PHYSICAL REVIEW E **91**, 012111 (2015)

Explicit expression for the Stokes-Einstein relation for pure Lennard-Jones liquids

Norikazu Ohtori[1,*] and Yoshiki Ishii[2]
[1]*Faculty of Science, Niigata University, 8050 Ikarashi 2-no cho, Nishi-ku, Niigata 950-2181, Japan*
[2]*Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-no cho, Nishi-ku, Niigata 950-2181, Japan*

(Received 30 July 2014; revised manuscript received 10 October 2014; published 7 January 2015)

An explicit expression of the Stokes-Einstein (SE) relation in molecular scale has been determined for pure Lennard-Jones (LJ) liquids on the saturated vapor line using a molecular dynamics calculation with the Green-Kubo formula, as $D\eta_{\mathrm{sv}} = kT\xi^{-1}(N/V)^{1/3}$, where D is the self-diffusion coefficient, η_{sv} the shear viscosity, k the Boltzmann constant, T the temperature, ξ the constant, and N the particle number included in the system volume V. To this end, the dependence of D and η_{sv} on packing fraction, η, and T has been determined so as to complete their scaling equations. The equations for D and η_{sv} in these states are $m^{-1/2}(N/V)^{-1/3}(1-\eta)^4\epsilon^{-1/2}T$ and $m^{1/2}(N/V)^{2/3}(1-\eta)^{-4}\epsilon^{1/2}T^0$, respectively, where m and ϵ are the atomic mass and characteristic parameter of energy used in the LJ potentials, respectively. The equations can well describe the behaviors of D and η_{sv} for both the LJ and the real rare-gas liquids. The obtained SE relation justifies the theoretical equation proposed by Eyring and Ree, although the value of ξ is slightly different from that given by them. The difference of the obtained expression from the original SE relation, $D\eta_{\mathrm{sv}} = (kT/2\pi)\sigma^{-1}$, where σ means the particle size, is the presence of the $\eta^{1/3}$ term, since $(N/V)^{1/3} = (6/\pi)^{1/3}\sigma^{-1}\eta^{1/3}$. Since the original SE relation is based on the fluid mechanics for continuum media, allowing the presence of voids in liquids is the origin of the $\eta^{1/3}$ term. Therefore, also from this viewpoint, the present expression is more justifiable in molecular scale than the original SE relation. As a result, the $\eta^{1/3}$ term cancels out the σ dependence from the original SE relation. The present result clearly shows that it is not necessary to attribute the deviation from the original SE relation to any temperature dependence of particle size or to introduce the fractional SE relation for pure LJ liquids. It turned out that the η dependence of both D and η_{sv} is similar to that in the corresponding equations by the Enskog theory for hard sphere (HS) fluids, although the T dependence is very different, which means that the difference in the behaviors of D and η_{sv} between the LJ and HS fluids are traceable simply to their temperature dependence. Although the SE relation for the HS fluids also follows $D\eta_{\mathrm{sv}} = kT\xi^{-1}(N/V)^{1/3}$, the value of ξ is significantly different from that for the LJ liquids.

DOI: 10.1103/PhysRevE.91.012111 PACS number(s): 65.20.De, 66.10.cg, 66.20.Cy, 47.11.−j

I. INTRODUCTION

Since the Stokes-Einstein (SE) relation has been derived for macromolecule in Brownian motion in a dilute solution [1], the applicability has been discussed to various kinds of molecules and liquid states over a century [2,3]. Even in a recent decade, breakdown of the relation has become one of the topics in studies of nanoparticles [4,5]. Also in molecular scale, many studies regarding the applicability have been reported from the viewpoints of theory [6,7], simulation [8–15], and experiment [16–22]. However, mainly from the theoretical work side, the inapplicability of the relation had already been pointed out to liquids with finite concentrations in molecular scale [23,24], and several modified equations have been devised. The representative ones for simple liquids in molecular scale are those derived by Eyring and Ree [25] and Zwanzig [26], independently. Applying the vacancy theory to the evaluation of self-diffusion coefficient, D, and shear viscosity, η_{sv}, with some geometrical approximations, the former derived the equation

$$D\eta_{\mathrm{sv}} = \frac{kT}{\xi}(N/V)^{1/3}, \tag{1}$$

where k is the Boltzmann constant, T the absolute temperature, N/V the number density, and ξ is the number of nearest-neighbors lying in the same plane as the diffusing atom: $\xi = 6$ is given for close-packed systems [25] and 5.6 for real liquids [24]. The latter related D directly with η_{sv} using normal mode analysis [26] and derived

$$D\eta_{\mathrm{sv}} = kTC(N/V)^{1/3}, \tag{2}$$

where $C = 0.0658\,(2 + \eta_{\mathrm{sv}}/\eta_{\mathrm{lv}})$. The longitudinal viscosity η_{lv} is defined as $4\eta_{\mathrm{sv}}/3 + \eta_{\mathrm{bv}}$, where η_{bv} is the bulk viscosity. If we use a typical relation of $\eta_{\mathrm{bv}} = \eta_{\mathrm{sv}}/3$, $C = 0.171$ which corresponds to $\xi = 5.85$. In addition to these coefficients, the term of N/V in these equations differs from that of particle radius in the original SE relation,

$$D\eta_{\mathrm{sv}} = \frac{kT}{4\pi r_{\mathrm{S}}}\,(\text{slip condition})\,, \tag{3}$$

where r_{S} the Stokes radius [27]. The difference is crucial, since any breakdown in Eq. (3) might lead to the introduction of temperature dependence of atomic size or the fractional SE equation, but not so in Eqs. (1) or (2). However, many subsequent works [6–22] in the molecular scale have not paid much attention to the differences, and have simply compared their numerical results with the relations. Therefore, both the original and modified expressions have still not been justified in the molecular scale.

Here we focus on the Lennard-Jones (LJ) liquids. Such simple liquids, i.e., rare gases or the LJ liquids, are the extreme opposites to dilute solutions containing macromolecules in the hydrodynamic region. Nonetheless, even the breakdown has been discussed extensively in supercooled states [10,14] and even in normal liquid states [12]. The LJ potential at an

---

[*] ohtori@chem.sc.niigata-u.ac.jp

interatomic distance of r is given as

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

where ϵ and σ are the parameters characterizing potential depth and atomic size, respectively. In many studies, σ is assumed to correspond to the Stokes radius in Eq. (3). Since the LJ potential as well as the soft-core potential can be scaled with ϵ and σ [28,29], transport properties may be expressed with the necessary and sufficient independent variables. Furthermore, the LJ model can well express the realistic behaviors of them for rare-gas liquids. Therefore, the model is suitable for the study to elucidate the above-mentioned questions on the SE relation in molecular scale.

In this paper, we demonstrate that we can determine the explicit expression of the SE relation justifiable for the LJ liquids using the molecular dynamics calculation, and that number density is an appropriate variable for the expression in the pure states. Our approach for this purpose is to determine the explicit expressions of D and η_{sv}, respectively, using the necessary and sufficient independent variables. MD calculation is expected to give numerically exact solutions for a given model such as the LJ model. Furthermore, the present method is easy to apply to the mixtures. In a subsequent paper, we will present the results of mixtures, and suggest the expressions unified from molecular scale to hydrodynamic region.

II. CALCULATION

First, under the microcanonical ensemble, we express D and η_{sv} as dimensionless quantities in terms of appropriate units, i.e., σ for length, m for mass, ϵ/k for temperature, and $(m\sigma^2/\epsilon)^{1/2}$ for time [28,29], so that we obtain dimensionless quantities as

$$D(\sigma,\epsilon,m,N,V,E) = m^{-1/2}\sigma\epsilon^{1/2}D^*(N,V^*,E^*) \qquad (5)$$

and

$$\eta_{\mathrm{sv}}(\sigma,\epsilon,m,N,V,E) = m^{1/2}\sigma^{-2}\epsilon^{1/2}\eta^*_{\mathrm{sv}}(N,V^*,E^*), \qquad (6)$$

where E is the internal energy, $V^* = V/\sigma^3$, $E^* = E/\epsilon$, and D^* and η^*_{sv} are the dimensionless self-diffusion coefficient and shear viscosity, respectively. These show directly the mass dependence of $m^{-1/2}$ for D and $m^{1/2}$ for η_{sv}. Note that the product of Eqs. (5) and (6) apparently suggests σ^{-1} dependence. We will discuss this in detail later. Since packing fraction, η, is defined as $(\pi/6)\sigma^3(N/V)$, dimensionless number density, N/V^*, means η, and we can choose two variables among σ, N/V, and η to express D and η_{sv}, respectively. If we select N/V and η, as $\sigma = (6/\pi)^{1/3}(N/V)^{-1/3}\eta^{1/3}$, we obtain

$$D \propto m^{-1/2}(N/V)^{-1/3}\eta^{1/3}\epsilon^{1/2}D^*(N,V^*,E^*) \qquad (7)$$

and

$$\eta_{\mathrm{sv}} \propto m^{1/2}(N/V)^{2/3}\eta^{-2/3}\epsilon^{1/2}\eta^*_{\mathrm{sv}}(N,V^*,E^*). \qquad (8)$$

In summary, for the LJ liquids, the diffusion coefficient and shear viscosity can be expressed as

$$D(d,T) = D(m,N/V,\eta,T) = m^{-1/2}(N/V)^{-1/3}f(\eta,T) \qquad (9)$$

TABLE I. Parameters for the LJ potential, σ and ϵ, in the rare gas systems [30].

Atom	σ (nm)	ϵk^{-1} (K)
Ar	0.3405	119.8
Kr	0.3670	167.0
Xe	0.3924	257.4

and

$$\eta_{\mathrm{sv}}(d,T) = \eta_{\mathrm{sv}}(m,N/V,\eta,T) = m^{1/2}(N/V)^{2/3}g(\eta,T), \qquad (10)$$

where d is the density defined as mN/V.

MD calculations were carried out for Ar, Kr, and Xe using the NVE conditions. The particle number N was 864 and the cell volume V was determined from the experimental density [31,32] at each temperature. The parameters used in the LJ potentials are given in Table I [30]. The equations of motion were integrated using the velocity Verlet algorithm [33] with a time step of 10 fs and each run consisted of 200 000 steps: 2 ns. At each state, we have performed calculations of five runs to evaluate D, and 10 or 20 runs for η_{sv}, and then obtained the averages and the standard deviations, σ_{SD}, for them from the results. For all the present calculation results shown from Figs. 2 to 6, error bars are indicated as $\pm\sigma_{\mathrm{SD}}$ behind plotted symbols. The self-diffusion coefficient was evaluated using the Einstein equation [33] and corrected for the effect of the finite system size used in the periodic boundary condition, using the equation [34],

$$D = D_{\mathrm{PBC}} + 2.837297\frac{kT}{6\pi\eta_{\mathrm{sv}}}\left(\frac{N}{V}\right)^{1/3}N^{-1/3}, \qquad (11)$$

where D_{PBC} means the self-diffusion coefficient obtained under the present periodic boundary condition used. The shear viscosity was evaluated using the Green-Kubo formula [33] and uncorrected since the system size dependence is relatively weak [34].

Figure 1 shows the thermodynamic states calculated on the phase diagram of Ar which is based on the results of Ref. [35].

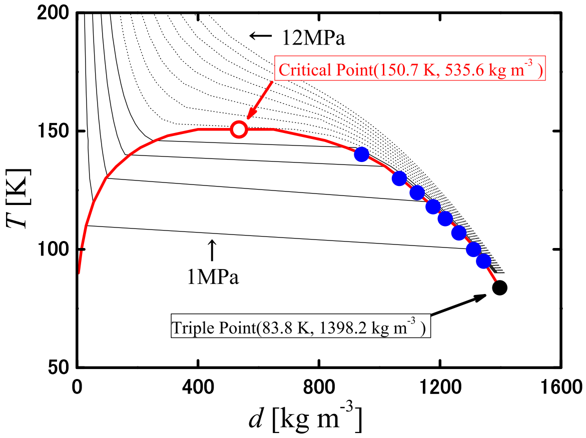

FIG. 1. (Color online) Thermodynamic states studied in this work, shown by blue closed circles, on the phase diagram of Ar [35].

In this work, in order to focus on the density dependence, we have sampled a range of states along the saturated vapor line which shows weak temperature dependence of η_{sv}. In these states, we have evaluated D and η_{sv} in order to compare them with the experimental results and the scaling equations to be determined in this study.

The calculations to determine the functional forms of $f(\eta,T)$ and $g(\eta,T)$ were performed for liquid Ar at a reference state of 1124.9 kg m^{-3} and/or 124 K. In these calculations, only one variable was changed, keeping all the other variables as constants. Changing the packing fraction can be achieved by scaling the atomic size σ. A more detailed description of the scaling method is given in Ref. [36].

III. RESULTS AND DISCUSSION

Figure 2 shows comparisons between the calculated and the experimental [32,37] results for Ar in the liquid states shown in Fig. 1. They are in good agreement with each other in η_{sv}, whereas some tendency of overestimation in D is found compared with the experimental results. Hard-sphere (HS) fluids based on the Enskog theory show the different behaviors from those in the LJ liquids mainly in the high- and low-mobile regions, respectively. The origin of these differences will be discussed later.

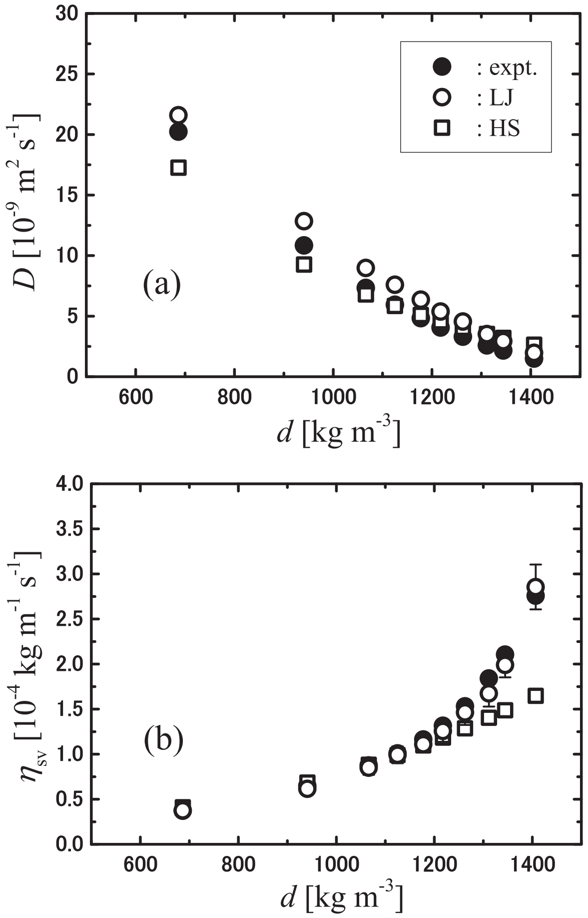

FIG. 2. (a) Self-diffusion coefficient and (b) shear viscosity of Ar in the liquid states on the saturated vapor line shown in Fig. 1. HS means the plots of calculated values using the Enskog formula in the same temperature and density.

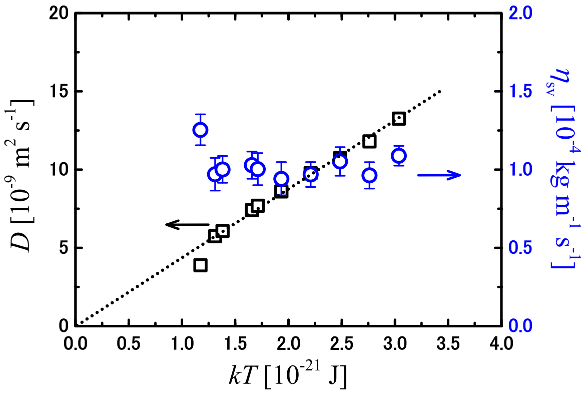

FIG. 3. (Color online) Temperature dependence of self-diffusion coefficient and shear viscosity calculated for liquid Ar at the constant density of 1124.9 kg m^{-3}.

Figure 3 shows the temperature dependence of D and η_{sv}, respectively, at the constant density of 1124.9 kg m^{-3}. It is very weak in η_{sv} and approximately linear in D. Figure 4(a) shows the obtained packing-fraction dependence under the

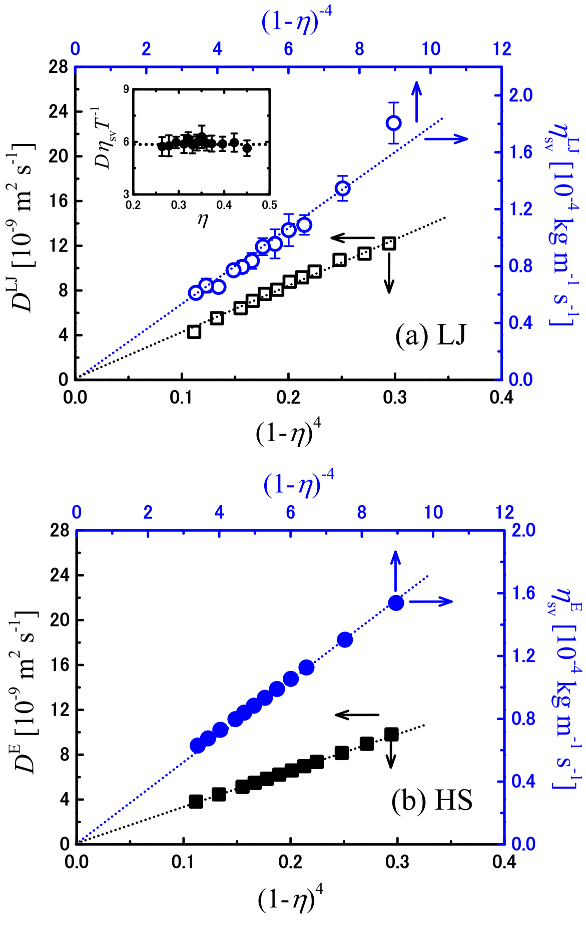

FIG. 4. (Color online) Packing-fraction dependence of self-diffusion coefficient and shear viscosity for (a) the LJ and (b) HS fluids under the constant density of 1124.9 kg m^{-3} and temperature of 124 K. HS means the results calculated using the Enskog formula in the same states as LJ.

constant density of 1124.9 kg m^{-3} and temperature of 124 K, which can be fitted to a simple equation as $(1-\eta)^4$ for D and $(1-\eta)^{-4}$ for η_{sv}, respectively. Although there still remains a little room to improve the fit using more complicated polynomial equations, the obtained results are enough for the present purpose. Whereas the temperature dependence of η_{sv} becomes noticeable near the triple point as shown in Fig. 3, except for this, we have confirmed the same variable dependence as stated above at all the states shown in Fig. 1. In addition, calculations to evaluate single-variable dependence on mass and number density of D and η_{sv} were also performed, and the same dependence as shown in Eqs. (9) and (10) was confirmed, respectively.

In summary, the self-diffusion coefficient and shear viscosity of simple LJ liquids should follow

$$D \propto m^{-1/2}(N/V)^{-1/3}(1-\eta)^4\epsilon^{-1/2}T \tag{12}$$

and

$$\eta_{\mathrm{sv}} \propto m^{1/2}(N/V)^{2/3}(1-\eta)^{-4}\epsilon^{1/2}T^0, \tag{13}$$

respectively. Figures 5(a) and 5(b) shows plots of all the calculated and the experimental results for liquids Ar [32,37], Kr [38], and Xe [38] on the saturated vapor lines as functions of Eqs. (12) and (13), respectively. Although, unfortunately, there are only little available experimental data for both Kr and Xe liquids, all the results shown in the figures are well expressed with the equations. Note that some deviations from the equation shown in Fig. 5(b) are traceable only to changes in temperature dependence near the triple point, as mentioned above.

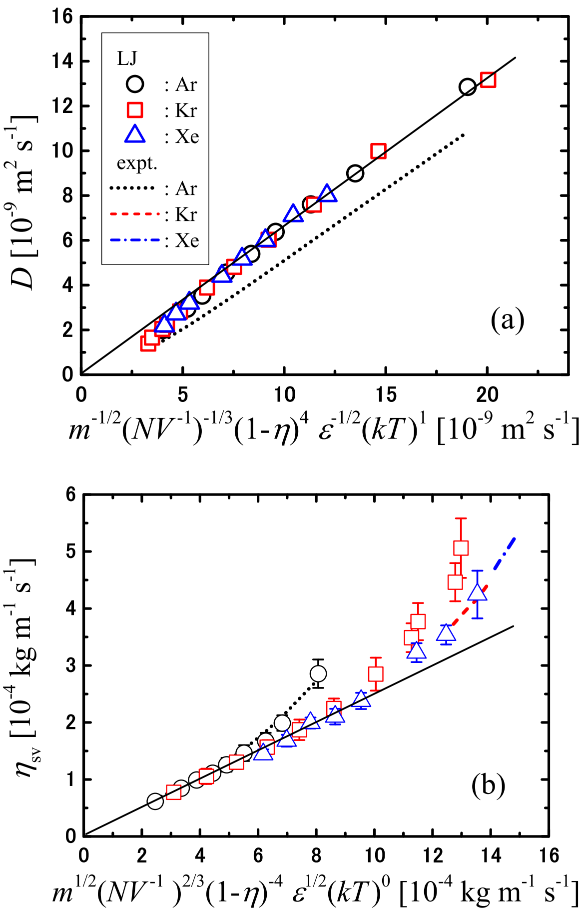

FIG. 5. (Color online) The calculated and experimental self-diffusion coefficient and shear viscosity of liquid Ar, Kr, and Xe on the saturated vapor lines as a function of mass, number density, packing fraction, and temperature. The solid straight lines are guides to the eye.

These scaling equations immediately give the SE relation for pure LJ liquids as a product between Eqs. (12) and (13): $D\eta_{\mathrm{sv}} \propto (N/V)^{1/3}T$. Figures 6(a) and 6(b) clearly show $D\eta_{\mathrm{sv}}/T$ can well be expressed not by σ^{-1} but by $(N/V)^{1/3}$. It should be noted that even near the triple point where the deviation of plot from the equation in abscissa in Fig. 5(b) becomes large, the obtained SE relation holds. Furthermore, we can see no significant dependence of $D\eta_{\mathrm{sv}}/T$ on the packing fraction which contains the particle size σ in Fig. 6(c). Since weak curvatures on the equations fitted to the packing-fraction dependence of D and η_{sv}, respectively, remain in Fig. 4(a), the direct products between the calculation results of D and η_{sv} are also shown as a function of η in the inset of Fig. 4(a). This also clearly shows that there is no significant dependence on η under these conditions.

If we would interpret these results on the basis of the original SE relation of Eq. (3), we might introduce any temperature dependence of atomic size or the fractional SE equations. However, clearly they are superfluous on the basis of the SE relation clarified in this work. It should also be noted that the expressions of the SE relation for the LJ liquids have nothing to do with the definition of particle size. Instead of σ as a scaling unit for length in the dimensional analysis, if we use a different unit, e.g., $\sigma/2$, it does not affect the present results. Therefore, in the study of applying the SE relation to pure LJ liquids, it does not make sense to discuss particle size and furthermore its temperature dependence. This idea is also supported by the fact that even near the triple point the obtained SE relation holds.

Here we recall that the product between Eqs. (5) and (6) suggests the σ^{-1} dependence in the SE relation. However, besides σ and T, the other variables does not cancel out, and the term of $\eta^{1/3}$ remains, which results in $\sigma^{-1}\eta^{1/3}$, i.e., $(N/V)^{1/3}$, dependence. It is worth considering the difference of the physical meanings between the present expression and the original SE relation, via the relation of $(N/V)^{1/3} = \sigma^{-1}(6/\pi)^{1/3}\eta^{1/3}$,since, to our knowledge, no one has ever done it. There are two points to be made clear. The first is that the presence of the $\eta^{1/3}$ term in the molecular scale converts the concept of particle size in the original SE relation to number density. The second point is really important and is that the presence or absence of the $\eta^{1/3}$ term characterizes the solvents which are treated as ensembles of particles or simply continuum media, respectively. That is, the expression of viscosity in the original SE relation is based on fluid mechanics for continuum media. Therefore, allowing the presence of voids in liquids means the departure from the original SE relation. As a result, the $\eta^{1/3}$ term cancels out the σ dependence from the original SE relation.

In order to reveal the significance of the $\eta^{1/3}$ term, though it may sound paradoxical, we apply the present expression to

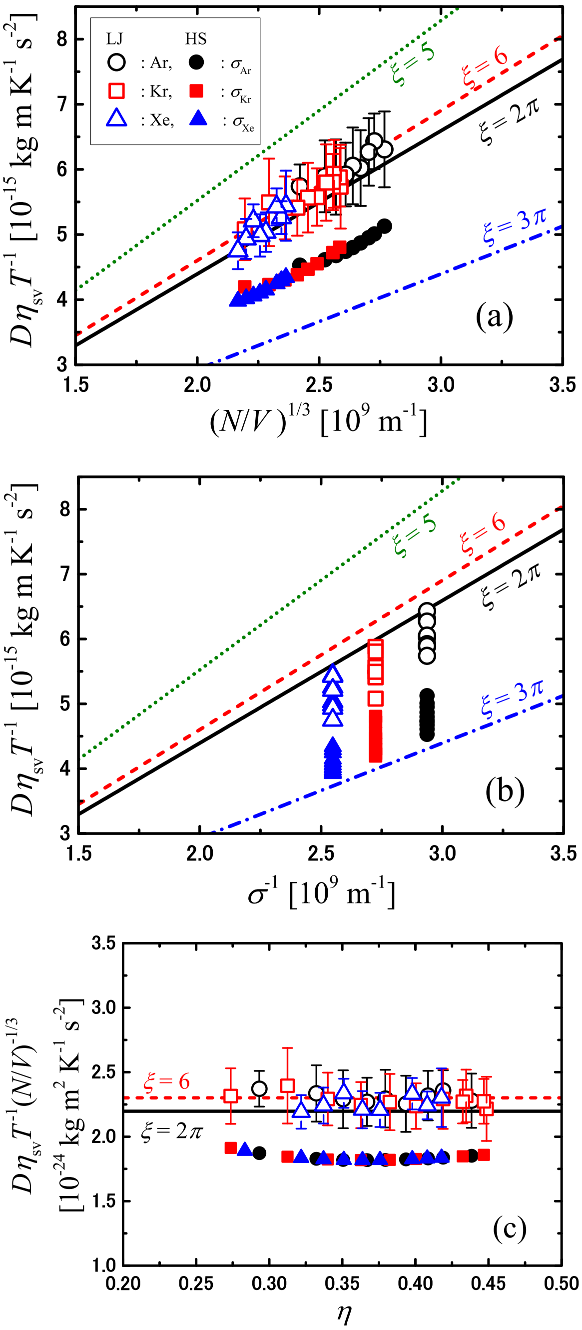

FIG. 6. (Color online) The Stokes-Einstein relation, $D\eta_{sv}/T$, based on the calculated self-diffusion coefficient and viscosity for Ar, Kr, and Xe on the saturated vapor lines as a function of (a) number density and (b) particle size, and (c) $(D\eta_{sv}/T)(N/V)^{-1/3}$ as a function of packing fraction. Closed symbols (HS) show the results from the Enskog formula with σ used in the present work instead of the hard-sphere diameters: σ_{Ar}, σ_{Kr}, and σ_{Xe} mean σ for Ar, Kr, and Xe, respectively.

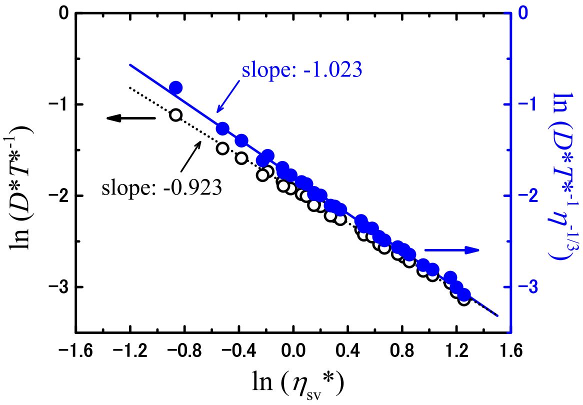

FIG. 7. (Color online) The fractional Stokes-Einstein relation based on all the calculated self-diffusion coefficient for Ar, Kr, and Xe on the saturated vapor lines as a function of the calculated viscosity. Closed and open circles show the plots with and without $\eta^{-1/3}$, respectively. The values of slope indicated were obtained by fit of all the data to the linear lines, respectively.

the fractional SE equation [12]:

$$\frac{D}{T} \propto \eta_{sv}^{-t}, \tag{14}$$

where t is a constant, $0 \leqslant t \leqslant 1$, which can be determined from the slopes of log-log plots. In the case where the original SE relation holds, obviously $t = 1$. Following the manner by Harris [12] using the dimensionless quantities, whereas the original SE relation can be expressed as

$$\frac{D^*}{T^*} \propto \eta_{sv}^{*\,-1}, \tag{15}$$

where $T^* = kT/\epsilon$, the present expression can be written as

$$\frac{D^*}{T^*}\eta^{-1/3} \propto \eta_{sv}^{*\,-1}. \tag{16}$$

Figure 7 clearly shows that the analysis based on the original SE relation may lead to the introduction of the fractional SE relation even for pure LJ liquids [12] but that based on the present expression will not need its help for them.

As shown in Fig. 6(a), the slope, $1/\xi$, is close to $1/2\pi$ or $1/6$ in the plot of $D\eta_{sv}/kT$ vs. number density. Therefore, the coefficient in the SE relation is not in entire agreement with those in the theoretical equations [24–26] given by Eqs. (1) and (2).

Lastly, we discuss the differences in the behaviors between the LJ liquids and the HS fluids based on the Enskog theory. The equations by the theory for self-diffusion coefficient, D^E [39], and shear viscosity, η_{sv}^E [40], in HS fluids are given, using the Carnahan-Starling approximation [41], as

$$D^E = 1.01896\frac{4\eta_{HS}}{y}D^0 \tag{17}$$

and

$$\eta_{sv}^E = 4\eta_{HS}\left[\frac{1.016}{y} + 0.8128 + 0.7835y\right]\eta_{sv}^0, \tag{18}$$

respectively, where η_{HS} is the packing fraction with hard-sphere diameter σ_{HS}, D^0 and η_{sv}^0 are the values of self-diffusion coefficient and shear viscosity at the low-density limit, respectively [27], given as

$$D^0 = \frac{3}{8\sigma_{HS}{}^2}\left(\frac{N}{V}\right)^{-1}\left(\frac{kT}{m\pi}\right)^{1/2}, \tag{19}$$

$$\eta_{\mathrm{sv}}^{0} = \frac{5}{16\sigma_{\mathrm{HS}}{}^{2}}\left(\frac{mkT}{\pi}\right)^{1/2}, \tag{20}$$

and

$$y \approx 4\eta_{\mathrm{HS}}\left(1-\tfrac{1}{2}\eta_{\mathrm{HS}}\right)/(1-\eta_{\mathrm{HS}})^{3}. \tag{21}$$

Using the relation, $\sigma_{\mathrm{HS}} = (6/\pi)^{1/3}(N/V)^{-1/3}\eta_{\mathrm{HS}}^{1/3}$, D^{E} and $\eta_{\mathrm{sv}}^{\mathrm{E}}$ have the dependence on mass and number density as $m^{-1/2}(N/V)^{-1/3}$ and $m^{1/2}(N/V)^{2/3}$, respectively, which is the same as those for the LJ liquids as shown in Eqs. (9) and (10). However, the same dependence on packing fraction between them, as shown in Figs. 4(a) and 4(b), is rather remarkable, since it suggests that not only doesn't the attractive part of the potential affect the behavior but also not the softness in the repulsive part. This is very different from the case of the thermal conductivity of simple liquids [42]. As a result, the difference between the LJ and HS fluids in the self-diffusion coefficient and viscosity shown in Fig. 2 can be attributed only to the differences in the temperature dependence shown in Fig. 3 and Eqs. (19) and (20).

In spite of the differences in temperature dependence, the expression for the SE relation for the HS fluids is quite similar to that for the LJ liquids: $D^{\mathrm{E}}\eta_{\mathrm{sv}}^{\mathrm{E}} \propto (N/V)^{1/3}\,T$. Figure 6 shows the same behaviors as those of the LJ liquids except for their coefficients: $D^{\mathrm{E}}\eta_{\mathrm{sv}}^{\mathrm{E}}/T$ can also well be expressed not by $\sigma_{\mathrm{HS}}^{-1}$ but by $(N/V)^{1/3}$. On the other hand, the coefficient in the SE relation is significantly different between the LJ liquids and the HS fluids. As the difference should be attributed to the softness of the repulsive part and/or the attractive part in the potential, the origin might be discussed using the Weeks-Chandler-Andersen potentials [42].

IV. CONCLUSIONS

We have successfully determined the expression of the SE relation justifiable for pure LJ liquids on the saturated vapor line using MD calculations with the GK formula. The expression clearly shows that N/V should be used instead of σ used in the original SE relation. It holds not only for the LJ liquids but also for the real rare-gas liquids, and furthermore for HS fluids. Therefore, the present results support the assumptions used in the theoretical work by Eyring and Ree. The expression can also be interpreted so that σ is converted to N/V in the molecular scale by the addition of $\eta^{1/3}$ into the original SE relation. As a result, the $\eta^{1/3}$ term cancels out the σ dependence from the original SE relation. It is worth noting that the presence of the $\eta^{1/3}$ term characterizes the solvent which is treated here not as continuum media but as ensembles of particles. In a subsequent paper, the importance of this additional factor will be shown again in the SE relation for the LJ-liquid mixtures. Allowing the presence of voids in liquids means the departure from the original SE relation.

ACKNOWLEDGMENT

This work was partially supported by Grant-in-Aid for Scientific Research (c) (Grant No. 24540397) from the Japan Society for the Promotion of Science.

[1] A. Einstein, *Investigation on the Theory of the Brownian Movement* (Dover, New York, 1956).
[2] R. M. Mazo, *Brownian Motion: Fluctuations, Dynamics, and Applications* (Oxford University Press, New York, 2002).
[3] K. L. Ngai, *Relaxation and Diffusion in Complex Systems* (Springer, New York, 2011).
[4] A. Tuteja, M. E. Mackay, S. Narayanan, S. Asokan, and M. S. Wong, Nano Lett. **7**, 1276 (2007).
[5] J. Liu, D. Cao, and L. Zhang, J. Phys. Chem. C **112**, 6653 (2008).
[6] K. Rah and B. C. Eu, Phys. Rev. E **60**, 4105 (1999).
[7] D. M. Heyes and N. H. March, Int. J. Thermophys. **20**, 267 (1999).
[8] D. M. Heyes, J. Chem. Soc. Faraday Trans. **79**, 1741 (1983).
[9] K. D. Hammonds and D. M. Heyes, J. Chem. Soc. Faraday Trans. **84**, 705 (1988).
[10] P. Bordat, F. Affouard, M. Descamps, and F. Müller-Plathe, J. Phys. Condens. Matter **15**, 5397 (2003).
[11] M. Cappelezzo, C. A. Capellari, S. H. Pezzin, and L. A. F. Coelho, J. Chem. Phys. **126**, 224516 (2007).
[12] K. R. Harris, J. Chem. Phys. **131**, 054503 (2009).
[13] Z. Li, Phys. Rev. E **80**, 061204 (2009).
[14] F. Affouard, M. Descamps, L.-C. Valdes, J. Habasaki, P. Bordat, and K. L. Ngai, J. Chem. Phys. **131**, 104510 (2009).
[15] M. Agarwal, A. Ganguly, and C. Chakravarty, J. Phys. Chem. B **113**, 15284 (2009).
[16] J. C. Bosma and J. A. Wesselingh, Trans. IChemE **77**, 325 (1999).
[17] J. E. Mungall, Geochim. Cosmochim. Acta **66**, 125 (2002).
[18] H. A. Kooijman, Ind. Eng. Chem. Res. **41**, 3326 (2002).
[19] J. Brillo, S. M. Chathoth, M. M. Koza, and A. Meyer, Appl. Phys. Lett. **93**, 121905 (2008).
[20] J. Brillo, A. I. Pommrich, and A. Meyer, Phys. Rev. Lett. **107**, 165902 (2011).
[21] B. A. Kowert, N. C. Dang, K. T. Sobush, and L. G. Seele III, J. Phys. Chem. A **107**, 1253 (2003).
[22] F. Mallamace, C. Branca, C. Corsaro, N. Leone, J. Spooren, H. E. Stanley, and S.-H. Chen, J. Phys. Chem. B **114**, 1870 (2010).
[23] H. A. Walls and W. R. Upthegrove, Acta Metallurgica **12**, 461 (1964).
[24] F. H. Ree, T. Ree, and H. Eyring, Ind. Eng. Chem. **50**, 1036 (1958).
[25] H. Eyring and T. Ree, Proc. Nat. Acad. Sci. **47**, 526 (1961).
[26] R. Zwanzig, J. Chem. Phys. **79**, 4507 (1983).
[27] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 4th ed. (Academic Press, London, 2013).
[28] E. Helfand and S. A. Rice, J. Chem. Phys. **32**, 1642 (1960).
[29] Y. Hiwatari, H. Matsuda, T. Ogawa, N. Ogita, and A. Ueda, Prog. Theo. Phys. **52**, 1105 (1974).
[30] M. F. Pas and B. J. Zwolinski, Mol. Phys. **73**, 471 (1991).
[31] H. M. Roder, C. A. Nieto de Castro, and U. V. Mardolcar, Int. J. Thermophys. **8**, 521 (1987).
[32] H. J. M. Hanley, R. D. McCarty, and W. M. Haynes, J. Phys. Chem. Ref. Data **3**, 979 (1974).
[33] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford Science, New York, 1989).

[34] I.-C. Yeh and G. Hummer, J. Phys. Chem. B **108**, 15873 (2004).

[35] R. Gilgen, R. Kleinrahm, and W. Wagner, J. Chem. Thermodyn. **26**, 383 (1994).

[36] N. Ohtori, Y. Ishii, Y. Togawa, T. Oono, and K. Takase, Phys. Rev. E **89**, 022129 (2014).

[37] J. J. van Loef, Physica **62**, 345 (1972).

[38] J. P. Boon, J. C. Legros, and G. Thomaes, Physica **33**, 547 (1967).

[39] D. M. Heyes, M. J. Cass, J. G. Powles, and W. A. B. Evans, J. Phys. Chem. B **111**, 1455 (2007).

[40] A. C. Brańka and D. M. Heyes, Phys. Rev. E **69**, 021202 (2004).

[41] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).

[42] Y. Ishii, K. Sato, M. Salanne, P. A. Madden, and N. Ohtori, J. Chem. Phys. **140**, 114502 (2014).