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## On the Kinetic Theory of Dense Fluids. XV. Some Comments on the Rice-Allnatt Theory

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In this paper it is shown that, within the framework of the Rice-Allnatt theory of transport phenomena in simple dense fluids, the cross-correlation functions of the soft and hard forces are exactly zero. A relation is found between the soft doublet and soft singlet friction coefficients, and an approximate theory is developed for the soft components of the shear viscosity and the thermal conductivity. The main assumption in this approximation is that of small step diffusion. The soft doublet friction coefficient which is derived in the first part of the paper is then used to calculate values for the soft force contribution to the viscosity and thermal conductivity. It is shown that the equilibrium properties of simple liquids are not known with sufficient accuracy to allow a complete test of the R-A theory, but that the expressions in this theory seem to be moderately insensitive to the equilibrium properties used.

## I. INTRODUCTION

ONE of the most active fields of research in the past 15 years has been the molecular theory of irreversible processes. The basic problem to be solved can be phrased in terms of two questions: (a) How do the time reversible equations of mechanics (or quantum mechanics) lead to a description of the approach to equilibrium? (b) Given a technique for describing the approach to equilibrium, what is the relationship between the macroscopic transport coefficients and the properties of the molecules comprising the system?

In the forefront of the efforts to answer Question (a) has been the work of Prigogine and co-workers.<sup>1</sup> Their analysis is directed towards extracting the approach to equilibrium and irreversible effects contained in the Liouville equation in the limit,  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V = \text{constant}$ , with  $N$  the number of molecules in the volume  $V$ . A result of the analysis is the derivation of non-Markoffian equations for the time evolution of the Fourier components of the distribution function—a result which arises from changes in the distribution function during the duration of a collision. It is concluded that Markoffian or Boltzmann-like equations are valid for the prediction of steady-state phenomena (such as transport of energy, momentum, mass, etc.) but are not valid for the description of the time evolution of the distribution function.

In principle, a solution of Problem (a) also provides a solution to Problem (b). For, once given the non-equilibrium distribution function, the fluxes of matter, momentum, and energy are readily obtained. In practice, the Prigogine solution cannot be used for the treatment of dense fluids because it is basically a perturbation expansion carried to infinite order. The method is useful for weakly interacting systems, where the ratio of the interaction energy to  $kT$  provides a small expansion parameter, or for very dilute systems, where the range of the potential divided by the mean

free path provides a small expansion parameter. In a liquid, however, every molecule is in continuous interaction with all its neighbors, and neither of the parameters mentioned is useful. It is the absence of a small parameter which accounts for most of the difficulty in treating dense fluids.

The only successful treatment of dissipation in the dense fluid phase is based on ideas introduced by Kirkwood<sup>2a</sup>. The guiding principle of Kirkwood's analysis is the description of the lower-order distribution functions only on a time scale such that a meaningful independent dynamical event can be defined. Transient effects during the establishment of the steady state and the approach to the steady state must be discussed using other techniques. We first note that a complete cluster expansion of the integrodifferential equation describing the  $n$  body distribution function can be obtained from a Kirkwood-type analysis, i.e., by use of coarse graining in time.<sup>2b</sup> In the steady state the resultant equations are identical with those derived by Prigogine, by Bogolubov, and by Green.<sup>3</sup> This may be taken as a validation of the conceptual approach (recall our earlier remark concerning steady-state phenomena). Kirkwood proposed to describe the motion of a molecule in a liquid as a quasi-Brownian motion. He then derived Fokker-Planck equations for the singlet and doublet distribution functions using the assumption that the mean momentum transfer in the fluctuating intermolecular field was small relative to the mean momentum.<sup>4</sup> This analysis has been criticized on the ground that large momentum transfers occur during strongly repulsive encounters. It is interesting that the Kirkwood relation between the friction constant and the autocorrelation function of the force acting on a molecule—probably the most valuable result of the analysis—when applied to the rigid-

<sup>2</sup> (a) J. G. Kirkwood, *J. Chem. Phys.* **14**, 180 (1946); (b) S. A. Rice, J. G. Kirkwood, and R. A. Harris, *Physica* **27**, 717 (1961).

<sup>3</sup> See, for example, S. A. Rice and H. L. Frisch, *Ann. Rev. Phys. Chem.* **11**, 187 (1960).

<sup>4</sup> See, also, J. Ross, *J. Chem. Phys.* **24**, 375 (1956).

\* NSF Cooperative Fellow.

<sup>1</sup> I. Prigogine, *Nonequilibrium Statistical Mechanics* (Interscience Publishers, Ltd., London, 1962), Vol. 1.

sphere fluid gives the same result as the Enskog theory.<sup>5</sup> It is clear that sufficient conditions have been formulated for the description of quasi-Brownian motion, but the necessary conditions have not yet been established. Nevertheless, the existence of a very short-range repulsive force contribution and a somewhat longer range attractive force contribution to the total intermolecular force suggests that a distinction be made between large and small momentum transfers.

Rice and Allnatt<sup>6,7</sup> have constructed a theory of transport within the framework of the Kirkwood philosophy. The theory divides the dissipative forces into hard and soft contributions and uses suitable but different dynamical descriptions for the two contributions. It is assumed that:

(a) The intermolecular pair potential may be represented as a rigid core and a superposed soft potential. The soft potential may have both repulsive and attractive parts provided only that the range is large relative to the range of a rigid-core potential.

(b) There exists a time  $\tau$  such that a dynamical event in  $\tau$  is independent of a prior dynamical event  $\tau$  earlier.

(c) The basic dynamical event in a liquid consists of a rigid-core encounter followed by quasi-Brownian motion in the rapidly fluctuating force field of the surrounding molecules. The analysis yields integrodifferential equations for the singlet and doublet distribution functions; the hard-core contribution leads to an Enskog-like modified Boltzmann kernel while the soft contribution gives rise to a Fokker-Planck term characterized by a friction constant defined by only the soft forces.

The consequences of the Rice-Allnatt theory for the special cases of ion mobility, thermal conductivity and viscosity have been examined by Rice and colleagues.<sup>8-11</sup> In all cases excellent agreement with experiment is obtained. At present it appears that the Rice-Allnatt theory provides a quantitative description of linear transport phenomena in liquids, but the meaning of this statement can only be fully ascertained when adequate equilibrium data become available. The dynamical assumptions of the Rice-Allnatt theory cannot at present be fully tested because of the lack of accurate equilibrium distribution functions.

In view of the excellent agreement between the predictions of the Rice-Allnatt theory and experiment, in this paper we examine and comment upon some of the details of the theory. In particular, we examine the

absence of cross terms between the hard and soft contributions to the friction and show that this is an exact consequence of the model; we examine the relationship between the doublet diffusion tensor and singlet diffusion coefficient and establish an approximate but useful connection; we introduce a simple approximation to the soft contribution to the dissipative processes and relate these to equilibrium properties of the liquid; and we also examine the stability of the Rice-Allnatt theoretical predictions to changes in the intermolecular potential and distribution functions.

## II. ON THE ABSENCE OF CROSS-CORRELATIONS

In the formulation of the Rice-Allnatt theory it is assumed that during a rigid-core encounter the soft potential due to the surrounding molecules remains constant and therefore that the soft force vanishes during this short interval. A consequence of this assumption is the absence in the final equations of cross terms between the hard and soft forces. Because this result has caused comment we present here an analysis of the cross correlation between the soft force  $\mathbf{F}^{(S)}$  and the hard force  $\mathbf{F}^{(R)}$ . In particular, we seek to evaluate the cross-correlation contribution to the integral

$$\int_0^\tau \langle \mathbf{F}(t) \cdot \mathbf{F}(t+s) \rangle ds = \int_0^\tau [\langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(R)}(t+s) \rangle + \langle \mathbf{F}^{(S)}(t) \cdot \mathbf{F}^{(S)}(t+s) \rangle + \langle \mathbf{F}^{(S)}(t) \cdot \mathbf{F}^{(R)}(t+s) \rangle + \langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(S)}(t+s) \rangle] ds, \quad (1)$$

where the angular brackets indicate an average over an equilibrium canonical ensemble. Let

$$C(s) = \langle \mathbf{F}^{(S)}(t) \cdot \mathbf{F}^{(R)}(t+s) \rangle_E + \langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(S)}(t+s) \rangle_E \\ = \langle \mathbf{F}^{(S)}(t) \cdot \mathbf{F}^{(R)}(t+s) \rangle_t + \langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(S)}(t+s) \rangle_t, \quad (2)$$

where we have used the subscript  $E$  for an ensemble average and the subscript  $t$  for a time average. The second line of Eq. (2) follows from the quasiergodic theorem<sup>12</sup> which equates time averages and ensemble averages at equilibrium. It is a general property of cross-correlation functions that<sup>13</sup>

$$\langle \mathbf{F}^{(S)}(t) \cdot \mathbf{F}^{(R)}(t+s) \rangle_t = \langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(S)}(t-s) \rangle_t, \quad (3)$$

whereupon, with the change of variable  $y = -s$ , one

<sup>5</sup> E. Helfand, *Phys. Fluids* **4**, 681 (1961).

<sup>6</sup> S. A. Rice and A. R. Allnatt, *J. Chem. Phys.* **34**, 2144 (1961).

<sup>7</sup> A. R. Allnatt and S. A. Rice, *J. Chem. Phys.* **34**, 2156 (1961).

<sup>8</sup> J. Naghizadeh and S. A. Rice, *J. Chem. Phys.* **36**, 2710 (1962).

<sup>9</sup> L. Ikenberry and S. A. Rice, *J. Chem. Phys.* **39**, 1561 (1963).

<sup>10</sup> B. Lowry and S. A. Rice (to be published).

<sup>11</sup> H. T. Davis, S. A. Rice, and L. Meyer, *J. Chem. Phys.* **37**, 947 (1962).

<sup>12</sup> R. Kurth, *Axiomatics of Classical Statistical Mechanics* (Pergamon Press, Ltd., London, 1960).

<sup>13</sup> See, for example, V. V. Solodovnikov, *Introduction to the Statistical Dynamics of Automatic Control Systems* (Dover Publications, Inc., New York, 1960).

finds after recognition that  $s$  and  $y$  are dummy variables

$$\begin{aligned} \int_0^\tau C(s) ds &= \int_0^\tau \langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(S)}(t-s) \rangle_t ds \\ &\quad + \int_0^\tau \langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(S)}(t+s) \rangle_t ds \\ &= \int_{-\tau}^\tau \langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(S)}(t+y) \rangle_t dy. \end{aligned} \quad (4)$$

The soft force at time  $t+y$  may be expanded about the soft force at time  $t$ , using

$$\mathbf{F}^{(S)}(t+y) = \mathbf{F}^{(S)}(t) + \Delta \mathbf{R}(y) \cdot \nabla \mathbf{F}^{(S)}(t) + \dots, \quad (5)$$

which leads to the relationship,

$$\begin{aligned} \int_0^\tau C(s) ds &= \int_{-\tau}^\tau [\langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(S)}(t) \rangle_t \\ &\quad + \langle \mathbf{F}^{(R)}(t) \cdot \Delta \mathbf{R}(y) \cdot \nabla \mathbf{F}^{(S)}(t) \rangle_t] dy + \dots \end{aligned} \quad (6)$$

We observe that the first term of Eq. (6) vanishes identically by the assumption inherent in the model that  $\mathbf{F}^{(S)} = 0$  during a rigid-core encounter. Note that this term vanishes no matter where in the interval of length  $\tau$  the rigid-core encounter occurs. To show this we merely need use the breakup,

$$\begin{aligned} \int_{-\tau}^\tau \langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(S)}(t) \rangle_t dy &= \int_{-\tau}^x \langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(S)}(t) \rangle_t dy \\ &\quad + \int_x^{x+} \langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(S)}(t) \rangle_t dy + \int_{x+}^\tau \langle \mathbf{F}^{(R)}(t) \cdot \mathbf{F}^{(S)}(t) \rangle_t dy, \end{aligned} \quad (7)$$

when the card-core collision occurs between  $x$  and  $x+$ . During the time  $-\tau \rightarrow x$ ,  $\mathbf{F}^{(R)}(t) = 0$ , during  $x \rightarrow x+$ ,  $\mathbf{F}^{(S)}(t) = 0$ , and during  $x+ \rightarrow \tau$ ,  $\mathbf{F}^{(R)}(t) = 0$ , so that the integral displayed is always zero. Consider now the second and higher unexhibited terms of Eq. (6). Using the quasiergodic theorem again we write

$$\begin{aligned} \int_{-\tau}^\tau \left\langle \mathbf{F}^{(R)}(t) \cdot \sum_{n=1}^\infty \left\{ \frac{\Delta \mathbf{R}(y)}{n!} \cdot \nabla_R \right\}^{(n)} \mathbf{F}^{(S)}(t) \right\rangle dy \\ = \left\langle \mathbf{F}^{(R)}(t) \cdot \sum_{n=1}^\infty \left[ \left\{ \int_{-\tau}^\tau \frac{\Delta \mathbf{R}(y)}{n!} dy \right\} \cdot \nabla_R \right]^{(n)} \mathbf{F}^{(S)}(t) \right\rangle, \end{aligned} \quad (8)$$

where we have again noted that  $\mathbf{F}^{(R)}(t)$  and  $\mathbf{F}^{(S)}(t)$  are never *simultaneously* nonzero. As a result of the preceding analysis, and the material presented in Appendix A, we conclude that

$$\int_0^\tau C(s) ds = 0. \quad (9)$$

We have thus shown that the assumptions made in the Rice-Allnatt theory lead, as originally stated, to the absence of cross correlation of the soft and hard forces

in the dissipative process. It is the model assumption, that  $\mathbf{F}^{(S)}(t) = 0$  during a hard-core encounter, which is responsible for the deletion of cross terms, and not any extra assumption or error in the analysis.

It is interesting to note that even for a potential without a rigid core, the cross correlations are small. If in Eq. (8) we expand  $\Delta \mathbf{R}(y)$  one finds

$$\begin{aligned} \mathbf{R}(t+y) &= \mathbf{R}(t) + \Delta \mathbf{R}(y) \\ &= \mathbf{R}(t) + y(p/m) + \dots \end{aligned} \quad (10)$$

The use of (10) in (8) shows that all odd powers of  $\Delta \mathbf{R}$  cause the expression in brackets to vanish. The first nonvanishing term is of order  $\tau^3$ , the retention of which would be inconsistent with the derivation of the Fokker-Planck portion of the transport equation.<sup>2</sup> The first term of Eq. (6) is different from zero if there is no rigid core in the potential, but the magnitude will be very small if the repulsive potential is steep. Indeed the integrand is of the order of magnitude of  $[\Delta \mathbf{R}(kT) \nabla^2 u^{(S)}] \mathbf{F}^{(R)}$ , where  $\Delta \mathbf{R}(kT)$  is the distance moved along the repulsive branch of the potential for an energy change of  $kT$ . For realistic potentials  $\Delta \mathbf{R}(kT)$  is very much smaller than the average molecular separation, while  $\int R^2 \nabla^2 u^{(S)} g_2 dR$  is of order of the soft friction constant. We therefore expect the integrand to be very small and the contribution of the cross correlation to be small relative to the contributions from the hard-hard and soft-soft force correlations even in the case of a general potential.

### III. APPROXIMATE RELATIONSHIP BETWEEN THE DOUBLET AND SINGLET DIFFUSION TENSORS

One of the thorniest problems in the theory of transport in liquids is the relationship between the doublet diffusion tensor and the singlet diffusion tensor. Because of the strong interactions between the molecules, the theory of the friction constant centers on the description of the motion of a pair of molecules under the combined influence of their mutual interaction and the force field generated by the surrounding molecules. It has been customary to assume that the pair diffusion tensor is approximately equal to the direct sum of the singlet diffusion tensors. This approximation<sup>2</sup> is valid when the distance between the molecules of the pair is large, but it cannot be correct at small-pair separation. Since it is the regime of small-pair separation which is most important for the study of liquids, the approximation made introduces possibly the most serious error in the theoretical analysis.

In this section we consider approximating the pair diffusion tensor in terms of the singlet diffusion tensor using a different scheme. Rice and Kirkwood<sup>14</sup> have shown that the average soft force acting on a molecule due to the  $N-1$  other molecules in the system may be

<sup>14</sup> S. A. Rice and J. G. Kirkwood, J. Chem. Phys. **31**, 901 (1959).

written in the form,

$$\langle \mathbf{F}_1^{(S)} \rangle = - (3kT\rho\tau)^{-1} \iint_0^\tau \nabla_{12}^2 u(R_{12}) \mathbf{u}_{12} \cdot \langle \mathbf{p}_{12} \Delta \mathbf{R}_{12}(s) \rangle^{1,2} \times f_0^{(2)} ds d^3 p_1 d^3 p_2 d^3 R_{12}, \quad (11)$$

where

$$\langle \mathbf{p}_{12} \Delta \mathbf{R}_{12}(s) \rangle^{1,2} = \int \mathbf{p}_{12} \Delta \mathbf{R}_{12}(s) \frac{f^{(N)}(\Omega_N)}{f^{(2)}(\Omega_2)} d\Omega_{N-2} \\ d\Omega_j = \prod_{i=1}^j d^3 R_i d^3 p_i; \\ \Omega_j = \{\mathbf{R}_1, \dots, \mathbf{R}_j, \mathbf{p}_1, \dots, \mathbf{p}_j\}. \quad (12)$$

Equation (11) is derived using the following two assumptions: (a) The average displacement of a molecule in a time  $\tau$  is small relative to the intermolecular spacing. This assumption permits us to use the expansion,

$$\nabla u[R_{12}(t+s)] = \nabla u[R_{12}(t)] + \Delta \mathbf{R}_{12}(s) \cdot \nabla \nabla u[R_{12}(t)] + \dots, \\ \mathbf{R}_{12}(t+s) = \mathbf{R}_{12}(t) + \Delta \mathbf{R}_{12}(s), \quad (13)$$

and neglect the higher terms which are not displayed in (13). (b) The distribution function in pair space may be adequately approximated as the product of the local equilibrium configuration distribution function and a momentum distribution function which is Maxwellian about the mean velocity. This assumption permits us to write

$$f^{(2)} = \rho^2 g_2^{(0)} \times \frac{\exp[-(\mathbf{p}_1 - m\mathbf{u})^2/2mkT] \exp[-(\mathbf{p}_2 - m\mathbf{u})^2/2mkT]}{(2\pi mkT)^3}, \quad (14)$$

which is then reduced to the form,

$$f^{(2)} = (\pi mkT)^{-3} \rho^2 g_2^{(0)} \exp(-\mathbf{p}_{12}^2/mkT) \times (1 + \mathbf{p}_{12} \cdot \mathbf{u}_{12}/kT), \quad (15)$$

by the substitutions  $2\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$ ,  $2\mathbf{p}_{12} = \mathbf{p}_2 - \mathbf{p}_1$ , followed by integration over  $d\mathbf{P}$ , expansion of the term involving  $\mathbf{p}_{12} \cdot \mathbf{u}_{12}$  in the exponential of (14) and finally neglecting terms of order  $\mathbf{u}^2$ . Rice and Kirkwood first considered (11) for the case that  $u$  is the total intermolecular pair potential, but their arguments only apply to  $u^{(S)}$  alone which is the case we prefer to discuss herein. The reason for using (11) only for the soft contribution to the potential arises from the observation that the series (13) will only converge rapidly if the product  $\Delta \mathbf{R} \cdot \nabla \nabla u$  is small. This requirement implies that  $\Delta \mathbf{R}$  is small and that  $u$  varies slowly in space. As in the Rice-Allnatt theory, we consider the potential to be the sum of a rigid-core repulsion and a soft potential, and consider in this section only the soft-force contribution to the

molecular friction. From

$$\zeta = \zeta_S + \zeta_H \quad (16)$$

and<sup>15</sup>

$$\langle \mathbf{F}_1 \rangle = \langle \mathbf{F}_1^{(S)} + \mathbf{F}_1^{(H)} \rangle = -(\zeta_S^{(1)} + \zeta_H^{(1)}) \mathbf{u}_{12}, \quad (17)$$

we find

$$\zeta_S^{(1)} = (3kT\rho\tau)^{-1} \iint_0^\tau \langle \mathbf{p}_{12} \cdot \Delta \mathbf{R}_{12}(s) \rangle^{1,2} \times \nabla_{12}^2 u(R_{12}) f_0^{(2)} d^3 p_1 d^3 p_2 d^3 R_{12} ds. \quad (18)$$

It is convenient to change the variable of integration from  $s$  to  $\Delta \mathbf{R}_{12}$  by using the relation,

$$\mathbf{p}_{12} (d\Delta \mathbf{R}_{12}(s)/ds) = (2\mathbf{p}_{12}\mathbf{p}_{12}/m); \\ (m/2) d\Delta \mathbf{R}_{12}(s) = \mathbf{p}_{12} ds, \quad (19)$$

whereupon

$$\tau^{-1} \int_0^\tau \langle \mathbf{p}_{12} \Delta \mathbf{R}_{12}(s) \rangle^{1,2} ds = \frac{1}{2} m \mathbf{D}_S^{(2)}, \quad (20)$$

$$\mathbf{D}_S^{(2)} = \frac{\langle \Delta \mathbf{R}_{12} \Delta \mathbf{R}_{12} \rangle^{1,2}}{2\tau}. \quad (21)$$

Clearly,  $\mathbf{D}_S^{(2)}$  is a function of  $\mathbf{R}_{12}$ . In place of the usual approximation ( $\mathbf{D}^{(2)} \Rightarrow D^{(0)}\mathbf{I} + D^{(1)}\mathbf{I}$ ) which is inaccurate at small distances, we seek an average representation of  $\mathbf{D}^{(2)}$  in the range of  $\mathbf{R}_{12}$  wherein the dominant contribution to (18) arises. That is, by a use of the mean value theorem and a separate calculation of  $\zeta_S^{(1)}$ , we choose an approximate value of  $\zeta_S^{(2)}$  which is density dependent but is not an explicit function of  $\mathbf{R}_{12}$ . From (20) and (18) and the use of the mean value theorem,

$$\zeta_S^{(1)} = \frac{n}{6\rho\zeta_S^{(2)}} \int_0^\infty \nabla_{12}^2 u(R_{12}) f_0^{(2)} d^3 p_1 d^3 p_2 d^3 R_{12}, \quad (22)$$

where we have also the isotropy of the liquid to integrate the tensor relation. In a separate analysis, Rice<sup>16</sup> has obtained the relationship,

$$\zeta_S^{(1)} = \frac{\rho}{36\pi mc^3} \left[ \int_0^\infty \nabla^2 u(R_{12}) g_2^{(0)}(R_{12}) d^3 R_{12} \right]^2, \quad (23)$$

which has been shown by Naghizadeh and Rice<sup>8</sup> to be an accurate representation of the singlet friction in liquid Ar. A combination of Eqs. (23) and (22) then leads to

$$\zeta_S^{(2)} = 6\pi m^2 c^3 \left[ \int_0^\infty \nabla^2 u(R_{12}) g_2^{(0)}(R_{12}) d^3 R_{12} \right]^{-1}, \quad (24)$$

or

$$\zeta_S^{(2)} = (\pi \rho m^2 c^3)^{\frac{1}{2}} (\zeta_S^{(1)})^{-\frac{1}{2}}. \quad (25)$$

The value of  $\zeta_S^{(2)}$  determined by (24) or (25) is for an intermediate but unknown intermolecular separation.

<sup>15</sup> This relation is found by inverting the linear phenomenological equation for the flux of matter in isothermal diffusion.

<sup>16</sup> S. A. Rice, Mol. Phys. 4, 305 (1961).

However, this approximation does weight that region of space from which come the important contributions to the molecular friction more than the use of asymptotic condition  $(\mathbf{D}^{(2)}(\infty) = D^{(1)}\mathbf{1} \oplus D^{(1)}\mathbf{1})$ .

The relationship between  $\zeta_s^{(2)}$  and  $\zeta_s^{(1)}$  expressed in Eq. (25) is interesting. It should be noted that (25) predicts that the temperature dependence of  $\zeta_s^{(2)}$  is very much smaller than that of  $\zeta_s^{(1)}$ . This is a confirmation of the analysis of the temperature dependence of self-diffusion and ion mobility by Rice and co-workers<sup>8,11</sup> since the direct correlation between a pair molecules leads to a negative contribution to the momentum autocorrelation function and thereby  $\zeta_s^{(1)}$  has a larger temperature coefficient than does  $\zeta_s^{(2)}$ . Before examining the numerical values of  $\zeta_s^{(2)}$ , we consider a representation of the soft force contribution to the transport coefficients evaluated by an approximate method based on the Rice-Kirkwood<sup>14</sup> small-step diffusion theory. The representation we now seek is more approximate than that of the Rice-Allnatt theory,<sup>6,7</sup> but has the advantage of relating the transport coefficients to equilibrium thermodynamic properties of the liquid, thereby avoiding the problem of the calculation of integrals involving poorly known pair distribution functions.

#### IV. APPROXIMATE REPRESENTATION OF THE TRANSPORT COEFFICIENTS

If the approximate analysis of transport in dense media proposed by Rice and Kirkwood<sup>14</sup> is repeated with the restrictions that (a) only the soft force contribution to the dissipation is computed in the small-step diffusion approximation, (b) the mean value approximation to  $\zeta_s^{(2)}$  is used in place of the asymptotic relationship between  $\zeta^{(2)}$  and  $\zeta^{(1)}$ , it is then found that

$$\eta_v(R > \sigma) = \frac{m\rho^2}{60\zeta_s^{(2)}} \int_{\sigma}^{\infty} R_{12}^2 \left[ u(R_{12})'' + \frac{4}{R_{12}} u(R_{12})' \right] \times g_2^{(0)}(R_{12}) d^3 R_{12}, \quad (26)$$

$$\phi_v(R > \sigma) = \frac{m\rho^2}{36\zeta_s^{(2)}} \int_{\sigma}^{\infty} R_{12}^2 \left[ u(R_{12})'' + \frac{1}{R_{12}} u(R_{12})' \right] \times g_2^{(0)}(R_{12}) d^3 R_{12}, \quad (27)$$

where  $\eta_v$  and  $\phi_v$  are the shear and bulk viscosities, respectively. For the potential considered in the Rice-Allnatt theory, the equation of state and the internal energy are<sup>17</sup>:

$$\begin{aligned} \frac{p}{\rho k T} &= 1 + \frac{2\pi\sigma^3\rho}{3} g_2(\sigma) \\ &\quad - \frac{\rho}{6kT} \int_{\sigma}^{\infty} R_{12} u'(R_{12}) g_2^{(0)}(R_{12}) d^3 R_{12}, \\ \frac{\langle u \rangle}{NkT} &= \frac{3}{2} + \frac{\rho}{2kT} \int_{\sigma}^{\infty} u(R_{12}) g_2^{(0)}(R_{12}) d^3 R_{12}. \end{aligned} \quad (28)$$

<sup>17</sup> T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956).

It will be noted that the integrands of (26), (27), and (28) are similar in structure. Following Rice and Kirkwood we introduce the definitions

$$\begin{aligned} B_6 &= 4\epsilon\rho \int_{\sigma}^{\infty} \left( \frac{\sigma}{R_{12}} \right)^6 g_2^{(0)}(R_{12}) d^3 R_{12}, \\ B_{12} &= 4\epsilon\rho \int_{\sigma}^{\infty} \left( \frac{\sigma}{R_{12}} \right)^{12} g_2^{(0)}(R_{12}) d^3 R_{12}, \end{aligned} \quad (29)$$

where we have now introduced explicitly the Lennard-Jones potential for the region  $\sigma < R < \infty$ . The use of Eqs. (29) in (28) leads to

$$\begin{aligned} (p/\rho k T) - 1 - \frac{2}{3}\pi\sigma^3\rho g_2(\sigma) &= (1/kT) (2B_{12} - B_6), \\ \langle u \rangle - \frac{3}{2}NkT = L &= \frac{1}{2}N(B_{12} - B_6), \end{aligned} \quad (30)$$

whereupon

$$\eta_v(R > \sigma) = \frac{m\rho}{10\zeta_s^{(2)}} \left[ -24 \frac{L}{N} + 15 \left( \frac{p}{\rho} - kT - \frac{2\pi\sigma^3\rho kT}{3} g_2(\sigma) \right) \right], \quad (31)$$

$$\phi_v(R > \sigma) = \frac{m\rho}{5\zeta_s^{(2)}} \left[ -4 \frac{L}{N} + 3 \left( \frac{p}{\rho} - kT - \frac{2\pi\sigma^3\rho kT}{3} g_2(\sigma) \right) \right]. \quad (32)$$

A similar argument may be used to reduce the soft-force contribution to the coefficient of thermal conductance to the form

$$\begin{aligned} \kappa(R > \sigma) &= \frac{kT\rho}{\zeta_s^{(2)}} \left( 6\alpha \frac{L}{N} + 6\Delta C_p - 6\alpha \frac{p}{\rho} + \frac{1}{4}k(\alpha T - 1) \right. \\ &\quad \times [1 + \frac{2}{3}\pi\sigma^3\rho g_2(\sigma)] - \frac{1}{4}kT(\frac{2}{3}\pi\sigma^3\rho) \\ &\quad \times \left. \left\{ \frac{\partial g_2(\sigma)}{\partial T} - \alpha g_2(\sigma) \right\} \right), \end{aligned} \quad (33)$$

with  $\alpha$  the coefficient of thermal expansion of the liquid and  $\Delta C_p = C_p(\text{liquid}) - \frac{3}{2}k$ .

The reader should note that in this paper we have normalized the distribution function differently than in the Rice-Kirkwood analysis.

#### V. SOME NUMERICAL CALCULATIONS

We have on several occasions remarked that the Rice-Allnatt theory was in good agreement with the observed transport coefficients. How meaningful is this statement? As is well known, the available pair correlation functions of either experimental or theoretical origin are very poor. In this section we examine some of the consequences of the errors in  $g_2(R)$  and  $u(R)$ . Attention is focused on the coefficients of thermal conductance and shear viscosity.

Let us first examine the accuracy with which the radial distribution function and potential reproduce the equilibrium internal energy and pressure of the liquid. It is well known that the calculation of the pressure is inordinately sensitive to the relative posi-

tions of the minimum of  $u(R)$  and the first maximum of  $g_2(R)$ ,<sup>18</sup> and that the internal energy is less sensitive to errors than is  $p$ . In Table I there are displayed the theoretical and experimental values<sup>19</sup> of  $L$  [defined by Eq. (30)] for the potential parameters  $\epsilon=171\times 10^{-16}$  erg,  $\sigma=3.418\times 10^{-8}$  cm, and the same radial distribution functions used by Ikenberry and Rice in the theory of thermal conductance. The agreement, while not spectacularly good, is satisfactory. On the other hand, in Table II are displayed the calculated pressures. These are seen to be in very poor agreement with observation. The sensitivity of the calculated pressure to a change in well depth,  $\epsilon$ , with no change in  $\sigma$  is easily seen by comparison of the third and fourth columns of Table II. The change in well depth from  $\epsilon/k=123.8^\circ\text{K}$  to  $\epsilon=115^\circ\text{K}$  is within the experimental uncertainty of the potential. Indeed, it is found that no single set of parameters ( $\epsilon, \sigma$ ) adequately describes the temperature dependence of the second virial coefficient. At the high-temperature end of the experimental data the set ( $\epsilon/k=123.8^\circ\text{K}$ ,  $\sigma=3.418$  Å) fits, whereas at the low-temperature end the parameter set ( $\epsilon/k=115^\circ\text{K}$ ,  $\sigma=3.50$  Å) is required to effect a fit to the data.<sup>18</sup> This indicates that the Lennard-Jones potential is inadequate over the entire range and a different analytic form or a more flexible form of the potential is needed. Is the discrepancy between the calculated and observed pressures indicative of gross errors which vitiate the meaningfulness of any calculations of transport coefficients? We believe the answer to this question is no. Consider, for example, an alteration of the potential such as to make the pressure integral correct. This may be done in a variety of ways since all that is needed is a shift of the minimum of the potential relative to the first maximum of  $g_2(R)$ . Arbitrarily, we choose to alter  $u(R)$  by scaling the potential through introduction of a parameter  $c$ ,

$$u(R) = 4\epsilon[(\sigma/cR)^{12} - (\sigma/cR)^6], \quad (34)$$

but we do not alter  $g_2(R)$ . The values of the parameter  $c$  are entered in Table II from which it is seen that the small shift in potential which is required, of the order of 1%–2%, is within the uncertainty in  $u(R)$ . Although the procedure adopted is arbitrary, we assert that it is a useful technique for improving integrands which involve products of widely varying functions, each of which is subject to uncertainty. It is important to note that the shift required in  $u(R)$  is very small. Since the shape of  $u(R)$  is not completely correct and the parameters are subject to uncertainties greater than the shift required, we shall use the shifted potential as a test function to examine the numerical stability of the computed transport coefficients.

TABLE I. Theoretical and experimental internal energies for liquid Ar.

| $T(^{\circ}\text{K})$ | $p(\text{atm})$ | $L(\text{calc})$<br>(J) | $L(\text{obs})^a$ |
|-----------------------|-----------------|-------------------------|-------------------|
| 128                   | 50              | –5150                   | –3345             |
| 135.5                 | 100             | –5136                   | –3474             |
| 185.5                 | 500             | –5074                   | –3456             |

<sup>a</sup> See Ref. 19.

We proceed by first noting that the use of the shifted potential in Eq. (28) leads to only small changes in the computed values of  $L$ . Consider now the computation of the thermal conductivity. Ikenberry and Rice<sup>9</sup> have shown that  $\kappa(R>\sigma)$  depends on the difference between  $u(R)$  and  $Ru'(R)$ . Introduction of the shifted potential then, in effect, leads to the multiplication of  $\kappa(R>\sigma)$  by  $c$ , since the difference between  $u(R)$  and  $Ru'(R)$  causes cancellation of the effect of all but one of the powers of  $c$  which enter from (34). The computed thermal conductance is, therefore, essentially unaffected by the shift of the potential required to correct the pressure integral.

Consider now the computation of  $\eta_v(R>\sigma)$ . Lowry and Rice<sup>10</sup> have shown that in this case the integrand is of the form  $R^3u'(R)g_2^0(R)\psi_2(R)$  and all the functions vary widely as  $R$  ranges from  $\sigma$  to  $\infty$ . Moreover, the function  $\psi_2(R)$  is determined from the solution of a differential equation, the input of which requires  $g_2(R)$ . We may therefore expect  $\eta_v(R>\sigma)$  to be very sensitive to the relative positions of  $u(R)$ ,  $g_2(R)$ , and  $\psi_2(R)$ . Detailed calculation shows that the introduction of the scaled potential leads to 25% changes in  $\eta_v(R>\sigma)$  but only 5% changes in the total shear viscosity. For example, at 100 atm and 133.5°K, the raw potential leads to  $\eta_v(R>\sigma)=0.1844\times 10^{-3}$  P, whereas the scaled potential leads to  $\eta_v(R>\sigma)=0.2228\times 10^{-3}$  P. Correspondingly, the total computed shear viscosity changes from  $\eta_T=0.761\times 10^{-3}$  P to  $\eta_T=0.794\times 10^{-3}$  P. It should be noted that the shear viscosity is sensitive to  $\sigma$  in three ways:  $\sigma^5$  and  $\sigma^6$  appear in the equations, the hard-core contribution is quite important, and the hard-core contribution is sensitive to  $g_2(\sigma)$ . In all, it appears that the shear viscosity is much more sensitive to the potential and to  $g_2(R)$  than is the thermal conductance (compare pressure and internal energy). Within the uncertainties of our knowledge of  $u(R)$  and the inadequacy of  $g_2(R)$ , it still appears that the computed viscosity is only variable by of order 25% within the range of possible variation of  $\epsilon$ ,  $\sigma$ , and  $g_2(\sigma)$ . Changes of  $g_2(R)$  cannot at present be investigated arithmetically because of the unavailability of suitable theoretical or experimental functions.

We conclude that the agreement between the Rice–Allnatt theory and experiment is meaningful since the possible changes in computed coefficients are bounded

<sup>18</sup> (a) M. Klein, Ph.D. thesis, Department of Physics, University of Maryland, 1962; (b) F. Buff, Ph.D. thesis, Department of Chemistry, California Institute of Technology, 1949.

<sup>19</sup> F. Dinn, *Thermodynamic Functions of Gases* (Butterworths Scientific Publications, Ltd., London, 1956), Vol. 2.

TABLE II. Theoretical and experimental pressures for liquid Ar.

| $T(^{\circ}\text{K})$ | $p(\text{obs})$ | $p(\text{calc})^a$<br>(atm) | $p(\text{calc})^b$ | $c$    |
|-----------------------|-----------------|-----------------------------|--------------------|--------|
| 128                   | 50              | -306                        | -190               | 0.9819 |
| 135.5                 | 100             | -228                        | -112               | 0.9827 |
| 185.5                 | 500             | +284                        | +398               | 0.9887 |

<sup>a</sup>  $(\epsilon/k)=123.8^{\circ}\text{K}$ .<sup>b</sup>  $(\epsilon/k)=115^{\circ}\text{K}$ .

in a reasonable domain. This conclusion is supported by the observation that agreement between theory and experiment exists in numerous cases of independent calculation. The likelihood that all such independent calculations are spuriously correct seems small.

We now turn to examine the relationship between the singlet and doublet friction constants and the approximate relationships for  $\eta_v(R>\sigma)$  and  $\kappa_v(R>\sigma)$ . From the experimental data of Naghizadeh and Rice we obtain values for the total singlet friction constant. From these data we obtain  $\zeta_s^{(1)}$  by using<sup>5</sup>

$$\zeta^{(1)} = \zeta_4^{(1)} + \zeta_s^{(1)},$$

$$\zeta_H^{(1)} = \frac{8}{3}\rho\sigma^2 g_v(\sigma) (\pi mkT)^{\frac{1}{2}}. \quad (35)$$

As seems usual in studies of transport phenomena, the relevant equilibrium data are hard to find. In Table III are listed the singlet and doublet friction constants for two temperatures and pressures in liquid Ar. Only at  $90^{\circ}\text{K}$  and 1.3 atm is there a measured velocity of sound. We have computed the velocity of sound for  $133.5^{\circ}\text{K}$  and 100 atm. Since the available thermodynamic data leave much to be desired, we restrict our attention to these two cases.

Examination of the entries in Table III immediately shows that  $2\zeta_s^{(2)}$  is less than  $\zeta_s^{(1)}$  at  $90^{\circ}\text{K}$  and 1.3 atm, but greater than  $\zeta_s^{(1)}$  at  $133.5^{\circ}\text{K}$  and 100 atm. From the fundamental relation,

$$D_s^{(2)} = (1/2\tau) [\langle \Delta R_1 \Delta R_1 \rangle^{1,2} + \langle \Delta R_2 \Delta R_2 \rangle^{1,2} + \langle \Delta R_1 \Delta R_2 \rangle^{1,2} + \langle \Delta R_2 \Delta R_1 \rangle^{1,2}], \quad (36)$$

we are led to conclude that the cross terms of (36) are negative at  $90^{\circ}\text{K}$  and positive at  $133.5^{\circ}\text{K}$ . This observation is consistent with the potential parameters, since  $90^{\circ} < \epsilon/k < 133.5^{\circ}$ , and we would expect, on the average, attraction at  $90^{\circ}\text{K}$  and repulsion at  $133.5^{\circ}\text{K}$ . The existence of negative contributions to the momentum autocorrelation function is sensibly independent of the potential parameters; it is determined mainly by the statistical geometry of the liquid.

Consider now the adequacy of the approximate formulae derived to represent the experimental data. As can be seen from Table III, the agreement between experiment and calculation is considerably poorer than

in the case of the full kinetic theory. It is our opinion that this discrepancy arises mainly from the inaccuracy of our representation of  $\zeta_s^{(2)}$ . Note, however, that the current version of the theory is an improvement on the original analysis of Rice and Kirkwood (which used the asymptotic approximation to  $\zeta_s^{(2)}$ ). We conclude that the approximate relationships for  $\kappa(R>\sigma)$  and  $\eta_v(R>\sigma)$  are useful (note the correct temperature dependence of  $\kappa$ ) but not quantitative representations of the properties of a real liquid.

## VI. CONSISTENCY CONDITIONS

We conclude this paper with a brief discussion of two conditions which the Rice-Allnatt theory must satisfy, and the implications of these two conditions.

Consider first the adequacy of a friction constant formalism. Gray and Suddaby and Gray<sup>20,21</sup> have shown that the total force autocorrelation function definition of the friction constant is correct if

$$(\zeta_s^{(1)}/m)\tau_1 < 0.71, \quad (37)$$

where  $\tau_1$  is the time for which the force autocorrelation

TABLE III. Theoretical and experimental doublet friction coefficients, shear viscosities and thermal conductivities of liquid Ar.<sup>a</sup>

| $T$                      | $90^{\circ}$                             | $133.5^{\circ}\text{K}$                  |
|--------------------------|--|--|
| $p$                      | 1.3 atm                                  | 100 atm                                  |
| $\zeta_s^{(1)}$          | $3.65 \times 10^{-10}$ g/sec             | 2.12 g/sec                               |
| $\zeta_s^{(2)}$          | $1.70 \times 10^{-10}$ g/sec             | 1.49 g/sec                               |
| $\eta_k$                 | $0.031 \times 10^{-3}$ P                 | $0.059 \times 10^{-3}$ P                 |
| $\eta_v(\sigma)$         | $0.201 \times 10^{-3}$ P                 | $0.512 \times 10^{-3}$ P                 |
| $\eta_v(>\sigma)$        | $1.455 \times 10^{-3}$ P                 | $0.707 \times 10^{-3}$ P                 |
| $\eta_T$                 | $1.687 \times 10^{-3}$ P                 | $1.278 \times 10^{-3}$ P                 |
| $\eta_T^{\text{asym}}$   | $1.587 \times 10^{-3}$ P                 | $1.576 \times 10^{-3}$ P                 |
| $\eta_{\text{obs}}$      | $2.39 \times 10^{-3}$ P                  | $1.02 \times 10^{-3}$ P                  |
| $\kappa_k$               | $0.02 \times 10^{-4}$ cal/deg<br>cm sec  | $0.07 \times 10^{-4}$ cal/deg<br>cm sec  |
| $\kappa_v(\sigma)$       | $0.08 \times 10^{-4}$ cal/deg<br>cm sec  | $0.08 \times 10^{-4}$ cal/deg<br>cm sec  |
| $\kappa_v(>\sigma)$      | $0.996 \times 10^{-4}$ cal/deg<br>cm sec | $0.695 \times 10^{-4}$ cal/deg<br>cm sec |
| $\kappa_T$               | $1.096 \times 10^{-4}$ cal/deg<br>cm sec | $0.845 \times 10^{-4}$ cal/deg<br>cm sec |
| $\kappa_T^{\text{asym}}$ | $1.030 \times 10^{-4}$ cal/deg<br>cm sec | $1.126 \times 10^{-4}$ cal/deg<br>cm sec |
| $\kappa_{\text{obs}}$    | $2.96 \times 10^{-4}$ cal/deg<br>cm sec  | $1.86 \times 10^{-4}$ cal/deg<br>cm sec  |

<sup>a</sup> All entries for the soft contribution are computed from the approximate theory discussed herein. For the results of the full kinetic theory see Refs. 9 and 10.

<sup>20</sup> A. Suddaby and P. Gray, Proc. Phys. Soc. (London) LXXV, 109 (1960).

<sup>21</sup> P. Gray (private communication).



function goes through a minimum. It is also necessary that  $\tau_1$  be much less than the time between rigid-core encounters. In principle the time  $\tau_1$  can be obtained from neutron diffraction data. At present there is not available a final experimental value for liquid Ar, but  $\tau_1$  is reliably estimated<sup>22</sup> to be  $5 \times 10^{-14}$  sec. Now, the time between rigid-core encounters is easily calculated and found to be of order  $10^{-12}$  sec for liquid Ar ( $0.872 \times 10^{-12}$  sec,  $0.855 \times 10^{-12}$  sec, and  $0.732 \times 10^{-12}$  sec at  $128^\circ$ ,  $133.5^\circ$ , and  $185.5^\circ\text{K}$ , respectively). From the experimental value of  $\zeta_S^{(1)}$  we find

$$\zeta_S^{(1)}/m\tau_1 = 0.226 < 0.71,$$

consistent with the requirement on the force autocorrelation function integral, thereby validating the use of a friction constant formalism.

As a final consideration we examine the meaning of the orthogonality conditions defining the solution to the Rice-Allnatt equation. It will be recalled that a linear integrodifferential equation

$$\lambda \int dy K(x, y) G(y) = S(x) \quad (38)$$

has unique solutions if and only if the inhomogeneity is orthogonal to the solutions,  $G_h(y)$ , of the associated homogeneous equation<sup>23</sup>

$$\lambda \int dy K(x, y) G_h(y) = 0. \quad (39)$$

The orthogonality conditions<sup>24</sup>

$$\int G_h(y) S(y) dy = 0 \quad (40)$$

for the Rice-Allnatt equation are an expression of the conservation of mass, momentum, and kinetic energy. But in a many-body problem of the type posed by transport phenomena in a liquid, what meaning is to be attributed to these conservation conditions? We need make no comment on the conservation of mass since this is unaffected by the presence of intermolecular forces. On the other hand, the conservation of momentum and of kinetic energy require some comment.

The basic physical content of the Rice-Allnatt theory is embodied in the separation of the rigid-core encounter from the quasi-Brownian motion due to the fluctuating soft force field of the molecules. Corresponding to this separation is the implication that the

equation of state, during *and only during* a rigid-core encounter, is that of a rigid-sphere fluid. The equation of state of the fluid during the quasi-Brownian motion is unrestricted, i.e., it is determined solely by  $u(R)$  and the temperature and density. An examination of the orthogonality conditions as applied to the Rice-Allnatt solution confirms this observation. The required orthogonality, as applied to momentum, is obtained when the equation of state is used to reduce the thermal expansion,  $\alpha$ , and the specific heat  $C_V$  and  $(\partial p/\partial T)_\rho$  to molecular terms. Thus the conservation of momentum in the time interval  $0$  to  $0+$  is a consequence of the reduction of the many-body dynamics to a two-body problem effected by the use of the rigid-core potential. During the interval  $0+$  to  $\tau$ , only the Fokker-Planck operator is nonvanishing, and this operator conserves momentum in the local equilibrium iterative scheme used to solve the equation.<sup>25</sup>

It is now apparent that the conservation of kinetic energy in the time interval  $0$  to  $0+$  is again a consequence of the fact that the equation of state during this time interval is that of a rigid-sphere fluid. For such a fluid, the only contribution to the internal energy arises from the kinetic energy. But in the interval  $0+$  to  $\tau$  the molecule moves in the soft-force field of the surrounding molecules. The conservation of kinetic energy is a consequence of the division of forces in the Fokker-Planck equation. What is effected, in the Fokker-Planck equation, is a division of the total intermolecular force into a systematic component, treated as an external force, and a momentum operator representing the fluctuating force. Again, this momentum operator conserves the kinetic energy in the local equilibrium iterative scheme used to solve the equation.

Suppose now we consider a relaxation of the condition that the potential have a rigid core. We have already noted that the cross terms which are rigorously zero in the Rice-Allnatt theory will be small. It is probable that they can be neglected with small consequent error if the repulsive potential is steep. It is interesting to note that the average excess energy per molecule over the energy of an ideal gas is approximately

$$\left[\frac{2}{3} - (1/\rho C_V) (\partial p/\partial T)_\rho\right],$$

when measured in units of  $\frac{3}{2}kT$ . This factor appears in the perturbation term of the rigid-core part of the Rice-Allnatt equation, and may be interpreted as a measure of the change in average potential energy due to the change in location before and after a nonrigid-core repulsive encounter. We therefore speculate, and at the moment can do no more than speculate, that an equation very similar in structure to the Rice-Allnatt equation will be an apt description of transport in a fluid with arbitrary intermolecular potential. In a

<sup>22</sup> K. S. Singwi (private communication).

<sup>23</sup> See, for example, R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1954), Vol. 1.

<sup>24</sup> The Rice-Allnatt equation of transport is not a Fredholm integrodifferential equation of either the first or the second kind. The orthogonality conditions as stated above need not hold; however, in the interval  $(0, 0+)$  or in the limit  $\zeta_S^{(1)} \rightarrow 0$ , they must be satisfied. This provides a good consistency check on the Rice-Allnatt equation.

<sup>25</sup> J. L. Lebowitz, H. L. Frisch, and E. Helfand, *Phys. Fluids* **3**, 325 (1960).

sense, this speculation supports the argument that the Rice-Allnatt model can be applied meaningfully to real liquids which, of course, do not have molecules with rigid cores.

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### APPENDIX A

In Sec. II it was demonstrated that the cross correlations implicit in the autocorrelation function of the total force are negligible. This demonstration depends strongly on one of the model assumptions in the Rice-Allnatt theory; that during a rigid-core encounter the soft potential due to the surrounding molecules remains constant and therefore that the soft force vanishes during this short interval. If this assumption is relaxed, and indeed it ought to be for real fluids, the demonstration fails and the cross correlations become non-zero. Even for the model fluid, although two particles immediately before a hard-core collision are acted upon by a relatively constant soft potential, arising from the  $N-2$  other particles, the soft potential between the colliding pair is certainly not constant. It can be shown that if the condition that the total soft potential be constant is relaxed, the Rice-Allnatt theory remains essentially unchanged in structure.

In their paper Rice and Allnatt, after assuming the pairwise additivity of the intermolecular potential, and after introducing the notion of time smoothing to reduce the hierarchy of equations, integrate the Liouville equation. They thereby arrive at an equation of transport

$$(\partial \tilde{f}^{(1)}(1)/\partial t) + (\mathbf{p}_1/m) \cdot \nabla_{\mathbf{R}_1} \tilde{f}^{(1)}(1) = \Omega_R + \Omega_S, \quad (A1)$$

where

$$\Omega_S = -\tau^{-1} \int_0^\tau \cdots \int \mathbf{F}_{12}^{(S)} \cdot \nabla_{\mathbf{p}_1} f^{(2)}(\mathbf{R}_1 \mathbf{R}_2 \mathbf{p}_1 \mathbf{p}_2; t+s) d\mathbf{R}_2 d\mathbf{p}_2 ds, \quad (A2)$$

and

$$\Omega_R = -\tau^{-1} \int_0^\tau \iint \mathbf{F}_{12}^{(R)} \cdot \nabla_{\mathbf{p}_1} f^{(2)}(\mathbf{R}_1 \mathbf{R}_2 \mathbf{p}_1 \mathbf{p}_2; t+s) d\mathbf{R}_2 d\mathbf{p}_2 ds. \quad (A3)$$

According to Rice and Allnatt, "the force on molecule 1 due to molecule 2,  $\mathbf{F}_{12}$ , has been separated into two parts,  $\mathbf{F}_{12}^{(R)}$ , the repulsive force between molecules 1 and 2, and  $\mathbf{F}_{12}^{(S)}$  the attractive part between the mole-

cules." The point at which it is assumed that no soft force acts on a pair of particles while they are in hard-core interaction follows the introduction of the phase-space transformation function or propagator (like Ross and Kirkwood) into  $\Omega_R$ . This assumption permits the introduction of a Liouville equation for the propagator in the interval  $(0, 0+)$ . One can relax this condition quite easily and be left with essentially the same form for  $\Omega_R$  except that now instead of just  $\mathbf{F}_{12}^{(R)}$  in  $\Omega_R$  there also appears  $\mathbf{F}_{12}^{(S)}$ :

$$\Omega_R = -\tau^{-1} \int_0^\tau \cdots \int (\mathbf{F}_{12}^{(R)} + \mathbf{F}_{12}^{(S)}) \cdot \nabla_{\mathbf{p}_1} f^{(2)}(\mathbf{R}_1 \mathbf{R}_2 \mathbf{p}_1 \mathbf{p}_2; t+s) d\mathbf{R}_2 d\mathbf{p}_2 ds. \quad (A4)$$

In this description a soft pair force acts on the particles immediately before and after the hard-core collision. Note that the soft force is only a two-particle force; the remaining  $(N-2)$  particle force field is assumed to be zero during the encounter, as is suggested by calculated average potentials from cell models of liquids.

Carrying through the analysis in precisely the same way that Rice and Allnatt do, we find that

$$\begin{aligned} \Omega_R = & \int_0^\tau \tau^{-1} \int [g^{(2)}(\mathbf{R}_1, \mathbf{R}_1 + \sigma \mathbf{k}) f^{(1)}(\mathbf{R}_1, \mathbf{p}_1 - \Delta \mathbf{p}_1) \\ & \times f^{(1)}(\mathbf{R}_1 + \sigma \mathbf{k}, \mathbf{p}_2 - \Delta \mathbf{p}_2) - g^{(2)}(\mathbf{R}_1, \mathbf{R}_1 - \sigma \mathbf{k}) f^{(1)}(\mathbf{R}_1, \mathbf{p}_1) \\ & \times f^{(1)}(\mathbf{R}_1 - \sigma \mathbf{k}, \mathbf{p}_2)] d\mathbf{R}_2 d\mathbf{p}_2 ds. \end{aligned} \quad (A5)$$

We may now expand the integrand around the point  $\mathbf{R}_1$ , and introduce the differential scattering cross section in the same way as do Rice and Allnatt:

$$\begin{aligned} \Omega_R = & g_0^{(2)}(\sigma) \int [\tilde{f}^{(1)}(\mathbf{R}_1, \mathbf{p}_1 - \Delta \mathbf{p}_1) \tilde{f}^{(1)}(\mathbf{R}_1, \mathbf{p}_2 - \Delta \mathbf{p}_2) \\ & - \tilde{f}^{(1)}(\mathbf{R}_1, \mathbf{p}_1) \tilde{f}^{(1)}(\mathbf{R}_1, \mathbf{p}_2)] \left| \frac{\mathbf{p}_1}{m} - \frac{\mathbf{p}_2}{m} \right| b db d\epsilon d\mathbf{p}_2 \\ & + g_0^{(2)}(\sigma) \int [\tilde{f}^{(1)}(\mathbf{R}_1, \mathbf{p}_1 - \Delta \mathbf{p}_1) \sigma \mathbf{k} \cdot \nabla_{\mathbf{R}_1} \tilde{f}^{(1)}(\mathbf{R}_1, \mathbf{p}_2 - \Delta \mathbf{p}_2) \\ & + \tilde{f}^{(1)}(\mathbf{R}_1, \mathbf{p}_1) \sigma \mathbf{k} \cdot \nabla_{\mathbf{R}_1} \tilde{f}^{(1)}(\mathbf{R}_1, \mathbf{p}_1)] \left| \frac{\mathbf{p}_1}{m} - \frac{\mathbf{p}_2}{m} \right| b db d\epsilon d\mathbf{p}_2. \end{aligned} \quad (A6)$$

Now

$$\Delta \mathbf{p}_1 = \Delta \mathbf{p}_1^{(H)} + \Delta \mathbf{p}_1^{(S)}, \quad (A7)$$

and

$$\Delta \mathbf{p}_2 = \Delta \mathbf{p}_2^{(H)} + \Delta \mathbf{p}_2^{(S)},$$

where  $\Delta \mathbf{p}_1^{(H)}$  and  $\Delta \mathbf{p}_1^{(S)}$  are the changes in the momentum due to the hard-core force and soft force acting on Particle 1 during the interval  $(0, 0+)$ , respectively. The distribution functions may be expanded about  $\mathbf{p}_1 - \Delta \mathbf{p}_1^{(H)}$  and  $\mathbf{p}_2 - \Delta \mathbf{p}_2^{(H)}$  because  $\Delta \mathbf{p}_1^{(S)}$  and  $\Delta \mathbf{p}_2^{(S)}$  are small in the time interval considered. We find

$$\Omega_R = \Omega_R^{RA} + \Delta \Omega_R, \quad (A8)$$

where  $\Omega_R^{RA}$  is the term which Rice and Allnatt find and  $\Delta\Omega_R$  is the correction to this term due to the presence of  $\mathbf{F}_{12}^{(S)}$ :

$$\begin{aligned} \frac{\Delta\Omega_R}{g_0^{(2)}(\sigma)} = & \iint [\Delta\mathbf{p}_1^{(S)} \cdot \nabla_{\mathbf{p}_1} \tilde{f}^{(1)}(\mathbf{p}_1 - \Delta\mathbf{p}_1^{(H)}) \Delta\mathbf{p}_2^{(S)} \\ & \cdot \nabla_{\mathbf{p}_2} \tilde{f}^{(1)}(\mathbf{p}_2 - \Delta\mathbf{p}_2^{(H)})] \left| \frac{\mathbf{p}_1}{m} - \frac{\mathbf{p}_2}{m} \right| bdbd\epsilon d\mathbf{p}_2 \\ & - \iint [\Delta\mathbf{p}_2^{(S)} \cdot \nabla_{\mathbf{p}_2} \tilde{f}^{(1)}(\mathbf{p}_2 - \Delta\mathbf{p}_2^{(H)}) \tilde{f}^{(1)}(\mathbf{p}_1 - \Delta\mathbf{p}_1^{(H)}) \\ & + \Delta\mathbf{p}_1^{(S)} \cdot \nabla_{\mathbf{p}_1} \tilde{f}^{(1)}(\mathbf{p}_1 - \Delta\mathbf{p}_1^{(H)}) \tilde{f}^{(1)}(\mathbf{p}_2 - \Delta\mathbf{p}_2^{(H)})] \\ & \times \left| \frac{\mathbf{p}_1}{m} - \frac{\mathbf{p}_2}{m} \right| bdbd\epsilon d\mathbf{p}_2 \\ & - \iint [\Delta\mathbf{p}_1^{(S)} \cdot \nabla_{\mathbf{p}_1} \tilde{f}^{(1)}(\mathbf{p}_1 - \Delta\mathbf{p}_1^{(H)}) \sigma \mathbf{k} \cdot \nabla_{\mathbf{R}_{12}} \tilde{f}^{(1)}(\mathbf{p}_2 - \Delta\mathbf{p}_2^{(H)}) \\ & + \Delta\mathbf{p}_2^{(S)} \cdot \nabla_{\mathbf{p}_2} \tilde{f}^{(1)}(\mathbf{p}_2 - \Delta\mathbf{p}_2^{(H)}) \sigma \mathbf{k} \cdot \nabla_{\mathbf{R}_{12}} \tilde{f}^{(1)}(\mathbf{p}_1 - \Delta\mathbf{p}_1^{(H)})] \\ & \times \left| \frac{\mathbf{p}_1}{m} - \frac{\mathbf{p}_2}{m} \right| bdbd\epsilon d\mathbf{p}_2 + \iint \Delta\mathbf{p}_1^{(S)} \cdot \nabla_{\mathbf{p}_1} \tilde{f}^{(1)}(\mathbf{p}_1 - \Delta\mathbf{p}_1^{(H)}) \sigma \mathbf{k} \\ & \cdot \nabla_{\mathbf{R}_{12}} \{ \Delta\mathbf{p}_1^{(S)} \cdot \nabla_{\mathbf{p}_1} \tilde{f}^{(1)}(\mathbf{p}_2 - \Delta\mathbf{p}_2^{(H)}) \} \left| \frac{\mathbf{p}_1}{m} - \frac{\mathbf{p}_2}{m} \right| bdbd\epsilon d\mathbf{p}_2. \end{aligned} \quad (\text{A9})$$

By definition,

$$\Delta\mathbf{p}_1^{(S)} = \int_0^{\tau'} \mathbf{F}_{12}^{(S)} ds = \mathbf{F}_{12}^{(S)} \tau', \quad (\text{A10})$$

where  $\tau'$  is the duration of the hard-core collision. Thus

$$\Delta\mathbf{p}_1^{(S)} \approx \mathbf{0}, \quad \Delta\mathbf{p}_2^{(S)} \approx \mathbf{0} \quad (\text{A11})$$

for a hard-core collision, and  $\Delta\Omega_R$  may be neglected relative to  $\Omega_R$ . The Rice-Allnatt results are thereby retrieved with conditions relaxed from those originally stated.

It becomes obvious that when the assumption that the soft force vanishes during the rigid-core encounter is relaxed the cross correlations are nonzero. But it has just been demonstrated that the Rice-Allnatt equation is structurally unchanged. Clearly, this is true even when the  $n$ -particle soft force is considered, provided only that the soft potential is continuous. An inference that can be drawn is that the Fokker-Planck kernel in the Rice-Allnatt equation contains the cross correlations implicitly. Thus, it seems that the friction coefficient in this kernel arises not only from the soft-force autocorrelation function, but also from the cross correlations projected by the hard-core encounter. This correction may be seen to affect the computation of the friction constant alone and not the structure of the Rice-Allnatt theory.

## APPENDIX B<sup>26</sup>

The development of the small-step diffusion model given by Rice and Kirkwood<sup>14</sup> has been summarized in Sec. IV. In this Appendix we show that the development contains an unstated approximation as it stands, but that all the results may be retrieved with a minor modification to the formalism.

The hypothesis of molecular chaos is introduced as the assumption that a time  $\tau$  exists which is short enough that the average change in relative displacement  $\Delta\mathbf{R}_{12}(\tau)$  is small [Eq. (13)], but nevertheless long enough for  $\langle \Delta\mathbf{R}_{12}(\tau) \Delta\mathbf{R}_{12}(\tau) \rangle^{1,2}$  to reach an asymptotic form  $2\mathbf{D}_S^{(2)}\tau$ , thus allowing the introduction of the generalized pair diffusion tensor  $\mathbf{D}_S^{(2)}$  in Eq. (21). Now, the definition of a diffusion coefficient necessarily involves a time scale  $\tau$  long compared to times in which the momentum retains significant correlation with its initial value, so that Eq. (19),

$$\frac{m}{2} d[\Delta\mathbf{R}_{12}(s)] = \mathbf{p}_{12} ds,$$

is not valid during the whole of an interval  $\tau$ , but only during that fraction for which the molecular trajectories are approximately linear, since  $\mathbf{p}_{12}$  is the initial momentum  $\mathbf{p}_{12}(0)$  at  $s=0$ . The relation valid throughout  $\tau$  is

$$\frac{m}{2} d[\Delta\mathbf{R}_{12}(s)] = \mathbf{p}_{12}(s) ds. \quad (\text{B1})$$

Equation (20) is therefore written without approximation as

$$\begin{aligned} \frac{m}{2} \mathbf{D}_S^{(2)} &= \tau^{-1} \int_0^\tau \langle \mathbf{p}_{12}(s) \Delta\mathbf{R}_{12}(s) \rangle^{1,2} ds \\ &= \tau^{-1} \int_0^\tau \langle \mathbf{p}_{12}(0) \Delta\mathbf{R}_{12}(s) \rangle^{1,2} ds \\ &\quad + \tau^{-1} \int_0^\tau \langle \Delta\mathbf{p}_{12}(s) \Delta\mathbf{R}_{12}(s) \rangle^{1,2} ds. \end{aligned} \quad (\text{B2})$$

We can show, however, that the last term on the right of (B2) is zero, under certain circumstances. We write

$$\Delta\mathbf{R}_{12}(s) = \frac{2}{m} \int_0^s \mathbf{p}_{12}(s') ds'$$

so that

$$\begin{aligned} \langle \Delta\mathbf{p}_{12}(s) \Delta\mathbf{R}_{12}(s) \rangle^{1,2} &= \frac{2}{m} \int_0^s [\langle \mathbf{p}_{12}(s) \mathbf{p}_{12}(s') \rangle^{1,2} \\ &\quad - \langle \mathbf{p}_{12}(0) \mathbf{p}_{12}(s') \rangle^{1,2}] ds'. \end{aligned} \quad (\text{B3})$$

We remark that the average used here is that for which the initial positions and momenta of Molecules 1 and 2

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are held fixed. Thus, while  $\langle \mathbf{p}_{12}(0) \mathbf{p}_{12}(s') \rangle^{1,2}$  can be determined by means of the appropriate bivariate probability distribution for  $\mathbf{p}_{12}(0)$  and  $\mathbf{p}_{12}(s')$  to be simply  $\frac{1}{3} p_{12}^2(0) \mathbf{1} \psi(s')$ , where  $\psi$  is the normalized correlation function (we assume that the momentum is a stationary random process, and for simplicity restrict our attention to the case in which different components are uncorrelated; the argument can be generalized, but is in any case consistent with the assumption of isotropy), the determination of  $\langle \mathbf{p}_{12}(s) \mathbf{p}_{12}(s') \rangle^{1,2}$  requires a knowledge of the trivariate distribution for  $\mathbf{p}_{12}(0)$ ,  $\mathbf{p}_{12}(s)$  and  $\mathbf{p}_{12}(s')$ . The result is in general a function of  $\psi(s)$ ,  $\psi(s')$ , and  $\psi(s-s')$  for which (B3) does not vanish. For example, consider the case that the momentum is a Gaussian process, though not necessarily Markovian. It can be shown that

$$\langle \mathbf{p}_{12}(s) \mathbf{p}_{12}(s') \rangle^{1,2} = \{ \sigma^2 [\psi(s-s') - \psi(s)\psi(s')] + \frac{1}{3} p_{12}^2(0) \psi(s)\psi(s') \} \mathbf{1}, \quad (\text{B4})$$

where  $\sigma^2 = \frac{1}{3} \langle p_{12}^2 \rangle$ , for the average subject to fixed initial  $\mathbf{p}_{12}(0)$ . Substitution of (B4) in (B3) does not cause the latter to vanish. However, if we average (B4) over  $\mathbf{p}_{12}(0)$ , we obtain

$$\langle \langle \mathbf{p}_{12}(s) \mathbf{p}_{12}(s') \rangle^{1,2} \rangle = \sigma^2 \psi(s-s') \mathbf{1}, \quad (\text{B5})$$

so that (B3) becomes

$$\langle \langle \Delta \mathbf{p}_{12}(s) \Delta \mathbf{R}_{12}(s) \rangle^{1,2} \rangle = \frac{2\sigma^2}{m} \mathbf{1} \int_0^s [\psi(s-s') - \psi(s')] ds'. \quad (\text{B6})$$

It is now a simple matter to show that the *integrand* of (B6) vanishes identically. Thus Eq. (21) is correct (i.e., not an approximation) if the average  $\langle \dots \rangle^{1,2}$  is subject only to the fixed initial *positions* of Molecules 1 and 2. It can be seen that the necessary modification to the formalism makes no difference to the results, since these concern only the interaction contributions to the transport coefficients.

### APPENDIX C

Minor errata in a previous paper,<sup>26</sup> J. Chem. Phys. **34**, 2144 (1961):

$$\begin{aligned} \mathbf{K} = & \left[ \frac{f_0^{(1)}(1)}{g(\sigma)} \right] \left( \frac{2kT}{m} \right)^{\frac{1}{2}} \left[ \frac{3}{2} + \alpha T - W_1^2 \right] \mathbf{W}_1 \\ & + f_0^{(1)}(1) \left( \frac{2\pi\sigma^3}{15\nu} \right) \left( \frac{2kT}{m} \right)^{\frac{1}{2}} \left[ -\frac{5}{2} + 10\alpha T - 3W_1^2 \right] \mathbf{W}_1, \quad (\text{43a}) \end{aligned}$$