}^N \langle \mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r}); f \rangle - \mathbf{u} \sum_{k=1}^N m \langle \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \right] = 0 \end{aligned}$$

by (3.1) and (3.2).

When (6.17) is substituted into (6.16) and (6.18) added to this equation, we obtain

$$\begin{aligned} & \nabla_{\mathbf{r}} \cdot (\mathbf{q} - \mathbf{u} \cdot \sigma_V) \\ &= \nabla_{\mathbf{r}} \cdot \left[\sum_{k=1}^N \left\langle \frac{m}{2} \left| \frac{\mathbf{p}_k}{m} - \mathbf{u} \right|^2 \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \right. \\ & \quad + \frac{1}{2} \sum_{j \neq k} \left\langle V(R_{kj}) \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \\ & \quad - \frac{1}{2} \sum_{j \neq k} \left\langle \frac{V'(R_{kj})}{R_{kj}} \mathbf{R}_{kj} \mathbf{R}_{kj} \cdot \frac{\mathbf{p}_k}{m} \left\{ 1 - \frac{1}{2} \mathbf{R}_{kj} \cdot \nabla_{\mathbf{r}} + \dots \right. \right. \\ & \quad \left. \left. + \frac{1}{n!} (-\mathbf{R}_{kj} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \right\} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \right], \quad (6.19) \end{aligned}$$

where $|\mathbf{p}_k/m - \mathbf{u}|$ is the magnitude of the vector $(\mathbf{p}_k/m) - \mathbf{u}$.

We shall now define the point function heat current

density, the most apparent solution of (6.19), as

$$\mathbf{q}(\mathbf{r}; t) = \mathbf{q}_K(\mathbf{r}; t) + \mathbf{q}_V(\mathbf{r}; t) \quad (6.20)$$

$$\mathbf{q}_K(\mathbf{r}; t) = \sum_{k=1}^N \left\langle \frac{m}{2} \left| \frac{\mathbf{p}_k}{m} - \mathbf{u} \right|^2 \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \quad (6.21)$$

$$\begin{aligned} \mathbf{q}_V(\mathbf{r}; t) &= \mathbf{u} \cdot \left[\sigma_V - \frac{1}{2} \sum_{j \neq k} \langle V(R_{kj}) \mathbf{1} \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \right] \\ & \quad + \frac{1}{2} \sum_{j \neq k} \left\langle \left[V(R_{kj}) \mathbf{1} - \frac{V'(R_{kj})}{R_{kj}} \mathbf{R}_{kj} \mathbf{R}_{kj} \left\{ 1 + \dots \right. \right. \right. \\ & \quad \left. \left. \left. + \frac{1}{n!} (-\mathbf{R}_{kj} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \right\} \right] \cdot \frac{\mathbf{p}_k}{m} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \quad (6.22) \end{aligned}$$

where $\mathbf{1}$ is the unit tensor of the second rank.

\mathbf{q}_V may be expressed in terms of the pair density and particle current density in pair space by introducing into (6.22) a new δ -function $\delta(\mathbf{R}_{kj} - \mathbf{R})$, and integrating over \mathbf{R} .

$$\begin{aligned} \mathbf{q}_V(\mathbf{r}; t) &= \mathbf{u} \cdot \left[\sigma_V - \frac{1}{2} \sum_{j \neq k} \left\langle \int_{3 \text{ fold}} \delta(\mathbf{R}_{kj} - \mathbf{R}) \right. \right. \\ & \quad \left. \left. \times V(R) \mathbf{1} \delta(\mathbf{R}_k - \mathbf{r}) d\mathbf{R}; f \right\rangle + \frac{1}{2} \sum_{j \neq k} \left\langle \int_{3 \text{ fold}} \delta(\mathbf{R}_{kj} - \mathbf{R}) \right. \right. \\ & \quad \left. \left. \times \left[V(R) \mathbf{1} - \frac{V'(R)}{R} \mathbf{R} \mathbf{R} \left\{ 1 + \dots \right. \right. \right. \right. \\ & \quad \left. \left. \left. + \frac{1}{n!} (-\mathbf{R} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \right\} \right] \cdot \frac{\mathbf{p}_k}{m} \delta(\mathbf{R}_k - \mathbf{r}) d\mathbf{R}; f \right\rangle \right]. \end{aligned}$$

Commuting the integrations over \mathbf{R} with the phase integrals and the summations we obtain

$$\begin{aligned} \mathbf{q}_V(\mathbf{r}; t) &= \mathbf{u} \cdot \left[\sigma_V - \frac{1}{2} \int_{3 \text{ fold}} V(R) \mathbf{1} \sum_{j \neq k} \langle \delta(\mathbf{R}_{kj} - \mathbf{R}) \right. \\ & \quad \left. \times \delta(\mathbf{R}_k - \mathbf{r}); f \rangle d\mathbf{R} \right] + \frac{1}{2} \int_{3 \text{ fold}} \left[V(R) \mathbf{1} - \frac{\mathbf{R} \mathbf{R}}{R} V'(R) \right. \\ & \quad \left. \times \left\{ 1 - \frac{1}{2} \mathbf{R} \cdot \nabla_{\mathbf{r}} + \dots - \frac{1}{n!} (-\mathbf{R} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \right\} \right. \\ & \quad \left. \cdot \left[\sum_{j \neq k} \left\langle \frac{\mathbf{p}_k}{m} \delta(\mathbf{R}_{kj} - \mathbf{R}) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \right] d\mathbf{R}. \end{aligned}$$

The product $\delta(\mathbf{R}_{kj} - \mathbf{R}) \delta(\mathbf{R}_k - \mathbf{r})$ is equivalent to the product $\delta(\mathbf{R}_k - \mathbf{r}) \delta(\mathbf{R}_j - \mathbf{r} - \mathbf{R})$. Consequently, referring to the definitions (3.8) and (3.10) and replacing σ_V by

its value given in (5.15), the above equation becomes

$$\begin{aligned} \mathbf{q}_V(\mathbf{r}; t) = & -\frac{1}{2} \mathbf{u}(\mathbf{r}; t) \cdot \int \left[V(R) \mathbf{1} - \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \right] \left\{ 1 - \frac{1}{2} \mathbf{R} \cdot \nabla_{\mathbf{r}} \right. \\ & + \dots + \frac{1}{n!} (-\mathbf{R} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \left. \right\} \rho^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R}; t) d\mathbf{R} \\ & + \frac{1}{2} \int \left[V(R) \mathbf{1} - \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \right] \left\{ 1 - \frac{1}{2} \mathbf{R} \cdot \nabla_{\mathbf{r}} + \dots \right. \\ & + \frac{1}{n!} (-\mathbf{R} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \left. \right\} \cdot \mathbf{j}_1^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R}; t) d\mathbf{R}. \quad (6.23) \end{aligned}$$

In the interior of a fluid $\rho^{(2)}$ and $\mathbf{j}_1^{(2)}$ are very slow functions of \mathbf{r} ; consequently, as explained in the preceding section, all terms in the brace beyond the first may be neglected. Equation (6.23) then reduces to

$$\begin{aligned} \mathbf{q}_V(\mathbf{r}; t) = & -\frac{1}{2} \int \left[V(R) \mathbf{1} - \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \right] \\ & \cdot [\mathbf{j}_1^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R}; t) - \mathbf{u}(\mathbf{r}; t) \rho^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R}; t)] d\mathbf{R}. \quad (6.24) \end{aligned}$$

What are the physical interpretations of the various terms comprising \mathbf{q} ? The interpretation is somewhat easier viewed from a coordinate frame moving with the local velocity \mathbf{u} . \mathbf{q}_K represents the current density of kinetic energy due to the macroscopically imperceptible random molecular motion. It is this term which occurs in the kinetic theory of gases. The terms in \mathbf{q}_V involving $V(R)$ (but not its derivative) represent the current density of potential energy due to this same random motion. The terms in \mathbf{q}_V involving $V'(R)$, when dotted into an element of area $d\mathbf{S}$, represent the work per unit time done on molecules on one side of $d\mathbf{S}$ by molecules on the other. Work is done on the former as they move (due to their macroscopically imperceptible random motion) through the force field of the latter.

COMPILATION OF RESULTS

The equations of phenomenological hydrodynamics for a single component, single phase system are relations among certain macroscopic observables—mass density, fluid velocity, body force density, energy density, stress tensor, and heat current density. Using classical statistical mechanics, we have found that it is possible to define the corresponding microscopic observables and that equations identical in form to the hydrodynamical equations relate these quantities. The macroscopic equations may be obtained from the microscopic (or point function) equations by averaging over a microscopically large though macroscopically small space domain determined by the resolution of one's measurements and

averaging over a time interval of the order of the relaxation time of one's measuring instruments.

The microscopically correct hydrodynamical equations are the continuity equation:

$$\frac{\partial}{\partial t} \rho(\mathbf{r}; t) = -\nabla_{\mathbf{r}} \cdot [\rho(\mathbf{r}; t) \mathbf{u}(\mathbf{r}; t)], \quad (1.1)$$

the equation of motion (momentum transport equation):

$$-\frac{\partial}{\partial t} [\rho \mathbf{u}] + \nabla_{\mathbf{r}} \cdot [\rho \mathbf{u} \mathbf{u}] = \mathbf{X} + \nabla_{\mathbf{r}} \cdot \boldsymbol{\sigma}, \quad (1.2)$$

and the energy transport equation

$$\frac{\partial E}{\partial t} + \nabla_{\mathbf{r}} \cdot [E \mathbf{u} + \mathbf{q} - \mathbf{u} \cdot \boldsymbol{\sigma}]. \quad (1.4)$$

The quantities appearing in the above equations are defined as follows:¶

$$\rho(\mathbf{r}; t) = \sum_{k=1}^N m_k \langle \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \quad (3.1)$$

= mass density at \mathbf{r} .

$$\mathbf{u}(\mathbf{r}; t) = \frac{1}{\rho(\mathbf{r}; t)} \sum_{k=1}^N \langle \mathbf{p}_k \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \quad (3.2)$$

= mean molecular velocity (fluid velocity) at \mathbf{r} .

$$\mathbf{X}(\mathbf{r}; t) = - \sum_{k=1}^N [\nabla_{\mathbf{r}} \psi_k(\mathbf{r})] \langle \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \quad (3.6)$$

= body force per unit volume due to external fields at \mathbf{r} .

$$E(\mathbf{r}; t) = E_K + E_{\psi} + E_V \quad (1.3)$$

= internal energy density at \mathbf{r} , where

$$E_K(\mathbf{r}; t) = \sum_{k=1}^N \left\langle \frac{\mathbf{p}_k^2}{2m_k} \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \quad (3.3)$$

= kinetic energy density,

$$E_{\psi}(\mathbf{r}; t) = \sum_{k=1}^N \psi_k(\mathbf{r}) \langle \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \quad (3.5)$$

= potential energy density associated with external fields, and

$$E_V(\mathbf{r}; t) = \frac{1}{2} \sum_{j \neq k} \sum \langle V_{jk} \delta(\mathbf{R}_k - \mathbf{r}); f \rangle \quad (3.7)$$

¶ The bracket notation $\langle \cdot; f \rangle$ means the expectation value of the quantity appearing to the left of the semicolon over an ensemble having a probability distribution function, $f(\mathbf{R}_1, \dots, \mathbf{R}_N; \mathbf{p}_1, \dots, \mathbf{p}_N; t)$.

=potential energy density due to molecular interaction. (In defining E_V it is assumed that the potential energy of interaction between two molecules is localized half at each molecule.)

These definitions are completely general. The other quantities, however, appearing in the above hydrodynamical equations, σ and q , have been defined only for a single component, single phase system in which the intermolecular force is central, depending on range only. Their definitions follow.

$$\sigma(\mathbf{r}; t) = \sigma_K + \sigma_V \quad (5.12)$$

=stress tensor at \mathbf{r} , where

$$\sigma_K = - \sum_{k=1}^N m \left\langle \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \quad (5.13)$$

=kinetic contribution to stress tensor. (This is the dominant term for gases, but relatively unimportant for liquids.) And

$$\sigma_V(\mathbf{r}; t) = \frac{1}{2} \int \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \left\{ 1 - \frac{1}{2} \mathbf{R} \cdot \nabla_{\mathbf{r}} + \dots \right. \\ \left. \frac{1}{n!} (-\mathbf{R} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \right\} \rho^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R}; t) d\mathbf{R} \quad (5.15)$$

=intermolecular force contribution to stress tensor. (This is the dominant term for liquids.)

$$\mathbf{q}(\mathbf{r}; t) = \mathbf{q}_K + \mathbf{q}_V \quad (6.20)$$

=heat current density at \mathbf{r} , where

$$\mathbf{q}_K(\mathbf{r}; t) = \sum_{k=1}^N \left\langle \frac{m}{2} \left| \frac{\mathbf{p}_k}{m} - \mathbf{u} \right|^2 \left(\frac{\mathbf{p}_k}{m} - \mathbf{u} \right) \delta(\mathbf{R}_k - \mathbf{r}); f \right\rangle \quad (6.21)$$

=heat current due to transport of thermal kinetic energy, and

$$\mathbf{q}_V(\mathbf{r}; t) = -\frac{1}{2} \mathbf{u}(\mathbf{r}; t) \cdot \int \left[V(R) \mathbf{1} - \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \right. \\ \left. \times \left\{ 1 - \frac{1}{2} \mathbf{R} \cdot \nabla_{\mathbf{r}} + \dots + \frac{1}{n!} (-\mathbf{R} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \right\} \right] \\ \times \rho^{(2)}(\mathbf{r}; \mathbf{r} + \mathbf{R}; t) d\mathbf{R} + \frac{1}{2} \int \left[V(R) \mathbf{1} - \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \right. \\ \left. \times \left\{ 1 - \frac{1}{2} \mathbf{R} \cdot \nabla_{\mathbf{r}} + \dots + \frac{1}{n!} (-\mathbf{R} \cdot \nabla_{\mathbf{r}})^{n-1} + \dots \right\} \right] \\ \cdot \mathbf{j}_1^{(2)}(\mathbf{r}; \mathbf{r} + \mathbf{R}; t) d\mathbf{R} \quad (6.23)$$

=contribution to heat current density by molecular interaction.

In the definitions of σ_V and \mathbf{q}_V the following quantities appear.

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}'; t) = \sum_{j \neq k} \langle \delta(\mathbf{R}_j - \mathbf{r}) \delta(\mathbf{R}_k - \mathbf{r}'); f \rangle \quad (3.8)$$

=pair density at \mathbf{r} and \mathbf{r}' , the probability per (unit volume)² that one particle (any particle) will be at \mathbf{r} and another at \mathbf{r}' .

$$\mathbf{j}_1^{(2)}(\mathbf{r}, \mathbf{r}'; t) = \sum_{k \neq i} \left\langle \frac{\mathbf{p}_k}{m_k} \delta(\mathbf{R}_k - \mathbf{r}) \delta(\mathbf{R}_i - \mathbf{r}'); f \right\rangle \quad (3.10)$$

=projection onto the space of \mathbf{r} of the particle current density at \mathbf{r}, \mathbf{r}' in pair space, =particle current density at \mathbf{r} if another particle is at \mathbf{r}' multiplied by the particle density at \mathbf{r}' .

The differential operator, $\nabla_{\mathbf{r}}$, occurring in the definitions of σ_V and \mathbf{q}_V operate on $\rho^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R}; t)$ and $\mathbf{j}_1^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R}; t)$ with \mathbf{R} held fixed. Since in the interior of a fluid $\rho^{(2)}$ and $\mathbf{j}_1^{(2)}$ are slow functions of \mathbf{r} (holding \mathbf{R} fixed), changing negligibly for \mathbf{r} varying by a displacement whose length is of the order of the "range" of intermolecular forces, all terms beyond the first may be neglected in the brace appearing in the definitions of σ_V and \mathbf{q}_V . This yields the simplified expressions:

$$\mathbf{q}_V(\mathbf{r}; t) = \frac{1}{2} \int \left[V(R) \mathbf{1} - \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \right] \\ \cdot [\mathbf{j}_1^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R}; t) - \mathbf{u}(\mathbf{r}; t) \rho^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{R}; t)] d\mathbf{R} \quad (6.24)$$

$$\sigma_V(\mathbf{r}; t) = \frac{1}{2m^2} [\rho(\mathbf{r}; t)]^2 \int \frac{\mathbf{R}\mathbf{R}}{R} V'(R) g^{(2)}(\mathbf{r}; \mathbf{R}; t) d\mathbf{R} \quad (5.17)$$

where the correlation function $g^{(2)}$ is defined by

$$\rho^{(2)}(\mathbf{r}; \mathbf{r} + \mathbf{R}; t) = \frac{1}{m^2} \rho(\mathbf{r}; t) \rho(\mathbf{r} + \mathbf{R}; t) g^{(2)}(\mathbf{r}; \mathbf{R}; t). \quad (5.16)$$

The pressure is defined by

$$P(\mathbf{r}; t) = -\frac{1}{3} \text{Trace} \sigma(\mathbf{r}; t). \quad (5.18)$$

In an ensemble which is in equilibrium with a temperature T , the pressure is

$$P_{eq} = \frac{\rho}{m} kT - \frac{2\pi}{3} \left(\frac{\rho}{m} \right)^2 \int R^3 V'(R) g^{(2)}(R) dR. \quad (5.21)$$

This is the equation of state, obtainable by other methods as well.

APPENDIX

The part of the stress tensor at the point \mathbf{r} due to intermolecular forces is defined so that

$$\sigma_V(\mathbf{r}; t) \cdot d\mathbf{S} = \text{"the force acting across } d\mathbf{S}." \quad (A.1)$$

First we imagine a plane tangent to dS at \mathbf{r} . This plane divides the fluid into two parts. That portion into which the vector $d\mathbf{S}$ points we shall refer to as "outside of dS ;" the other portion is "inside of dS ."

The interaction forces acting on the fluid are all between pairs of molecules. Let us say that the force between a pair of molecules "acts across dS " if the line of centers between these molecules intersects dS between the molecules. This can only happen (for infinitesimal dS) if one molecule of the pair is "inside dS " and the other is "outside." By convention, the "force acting across dS " is the force acting on the molecule inside dS .

If a molecule is located at \mathbf{r}' inside dS , and another at $\mathbf{r}'+\mathbf{R}$ outside of dS , then the force acting on the molecule at \mathbf{r}' is

$$(\mathbf{R}/R)V'(R). \quad (\text{A.2})$$

This force "acts across dS " only if $\mathbf{r}'+\alpha\mathbf{R}$ terminates on dS for some α between 0 and 1.

Keeping \mathbf{R} fixed, the volume of the element at \mathbf{r}' , over which $\mathbf{r}'+\alpha\mathbf{R}$ terminates on dS for α between α_0 and $\alpha_0+d\alpha$, is $d\mathbf{S}\cdot\mathbf{R}d\alpha$.

The probability of finding a molecule (any molecule) in this volume and another at $\mathbf{r}'+\mathbf{R}$ with the relative displacement \mathbf{R} ranging over a volume $d\mathbf{R}$ is

$$\rho^{(2)}(\mathbf{r}', \mathbf{r}'+\mathbf{R})(d\mathbf{S}\cdot\mathbf{R}d\alpha)d\mathbf{R} \\ = \rho^{(2)}(\mathbf{r}-\alpha\mathbf{R}; \mathbf{r}-\alpha\mathbf{R}+\mathbf{R})(d\mathbf{S}\cdot\mathbf{R}d\alpha)d\mathbf{R}. \quad (\text{A.3})$$

The error in replacing \mathbf{r}' by $\mathbf{r}-\alpha\mathbf{R}$ is an infinitesimal of a higher order, since the difference between \mathbf{r}' and $\mathbf{r}-\alpha\mathbf{R}$ is an infinitesimal (the vector from \mathbf{r} to some other point on dS).

The total force acting across dS is, therefore, the integral of the product of (A.2) and (A.3).

"The force acting across dS "

$$= d\mathbf{S} \cdot \int \left\{ \int_0^1 \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \rho^{(2)}(\mathbf{r}-\alpha\mathbf{R}, \mathbf{r}-\alpha\mathbf{R}+\mathbf{R}) d\alpha \right\} d\mathbf{R} \quad (\text{A.4})$$

where \mathbf{R} ranges over those values only for which $\mathbf{R}\cdot d\mathbf{S}$ is positive (i.e., \mathbf{R} from the inside toward the outside).

|| This definition of the force "acting across dS " is quite arbitrary, and with another definition we would obtain a different expression for the point function stress tensor. But all definitions must have this in common—that the stress between a pair of molecules be concentrated near the line of centers. When averaging over a domain large compared with the range of intermolecular force, these differences are washed out, and the ambiguity remaining in the macroscopic stress tensor is of negligible order.

Making the change of variable, $\gamma=1-\alpha$, the brace in Eq. (A.4) becomes

$$\left\{ \right\} = \int_0^1 \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \rho^{(2)}(\mathbf{r}+\gamma\mathbf{R}-\mathbf{R}; \mathbf{r}+\gamma\mathbf{R}) d\gamma \\ = \int_0^1 \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \rho^{(2)}(\mathbf{r}+\gamma\mathbf{R}; \mathbf{r}+\gamma\mathbf{R}-\mathbf{R}) d\gamma,$$

where we have used the symmetry of $\rho^{(2)}$ with respect to its two arguments. Changing the name of the integration variable γ back to α one notes that the brace is an even function of the vector \mathbf{R} . Consequently, (A.4) may be written:

"The force acting across dS "

$$= d\mathbf{S} \cdot \frac{1}{2} \int \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \left[\int_0^1 \rho^{(2)}(\mathbf{r}-\alpha\mathbf{R}; \mathbf{r}-\alpha\mathbf{R}+\mathbf{R}) d\alpha \right] d\mathbf{R} \quad (\text{A.5})$$

3 fold

where the integration over \mathbf{R} now extends over all space. Since dS was arbitrarily chosen through \mathbf{r} , we obtain on comparing (A.1) and (A.5)

$\sigma_V(\mathbf{r}; t)$

$$= \frac{1}{2} \int \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \left[\int_0^1 \rho^{(2)}(\mathbf{r}-\alpha\mathbf{R}, \mathbf{r}-\alpha\mathbf{R}+\mathbf{R}; t) d\alpha \right] d\mathbf{R}. \quad (\text{A.6})$$

3 fold

$\rho^{(2)}$, appearing in (A.6), may be expanded in a Taylor's series in α .

$$\rho^{(2)}(\mathbf{r}-\alpha\mathbf{R}; \mathbf{r}-\alpha\mathbf{R}+\mathbf{R}) = \left\{ 1 - \alpha\mathbf{R}\cdot\nabla_{\mathbf{r}} + \frac{\alpha^2}{2}(\mathbf{R}\cdot\nabla_{\mathbf{r}})^2 + \dots \right. \\ \left. + \frac{\alpha^{n-1}}{(n-1)!}(-\mathbf{R}\cdot\nabla_{\mathbf{r}})^{n-1} + \dots \right\} \rho^{(2)}(\mathbf{r}, \mathbf{r}+\mathbf{R}) \quad (\text{A.7})$$

where it is understood that \mathbf{R} is to be held constant when operating with $\nabla_{\mathbf{r}}$.

Substituting (A.7) into (A.6) and integrating over α from 0 to 1, we obtain:

$$\sigma_V(\mathbf{r}; t) = \frac{1}{2} \int \frac{\mathbf{R}\mathbf{R}}{R} V'(R) \left\{ 1 - \frac{1}{2}\mathbf{R}\cdot\nabla_{\mathbf{r}} + \dots \right. \\ \left. + \frac{1}{n!}(-\mathbf{R}\cdot\nabla_{\mathbf{r}})^{n-1} + \dots \right\} \rho^{(2)}(\mathbf{r}, \mathbf{r}+\mathbf{R}; t) d\mathbf{R}. \quad (\text{A.8})$$

3 fold

This is identical to the expression given in Eq. (5.15).