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Bulk viscosity in the case of the interatomic potential depending on density

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We derive a formula for the bulk viscosity ζ in a density-dependent-potential system. This is a generalization of the bulk-viscosity formula for the density-independent-potential system which has been proposed recently by us. In our formulas, the bulk viscosity is expressed by using microscopic quantities such as interatomic potentials and pair distribution functions. This has an outstanding advantage of providing the relation between such microscopic information and a macroscopic quantity ζ. On the other hand, in all formulas proposed previously, ζ is expressed in terms of pressure, a macroscopic quantity, and it is difficult to discuss this relation. We apply our formula to a model liquid metal in which the interatomic potential varies with density. Our calculated results show that ζ increases in the density region where the interatomic potential changes from one type to another. These results agree qualitatively with the experimental results about liquid mercury.

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I. INTRODUCTION

The bulk viscosity ζ of a fluid is related to the difference between the pressure p' under compression or expansion and the pressure p under no volume change; ζ also depends on the compression speed [1]. The bulk viscosity is described as follows. Let us consider two N-particle systems, denoted by 1 and 2. Suppose that system 1 is either compressed or expanded adiabatically, then its volume changes gradually, say, from $V+\delta V/2$ to $V-\delta V/2$ during the time interval δt, where $|\delta V| \ll V$ and δV is either positive or negative depending on whether the system is compressed or expanded. This naturally means that system 1 is in a nonequilibrium state. When the volume becomes exactly V during this volume-changing process, we write the pressure and the total energy of system 1 as p' and E, respectively. We assume that system 2 is in an equilibrium state with a constant volume V and total energy E, which is the same value as that in system 1 when the volume becomes exactly V. We write the pressure in system 2 as p. The bulk viscosity ζ is defined as the coefficient in the linear relation between the volume-changing rate $\dot{V}/V$ in system 1 and the pressure difference $p'-p$ and is expressed as

$$p'-p=-\zeta\dot{V}/V, \tag{1}$$

where $\dot{V}\equiv\lim_{\delta t\to 0}\delta V/\delta t$.

The bulk viscosity ζ is one of the transport coefficients in the constitutive equations of hydrodynamics. Several experimental studies have shown that the bulk viscosity plays an important role in understanding acoustics on the microscopic level [2,3]. As a consequence, it is an interesting task to formulate the macroscopic quantity ζ in terms of microscopic information such as interatomic potentials and atomic pair distribution functions. We have achieved this task recently in the case of interatomic potentials, which are independent of density.

In this paper, we propose the generalized form of this formula to density-dependent-potential systems. The consideration of the density dependence of interatomic potentials becomes important in metallic systems where the existence of mobile electrons inevitably makes interionic potentials density dependent. It must be definitely kept in mind that, when we say, ‘‘interatomic potentials depend on density,’’ this density is by no means the number density n_{atom} of atoms (or to be more precise the number density n_{ion} of ions in the case of a metallic system), but is rather the number density n_e of mobile electrons. Since, in general, $n_e=zn_{\text{atom}}$, z being the valence number, the formulations derived therefrom are often expressed for simplicity in terms of n_{atom} instead of n_e, which occasionally causes a misunderstanding. Though it may sound superfluous to mention this point, we nevertheless feel it worthwhile to emphasize that the origin for the density dependence of interatomic potentials is mobile electrons. The present paper is the first work that evaluates ζ in systems with density-dependent pair potentials.

In all conventional methods proposed in the last century, ζ is expressed in terms of pressure, which is a macroscopic quantity. Among them are included the Green-Kubo formula [4–7], the Heyes method [8,9] and the Hoover *et al.* method [10,11]. On the other hand, our formula demonstrated in a series of papers [12,13] is advantageous as stated in the above in the sense that ζ is directly derived from microscopic quantities such as interatomic potentials. The relationship among these conventional methods and our formula has been discussed at full length in one [13] of our previous papers.

The outline of the present paper is stated as follows. In Sec. II, we provide a physical insight into the mechanism

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that is responsible for the bulk viscosity, and give a review of our recently proposed formula for ζ described by the interatomic potential and the pair distribution function [12,13]. In Sec. III, we explain the concept and significance of density-dependent potentials, particularly in connection with the possibility of applications to metallic fluids, and derive a formula for ζ to be useful for potentials dependent on density. In Sec. IV, we propose a density-dependent model potential of liquid mercury and apply the new formula to model potential. We then calculate ζ in this system by performing molecular dynamics (MD) simulations on the basis of the formula we have obtained. We also give detailed discussions by placing much emphasis on the compression between our theoretical results and the experimental data. Concluding remarks are found in Sec. V.

II. FORMULA FOR THE BULK VISCOSITY IN A SYSTEM WITH DENSITY-INDEPENDENT POTENTIALS

For the sake of convenience to our main purpose in the present paper, we first give a brief review of the derivation of our previous formula for the bulk viscosity in a density-independent system.

An important point to make is that an authentic microscopic quantity characteristic of a system is interatomic potentials, which, throughout the series of our papers, we approximate by the sum of pair potentials $\phi(r,\rho)$, where r is the distance between the particles under consideration. Equilibrium atomic distribution functions such as an equilibrium pair distribution function are determined from the interatomic potentials for any pair of thermodynamic quantities, say, for density $\rho \equiv mN/V$, where m is the particle mass and entropy S. All volume changes are performed adiabatically in this paper. Therefore, the entropy is regarded as constant in the linear response theory. We then omit argument S from our expressions; for example, the pair distribution function is described as $g_0(r,\rho)$ instead of $g(r,\rho,S)$, where subscript 0 denotes the equilibrium state. On the other hand, in the nonequilibrium system, during compression or expansion, the pair distribution function $g(r)$ changes with time. Therefore, we write it as $g(r,t)$.

To explain the origin of the bulk viscosity, it is convenient to use the well-known virial equation:

$$p' = \frac{Nk_{\mathrm{B}}T}{V} - \frac{\rho^2}{6m^2}\int_0^\infty r\frac{d\phi(r)}{dr}g(r,t)4\pi r^2 dr, \tag{2}$$

where k_{B} is the Boltzmann constant, T is temperature. In the case of compression, for example, $g(r,t)$ is also compressed in the sense that the nonequilibrium $g(r,t)$ is shifted towards smaller values of r when compared to $g_0(r,\rho)$ as shown in Fig. 1. This means that the peak of $g(r,t)$ moves towards the region of r where the pair potential $\phi(r)$ is more repulsive, and accordingly, $-d\phi(r)/dr$ is larger. Therefore, Eq. (2) indicates that this shift makes the nonequilibrium pressure p' higher than the equilibrium pressure p. This is a qualitative interpretation of the origin of the bulk viscosity. A discussion analogous to this is of course possible in the case of expansion as well.

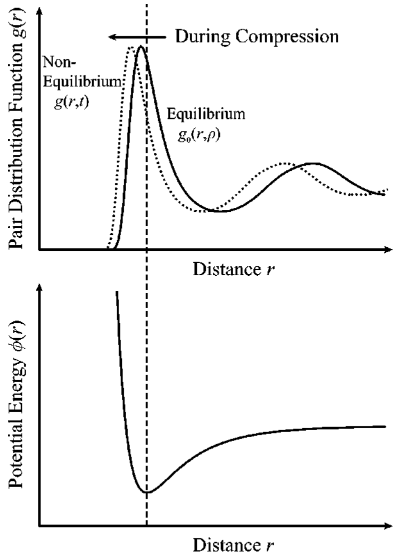

FIG. 1. The qualitative interpretation of the origin of the bulk viscosity. During compression of fluids, $g(r,t)$ is also compressed and the peak position is shifted away from that of the equilibrium $g_0(r,\rho)$ to the inside. This results in the movement of the $g(r,t)$ peak to the strong repulsive position and makes the nonequilibrium pressure p' higher than the equilibrium pressure p.

In order to analyze the effects of the volume change on $g(r,t)$, it is convenient to divide the time derivative of $g(r,t)$ into two terms, such that the first term represents *uniform* contraction or expansion [14,15] due to the compression, while the second term takes care of the difference between the effects of accurate and uniform volume change. For simplicity, we assume that the second term is governed by the Debye relaxation with a single relaxation time. The Debye relaxation is the simplest type of relaxation and is widely used as an appropriate approximation [2,3]. As a result, we obtain the time evolution of $g(r,t)$ in the form

$$\left(\frac{\partial g(r,t)}{\partial t}\right)_r = \frac{\dot{\rho}}{3\rho}r\left(\frac{\partial g(r,t)}{\partial r}\right)_t - \frac{1}{\tau}\{g(r,t)-g_0(r,\rho)\}, \tag{3}$$

where τ is the relaxation time of $g(r,t)$.

In order to solve the time development of Eq. (3), we carry out a perturbation expansion of the nonequilibrium $g(r,t)$ from the equilibrium $g_0(r,\rho)$. The difference of $g(r,t)$ from $g_0(r,\rho)$ is important only when the fluid is compressed more slowly than τ, that is, $\tau|\dot{\rho}|/\rho \ll 1$. This is because the bulk viscosity is only observed experimentally under this condition [2,3,16]. We then take $\tau\dot{\rho}/\rho$ as a perturbation-expansion parameter and finally represent the nonequilibrium $g(r,t)$ in terms of equilibrium $g_0(r,\rho)$,

$$g(r,t) = g_0(r,\rho) + \tau\frac{\dot{\rho}}{3\rho}\left\{r\left(\frac{\partial g_0(r,\rho)}{\partial r}\right)_\rho - 3\rho\left(\frac{\partial g_0(r,\rho)}{\partial \rho}\right)_r\right\} + O\left(\left[\tau\frac{\dot{\rho}}{\rho}\right]^2\right). \tag{4}$$

In order to derive the expression of bulk viscosity using Eq. (4), we calculate the difference between the pressure during the compression and that of the equilibrium system. In the case of a system in which $\phi(r)$ does not depend on density, the pressure is calculated from $g(r,t)$ by the virial theorem (2). According to the definition of the bulk viscosity, a discussion must take place about the difference of the pressure in system 1, which is compressed adiabatically and gradually from that in the volume-constant system 2. The pressure in system 1 must be compared to that of the equilibrium system 2, which has the same total energy, volume, and number of particles. For this reason, the temperature during the adiabatic compression is different from the temperature of the equilibrium system. We calculate these two temperatures using the fact that the value of the total energy is the same in these systems. As a consequence, we get a formula for the bulk viscosity ζ from the pressure difference $p'-p$ as

$$\zeta=-\frac{\rho^2}{18m^2}\tau\int_0^\infty\left\{r\frac{d\phi(r)}{dr}+2\phi(r)\right\}$$

$$\times\left\{r\left(\frac{\partial g_0(r,\rho)}{\partial r}\right)_\rho-3\rho\left(\frac{\partial g_0(r,\rho)}{\partial\rho}\right)_r\right\}4\pi r^2dr. \quad (5)$$

The Debye relaxation is assumed in this derivation. However, we can show that our formula is exactly equivalent to the Green-Kubo formula and the Heyes method, by determining τ as

$$\tau=\int_0^\infty\frac{\Delta p(t)}{\Delta p(+0)}dt, \quad (6)$$

where $\Delta p(t)$ is the difference between the pressure $p(t)$ at time t after the sudden compression and the pressure $p(\infty)$ after reaching equilibrium, i.e., $\Delta p(t)=p(t)-p(\infty)$ [13]. $\Delta p(+0)$ is the difference between the pressure $p(+0)$ just after the sudden compression and $p(\infty)$. This formula was applied to the Lennard-Jones fluid near its triple point in Refs. [12,13]. The obtained value shows excellent agreement with the results of the Green-Kubo formula and the Heyes method.

III. FORMULA FOR THE BULK VISCOSITY IN A SYSTEM WITH DENSITY-DEPENDENT POTENTIALS

Before deriving the expression of the bulk viscosity in density-dependent potentials, we derive the expression of pressure in this system. The definition of pressure is given by

$$p=-\left(\frac{\partial F}{\partial V}\right)=\frac{k_\mathrm{B}T}{Q_N}\left(\frac{\partial Q_N}{\partial V}\right)_T, \quad (7)$$

where Q_N is a configurational partition function expressed by

$$Q_N=\frac{1}{N!}\int_V\cdots\int_V\exp\{-\beta\Phi_N(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N,V)\}d\boldsymbol{r}_1\ldots d\boldsymbol{r}_N$$

$$=\frac{V^N}{N!}\int_0^1\cdots\int_0^1\exp\{-\beta\Phi_N(V^{1/3}\boldsymbol{s}_1,\ldots,V^{1/3}\boldsymbol{s}_N,V)\}$$

$$\times d\boldsymbol{s}_1\cdots d\boldsymbol{s}_N. \quad (8)$$

The coordinates of atoms are scaled as $\boldsymbol{r}_i\equiv V^{1/3}\boldsymbol{s}_i$ for the volume derivative of Q_N in Eq. (7). Accordingly, the volume derivative of Q_N is determined as

$$\left(\frac{\partial Q_N}{\partial V}\right)_T=\frac{N}{V}Q_N-\beta\frac{V^N}{N!}\int_0^1\cdots\int_0^1 e^{-\beta\Phi_N(V^{1/3}\boldsymbol{s}_1,\ldots,V^{1/3}\boldsymbol{s}_N,V)}$$

$$\times\frac{\partial\Phi_N}{\partial V}d\boldsymbol{s}_1\cdots d\boldsymbol{s}_N, \quad (9)$$

where Φ_N is the total potential energy in the N-body system. In the case where $\phi(r)$ does not depend on density, it is written as

$$\Phi_N(\boldsymbol{r}^{(N)})=\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\phi(r_{ij}), \quad (10)$$

where $\boldsymbol{r}^{(N)}$ denote the N-particle coordinates. The volume derivative of $\Phi(r)$ is calculated by

$$\frac{\partial\Phi_N}{\partial V}=\frac{1}{6V}\sum_{i=1}^{N}\sum_{j\neq i}^{N}r_{ij}\frac{d\phi(r_{ij})}{dr_{ij}}. \quad (11)$$

In the case where $\phi(r)$ depends on density, i.e., on volume V, the total potential energy $\Phi_N(\boldsymbol{r}^{(N)},V)$ is written as

$$\Phi_N(\boldsymbol{r}^{(N)},V)=\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\phi(r_{ij},V). \quad (12)$$

Then, the volume derivative of Φ_N is described by

$$\frac{\partial\Phi_N}{\partial V}=\frac{1}{6V}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\left\{\left(r_{ij}\frac{\partial\phi(r_{ij},V)}{\partial r_{ij}}\right)_V+\left(V\frac{\partial\phi(r_{ij},V)}{\partial V}\right)_r\right\}. \quad (13)$$

The pressure in this system includes an extra term $V[\partial\phi(r,V)/\partial V]$, in addition to the pressure in a density-independent-potential system. According to Eqs. (7), (9), and (13), the pressure in the density-dependent-potential system becomes

$$p=\frac{Nk_\mathrm{B}T}{V}-\frac{n^2}{6}\int_0^\infty\left\{\left(r\frac{\partial\phi(r,V)}{\partial r}\right)_V+\left(3V\frac{\partial\phi(r,V)}{\partial V}\right)_r\right\}$$

$$\times g_0(r,V)4\pi r^2dr. \quad (14)$$

This equation is rewritten by using density ρ instead of volume V in the form

$$p=\frac{Nk_{\mathrm{B}}T}{V}-\frac{\rho^2}{6m^2}\int_0^\infty\left\{\left(r\frac{\partial\phi(r,\rho)}{\partial r}\right)_\rho-\left(3\rho\frac{\partial\phi(r,\rho)}{\partial\rho}\right)_r\right\}\times g_0(r,\rho)4\pi r^2dr. \tag{15}$$

The nonequilibrium $g(r,t)$ in this system is also expressed as Eq. (4). By using Eq. (15) in lieu of Eq. (2), our formula for ζ in the $\phi(r,\rho)$ system finally becomes

$$\zeta=-\frac{\rho^2}{18m^2}\tau\int_0^\infty\left\{\left(r\frac{\partial\phi(r,\rho)}{\partial r}\right)_\rho+2\phi(r,\rho)-\left(3\rho\frac{\partial\phi(r,\rho)}{\partial\rho}\right)_r\right\}\times\left\{r\left(\frac{\partial g_0(r,\rho)}{\partial r}\right)_\rho-3\rho\left(\frac{\partial g_0(r,\rho)}{\partial\rho}\right)_r\right\}4\pi r^2dr. \tag{16}$$

In the case where $\phi(r,\rho)$ does not depend on density, this equation results in Eq. (5) because $\partial\phi(r,\rho)/\partial\rho=0$.

IV. APPLICATION

A. Model potential

Density-dependent potentials are frequently used as models of liquid metals [17]. As an example of a density-dependent potential, we propose a model potential of liquid mercury. We compare our results with experimental data of ζ in mercury, measured from the sound attenuation coefficient [2,3]. We assume that the density dependence of the potential is defined by

$$\phi(r,\rho)\equiv f(\rho)\phi_1(r)+[1-f(\rho)]\phi_2(r), \tag{17}$$

where $\phi_1(r)$ and $\phi_2(r)$ are two different kinds of density-independent potentials. Function $f(\rho)$ with the range of values $0\leqslant f(\rho)\leqslant 1$ is introduced to describe the transition of the potential from $\phi_1(r)$ to $\phi_2(r)$ as $f(\rho)$ changes from unity to zero. For our purpose of investigating the change of ζ accompanying the metal-to-nonmetal (MNM) transition on the decrease in density, it is appropriate to assume that $\phi_1(r)$ and $\phi_2(r)$ are potential for the high and low density regions, respectively. As $\phi_1(r)$, we choose the mercury potential calculated by Jank and Hafner [18], while as $\phi_2(r)$ we use the Lennard-Jones potential. We take the Lennard-Jones parameters such that the depth $\epsilon=1326$ K, and the diameter $\sigma=2.63$ Å, determined by fitting the Lennard-Jones critical temperature and critical density [19–21] to the experimental values of those for mercury. These potentials are shown in Fig. 2.

In liquid mercury, the MNM transition occurs at $\rho=8$–9 g/cm^3 [22,23]. We therefore propose a simple model for $f(\rho)$ according to the decrease of ρ from metallic to nonmetallic values in the form

$$f(\rho)=\begin{cases}2(\rho-9)/9 & (10<\rho\leqslant 13.5\ \ \mathrm{g/cm^3})\\ (\rho-8)^2/18 & (8<\rho\leqslant 10\ \ \mathrm{g/cm^3})\\ 0 & (\rho\leqslant 8\ \ \mathrm{g/cm^3}).\end{cases} \tag{18}$$

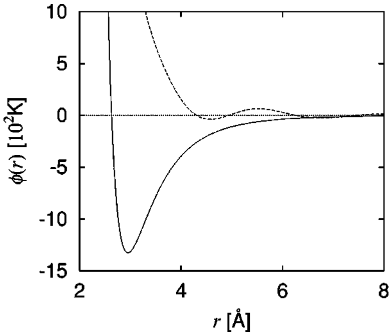

FIG. 2. The interatomic potentials $\phi_1(r)$ and $\phi_2(r)$. The dashed line is $\phi_1(r)$ in the high density region calculated by Jank and Hafner [18]. The solid line is the Lennard-Jones potential $\phi_2(r)$ in the low density region.

This density dependence of $f(\rho)$ is presented in Fig. 3.

In this dependence of $\phi(r,\rho)$ on ρ, our formula for ζ finally becomes

$$\zeta=-\frac{\rho^2}{18m^2}\tau\int_0^\infty\left\{r\left(\frac{\partial\phi(r,\rho)}{\partial r}\right)_\rho+2\phi(r,\rho)-3\rho\frac{df(\rho)}{d\rho}[\phi_1(r)-\phi_2(r)]\right\}\times\left\{r\left(\frac{\partial g_0(r,\rho)}{\partial r}\right)_\rho-3\rho\left(\frac{\partial g_0(r,\rho)}{\partial\rho}\right)_r\right\}4\pi r^2dr. \tag{19}$$

Equation (16) is generally used in the density-dependent potential. On the other hand, Eq. (19) is an expression only for the system in which the potential dependence is written as Eq. (17).

B. Molecular dynamics simulations

In order to evaluate $g_0(r,\rho)$ and τ in our formula, microcanonical MD simulations are performed under the following conditions. The number of particles N is 256 with periodic boundary conditions in the cubic unit cell with side length L. The temperature is set to 1800 K. The time step is $\delta t=5.6$ fs. The equation of motion is integrated by the sixth-

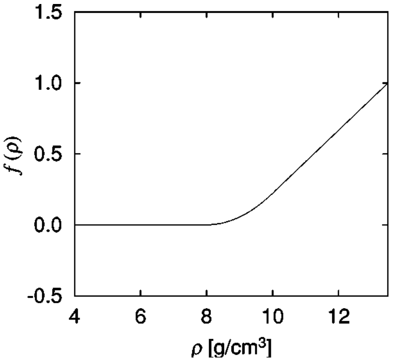

FIG. 3. Function $f(\rho)$ describing the potential change from $\phi_1(r)$ to $\phi_2(r)$.

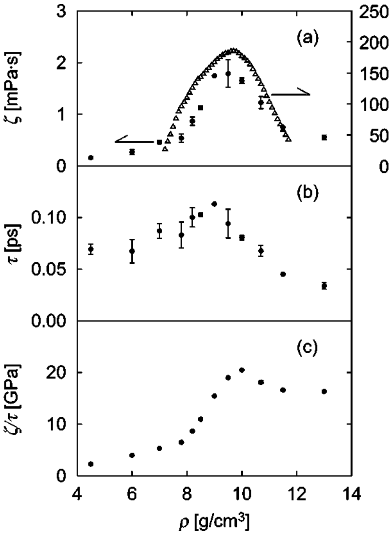

FIG. 4. The density dependence of (a) ζ, (b) τ, and (c) ζ/τ. Filled circle, the simulation results; open triangle, the experimental results for liquid mercury. These results agree qualitatively with one another.

order Gear's predictor-corrector algorithm. The cutoff radius r_c is taken as $L/2$. The cutoff correction is made for pressure and potential energy.

For the purpose of calculating the density derivative of the pair distribution function $\partial g_0(r,\rho)/\partial\rho$, we perform MD simulations in two systems with slightly different densities ρ and $\rho+\Delta\rho(\Delta\rho/\rho=0.02)$, and calculate $g_0(r,\rho)$ and $g_0(r,\rho+\Delta\rho)$ so that we approximate the derivative by the difference divided by $\Delta\rho$.

The time steps are taken as follows. First, microcanonical MD simulations are performed at the equilibrium for 200 steps in the density ρ. The pair distribution function $g_0(r,\rho)$ is determined from these simulations. Secondly, for the purpose of estimating τ and $[\partial g_0(r,\rho)/\partial\rho]_r$, the volume is changed uniformly, instantaneously, and adiabatically. Third, we continue the MD simulations over 400 steps for the observation of the pressure relaxation. The relaxation time τ is estimated by making use of Eq. (6), which describes the pressure relaxation from an instantaneous to equilibrium value. Finally, microcanonical MD simulations are performed at the equilibrium over 200 steps in density $\rho+\Delta\rho$. The equilibrium pressure $p(\infty)$ at $\rho+\Delta\rho$ and $g_0(r,\rho+\Delta\rho)$ is determined from these simulations.

In order to improve the statistical accuracy, MD simulations are performed by starting from 1600 different initial conditions. For the purpose of estimating the error bar, we divide the results of the 1600 initial conditions into two sets, each starting from different 800 initial conditions. Two values of ζ are determined from these two different sets of results. The error bar is determined from the standard deviation of these two values of ζ.

C. Results and discussion

The simulated results of the bulk viscosity ζ are shown in Fig. 4. We observe that it increases in the MNM transition region with a peak at $\rho=9.5$ g/cm^3. This figure also contains the experimental values of ζ in liquid mercury, which are estimated from the sound attenuation coefficients α and the sound velocity data [2,3]. The critical attenuation is separated from the normal sound attenuation coefficient [24]. The experimental data also has a peak in the MNM transition region. Although the experimental data are hundred times larger than the simulation results, the behavior of our bulk-viscosity data agrees qualitatively with the experimental results. This explains the peak of ζ theoretically.

In order to investigate the behavior of the bulk viscosity in more detail, we also show, in Fig. 4, the results of τ and ζ/τ, including the integral of Eq. (19). The discussion on the reason for the increase in ζ is conducted in the following way for the two density regions (1) $\rho<9.5$ g/cm^3 and (2) $\rho>9.5$ g/cm^3.

1. Analysis concerning the behavior of ζ for $\rho<9.5$ g/cm^3

In this low density region, ζ increases according to the increase in ρ. The increase in ζ/τ in this region is as much as nine times, while the increase in τ is only by a factor 1.6. Among other features, the increase of ζ/τ gives the most dominant contribution to the increase in ζ within this region. The term containing $3\rho[df(\rho)/d\rho][\phi_1(r)-\phi_2(r)]$ in the integrand is zero at a density lower than 8 g/cm^3. This term takes nonzero values only in the region of the density ($\rho>8$ g/cm^3) and causes the increase in ζ in this region.

The bulk viscosity originates from the fact that the peak position of the nonequilibrium $g(r,t)$ is shifted away from that of the equilibrium $g_0(r,\rho)$ towards smaller values of r. Because of this movement, the nonequilibrium pressure p' is higher than the equilibrium pressure p as shown in Fig. 1. In our model, the interatomic potential depends on density. The repulsive part of $\phi(r,\rho)$ moves towards larger values of r by the compression, while the $g(r,t)$ shifts towards smaller values of r as in Fig. 5. As a consequence, the nonequilibrium pressure p' is much higher than that in a density-independent-potential system, and the bulk viscosity increases in the transition region of $\phi(r)$. In other words, the increase in ζ is caused by the density dependence of $\phi(r,\rho)$, and is expressed by the term containing $3\rho df(\rho)/d\rho[\phi_1(r)-\phi_2(r)]$.

2. Analysis concerning the behavior of ζ for $\rho>9.5$ g/cm^3

According to the increase of density beyond $\rho=9.5$ g/cm^3, ζ decreases. The most dominant contribution in this region comes from τ rather than from ζ/τ. The integral part for ζ/τ is almost constant. On the other hand, τ decreases to one-third of the value at $\rho=9.5$ g/cm^3. This phenomenon is explained as follows. The repulsive part shifts to the larger value of r by the increase of density. This movement means that the effective sizes of the atoms become larger and the atoms collide with one another more frequently. The relaxation time τ, therefore, becomes shorter.

As described above, we explained the increase mechanism of ζ in the density region of $\rho=9$–10 g/cm^3. It becomes possible only by our formula to discuss the origin of the increase of ζ from the ρ dependence of $\phi(r,\rho)$ in detail

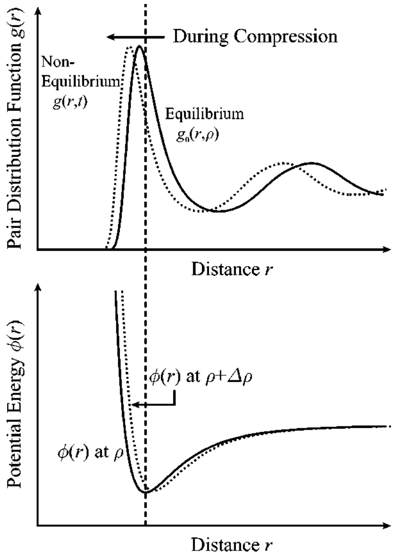

FIG. 5. The illustration of the behavior of $\phi(r,\rho)$ and $g(r,t)$. The repulsive part of $\phi(r,\rho)$ moves towards larger values of r by the compression while accompanying the $g(r,t)$ shifts towards smaller values of r. The nonequilibrium pressure p' is much higher than that for a density-independent-potential system.

as presented in this paper. By the previous methods, it was not possible to investigate the ζ increase mechanism, because ζ is not described in terms of microscopic properties as is the case by our method.

The experimental value is hundred times larger than that of our simulation results. In real mercury, all atoms do not transform at the same time from a metallic to nonmetallic state at a certain density, as assumed in a model system. There exist both metallic clusters and nonmetallic clusters simultaneously in the MNM transition region. These clusters cause group motions of atoms, and the relaxation time becomes longer. As a result, the bulk viscosity is expected to be larger. If we take the effects of such metallic clusters into account, the quantitative gap between the experimental and theoretical values will be narrowed concerning the relaxation time and the peak height in ζ. Therefore, a remarkable point is that even a simple model as ours can reproduce the behavior of ζ, in general, and the existence of the peak, in particular, in the ζ-ρ curve.

V. CONCLUSION

We derive a formula for the bulk viscosity ζ in a density-dependent-potential system. This is a generalization of the bulk-viscosity formula for the density-independent system which we have proposed recently. The bulk viscosity is expressed in terms of microscopic quantities such as interatomic potentials and pair distribution functions in our formula. This is an outstanding advantage when compared to the previously proposed formulas, in all of which ζ is expressed in terms of pressure. We apply our formula to a model liquid metal in which the interatomic potential varies with density. We show that ζ increases in the density region where the interatomic potential changes from nonmetallic to metallic. This result agrees qualitatively with the experimental results of liquid mercury. The increase of ζ is caused by the shift of the interatomic potential towards larger values of r. This shift leads to (1) the increase of ζ/τ in the region of $\rho=8-10$ g/cm^3 and (2) the decrease of τ in the region of $\rho>9.5$ g/cm^3. We conclude that this is the mechanism for the increase of the bulk viscosity ζ in the MNM transition region.

In order to deal with liquid metals by MD simulations, we have used the model of the pair potential depending on density. Besides this kind of model, there is also the method with a functional of the electronic density, such as the embedded atom method [25,26]. In the latter method, however, the thermodynamic quantities (energy, pressure, etc.) are not described by pair distribution functions. The embedded atom method is, therefore, not capable of being incorporated with our formula. The behavior of liquid mercury is essentially explained by the model of the pair potential depending on density.

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