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Theoretical evaluation of bulk viscosity: Expression for relaxation time

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A theoretical calculation of bulk viscosity has been carried out by deriving an expression for the relaxation time which appears in the formula for bulk viscosity derived by Okumura and Yonezawa. The expression involved a pair distribution function and interaction potential. Numerical results have been obtained over a wide range of densities and temperatures for Lennard-Jones fluids. It is found that our results provide a good description of bulk viscosity as has been judged by comparing the results with nonequilibrium molecular dynamics results. In addition, our results demonstrate the importance of the multiparticle correlation function.

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I. INTRODUCTION

Shear viscosity is a well-studied transport coefficient and describes the irreversible resistance of a fluid to shearing forces. However, bulk viscosity, measuring the irreversible resistance of the fluid to dilatational—i.e., volume-changing forces—has drawn comparatively less attention. Bulk viscosity can be considered as a measure of resistance offered by a medium subjected to the forces of compression or expansion. It is one of the parameters which appear in the constitutive equation of the hydrodynamics or in the Navier-Stokes equation and hence is an important parameter describing the kinetics of fluids. It plays a significant role in investigating acoustics on microscopic grounds [1,2], in understanding the intermolecular forces of attraction, and investigating the dynamical structure factor, a quantity which is directly measurable in neutron diffraction experiments. Nevertheless, there exist [3–6] some estimates for the bulk viscosity of various liquids, which encourages one to study this quantity using a microscopic approach. Microscopically, one can study bulk viscosity by the Green-Kubo method which expresses it [7] as a time integral of the bulk stress-time autocorrelation function.

Another equivalent approach to calculate bulk viscosity is through the evaluation of longitudinal and shear viscosity by exploiting the relation $\eta_B = \eta_l - 4/3\,\eta_s$, where η_B, η_l, and η_s are, respectively, bulk, longitudinal, and shear viscosities. The longitudinal and shear viscosities can be estimated through knowledge of the time development of longitudinal and transverse stress autocorrelation functions. For dilute gases, the bulk viscosity becomes zero whereas for the dense fluid its magnitude is comparable to that of shear viscosity as shown in our previous paper [8].

In principle, there are three different routes to estimate the bulk viscosity: (i) experiment, (ii) computer simulation, and (iii) direct calculation. However, in practice, experimental determination of bulk viscosity is difficult and can only be accomplished indirectly through sound attenuation measurements. For the second route, recently, Okumora and Yonezawa [9] derived an approximate formula for the calculation of bulk viscosity. In this paper, a method which employs this formula for direct calculation (the third route) of this parameter has been proposed.

The formula proposed directly involves the pair correlation function $g(r)$, density derivative of $g(r)$, and interaction potential. In addition, it involves relaxation time. Until now, there exists no theoretical way to calculate this relaxation time. In this paper, an attempt has been made to calculate the relaxation time based on microscopic considerations. The numerical calculations for bulk viscosity from this formula have been carried out for Lennard-Jones (LJ) fluids over a wide range of densities and temperatures. Results have been compared with those obtained by nonequilibrium molecular dynamics (MD) simulations [10] and the Green-Kubo method. It has been found that our results for bulk viscosity are in very good agreement with both.

The layout of the paper is as follows. In the next section we briefly present the formula derived by Okumura and Yonezawa. In Sec. III the expression for the relaxation time is presented. Section IV contains the result and discussion. The summary and conclusion are given in Sec. V.

II. THEORY: APPROXIMATE FORMULA FOR BULK VISCOSITY

Recently, Okumura and Yonezawa [9] derived an approximate formula for the calculation of bulk viscosity which we present it briefly here. The bulk viscosity η_B is defined as

$$\bar{P} - P = -\eta_B \frac{\dot{V}}{V}, \tag{1}$$

where $\bar{P}$ is the pressure in a fluid being compressed or expanded, P is the pressure at constant volume, and $\frac{\dot{V}}{V}$ is the volume-changing rate. Using the virial definition, $\bar{P}$ can be as written as

$$\bar{P} = \frac{Nk_BT}{V} - \frac{n^2}{6}\int_0^\infty r\frac{du(r)}{dr} g(r,t) 4\pi r^2 dr. \tag{2}$$

Here it may be noted that the nonequilibrium pair distribution function $g(r,t)$ is a function of the distance r as well as time t. During compression, $g(r,t)$ is also compressed. For example, the peak position of nonequilibrium $g(r,t)$ is shifted towards smaller r. The equilibrium distribution function is treated as a function of r, volume per particle, ν $(=V/N)$, and entropy per particle, s, and is represented by $g_0(r,\nu,s)$. Thus the equilibrium pressure P is calculated using $g_0(r,\nu,s)$ from the following equation:

$$P=\frac{Nk_BT}{V}-\frac{n^2}{6}\int_0^\infty r\frac{du(r)}{dr}g_0(r,\nu,s)4\pi r^2dr. \tag{3}$$

In cases where the relaxation of $g(r,t)$ could not be described by a single relaxation time, the treatment of the relaxation becomes more complicated. However, the Debye relaxation is the simplest type of relaxation and is widely used as an appropriate approximation [2,11]. The time evolution of $g(r,t)$ in the course of compression is given as

$$\left(\frac{\partial}{\partial t}g(r,t)\right)_r=-\frac{\dot{L}}{L}r\left(\frac{\partial}{\partial r}g(r,t)\right)_t-\frac{1}{\tau}[g(r,t)-g_0(r,\nu(t),s(t))]. \tag{4}$$

In the above equation, $L=(V)^{1/3}$ and τ is the relaxation time of $g(r,t)$. This equation is most important step for achieving our formula of the bulk viscosity. The pressure $\bar{P}$ during compression is determined using $g(r,t)$ as

$$\bar{P}=\frac{Nk_BT'}{V}-\frac{n^2}{6}\int_0^\infty r\frac{du(r)}{dr}g(r,t)4\pi r^2dr. \tag{5}$$

In the above equation, T' is the temperature during compression which is given as

$$T'=T+\frac{n}{3k_BT}\tau\frac{\dot{L}}{L}\int_0^\infty u(r)\left[r\left(\frac{\partial}{\partial r}g_0(r,\nu,s)\right)+3\nu\left(\frac{\partial}{\partial \nu}g_0(r,\nu,s)\right)_{r,s}\right]4\pi r^2dr. \tag{6}$$

By inserting Eqs. (5) and (3) into Eq. (1) and making use of Eq. (6), the approximate formula for bulk viscosity is given as

$$\eta_B=-\frac{n^2}{18}\tau\int_0^\infty\left(r\frac{du}{dr}+2u(r)\right)\left[r\left(\frac{\partial}{\partial r}g_0(r,\nu,s)\right)_{\nu,s}+3\nu\left(\frac{\partial}{\partial \nu}g_0(r,\nu,s)\right)_{r,s}\right]4\pi r^2dr. \tag{7}$$

This formula expresses the bulk viscosity, using the microscopic information of $u(r)$ and $g_0(r,\nu,s)$. Here, it may be noted that the above formula involves a density derivative of the pair distribution function and hence also includes the effect of multiparticle correlation functions. Further, it can also be observed that the above formula involves a single relaxation time as a multiplier and, therefore, is different from Mori's memory function approach. However, it has the advantage that the method can safely be applied to two-dimensional systems as it avoids the logarithmic divergence. Moreover, computer simulation results of this formula are similar to those obtained by Malbrunot *et al.* [12], Hoover *et al.* [13] and also by Heyes [10]. To make it more useful for theoretical calculations, we need to know the relaxation time and density dependence of $g(r)$. In the next section we propose a method to calculate the relaxation time.

III. EXPRESSION FOR THE RELAXATION TIME

The equation which describes the relaxation time in Eq. (7) is given as

$$\tau=\int_0^\infty\frac{\Delta P(t)}{\Delta P(+0)}dt, \tag{8}$$

where $\Delta P(t)=P(t)-P(\infty)$, $P(\infty)$ is the equilibrium pressure. In fact, it refers to the manner in which $P(t)$ approaches equilibrium pressure. We assume that the decay of $\Delta P(t)$ is Gaussian, such that

$$\Delta VP(t)=\Delta VP(0)e^{-t^2/2\tau'^2}. \tag{9}$$

Therefore, Eq. (8) can be written as

$$\tau=\int_0^\infty\frac{\Delta VP(t)}{\Delta VP(0)}dt=\int_0^\infty e^{-t^2/2\tau'^2}dt. \tag{10}$$

Thus the relaxation time is obtained to be

$$\tau=\sqrt{\frac{\pi}{2}}\tau'. \tag{11}$$

We propose [14] to calculate τ' from the second time derivative of the correlation of displacement and force exerted by particle at a given time, normalized to idealized pressure. To obtain expression for τ' we use

$$P(t)V=\langle r_i(t)F_i(0)\rangle. \tag{12}$$

By comparing the Taylor expansion of the Eq. (12) with that of Eq. (9) the expression for τ' can be obtained and is given as

$$\tau'^{-2}=\frac{1}{k_BT}\frac{d^2}{dt^2}\langle r_i(t)F_i(t)\rangle|_{t=0}. \tag{13}$$

Thus, time τ in Eq. (8) is not different from that in Eq. (12). Following the definition of F_i,

$$F_i=-\nabla_iU(r), \tag{14}$$

and of $\ddot{F}_{i\alpha}$,

$$\ddot{F}_{i\alpha}=-\left(\frac{\partial^3U(r)}{\partial r_{i\alpha}\,\partial r_{j\alpha}\,\partial r_{j'\alpha}}v_{j\alpha}v_{j'\alpha}+\frac{\partial^2U(r)}{\partial r_{i\alpha}\,\partial r_{j\alpha}}\dot{V}_{j\alpha}\right), \tag{15}$$

and making use of the Yvon theorem, we obtain a relevant expression from which, on carrying out angular integration, one obtains

TABLE I. The analysis of two contributions C_1 and C_2 (in units of ϵ/σ^6) appearing in the definition of viscosity at various densities ($n^\star$) and temperatures ($T^\star$). C_1 and C_2 are defined in Eqs. (18) and (19). The contribution C_2 representing the multiparticle contribution.

T^*	n^*	C_1	$-C_2$	C_1+C_2	100 C_2/C_1
0.71	0.800	29	8.6	21.4	30.0
0.700	0.844	33	11.0	22.0	34.1
0.72	0.884	40	16.0	24.0	40.0
0.73	0.928	48	22.0	26.0	46
1.23	0.419	7.09	0.17	6.92	2.4
1.25	0.500	10.32	0.7	9.61	6
1.19	0.584	14.6	1.6	13.0	11
1.28	0.600	16.0	2.17	13.83	13.5
1.16	0.844	41.8	15.0	26.8	35
1.21	0.966	69	34.0	35	49
1.81	0.400	6.8	0.4	6.4	5
1.83	0.500	11.4	1.17	10.23	10.2
1.81	0.700	27.5	6.5	21	23
1.84	0.743	33	9.0	24	27
1.90	0.801	42	13.5	28.5	32
1.88	0.966	79	37.0	42.0	46.7
2.47	0.450	9.62	0.94	8.68	9.8
2.48	0.500	12.4	1.52	10.88	12.2
2.5	0.600	19	3.50	10.5	18
2.56	0.743	36	10.03	26	28
2.5	0.803	45	15.06	29.94	30.8
2.53	0.909	68.6	28.71	39.9	42
3.46	0.400	7.8	0.74	7.06	9.4
3.46	0.500	13.5	1.88	11.62	14
3.41	0.600	21.5	4.18	17.32	19.4
3.5	0.700	32.8	8.50	24.3	24
3.54	0.803	49	16.61	32.4	34
3.48	0.909	72.5	30.50	42.0	42

TABLE II. Values of relaxation time τ as given by Eqs. (11) and (16) in units of $\sqrt{m\sigma^2/\epsilon}$ and η_B and η_B(MD) in units of $\sigma^2/\sqrt{m\epsilon}$ for LJ fluids for few densities and temperatures.

T^*	n^*	τ	η_B	η_B(MD)
0.71	0.800	0.058	1.18	1.34
0.700	0.844	0.055	1.21	1.47
0.72	0.884	0.051	1.23	1.19 (1.09) [16](1.20)[9]
0.73	0.928	0.047	1.25	1.56
1.23	0.419	0.084	0.58	0.36
1.25	0.500	0.076	0.73	
1.19	0.584	0.070	0.88	0.78
1.28	0.600	0.067	0.91	0.801
1.16	0.844	0.047	1.30	1.50
1.21	0.966	0.040	1.37	1.83

$$\tau'^{-2} = \frac{8\pi n}{3m}\int_0^\infty g(r) r^2\left[\frac{d^2u(r)}{dr^2} + \frac{2}{r}\frac{du(r)}{dr}\right]dr. \qquad (16)$$

Numerically evaluating τ' and after inserting the results into Eq. (11), the bulk viscosity is obtained from Eq. (7) in the next section.

IV. CALCULATIONS AND RESULTS

In order to calculate the bulk viscosity from Eq. (7) and relaxation time from Eq. (16), we require the pair potential, equilibrium distribution function $g(r)$ and its density derivative. For pair potential we make use of Lennard-Jones potential defined as

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \qquad (17)$$

where ϵ and σ are two parameters of the LJ potential.

For the equilibrium distribution function we use theory of Sung and Chandler [15] based on optimized cluster theory. For the purpose of calculation of the effect of two parts of formula (7) of bulk viscosity, we write these two integrals separately as

$$C_1 = -\frac{n^2}{18}\int_0^\infty\left(r\frac{du(r)}{dr} + 2u(r)\right) r\frac{\partial}{\partial r}g(r) \qquad (18)$$

and

$$C_2 = +\frac{n^3}{6}\int_0^\infty\left(r\frac{du(r)}{dr} + 2u(r)\right)\frac{\partial}{\partial n}g(r). \qquad (19)$$

In order to obtain the density derivative of the equilibrium distribution function we have used a five-point differential formula. The $g(r)$ was calculated for different densities with $\Delta n^* = 0.005$. For evaluating the integrals, we have used the Gauss quadrature method. The values thus obtained for C_1 and C_2 are given in Table I for various reduced densities $n^\star$ ($=n\sigma^3$) and temperatures $T^\star$ ($=k_BT/\epsilon$).

It can be seen from Table I that C_1 is positive whereas C_2 is negative. It is further seen that both C_1 and $-C_2$ increase with an increase in density and temperature. Here it may be noted that C_1 and C_2 do not involve temperature explicitly. The temperature dependence of C_1 and C_2 is only through the dependence of $g(r)$ on temperature. C_2 involves the density derivative of $g(r)$, implying that it also contains the effect of the higher-order static correlation function. The increase of C_2/C_1 with density may imply that the role of triplet correlation increases with an increase in density. It can also be seen from Table I that C_1+C_2 increases with an increase in density and an increase in temperature.

The values of relaxation time $\tau^\star$ ($=\tau\sqrt{\epsilon/m\sigma^2}$) obtained from Eqs. (16) and (11) are given in Table II. It is seen that $\tau^\star$ decreases with an increase in density and an increase in temperature. From the values of $\tau^\star$ it can be seen that with an increase in temperature, $\Delta VP(t)$ decays faster. On the other hand, it decays slower with a decrease in density at a given temperature.

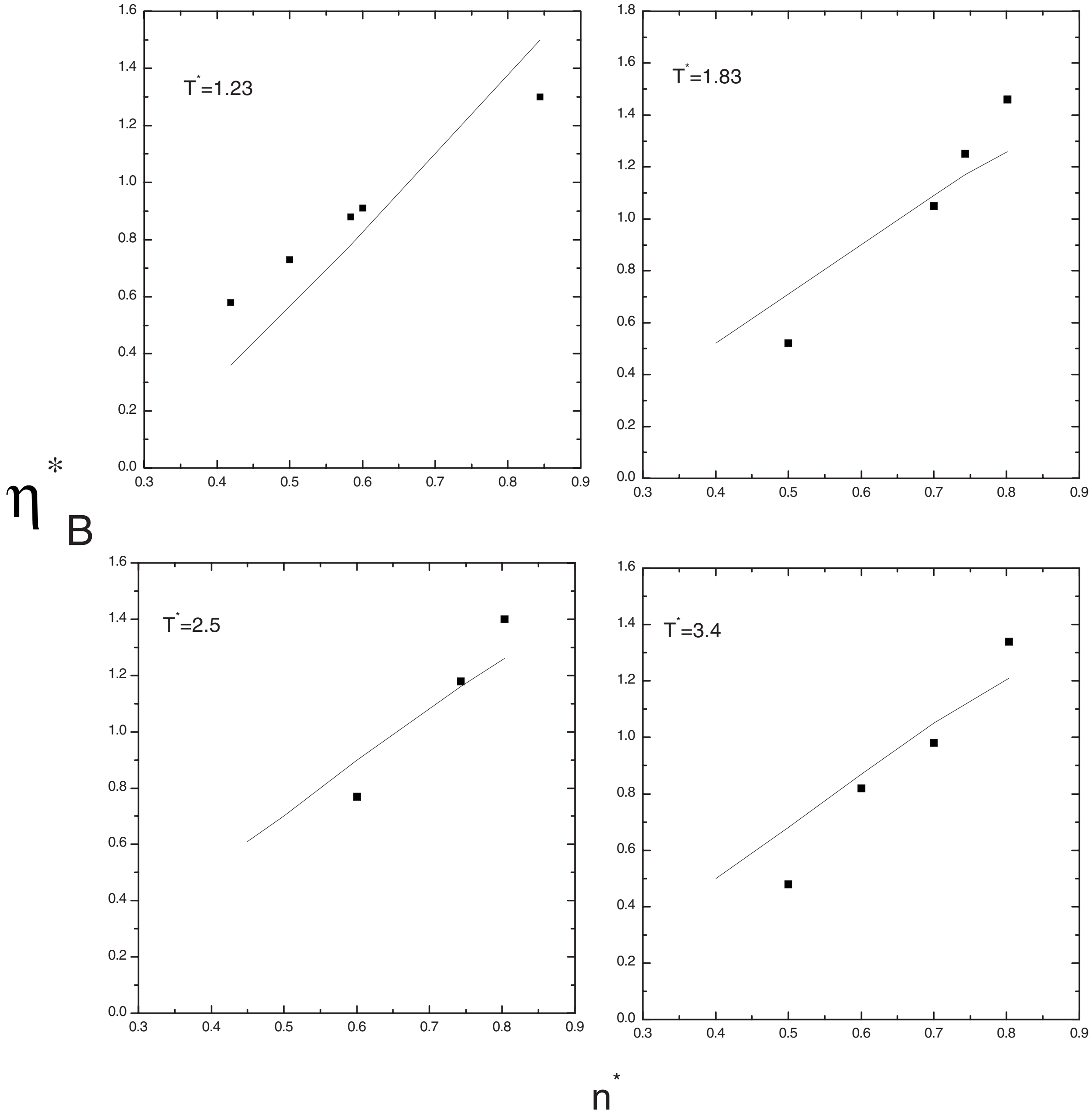

FIG. 1. Variation in the bulk viscosity $\eta_B^\star$ $(=\eta_B\sigma^2/\sqrt{m\epsilon})$ with reduced density n^* at various temperatures. Solid lines are our results, and solid squares are results of MD simulations of Heyes [10].

The results obtained for $\eta_B^\star$ $(=\eta_B\sigma^2/\sqrt{m\epsilon})$ are given in Table II along with $\eta^\star$(MD) representing nonequilibrium molecular dynamics values of Heyes [10]. The Green-Kubo value for bulk viscosity [16] and the value obtained by Okumura and Yonezawa [9] are also shown at the triple point in Table II. The results for bulk viscosity are shown in Fig. 1, where the solid line represents our results and solid squares represent MD results of Heyes [10]. It can be seen from the figure that our method provides results which are in good agreement with simulation results for Lennard-Jones fluids.

V. SUMMARY AND CONCLUSION

We have proposed a method for the theoretical calculation of bulk viscosity from a formula proposed by Okumura and Yonezawa. This formula includes the interaction potential, density, and distance derivatives of the pair distribution function and relaxation time. Since theoretical evaluation of the relaxation time was not known yet, therefore we have proposed a method based on microscopic considerations to calculate the relaxation time. The expression of relaxation time has also been numerically calculated. We have obtained bulk viscosity of Lennard-Jones fluids for a wide range of densities and temperatures. The results obtained from our method have been compared with nonequilibrium molecular dynamic simulation of Heyes [10] and at a triple point with results of Okumura and Yonezawa [9] and the Green-Kubo method. It is a found that our method provides a good description of bulk viscosity as has been judged by a comparison of the results.

[1] H. Kohno and M. Yao, J. Phys.: Condens. Matter **11**, 5399 (1999).

[2] H. Kohno, K. Okado, Y. Kajihara, Y. Hiejima, and M. Yao, J. Non-Cryst. Solids **250-252**, 139 (1999).

[3] N. H. March and M. P. Tosi, *Introduction to Liquid State Physics* (World Scientific, Singapore, 2002).

[4] J. Levesque, L. Verlet, and J. Kurkijarvi, Phys. Rev. A **7**, 1690 (1973).

[5] A. V. Narasimham, Can. J. Phys. **45**, 3925 (1967).

[6] A. V. Narasimham, Indian J. Pure Appl. Phys. **31**, 281 (1993).

[7] D. A. McQuaire, *Statistical Mechanics* (Harper and Row, New York, 1976).

[8] A. H. Zaheri, S. Srivastava, and K. Tankeshwar, J. Phys.: Condens. Matter **15**, 6683 (2003).

[9] H. Okumura and F. Yonezawa, J. Chem. Phys. **116**, 7400 (2002).

[10] D. M. Heyes, J. Chem. Soc., Faraday Trans. 2 **80**, 1363 (1984).

[11] B. Y. Baharudim, D. A. Jackson, and P. E. Schoen, Phys. Lett. **51A**, 409 (1975).

[12] P. Malbrunot, A. Boyer, E. Charles, and H. Abachi, Phys. Rev. A **27**, 1523 (1983).

[13] W. G. Hoover, A. J. C. Ladd, R. B. Hickman, and B. L. Holian, Phys. Rev. A **21**, 1756 (1980).

[14] N. K. Ailawadi and R. Bansal, Phys. Rev. A **18**, 1717 (1978).

[15] S. Sung and D. Chandler, J. Chem. Phys. **56**, 4986 (1972).

[16] C. Hoheisel, R. Vogelsang, and M. Schoen, J. Chem. Phys. **87**, 7195 (1987).