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Transport coefficients of hard-sphere mixtures: Theory and Monte Carlo molecular-dynamics calculations for an isotopic mixture

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The thermal transport properties of mixtures can be formulated in a number of ways, depending on the choice of driving forces for the transport of heat and matter, without violating the Onsager conditions. Here we treat transport in mixtures based on the driving forces $-\nabla \ln T$ and $-T\nabla(\mu_a/T)$, with T the temperature and μ_a the specific chemical potential, to obtain the Green-Kubo expressions and the Enskog theory for the corresponding transport coefficients which seem most amenable to molecular-dynamics evaluation. The transport properties of a hard-sphere mixture (mass ratio of 0.1, diameter ratio of 1.0, at a volume of three times close-packed volume), calculated by a Monte Carlo, molecular-dynamics method based on the Green-Kubo formulas, are compared with the predictions of the Enskog theory. The long-time behavior of the Green-Kubo time-correlation functions for shear viscosity, thermal conductivity, thermal diffusion, and mutual diffusion are found to be in good agreement with the predictions of mode-coupling theory. Except for viscosity, the contribution of the long-time tails to the transport coefficients is found to be significant. We obtain values, relative to Enskog, of 1.016 ± 0.007 for shear viscosity, 1.218 ± 0.009 for thermal conductivity, 1.267 ± 0.026 for thermal diffusion, and 1.117 ± 0.008 for mutual diffusion.

I. INTRODUCTION

The theoretical study of the transport properties of mixtures has had a striking resurgence in recent years, arising at least in part from the need to understand the behavior of the multicomponent fluid mixtures which are important in a great variety of natural and industrial systems. This intensified interest has been manifested in both analytic theory and computer simulations. Our aim in the present series of papers is to focus the mainstream of these developments onto simple model systems so as (1) to develop a comprehensive assessment of analytic theory and the extent to which it can describe transport processes, and (2) to explore the power and limitations of computer simulations with respect to transport in mixtures.

Hard-sphere models are prominent in the kinetic theory of fluids in that an explicit theory of transport properties, beyond the low-density limit, has been developed only for such models. For single-component fluids, the high-density theory developed by Enskog[1,2] was based from the outset on a hard-sphere model. Extensions to soft interactions have thus far proven elusive, although *ad hoc* methods for applying the Enskog theory to arbitrary systems exist, viz., the so-called modified Enskog theory.

The Enskog theory was revised by van Beijeren and Ernst[3,4] who resolved certain ambiguities in the earlier versions. The extension of the theory to mixtures[4] resulted in the correction of the earlier applications to binary mixtures by Thorne[2] and to multicomponent mixtures by Tham and Gubbins.[5] The van Beijeren–Ernst developments, the so-called revised Enskog theory, yielded a theory consistent with the Onsager reciprocity relations in all cases.

Explicit calculations for the revised Enskog theory were made by Lopez de Haro, Cohen, and Kincaid in a series of papers giving the general development,[6] the mutual diffusion constant,[7] and the thermal diffusion constant.[8] Our principal aim is to test that theory quantitatively.

In a test of the accuracy of the Enskog theory for single-component fluids, Alder and Wainwright[9] first used the molecular-dynamics method to evaluate the equilibrium time-correlation functions which occur in the Green-Kubo theory of transport coefficients. It was through these studies that the long-time tail of the velocity autocorrelation function was first observed and explained hydrodynamically,[10] subsequently being compared[11,12] with the theoretical predictions of the kinetic theory[13,14] and mode-coupling theory.[15–17] While the effect of these long-time tails was to cause a rather substantial increase in the self-diffusion constant beyond the Enskog value at certain intermediate fluid densities, the effect was rather minor at other densities. In any case, the existence of slow, algebraic decay of the time-correlation functions which appear in the Green-Kubo formulas makes it essential that the tail contributions to the transport coefficients be explicitly taken into account.

For other transport coefficients, the comparison between theory and molecular-dynamics calculations has been only partially understood. Alder and Wainwright reported values of the thermal conductivity[18] of hard spheres in substantial agreement with the Enskog theory over the entire fluid regime. For shear viscosity, these authors reported similar agreement for densities well below the fluid-solid phase transition, near which the viscosity increases substantially above the Enskog value.

The mode-coupling theory predicts only small long-time contributions for shear viscosity. Only through the extension of the theory to shorter wavelengths in the so-called extended mode-coupling theory[19] has it been possible to understand the long-time effects associated with the enhanced viscosity at high densities.[20]

For mixtures, the study of transport properties through molecular-dynamics calculations has quite a limited literature. Surprisingly, perhaps, the most extensive work has been concerned with soft interaction potentials rather than hard-core potentials. The self-diffusion constant in a mixture of Lennard-Jones particles was studied by Jacucci and McDonald[21] and by Hoheisel and Deiters[22] using methods based on the Green-Kubo formalism. The self-diffusion of mixtures of hard disks was the subject of a molecular-dynamics study by Clifford and Dickinson.[23] The first investigation of the "thermal" transport coefficients was the Green-Kubo calculation of Jolly and Bearman[24] who studied the mutual diffusion constant for the same mixture studied by Jacucci and McDonald. Schoen and Hoheisel[25,26] extended these calculations to greater precision and to a wider range of parameters. Vogelsang and Hoheisel[27] calculated the thermal conductivity of Lennard-Jones mixtures, also using the Green-Kubo method. Finally, MacGowan and Evans[28] used a nonequilibrium molecular dynamics to calculate the coefficients for mutual diffusion, thermal diffusion, and thermal conduction, also for Lennard-Jones mixtures. Their mutual diffusion coefficients appear to disagree with the earlier results rather substantially.

The aim of the present study is rather different from the previous work. Here our principal goal is the comparison between theory and numerical simulations not only for mutual diffusion but also for shear viscosity, thermal conductivity, and thermal diffusion. While such a comparison may seem straightforward, it is well-known that the separation of energy transport into a thermal and a diffusive part is not unique for mixtures, a fact that has led to great confusion among both theorists and experimentalists. In his classical monograph, de Groot[29] discusses at least three distinct systems of phenomenological fluxes and gradients. Other such separations and other definitions of transport coefficients have been made to accommodate either theory or experiment or both. Evidently, then, some care must be exercised in selecting the system of fluxes and forces, in adopting the correct Green-Kubo expressions for that choice, and in obtaining theoretical results for both the revised Enskog theory and for the long-time tails of the time-correlation functions for that same choice. In view of the ample opportunities for confusion in this field, it is hardly surprising that the literature is replete with disagreements, both real and apparent.

In view of the above, we initiate our study with an outline of the theory, beginning in Sec. II with the phenomenological description of transport in multicomponent mixtures, turning to the microscopic Green-Kubo theory in Sec. III, and providing the specialization of the revised Enskog theory for our choice of fluxes and forces in Sec. IV. In Sec. V, we quote the results of mode-coupling theory for the long-time behavior of the Green-Kubo time-correlation functions, which is the subject of a separate paper.[30] Finally, in Sec. VI, we discuss the results of a Monte Carlo, molecular-dynamics calculation of the various transport coefficients and a brief comparison with the theory. Subsequent papers will deal with more extensive calculations.

II. PHENOMENOLOGICAL TRANSPORT THEORY

As mentioned in the Introduction, de Groot[29] introduced three distinct choices of the fluxes and forces for energy transport in a multicomponent mixture. For the present purpose, our choice is dictated principally by our desire to optimize the molecular-dynamics calculations of the transport coefficients (via the Green-Kubo formulas) in the sense that our choice should lead to the greatest accuracy. Indeed, we find the choice of fluxes and forces to be particularly critical in this respect. Nonetheless, using our results and the values of the partial specific enthalpies and chemical potentials, say, from an approximate analytic equation of state, one can readily transform to the other systems of fluxes and forces.

A. Conservation equations

We consider a d-dimensional ($d=2$ or 3), nonequilibrium fluid system consisting of n_s distinct species. At position $\mathbf{r}$ and time t, let the system have pressure p, temperature T, and specific entropy s, with mass density ρ_a, and flow velocity $\mathbf{v}_a$ of each species. Consider the conservation laws, in the absence of chemical reactions and external forces. The "continuity" equation for species a is[29]

$$\frac{\partial \rho_a}{\partial t} = -\nabla\cdot(\rho_a \mathbf{v}_a) \; . \tag{1}$$

Summation of the continuity equation over all species yields the overall continuity equation

$$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla}\cdot(\rho \mathbf{v}) \; , \tag{2}$$

in which ρ is the overall mass density and $\mathbf{v}$ is the mass-averaged flow velocity

$$\mathbf{v} = \rho^{-1}\sum_a \rho_a \mathbf{v}_a \; . \tag{3}$$

The equation of motion is

$$\rho\frac{\partial \mathbf{v}}{\partial t} + \rho\mathbf{v}\cdot\nabla\mathbf{v} = -\boldsymbol{\nabla}\cdot\mathbf{P} \; , \tag{4}$$

in which $\mathbf{P}$ is the pressure tensor. Finally, the entropy transport equation is written as

$$\rho\frac{\partial s}{\partial t} + \rho\mathbf{v}\cdot\boldsymbol{\nabla} s = -\boldsymbol{\nabla}\cdot\mathbf{J}_s + \Omega \; , \tag{5}$$

in which Ω is the entropy production and $\mathbf{J}_s$ is the entropy current, which can be written in terms of the heat current $\mathbf{J}_q$ and the diffusion current $\mathbf{J}_a$ as

$$\mathbf{J}_s = \frac{1}{T}\left[\mathbf{J}_q - \sum_a \mu_a \mathbf{J}_a\right] \; , \tag{6}$$

in which we use sums over Roman indices, $a,b,\ldots,$ for sums over the n_s species. The specific chemical potential μ_a of species a is defined in terms of the (extensive) Gibbs free energy $G(T,p,\{M_a\})$ of a system having masses $\{M_a\}=\{M_1,M_2,\ldots,M_{n_s}\}$ of the various species

$$\mu_a(T,p,\{c_a\})=\left(\frac{\partial G}{\partial M_a}\right)_{T,p,\{M_{b\neq a}\}}, \tag{7}$$

in which we define the thermodynamic state by T, p, and the n_s-1 independent mass fractions, $\{c_a\}=\{c_1,c_2,\ldots,c_{n_s-1}\}$. The currents are defined by

$$\begin{aligned}\mathbf{J}_a&=\rho_a(\mathbf{v}_a-\mathbf{v})\ ,\\ \mathbf{J}_q&=\mathbf{J}_e-(\rho e\mathbf{v}+\mathbf{P}\cdot\mathbf{v})\ ,\end{aligned} \tag{8}$$

where e is the total specific energy, $e=\frac{1}{2}v^2+u$, u is the specific internal energy, and $\mathbf{J}_e$ is the total energy current, which satisfies the energy continuity equation

$$\frac{\partial(\rho e)}{\partial t}=-\nabla\cdot\mathbf{J}_e\ . \tag{9}$$

By virtue of the assumption of "local equilibrium," u is taken to be a known function of the local thermodynamic state $T,p,\{c_a\}$.

B. Linear phenomenological laws

The hydrodynamic equations are completed by expressing the heat current and pressure tensor as linear functions of the gradients. The pressure tensor in the Newtonian approximation for a d-dimensional fluid is

$$\mathbf{P}=p\mathbf{1}-\eta[\nabla\mathbf{v}+(\nabla\mathbf{v})^\dagger]+[(2/d)\eta-\zeta](\nabla\cdot\mathbf{v})\mathbf{1}\ , \tag{10}$$

in which η is the shear viscosity coefficient, ζ is the bulk viscosity, $(\nabla\mathbf{v})^\dagger$ denotes the transpose of the dyadic tensor, and $\mathbf{1}$ denotes the unit tensor.

In nonequilibrium thermodynamics, the heat and diffusion fluxes are written as linear functions of their "canonical" forces, i.e., fluxes $\mathbf{J}_i$ and forces $\mathbf{X}_i$ such that the entropy production has the Onsager form

$$\Omega=\frac{1}{T}\sum_i\mathbf{J}_i\cdot\mathbf{X}_i\ . \tag{11}$$

For the heat and matter transport, de Groot[29] details three distinct choices of fluxes and forces which we designate as "mainstream," "prime," and "double prime" corresponding to his unprimed, singly primed, and doubly primed choices. In each case, the viscous contributions Ω_η remain the same, so the entropy production takes the form

$$\Omega=\Omega_u+\Omega_\eta\ , \tag{12}$$

in which[31]

$$\Omega_\eta=\frac{1}{T}\{\eta[\nabla\mathbf{v}+(\nabla\mathbf{v})^\dagger]-[(2/d)\eta-\zeta](\nabla\cdot\mathbf{v})\mathbf{1}\}:\nabla\mathbf{v}\ . \tag{13}$$

In the mainstream system, de Groot uses the fluxes $\mathbf{J}_q$ and $\mathbf{J}_a$ with corresponding forces

$$\begin{aligned}\mathbf{X}_u&=-\frac{1}{T}\nabla T\ ,\\ \mathbf{X}_a&=-T\nabla\left(\frac{\mu_a}{T}\right)\ ,\end{aligned} \tag{14}$$

respectively. In the prime system used, for example, by Green[32] in his study of the Green-Kubo relations for mixtures and by Pomeau[33] in his theory for the long-time behavior of the time-correlation functions for mixtures, the forces

$$\begin{aligned}\mathbf{X}'_u&=\mathbf{X}_u\ ,\\ \mathbf{X}'_a&=-\nabla\mu_a=\mathbf{X}_a+\mu_a\mathbf{X}_u\ ,\end{aligned} \tag{15}$$

have canonical fluxes

$$\begin{aligned}\mathbf{J}'_q&=\mathbf{J}_q-\sum_a\mu_a\mathbf{J}_a\ ,\\ \mathbf{J}'_a&=\mathbf{J}_a\ .\end{aligned} \tag{16}$$

Finally, the double-prime system is based on forces

$$\begin{aligned}\mathbf{X}''_u&=\mathbf{X}_u\ ,\\ \mathbf{X}''_a&=\mathbf{X}_a+h_a\mathbf{X}_u\ ,\\ &=-(\nabla\mu_a+s_a\nabla T)\ ,\end{aligned} \tag{17}$$

in which h_a is the partial specific enthalpy,

$$h_a=\left(\frac{\partial H}{\partial M_a}\right)_{T,p,\{M_{b\neq a}\}}, \tag{18}$$

[with $H(T,p,\{M_a\})$ the enthalpy], and s_a is the partial specific entropy

$$s_a=\left(\frac{\partial S}{\partial M_a}\right)_{T,p\{M_{b\neq a}\}}, \tag{19}$$

in which S is the total (extensive) entropy. It follows that

$$\begin{aligned}\mathbf{J}''_q&=\mathbf{J}_q-\sum_a h_a\mathbf{J}_a\ ,\\ \mathbf{J}''_a&=\mathbf{J}_a\ .\end{aligned} \tag{20}$$

It is perhaps worth noting that X''_a can also be written,

$$\mathbf{X}''_a=-\nabla_T\mu_a\ , \tag{21}$$

in which the isothermal gradient for any intensive thermodynamic function g is defined by

$$\nabla_T g(T,p,\{c_a\})=\nabla g-\left(\frac{\partial g}{\partial T}\right)_{p,\{c_a\}}\nabla T\ . \tag{22}$$

Thus, in the double-prime system the diffusion force has no contribution from the temperature gradient in the sense that the term arising from the temperature dependence of the chemical potential has been subtracted off.

The hydrodynamic modes, which are used in mode-coupling theory for the long-time behavior of the time-correlation functions, can be formulated in terms of any of the three forms of the forces and fluxes. The prime set, used for example by Pomeau,[33] would appear to be particularly unfortunate for the present calculations in that the fluxes and forces (and thence the transport coefficients) contain properties of the system which are either difficult to evaluate or undesirable to specify. The latter can be seen from the expression for the chemical potential of a three-dimensional ideal gas,

$$\mu_a = \frac{3k_BT}{2m_a}\ln(2\pi\hbar^2) - \frac{3k_BT}{2m_a}\ln m_a - \frac{5k_BT}{2m_a}\ln(k_BT) + \frac{k_BT}{m_a}\ln(x_a p) , \tag{23}$$

in which $2\pi\hbar$ is Planck's constant and x_a is the mole fraction of species a. Thus X'_a, Eq. (15), contains a term in the temperature gradient involving Planck's constant. Not surprisingly, Planck's constant also appears explicitly, for example, in the Green-Kubo expression for the prime thermal conductivity, resulting, as it turns out, in a dependence of the transport coefficient on the thermal wavelengths of the particles. On the other hand, neither X_a nor X''_a contains this term in $\hbar$. While clearly there is nothing wrong with this property of the prime set, it is clearly advantageous to avoid reporting results which apply only for specific values of the thermal wavelengths. As a result, our considerations will be limited for the most part to the mainstream and double-prime systems.

The linear transport coefficients are defined in the standard fashion,

$$\begin{aligned} \mathbf{J}_a &= \sum_b L_{ab}\mathbf{X}_b + L_{au}\mathbf{X}_u , \\ \mathbf{J}_q &= \sum_a L_{ua}\mathbf{X}_a + L_{uu}\mathbf{X}_u , \end{aligned} \tag{24}$$

in which the L_{ab} are the mutual diffusion coefficients, the L_{au} and L_{ua} are the thermal diffusion coefficients, and L_{uu} is the thermal conductivity. Similar expressions define the prime and double-prime transport coefficients. The Onsager reciprocity relations for the mainstream transport coefficients are

$$\begin{aligned} L_{ab} &= L_{ba} , \\ L_{ua} &= L_{au} , \end{aligned} \tag{25}$$

while the definition of the diffusion current, Eq. (8), whereby $\sum_a \mathbf{J}_a = 0$ yields

$$L_{aa} = \sum_{b \neq a} L_{ab} . \tag{26}$$

For the case of a binary mixture, these relations reduce the number of independent thermal transport coefficients to three, viz., L_{11}, L_{1u}, and L_{uu}.

The relationships among the various sets of transport coefficients can readily be obtained by writing the fluxes in the target system in terms of the fluxes in the source system. Thus, to obtain the prime coefficients in terms of the mainstream, we write the prime fluxes in the form Eq. (16), substitute the linear relations, Eq. (24), for the mainstream fluxes, and write the mainstream forces in terms of the prime forces through Eq. (15). Using the second of the Onsager relations, Eq. (25), and comparing the result with the prime version of the linear laws, we thereby obtain

$$\begin{aligned} L'_{ab} &= L_{ab} , \\ L'_{ua} &= L_{ua} - \sum_b \mu_b L_{ba} , \\ L'_{uu} &= L_{uu} - 2\sum_a \mu_a L_{ua} + \sum_a \sum_b \mu_a \mu_b L_{ab} . \end{aligned} \tag{27}$$

One can readily obtain the inverse relations in a similar manner as

$$\begin{aligned} L_{ab} &= L'_{ab} , \\ L_{ua} &= L'_{ua} + \sum_b \mu_b L'_{ba} , \\ L_{uu} &= L'_{uu} + 2\sum_a \mu_a L'_{ua} + \sum_a \sum_b \mu_a \mu_b L'_{ab} . \end{aligned} \tag{28}$$

Similarly, the double-prime set is found to be

$$\begin{aligned} L''_{ab} &= L_{ab} , \\ L''_{ua} &= L_{ua} - \sum_b h_b L_{ba} , \\ L''_{uu} &= L_{uu} - 2\sum_a h_a L_{ua} + \sum_a \sum_b h_a h_b L_{ab} , \end{aligned} \tag{29}$$

which can also be readily inverted.

III. MICROSCOPIC THEORY

The microscopic calculation of transport coefficients is based on Green-Kubo theory. Unfortunately, the literature on the subject is untrustworthy for the most part so that considerable care must be exercised in the use of so-called standard references. For the present purposes, we refer to the development by Green,[32] although some minor correction is needed in this case also. Because Green derived expressions for the transport coefficients based on the prime fluxes and forces, we shall further transform these to obtain expressions appropriate to the mainstream and double-prime systems.

A. Dynamical system

We consider a fluid system at the temperature T contained in cubic volume $V = L^3$. The system consists of N particles, N_1 having mass m_1, N_2 having mass $m_2, \ldots,$ and N_{n_s} having mass m_{n_s}.

The system is assumed to evolve with time under the Newtonian equations of motion, subject to a two-body, central interaction potential $u_{ab}(r)$ acting between particles of species a and b at a separation r. If we denote the particle positions by $r^N = \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$ and the particle velocities by $v^N = \{\mathbf{v}_1, \mathbf{v}_2, \ldots, \mathbf{v}_N\}$, then the potential energy is the sum of pairwise additive terms,

$$\begin{aligned} U_0 &= \sum_{i<j} u_{s_i s_j}(r_{ij}) , \\ \mathbf{r}_{ij} &= \mathbf{r}_i - \mathbf{r}_j , \end{aligned} \tag{30}$$

in which we denote the species index of particle i by s_i and in which $r_{ij}=|\mathbf{r}_{ij}|$. To simplify the notation, however, for the i,j interaction, we write, hereafter,

$$\phi_{ij}(r_{ij})=u_{s_i s_j}(r_{ij}) \ . \tag{31}$$

For the case of hard-disk or hard-sphere mixtures, which will be our principal concern, the interaction potential is singular,

$$\begin{aligned} u_{ab}(r) &= \begin{cases} 0 & \text{if } r \geq \sigma_{ab} \ , \\ \infty & \text{otherwise} \ , \end{cases} \\ \sigma_{ab} &= (\sigma_a+\sigma_b)/2 \ , \end{aligned} \tag{32}$$

in which σ_a is the diameter of species a. (In the discussion which follows, we shall speak of the hard-sphere interaction to indicate the two- or three-dimensional case. Only in Secs. IV and VI will we specialize to three dimensions.)

In numerical calculations, the system typically is far from macroscopic size. In order to minimize surface effects, we employ the usual periodic-boundary conditions in which the N-particle system is replicated throughout space through translation by $\boldsymbol{\nu}L$ for all d vectors $\boldsymbol{\nu}$ having integer components. Thus the total potential energy of the system becomes

$$\begin{aligned} U(r^N) &= \sum_{\boldsymbol{\nu}} U_{\boldsymbol{\nu}}(r^N) \ , \\ U_{\boldsymbol{\nu}}(r^N) &= {\sum_{i\leq j}}' \phi_{ij}(|\mathbf{r}_{ij}+\boldsymbol{\nu}L|) \ , \end{aligned} \tag{33}$$

in which the prime on the i,j sum denotes the omission of the $j=i$ term for $\boldsymbol{\nu}=\mathbf{0}$, as in Eq. (30).

In order to be specific in the face of periodic-boundary conditions, we further define the position $\mathbf{r}_i(t)$ to be the integral of the velocity $\mathbf{v}_i(t)$. This definition is sometimes called the "infinite checkerboard" description in which the $\mathbf{r}_i(t)$ move continuously throughout the periodic cells. It is to be distinguished from the discontinuous definition whereby the particle remains within the "primary" or $\boldsymbol{\nu}=0$ cell.

B. Green-Kubo formulas

Green[32] derived the Green-Kubo formulas for a multicomponent mixture. These can be written in the usual form of a sum of kinetic, cross, and potential terms as

$$L_\alpha = L_\alpha^{(KK)}+L_\alpha^{(K\phi)}+L_\alpha^{(\phi K)}+L_\alpha^{(\phi\phi)} \ , \tag{34}$$

in which

$$\begin{aligned} L_\alpha^{(AB)} &= \lim_{t\to\infty} \operatorname{tlim} L_\alpha^{(AB)}(t) \ , \\ L_\alpha^{(AB)}(t) &= \int_0^t ds\, \rho_\alpha^{(AB)}(s) \ , \end{aligned} \tag{35}$$

with $A,B \in \{K,\phi\}$, for transport coefficient $\alpha \in \{ab, au, uu, \eta\}$ representing the mutual diffusion constant, the thermal diffusion constant, the thermal conductivity, and the shear viscosity, respectively. Here tlim denotes the thermodynamic limit of large system size and $\rho_\alpha(t)$ are time-correlation functions of the form

$$\rho_\alpha^{(AB)}(t) = \frac{\beta}{n_\alpha V} \langle \mathcal{J}_{\alpha_1}^{(A)}(0)\cdot \mathcal{J}_{\alpha_2}^{(B)}(t) \rangle \ , \tag{36}$$

in which

$$\mathcal{J}_{\alpha_i} = \mathcal{J}_{\alpha_i}^{(K)}+\mathcal{J}_{\alpha_i}^{(\phi)}$$

are microscopic currents, $\beta=1/(k_B T)$, and $n_\alpha=d$, except for the case of the viscosity for which $n_\eta=1$. The subscripts α_1 and α_2 denote the first and second subscripts of α, respectively, except for the case of shear viscosity for which both α_1 and α_2 are η. The angular brackets denote an average over an equilibrium, statistical-mechanical ensemble.

Analogous relations relate the prime transport coefficients, the prime time-correlation functions, and the prime microscopic currents, as well as the double-prime quantities.

The microscopic currents for the prime system reduce, for an equilibrium ensemble (Green treats a generalized ensemble), to

$$\begin{aligned} \mathcal{J}'_a(t) &= \mathcal{J}_a'^{(K)}(t) \ , \\ &= \sum_j^{(a)} m_{s_j}\mathbf{v}_j(t) - c_a \sum_j m_{s_j}\mathbf{v}_j(t) \ , \\ \mathcal{J}_u'^{(K)}(t) &= \mathbf{B}^{(K)}(t) - \sum_a \mu_a \mathcal{J}'_a(t) - h\sum_i m_{s_i}\mathbf{v}_i(t) \ , \\ \mathcal{J}_u'^{(\phi)}(t) &= \mathbf{B}^{(\phi)}(t) \ , \\ \mathcal{J}_\eta^{(A)}(t) &= T_{xy}^{(A)}(t) \ , \end{aligned} \tag{37}$$

in which $\sum_j^{(a)}$ denotes the sum over particles of species a and in which $\mathbf{B}$ is the total microscopic energy flux,

$$\begin{aligned} \mathbf{B} &= \mathbf{B}^{(K)}+\mathbf{B}^{(\phi)} \ , \\ \mathbf{B}^{(K)} &= \sum_i e_i\mathbf{v}_i \ , \\ \mathbf{B}^{(\phi)} &= \tfrac{1}{2}\sum_{\boldsymbol{\nu}} {\sum_{i,j}}' (\mathbf{r}_{ij}+\boldsymbol{\nu}L)\mathbf{F}_{ij}(\mathbf{r}_{ij}+\boldsymbol{\nu}L)\cdot\mathbf{v}_i \ , \\ e_i &= \tfrac{1}{2}\left[m_{s_i}v_i^2 + \sum_{\boldsymbol{\nu}} {\sum_j}' \phi_{ij}(|\mathbf{r}_{ij}+\boldsymbol{\nu}L|) \right] \ , \end{aligned} \tag{38}$$

e_i is the energy of particle i, $\mathbf{T}$ is the microscopic stress tensor,

$$\begin{aligned} \mathbf{T} &= \mathbf{T}^{(K)}+\mathbf{T}^{(\phi)} \ , \\ \mathbf{T}^{(K)} &= \sum_i m_{s_i}\mathbf{v}_i\mathbf{v}_i \ , \\ \mathbf{T}^{(\phi)} &= \tfrac{1}{2}\sum_{\boldsymbol{\nu}} {\sum_{i,j}}' (\mathbf{r}_{ij}+\boldsymbol{\nu}L)\mathbf{F}_{ij}(|\mathbf{r}_{ij}+\boldsymbol{\nu}L|) \ , \end{aligned} \tag{39}$$

and $\mathbf{F}_{ij}(r)$ is the force,

$$\mathbf{F}_{ij}(r) = -\boldsymbol{\nabla}\phi_{ij}(r) \ .$$

Both $\mathbf{B}$ and $\mathbf{T}$ are written as sums of kinetic and potential parts. Our calculations have not included the bulk viscosity so we do not consider it here.

To obtain the microscopic currents appropriate to the mainstream transport coefficients, we substitute the prime versions of Eqs. (35) and (36) into the relation between mainstream and prime transport coefficients, Eq. (28). With suitable rearrangement of the microscopic currents, we obtain the following:

$$\begin{gathered}\mathcal{J}_a(t)=\mathcal{J}'_a(t)\,,\\ \mathcal{J}_u^{(K)}(t)=\mathbf{B}^{(K)}(t)-h\sum_i m_{s_i}\mathbf{v}_i\,,\\ \mathcal{J}_u^{(\phi)}(t)=\mathbf{B}^{(\phi)}(t)\,.\end{gathered}\tag{40}$$

We note that the microscopic heat current no longer contains the chemical potentials and is therefore more readily computed than the prime version. Moreover, for the so-called molecular-dynamics ensemble, having fixed volume, energy, and linear momentum, the latter normally being set to zero, the term in the specific enthalpy vanishes, whence the heat current is dependent only on the phase, $x^{(N)}(t)$.

For the double-prime transport coefficients, the microscopic currents follow from substituting the double-prime versions of Eqs. (35) and (36) into Eq. (29). We obtain

$$\begin{gathered}\mathcal{J}''_a(t)=\mathcal{J}_a(t)\,,\\ \mathcal{J}_u''^{(K)}(t)=\mathcal{J}_u^{(K)}(t)-\sum_a h_a\mathcal{J}_a(t)\,,\\ \mathcal{J}_u''^{(\phi)}(t)=\mathbf{B}^{(\phi)}(t)\,.\end{gathered}$$

We see that the double-prime heat current is similar to the mainstream in not containing the chemical potentials but is complicated by the presence of the partial specific enthalpies which would normally be a little difficult to evaluate with precision. Indeed, Vogelsang and Hoheisel[27] in their calculation of the double-prime thermal conductivity of the Lennard-Jones fluid simply estimated the magnitude of this contribution to be small.

For the case of hard-sphere interactions, Eq. (32), the potential terms in Eqs. (38) and (39) are singular. Expressions suitable for hard spheres can be obtained by calculating the energy current and the momentum current across an elementary area in the N-particle system, taking into account the periodic-boundary conditions. One obtains

$$\begin{aligned}\mathbf{B}^{(\phi)}=\tfrac{1}{4}\sum_{\gamma=1}^{\infty}\delta(t-t_\gamma)[\mathbf{r}_{ij}(t_\gamma)+\boldsymbol{\nu}_\gamma L]m_{s_i}\Delta\mathbf{v}_i(t_\gamma)&\\ \times[\mathbf{v}_i(t_\gamma)+\mathbf{v}'_i(t_\gamma)+\mathbf{v}_j(t_\gamma)+\mathbf{v}'_j(t_\gamma)]\,,&\end{aligned}\tag{41}$$

for the potential part of the energy flux and

$$T^{(\phi)}=\sum_{\gamma=1}^{\infty}\delta(t-t_\gamma)[\mathbf{r}_{ij}(t_\gamma)+\boldsymbol{\nu}_\gamma L]m_{s_i}\Delta\mathbf{v}_i(t_\gamma)\tag{42}$$

for the potential part of the stress tensor.[34] Here t_γ is defined to be the time of the γth collision and i and j denote the particles involved in that collision. In general, these particles need not be in contact, but periodic image $\mathbf{r}_i+\boldsymbol{\nu}_\gamma L$ is defined as being in collision with $\mathbf{r}_j$ at time t_γ. The symbols, $\mathbf{v}_i$ and $\mathbf{v}'_i$, specify the pre- and post-collision velocities, and

$$\Delta\mathbf{v}_i=\mathbf{v}'_i-\mathbf{v}_i\,.$$

While it is not possible to directly compute time-correlation functions involving the potential terms because of the δ functions in the time, one can readily compute time integrals by interchanging the time integral with the ensemble average. We write the time-dependent transport coefficients, defined by the second of Eq. (35), as a time-correlation function by taking the time integral within the ensemble average in Eq. (36), where

$$\begin{gathered}L_\alpha^{(AB)}(t)=\frac{\beta}{n_\alpha V}\langle\mathcal{J}_{\alpha_1}^{(A)}(0)\cdot\mathcal{G}_{\alpha_2}^{(B)}(t)\rangle\,,\\ \mathcal{G}_{\alpha_i}^{(A)}(t)=\int_0^t ds\,\mathcal{J}_{\alpha_i}^{(A)}(s)\,.\end{gathered}\tag{43}$$

While the kinetic and the $(K\phi)$ cross terms are seen to no longer contain δ functions, the potential terms and the (ϕK) cross terms do. To evaluate these, we consider the so-called Einstein functions,

$$S_\alpha^{(AB)}(t)=\frac{\beta}{2tn_\alpha V}\langle\mathcal{G}_{\alpha_1}^{(A)}(t)\cdot\mathcal{G}_{\alpha_2}^{(B)}(t)\rangle\,.\tag{44}$$

Observe that

$$\begin{gathered}\frac{d}{dt}tS_\alpha^{(AA)}(t)=M_\alpha^{(AA)}(t)\,,\\ \frac{d}{dt}tS_\alpha^{(K\phi)}(t)=\tfrac{1}{2}[M_\alpha^{(K\phi)}(t)+M_\alpha^{(\phi K)}(t)]\,,\\ M_\alpha^{(AB)}(t)=\frac{\beta}{n_\alpha V}\langle\mathcal{J}_{\alpha_1}^{(A)}(t)\cdot\mathcal{G}_{\alpha_2}^{(B)}(t)\rangle\,.\end{gathered}\tag{45}$$

It can be shown using the Liouville theorem and the dynamic reversibility of the trajectory that

$$M_\alpha^{(AB)}(t)=L_\alpha^{(AB)}(t)\,.\tag{46}$$

Thus, for hard spheres, we are forced by the presence of the δ functions in the potential parts of the energy current and the stress tensor to evaluate the time-dependent transport coefficients through differentiation of the Einstein functions.

IV. ENSKOG THEORY

The revised Enskog theory was applied to hard-sphere mixtures by Lopez de Haro *et al.*,[6] referred to as LCK hereafter. In view of the various possible choices for fluxes and forces, it is essential that we ascertain the choice made in that paper. By substituting the energy current $\mathbf{J}_e$ from Eq. (8) and the total energy e into the energy continuity relation, Eq. (9), and observing that for hard spheres the specific internal energy is given by

$$u=\frac{d}{2}nk_BT/\rho\,,$$

one readily obtains the energy equation, Eq. (9c), of LCK. Therefore, the LCK heat current $\mathbf{J}_q$ is identical with ours.

The Enskog theory, specialized to the $d=3$ case, yields the following expressions for the fluxes of mass, momentum, and heat in terms of the gradients of velocity, temperature, and number density:[6]

$$\mathbf{J}_a = -\frac{\rho_a}{2n}\left[\sum_b d_{a,0}^{(b)}\mathbf{d}_b - a_0^{(a)}\nabla \ln T\right] ,$$

$$\mathbf{P} = -\left[\sum_a K_a' \frac{n_a k_B T}{n} b_0^{(a)} + \tfrac{8}{15}C\right]\langle\langle \nabla \mathbf{v}\rangle\rangle$$

$$-\left[\frac{4}{9}C + \frac{2k_B T}{n}\sum_a\sum_b \rho b_{ab} M_{ba}\chi_{ab} n_a h_1^{(a)}\right](\nabla\cdot\mathbf{v})\mathbf{1} ,$$

$$\mathbf{J}_q = -\tfrac{5}{4}k_B T\sum_a \frac{K_a n_a}{n}\left[a_1^{(a)}\nabla \ln T - \sum_b d_{a,1}^{(b)}\mathbf{d}_b\right]$$

$$-\tfrac{4}{3}k_B T\sum_a\sum_b\left[\frac{2\pi m_a m_b k_B T}{m_a+m_b}\right]^{1/2}\frac{n_a n_b \sigma_{ab}^4\chi_{ab}}{m_a+m_b}\nabla \ln T$$

$$+k_B T\sum_a\sum_b \frac{\rho b_{ab}(M_{ab}-M_{ba})\chi_{ab}}{m_a}\mathbf{J}_a$$

$$+k_B T\sum_a\left[\frac{5}{2}+\sum_b \rho b_{ab}\chi_{ab}\right]\frac{\mathbf{J}_a}{m_a} . \tag{47}$$

The last term has been corrected by removing a numerical factor of $\frac{5}{2}$ from the final $\sum_b$.[35] In Eq. (47) we have the definitions

$$\begin{aligned}
M_{ab} &= m_a/(m_a+m_b) ,\\
C &= \sum_a\sum_b\left[\frac{2\pi m_a m_b k_B T}{m_a+m_b}\right]^{1/2} n_a n_b \sigma_{ab}^4\chi_{ab} ,\\
K_a &= 1+\tfrac{12}{5}\sum_b \rho b_{ab} M_{ab} M_{ba}\chi_{ab} ,\\
K_a' &= 1+\tfrac{4}{5}\sum_b \rho b_{ab} M_{ba}\chi_{ab} ,\\
b_{ab} &= 2\pi n_b \sigma_{ab}^3/3\rho ,\\
\mathbf{d}_a &= \mathbf{Z}_a + \frac{1}{n}\sum_b E_{ab}\nabla n_b ,\\
\mathbf{Z}_a &= \frac{\rho_a}{n\rho k_B T}\nabla p + \sum_b \frac{n_a}{n}(\delta_{ab}+2\rho b_{ab} M_{ab}\chi_{ab})\nabla \ln T ,\\
E_{ab} &= \frac{\rho_a}{k_B T}\left[\frac{\partial \mu_a}{\partial n_b}\right]_{T,\{n_{c\neq b}\}} ,
\end{aligned} \tag{48}$$

in which n_a is the number density of species a, χ_{ab} is the pair-correlation function at contact, and δ_{ab} is the Kroeneker δ. The symbol $\langle\langle \mathbf{X}\rangle\rangle$ denotes the traceless, symmetrized form of the tensor $\mathbf{X}$.[2] (Note that our expression for E_{ab} differs from LCK in the presence of an additional factor of m_a because LCK uses the chemical potential per particle rather than per unit mass.) The $a_i^{(a)}$, $b_i^{(a)}$, $d_{a,i}^{(b)}$, and $h_i^{(a)}$ are expansion coefficients in the Sonine polynomial expansion. We observe that LCK specify the thermodynamic state through the temperature T and the n_s number densities.

In the LCK development, Eqs. (47) were used to find explicit transport coefficients in forms convenient for experimental comparison; except for the viscosity for which no ambiguity exists, these are not the same transport coefficients defined in Sec. III. As a result, we derive here the Enskog values of the transport coefficients, particularly for the mainstream system. Given, for example, an approximate analytic equation of state, one can readily obtain the prime and double-prime sets from these. Our aim, then, is to write Eqs. (47) in the form of Eqs. (24), with forces, Eqs. (14). We begin by eliminating the gradient of the number densities by rewriting $\mathbf{d}_a$ in terms of gradients of chemical potential and temperature

$$\mathbf{d}_a = \mathbf{Z}_a + \frac{\rho_a}{n k_B T}\left\{T\nabla(\mu_a/T) + \left[\mu_a - T\left[\frac{\partial \mu_a}{\partial T}\right]_{\{n_b\}}\right]\nabla \ln T\right\} . \tag{49}$$

For the hard-sphere fluid, we can write

$$\begin{aligned}
\mu_a &= \mu_a^{(0)} + k_B T q(\{n_b\}) ,\\
\mu_a^{(0)} &= \frac{k_B T}{m_a}\ln\lambda_a^3 ,
\end{aligned} \tag{50}$$

in which the function q is independent of the temperature and λ_a is the thermal wavelength,

$$\lambda_a = \frac{2\pi\hbar^2}{m_a k_B T} .$$

Thus the term in the chemical potential appearing in Eq. (49) becomes

$$\mu_a - T\left[\frac{\partial \mu_a}{\partial T}\right]_{\{n_b\}} = \frac{3k_B T}{2m_a} . \tag{51}$$

Substituting Eq. (51) into Eq. (49) and thence into the expression for $\mathbf{J}_a$ in Eq. (47), and using the expression for $\mathbf{Z}_a$ from the same equation, as well as the identity,

$$\sum_b d_{a,i}^{(b)}\rho_b = 0 , \tag{52}$$

to eliminate the term in the pressure gradient, we obtain the first of Eq. (24), with mutual diffusion constant,

$$L_{ab}^{E} = \frac{\rho_a\rho_b}{2n^2 k_B T} d_{a,0}^{(b)} , \tag{53}$$

and thermal diffusion constant,

$$L_{au}^{E} = \frac{5\rho_a}{4n^2}\sum_b K_b'' n_b d_{a,0}^{(b)} - \frac{\rho_a}{2n}a_0^{(a)} , \tag{54}$$

in which

$$K_a'' = 1+\tfrac{4}{5}\sum_b \rho b_{ab} M_{ab}\chi_{ab} .$$

We note that no assumption of vanishing pressure gradient has been introduced.

In similar fashion, Eq. (47) yields an equation of the form of the second of Eq. (24), with thermal diffusion constant,

$$L_{ua}^{E}=-\frac{5\rho_a}{4n^2}\sum_b (K_b n_b d_{b,1}^{(a)}-K_b'' n_b d_{b,0}^{(a)}) \tag{55}$$

and thermal conductivity

$$\begin{aligned}L_{uu}^{E}=&\frac{5k_BT}{4n}\sum_a K_a n_a\left[a_1^{(a)}-\tfrac{5}{2}\sum_b \frac{K_b'' n_b}{n}d_{a,1}^{(b)}\right]\\&+\frac{4k_BT}{3}\sum_a\sum_b\left[\frac{2\pi m_a m_b k_BT}{m_a+m_b}\right]^{1/2}\frac{n_a n_b \sigma_{ab}^4\chi_{ab}}{m_a+m_b}\\&+\frac{5k_BT}{2}\sum_a\frac{K_a'' L_{au}^{E}}{m_a}\ .\end{aligned}\tag{56}$$

For completeness, we also give the shear viscosity coefficient,

$$\eta^E=L_\eta^E=\tfrac{1}{2}\sum_a \frac{K_a' n_a k_BT}{n}b_0^{(a)}+\tfrac{4}{15}C\ . \tag{57}$$

It should be noted that the Onsager reciprocity relations evidently require that

$$\begin{aligned}&d_{a,0}^{(b)}=d_{b,0}^{(a)}\ ,\\&a_0^{(a)}=\frac{5}{2n}\sum_b K_b n_b d_{b,1}^{(a)}\ .\end{aligned}\tag{58}$$

While we have not proven these equations, they evidently are true in that the Onsager relations were established in general.[4] Our numerical calculations, described below, also are consistent with these relations.

V. MODE-COUPLING THEORY

The long-time behavior of the time correlation functions for mixtures was first studied by Pomeau[33] using the Landau-Placzeck theory. Wood[30] has revisited the problem using the mode-coupling theory, as developed by Ernst *et al.*,[15–17] and considered the mainstream and double-prime systems in addition to the prime hydrodynamics of Pomeau. Because the form of the mode-coupling results depends on the form of the starting hydrodynamic equations, it is evident that the long-time tails for a given set of time-correlation functions will have different forms when expressed in terms of the different set of transport coefficients.

Wood[30] considered the case of a binary mixture in d dimensions, assuming that the equation of state and transport coefficients are known. In addition to confirming, except for numerous apparent misprints, the results of Pomeau[33] for the long-time tails in the prime system of fluxes and forces, he also obtained relatively simple expressions for the tails for the double-prime system and somewhat more complicated expressions for the mainstream system. In this section we display the mode-coupling results for the latter.

The general form of the long-time tail for transport coefficient L_α is

$$\rho_\alpha(t)\sim k_\alpha t^{-d/2}\ . \tag{59}$$

It is perhaps simplest to write the coefficient k_α in terms of the double-prime transport coefficients rather than the mainstream coefficients. For mutual diffusion, then, the coefficient is

$$k_{11}=\frac{d-1}{d\beta^2\mu_w(\eta_+-\eta_-)}\sum_{\tau=+,-}\tau\frac{\eta_\tau-L_{uu}''/c_pT}{[4\pi(\eta+\eta_\tau)/\rho]^{d/2}}\ , \tag{60}$$

in which

$$\begin{aligned}&\eta_\pm=\tfrac{1}{2}(\mu_w L_{11}''+L_{uu}''/c_pT\pm\mathcal{D}^{1/2})\ ,\\&\mathcal{D}=\left[\frac{L_{uu}''}{c_pT}-\mu_w L_{11}''\right]^2+4\frac{\mu_w}{c_pT}(L_{u1}'')^2\ ,\\&\mu_w=\left[\frac{\partial(\mu_1-\mu_2)}{\partial c_1}\right]_{T,p}\ ,\end{aligned}\tag{61}$$

and in which c_p is the specific constant-pressure heat capacity. For thermal diffusion, the coefficient is

$$k_{u1}=\frac{d-1}{d\mu_w\beta^2(\eta_+-\eta_-)}\frac{c_pT}{L_{u1}''}\sum_{\tau=+,-}\tau\frac{(\eta_\tau-L_{uu}''/c_pT)[\eta_\tau-\mu_wL_{11}''+(h_1-h_2)L_{u1}''/c_pT]}{[4\pi(\eta+\eta_\tau)/\rho]^{d/2}}\ . \tag{62}$$

For thermal conductivity, the long-time tail coefficient is

$$k_{uu}=\frac{c^2}{d\beta^2}\frac{1}{(4\pi\Gamma_s)^{d/2}}+\frac{d-1}{d\mu_w\beta^2(\eta_+-\eta_-)}\left[\frac{c_pT}{L_{u1}''}\right]^2\sum_{\tau=+,-}\tau\frac{(\eta_\tau-L_{uu}''/c_pT)[\eta_\tau-\mu_wL_{11}''+(h_1-h_2)L_{u1}''/c_pT]^2}{[4\pi(\eta+\eta_\tau)/\rho]^{d/2}}\ , \tag{63}$$

in which c is the adiabatic sound speed

$$c^2=\left[\frac{\partial p}{\partial\rho}\right]_{s,c_1} \tag{64}$$

and Γ_s is the acoustic damping constant

$$\begin{aligned}&\Gamma_s=\frac{1}{\rho}\left[\frac{2(d-1)}{d}\eta+\zeta\right]+\Gamma_{su}\ ,\\&\Gamma_{su}=\frac{\gamma-1}{\rho c_pT}\left[L_{uu}''-2\frac{\rho c_pT\mu_p}{\chi}L_{u1}''+\left[\frac{\rho c_pT\mu_p}{\chi}\right]^2L_{11}''\right]\ ,\end{aligned}\tag{65}$$

in which

$$\chi = \frac{T}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{p,c_1} \tag{66}$$

is related to the usual volume coefficient of thermal expansion and

$$\mu_p = \left(\frac{\partial(\mu_1-\mu_2)}{\partial p}\right)_{T,c_1} . \tag{67}$$

By virtue of Eq. (29) relating the double-prime transport coefficients to the mainstream coefficients, we regard these expressions as providing the mainstream long-time tails in terms of the mainstream transport coefficients.

VI. MONTE CARLO MOLECULAR-DYNAMICS CALCULATIONS

In this section, we discuss the evaluation of the transport coefficients directly from the Green-Kubo formulas for a 50-50 binary mixture of hard spheres ($d=3$), each species having diameter σ, but the particles of species 2 having a mass of $0.1m_1$. Because the thermodynamic and transport variables have a trivial dependence on temperature for hard spheres, we specify the state through the volume relative to close-packing for which we have

$$\begin{aligned} V &= 3V_0 , \\ V_0 &= \tfrac{1}{2}\sqrt{2}N\sigma^3 . \end{aligned} \tag{68}$$

The system is the same one treated earlier by Kincaid and Erpenbeck[36] for mutual diffusion.

A. Numerical methods

The numerical calculation of the transport coefficients has been described in some detail in previous publications[37,11] dealing especially with self-diffusion in one-component systems. The present calculations are entirely analogous, except that different time-correlation functions are evaluated. We compute Monte Carlo estimates for the various time-correlation functions discussed in Sec. III in the "molecular-dynamics" ensemble, i.e., the submicrocanonical ensemble characterized by vanishing total linear momentum and specified values for the number of particles N_1 and N_2, the volume V, and the energy E. The Monte Carlo procedure yields a sequence of initial phases $\{x_k^N, k=1,2,\ldots,N_{\rm tr}\}$ sampled from the appropriate distribution function. The molecular-dynamics method is used to generate a trajectory beginning at each x_k^N, from which values for the various time-correlation functions can be obtained for a sequence of times, using the expressions for the microscopic currents $\mathcal{J}_{\alpha_i}$ and their integrals $\mathcal{G}_{\alpha_i}$ given in Sec. III. In our calculations, the time-correlation functions are computed at times as

$$t_0, t_0+k_1\Delta t, \ldots, t_0+n_1k_1\Delta t, t_0+(n_1k_1+k_2)\Delta t, \ldots, t_0+(n_1k_1+n_2k_2)\Delta t, \ldots , \tag{69}$$

in which t_0 denotes a "time origin," the n_i and k_i are integers, and the time step Δt is chosen relative to the Boltzmann mean free time t_{00} to be

$$\begin{aligned} \Delta t &= 0.05t_{00} , \\ t_{00} &= \frac{N(N-1)}{\sum_a \sum_b N_a(N_b-\delta_{ab})\sigma_{ab}^2[(m_a+m_b)/2m_am_b]^{1/2}} . \end{aligned} \tag{70}$$

For the present calculations we choose $k_1=1$, $n_1=30$, $k_2=5$, $n_2=14$, $k_3=15$, $n_3=60$, so that the final time t_f for which the time-correlation functions are calculated is $50t_{00}$, which corresponds roughly to 100 actual mean free times at the present density.

For each trajectory the values of the time-correlation functions are averaged over time origins which are spaced at five time-step intervals. Because each trajectory is generated out to a time $N_{\rm stp}\Delta t$ which far exceeds t_f, the extent of time averaging on a given trajectory is large. The time-averaged values are then averaged over the $N_{\rm tr}$ trajectories providing the estimates for the ensemble averages, as well as their statistical uncertainties by virtue of the statistical independence of the starting phases for successive trajectories. This independence is achieved by the use of independent sampling for the velocities of the particles, coupled with a Metropolis Monte Carlo procedure in configuration space consisting of 200 attempted moves per particle between phase x_i^N and x_{i+1}^N. The parameters $N_{\rm tr}$ and $N_{\rm stp}$ for the present calculations, as well as the total number of collisions N_c, are listed in Table I, which also includes results to be discussed below.

B. Evaluation of theoretical results

In order to evaluate the theoretical results for the hard-sphere mixture at $V/V_0=3$, we observe that the calculation of the long-time tails requires both the equation of state (including the free energy) and the transport coefficients. For the latter we use the Enskog approximation which also depends on the equation of state. While for the present isotopic mixture, whose thermodynamic properties are just those of the single-component system, an extremely accurate equation of state is available,[38] for the general hard-sphere mixture no comparable representation exists. Therefore, we follow Lopez de Haro

TABLE I. Parameters and results for the Monte Carlo molecular-dynamics calculations in the submicrocanonical ensemble having zero linear momentum for the transport properties of 50% mixtures of hard spheres having equal diameters and a mass ratio of 0.1 at a volume of three times close-packed volume. N is the number of particles, N_{tr} is the number of distinct trajectories, N_c is the total number of collisions, in millions, N_{stp} is the number of time steps, in thousands, for each trajectory, each step of length $0.05t_{00}$, with t_{00} the Boltzmann mean free time. The results include the mean free time, t_0, and the time-dependent transport coefficients, $\hat{L}_\alpha(t_f)$, reduced by the Enskog transport coefficients, for the shear viscosity ($\alpha=\eta$), the thermal conductivity ($\alpha=uu$), the thermal diffusion ($\alpha=u1$), and the mutual diffusion ($\alpha=11$). The time, $t_f=50t_{00}$, is the longest time for which the time-correlation functions were evaluated. The values in parentheses denote the statistical uncertanties (one standard deviation) in the low-order digit of the mean.

N	N_{tr}	N_c	N_{stp}	t_0/t_{00}	$\hat{L}_\eta(t_f)$	$\hat{L}_{uu}(t_f)$	$\hat{L}_{u1}(t_f)$	$\hat{L}_{11}(t_f)$
108	60	40	120	0.480 93(9)	1.007(13)	1.038(14)		0.988(14)
500	95	205	84	0.485 34(6)	1.007(12)	1.115(16)	1.177(20)	1.054(14)
1372	217	184	12	0.485 54(4)	1.024(23)	1.133(27)	1.186(35)	1.054(24)
4000	100	103	5	0.485 86(5)	1.085(58)	1.004(64)	1.094(76)	1.133(60)

et al.[6-8] in using the Carnahan-Starling[39,40] approximation which applies for arbitrary diameters, masses, and volumes

$$\chi_{ab}=\frac{1}{1-\zeta_3}\left[1+3\frac{\sigma_a\sigma_b\zeta_2}{(\sigma_a+\sigma_b)(1-\zeta_3)}+2\left[\frac{\sigma_a\sigma_b\zeta_2}{(\sigma_a+\sigma_b)(1-\zeta_3)}\right]^2\right],$$

$$p=\frac{6k_BT}{\pi}\left[\frac{\zeta_0}{1-\zeta_3}+\frac{3\zeta_1\zeta_2}{(1-\zeta_3)^2}+\frac{(3-\zeta_3)\zeta_2^3}{(1-\zeta_3)^3}\right], \tag{71}$$

$$\frac{m_a\mu_a}{k_BT}=\ln\frac{n_a\lambda_a^3}{1-\zeta_3}+\frac{\pi p\sigma_a^3}{6k_BT}+\sum_{i=1}^{3}\sigma_a^i f_i ,$$

in which

$$\zeta_i(V,\{M_a\})=\frac{\pi}{6V}\sum_a\frac{M_a\sigma_a^i}{m_a},$$

$$f_1=\frac{3\zeta_2}{1-\zeta_3},$$

$$f_2=\frac{3\zeta_1}{1-\zeta_3}+\frac{9\zeta_2^2}{2(1-\zeta_3)^2}+\frac{3\zeta_2^2}{\zeta_3^2}\left[\ln(1-\zeta_3)+\frac{\zeta_3}{1-\zeta_3}-\frac{\zeta_3^2}{2(1-\zeta_3)^2}\right],$$

$$f_3=-\frac{\zeta_2^3}{\zeta_3^3}\left[2\ln(1-\zeta_3)+\frac{\zeta_3(2-\zeta_3)}{1-\zeta_3}\right].$$

Kincaid provided us with the FORTRAN programs which LCK describe for computing the Enskog transport coefficients. We modified these so as to yield the mainstream transport coefficients, Eqs. (53)–(57), as well as the double-prime coefficients, Eq. (29), using the partial specific enthalpies, Eq. (18), which become for hard spheres,

$$h_a=\frac{3k_BT}{2m_a}+pv_a , \tag{72}$$

where v_a is the partial specific volume. The latter can be evaluated in the Carnahan-Starling approximation using the identity

$$v_a=\frac{\left[\dfrac{\partial p}{\partial M_a}\right]_{T,V,\{M_{b\neq a}\}}}{\left[\dfrac{\partial p}{\partial V}\right]_{T,\{M_b\}}},$$

with the pressure from Eq. (71). We have used the highest "Enskog approximation" (i.e., highest degree Sonine polynomial expansion) for which the FORTRAN package was designed, namely, the tenth approximation.

In similar fashion, we determine the long-time tails of the time-correlation functions from these double-prime transport coefficients, obtaining the required thermodynamic quantities from Eq. (71). For example, to obtain μ_w we use

$$\left[\frac{\partial\mu_a}{\partial c_1}\right]_{T,p}=\sum_b\left[\frac{\partial\tilde{\mu}_a}{\partial n_b}\right]_{T,\{n_{c\neq b}\}}\left[\frac{\partial n_b}{\partial c_1}\right]_{T,p},$$

$$\left[\frac{\partial n_1}{\partial c_1}\right]_{T,p}=-\frac{1}{J_0}\left[\frac{\partial p}{\partial n_2}\right]_{T,n_1},$$

$$\left[\frac{\partial n_2}{\partial c_1}\right]_{T,p}=\frac{1}{J_0}\left[\frac{\partial p}{\partial n_1}\right]_{T,n_2}, \tag{73}$$

$$J_0=-\frac{m_1m_2}{(m_1n_1+m_2n_2)^2}\sum_a n_a\left[\frac{\partial p}{\partial n_a}\right]_{T,\{n_{b\neq a}\}},$$

$$\tilde{\mu}_a=\mu_a-\frac{\pi}{6}p\sigma_a^3/m_a ,$$

which can be readily evaluated from Eq. (71).

C. Numerical results

Our calculations include the study of systems of 108, 500, 1372, and 4000 particles. The parameters for each of these calculations are given in Table I, including the time steps per trajectory N_{stp} and the number of trajectories N_{tr}. Observe that for the larger systems the trajectories are relatively short on the basis of the number of collisions per particle. Because the number of trajectories for the larger systems is not proportionately larger, the calculations for the larger systems, especially the 4000-particle system, are relatively less extensive when applied to the calculation of time-correlation functions for the transport properties studied here.

Our results consist of the time-dependent transport coefficients, either evaluated directly from Eq. (43), as in the case of mutual diffusion and thermal diffusion, or through differentiation, Eq. (45), of the Einstein function, Eq. (44), as in the case of the thermal conductivity and the viscosity. We define reduced transport coefficients relative to the Enskog values (in the tenth Sonine approximation) by adding a caret over the symbol, e.g.,

$$\hat{L}_\alpha = L_\alpha / L_\alpha^E \ . \tag{74}$$

The Enskog transport coefficients are evaluated as outlined above, yielding

$$\begin{aligned} L_{uu}^E &= 3.919\,743\,0 \frac{m_1}{(m_1\beta)^{3/2}\sigma_1^2} \ , \\ L_{u1}^E &= -0.054\,992\,8 \frac{m_1}{(m_1\beta)^{1/2}\sigma_1^2} \ , \\ L_{11}^E &= 0.002\,116\,4 \frac{m_1(m_1\beta)^{1/2}}{\sigma_1^2} \ , \\ L_\eta^E &= 0.293\,786\,2 \frac{m_1}{(m_1\beta)^{1/2}\sigma_1^2} \ . \end{aligned} \tag{75}$$

In similar fashion we define a reduced time relative to the mean free time

$$\hat{t} = t / t_0 \ , \tag{76}$$

which we estimate numerically from the collision rate

$$t_0 = \left\langle \frac{t_l N(N-1)}{2N_c} \right\rangle \ , \tag{77}$$

in which N_c is the number of collisions on a trajectory extending to time t_l. The observed values of t_0 relative to the Boltzmann expression, Eq. (70), are given in Table I.

The time-dependent thermal conductivity for the 500-particle system is shown as a function of time in Fig. 1. The arrow in the figure marks the time $t_a = L/c$ required for an acoustic wave to transverse the 500-particle system. For self-diffusion, finite-system effects were found to become important for larger values of the time.[11] The form of the dependence on time is similar to that shown by the other transport coefficients, except at early times. (The fact that, for hard spheres, the time-dependent transport coefficients for certain transport properties are nonzero at $t=0$ is related to the presence of δ functions in the corresponding microscopic current; we will discuss this further in a future article.) The values of $\hat{L}_\alpha(t_f)$, the transport coefficients at the longest times considered in these calculations, are given in Table I. For each transport coefficient, these values are plotted against $1/N$ in Fig. 2 to show the approach to the thermodynamic limit. The least-squares fit of the results to a $1/N$ form yields values for the thermodynamic limit given in Table II. The least-squares lines are also shown in Fig. 2.

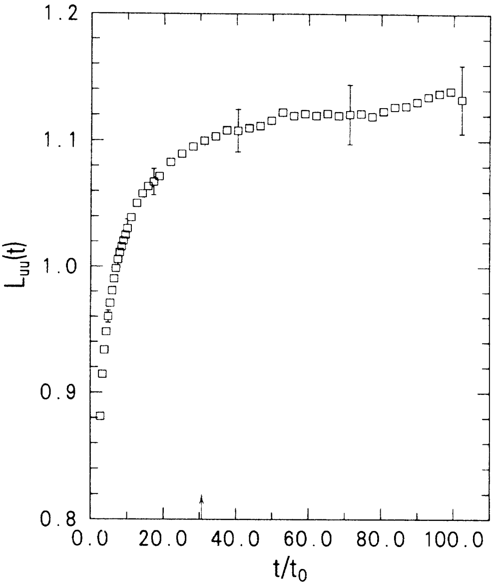

FIG. 1. Time-dependent thermal conductivity $\hat{L}_{uu}(t)$, relative to the Enskog value, for a 50-50 binary hard-sphere mixture having mass ratio of 0.1 and diameter ratio of 1.0 at a volume of three times close packing, as a function of the time t, relative to the observed mean free time t_0, for a 500-particle system. The arrow shows the acoustic wave traversal time for the system. The error bars represent ±1 standard deviation about the mean.

In addition to the time-dependent transport coefficients, we also compute the various Green-Kubo time-correlation functions, Eq. (36). For the case of thermal conductivity, these are plotted against $\hat{t}^{-3/2}$ in Fig. 3 for time greater than $16t_0$ for each of the four system sizes. Also shown are the mode-coupling predictions for the long-time tail. We observe that statistical uncertainties associated with the 4000-particle results are relatively large and do little to substantiate the mode-coupling result. While the 108-particle data appear to lie somewhat below the theoretical prediction, the 500- and 1372-particle results appear to agree well with the theory for times greater than $35t_0$.

For the thermal diffusion, a similar comparison is shown in Fig. 4. The 108-particle calculations did not include the thermal diffusion, however, so only three sets of data are plotted. Again, the results for $N=500$ and 1372 appear to support the mode-coupling results for times beyond about 35 collisions.

For the mutual diffusion coefficient, the Monte Carlo molecular-dynamics (MCMD) results are compared with the theory in Fig. 5. The agreement appears qualitatively reasonable perhaps for somewhat earlier times, say, for $t > 26t_0$.

Finally, for the shear viscosity coefficient, we show the comparison between theory and MCMD results in Fig. 6.

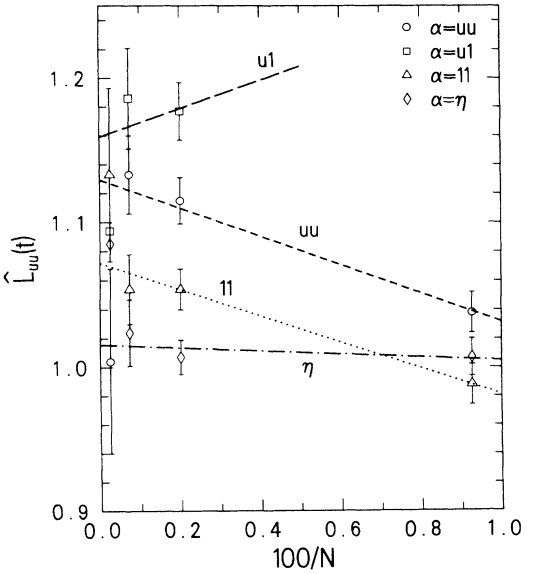

FIG. 2. Reduced transport coefficients $\hat{L}_\alpha(t_f)$ for a 50-50 binary hard-sphere mixture having mass ratio of 0.1 and diameter ratio of 1.0, evaluated at a time t_f (see Table I) of approximately 100 mean free times, as a function of the reciprocal of the total number of particles N, showing the dependence on system size. The various transport coefficients are $\alpha = uu$ for thermal conductivity, $u1$ for thermal diffusion, 11 for mutual diffusion, and η for shear viscosity. The lines are a weighted linear least-squares fit for each set of data. To avoid confusion, the error bars (± 1 standard deviation) are not shown for all of the $N = 4000$ data; see Table I for the values.

Except for the relatively imprecise $N = 4000$ results, the agreement remains adequate. Note that the theoretical tail is quite small in this case and that the time-correlation function appears to be indistinguishable from zero over most of the range of time which is displayed.

To estimate the complete transport coefficient, we add the mode-coupling long-time tail contribution, starting at a time t_m, to the infinite-system extrapolation for $\hat{L}_\alpha(t_m)$, where t_m is sufficiently large so that the difference between the mode-coupling prediction and the large-system limit of the actual tail is negligible. Our comparisons in Figs. 3–6 suggest that t_m should be at least $35t_0$. In Table II, we show the results for two choices for t_m, viz., about $35t_0$ and the longest time t_f for which $\hat{L}_\alpha(t)$ is computed, as previously discussed. In each case, we assign a statistical uncertainty to the final estimate, based on the uncertainty in $\hat{L}_\alpha(t_m)$. Because this uncertainty increases with time, it is evident that the choice, $t_m = 35t_0$, will lead to a smaller uncertainty. Nonetheless the results from these two choices are in statistical agreement. In view of the agreement suggested by Figs. 3–6, the $t_m = 35t_0$ estimate would appear to be justified although the magnitude of the systematic error cannot be estimated by this simple approach.

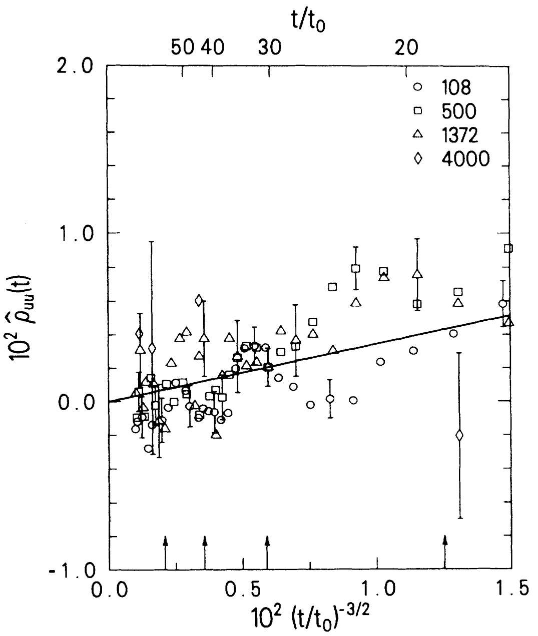

FIG. 3. Reduced autocorrelation function for thermal conductivity $\hat{\rho}_{uu}(t)$ for a 50-50 binary hard-sphere mixture having mass ratio of 0.1 and diameter ratio of 1.0, plotted against $(t/t_0)^{-3/2}$, where t is the time and t_0 is the mean free time, for systems of $N = 108$ to 4000 particles. The line shows the long-time tail predicted by mode-coupling theory. The arrows show the acoustic-wave traversal time for the systems, with the rightmost arrow for the fewest particles. The error bars represent ± 1 standard deviation about the mean and are found to be essentially independent of time, for a given value of N. Only a few of the data are shown for the 4000-particle system because of their relatively large error bars.

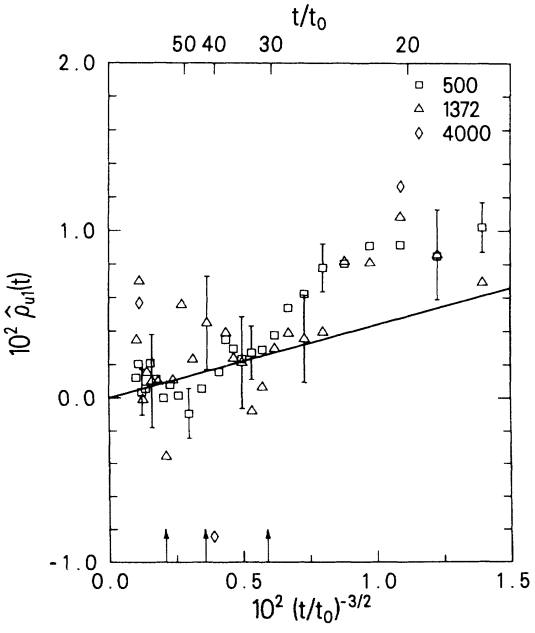

FIG. 4. As in Fig. 3, but for the thermal-diffusion time-correlation function $\hat{\rho}_{u1}(t)$.

TABLE II. The transport coefficients $\hat{L}_\alpha$, relative to the Enskog values, evaluated by least-squares extrapolation of the Monte Carlo molecular-dynamics values to the thermodynamic limit. Results for two choices for t_m are given. In each case, the values $\hat{L}_\alpha(t_m)$ are incremented by the theoretical long-time tail contributions to form the estimates $\hat{L}_\alpha^{(i)}$ of the full transport coefficients; $i=1$ corresponds to a $t_m=35t_0$ and $i=2$ to $t_m=t_f$. The χ^2 values are the goodness-of-fit parameters for the least squares, having three degrees of freedom except for the thermal diffusion coefficient, which contains two degrees of freedom. The values in parentheses denote the statistical uncertainties (one standard deviation) in the low-order digit of the mean.

α	$\hat{L}_\alpha(35t_0)$	χ^2	$\hat{L}_\alpha^{(1)}$	$\hat{L}_\alpha(t_f)$	χ^2	$\hat{L}_\alpha^{(2)}$
η	1.00012(74)	0.3	1.0156(74)	1.0158(130)	1.9	1.0240(130)
uu	1.1009(88)	6.0	1.2181(88)	1.1294(165)	4.0	1.1966(165)
$u1$	1.1168(263)	1.1	1.2670(263)	1.1591(474)	1.1	1.2451(474)
11	1.0426(75)	0.2	1.1170(75)	1.0719(146)	1.3	1.1143(146)

VII. CONCLUSIONS

We list here what seem to be the most important conclusions that can be drawn from this work.

(1) The transport coefficients for mixtures can be defined in a variety of ways by virtue of the fact that the separation of the heat current into a thermal and a diffusive part is not unique, even when subject to the Onsager conditions. From the point of view of molecular dynamics calculations, the mainstream choice of fluxes and forces, with driving forces of $-T^{-1}\nabla T$ and $-T\nabla(\mu_a/T)$, yields Green-Kubo expressions which do not require knowledge of the partial specific enthalpies for the system and are, therefore, more easily applied.

(2) For the mass and diameter ratio studied here at a volume of three times close packing, the long-time behavior of the time-correlation functions for shear viscosity, thermal conductivity, thermal diffusion, and mutual diffusion appears to agree (within their statistical uncertainties) with the predictions of the mode-coupling theory. Except for the strong evidence for agreement in the case of one-component self-diffusion,[11,12] the present evidence seems to be the first to support mode-coupling theory for other time-correlation functions. Whether this agreement holds for other densities and for other mass and diameter ratios remains to be seen.

(3) The results for the hard-sphere transport coefficients for the isotopic mixture show significant deviations from the Enskog theory. These deviations arise principally from the long-time tails of the time correlation functions, as can be seen from Table II. The values of $\hat{L}_\alpha(35t_0)$ show quite modest deviations from unity, even though the time is long compared to the Enskog decay time. The additional contributions for longer times are small for shear viscosity, but increasingly large for mutual diffusion (7%), thermal diffusion (11%), and thermal conductivity (15%). This result contrasts with the conclusion of Alder, Gass, and Wainwright[18] for the

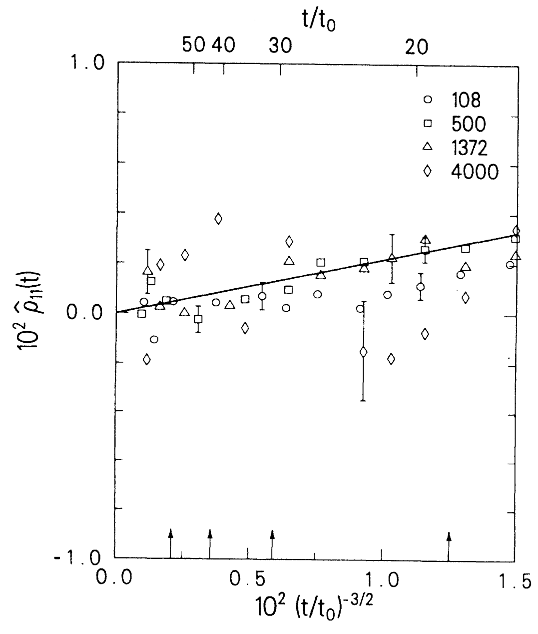

FIG. 5. As in Fig. 3, but for the mutual-diffusion time-correlation function $\hat{\rho}_{11}(t)$.

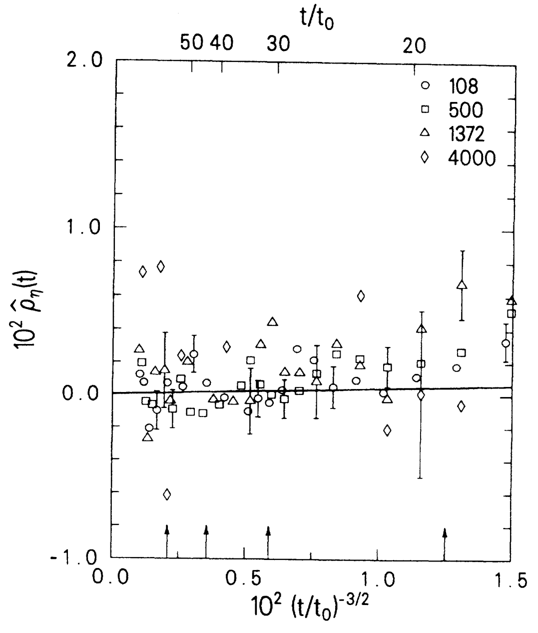

FIG. 6. As in Fig. 3, but for the shear-viscosity time-correlation function $\hat{\rho}_\eta(t)$.

thermal conductivity of a single-component, hard-sphere fluid but agrees with their observations for shear viscosity.

(4) The present results suggest that further study of the parameter space for hard-sphere mixtures is in order. Calculations for other densities and for a number of other mass and diameter ratios are now in progress.

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