PHYSICAL REVIEW B **71**, 094209 (2005)

Scaling law for diffusion coefficients in simple melts

G. X. Li, C. S. Liu,* and Z. G. Zhu

Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei 230031, People's Republic of China

(Received 18 August 2004; revised manuscript received 28 January 2005; published 30 March 2005)

Employing realistic many-body potentials for a series of simple melts, including Ag, Al, Au, Co, Cu, Mg, Ni, Pb, Pd, Pt, Rh, and Si, we tested by molecular-dynamics simulation the scaling laws of diffusion coefficients with different expressions of the reduction parameters. Our simulation results give sound support to the universal excess entropy scaling laws proposed by Rosenfeld [Phys. Rev. A **15**, 2545 (1977)] and Dzugutov [Nature (London) **381**, 137 (1996)] for transport coefficients in liquid metals. In particular, we find that excess entropy (S_{ex}) universally scales with temperature as $S_{ex}=-E_S/T$. When the diffusion coefficient is scaled as Dzugutov suggested, E_S is essentially identical to the Arrhenius activation energy, indicating that the entropic component in the Arrhenius activation energy is solely responsible for controlling the diffusion rate. Thus, there exists a link between the scaling law and the Arrhenius law, i.e., the excess entropy scaling law for the diffusion coefficient can be interpreted as a straightforward extension of the Arrhenius law.

DOI: 10.1103/PhysRevB.71.094209 PACS number(s): 66.10.−x, 61.20.Ja

I. INTRODUCTION

Transport coefficients, such as diffusion coefficient of liquids, are of immense importance not only for understanding liquid structures and thermophysical behaviors of liquids, but also for studying their flow behavior in practical engineering applications. Despite their fundamental importance, however, the transport coefficients remain elusive quantities. For example, the liquid diffusion coefficient is very difficult to be measured experimentally for high-temperature melts such as liquid metals and liquid semiconductors. It is not fully understood how the diffusion coefficient depends on the structure and thermodynamics of the liquid. To find a relation between liquid transport coefficients and structural properties remains one of the most challenging tasks in the field of condensed matter. A first attempt in this direction was probably made by Rosenfeld in 1977,[1] where the transport coefficients are expressed in terms of the corresponding internal entropies to reveal some universal characteristics. Rosenfeld[1,2] defined the reduced coefficient of self-diffusion, D, which is scaled by the macroscopic reduction parameters (density and temperature), namely a mean interparticle distance, $d=\rho^{-1/3}$, and the thermal velocity, $v=(k_BT/m)^{1/2}$:

$$D_R^* = D\frac{\rho^{1/3}}{(k_BT/m)^{1/2}}, \tag{1}$$

where ρ is the number density, T is the absolute temperature, k_B is the Boltzmann constant, and m is the atomic mass. The reduced diffusion coefficient was shown to be correlated to the excess entropy (S_{ex}) in a quasi-universal behavior:

$$D_R^* \approx 0.6e^{0.8S_{ex}}, \tag{2}$$

where S_{ex} is in units of k_B. Note that the reduction parameter of the diffusion coefficient by Rosenfeld is

$$D_R^0 = \frac{(k_BT/m)^{1/2}}{\rho^{1/3}}. \tag{3}$$

A few years ago, Dzugutov[3] proposed a similar universal scaling law on the basis of two main propositions. First, the transfer of energy and momentum in the liquid is mainly governed by the uncorrelated binary collisions described by the Enskog theory. Then, the diffusion coefficient is expressed in dimensionless units via

$$D_D^* = \frac{D}{\sigma^2\Gamma}, \tag{4}$$

that is, the reduction parameter of the diffusion coefficient is

$$D_D^0 = \sigma^2\Gamma, \tag{5}$$

where σ is the hard sphere diameter that corresponds practically to the position of the first peak of the pair correlation function $g(r)$ and Γ is the collision frequency according to the Enskog theory of atomic transport, $\Gamma=4\sigma^2g(\sigma)\rho\sqrt{\pi k_BT/m}$. Second, the frequency of the local structural relaxations, which defines the rate of the cage diffusion, is obviously proportional to the number of accessible configurations. In an equilibrium system, the constraints imposed by the structural correlations reduce this configuration number by a factor of $e^{S_{ex}}$. Thus, D_D^* and $e^{S_{ex}}$ must be connected by a universal linear relationship. For several model liquids including Pb, Cu, Lennard-Jones (LJ), and hard sphere systems, Dzugutov demonstrated that the universal scaling law of the diffusion coefficient is expressed by

$$D_D^* = 0.049e^{S_{ex}}. \tag{6}$$

In the original Dzugutov work, S_{ex} was approximated by the two-body contribution which is denoted by S_2 and is given by

$$S_2 = -2\pi\rho\int_0^\infty \{g(r)\ln[g(r)] - [g(r) - 1]\}r^2 dr. \qquad (7)$$

In addition, the scaling law also remains applicable to atomic transport in a quasicrystal and to silver-ion diffusion in the solid-state ionic conductor α-AgI.[3] For liquid metals modeled by the embedded atom potentials, some scatter in the data is observed, especially for liquid silicon modeled by the Stillinger-Weber potential; however, with the use of the more accurate excess entropy calculation rather than the S_2 form, there appears to be less scatter in the data.[4]

If true, in view of the absence of a unifying quantitative description of atomic transport in liquids, the scaling law is important for estimating unknown diffusion coefficients from diffraction measurements and for providing guidelines for theoretical analysis. So, it needs us to perform further studies in order to confidently label the universal scaling law and use it. On the one hand, lots of simulation results give the support to the scaling law,[3–7] and using mode coupling theory Samanta and co-workers[8] derived a new universal scaling relation of diffusion and reproduced the scaling law of Dzugutov. However, on the other hand, little is known of the nature of the scaling law and it is difficult to perform an experimental test because at certain temperatures both the diffusion data and the diffraction data are unavailable.

As mentioned above, using different reduction parameters of the diffusion coefficients, both Rosenfeld and Dzugutov obtained similar scaling laws relating the transport coefficients to the excess entropy, which means the choice of the reduction parameters is not unique. On the basis of the corresponding states principle, the reduced form of the diffusion coefficient could be formulated as the following:[9,10]

$$D_C^0 = \frac{\varepsilon^{1/2}\sigma}{m^{1/2}}. \qquad (8)$$

Here ε is the energy characteristic for the interatomic potential. It is interesting to see whether or not there exists the similar scaling relation on the diffusion, which may help us to understand the inside of the scaling law.

In the present work, using realistic many-body potentials for a series of simple melts, including Ag, Al, Au, Co, Cu, Mg, Ni, Pb, Pd, Pt, Rh, and Si, we first examine the scaling laws for different expressions of the reduction parameters as shown in Eqs. (3), (5), and (8), and then further explore the temperature dependence of the original and reduced diffusion coefficients and the excess entropy in order to throw light on the inside of the scaling laws. The rest of the paper is organized as follows: in Sec. II, the computational methods are described; in Secs. III and IV, the results are presented and discussed, respectively; and finally, the conclusions are given in Sec. V.

II. COMPUTATIONAL METHODS

The second-moment approximation of the tight-binding scheme (TB-SMA)[11] is a well-studied semi-empirical many-body interaction potential that has been widely used in numerical simulation studies in metals and alloys. For example, the melting and the dynamic properties such as the diffusion constants and viscosities of the fcc transition metals (including Ni, Pd, Pt, Cu, Ag, and Au) and simple fcc metals (including Al, Pb) in the liquid phase,[12] the cooling rate dependence of crystallization for liquid Cu,[13] the high temperature hcp-bcc transition in Zr,[14] and the structural and dynamic properties of Cu-Au bimetallic clusters[15] have been well investigated by using this potential. In the present paper, we employed TB-SMA to study the transport and structure properties of a series of simple and transition metals, including Ag, Al, Au, Co, Cu, Mg, Ni, Pb, Pd, Pt, and Rh. To make a comparison and test the effect of the interparticle interaction, the *glue* potential[16] was also employed to study Al, and the Stillinger-Weber (SW) potential[17] and the Tersoff potential[18] were employed to study liquid Si. The glue potential[16] can correctly reproduce many basic properties of Al in crystalline and noncrystalline phases. Using this potential, Sun and Gong have successfully studied the structural properties and glass transition in Al clusters;[19] Liu *et al.*[20] have investigated the cooling rate dependence of some microscopic and macroscopic quantities of liquid Al during rapid solidification. Using the Stillinger-Weber potential, Yu, Wang, and Stroud[21] have studied the structure and dynamics of liquid Si. The Tersoff potential has been used to investigate the validity of this potential for liquid Si[22,23] and it is found that this potential is very useful for the structural analysis of liquid Si, though the Tersoff potential overestimates greatly the melting temperature.

The computer simulations are based on constant-pressure molecular dynamics (MD) simulation[24] except for liquid Si. The simulated system consists of 500 atoms in a cubic cell with periodic boundary conditions. The Newtonian equations of motion are integrated using the velocity-Verlet algorithm. First, the system is heated up to liquid state. Then the system is run for 50 000 time steps to guarantee an equilibrium liquid state. Next the temperature is decreased for 30 000 time steps and run for 50 000 time steps to get another equilibrium state. For each of the recorded configurations, another run of 12 000 time steps at the given temperature is performed in order to collect data for analyzing the diffusion coefficient and the excess entropy. The MD calculations of liquid Si were performed under constant volume and constant temperature conditions. For the case of Tersoff potential, the temperatures studied are 3000, 3200, 3400, 3600, and 3800 K. For the case of the SW potential, the temperatures studied are 1700, 1800, 1900, 2000, and 2100 K. The corresponding densities are 2.61, 2.59, 2.57, 2.55, and 2.53 g cm^{-3}, which agree with the experimental data of liquid Si. The system consists of 512 atoms. First, we melted the diamond lattice to obtain an initial configuration. Then, the system was heated up to a desired temperature by rescaling the velocities of the particles. The system is run for 30 000 time steps to guarantee an equilibrium liquid state. Another run of 12 000 time steps at the given temperature is performed for analyzing the diffusion coefficient and the excess entropy. The diffusion coefficient is calculated from the integral of the velocity-velocity correlation functions. The excess entropy, S_{ex}, is approximately calculated from Eq. (7), where $g(r)$ are obtained by averaging 20 configurations sampled during the run of 12 000 time steps.

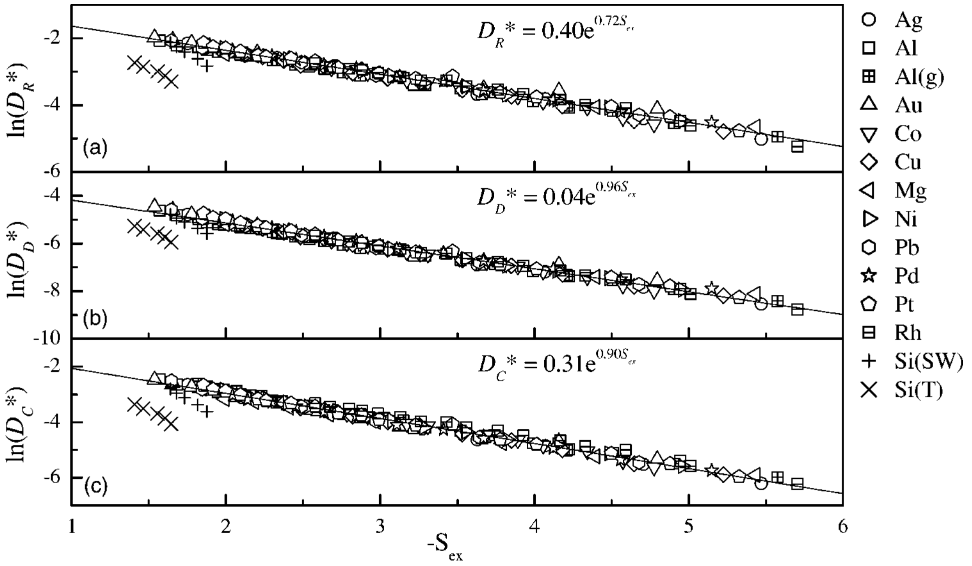

FIG. 1. The reduced diffusion coefficients D^* as a function of the excess entropy S_{ex}. D_R^*, D_D^* and D_C^* are scaled by Eqs. (3), (5), and (8), respectively. Entropy is expressed in units of κ_B. The solid lines, being the best fit to the data, represent the present scaling law of equations given in (a), (b), and (c).

III. RESULTS

Figure 1 shows the reduced diffusion coefficients as a function of the excess entropy for three different choices of reduced parameters, respectively. We find that, based on three different choices of the reduction parameters D^0 as defined by Eqs. (3), (5), and (8), the scaling laws of diffusion coefficients hold rather well for all simulated liquids but liquid Si. So the present results not only give the sound support to early attempts at finding the universal scaling laws by Rosenfeld and Dzugutov for transport coefficients in liquid metals, but also tell us that there are many choices of the reduction parameters to find the scaling laws of the type $D^* = Ae^{BS_{ex}}$. The magnitude of A and B depends on the choice of the reduction parameters. In addition, the difference of results for liquid Al modeled by TB-SMA and glue potentials is very small, but the difference of the results for liquid Si modeled by SW and Tersoff potentials is large, which results from the Tersoff potential overestimating greatly the melting temperature. From this figure, we can also observe that the slope of the line for the case of liquid Si is higher than that for liquid metals.

As is well known, the temperature dependence of the diffusion coefficient in liquid phase exhibits an Arrhenius-type relationship even though no rigorous theoretical explanation has been given,

$$D = D_0 \exp\left(-\frac{E}{k_B T}\right), \tag{9}$$

where D_0 and E are constants; D_0 is generally referred to as the diffusion preexponential factor, and E is called the activation energy. We plotted the natural logarithm of original diffusion coefficients (D) and reduced diffusion coefficients (D_R^*, D_D^*, and D_C^*) against the reciprocal temperature in Fig. 2. It is interesting that not only the original diffusion data but also the reduced diffusion coefficients can be linearly fitted with a high degree of accuracy. A glance at Figs. 2(b)–2(d)

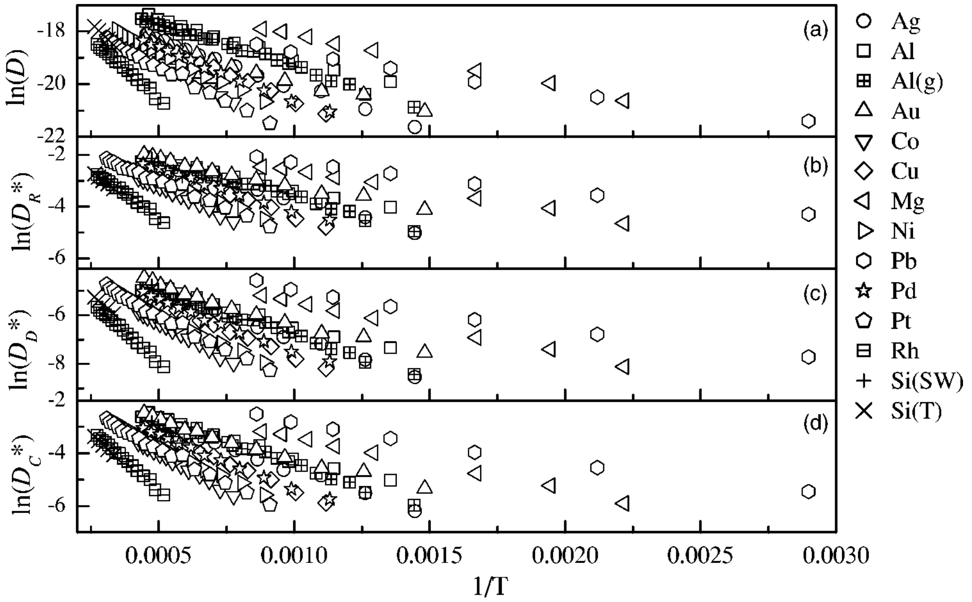

FIG. 2. The Arrhenius plots for the original diffusion coefficiet and reduced diffusion coefficients via three different reduction parameters D^0 as defined by Eqs. (3), (5), and (8).

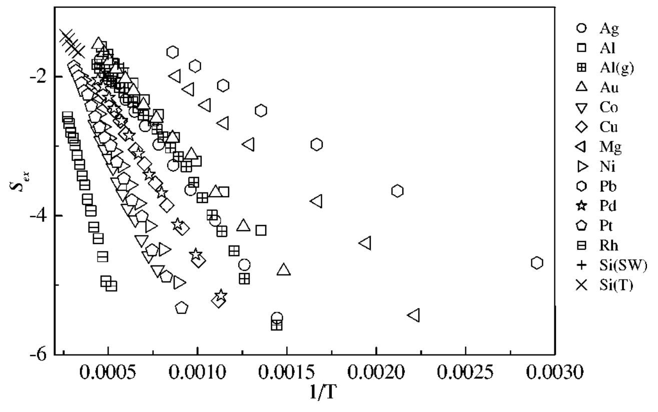

FIG. 3. The excess entropy S_{ex} (in units of k_B) versus reciprocal temperature.

shows that the reduced diffusion coefficients D_R^*, D_D^*, and D_C^* exhibit the identical temperature dependence for all studied liquids. These linear fits of semilog curves of D, D_R^*, D_D^*, and D_C^* yield the intercepts (I_{un}, I_R, I_D, and I_C) and the slopes (E_{un}, E_R, E_D, and E_C), which are shown in Fig. 4. Figure 3 shows the excess entropy versus the reciprocal temperature. This figure indicates that there exists a linear relationship between S_{ex} and $1/T$, similar to that between the natural logarithm of D (or D^*) and $1/T$. For every studied liquid, the intercept I_S and the absolute value of slope E_S obtained by the linear fitting of S_{ex} and $1/T$ are also shown in Fig. 4. Note that E_S has the dimensionality of energy. It is natural that the functional form linking the diffusion coefficient and the excess entropy is D (or D^*) $\sim\exp(S_{ex})$, because D (or D^*) $\sim\exp(-1/T)$ and $S_{ex}\sim -1/T$.

Let us now evaluate the relationships $S_{ex}\sim -1/T$ and D (or D^*) $\sim\exp(-1/T)$. As can be seen from Fig. 4(a), for various liquids I_S fluctuates around zero and is close to zero, which indicates that the expression ($S_{ex}=-E_S/T$) provides a universal link between S_{ex} and $1/T$; in other words, the excess entropy S_{ex} universally scales with temperature as $-E_S/T$. I_R, I_D, and I_C for various liquids, with a notable exception of liquid Si modeled by SW potential, fluctuate around −0.94, −3.24, and −1.16, respectively. Compared to I_R, I_D, and I_C, I_{un} fluctuates more strongly. In a word, for all studied liquids, with the exception of SW-modeled liquid Si, I_S, I_R, I_D, and I_C are nearly independent on the element species. As can be seen from Fig. 4(b), for liquid elements except liquid Si E_{un}, E_D, E_C, and E_S are almost equal to the same magnitude. E_R is always smaller than E_{un}, E_D, E_C, and E_S. The ratio of the activation energy E_{un}, E_R, E_D, and E_C obtained from the diffusion coefficients to the activation energy E_S obtained from the entropy for various liquid elements shown in Fig. 5 indicates a much clearer relationship. For various liquids, with the exception of liquid Si, E_{un}/E_S, E_R/E_S, E_D/E_S, and E_C/E_S keep constants 0.90, 0.72, 0.96, and 0.90, respectively, that is, E_{un}/E_S, E_R/E_S, E_D/E_S, and E_C/E_S exhibit the independence of liquid species.

Figure 6 presents the reduction parameters D^0 as defined by Eqs. (3), (5), and (8) for various liquids as a function of temperature. It is apparent that with the increase of temperature, D_R^0 increases, D_D^0 slightly decreases, and D_C^0 keeps a constant. Therefore, for three different choices of the reduction parameters, they are different from the parameters (A and B) entering the scaling law of diffusion coefficients ($D^*=Ae^{BS_{ex}}$): for $D_R^0=(k_BT/m)^{1/2}/\rho^{1/3}$, $B=0.72$; for $D_D^0=\sigma^2\Gamma$, $B=0.96$; and for $D_C^0=\varepsilon^{1/2}\sigma/m^{1/2}$, $B=0.90$.

IV. DISCUSSIONS

What is the nature and the origin of the scaling law ($D^*=Ae^{BS_{ex}}$) for the transport coefficients? Why do A and B depend on the choice of the reduction parameters? Why does the scaling law in liquid metals not hold for liquid Si? Keeping these questions in mind, we make the following discussions.

On the basis of the obtained results as shown in Figs. 2–5, we think that there are four reasons for the scaling law of diffusion coefficients as $D^*=Ae^{BS_{ex}}$ in liquid metals. (1) The original and reduced diffusion coefficients hold the Arrhenius relationship $[D=D_0\exp(-E/k_BT)]$; note that the diffusion

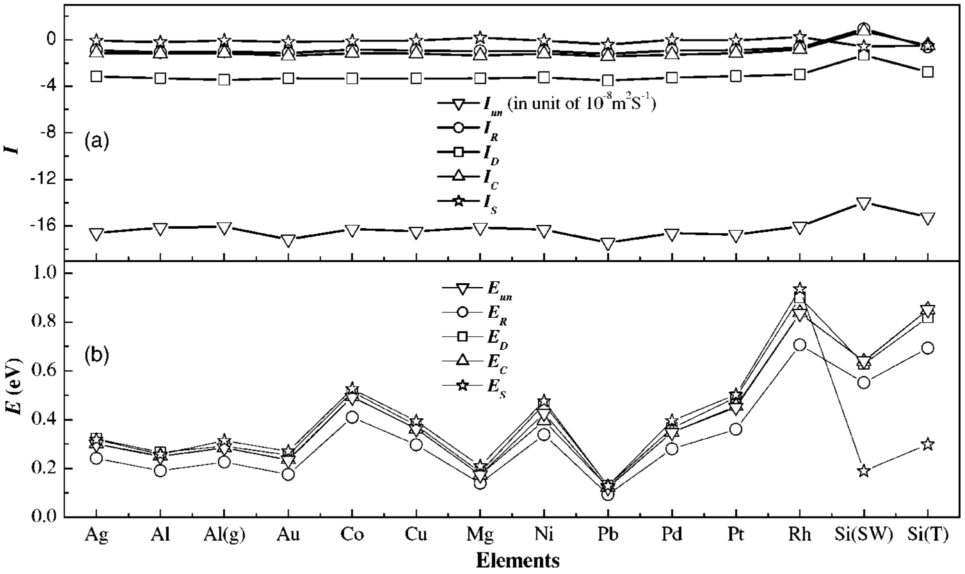

FIG. 4. The intercepts (I_{un}, I_R, I_D, I_C, and I_S) and the slopes (E_{un}, E_R, E_D, E_C, and E_S) for various liquids. These linear fits of semilog curves of the original and reduced diffusion coefficients (D, D_R^*, D_D^*, and D_C^*) yield the intercepts (I_{un}, I_R, I_D, and I_C) and the slopes (E_{un}, E_R, E_D, and E_C).

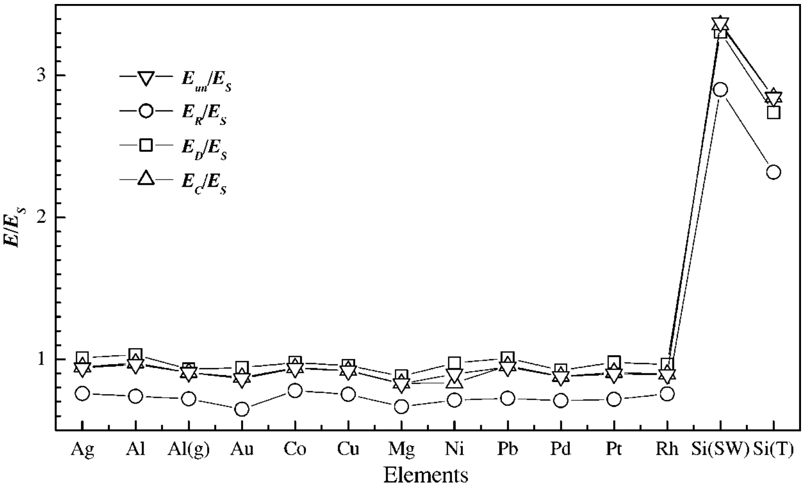

FIG. 5. E_{un}/E_S, E_R/E_S, E_D/E_S, E_C/E_S for various liquids and E_{un}, E_R, E_D, E_C, and E_S are described as in Fig. 4 and in the text.

preexponential factor D_0 and the activation energy E are dependent on liquid species. (2) The excess entropy S_{ex} universally scales with temperature as $S_{ex}=-E_S/T$; note that E_S depends on liquid species, too. (3) The reduction parameters D^0 as defined by Eqs. (3), (5), and (8) eliminate the element dependence of the diffusion preexponential factor, which is suggested by the element independence of I_R, I_D, and I_C. (4) E_R/E_S, E_D/E_S, and E_C/E_S exhibit the element independence, even though the activation energies obtained from the reduced diffusion coefficients and the excess entropy are dependent on liquid species. Our present results show that the scaling laws for the diffusion coefficient and the Arrhenius law are linked via the relationship connecting the excess entropy and the temperature as $S_{ex}=-E_S/T$. That is, if $D^*=Ae^{BS_{ex}}$ plus $S_{ex}=-E_S/T$, then it is natural that the diffusion coefficient exhibits an Arrhenius relationship; if $D=D_0\exp(-E/k_BT)$ and $S_{ex}=-E_S/T$, then the diffusion coefficient scales with the excess entropy as $e^{S_{ex}}$. There is an additional result in the supercooled liquids by Dzugutov[5,25] that supports the present finding. In a supercooled liquid the Arrhenius law is no longer observed; Dzugutov showed that the scaling law is not obeyed.

The parameters (A and B) entering the scaling law that connects D^* and S_{ex} depend on the choice for the reduced diffusion coefficient. When the reduced parameter was postulated to be $D_R^0=(k_BT/m)^{1/2}/\rho^{1/3}$ by Rosenfeld,[1] $B=0.72$; when it was assumed to be $D_D^0=\sigma^2\Gamma$ by Dzugutov,[3] $B=0.96$; when it was formulated as $D_C^0=\varepsilon^{1/2}\sigma/m^{1/2}$ on the basis of the corresponding states principle,[9,10] $B=0.90$. D_R^0, D_D^0, and D_C^0 exhibit different temperature dependence as shown in Fig. 6, so B has different values in the different cases. Let us restate the details of the different postulates of the reduced parameter D^0 by Rosenfeld[1,2] and Dzugutov.[3] Rosenfeld defined the dimensionless diffusion coefficient as Eq. (1) by choosing macroscopic reduction parameters, namely, a mean interparticle distance $d=(V/N)^{1/3}=\rho^{-1/3}$ and the thermal velocity $\upsilon_{th}=(k_BT/m)^{1/2}$, which lead to $D_R^0=\rho^{-1/3}(k_BT/m)^{1/2}$. Dzugutov defined the dimensionless diffusion coefficient as Eq. (4) by choosing the hard-sphere diameter σ [being replaced by the position of the first peak of $g(r)$] and the Enskog collision frequency $\Gamma=4\sigma^2g(\sigma)\rho\sqrt{\pi k_BT/m}$, which provide a natural unit of length and a natural time scale for dynamics, respectively, thus leading to $D_D^0=\sigma^2\Gamma=4\sqrt{\pi}g(\sigma)\sigma^4\rho(k_BT/m)^{1/2}$. An im-

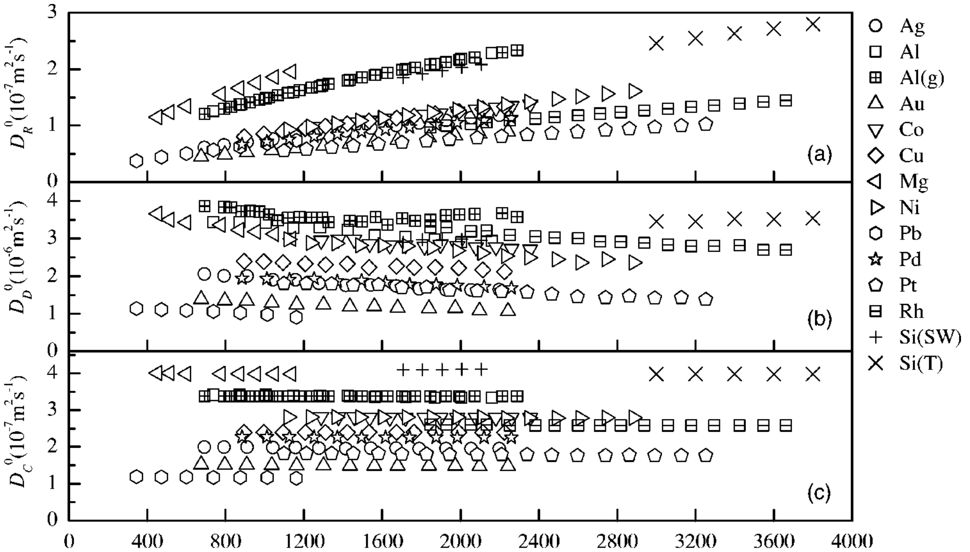

FIG. 6. The different reduction parameters D^0 as defined by Eqs. (3), (5), and (8) as a function of temperature.

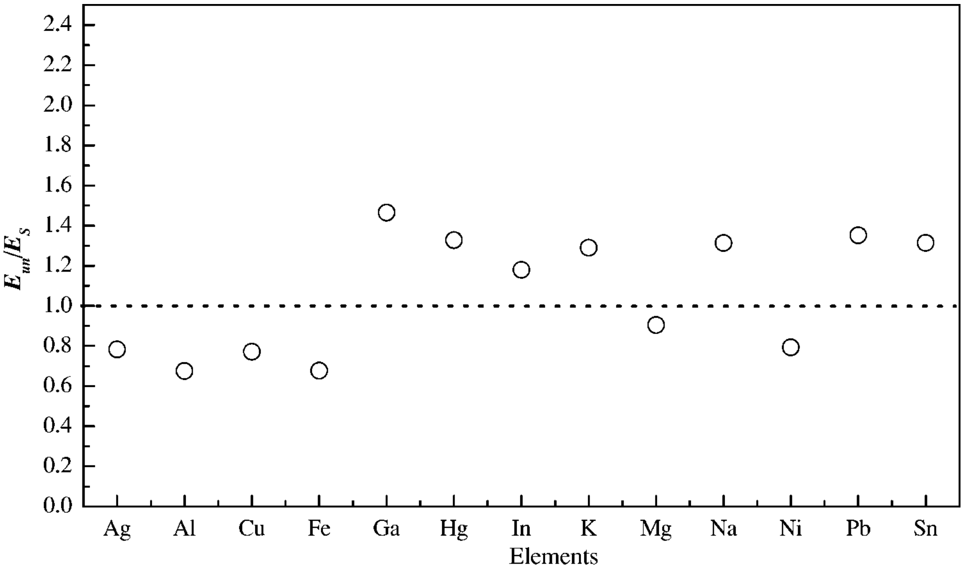

FIG. 7. The ratio of the experimental activation-energy E (in Ref. 26) to the activation energy E_S obtained from the experimental $g(r)$ data (in Ref. 27) for various liquid elements.

portant distinction of D_R^0 and D_D^0 is that D_D^0 includes $g(\sigma)$, which changes with temperature. In consequence, D_R^0 and D_D^0 show a different temperature dependence. It should be emphasized that, as demonstrated in Figs. 3 and 5, if the diffusion coefficient is scaled with D_D^0, E_D/E_S is essentially equal to 1, namely, E_S becomes identical to the Arrhenius activation energy. This makes it possible to avoid the empirical or fitting constant B in the general formulation of the scaling laws. Moreover, it indicates that the entropic component in the Arrhenius activation energy, which turns out to be TS_{ex}, is solely responsible for controlling the diffusion rate. A similar conclusion was reported in the case of a hard sphere by Dzugutov.[25]

Besides the above-mentioned distinction of reduced parameters D_R^0 and D_D^0, it should be stressed again that, as indicated in Sec. I, there exists a principal difference between the two scaling laws by Dzugutov and Rosenfeld. Dzugutov's scaling law is based on the postulate that both the diffusion rate and the rate of structural relaxation are proportional to the available phase-space volume which scales with the excess entropy as $e^{S_{ex}}$. As shown in Figs. 2 and 3, the diffusion coefficient holds the Arrhenius relationship and the excess entropy S_{ex} universally scales with temperature as $S_{ex}=-E_S/T$. Thus the diffusion coefficient scales with the excess entropy as $e^{S_{ex}}$, which directly supports this postulate.

We now turn our attention to the failure of the scaling laws in application liquid Si. As mentioned in Sec. I, Hoyt *et al.*[4] recently reported that the scaling law does not hold in the case of Si. They stressed the very different liquid structure observed in liquid Si from that in the examined metallic liquids: in liquid Si, besides the first peak in $g(r)$ there exists a small peak on the high-r side; in liquids characterized by central force potentials the first peak in $g(r)$ is very sharp. So, in liquid Si, the first neighbor shell actually consists of two closely spaced shells. They proposed that the collision frequency $\Gamma[=4\sigma^2 g(\sigma)\rho\sqrt{\pi k_B T/m}]$ developed for hard-sphere systems is no longer appropriate. Thus the Dzugutov scaling law fails for the case of Si. According to our present simulation results, we obtained a different explanation for the failure of the scaling law. As can be seen in Fig. 3, in liquid Si the excess entropy (S_{ex}) scales with temperature as $S_{ex}=-E_S/T$, like that in simulated metallic liquids. The most notable feature of Fig. 5 is that the values of E_R/E_S, E_D/E_S, and E_C/E_S of liquid Si are much larger than those of the examined metallic liquids, which results in the failure of the scaling laws in presently simulated Si. The very different behaviors of E_R/E_S, E_D/E_S, and E_C/E_S for the case of Si from those for the case of metals may suggest the calculated E_R, E_D, and E_C may be inaccurate from the SW and Tersoff potentials, and particularly the calculation of excess entropy by the two-body approximation is not accurate for the case of Si due to the complicated local structures in liquid Si, which gives rise to the wrong result of E_S. In other words, for liquid metals it is reasonable to expect that the excess entropy could be calculated approximately in terms of the two body contribution, but for liquid Si it is unreasonable. This is supported by the difference in the slope of the line for liquid Si between our result and Hoyt *et al.*'s result: The slope of the line for liquid Si is higher than that for liquid metals in our case, whereas the slopes of the line for liquid Si obtained by Hoyt *et al.* is slightly lower.[4] We calculated the excess entropy by the two-body approximation given by Eq. (7), while Hoyt *et al.* calculated the actual excess entropy. Thus further works are needed to explore the source of the failure for the case of Si.

Based on our present results, we believe that a key reason for the scaling law of diffusion in liquid metals is the element independence of E_R/E_S, E_D/E_S, and E_C/E_S, namely, E_S is essentially identical to the Arrhenius activation energy. This may provide an easy way to test the scaling law of diffusion by experimental data. Using the self-difusivity data in Tables 7.2 and 7.3 of Ref. 26 and $g(r)$ data in Ref. 27, we first calculated the excess entropy by the two-body approximation, then obtained E_S through the plot of S_{ex} against $1/T$, and finally pictured E_{un}/E_S for various liquid metals in Fig. 7. As can be seen from this figure, the magnitude of E_{un}/E_S is 0.68–1.46, fluctuating around 1.06 for various elements. The result is in agreement with the simulation result to some extent, but the fluctuation is stronger. This may result from the error due to the limited $g(r)$ data. The $g(r)$ data are available at three to five different temperatures, and E_S is obtained from the slope of the line of S_{ex} versus $1/T$. To make an accurate comparison between the simulation and experiment results, the experimental data on $g(r)$ at more temperatures are necessary.

V. CONCLUSIONS

Using realistic many-body potentials for a series of simple melts, including Ag, Al, Au, Co, Cu, Mg, Ni, Pb, Pd, Pt, Rh, and Si, we examined the scaling laws of diffusion with different expression of the reduction parameters. Then we further explore the temperature dependence of the original and reduced diffusion coefficients and the excess entropy. Our simulation results give the sound support to early attempts at finding the universal scaling laws by Rosenfeld and Dzugutov for transport coefficients in liquid metals. Our analysis indicates that there are four reasons for the scaling law of diffusion. (1) The diffusion coefficient usually shows the Arrhenius relationship. (2) The expression ($S_{ex}=-E_S/T$) provides a universal link between excess entropy and temperature. (3) The reduction parameters D^0 as defined by Eqs. (3), (5), and (8) eliminate the element dependence of the diffusion preexponential. (4) The ratio of the activation energy E_{un}, E_R, E_D, and E_C to the activation energy E_S for various metallic liquids exhibits the element independence, even though all activation energies are dependent on liquid species. So we can conclude that there exists a link between the examined scaling law and the Arrhenius law from the excess entropy universally scaling with temperature. When the diffusion coefficient is scaled as Dzugutov suggested, E_S is essentially identical to the Arrhenius activation energy, indicating that the entropic component in the Arrhenius activation energy is solely responsible for controlling the diffusion rate, and this makes it possible to avoid the empirical constant B in the general formulation of the scaling laws. Our present results also directly support the postulate by Dzugutov that both the diffusion rate and the rate of structural relaxation are proportional to the available phase-space volume which scales as $e^{S_{ex}}$. The failure of liquid Si to obey the scaling law may mainly be due to the unreasonable estimation of excess entropy. Our present results not only help us understand the nature of the scaling law of diffusion, but also provide an easy way to test the scaling law of diffusion by experimental data.

ACKNOWLEDGMENTS

We thank Dr. D. Y. Sun for valuable discussions. This work was supported through the National Natural Sciences Foundation of China under Grant Nos. 10174082 and 10374089, and by the Center for Computational Science, Hefei Institutes of Physical Sciences.

---

*Author to whom correspondence should be addressed. E-mail: csliu@issp.ac.cn

[1] Y. Rosenfeld, Phys. Rev. A **15**, 2545 (1977).

[2] Y. Rosenfeld, J. Phys.: Condens. Matter **11**, 5415 (1999).

[3] M. Dzugutov, Nature (London) **381**, 137 (1996).

[4] J. J. Hoyt, M. Asta, and B. Sadigh, Phys. Rev. Lett. **85**, 594 (2000).

[5] M. Dzugutov, J. Phys.: Condens. Matter **11**, A253 (1999).

[6] I. Yokoyama, Physica B **269**, 244 (1999).

[7] T. Arai and T. Shirasuna, J. Non-Cryst. Solids **312–314**, 208 (2002).

[8] A. Samanta, Ali Sk. Musharaf, and S. K. Ghosh, Phys. Rev. Lett. **87**, 245901 (2001); **92**, 145901 (2004).

[9] E. Helfand and S. A. Rice, J. Chem. Phys. **32**, 1642 (1960).

[10] J. L. Bretonnet, J. Chem. Phys. **120**, 11100 (2004).

[11] F. Cleri and V. Rosato, Phys. Rev. B **48**, 22 (1993).

[12] L. Gomez, A. Dobry, and H. T. Diep, Phys. Rev. B **55**, 6265 (1997); M. M. G. Alemany, O. Dieguez, C. Rey, and L. J. Gallego, *ibid.* **60**, 9208 (1999).

[13] C. S. Liu, J. Xia, Z. G. Zhu, and D. Y. Sun, J. Chem. Phys. **114**, 7506 (2001).

[14] F. Willaime and C. Massobrio, Phys. Rev. Lett. **63**, 2244 (1989).

[15] M. J. Lopez, P. A. Marcos, and J. A. Alonso, J. Chem. Phys. **104**, 1056 (1996).

[16] F. Ercolessi and J. B. Adams, Europhys. Lett. **26**, 583 (1994).

[17] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).

[18] J. Tersoff, Phys. Rev. B **38**, 9902 (1988); **39**, 5566 (1989).

[19] D. Y. Sun and X. G. Gong, Phys. Rev. B **57**, 4730 (1998).

[20] C. S. Liu, Z. G. Zhu, J. Xia, and D. Y. Sun, J. Phys.: Condens. Matter **13**, 1873 (2001).

[21] W. Yu, Z. Q. Wang, and D. Stroud, Phys. Rev. B **54**, 13 946 (1996).

[22] M. Ishimaru, K. Yoshida, and T. Motooka, Phys. Rev. B **53**, 7176 (1996); M. Ishimaru, K. Yoshida, T. Kumamoto, and T. Motooka, *ibid.* **54**, 4638 (1996).

[23] C. S. Liu, Z. G. Zhu, J. Xia, and D. Y. Sun, Phys. Rev. B **60**, 3194 (1999); Z. G. Zhu and C. S. Liu, Phys. Rev. B **61**, 9322 (2000).

[24] H. C. Andersen, J. Chem. Phys. **72**, 2383 (1980); D. Brown and J. H. R. Clarke, Mol. Phys. **51**, 1243 (1984).

[25] M. Dzugutov, Phys. Rev. E **65**, 032501 (2002).

[26] T. Iita and R. I. L. Guthrie, *The Physical Properties of Liquid Metals* (Clarendon, Oxford, 1988).

[27] Y. Waseda, *The Structure of Non-Crystalline Materials* (McGraw-Hill, New York, 1980).