Analog of the Stokes-Einstein Relation for Bulk Viscosity

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An analog of the Stokes-Einstein relation is derived for the bulk viscosity of simple fluids by means of statistical mechanics. The formula is used to calculate the bulk viscosity with the self-diffusion coefficient available either from experiment or from numerical simulations. The results are in good agreement with experiment with regard to the density and temperature dependence.

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Of all transport coefficients of fluids, the bulk viscosity probably is the least studied experimentally and theoretically despite its importance for accounting for ultrasonic wave absorption and dispersion. On the theoretical side, the kinetic theory developed by Rice and Allnatt [1] provides a practicable method of computation and received some experimental attention [2–7] in the 1960s, but still remains to be further studied from the theoretical standpoint. There are some other kinetic theory methods [8,9], but they have not been followed up for comparison with experiment to a noticeable extent except for the modified Enskog theory result [10], which unfortunately holds for hard spheres only. There are some results obtained for bulk viscosity by molecular dynamics simulation methods [11–13] performed on the basis of the linear response theory formula. Recently, a formal expression for the bulk viscosity of a simple fluid has been also obtained on the basis of the generalized Boltzmann equation [14], but, since the formula involves a many-particle collision bracket integral requiring the solution of a many-particle collision problem, it still awaits for theoretical methods to compute it in an adequate accuracy.

In this Letter, we present a method of calculating the bulk viscosity of a simple liquid from the information available for the self-diffusion coefficient, equilibrium pair correlation function, and other attributes of the liquid. In this method, recognizing the significance of density variation for transport properties and using the method of statistical mechanics, we obtain a relation of the bulk viscosity to the self-diffusion coefficient, which is in fact rather akin to the well-known Stokes-Einstein relation [15] between the shear viscosity and the self-diffusion coefficient, and the present result may be regarded as a bulk viscosity analog of the Stokes-Einstein relation. The present method starts with the stress tensor as in the method used by Kirkwood, Buff, and Green [16], by which shear and bulk viscosities are calculated, but differs from theirs in the treatment of the stress tensor and in the result obtained for the bulk viscosity. In fact, the zero density limit of their bulk viscosity result is incorrect since the bulk viscosity of a dilute monatomic gas is equal to zero, as is well established experimentally and theoretically.

The bulk viscosity is defined by the linear thermodynamic force-flux relation [14,17]:

$$\Delta = -\eta_b \nabla \cdot \mathbf{u}\,, \tag{1}$$

where the excess normal stress Δ is defined by $\Delta = \frac{1}{3}\,\mathrm{Tr}\mathbf{P} - p$, with $\mathbf{P}$ denoting the stress tensor of the fluid and p the hydrostatic pressure; $\mathbf{u}$ is the velocity of the fluid particle; η_b is the bulk viscosity. Equation (1) indicates that, if the temperature is kept fixed, the excess normal stress is driven by compression/dilatation of the fluid. In the kinetic theory of fluids [1,9,14], the bulk viscosity coefficient η_b is given in terms of a collision bracket integral or a time correlation function. The present method does not require them to evaluate η_b.

Suppose, for example, a sound wave propagates through the fluid. The response to the compressional effects by the system will result in a local volume change of the fluid, which is associated with the bulk viscosity. Here we propose to exploit this density variation in the fluid to calculate the bulk viscosity.

A longitudinal sound wave passing through a fluid periodically compresses the fluid and thus creates a density variation in the direction of the wave. We will designate the direction of the wave propagation as the z direction in the Cartesian coordinate system. The z (longitudinal) component of the normal stress P_{zz} then is equal to the hydrostatic pressure p: $P_L \equiv P_{zz} = p$. Since the density does not vary in the transversal direction, the transversal components of the normal stress P_{xx} and P_{yy} are not the same as the longitudinal component P_{zz}. However, by symmetry $P_{xx} = P_{yy} \equiv P_T$. Therefore the density variation induces a nonvanishing normal stress difference $\mathcal{N} = P_T - P_L \neq 0$, which now is related to Δ by the equation $\Delta = \frac{2}{3}\,\mathcal{N} = \frac{2}{3}\,(P_T - P_L)$. This indicates that the normal stress difference is associated with the bulk viscosity in this situation.

The self-diffusion is driven by a density variation in space. It is described by the relation [18]

$$\rho \mathbf{u} = -D \nabla \rho\,, \tag{2}$$

where D is the self-diffusion coefficient, which depends on density as well as temperature. Equation (2) is Fick's law for self-diffusion. According to the result by the kinetic theory of fluids, the self-diffusion coefficient [17] depends on density as $D = D_0/\rho$, where D_0 may be regarded as a constant independent of ρ to the lowest order approximation. However, D_0 may depend on temperature. To be more precise, D_0 is generally represented in a series in ρ, but only the leading term is found to be sufficient for the discussion. Since the density does not change in the transversal direction in the present problem, differentiation of Eq. (2) with respect to z yields

$$-\frac{\partial u_z}{\partial z} = -\frac{2D}{\rho^2}\left(\frac{\partial \rho}{\partial z}\right)^2 + \frac{D}{\rho}\frac{\partial^2 \rho}{\partial z^2} \approx -\frac{2D}{\rho^2}\left(\frac{\partial \rho}{\partial z}\right)^2, \tag{3}$$

where the second derivative of ρ, being small, may be neglected. Upon substitution of Eq. (3) into Eq. (1), there follows the equation

$$P_T - P_L = -\frac{3\eta_b D}{\rho^2}\left(\frac{\partial \rho}{\partial z}\right)^2. \tag{4}$$

The stress tensor $\mathbf{P}$ can be calculated in terms of intermolecular forces and the dynamic pair distribution function for a nonequilibrium simple fluid by using the Irving-Kirkwood method [19]. It can be written in the form

$$\begin{aligned}\mathbf{P}(\mathbf{r},t) = &\int d\mathbf{p}\, m\mathbf{C}\mathbf{C}f(\mathbf{p},\mathbf{r},t) \\ &- \frac{1}{2}\int_0^1 d\lambda \int d\mathbf{r}_{12}\,\frac{\mathbf{r}_{12}\mathbf{r}_{12}}{r_{12}} \\ &\times v'(r_{12})\rho^{(2)}[\mathbf{r} - \lambda\mathbf{r}_{12}, \mathbf{r} + (1-\lambda)\mathbf{r}_{12}, t],\end{aligned} \tag{5}$$

where $f(\mathbf{p},\mathbf{r},t)$ is the singlet distribution function of momentum $\mathbf{p}$, position $\mathbf{r}$ at time t, m is the mass, $\mathbf{C} = \mathbf{p}/m - \mathbf{u}$ is the peculiar velocity, $v(r_{12})$ is the intermolecular potential energy, $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$, $v'(r_{12}) = \partial v(r_{12})/\partial r_{12}$, and $\rho^{(2)}$ is the dynamic pair correlation function (PCF). At equilibrium, the formula becomes time independent, because the PCF becomes independent of time. The first term (kinetic contribution to $\mathbf{P}$) on the right of Eq. (5) does not contribute to $P_N - P_T$, and, if the density gradient is small, it is possible to show that $P_N - P_T$ to the lowest order approximation is given in terms of the equilibrium PCF:

$$\begin{aligned}P_N - P_T = \frac{1}{4}\int_0^1 d\lambda \int d\mathbf{r}_{12}\left(r_{12} - \frac{3z_{12}^2}{r_{12}}\right)v'(r_{12}) \\ \times \rho^{(2)}[r_{12}, z_1 - \lambda z_{12}, z_1 + (1-\lambda)z_{12}].\end{aligned} \tag{6}$$

Since the fluid is locally nonuniform, the PCF may be expressed as

$$\begin{aligned}\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \rho(z_1 - \lambda z_{12})\rho[z_1 + (1-\lambda)z_{12}] \\ \times g[r_{12}, z_1 - \lambda z_{12}, z_1 + (1-\lambda)z_{12}],\end{aligned} \tag{7}$$

where $\mathbf{r}_1 = \mathbf{r} - \lambda\mathbf{r}_{12}$, $\mathbf{r}_2 = \mathbf{r} + (1-\lambda)\mathbf{r}_{12}$. By expanding the density up to the first order in density derivative, we find

$$\rho(z_1 - \lambda z_{12})\rho[z_1 + (1-\lambda)z_{12}] = \rho^2(z_1) + (1-2\lambda)z_{12}\rho(z_1)\frac{\partial \rho}{\partial z_1} - \lambda(1-\lambda)z_{12}^2\left(\frac{\partial \rho}{\partial z_1}\right)^2. \tag{8}$$

To the lowest order approximation, the PCF $g(\rho)$ may be approximated by the one evaluated at a mean density $\overline{\rho}$ suitably chosen. If the density variation has a range 2ξ, then the expansion for $\rho(z)$ is confined to $-\xi \le z_{12} \le \xi$. The range 2ξ may depend on temperature T; it may be larger than the range $r_{\max}$ of intermolecular forces near the critical point where the density fluctuation is long ranged, but may be quite small and on the order of the size of one or two molecules if T is sufficiently away from the critical temperature T_c. This finite range of density variation will be taken care of by inserting the factor $\zeta(|z_{12}| - \xi)$, where $\zeta(x) = 1$ for $x < 0$ and 0 for $x > 0$. If T is near T_c, the range of density fluctuation is long and expected to be larger than $r_{\max}$, that is, $\xi \ge r_{\max}$, and $\xi \le r_{\max}$ if T is sufficiently away from T_c.

When the expansion (8) is substituted into Eq. (6) and the integration is performed over λ, the first two terms on the right of Eq. (8) vanish. Taking integration over the relative coordinates, we obtain

$$(P_T - P_L)(z) = -\omega(z,T)\left(\frac{\partial \rho}{\partial z}\right)^2 = -\frac{3\eta_b D}{\rho^2}\left(\frac{\partial \rho}{\partial z}\right)^2. \tag{9}$$

Here, the factor $\omega(z,T)$ is given by

$$\omega(z,T) = \frac{2\pi}{45}\int_0^\infty dr\, r^5 v'(r_{12})g(r_{12},\overline{\rho})\zeta(|z_{12}| - \xi). \tag{10}$$

This factor ω depends on both density and temperature because g depends on both. The second equality of Eq. (9) follows from Eq. (4) for $P_T - P_L$. Therefore there follows the expression

$$\eta_b(z,T) = \frac{\rho^2\omega(z,T)}{3D(z,T)}. \tag{11}$$

By taking average of η_b over the range 2ξ of density fluctuations, we obtain

$$\langle \eta_b(z,T) \rangle = \frac{1}{2\xi} \int_{-\xi}^{\xi} dz \, \frac{\rho^2(z)\omega(z,T)}{3D(z,T)} \,. \qquad (12)$$

The integrand of this integral depends on z through $\rho(z)$. By the mean value theorem $\langle \eta_b \rangle = \eta_b(\rho_\xi)$, where ρ_ξ is the density value within the range of 2ξ, in which the density varies between the uniform bulk value and a maximum. Since this difference in density, however, is small and the value of ρ_ξ should be practically equal to the bulk density value, we take $\rho_\xi \simeq \rho$ and thus obtain the bulk viscosity:

$$\eta_b(\rho,T) = \frac{\rho^2 \omega(\rho,T)}{3D(\rho,T)} \,. \qquad (13)$$

It is a bulk viscosity analog of the Stokes-Einstein relation [15] relating the shear viscosity to D. We will test this relation against experimental data.

The range of density variation ξ varies with temperature and, at the minimum, can be of the same order of magnitude as the size of the first coordination shell of the liquid, that is, roughly the size of the cavity around a particle, not the whole intermolecular force range. In this case, the integrals in Eq. (6) have a cutoff well inside $r_{\max}$, and this makes the value of the integral sensitive to the value of ξ chosen because the pair correlation function oscillates. To adjust the value of $\omega(\rho,T)$, it was found easier to simply replace the cutoff factor $\zeta(|z_{12}| - \xi)$ with a numerical factor α. Thus, we write the factor $\omega(\rho,T)$ in the form

$$\omega(\rho,T) = \alpha \, \frac{2\pi}{45} \int_0^\infty dr \, r^5 v'(r) g(r,\overline{\rho},T) \,. \qquad (14)$$

It is found that $\alpha < 1$ when $\xi \le r_{\max}$, whereas $\alpha = 1$ when $\xi \ge r_{\max}$.

We have calculated the bulk viscosity of liquid argon at temperatures close to the critical point or higher and also in the neighborhood of the triple point by using formula (13) with the D values available from the literature. In both cases, the Lennard-Jones potential is employed for the potential function $v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where the well depth ϵ is taken to be $\epsilon/k_B = 119.8$ K, k_B is the Boltzmann constant, and $\sigma = 3.405$ Å. The equilibrium PCF is obtained from the Percus-Yevick integral equation, which was numerically solved.

In the region of temperature near or beyond the critical point ($T \ge 130$ K), the range of density fluctuations 2ξ is assumed to be comparable to or larger than $r_{\max}$. Thus $\alpha = 1$ is taken in the formula (14) to be used for computing the bulk viscosity. *Therefore in this case there is no adjustable parameter other than the potential parameters* which are taken with the values used in the literature. The numerical results so calculated with Eqs. (13) and (14) are compared with the experimental values reported in the literature in Fig. 1. For this calculation, we have used the values of D by using a formula obtained by fitting the experimental values of Naghizadeh and Rice [20] to an analytical form. We have also used the formula for D proposed by Heyes [21] who obtained it by fitting his simulation data [Eq. (4) of Ref. [21]]. In Fig. 1(a), the temperature dependence of the bulk viscosity is presented for argon around the critical point. The solid curve in Fig. 1(a) is the prediction with the values of the experimental D reported in Ref. [20], and the broken curve is the prediction with D obtained from the Heyes formula [21]. The filled circles are the experimental values reported in Ref. [3]. In Fig. 1(b), the density dependence of the bulk viscosity is presented at $T = 234.5$ K. It is the only temperature for the case of $\xi \ge r_{\max}$ for which the experimental density dependence is available. The solid line is the prediction by the present theory, whereas the double concentric circles are the experimental values in Ref. [4]. The broken curve is the prediction with the values of D given by the Heyes formula. It is remarkable that Eq. (13) is in qualitative and quantitative agreement with experiment with $\alpha = 1$, i.e., without an adjustable parameter, in this case.

In the neighborhood of the triple point, the range of density fluctuations was found to be much less than the intermolecular force range. We found the value of ξ is in the neighborhood of 2σ, which corresponds to $\alpha = 0.21$. With this value of α inserted in Eq. (14) for $\omega(\rho,T)$, the bulk viscosities are calculated from Eq. (13). In Fig. 2(a), the temperature dependence of η_b at $\rho = 1.408$ g/cm^3

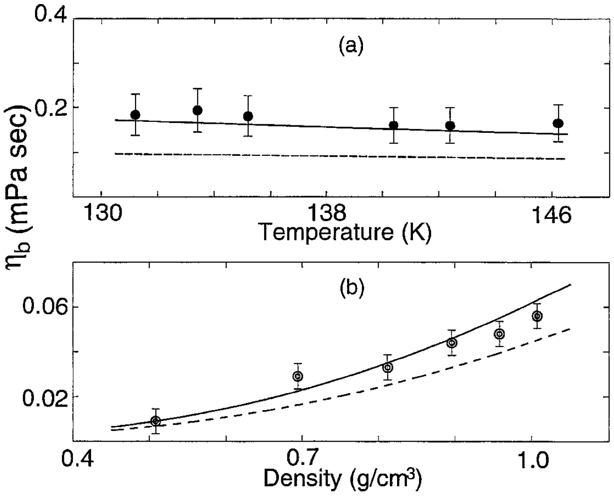

FIG. 1. (a) η_b vs temperature at $\rho = 1.062$ g/cm^3 for argon near the critical temperature. Solid curve: η_b calculated with $D_{\rm NR}$ (D calculated from a formula fitted to the Naghizadeh-Rice data [20]). Broken curve: η_b calculated with the Heyes formula [21] for D. (b) η_b vs density at $T = 234$ K for argon. Solid curve: the present theory; double concentric circles: experimental data in Ref. [4]. The values of D are calculated from the formula for $D_{\rm NR}$. $\alpha = 1$ for the theoretical η_b in the present comparison.

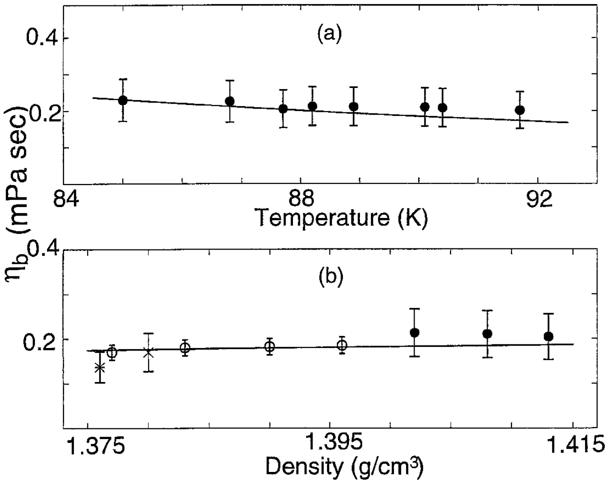

FIG. 2. (a) η_b vs temperature at $\rho = 1.408$ g/cm^3 for argon near the triple point. Solid circles: the experimental values in Ref. [3]; solid curve: the present theory with D computed from D_{NR}. (b) η_b vs density at $T = 90$ K for argon computed with D_{NR}. The symbols are $*$ (Ref. [7]), $\times$ (Ref. [2]), ○ (Ref. [6]), and ● (Ref. [3]). $\alpha = 0.21$ for the theoretical η_b.

is presented in comparison with the experimental values (closed circles) reported in Ref. [3]. In Fig. 2(b), the density dependence of η_b at $T = 90$ K is presented in comparison with experimental data reported in Ref. [7] (asterisks), Ref. [2] (crosses), Ref. [6] (open circles), and Ref. [3] (closed circles). For both sets of η_b values calculated, we have used the D values obtained from the formula fitted to the data of D reported in Ref. [20]. Since the Heyes formula for D is less satisfactory at high ρ and low T, it was not used for the purpose of comparison made in Figs. 2(a) and 2(b). With a single parameter value of α, Eq. (13) predicts η_b in good agreement with experiment with regard to the ρ and T dependence.

We have not made comparison with the molecular dynamics (MD) simulation results [13], which have been obtained from the Kubo formula, since, when compared with experiments, they are off the experimental values by 14%-140% according to the values reported by Borgelt *et al.* [13]. Analysis [12] of the MD simulations mentioned shows that they suffer from the presence of a long-time tail in the autocorrelation function, which seems to make accurate evaluation of η_b rather difficult. Therefore the present theoretical result raises a new hope for studying bulk viscosity, a rather difficult quantity to compute in a good accuracy.

In conclusion, in this Letter we have presented an analog of the Stokes-Einstein relation for the bulk viscosity of a simple fluid, which is derived by means of statistical mechanics. The formula predicts the bulk viscosity in the temperature range above 130 K in agreement with experiment without an adjustable parameter. As the temperature approaches the triple point, a cutoff parameter is required, but with a single choice of parameter α multiplying the integral for $\omega(\rho, T)$ instead of the cutoff parameters, the bulk viscosity computed by the present theory agrees with experiment with regard to the density and temperature dependence. Therefore the bulk viscosity analog of the Stokes-Einstein relation presented appears to be of practical utility for calculating the bulk viscosity of simple fluids, because it is so simple.

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