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Relation of shear viscosity and self-diffusion coefficient for simple liquids

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A Stokes-Einstein-type relation is derived for the potential part of the shear viscosity of a simple liquid by means of statistical mechanics. The product of the shear viscosity and the self-diffusion coefficient is shown to be expressible in terms of the pair correlation function and the intermolecular force as well as the density. The shear viscosity formula, consisting of kinetic and potential parts and given in terms of the self-diffusion coefficient, is tested against experimental data with regard to the temperature and density dependence of the shear viscosity. Given the self-diffusion coefficient determined by experiment or simulations, the viscosity formula involving the Stokes-Einstein relation obtained produces the shear viscosity of argon, krypton, and xenon, in good agreement with experiment in the case of temperatures well away from the triple point. However, in the neighborhood of the triple point of argon examined, a cutoff parameter, which is a measure of the range of density variation, is needed to account for the experimental data. The applicability of the Stokes-Einstein relation to molecular particles is assessed, and it is found to remain applicable in the range of density and temperature examined. [S1063-651X(99)05710-4]

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I. INTRODUCTION

Transport coefficients of fluids constitute an important class of thermophysical properties necessary in materials applications. Kinetic theories of transport processes have been pursued for a long time in statistical mechanics for the explicit purpose of calculating them in terms of intermolecular forces. However, the molecular theory to calculate them by means of statistical mechanics is rather challenging and, faced with the enormous difficulty of solving many-particle dynamics, the challenge has been increasingly met in recent years by developing various numerical simulation methods [1–3]. Numerical simulation methods allow us to compute some particular aspects of transport coefficients, but they still need inputs from theoretical investigations of the interrelationships of various transport processes and accompanying transport coefficients, as well as some subtle conceptual aspects of the problems involved. Therefore theoretical studies and some analytical results or models, if possible to obtain, can be very valuable for the overall aim of endeavors in research in transport properties of matter. The work presented here is a contribution to that end.

There are known some simple relations between transport coefficients, which have been experimentally verified to hold. They serve not only as means to compute one transport coefficient from another but also as verifications of the internal consistency of the phenomenological theory employed to calculate them. Indeed, the solutions of the kinetic equations of fluids employed predict certain relations between transport coefficients in the limits of density, and it is thereby possible to provide phenomenological relations with molecular theory foundations. For example, in Boltzmann kinetic theory the first order Chapman-Enskog solution of the Boltzmann equation yields a relation between the shear viscosity and the thermal conductivity (which is known as the Eucken relation [4]), the Nernst-Einstein relation for mobility [4], or a relation [4] between the shear viscosity and the self-diffusion coefficient, which are linearly proportional to each other with a proportionality constant.

$$\eta = C(T)\rho D, \tag{1}$$

where η and D are the shear viscosity and the self-diffusion coefficient of a monatomic gas, respectively, and $C(T)$ is a constant weakly dependent on temperature for non-hard-sphere potentials, but a simple numerical constant in the case of hard spheres: $C(T)=0.831$.

In the case of a hard sphere immersed in a viscous medium, the well known Stokes-Einstein relation [5] is another example that holds between the shear viscosity and the diffusion coefficient of the particle:

$$\eta D = \frac{k_B T}{c\pi R}. \tag{2}$$

Here R is the hard sphere radius, which is assumed to be much larger than the solvent molecular radius and may be treated as an adjustable parameter in the case of molecular particles, and c is equal to 6 in the case of the stick boundary condition and 4 in the case of the slip boundary condition. This macroscopically derived relation in fact often works impressively even if the diffusing particle is of a size comparable to the solvent molecule. Why this should be so has not as yet been satisfactorily explained by a molecular theory, but will be examined in the present work. On the other hand, there are some cases where there exist deviations from the relation in the case of some molecular fluids [6,7] and also some evidence of sizable deviations in the case of supercooled liquids [8–14]. See Mohanty's paper [15] for a

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review of the situation on supercooled liquids. Some attempts [16–18] have recently been made to understand the deviations.

There have been some derivations of the Stokes-Einstein relation made by using the absolute reaction rate theory [19], which yields an intuitive formula involving adjustable parameters, generalized hydrodynamics [20], the tagged particle kinetic theory [21], mode coupling theory [22], and a kinetic theory of ellipsoidal particles [23]; however, the derivations are mathematically rather involved and require a considerable amount of work even just to follow them. There also have been derivations of a relation based [24,25] on the autocorrelation function for the diffusion coefficient, but they require an assumption of the relaxation time and identifications of the elastic and shear moduli with the longitudinal and shear viscosities on the basis of physical arguments. Therefore, it is reasonable to conclude that a statistical mechanical derivation of the relation is still an interesting subject of study.

On the phenomenological side of the study of the relation, in the case of polyatomic liquids a number of authors [26,27] have suggested on empirical grounds that the Stokes-Einstein relation should be modified to the form [28]

$$\eta^{\epsilon}D=C(T), \tag{3}$$

where the exponent ϵ is a parameter less than unity but varying with temperature and the nature of the solvent. In Refs. [26, 27] cited, this formula, with an appropriately chosen value of the parameter ϵ, was shown to correlate with experimental data on polyatomic molecules such as hydrocarbons, tetramethylsilane, and benzene, to cite a few examples.

Since the dilute gas relation [Eq. (1)] and the relation [Eq. (2)] holding for liquids are so different with regard to the exponent of D, and are in fact in an inverse relation to each other with regard to the D dependence, a conventional Chapman-Enskog-type solution method for a kinetic equation is unlikely to produce the Stokes-Einstein relation for liquids. Such a diametrically opposite density dependence of the $\eta - D$ relation suggests that it is important to understand how the crossover behavior enters into the kinetic theory of the relation. The derivation of such a relation, which exhibits a crossover behavior, should be interesting even for simple liquids. Also, a generalized form of the Stokes-Einstein relation for complex liquids promises to be an even more interesting and worthwhile problem in the kinetic theory of liquids, especially because the self-diffusion coefficients are the easiest among transport coefficients to simulate on a computer; thus such a relation can provide a relatively simple method of computing viscosities for complex liquids. We therefore consider the present line of investigation to be the first step in such a direction of work.

In this paper we would like to report a simple method of deriving the Stokes-Einstein relation, or a general form of it, by means of statistical mechanics in the form

$$\eta_p D=C'(T,\rho), \tag{4}$$

where η_p is the potential part of the shear viscosity, and $C'(T,\rho)$ is given in terms of the density, the pair correlation function, and the intermolecular force. This method rests on the recognition of the importance of bulk density variations that occur when a stress is applied to a liquid. This is an effect which has not traditionally been taken into account when a theory of transport processes is developed. Therefore, despite the derivation of an old well known result, it represents a fresh viewpoint on the problem. The present method is sufficiently general as to suggest that it should be possible to obtain a similar expression for polyatomic liquids.

In Sec. II a Stokes-Einstein relation is derived for simple liquids subjected to shearing perturbation by using a kinetic theory method. The derivation exploits the bulk density variation that occurs in the molecular length scale in the liquid as it is sheared. A formula similar to the Stokes-Einstein relation, which holds only for a sufficiently large hard sphere in a viscous medium, is obtained for the potential part of the shear viscosity in terms of the density, temperature, and pair correlation function of the liquid. This relation can used for calculating the shear viscosity of a simple liquid from the data on the self-diffusion coefficient of the liquid, either known experimentally or from simulations. The original Stokes-Einstein formula is valid if the assumption is made that the hard sphere radius is much larger than that of the solvent molecule, so that the solvent can be treated as a continuous medium. The formula obtained in this work does not require the usual assumption mentioned. In Sec. III the relation is applied to calculate the density and temperature dependence of the shear viscosity of argon, and the density dependence of the shear viscosity of krypton and xenon. They all are in good agreement with experiment. The applicability of the Stokes-Einstein relation to molecular particles is also assessed in this section. A discussion and concluding remarks are given in Sec. IV.

II. STOKES-EINSTEIN RELATION FOR A SIMPLE LIQUID

Consider a simple liquid of molecular mass m contained in volume V at temperature T. It will be assumed that particles interact through pairwise additive potentials. A kinetic theory can be developed for the fluid, and, if the system is near equilibrium and subject to a small velocity gradient caused by a shearing perturbation, then the shear stress $\mathbf{\Pi}$ has the following linear relationship [29] with the velocity gradient:

$$\mathbf{\Pi}=-2\eta[\nabla\mathbf{u}]^{(2)}, \tag{5}$$

where η is the shear viscosity, and $[\nabla\mathbf{u}]^{(2)}$ is the traceless symmetric part of the velocity gradient $\nabla\mathbf{u}$, namely,

$$[\nabla\mathbf{u}]^{(2)}=\tfrac{1}{2}[\nabla\mathbf{u}+(\nabla\mathbf{u})^{t}]-\tfrac{1}{3}\boldsymbol{\delta}\nabla\cdot\mathbf{u}. \tag{6}$$

Here the superscript t denotes the transpose of the tensor and the symbol $\boldsymbol{\delta}$ stands for the unit second rank tensor. The assumption made for Eq. (5) is that $\|[\nabla\mathbf{u}]^{(2)}\|$ is small in magnitude, so that the linear relationship holds between the stress and the velocity gradient. The shear stress $\mathbf{\Pi}$ is also the traceless symmetric part of the stress (pressure) tensor $\mathbf{P}$:

$$\mathbf{\Pi}=\tfrac{1}{2}[\mathbf{P}+\mathbf{P}^{t}]-\tfrac{1}{3}\boldsymbol{\delta}\mathrm{Tr}\mathbf{P}. \tag{7}$$

In the kinetic theory of liquids based on the generalized Boltzmann equation [29], the shear viscosity is given in terms of a collision bracket integral of the virial tensor,

$$\eta = \frac{2p^2 g}{k_B T\, R^{(1)}}, \tag{8}$$

where

$$g = \left(\frac{m_r}{2k_B T} \right)^{1/2} (nd)^{-2},$$

with m_r and d denoting a mean mass and a mean radius of the molecules, respectively, and $R^{(1)}$ the collision bracket integral defined by [30]

$$R^{(1)} = \frac{1}{5n^2 d^3 (k_B T)^2} \int dx^{(N)} F_e^{(N)} \times \sum_{j=1}^{N} h_j^{(1)} \delta(\mathbf{r}_j - \mathbf{r}) : i \hat{T}^{(N)} \sum_{k=1}^{N} h_k^{(1)}. \tag{9}$$

Here $dx^{(N)} = d\mathbf{r}_1 \ldots d\mathbf{r}_N d\mathbf{p}_1 \ldots d\mathbf{p}_N$, with $\mathbf{r}_i$ and $\mathbf{p}_i$ denoting the position and momentum of particle i. Other symbols in this expression are $i = \sqrt{-1}$. $F_e^{(N)}$ is the equilibrium distribution function,

$$\hat{T}^{(N)} = T^{(N)} d \left(\frac{m_r}{2k_B T} \right)^{1/2}, \tag{10}$$

with $T^{(N)}$ denoting the collision operator of N particles, and $h_j^{(1)}$ is the traceless symmetric part of the virial tensor:

$$h_j^{(1)} = [m\mathbf{C}_j\mathbf{C}_j]^{(2)} - \tfrac{1}{2} \sum_{l \neq j}^{N} \frac{[\mathbf{r}_{jl}\mathbf{r}_{jl}]^{(2)}}{r_{jl}} v'_{jl}, \tag{11}$$

$$v'_{jl} = \frac{\partial v_{jl}}{\partial r_{jl}} \quad (r_{jl} = |\mathbf{r}_{jl}| = |\mathbf{r}_j - \mathbf{r}_l|). \tag{12}$$

Here $\mathbf{C}_j$ is the peculiar velocity of particle j defined by

$$\mathbf{C}_j = \frac{\mathbf{p}_j}{m} - \mathbf{u}, \tag{13}$$

with $\mathbf{u}$ denoting the fluid velocity, and v_{jl} is the intermolecular potential of particles j and l. The collision operator $T^{(N)}$ is the solution of the classical N-particle Lippmann-Schwinger equation; it may be expanded into a cluster expansion which reduces to the Boltzmann collision integral in the dilute gas limit. For details about the N-particle collision operator, the reader is referred to Ref. [29]. Since it requires the solution of many-particle collision dynamics it is not trivial to calculate the collision bracket integrals except for the kinetic contribution—namely, the term $[m\mathbf{C}_j\mathbf{C}_j]^{(2)}$ in $h_j^{(1)}$ which represents the momentum transfer per unit time—in the case of hard spheres, the problem of calculating η remains largely unsolved at present. We look for an alternative procedure of computing the shear viscosity.

To begin with, it is useful to observe that the shear viscosity may be decomposed into kinetic and potential contributions, namely,

$$\eta = \eta_k + \eta_p. \tag{14}$$

Both contributions depend on density ρ as well as on temperature T. However, there exists a density-independent limit

$$\lim_{\rho \to 0} \eta(\rho) = \eta_k^0, \tag{15}$$

which is the Chapman-Enskog viscosity. It can be verified that this is indeed the case, if the density expansion [30] of the collision bracket integral $R^{(1)}$ is calculated by using a cluster expansion of the collision operator $T^{(N)}$. To see this we define the collision bracket integral $R_0^{(1)}$ for the kinetic part by the formula

$$R_0^{(1)} = \frac{1}{5n^2 d^3 (k_B T)^2} \int dx^{(N)} F_e^{(N)} \times \sum_{j=1}^{N} [m\mathbf{C}_j\mathbf{C}_j]^{(2)} \delta(\mathbf{r}_j - \mathbf{r}) : i \hat{T}^{(N)} \sum_{k=1}^{N} [m\mathbf{C}_k\mathbf{C}_k]^{(2)}. \tag{16}$$

Then it is possible to identify η_k in the form

$$\eta_k = \frac{2p^2 g}{k_B T\, R_0^{(1)}}, \tag{17}$$

and η_p with the statistical mechanical formula

$$\eta_p = \frac{2p^2 g}{k_B T} \frac{1}{R_0^{(1)}} (R_0^{(1)} - R^{(1)}) \frac{1}{R^{(1)}}. \tag{18}$$

The leading term in the density expansion of the collision bracket integral $R_0^{(1)}$ can be shown [30] to be the Chapman-Enskog collision bracket integral of the Boltzmann kinetic theory [4]. Since the density-dependent part of η_k is relatively smaller than the density-dependent potential part, η_k^0 may be used for η_k in the lowest order approximation for the kinetic part:

$$\eta_k \approx \eta_k^0(T). \tag{19}$$

The potential contribution η_p evidently has to do with the intermolecular interactions. It depends strongly on both temperature and density. This is the part that will be calculated alternatively to the method using the collision bracket integral presented earlier. Consequently, except for showing that η is decomposable into kinetic and potential parts, the kinetic theory expression for η_p is not used at all in this work. All we need from the kinetic theory of transport coefficients is the decomposition of η [Eq. (14)], Newton's law of viscosity [Eq. (5)], and the Chapman-Enskog result for η_k^0, as shown below. It should be noted that on the right hand side of Eq. (18) there are cross terms between the kinetic and potential parts of the virial tensor $h_j^{(1)}$. Since the cross terms are generally smaller than the purely potential part, they will be neglected in the present work.

According to the method of Irving and Kirkwood [31] the stress tensor of a nonequilibrium inhomogeneous liquid can be calculated in terms of the dynamic pair correlation function in the form

$$\mathbf{P}=\mathbf{P}_k+\mathbf{P}_v\,, \tag{20}$$

where

$$\mathbf{P}_k(\mathbf{r},t)=\int d\mathbf{p}\, m\mathbf{C}\mathbf{C}f(\mathbf{p},\mathbf{r},t), \tag{21}$$

$$\mathbf{P}_v(\mathbf{r},t)=-\tfrac{1}{2}\int_0^1 d\lambda\int d\mathbf{r}_{12}\,\frac{\mathbf{r}_{12}\mathbf{r}_{12}}{r_{12}}\,v'(r_{12})\times\rho^{(2)}(\mathbf{r}-\lambda\mathbf{r}_{12},\mathbf{r}+(1-\lambda)\mathbf{r}_{12},t). \tag{22}$$

In these expressions $\mathbf{p}$ is the momentum of the particle, $v'(r_{12})$ is the derivative of the pair potential already defined, $r_{12}=|\mathbf{r}_{12}|=|\mathbf{r}_1-\mathbf{r}_2|$, $f(\mathbf{p},\mathbf{r},t)$ is the nonequilibrium singlet distribution function normalized to ρ,

$$\rho(\mathbf{r},t)=\int d\mathbf{p}\, f(\mathbf{p},\mathbf{r},t), \tag{23}$$

and $\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2,t)$ is the dynamic pair configuration distribution function. It should be noted that if the full virial tensor $\mathbf{V}_j$ is used, which is defined by [32]

$$\mathbf{V}_j=m\mathbf{C}_j\mathbf{C}_j\,\delta(\mathbf{r}_j-\mathbf{r})-\tfrac{1}{2}\int_0^1 d\lambda\times\sum_{j\neq k=1}^{N}\frac{\mathbf{r}_{jk}\mathbf{r}_{jk}}{r_{jk}}\,v'(r_{jk})\exp\left(-\lambda\mathbf{r}_{jk}\cdot\frac{\partial}{\partial\mathbf{r}}\right)\delta(\mathbf{r}_k-\mathbf{r}); \tag{24}$$

then the stress tensor is given by the average in the N-particle phase space

$$\mathbf{P}(\mathbf{r},t)=\int d\mathbf{r}^{(N)}\int d\mathbf{p}^{(N)}\sum_{j=1}^{N}\mathbf{V}_jF^{(N)}(\mathbf{r}^{(N)},\mathbf{p}^{(N)},t). \tag{25}$$

Here $F^{(N)}(\mathbf{r}^{(N)},\mathbf{p}^{(N)},t)$ is the dynamic distribution function depending on N-particle position and momentum vectors $\mathbf{r}^{(N)}$ and $\mathbf{p}^{(N)}$. It obeys the generalized Boltzmann equation [29]. Therefore $h_j^{(1)}$ is an approximation of the traceless symmetric part of $\mathbf{V}_j$ where the exponential displacement operator $\exp[-\lambda\mathbf{r}_{jk}\cdot(\partial/\partial\mathbf{r})]$ in Eq. (24) is set equal to unity:

$$h_j^{(1)}\delta(\mathbf{r}_j-\mathbf{r})=[\mathbf{V}_j]^{(2)}(\lambda=0). \tag{26}$$

The dynamic pair distribution function in Eq. (22) may be written in the form

$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2,t)=\rho(\mathbf{r}_1,t)\rho(\mathbf{r}_2,t)g(\mathbf{r}_1,\mathbf{r}_2,t), \tag{27}$$

where $g(\mathbf{r}_1,\mathbf{r}_2,t)$ is the dynamic pair correlation function, which depends on density as well as the velocity gradient for the nonequilibrium system under consideration. Therefore, there follow the expressions for the traceless symmetric part of $\mathbf{P}$:

$$\mathbf{\Pi}_k(\mathbf{r},t)=\int d\mathbf{p}[m\mathbf{C}\mathbf{C}]^{(2)}f(\mathbf{p},\mathbf{r},t), \tag{28}$$

$$\mathbf{\Pi}_v(\mathbf{r},t)=-\tfrac{1}{2}\int_0^1 d\lambda\int d\mathbf{r}_{12}\,\frac{[\mathbf{r}_{12}\mathbf{r}_{12}]^{(2)}}{r_{12}}\,v'(r_{12})\times\rho^{(2)}(\mathbf{r}-\lambda\mathbf{r}_{12},\mathbf{r}+(1-\lambda)\mathbf{r}_{12},t). \tag{29}$$

Here the symbol $[\mathbf{A}]^{(2)}$ denotes the traceless symmetric part of tensor $\mathbf{A}$ as in Eq. (6). Adding these two components, we obtain the traceless symmetric part $\mathbf{\Pi}$ of $\mathbf{P}$:

$$\mathbf{\Pi}=[\mathbf{P}]^{(2)}=\mathbf{\Pi}_k+\mathbf{\Pi}_v\,. \tag{30}$$

The two components must be calculated for the corresponding viscosities.

A. Kinetic part η_k

The kinetic part of the shear viscosity is obviously related to the kinetic part of the stress tensor, and this relation, although already discussed from the viewpoint of the collision bracket integral, can be examined from the standpoint of the stress tensors given in Eqs. (28) and (29). This is the aim of this subsection.

Since we are interested in the linear process occurring near equilibrium, it is sufficient to expand the singlet distribution function in the leading moments. It is assumed that the temperature is uniform. Therefore, there is only the stress tensor to consider. The singlet distribution function then can be written in the form

$$\begin{aligned}f&=f_0[1+m\mathbf{C}\cdot\mathbf{C}A+[m\mathbf{C}\mathbf{C}]^{(2)}:\mathbf{B}]\\&\equiv f_0(\mathbf{w})[1+k_BT\mathbf{w}\cdot\mathbf{w}A+k_BT[\mathbf{w}\mathbf{w}]^{(2)}:\mathbf{B}],\end{aligned} \tag{31}$$

where f_0 is the local equilibrium Maxwell distribution function

$$\begin{aligned}f_0&=\rho(2\pi mk_BT)^{-3/2}\exp\left(-\frac{mC^2}{2k_BT}\right)\\&=\rho(2\pi mk_BT)^{-3/2}\exp(-\tfrac{1}{2}w^2),\end{aligned} \tag{32}$$

with the reduced peculiar velocity defined by

$$\mathbf{w}=\sqrt{m\beta}\,\mathbf{C}\qquad\left(\beta=\frac{1}{k_BT}\right).$$

A and $\mathbf{B}$ are the scalar and tensor moments to be determined. Since the normalization is preserved, it follows that

$$\rho=\int d\mathbf{p}\, f(\mathbf{p},\mathbf{r},t)=\int d\mathbf{p}f_0(\mathbf{p}). \tag{33}$$

Multiply $m\mathbf{C}\cdot\mathbf{C}$ to f and integrate over $\mathbf{p}$ to obtain

$$\mathrm{Tr}\mathbf{P}_k=\int d\mathbf{p}\, m\mathbf{C}\cdot\mathbf{C}f(\mathbf{p},\mathbf{r},t)=3\rho k_BT+15\rho(k_BT)^2A.$$

Therefore

$$A=\frac{1}{5k_BT}\left(\frac{1}{3\rho k_BT}\mathrm{Tr}\mathbf{P}_k-1\right)\equiv\frac{\Delta_k}{5\rho(k_BT)^2}. \tag{34}$$

Multiplying $[m\mathbf{C}\mathbf{C}]^{(2)}$ by f and integrating over $\mathbf{p}$, we obtain

$$\mathbf{\Pi}_k = \int d\mathbf{p}[m\mathbf{CC}]^{(2)} f(\mathbf{p},\mathbf{r},t) = \int d\mathbf{p}\, f_0 [m\mathbf{CC}]^{(2)} \times [m\mathbf{CC}]^{(2)}:\mathbf{B} = 2\rho(k_BT)^2[\mathbf{B}]^{(2)}.$$

This means that the tensor $[\mathbf{B}]^{(2)}$ is given by

$$[\mathbf{B}]^{(2)} = \frac{\mathbf{\Pi}_k}{2\rho(k_BT)^2}. \tag{35}$$

Collecting these results, we finally obtain

$$f = f_0(\mathbf{w})\left[1 + \mathbf{w}\cdot\mathbf{w}\frac{\Delta_k}{5\rho k_BT} + [\mathbf{ww}]^{(2)}:\frac{\mathbf{\Pi}_k}{2\rho k_BT}\right]. \tag{36}$$

There remains the problem of determining $\mathbf{\Pi}_k$ in terms of the shear rate or, more generally, the velocity gradient. For that the kinetic theory must be sought for help, and we may use expression (17). Calculating this formula to the lowest order in density making use of the well established procedure in the dilute gas kinetic theory, we can obtain the results for η_k^0 as follows:

$$\mathbf{\Pi}_k = -2\eta_k^0[\nabla\mathbf{u}]^{(2)} \tag{37}$$

and

$$\eta_k^0 = \frac{3\Omega_1^{(2)}(2)}{5\Omega_{12}^{(1)}(1)}\rho D_0 \equiv c\rho D_0. \tag{38}$$

Here $\Omega_1^{(2)}(2)$ and $\Omega_{12}^{(1)}(1)$ are collision bracket integrals [4], and D_0 is the Chapman-Enskog self-diffusion coefficient [4]. Tables for the collision bracket integrals for the Lennard-Jones potential are available in the literature [33]. From the tabulated values for the collision bracket integrals, we find that the ratio $\Omega_1^{(2)}(2)/\Omega_{12}^{(1)}(1)$ is approximately 1.1 for the Lennard-Jones potential, and thus $c \simeq 0.7$. It must be noted that the formula in Eq. (38) is an approximation of η_k, since the singlet distribution function f is not a dilute gas singlet distribution function and therefore the viscosity coefficient η_k is density dependent. To take this into account we may replace D_0 *ad hoc* with a density-dependent self-diffusion coefficient, for example the full self-diffusion coefficient D, and set

$$\eta_k = c\rho D. \tag{39}$$

However, this procedure is not firmly based on mathematical analysis, but empirical. Nevertheless, the result may turn out to be useful.

B. Potential part η_p

To calculate the potential part alternatively to the method of Eq. (18), the pair correlation function must be examined with regard to the $\mathbf{r}_{12}$ dependence of density $\rho(\mathbf{r}-\lambda\mathbf{r}_{12})$ and $\rho(\mathbf{r}+(1-\lambda)\mathbf{r}_{12})$. This $\mathbf{r}_{12}$ dependence of the bulk density indicates that the potential part of the stress tensor varies over the length scale of intermolecular distance, and it can have a significant effect since the shearing perturbation is accompanied by shear waves. To be specific we will consider a plane Couette flow configuration in which flow is in the x direction, and the velocity gradient in the z direction. The y direction is neutral. It is important to recognize that the fluid is compressible. Expansion of the bulk densities in series of $\lambda\mathbf{r}_{12}$ yields

$$\rho(\mathbf{r}-\lambda\mathbf{r}_{12})\rho(\mathbf{r}+(1-\lambda)\mathbf{r}_{12}) = \rho^2(\mathbf{r}) + (1-2\lambda)\rho(\mathbf{r})\left(\frac{\partial\rho}{\partial\mathbf{r}}\right)\cdot\mathbf{r}_{12} - \lambda(1-\lambda) \times\left[\left(\frac{\partial\rho}{\partial\mathbf{r}}\right)\cdot\mathbf{r}_{12}\right]^2 + O(r_{12}^3). \tag{40}$$

Since the density gradient is expected to be small, only the first order derivative terms will be retained. The dynamic pair correlation function $g(\mathbf{r}_1,\mathbf{r}_2,\rho,t)$ will be approximated by the equilibrium pair correlation function to the lowest order because the system is near equilibrium. Furthermore, it will be evaluated at a suitable mean density $\overline{\rho}$, which will be specified later. The main reason for this approximation is a practical one because otherwise it will be necessary to solve an integral equation for $g(\mathbf{r}_1,\mathbf{r}_2,\rho)$ where the density varies in space, but such an integral equation is impractical to solve because it involves three-dimensional integrals requiring too large computational resources. In any case, it does not change so rapidly with regard to the density in the dense liquid regime, and the approximation is reasonable. By using expansion (40) and the approximate pair correlation function $g(\mathbf{r}_1,\mathbf{r}_2,\overline{\rho})$, we obtain the xz component of $\mathbf{\Pi}_v$ necessary for the plane Couette flow configuration in the following form:

$$\begin{aligned}\Pi_{vxz} &= \frac{1}{12}\int d\mathbf{r}_{12}\frac{x_{12}z_{12}}{r_{12}}v'(r_{12})g(r_{12},\overline{\rho})\mathbf{r}_{12}\mathbf{r}_{12}:\frac{\partial\rho}{\partial\mathbf{r}}\frac{\partial\rho}{\partial\mathbf{r}}\\ &= \frac{1}{6}\int d\mathbf{r}_{12}\frac{(x_{12}z_{12})^2}{r_{12}}v'(r_{12})g(r_{12},\overline{\rho})\frac{\partial\rho}{\partial x}\frac{\partial\rho}{\partial z}\\ &= \frac{2\pi}{45}\int_0^\infty dr\, r^5 v'(r)g(r,\overline{\rho})\frac{\partial\rho}{\partial x}\frac{\partial\rho}{\partial z}.\end{aligned} \tag{41}$$

Since the bulk density variation is expected to be limited to a range of distance of the order of intermolecular force at most, it is appropriate to insert a cutoff factor defined by

$$\zeta(\xi-|\mathbf{r}_{12}|) = 1-\theta(\xi-|\mathbf{r}_{12}|),$$

where $\theta(\xi-|r_{12}|)$ is the Heaviside step function:

$$\theta(x) = \begin{cases}1 & \text{for } x \geqslant 0\\ 0 & \text{for } x < 0.\end{cases}$$

Here ξ is the cutoff distance which can be as small as about 2σ in the low temperature regime, and as large as the intermolecular force range $r_{\max}$ at higher temperatures. Thus we finally obtain

$$\Pi_{vxz} = \frac{1}{3}\omega(\rho)\frac{\partial\rho}{\partial x}\frac{\partial\rho}{\partial z}, \tag{42}$$

where

$$\omega(\rho) = \frac{2\pi}{15}\int_0^\infty dr\, r^5 v'(r)g(r,\overline{\rho})\zeta(\xi-|\mathbf{r}|). \tag{43}$$

In the case of a single component fluid under consideration, the velocity u^* of the diffusing tracer particle is related to the density gradient in the following manner [34]:

$$\rho\mathbf{u}^*(\mathbf{r})=-D\frac{\partial\rho}{\partial\mathbf{r}}, \tag{44}$$

where D is the self-diffusion coefficient. This tracer particle velocity is opposite to the velocity of the bulk fluid against which the diffusing tracer particle moves, that is,

$$\mathbf{u}^*(\mathbf{r})=-\mathbf{u}(\mathbf{r}). \tag{45}$$

This means that

$$\rho\mathbf{u}(\mathbf{r})=D\frac{\partial\rho}{\partial\mathbf{r}}. \tag{46}$$

Therefore, if the density variation with $\mathbf{r}$ is small so that the second derivative is negligible, then the velocity gradient for the Couette flow is given by

$$\frac{\partial u_x}{\partial z}=\frac{\partial}{\partial z}D\frac{\partial\rho}{\partial x}\approx-\frac{2D}{\rho^2}\frac{\partial\rho}{\partial x}\frac{\partial\rho}{\partial z}, \tag{47}$$

for which we have used the property of $D\approx D'/\rho$, where D' is approximately independent of ρ. The removal of this assumption does not basically change the essential result. Since for the plane Couette flow configuration

$$\Pi_{vxz}=-\eta_p\frac{\partial u_x}{\partial z}, \tag{48}$$

use of Eq. (47) yields Π_{vxz} in the form

$$\Pi_{vxz}=\frac{2\eta_p D}{\rho^2}\frac{\partial\rho}{\partial x}\frac{\partial\rho}{\partial z}. \tag{49}$$

This result should be compared with Eq. (42). We thus obtain the potential part of the shear viscosity in the form

$$\eta_p=\frac{\rho^2\omega(\rho)}{6D}. \tag{50}$$

Since the density in this expression changes over the range of 2ξ this formula should be averaged over the distance. Thus we obtain

$$\langle\eta_p\rangle=\frac{1}{2\xi}\int_{-\xi}^{\xi}d\xi\,\eta_p(\rho(\xi)). \tag{51}$$

By the mean value theorem there exists a ξ_m for which

$$\langle\eta_p\rangle=\eta_p(\rho(\xi_m)). \tag{52}$$

Since the density variation in the interval of 2ξ is small and around the bulk density value ρ, the density $\rho(\xi_m)$ at $\xi=\xi_m$ satisfying the mean value theorem should be practically the same as the bulk density to a good approximation. This suggests that we take $\overline{\rho}=\rho(\xi_m)\simeq\rho$. Thus it is permissible to take

$$\langle\eta_p\rangle=\eta_p(\rho(\xi_m))\simeq\eta_p(\rho)=\frac{\rho^2\omega(\rho)}{6D}. \tag{53}$$

This relation is similar to the Stokes-Einstein relation except for the factor $\rho^2\omega(\rho)$ which depends on density, temperature, and intermolecular potential parameters. By combining the kinetic and potential parts [Eqs. (39) and (53)], we finally obtain the shear viscosity of the fluid in the form

$$\eta=c\rho D_0+\frac{\rho^2\omega(\rho)}{6D}. \tag{54}$$

In the limit of vanishing density, this formula gives rises to the Chapman-Enskog viscosity of the gas which is independent of density, whereas in the limit of high densities in the liquid regime it takes the Stokes-Einstein form since the second term on the right is dominant over the Chapman-Enskog contribution. Therefore formula (54) explains how the Chapman-Enskog prediction of the $\eta-D$ relation crosses over to the Stokes-Einstein form of the $\eta-D$ relation as the density increases from the dilute gas regime to the liquid regime. We see that in the dilute gas regime the momentum relaxation dominates, since the intermolecular part of the stress relaxes faster than the momentum transfer rate (momentum flux) owing to frequent collisions of relatively long mean free paths, whereas in the liquid density regime the stress arising from the intermolecular interactions dominates since it relaxes more slowly than the momentum transfer rate owing to the more constrained configuration of the particles at a liquid density.

The formula derived suggests that if there are data, experimental or simulation, available for D, then the shear viscosity can be calculated from Eq. (54). Since the self-diffusion coefficient is much easier to simulate than the shear viscosity, formula (54) can be quite useful in practice, provided it is sufficiently reliable. The utility of the formula is tested against experimental data in the following.

We examine the Stokes-Einstein relation for η_p in some detail. First, expressed in reduced quantities $\chi=r/\sigma$, $v^*=v/k_BT$, and $\varrho^*=\pi\sigma^3\rho/6$, the $\rho^2\omega(\rho)$ factor can be given in the form

$$\frac{1}{6}\rho^2\omega(\rho)=\frac{4}{5}\varrho^{*2}\hat{\omega}(\varrho^*)\frac{k_BT}{\pi\sigma}, \tag{55}$$

where

$$\hat{\omega}(\varrho^*,T^*)=\int_0^\infty d\chi\,\chi^5\frac{dv^*}{d\chi}g(\chi,\varrho^*)\zeta(\hat{\xi}-|\chi|), \tag{56}$$

with $\hat{\xi}=\xi/\sigma$. Therefore the numerical factor c in the Stokes-Einstein relation is replaced by a density- and temperature-dependent factor

$$c^{-1}\Rightarrow\frac{4R}{5\sigma}\varrho^{*2}\hat{\omega}(\varrho^*,T^*). \tag{57}$$

That is,

$$\eta_pD=\frac{k_BT}{\pi R}\left[\frac{4R}{5\sigma}\varrho^{*2}\hat{\omega}(\varrho^*,T^*)\right]. \tag{58}$$

Because the particle diffusing through the medium is the same molecule as the molecules comprising the medium, a non-numerical factor depending on T^* and ϱ^* in Eq. (58) is understandable. The factor in the square brackets in Eq. (58) replaces 6^{-1} in the case of the stick boundary condition, and 4^{-1} in the case of the slip boundary condition, in the Stokes-Einstein relation.

In fact, since R is generally a parameter that can be different from the radius of the molecule if the Stokes-Einstein relation is applied to particles of a molecular size, one may infer a molecular expression for R from Eq. (58) if one insists it be the Stokes-Einstein relation

$$\begin{aligned}\frac{\sigma}{2R} &= \frac{12}{5}\varrho^{*2}\hat{\omega}(\varrho^*,T^*) \quad \text{for the stick boundary condition} \\ &= \frac{8}{5}\varrho^{*2}\hat{\omega}(\varrho^*,T^*) \quad \text{for the slip boundary condition.}\end{aligned} \tag{59}$$

If the Stokes-Einstein relation is obeyed, the right hand side should be equal to unity. If η is used instead of η_p, then we find, from Eq. (54)

$$\begin{aligned}\frac{\sigma}{2R} &= \frac{3\pi\sigma}{k_BT}c\rho D_0 D + \frac{12}{5}\varrho^{*2}\hat{\omega}(\varrho^*,T^*) \quad \text{for the stick boundary condition} \\ &= \frac{2\pi\sigma}{k_BT}c\rho D_0 D + \frac{8}{5}\varrho^{*2}\hat{\omega}(\varrho^*,T^*) \quad \text{for the slip boundary condition.}\end{aligned} \tag{60}$$

Here one may replace $c\rho D_0$ with η_k^0. These relations will be assessed to see if the Stokes-Einstein relation is obeyed for molecules.

Formula (54) is reminiscent of the one derived by Kirkwood, Buff, and Green [35], who obtained it by using a different method which requires solutions for the hierarchy of kinetic equations for Brownian particles. These kinetic equations are Fokker-Planck equations that Kirkwood derived in his earlier paper [36] for reduced distribution functions for particles immersed in their own kind of particles which are treated as a continuous medium bombarding the particles of interest. In fact, their equation can be given the same form as Eq. (54) if an approximate form is taken for the ψ_2 factor appearing in their equation except for the different numerical coefficients emerging thereby. For example, if the lowest order approximation is taken for ψ_2, namely, $\psi_2 \approx r^2/2$ [see Eq. (31) of Ref. [35]], then from Eq. (10) of Ref. [35] we have the viscosity formula

$$\eta = \frac{1}{2}\rho D + \frac{\rho^2\omega_{\mathrm{KBM}}(\rho)}{6D}, \tag{61}$$

where

$$\omega_{\mathrm{KBM}}(\rho) = \frac{\pi}{5}\int_0^\infty dr r^5 v'(r) g(r,\rho). \tag{62}$$

This must be compared with Eq. (43). We thus find that, apart from the cutoff factor, there holds the following relation for the multiplicative factors:

$$\omega(\rho) = \frac{2}{3}\omega_{\mathrm{KBM}}(\rho). \tag{63}$$

It is remarkable that this relation arises despite the fact that the method of Kirkwood, Buff, and Green is quite different from the present method. This suggests that the Kirkwood-Buff-Green method seems to merit a more careful investigation. In this connection it should be noted that the Rice-Allnatt theory [37] also gives formulas for viscosities in terms of a hard sphere friction constant in forms reminiscent of the viscosity formula presented here, but they are more complicated than either Eqs. (54) or (61).

In the derivation of formula (54) the coupling between the momentum transfer part $[m\mathbf{C}_j\mathbf{C}_j]^{(2)}$ and the virial part $[m\mathbf{r}_{ij}\mathbf{r}_{ij}]^{(2)}v'_{ij}/r_{ij}$ of the tensor $h_j^{(1)}$ has been neglected. Near equilibrium, the contribution from the coupling of these terms is negligible, but it may become non-negligible in the supercooled liquid regime. In such a case Eq. (54) may require a correction. Since investigation of this aspect also requires an improved method of computing the pair correlation function beyond the Percus-Yevick integral equation used in this work, it will be deferred to a future work.

III. COMPARISON WITH EXPERIMENT

A. Shear viscosity

To see the utility of the formula presented, we calculate the shear viscosity of argon with regard to its density and temperature dependence as well as the density dependence of krypton and xenon, and compare the results with experimental data available in the literature. The temperature dependence for krypton and xenon is not calculated because of the absence of experimental data to compare with. The values of the self-diffusion coefficient D are computed with either the formula obtained by fitting the Naghizadeh-Rice data [38] to a mathematical form or the formula proposed by Heyes [39] on the basis of the molecular dynamics simulation results.

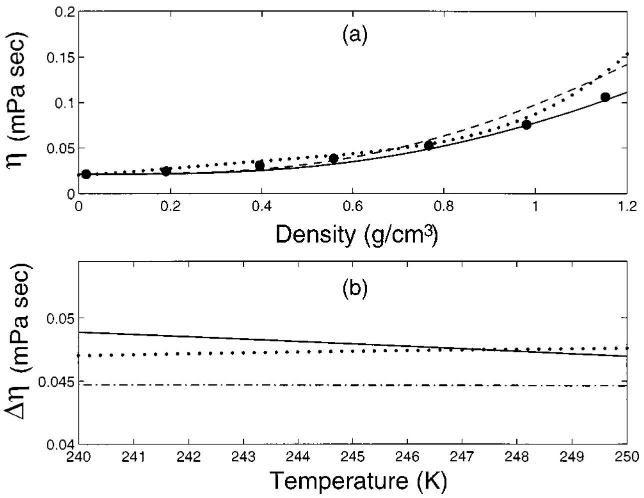

FIG. 1. (a) Density dependence of shear viscosity at $T=273.0\,\mathrm{K}$. The dotted curve is the prediction by the Haynes formula. The solid and dashed curves are the theoretical shear viscosities calculated with D_{Heyes} and $D_{\text{Naghizadeh-Rice}}$, respectively. The experimental value of η_k^0 is used in place of the Chapman-Enskog shear viscosity. The filled circles (●) are the experimental values reported in Ref. [42]. (b) Temperature dependence of $\Delta\eta=\eta-\eta_k^0$ at $\rho=0.9\,\mathrm{g/cm^3}$. The solid curve is for the theoretical excess shear viscosities calculated with D_{Heyes}, and the dotted and broken curves are the experimental temperature dependence computed with the empirical formulas of Haynes [41] and Younglove and Hanley [43], respectively. The value of parameter α in this case is equal to unity.

The pair correlation function appearing in the expression for $\omega(\rho)$ was obtained from the numerical solution of the Percus-Yevick integral equation [40] for the pair correlation function. With the so obtained pair correlation function, the integral is numerically evaluated at different temperatures and densities.

In Fig. 1(a) the shear viscosity of argon at $T=273.0\,\mathrm{K}$ is plotted against the density, and the density dependence is compared with that predicted by the Haynes formula [41], which was obtained by fitting his experimental data. The potential parameters for argon are $\sigma=3.40\,\text{Å}$ and $\epsilon/k_BT=119.8\,\mathrm{K}$ [33]. The dotted curve is the prediction by the Haynes formula. The solid and broken curves are the theoretical values of the present theory, which have been computed with the values of D by using the Heyes formula and the Naghizadeh-Rice formula, respectively. The D values obtained by the former will be called D_{Heyes}, and those obtained by the latter will be called $D_{\text{Naghizadeh-Rice}}$. In all of the calculations for this figure the experimental value of the dilute gas viscosity has been used for $\eta_k^0=c\rho D_0$. The reason for not using the Chapman-Enskog value for η_k^0 is that it is about 10% lower than the experimental value at $T=273.0\,\mathrm{K}$, and 4–5% in the range of $T=240–250\,\mathrm{K}$, whereas it agrees well with the experimental values around the triple point. Since the principal aim here is to test the formula for the excess shear viscosity η_p, the part obeying the Stokes-Einstein form, we feel it appropriate to remove the uncertainty in the kinetic part of η, namely, η_k^0. The filled circles are the experimental values of Ref. [42]. In this case, the value of the parameter α is taken to be equal to unity, which implies that the range of density variation is equal to or larger than the intermolecular force range $r_{\max}\equiv|\mathbf{r}_{12}|_{\max}$. Thus the viscosity values computed are free from parameters other than potential parameters. Agreement with experiment is good. In Fig. 1(b) the temperature dependence of the shear viscosity at $\rho_m=m\rho=0.9\,\mathrm{g/cm^3}$ is presented for the temperature range indicated. The solid curve is for the excess viscosity calculated with D_{Heyes}, the dotted curve is computed by the empirical formula reported by Haynes [41], and the dash-dotted curve is obtained with the formula reported by Younglove and Hanley [43]. The latter two curves are therefore experimental. In this case, the value of α is equal to unity. The temperature dependence by the present theory shows a negative temperature derivative of $\Delta\eta$, as do the Younglove-Hanley formula and molecular dynamic simulation data [44], whereas the Haynes formula [41] shows a positive temperature derivative. On physical grounds the temperature gradient of $\Delta\eta$ is expected to be negative.

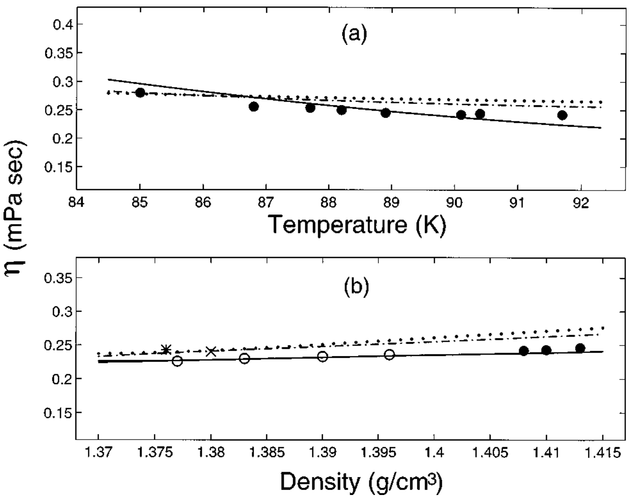

FIG. 2. (a) Temperature dependence of shear viscosity at $\rho=1.408\,\mathrm{g/cm^3}$. The solid curve is the theoretical shear viscosity calculated with $D_{\text{Naghizadeh-Rice}}$ [38]. In this case, the Chapman-Enskog shear viscosity was used for the kinetic part of η. The dotted and dash-dotted curves are the experimental temperature dependence calculated with the empirical formulas of Haynes [41] and Younglove and Hanley [43]. The filled circles (●) are experimental values as reported in Ref. [45] whose authors obtained them by interpolating/extrapolating the data reported in Refs. [46–48]. (b) Density dependence of shear viscosity at $T=90.0\,\mathrm{K}$. The meanings of the curves are the same as in (a). The symbols represent the following data ○ from Ref. [49], * from Ref. [50], × from Ref. [51], and ● from Ref. [45]. The value of parameter α in this case is equal to 0.175, which corresponds to the cutoff parameter value $\xi\approx2\sigma$.

The critical density and temperature of argon are, respectively, $\rho_c=0.533\,\mathrm{g/cm^3}$ and $T_c=151\,\mathrm{K}$, whereas at the triple point $\rho=1.42\,\mathrm{g/cm^3}$ and $T=85\,\mathrm{K}$. The empirical value of the viscosity at the triple point is 0.289 mPa s according to the Younglove-Hanley formula and 0.282 mPa s according to the Haynes formula. As the temperature approaches the triple point of argon, the value of parameter α is found to be less than unity. For Figs. 2(a) and 2(b) we have chosen $\alpha=0.175$, which approximately corresponds to the cutoff parameter value $\xi\approx2\sigma$. In Fig. 2(a) the temperature dependence of the shear viscosity of argon at $\rho_m=1.408\,\mathrm{g/cm^3}$ is shown. The solid curve is the theoretical shear viscosity

TABLE I. Ratio of η_b to η at $T=273.0$ K.

	η (mPa s)				η_b (mPa s)			η_b/η		
ρ_m	$D_{N\text{-}R}$ [a]	D_{Heyes}	Expt. [b]	Expt. [c]	$D_{N\text{-}R}$	D_{Heyes}	Expt. [b]	$D_{N\text{-}R}$	D_{Heyes}	Expt. [b]
0.508	0.032	0.028	0.0365	0.033 (0.033)	0.009	0.0066	0.009	0.28	0.24	0.25
0.694	0.052	0.043	0.051	0.044 (0.044)	0.022	0.016	0.029	0.42	0.31	0.57
0.812	0.071	0.056	0.060	0.054 (0.055)	0.035	0.025	0.033	0.49	0.45	0.55
0.896	0.087	0.068	0.067	0.063 (0.065)	0.046	0.033	0.044	0.53	0.49	0.66
0.958	0.10	0.078	0.073	0.071 (0.074)	0.055	0.040	0.048	0.55	0.51	0.66
1.008	0.11	0.086	0.08	0.079 (0.083)	0.063	0.045	0.056	0.57	0.52	0.70

[a] $D_{N\text{-}R}$ is $D_{\text{Naghizadeh-Rice}}$. The columns $D_{N\text{-}R}$ and D_{Heyes} represent the theoretical values of viscosities computed with $D_{N\text{-}R}$ and D_{Heyes} for the self-diffusion coefficient. The viscosities quoted are in the units of mPa s. The viscosities computed with the Younglove-Hanley and Haynes formulas are experimental.

[b] Experimental values reported in Ref. [53].

[c] The Younglove-Hanley formula. The numbers in parentheses are from Haynes' formula.

computed with $D_{\text{Naghizadeh-Rice}}$ and the Chapman-Enskog shear viscosity is used for the kinetic part of η, namely, $\eta_k^0 = \eta_{\text{Chapman-Enskog}}$. As mentioned in connection with Fig. 1, the Chapman-Enskog shear viscosity at the temperatures of interest here agrees well with experiment. Because D_{Heyes} was considered inapplicable in the temperature range considered here, the viscosity was not calculated with it. The dotted (···) and dash-dotted (-·-) curves are computed with the Haynes [41] and Younglove-Hanley formulas [43], respectively, which are empirical. The filled circles (●) are the experimental data as quoted in Ref. [45], whose authors, to obtain them, either interpolated or extrapolated the data reported in Refs. [46], [47], [48]. The slopes of the shear viscosity are seen to be negative, that is, the temperature derivative of η is negative as expected. The qualitative behavior of the theoretical prediction shows a correct tendency. In Fig. 2(b) the density dependence of the shear viscosity at $T=90.0$ K is presented. The meanings of the curves are the same as in Fig. 2(a). The symbols represent experimental data: ○ from Ref. [49], $*$ from Ref. [50], $\times$ from Ref. [51], and ● from Ref. [45]. The theoretical prediction, with one adjustable parameter, agrees well with experiment in the density range where experimental values are available. It can be shown [52] that the bulk viscosity η_b also obeys a Stokes-Einstein relation similar to the potential part of η presented in this work:

$$\eta_b = \frac{\rho^2 \omega(\rho)}{9D} = \frac{2}{3}\,\eta_p . \tag{64}$$

Therefore, it is possible to calculate the ratio η_b/η. The value of this ratio in the neighborhood of the triple point is found to be about 0.77, whereas the experimental values are on the average 0.85 from Ref. [45], 0.78 from Ref. [49], 0.56 from Ref. [50], and 0.69 from Ref. [51]. Therefore, the theoretical value is comparable to the mean value 0.72 of the experimental values. On the other hand, at $T=273.0$ K its value changes from 0 to ~0.6 as the density increases from 0 to 1.0 g/cm^3, as indicated by some of the higher density values shown in Table I. The ratio clearly vanishes as the density vanishes since $\eta_b \sim \rho^3$ as $\rho \to 0$.

These comparisons of the ratio η_b/η indicate the formulas obtained for the viscosities in the present theory have qualitatively correct and mutually consistent properties, and therefore are reliable. Note that because of the kinetic contribution to η, the values of the ratio η_b/η are a little lower than the ratio of η_b to η_p, which is 2/3.

To ascertain the applicability of the shear viscosity formula to other simple fluids we have calculated the density dependence of krypton at $T=298.1$ K and of xenon at $T=373.1$ K. The results are presented in Figs. 3(a) and 3(b).

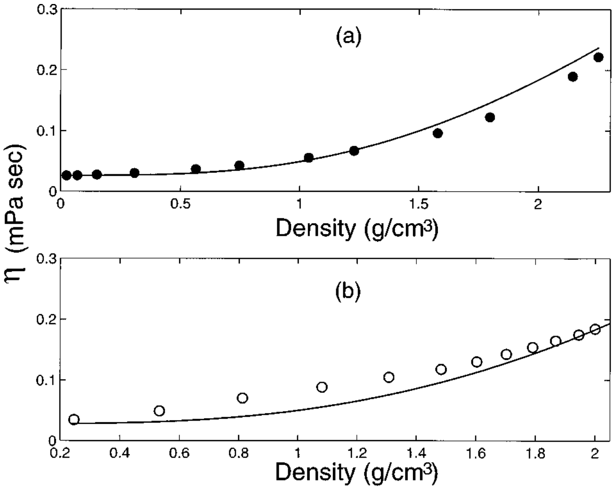

FIG. 3. (a) The density dependence of η of krypton at $T=298.1$ K ($T^*=1.74$). The solid curve is theoretical and the filled circles are the experimental values reported by Trappeniers *et al.* [54]. (b) The density dependence of η of xenon at $T=373.1$ K ($T^*=1.69$). The solid curve is theoretical and the open circles are the experimental values reported by Reynes and Thodos [55].

The potential parameters for krypton are $\sigma = 3.60$ Å and $\epsilon/k_B = 171$ K, whereas $\sigma = 4.10$ Å and $\epsilon/k_B = 221$ K in the case of xenon. The values of the potential parameters were taken from Refs. [33, 50]. These parameters give rise to the reduced temperature at $T^* = 1.74$ for krypton and $T^* = 1.69$ for xenon. Therefore, the two fluids are at comparable reduced temperatures. For the calculation of the shear viscosities of these fluids, the value of the parameter α is set equal to unity. Therefore, the viscosity formula involves the potential parameters only. The density dependence of the shear viscosity is presented for krypton in Fig. 3(a), where the solid curve is the theoretical density dependence whereas the filled circles are the experimental values reported by Trappeniers *et al.* [54]. The Chapman-Enskog shear viscosity is used for the kinetic part of η, which was found to agree well with experiment. In Fig. 3(b) the density dependence of the shear viscosity of xenon is presented, where the solid curve is the theoretical density dependence calculated with the Chapman-Enskog shear viscosity for the kinetic part of η, and the open circles are the experimental values reported in Ref. [55]. In this case the Chapman-Enskog shear viscosity was found to underestimate the experimental viscosities slightly at low densities. Agreement with experiment and theory is not as good as for the case of krypton at intermediate densities, but the density dependence is found to be qualitatively correct. Since the law of corresponding states was reported [56,57] to be obeyed by simple fluids such as argon, krypton, and xenon examined here, agreement between experiment and theory in the case of krypton and xenon could have been expected. Nevertheless, the comparison presented for krypton and xenon assures us of the reliability of the viscosity formula derived in this work, and verifies the law of corresponding states for the fluids considered.

B. Assessment of the Stokes-Einstein relation

The viscosity formula [Eq. (54)] does not appear to be a Stokes-Einstein relation at first glance. Nevertheless, it can account for the experimental density and temperature dependence of simple fluids, and thus is useful in practice. It will be useful to see if the Stokes-Einstein relation (2) can be understood for molecular particles in terms of the formula. For this we examine the relations given in Eqs. (59) and (60). If $\sigma/2R$ remains constant with regard to temperature and density, and is equal to unity, then it is possible to conclude that the Stokes-Einstein relation is valid even for particles of a molecular size comparable to the solvent molecules. The assessment of the relation will be made for argon. In Fig. 4 the values of $2R/\sigma$ are plotted against density and temperature in panel (a) and (b) respectively. The broken (- - -) and dotted (···) lines are results computed for slip and stick boundary conditions with the formulas in Eq. (59), respectively, and the solid (—) and dash-dotted (- · -) lines are the results computed for slip and stick boundary conditions with the formulas in Eq. (60), respectively. The density dependence is computed for argon at $T = 273.0$ and the temperature dependence is computed at $\rho_m = 1.0$ g/cm^3. The value of parameter α is unity for the figures. The density dependence of $2R/\sigma$ is almost absent if the full viscosity η is used for the Stokes-Einstein relation, although the values for the different boundary conditions used differ by an almost constant factor. On the other hand, the Stokes-Einstein relation for η_p shows a density dependence, but has no temperature dependence. In Fig. 5 the density and temperature dependences of $2R/\sigma$ are examined in the case of argon near the triple point, at $T = 90$ K for the density dependence and at $\rho_m = 1.408$ g/cm^3 for the temperature dependence. For these figures $\alpha = 0.175$. The meanings of the lines are the same as in Fig. 4. *The values of $2R/\sigma$ are seen to remain virtually constant for all cases, indicating that the Stokes-Einstein relation is obeyed. These figures suggest that in the density and temperature ranges examined here the Stokes-Einstein relation remains valid for η, even if the particle is of a molecular size*, and that the question of slip or stick boundary condition is irrelevant from the viewpoint of statistical mechanics and if one is prepared to take R as an adjustable parameter that

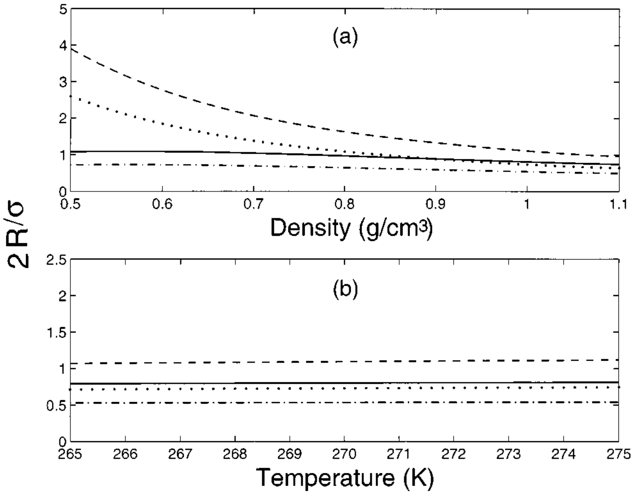

FIG. 4. (a) Density dependence of $2R/\sigma$ for argon at $T = 273.0$ K. (b) Temperature dependence for argon at $\rho_m = 1.0$ g/cm^3. For these figures, $\alpha = 1$. The broken (- - -) and dotted (···) lines are computed with Eq. (59) for the slip and stick boundary condition, respectively. The solid (—) and dash-dotted (-·-) lines are computed with Eq. (60) for the slip and stick boundary conditions, respectively.

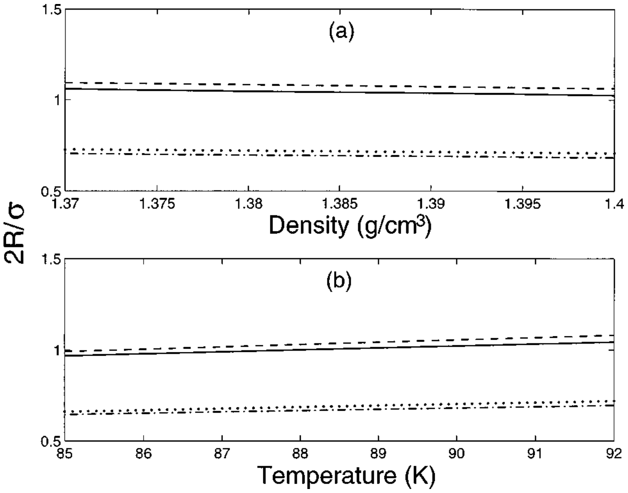

FIG. 5. (a) Density dependence of $2R/\sigma$ for argon at $T = 90$ K. (b) Temperature dependence of argon at $\rho_m = 1.408$ g/cm^3. For these figures, $\alpha = 0.175$. The meanings of the lines are the same as in Fig. 4.

should be taken with a value in the neighborhood of $\sigma/2$. Since the validity of the Stokes-Einstein relation for molecules has been a focus of attention in the literature, as mentioned in Sec. I the assessment made here of the relation provides useful insight into the question. In any case, from the perspective of Eq. (54) the question of the validity of the Stokes-Einstein relation for molecular particles is irrelevant because it itself is a relation holding for fluids consisting of molecular particles.

IV. DISCUSSION AND CONCLUDING REMARKS

In this paper, by means of statistical mechanics, we have derived a relation of the shear viscosity to the self-diffusion coefficients for a simple liquid in which the potential part of the shear viscosity bears a resemblance to the well-known Stokes-Einstein relation for a hard sphere immersed in a continuous medium. The coefficient in the relation is given in terms of density, molecular parameters, and the pair correlation function of the fluid. The relation may be regarded as a generalization of the Stokes-Einstein relation. The formula derived for the relation of shear viscosity and the self-diffusion coefficient is reminiscent of the expression for the shear viscosity derived by Kirkwood, Buff, and Green [35] in 1949. The latter can be shown to take the present form, apart from the constant numerical factor, in the lowest order approximation for ψ_2 appearing in their formula for the shear viscosity. This seems to suggest that the Kirkwood kinetic equation for Brownian particles [36] may be worth a fresh investigation, although its variant was already proposed in the form of Rice-Allnatt theory [37] which was used to calculate transport coefficients. As far as the mathematical structure goes with regard to the friction constant dependence, the present result is also reminiscent of the shear viscosity formula of the Rice-Allnatt theory despite the difference in the methods of derivation of the viscosity formula.

The present theory for the relation of η to D exploits the minute bulk density variations which occur when the fluid is sheared or compressed by an external agency. This is an effect which is traditionally ignored when a theory of transport processes is developed in the Chapman-Enskog line of approach. Neglect of such an effect within the bounds of the traditional line of approach to the transport theory is quite legitimate when the collisional contributions are calculated from the solutions of the kinetic equations, but the effect becomes significant when some relations are sought between transport coefficients such as viscosities and the self-diffusion coefficient of the fluid, especially in the liquid density regime. As a matter of fact, such a density variation appears in the free energy functional in the van der Waals theory of inhomogeneous fluids [58] where the bulk density variation is taken into account by including a quadratic form of first density derivative with respect to space. In the Kirkwood line of transport theory such an effect is taken into account in the sense that the kinetic equation for the singlet distribution function is solved together with the kinetic equation for the dynamic pair correlation function, whereas, for example, in the linear response theory it is not taken into consideration.

Since it is not possible to acquire numerically reliable analytical solutions for transport properties of dense gases and liquids by means of statistical mechanics, and the only practicable option is numerical simulation methods [1–3], it is useful to develop relations between transport coefficients which can be made use of to compute one transport coefficient from another. In this regard the formula we have derived here and a further improvement of it can be very useful from a practical viewpoint, because the self-diffusion coefficient is the simplest of transport coefficients to compute by means of a numerical simulation method. Its simulation requires the least amount of technical and conceptual problems to resolve in implementing the numerical simulation method. In contrast to this, simulations for viscosities, although often practiced, are not as simple to implement, because of the required boundary conditions, viscous heating, numerical instabilities that may arise as the shear rate increases, and a large signal to noise ratio in the small shear rate regime.

Although not directly applicable to supercooled liquids and complex liquids, the viscosity formula derived in this work has a potentially useful feature which, when properly generalized, may be helpful for understanding the deviations from the Stokes-Einstein relation which have been experimentally observed in glass-forming liquids as mentioned in Sec. II, because the present approach may provide molecular theory expressions for the parameters replacing c and R in the Stokes-Einstein relation for such complex liquids.

In conclusion, the derivation of the formula presented for the shear viscosity is relatively simple. Although it has an adjustable parameter in the case of low temperatures near the triple point where the density variation is short ranged and of the order of a couple of molecular diameters, the formula is not only easy to use and practical in accounting for the temperature and density dependence of experimental data of simple fluids such as argon, krypton, and xenon, but it is also suggestive of the possibility of generalizations for more complex fluids. In the range of density and temperature examined, the Stokes-Einstein relation is found to remain applicable to particles of a molecular size.

ACKNOWLEDGMENT

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