

Phenomenological viscous factor in the nonequilibrium distribution function for liquids

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An improved formula of shear viscosity for liquids is presented by introducing a phenomenological viscous factor in the nonequilibrium term in the doublet distribution function, which improves an incomplete formula of shear viscosity presented in an early work of Born and Green. The phenomenological viscous factor effectively counts some higher-order interactions, and is constrained so that, in the limit of hard-sphere liquids, the magnitude of the improved formula of shear viscosity reduces to that of Enskog for dense fluids. The improved formula does not require any adjustable parameters except for the pair potential to describe liquids. In order to verify the improved formula, a liquid of Ar near the triple point is studied in detail. In addition, liquids of Pb in wide ranges of temperature are examined to test the temperature dependence of the phenomenological viscous factor. Here an available integral equation is employed to calculate the radial distribution function by prescribed pair potentials. One finds that the present formula is capable to describe the shear viscosity in accord with those of experimental data for both cases of Ar and Pb. The phenomenological viscous factor plays a crucial role in the evaluation of shear viscosity for liquids.

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I. INTRODUCTION

The transport phenomena of fluids is most important in the nonequilibrium statistical mechanics in aspects of knowing the detail dynamics of molecules in fluids as well as the practical quantities of crystal and noncrystal formations from fluids.

The most well-known formulation of the transport phenomena by means of statistical mechanics called kinetic theory is based on a formalism of the singlet distribution function of the Chapman-Enskog method [1], by which one may evaluate the transport coefficients of diffusion, viscous flow, and thermal conductivity independently. In the framework of the Chapman-Enskog method, formulas of the transport coefficients for dense fluids, being assumed as the hard-sphere constituents, were firstly derived by Enskog [1], and, up to present, considerable efforts have been devoted to extending it to realistic dense fluids. In a recent work [2] along this line, the pair potential to describe a realistic dense fluid is approximated as superposition of the square-well potentials, which enables one to directly use the Chapman-Enskog method. The theoretical evaluation performed in [2] for the transport coefficients of liquid Ar shows good agreement with the results of experimental data and computer simulations. In this evaluation, however, some adjustable parameters except for the pair potential to describe liquid Ar are involved.

On the other hand, by generalizing the work of Kirkwood and co-workers [3], Rice and Allnatt (RA) [4,5] obtained more complete equations, involving the Brownian motion, for the transport coefficients of a realistic dense fluid. The RA theory treats the singlet and doublet distribution functions, and truncates the higher-order terms in the so-called Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy [6], by adopting a generalized superposition approximation [4] for the triplet distribution function. From the RA theory, one may, in principle, evaluate all the transport coef-

ficients without any adjustable parameters except for the pair potential to describe a realistic dense fluid. However, due to the difficulty in evaluation for the friction constant, they had to use experimental diffusion data in order to obtain the other transport coefficients. Their results [5] showed overall agreement with the experiments, existing at that time, for the transport coefficients of shear and bulk viscosities and thermal conductivity of liquid Ar. Since then, there appeared a report of a precise experiment [7] for the bulk viscosity, and also a critical comparison [8] for the RA theory with accurate computer simulations for the shear viscosity and the thermal conductivity. Unfortunately, these works indicate that the RA theory is not suitable to use for predictions of transport coefficients for dense fluids. One ought to seek, therefore, an alternative approach to describe the transport phenomena for dense fluids.

One of the alternative approaches for the transport phenomena would be the one based on the time-dependent correlation functions [9], which has been developed by guidance of computer simulations. Following such an approach, one may describe detail dynamics of molecules in a fluid such as the autocorrelation functions, from which one may evaluate transport coefficients in a certain limit. One would thus expect to evaluate reasonably accurate transport coefficients for various liquids by such an approach. However, we do not follow such an approach. Rather, we revive an early work [10] of Born and Green (BG) for the following reasons. Firstly, although there was a caution [11] (see the next paragraph) to use the BG formula of shear viscosity presented in [10], it was known that the temperature dependences of shear viscosity evaluated by the BG formula were in accord with experimental data for some various liquid metals [12]. Secondly, in the limit of hard-sphere liquids, the BG formula of shear viscosity reduces to that of Enskog with a constant factor, so that the BG formula may be regarded as a simply generalized Enskog formula extended to a realistic dense fluid. Thirdly, as we shall see in the next section, the BG

formula of shear viscosity is written in a quite simple form, so that, along the BG approach, one may expect to deduce practical formulas of the transport coefficients for various liquids.

The BG approach was developed in parallel, but in a different manner, with that of Kirkwood and co-workers [3]. The most essential difference between these approaches is in consideration for the Brownian motion. The approach of Kirkwood and co-workers [3] directly connected the equation of the Brownian motion, which eventually enables one to evaluate the transport coefficients in a certain approximation without any adjustable parameters except for the pair potential. On the other hand, the BG approach did not directly involve the equation of the Brownian motion, but extended the Chapman-Enskog method in a straightforward manner to a dense fluid. Namely, they assumed a form of the doublet distribution function analogous to that of the singlet distribution function as in the Chapman-Enskog method. Unlike the case of the singlet distribution function, a unknown quantity, being implemented in the nonequilibrium term relevant to the shear viscosity in the doublet distribution function, could not be solved. Thus, the BG formula of shear viscosity was derived from a dimensional analysis [11] for the term proportional to the nondivergent rate of strain tensor in the nonequilibrium term in the doublet distribution function, so that this formula involves one unknown quantity.

Recently, the BG formula of shear viscosity was employed [13] to speculate features of the pair potentials for liquid metals by using the experimental data for shear viscosity and radial distribution function (RDF). There the unknown quantity of the BG formula was regarded as a parameter to fit the experimental viscosities. Although within a limited analysis, using prescribed potential forms for liquid metals, the overall results obtained for some various liquid metals could explain the characteristics, such that the feature of the pair potential becomes longer ranged according to increase of the valence electrons of an atom in a liquid. It was noticed that the overall variations of the unknown quantity for the liquid metals are relatively small, and yet possess some regularity, which indicates that the unknown quantity may be replaced by some physical quantity.

In the present paper, we shall determine the unknown quantity in the BG formula of shear viscosity for liquids in a phenomenological manner as follows: It is known [14] that, for fluids of relatively lower density than that of a liquid, the shear viscosities evaluated by the Enskog formula agree with those obtained by computer simulations. Therefore, firstly, we constrain the unknown quantity so that, in the limit of hard-sphere liquids, the magnitude of the BG formula of shear viscosity reduces to that of Enskog. Secondly, without disturbing the above constraint, we implement an averaged cross section of momentum transfer of molecules for the unknown quantity, which would bring some viscous effect arising from higher order of interactions of molecules into the BG formula. Let us call the factor so determined as a phenomenological viscous factor, by which we are able to obtain an improved formula of shear viscosity for liquids.

Our improved formula for shear viscosity is expressed as an integral of a product of the derivative of pair potential and the RDF, and, thus, the formula does not require any adjust-

able parameters except for the pair potential. In order to verify our improved formula, one needs accurate calculations for the RDF by the pair potential. For this purpose, we shall employ a modified hypernetted chain (MHNC) equation presented in [15], and study a case of liquid Ar in detail, since the characteristics for this liquid are well investigated experimentally as well as theoretically. We shall then proceed to testing our improved formula for shear viscosity for liquid Pb, from which the temperature dependence of the phenomenological viscous factor may be verified.

The layout of this paper is as follows. In Sec. II, our phenomenological viscous factor and improved formula of shear viscosity are presented. The procedure to solve the MHNC equation is described in Sec. III. Then we proceed to Sec. IV for examination of our improved formula for liquid Ar and liquid Pb. There the numerical results are given. Section V is devoted to the summary and discussion.

II. THE PHENOMENOLOGICAL VISCOUS FACTOR

In a classical system of N equivalent molecules, the distribution function for the whole system at time t is defined by N position vectors and N momentum vectors of molecules. Assuming that the molecules are governed only by binary additive interactions, one obtains the BBGKY hierarchy [6]:

$$\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial f_1}{\partial \mathbf{r}_1} = \int \int \frac{\partial \varphi_{21}}{\partial \mathbf{r}_1} \cdot \frac{\partial f_2}{\partial \mathbf{p}_1} d\mathbf{r}_2 d\mathbf{p}_2, \quad (1)$$

where m is the mass of a molecule in the system, $f_1 = f_1(\mathbf{r}_1, \mathbf{p}_1; t)$ and $f_2 = f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2; t)$ are the singlet and doublet distribution functions, respectively, and $\varphi_{21} = \varphi(|\mathbf{r}_2 - \mathbf{r}_1|)$ is a binary interaction between a pair of molecules 1 and 2. The vectors of \mathbf{r} and \mathbf{p} correspond, respectively, to the positions and the momenta of molecules specified by the suffixes. The term in the integral of Eq. (1) connects the higher rank of distribution function, so that the equation for the doublet distribution function associates with an integral of terms connecting the triplelet distribution function by the respective binary interactions. The equation continues until N -molecule distribution function appears in the integral.

The pressure tensor of the system can be obtained [16,17] from Eq. (1) by multiplying with \mathbf{p}_1 and integrating over \mathbf{p}_1 :

$$\mathbf{P} = \int \left(\frac{1}{m} \mathbf{p}_1 \mathbf{p}_1 - m \mathbf{u} \mathbf{u} \right) f_1 d\mathbf{p}_1 - \frac{1}{2} \int \frac{\mathbf{r}_{21} \mathbf{r}_{21}}{r_{21}} \varphi'_{21}(r_{21}) \bar{n}_2(\mathbf{r}_{21}, \mathbf{r}_1; t) d\mathbf{r}_{21}, \quad (2)$$

where \mathbf{u} is the macroscopic velocity of fluid defined by

$$\mathbf{u} = \mathbf{u}(\mathbf{r}_1; t) = \frac{1}{n_1 m} \int \mathbf{p}_1 f_1(\mathbf{r}_1, \mathbf{p}_1; t) d\mathbf{p}_1 \quad (3)$$

with

$$n_1 = n_1(\mathbf{r}_1; t) = \int f_1(\mathbf{r}_1, \mathbf{p}_1; t) d\mathbf{p}_1, \quad (4)$$

r_{21} is the magnitude of $\mathbf{r}_{21} = \mathbf{r}_2 - \mathbf{r}_1$, and φ'_{21} is the first derivative concerning r_{21} . Here $\bar{n}_2(\mathbf{r}_{21}, (\mathbf{r}_1 + \mathbf{r}_2)/2; t) \equiv n_2(\mathbf{r}_1, \mathbf{r}_2; t)$:

$$n_2(\mathbf{r}_1, \mathbf{r}_2; t) = \iint f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2; t) d\mathbf{p}_1 d\mathbf{p}_2 \quad (5)$$

and the term in the last integral of Eq. (2) is obtained by a Taylor's expansion for \bar{n}_2 concerning the coordinate of the center of mass around \mathbf{r}_1 (see [17]).

By assuming certain forms for f_1 and \bar{n}_2 in the integrals of Eq. (2), one may obtain a formula of shear viscosity. The first integral of Eq. (2) is called the kinetic contribution governed by the singlet distribution function which is affected by some distortion due to the binary interaction. The second integral of Eq. (2) is called the potential contribution that dominates over the first one in high density fluids like liquids, so that we ignore the first one. In order to obtain a formula of shear viscosity for liquids, let us follow the procedure of Born and Green [10,17], assuming a form of nonequilibrium term in the doublet distribution function as

$$\bar{n}_2 = n_1^2 g(r_{21}) f_s a_s r_{21} \hat{\mathbf{r}}_{21} \cdot \frac{\partial}{\partial \mathbf{r}_1} \mathbf{u} \cdot \hat{\mathbf{r}}_{21}, \quad (6)$$

where $\hat{\mathbf{r}}_{21} = \mathbf{r}_{21}/r_{21}$, $g(r_{21})$ is the equilibrium RDF of a pair of molecules 1 and 2, and $(\partial/\partial \mathbf{r}_1)\mathbf{u}$ is the nondivergent rate of strain tensor. For later convenience, $a_s = (4m/\pi kT)^{1/2}$ is chosen, where k and T are the Boltzmann constant and the absolute temperature, respectively, and hence f_s is a nondimensional quantity. Substituting Eq. (6) into the second integral of Eq. (2), one may obtain a formula of shear viscosity for liquids as

$$\eta_s = f_s \frac{4}{15} \left(\frac{\pi m}{kT} \right)^{1/2} n_1^2 \int_0^\infty \varphi'_{21}(r_{21}) g(r_{21}) r_{21}^4 dr_{21}. \quad (7)$$

Since the unknown quantity f_s still remains in the above formula, this is essentially the same as the one presented in the BG approach [10].

Now let us constrain f_s in the formula (7) so that, in the limit of hard-sphere liquids, the magnitude of this formula reduces to the relevant term in the Enskog formula. By use of the convenient form for the hard-sphere pair potential [18]:

$$\varphi'(r_{21}) = -kT \delta(r_{21} - \sigma_0), \quad (8)$$

where σ_0 and $\delta(r)$ are the diameter of hard-sphere molecule and the Dirac δ function, respectively, we may rewrite the formula (7) as

$$|\eta_s| = f_s \frac{4}{15} (\pi m kT)^{1/2} n_1^2 g(\sigma_0) \sigma_0^4. \quad (9)$$

Since we ignore the kinetic contribution, this formula corresponds to the one in the Enskog formula derived from the collisional momentum transfer of molecular properties (the term with a quantity denoted by ϖ in [19]), which implies

$$f_s \rightarrow 1 \quad (10)$$

in the limit of hard-sphere liquids.

So far, we have not considered any contributions from the higher rank of the hierarchy. Such contributions may be partly taken into account by employing an averaged cross section for momentum transfer of molecules [20] known as $\Omega^{(2,2)}$ in [21] (equivalently $\Omega_{12}^2(2)$ in [1]). Maintaining the constraint given by Eq. (10), we implement this averaged cross section as

$$f_s = \frac{\Omega^{(2,2)}}{[\Omega^{(2,2)}]_{\text{hrdsph}}} \equiv \Omega^{(2,2)*}, \quad (11)$$

where $[\Omega^{(2,2)}]_{\text{hrdsph}}$ is the corresponding hard-sphere values, so that f_s reduces to unit in the limit of hard-sphere liquids. Substituting Eq. (11) into Eq. (7), we obtain an improved formula of shear viscosity for liquids.

Here one notices that the term of the averaged cross section in our formula for shear viscosity for liquids plays an opposite role to that in the ordinary formula for a dilute gas [1]. When the value of this cross section becomes larger, the shear viscosity decreases in the case of a dilute gas and increases in our case. This is due to two independent mechanisms of momentum transport; the former corresponds to the bodily movement of individual molecules through space and the latter to the action of interactions of molecules at a distance. The stronger interaction of molecules increases the shear viscosity in our case. Our formula of shear viscosity counts, therefore, some effect from higher order of interactions of molecules, together with the binary interaction in the integral of Eq. (7) which is originated from an internal force acting on a pair of molecules in a liquid. Except for the role of this cross section in the formula of shear viscosity, the choice of f_s is not unique. For instance, the higher power of the right-hand side of Eq. (11) also satisfies the above constraint. Therefore, our improved formula of shear viscosity must be verified by numerical evaluations.

III. THE INTEGRAL EQUATION

Since there is much work [22,23] on this subject, we only note here some formulas in order to explain our procedure to calculate the RDF by solving the MHNC equation [15]. The integral equation is written in a form

$$\begin{aligned} \ln g(r) = & -\beta \varphi^{\text{eff}}(r) \\ & + \frac{2\pi n}{r} \int_0^\infty [K(|r-t|) - K(|r+t|)] t [g(t) - 1] dt, \end{aligned} \quad (12)$$

and a kernel $K(y)$ of the MHNC equation is given by

$$K(y) = \int_{|y|}^\infty s [-\beta \varphi^{\text{eff}}(s) + g(s) - 1 - \ln g(s)] ds, \quad (13)$$

where $r = r_{21}$, $\beta = 1/kT$, $n = n_1$ for which we implement the number density of a liquid, and $\varphi^{\text{eff}}(r)$ is an effective pair potential defined with the bridge function $b(r)$ as

$$\varphi^{\text{eff}}(r) = \varphi(r) + b(r)/\beta. \quad (14)$$

The case of $b(r)=0$ corresponds to the ordinary hypernetted chain (HNC) equation [23], and the bridge function employed in the MHNC equation is

$$\begin{aligned} b(r) &= -C_{\text{PY}}(r) - 1 - \ln[-C_{\text{PY}}(r)], \quad r < \sigma_0 \\ &= g_{\text{PY}}(r) - 1 - \ln g_{\text{PY}}(r), \quad r > \sigma_0 \end{aligned} \quad (15)$$

where the analytical forms for $C_{\text{PY}}(r)$ and $g_{\text{PY}}(r)$ are given in [24], and σ_0 is treated as a parameter in the MHNC equation, but it does correspond to the diameter of hard-sphere molecule in the Percus and Yevick (PY) model [25]. Instead of this diameter, we use the corresponding packing fraction $f_{\text{PY}} = \pi\sigma_0^3 n/6$ for a parameter of the MHNC equation as in [15]. Let us call this parameter the MHNC parameter.

Our procedure to numerically solve the integral equation (12) is as follows. Taking a form of the RDF as

$$g(r) = \exp\{-\beta[\varphi^{\text{eff}}(r) + v(r)]\}, \quad (16)$$

we seek a self-consistent solution for $v(r)$ by iteration. We start with a trial $v(r)$, and calculate Eq. (12), then determine new input $v^{\text{new}}(r)$ by

$$v^{\text{new}}(r) = \alpha v^{\text{old}}(r) + (1 - \alpha)v^{\text{out}}(r), \quad (17)$$

where $v^{\text{old}}(r)$ is the first input, $v^{\text{out}}(r)$ is the resultant output, and then use $v^{\text{new}}(r)$ for input in the next calculation. Here we employed the empirical value $\alpha=0.95$ [23]. One should choose a trial $v(r)$ reasonably close to the real solution, otherwise the integral equation does not converge. For this purpose, we started from a solution [26] obtained by use of the PY model for the Lennard-Jones potential of the reduced temperature, $T^* = kT/\epsilon = 0.88$, and the reduced number density, $n^* = \sigma^3 n = 0.85$. The tabulated values of this solution at certain points for r are given in [26].

Since the function in the integral in the kernel (13) behaves smoothly, we employ Gauss integration to calculate the kernel. The necessary points for the Gauss integration are interpolated from the input quantity such as the trial $v(r)$ whose coordinates are given at certain points. The kernel so obtained also behaves smoothly, and, thus, we also employ Gauss integration to calculate the integral of Eq. (12). The necessary points for this Gauss integration are interpolated from the obtained kernel. This procedure would make the computational work shorter and easier than the calculation by the Simpson's integration.

In order to test the reliability of the RDF calculated by solving the integral equation (12), one evaluates thermodynamic quantities of the excess internal energy

$$U^{\text{ex}} = 2\pi n N_A \int_0^\infty \varphi(r) g(r) r^2 dr, \quad (18)$$

where N_A is Avogadro's number; the pressure

$$p = nkT - \frac{2\pi}{3} n^2 \int_0^\infty \varphi'(r) g(r) r^3 dr; \quad (19)$$

and the isothermal compressibility; and, then, compare these quantities as well as the feature of the RDF with those ob-

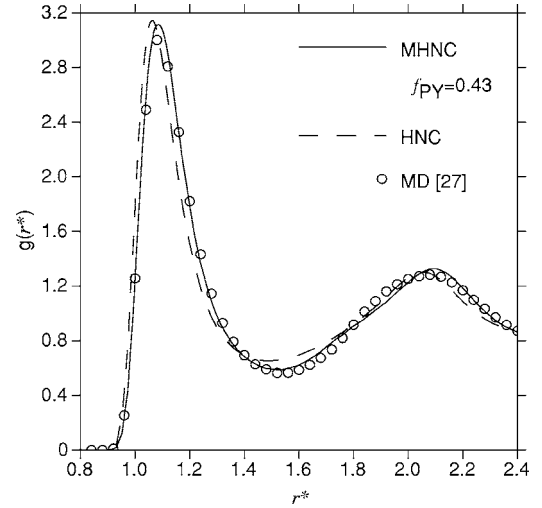


FIG. 1. The radial distribution functions for liquid Ar at 85 K. The Lennard-Jones potential, $T^* = kT/\epsilon = 0.719$ and $n^* = \sigma^3 n = 0.85$, is assumed for liquid Ar near the triple point (see the last paragraph in Sec. III). The solid and broken curves correspond to the results calculated by the MHNC and HNC equations, respectively. The circles are the results obtained by the MD simulation given in [27].

tained by computer simulations. We also follow this procedure, but we do not consider the isothermal compressibility, since an evaluation for this quantity involves some other errors associated with the numerical Fourier transformation of the RDF.

The most suitable liquids for testing our improved formula of shear viscosity presented in Sec. II would be those of Ar, which have been well investigated experimentally as well as theoretically. It is known [27,28] that a liquid of Ar near the triple point ($T=85$ K, $n=0.02125$ Å⁻³) is well described by the Lennard-Jones potential:

$$\varphi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (20)$$

with the potential parameters of $\epsilon=0.0102$ eV and $\sigma=3.42$ Å, corresponding to $T^*=0.719$ and $n^*=0.85$, respectively. The work of [15] showed that the RDF calculated by use of the MHNC parameter of 0.43 gives the thermodynamic quantities as well as the feature of the RDF comparable with those obtained by computer simulations. Therefore, in the next section, we firstly show our RDF calculated by use of the same MHNC parameter as well as the same potential parameters for this liquid, and confirm that our resultant quantities agree with those presented in [15,27].

IV. NUMERICAL RESULTS

By the procedure described in the previous section, we calculated the RDFs by the integral equation (12) for liquid Ar near the triple point. Figure 1 shows our calculated RDFs with the results obtained by a molecular dynamic (MD) simulation [27] (compare with Fig. 14 in [15]). The Table I compares our thermodynamic quantities evaluated by use of our RDF (calculated by the MHNC equation) with the results

TABLE I. The thermodynamic quantities and the shear viscosity for liquid Ar at 85 K.

	$U^{\text{ex}*}$	p^*	η_s (mPa s)
Present	-8.53	0.43	0.23
MD	-8.51	0.36	
	(-8.49)	(0.49)	(0.23)
Experiment			0.28

Here $U^{\text{ex}*} = \beta U^{\text{ex}}/N_A$ and $p^* = \beta p/n$. The corresponding value of $\Omega^{(2,2)*}$ is 1.882. The values in the second line are the results given in [27], whereas those in the third line (in the parentheses) are obtained by use of the radial distribution function interpolated from the one tabulated in [27]. The experimental shear viscosity ($T=84$ K, $n=0.02108 \text{ \AA}^{-3}$) is taken from the Table 1.2 in [29].

of the MD simulation [27]. One sees that our results are comparable with those of [15,27], which confirms the reliability of our procedure to calculate the RDF by the MHNC equation. By use of our RDF calculated for liquid Ar near the triple point, we then evaluated the shear viscosity by our formula (7) presented in Sec. III. The result is also given in the Table I, where one sees that our result is comparable with the experimental one.

We also evaluated the thermodynamic quantities as well as the shear viscosity by use of the RDF interpolated directly from the one tabulated in [27]. The results are also displayed in the Table I, where one notices that, even using the same RDF, our value evaluated for the pressure deviates from the one given in [27]. The reason for this is as follows. Since the sign of the derivative of the pair potential changes at the minimum point, correspondingly around the position of the first peak of the RDF, evaluations for the pressure and the shear viscosity are very sensitive to the relative shapes and positions of the pair potential and the RDF, especially in the inside region of the position of the first peak. The deviation of our value evaluated for the pressure from the one given in [27], even using the same RDF, is due to the error associated with the interpolation from the limited numbers of the points for the RDF tabulated in [27]. As for the shear viscosity, however, the relevant function in the integral possesses the power of r larger by one than that of the pressure [compare Eqs. (7) and (19)], so that the error associated with the interpolation acts less in the evaluation for the shear viscosity than that for the pressure.

Now let us examine the temperature dependence of f_s which is assumed as $\Omega^{(2,2)*}$ in the present work. Figure 2 shows the temperature dependence of f_s for the Lennard-Jones potential (20), where one sees that the variation of f_s for liquid Ar from the melting point of 84 K to the boiling point of 87 K is very small, and it changes only about 2%, so that, in the case of liquid Ar, an obvious examination for the temperature dependence of f_s cannot be expected. On the other hand, there are elaborate experimental data of the RDF and the shear viscosity for liquid metals over wide ranges of temperature [31,32], so that one expects a suitable example among liquid metals for this purpose. Figure 2 also shows such a variation in a case of liquid Pb from 613 K near the melting point to 1173 K, the pair potential of which we explain below.

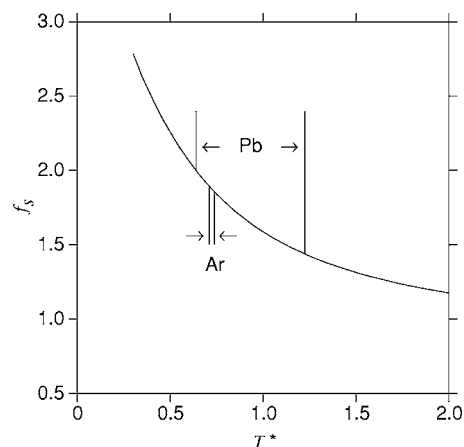


FIG. 2. The temperature dependence of f_s . The solid curve corresponds to f_s assumed as $\Omega^{(2,2)*}$. The values for $\Omega^{(2,2)*}$ are taken from the table in [30]. The regions indicated by the arrows correspond to 84–87 K for liquid Ar and 613–1173 K for liquid Pb. The pair potential for liquid Pb is assumed as the Lennard-Jones potential (see the text).

It is known that, due to the conduction electrons, the pair potentials for liquid metals differ from that of liquid Ar. However, the pair potentials for some liquid metals such as those of Cu and Ag indicate the similar features to that of the Lennard-Jones potential [13,33], which implies that some liquid metals may be described approximately by the Lennard-Jones potential. In order to test the temperature dependence of f_s , we choose liquid Pb, since the crystal structure of Pb is the same fcc as those of Cu and Ag, and the experimental RDF of liquid Pb at 613 K [31] possesses the height of the first peak as well as its oscillation similar to those of liquid Ar near the triple point. Therefore, we start with the RDF of liquid Ar near the triple point regarding as a first trial RDF for liquid Pb at 613 K, and seek the potential parameters, ϵ and σ , for this liquid Pb. Firstly the value of σ may be guessed by shifting the first trial RDF along the r -axis according to the experimental RDF of the liquid Pb, so as to let these RDFs have the same starting (rising) position of the first peak. By use of the value of σ so guessed and the corresponding experimental number density for the liquid Pb, an improved RDF may be calculated by the MHNC equation. The height of the first peak of the improved RDF, however, becomes slightly smaller than that of the first trial RDF. Thus, one adjusts the value of ϵ so as to get the same height of the experimental data. After some small corrections, but keeping $f_{pV}=0.43$, one reaches the RDF of liquid Pb at 613 K as shown in the Fig. 3. The final values of σ and ϵ for liquid Pb at 613 K are displayed in the Table II.

Now let us extend our potential to the regions of higher temperature. When one calculates the RDF at 1173 K by use of the same potential parameters obtained at 613 K, the resultant RDF, comparing with the experimental one, slightly shifts to the outer regions along the r -axis. We remedy this by introducing a temperature dependence in σ as

$$\sigma = \sigma_1 - (T/T_1 - 1)\alpha, \quad (21)$$

where $\sigma_1 = 2.96 \text{ \AA}$, $T_1 = 613 \text{ K}$, and $\alpha = 0.0985$. The pair potential so obtained is, thus, a temperature-dependent poten-

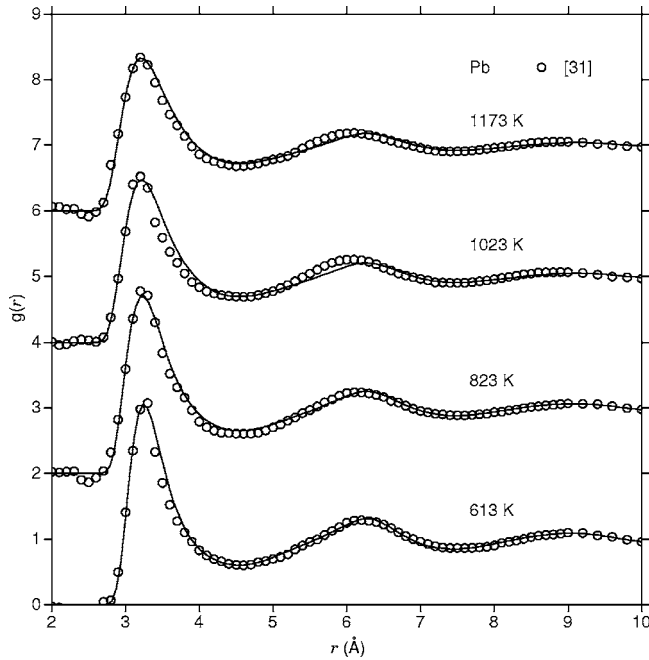


FIG. 3. The radial distribution functions for liquid Pb at four temperatures. The solid curves correspond to the results calculated by the MHNC equation with $f_{PY}=0.43$. The potential parameters for the corresponding temperatures are given in the Table II.

tial, by which we calculated the RDF at three other temperatures where the experimental data for the RDFs of liquid Pb are available. Here we also kept $f_{PY}=0.43$. The results are also shown in Fig. 3, and the potential parameters employed in the calculations are summarized in the Table II. There one can see that the overall features of our RDFs are in accord with those of the experimental data.

Employing our temperature-dependent potential, we calculated the RDFs for liquid Pb at additional ten points of temperature in the region of $T=450\text{--}1300$ K, where we employed an empirical formula of the density of liquid Pb given in [32]. We then evaluated the shear viscosities for liquid Pb by our formula (7) with the resultant RDFs at the corresponding temperatures. Figure 4 shows our results for the shear viscosity comparing with the experimental ones [34,35]. One sees clearly good agreement with the experimental ones, and that, without our f_s , neither the temperature dependence nor magnitude of the shear viscosity can be described.

TABLE II. The potential parameters and the corresponding values of f_s for liquid Pb.

T (K)	n (\AA^{-3})	σ (\AA)	T^*	n^*	$\Omega^{(2,2)*}$
613	0.0310	2.960	0.640	0.804	1.998
823	0.0302	2.926	0.859	0.757	1.715
1023	0.0295	2.894	1.068	0.715	1.536
1173	0.0287	2.870	1.225	0.679	1.438

Here $\epsilon=0.0825$ eV is employed at all the temperatures. The values in the column of n are the experimental data taken from [31], and those in the column of $\Omega^{(2,2)*}$ ($=f_s$) are interpolated from those tabulated in [30].

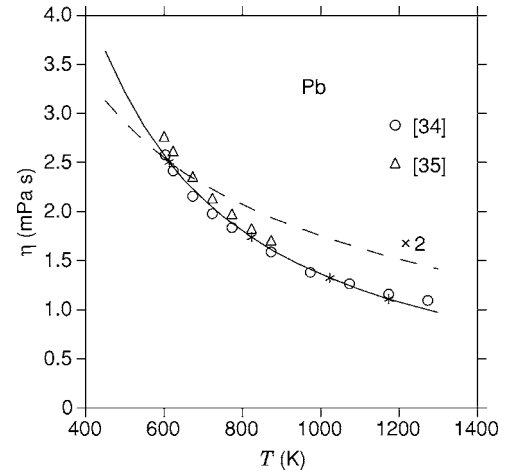


FIG. 4. The shear viscosities for liquid Pb. The solid curve corresponds to our evaluated result, whereas the broken one is two times as large as the result evaluated by setting $f_s=1$ at all temperatures. The points indicated by the asterisks correspond to those evaluated at the temperatures, where our calculated radial distribution functions, together with those of the experimental data, are shown in Fig. 3.

V. SUMMARY AND DISCUSSION

In this paper, we have presented an improved formula of shear viscosity for liquids by introducing a phenomenological viscous factor for the nonequilibrium term in the doublet distribution function. The magnitude of the improved formula is normalized by some factor so that, in the limit of hard-sphere liquids, the formula reduces to that of Enskog for dense fluids. We chose an average cross section of the momentum transfer of molecules for the phenomenological viscous factor, which effectively counts contribution from some higher order of interactions of molecules. This choice is not unique. We verified it by the numerical evaluation for the shear viscosities in the cases of liquid Ar near the triple point and liquid Pb in the wide ranges of temperature. For this purpose, we employed the MHNC equation to calculate reasonably accurate radial distribution functions for the liquids. The results for the shear viscosity as well as those for the radial distribution function are all in good agreement with the experiments. The phenomenological viscous factor plays a crucial role to describe the shear viscosity in aspects of its magnitude and its temperature dependence. Within the approximation of the prescribed Lennard-Jones potentials for the liquids, our present work showed that, consistently with the calculations for the radial distribution functions, one may evaluate the shear viscosity by the presented improved formula which does not require any adjustable parameters to fit any experimental transport coefficients.

In the evaluation for the shear viscosity at each temperature, we used a radial distribution function calculated by the MHNC equation which involves one parameter adjusted to a radial distribution function obtained by computer simulations. We kept the same value for this parameter in all the cases of liquid Pb in the wide ranges of temperature. This may cause some deviations in our calculated radial distribu-

tion functions from those obtained by computer simulations, since the value of this parameter in the MHNC equation slightly depends on temperature and density [36]. However, even considering such a variation of this parameter according to the temperature and density, there are alternative ways to seek pair potentials of liquids, although these would be more complicated than our procedure presented in the pre-

ceding section. The results so obtained would be still the similar to those in the present work.

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