



Revisiting scaling laws for the diffusion coefficients in simple melts based on the structural deviation from hard-sphere-like case

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ABSTRACT

Molecular simulations of a series of simple melts, including Al, Cu, Ni, Pt, Ti, Si and Ge, are used to study the scaling laws of diffusion coefficients proposed by Rosenfeld and Dzугutov. Our simulation results give strong support to the result that the scaling laws of diffusion coefficients hold true for simple liquids with isotropic many-body interactions but fail for systems with anisotropic interatomic interaction. The failure of the scaling laws in application liquid Si (*l*-Si) and liquid Ge (*l*-Ge) is connected to the fact that the excess entropy of them cannot be calculated approximately in terms of the two-body contribution and the original reduction parameters are no longer appropriate. In particular, since the ratio between the positions of the second and first peaks in structure factor (Q_2/Q_1) is a direct measure of the structural deviation from the hard-sphere-like case, the temperature dependence of Q_2/Q_1 was analyzed. Moreover, in comparison with 1.86, the value of Q_2/Q_1 for the hard-sphere-like case, we modified the scaling laws of diffusion coefficients proposed by Rosenfeld and Dzугutov. The modified scaling relations are appropriate not only for simple liquid metals, but also for *l*-Si and *l*-Ge with anisotropic interatomic interaction.

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1. Introduction

Diffusion phenomena play a very important role in various disciplines of applied science and considerable attention has been paid to the self-diffusivity in simple liquids resulting into various experimental and theoretical developments [1]. It has been demonstrated that the self-diffusivity D of several equilibrium simple fluids, when cast in an appropriately reduced form, shows an approximate scaling with S_{ex} , the excess entropy per particle of the fluid [2–10,12]. As summarized by Rosenfeld [3], the excess entropy scaling relation is a semi-quantitative model, rather than a theory. However, this type of empirical scaling behavior has great practical significance because it relates the dynamic quantity, D , that can be difficult to predict or measure to an experimentally accessible thermodynamic quantity, S_{ex} , which can be calculated directly from a computer simulation or estimated on the basis of knowledge of the pair correlation function.

Entropy scaling relation for the transport coefficients of liquids was first proposed by Rosenfeld [2,3]. Based on the success of variational hard-sphere thermodynamic perturbation theory and corresponding states arguments, he defined the reduced coefficient of self-diffusion, D_R , which is scaled by macroscopic reduction

parameters (density and temperature), namely a mean interparticle distance, $d = \rho^{-1/3}$ and thermal velocity, $v = (k_B T/m)^{1/2}$:

$$D_R = D \frac{\rho^{1/3}}{(k_B T/m)^{1/2}}, \quad (1)$$

where ρ is the number density, k_B is the Boltzmann constant, T is the temperature, and m is the particle mass. The reduced diffusion coefficient was shown to be correlated to the excess entropy in a quasi-universal behavior:

$$D_R \approx 0.6e^{0.8S_{ex}}, \quad (2)$$

where S_{ex} is in units of k_B . This form of the reduced self-diffusivity is suggested by an elementary kinetic theory for a dense medium of particles with thermal velocities but with a mean free path between collisions which is of the order of the average interparticle distance. Note that the reduction parameter of the diffusion coefficient by Rosenfeld is

$$D_{R0} = \frac{(k_B T/m)^{1/2}}{\rho^{1/3}}. \quad (3)$$

Recognizing that the relevant effects of the collisional events are mainly due to the harsh repulsion prevailing at small separations, Dzугutov [4] proposed another universal relation linking the diffusion coefficient and the excess entropy, from molecular dynamics calculations. The diffusion coefficient is expressed in dimensionless

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units via

$$D_D = \frac{D}{\sigma^2 \Gamma}, \quad (4)$$

that is, the reduction parameter of the diffusion coefficient is

$$D_{D0} = \sigma^2 \Gamma. \quad (5)$$

Here, 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 transition, $\Gamma = 4\pi\sigma^2\rho g(\sigma)(k_B T/m\pi)^{1/2}$, where $g(r)$ is the pair correlation function evaluated at the separation distance σ . Dzугutov demonstrated that the universal scaling law of the diffusion coefficient is expressed by

$$D_D = 0.049e^{S_{ex}}. \quad (6)$$

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

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

Because of the choice of macroscopic reduction parameters for the transport coefficient rather than microscopic potential parameters, the Rosenfeld scaling can be applied directly to real materials. From this point of view it can be even a more effective recipe than the Dzугutov scaling [3]. The Rosenfeld approach, where the exponential scaling is more general and holds for a wider range of liquids, even though the scaling parameters will depend on the functional form of the interaction potential and will be identical only for conformal potentials [11].

It is well known that most simple liquids with isotropic potentials obey these two scaling laws [2–10]. But at the same time, unlike the behavior of the simple metals, the data for liquid Si (*l*-Si) with anisotropic interatomic interactions significantly deviates from the excess entropy scaling laws of Rosenfeld and Dzугutov [5,6,13]. These systematic deviations are partly related to the fact that the excess entropy could be calculated approximately in terms of the two-body contribution for liquid metals with isotropic many-body interactions, but the two-body approximation is not accurate for the case of system with anisotropic interatomic interaction due to the complicated local structures [6]. Furthermore, Hoyt et al. [5] proposed that the collision frequency developed for hard-sphere systems is no longer appropriate for *l*-Si since the liquid structure observed in *l*-Si is very different from that in the metallic liquids: in *l*-Si, besides the first peak in $g(r)$ there exists a small peak in the high- r side while in liquids characterized by central force potentials the first peak in $g(r)$ is very sharp. Therefore, in *l*-Si, the first neighbor shell actually consists of two closely spaced shells. They replaced the quantity $\sigma^2 g(\sigma)$ with the sum $\sigma_1^2 g(\sigma_1) + \sigma_2^2 g(\sigma_2)$, where the subscripts 1 and 2 refer to the positions of the two closely spaced peaks in $g(r)$. This two-shell model was applied to a representative *l*-Si data point and the corrected data point is in quite good agreement with the embedded atom method potentials data. However, as mentioned by Hoyt et al. The two-shell model could not be applied to every data point because at high temperatures the two peaks in $g(r)$ merge to such an extent that the second position could not be defined.

In this general context it is desirable to construct an alternative reduction parameter of the diffusion coefficient which is appropriate for both simple liquids with isotropic interactions and systems with anisotropic interatomic interaction, such as *l*-Si and liquid Ge (*l*-Ge). For this purpose, we carry out Monte Carlo simulations and molecular dynamic simulations for several simple melts, including Al, Cu, Ni, Pt, Ti and Si as well as Ge, over wide range of equilibrium conditions, thereby obtaining information about the temperature dependence of structural properties and dynamic properties in the liquid state. Furthermore, we give two

modified reduction parameters of the diffusion coefficient using these structural properties.

The rest of the paper is organized as follows: in Section 2, the computational methods and details are described; in Section 3, the results are presented and discussed; finally, the conclusions are given in Section 4.

2. Computational method and details

The interparticle interactions of simple metals including Al, Cu, Ni, Pt and Ti were described by the second-moment approximation of the tight-binding scheme [14], which has been widely used in numerical simulation studies in metals and alloys [6,14–16]. According to this formalism, the potential energy U of a system can be written as

$$U = \sum_i \left\{ \sum_j A e^{-p(r_{ij}/r_0-1)} - \left(\sum_j \xi^2 e^{-2q(r_{ij}/r_0-1)} \right)^{1/2} \right\}, \quad (8)$$

where the sum is over all atoms in the system, r_{ij} represents the distance between atom i and j , and r_0 is the first-neighbors distance of the bulk crystal. The repulsive portion is a Born–Mayer pair-wise interaction. The attractive term mimics the form of the square root of the second moment of local density of states, and hence has a many-body character. In this paper, we use the value of parameters A , ξ , p and q as given by Cleri and Rosato [14]. The Stillinger–Weber (SW) potential [17] is employed to model *l*-Si and *l*-Ge atomic interaction. The SW potential has been widely used in studies of the liquid phase [17–20]. The calculated pair correlation function and its Fourier transform are in good agreement with experiments [20]. It takes the following form:

$$\Phi = \sum_{i < j} \varepsilon f_2(r_{ij}/\sigma) + \sum_{i < j < k} \lambda f_3(\vec{r}_i/\sigma, \vec{r}_j/\sigma, \vec{r}_k/\sigma). \quad (9)$$

Here f_2 is the pair interaction term, f_3 is the three-body interaction term which stabilized the tetrahedral structure of bulk Si, ε is the potential well depth, σ is the length parameter, and λ is the scaling factor which reflects the relative strength of the two- and three-body interactions. The functional forms and the associated parameter values of f_2 and f_3 can be found in Ref. [17]. The potential parameters we chose are: $\varepsilon = 3.315$ eV, $\sigma = 2.095$ Å and $\lambda = 21$ for *l*-Si as in Ref. [17], and $\varepsilon = 1.925$ eV, $\sigma = 2.181$ Å and $\lambda = 19.5$ for *l*-Ge as in Ref. [19].

As we know, the entropy can be calculated from the density of states as

$$S(N, E, V) = k_B \ln \Omega(N, E, V), \quad (10)$$

where k_B is the Boltzmann constant, and $\Omega(N, E, V)$ is the density of states. A novel Monte Carlo method has been proposed by Wang and Landau [21] for direct calculation of the density of states of systems as a function of one or more macroscopic observables like energy, temperature and volume. This method has drawn wide attention of researchers due to its straightforward implementation and wide applicability. Also it has been generalized for off-lattice simulations [22]. In the Wang–Landau algorithm the probability of observing a particular atomic configuration is inversely proportional to the density of states corresponding to the given state, that is to say, the new state is accepted with probability:

$$p(E_i, V_i \rightarrow E_j, V_j) = \min \left[\left(\frac{V_j}{V_i} \right)^N \frac{\Omega(E_i, V_i)}{\Omega(E_j, V_j)}, 1 \right], \quad (11)$$

where E_i and E_j are the energies of the initial and final states, V_i and V_j are the volumes of the initial and final states, respectively.

The density of states is initially set so $\Omega(E,V) = 1$, and the density of states is modified at every simulation step. For each visited states, the corresponding $\Omega(E,V)$ is updated according to $\Omega(E,V) = f \times \Omega(E,V)$, where f is an arbitrary convergence factor which tend to unity as the calculation proceeds. We also keep track of the histogram $H(E,V)$, counting the number of times each energy is visited. Once the histogram is sufficiently flat, f is reduced and $H(E,V)$ is reset to zero. These steps are repeated until f has become close to unity. With an accurate density of states, the partition function or the averages of other important thermodynamic quantities can be calculated directly, for example entropy can be computed by Eq. (10). Reweighting techniques [23] is employed for transforming $S(N,V,E)$ as a function of temperature. Since the density of states is modified every time the state is visited, a relative density of states and relative entropy are obtained only at the end of the simulation [21]. The difference between the relative entropy and the absolute entropy is a constant. In order to get the value of the constant, we select the Lennard–Jones (LJ) system as a reference system whose equation of states is known and then the absolute entropy is easy to obtain [24]. For the studied system at the state point (N_0, V_0, T_0) , the entropy of system of interest, denoted by $S(N_0, V_0, T_0)$, is evaluated by

$$S(N_0, V_0, T_0) = S_{LJ}(N_0, V_0, T_0) + \frac{1}{T} [\Delta U(N_0, V_0, T_0) - \Delta F(N_0, V_0, T_0)], \quad (12)$$

where $S_{LJ}(N_0, V_0, T_0)$ is the entropy of LJ system at the same state, $\Delta U(N_0, V_0, T_0)$ is the difference of internal energy between LJ system and the system of interest at the same state, and $\Delta F(N_0, V_0, T_0)$ is the difference of free energy between LJ system and the system of interest. According to the thermodynamic integration method it can be written as

$$\Delta F(N_0, V_0, T_0) = F(N_0, V_0, T_0) - F_{LJ}(N_0, V_0, T_0) = \int_0^1 d\lambda \left\langle \frac{\partial U_\lambda}{\partial \lambda} \right\rangle_\lambda, \quad (13)$$

where λ is the coupling parameter, which interpolates between the potential function U_{LJ} and U such that: $U_\lambda = (1-\lambda)U_{LJ} + \lambda U$. Once $S(N_0, V_0, T_0)$ has been obtained, using Eq. (10) with Eq. (12) we can obtain the absolute entropy. Then the excess entropy is calculated by subtracting the entropy of an equivalent ideal gas from the absolute entropy of the system.

Monte Carlo simulations for all the systems are carried out in the isobaric-isothermal (NPT) ensemble under cubic periodic boundary conditions at ambient pressure, with the systems consisting of 4000 particles. First we run short simulations in the canonical ensemble for both the low temperature and high temperature phases to get the energy range. Then the energy range is divided into a number of bins and we run the WL algorithm for 1×10^8 MC steps. We reduce the modification factor $\ln f \rightarrow 0.1 \ln f$. The system is run for 100 000 steps at the given temperature to guarantee an equilibrium liquid state, and $g(r)$ are obtained by averaging 50 configurations sampled during another run of 30 000 steps. To study the atomic self-diffusion coefficient $D(T)$ in liquids, we first follow the time-dependent mean-square displacement in the liquids. We start from the equilibrium liquid configuration generated by classical molecular dynamics. According to the Einstein formula, for sufficiently long time interval, $D(T)$ can be extracted from the equation:

$$D(T) = \lim_{t \rightarrow \infty} \frac{\langle |r(t) - r(0)|^2 \rangle}{6t}, \quad (14)$$

where $r(t)$ denotes an atom position at time t . The angular brackets denote an average over all the particles and also over all time origins.

3. Result and discussions

Since the pair correlation entropy can be obtained from the integral of the experimentally accessible pair distribution function. It is very attractive to obtain estimates of transport properties of liquids from the pair correlation entropy. The first step is evaluating the numerical validity of the pair correlation approximation for entropy scaling relation for the transport coefficients of liquids. Fig. 1 shows the reduced diffusion coefficients as a function of the pair correlation entropy for different choices of reduced parameters and the results are compared to the original best fit determined by Rosenfeld and Dzugutov, respectively. We find that the slopes of simple liquid metals are about -0.74 and -1.08 , which are very close to the ideal values -0.8 and -1.0 for different choice of reduced parameters as defined by Eqs. (3) and (5), respectively. The slopes of the lines of *l*-Si and *l*-Ge are much larger than the ideal values. In other words, based on different choices of the reduction parameters, the scaling laws of diffusion coefficients hold for all simulated liquids except *l*-Si and *l*-Ge. Fig. 2 shows the scaled diffusion coefficients vs the excess entropy for different choices of reduced parameters. The slopes of the lines of *l*-Si and *l*-Ge are closer to the ideal values, although the scaling laws of diffusion coefficients are also valid for simple liquid metals and fails for *l*-Si and *l*-Ge. That is to say, the pair correlation approximation has little effect on the entropy scaling laws for the case of simple liquid metals, but has significant effect on that of *l*-Si and *l*-Ge. We plot $S_{RMPE}/S_e\%$ as a function of temperature in Fig. 3, where $S_{RMPE} = S_e - S_2$ is the residual multi-particle entropy. From this figure, we can find that the error of the excess entropy caused by the pair correlation approximation is of the order of 30 % or less for simple liquid metals, but it is larger for *l*-Si and *l*-Ge. The results presented above reinforce the notion, that the excess entropy could be calculated approximately in terms of the two-body contribution for liquid metals, but the two-body approximation is not accurate for the case of *l*-Si and *l*-Ge.

The above results suggest that the deviations of *l*-Si and *l*-Ge from the scaling laws are partly due to the fact that the two-body approximation is not accurate for the case of them. However, the two-body approximation is not the only reason. It is helpful to recall the basic arguments originally made in justifying these semi-empirical relationships. For the scaling law of Rosenfeld, the

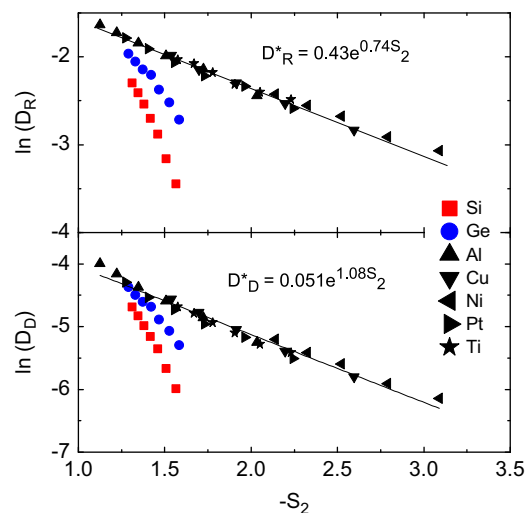


Fig. 1. The reduced diffusion coefficients as a function of the pair correlation entropy S_2 . D_R and D_D are scaled by Eqs. (3) and (5), respectively. Entropy is expressed in units of k_B . The solid lines, being the best fit to the data of simple liquid metals including Al, Cu, Ni, Pt and Ti, represent the present scaling law of equations given in the figure.

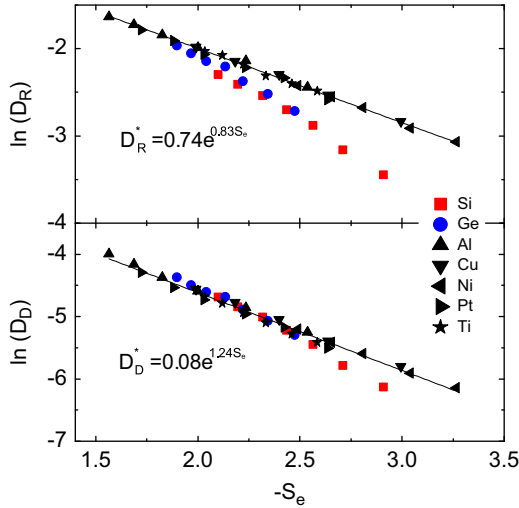


Fig. 2. The reduced diffusion coefficients vs the excess entropy S_e . D_R and D_D are scaled by Eqs. (3) and (5), respectively. Entropy is expressed in units of k_B . The solid lines, being the best fit to the data of simple liquid metals including Al, Cu, Ni, Pt and Ti, represent the present scaling law of equations given in the figure.

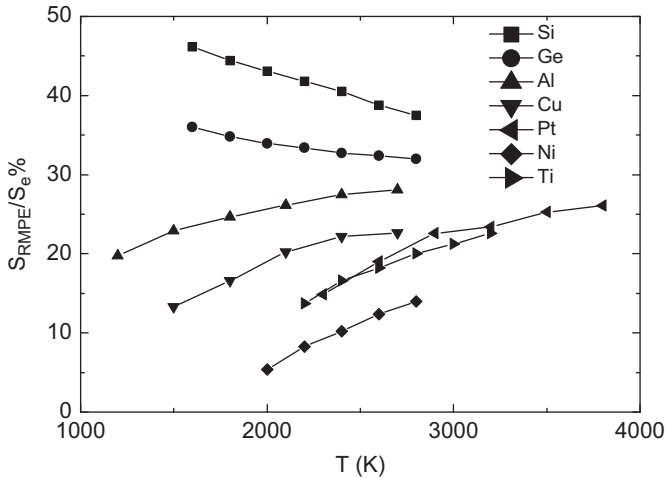


Fig. 3. Percentage contribution of the residual multiparticle entropy to the excess entropy, $S_{RMPE}/S_e\%$, as a function of temperature for simple melts.

kinetic coefficients are expressed in reduces units based on a mean free path between collisions which is of the order of the average interparticle distance and thermal velocities [2]. That is to say, the scaling law of Rosenfeld was based on the approximation that the structure of liquid can be adequately described by an effective hard-sphere system. Similarly, the Dzugutov scheme is based on two main propositions [4]. First, the transfer of energy and momentum in the liquid is mainly governed by the uncorrelated binary collisions described by the Enskog theory, and the Enskog parameter, Γ , provides the relevant microscopic information about the collision processes that mediate self-diffusion in the fluid. The second ideal central to the entropy scaling law is that the frequency of local structural relaxations in the liquid dictates cage diffusion and is proportional to the number of accessible configurations in the system. In other words, the Enskog approach is intrinsically a hard sphere collision theory that focuses on the first peak in $g(r)$. Thus, it is expected that the scaling laws without modification might only works on the hard-sphere-like fluid.

Concerning atomic structures in the liquid phase, Si and Ge are known to have several unusual features when compared to

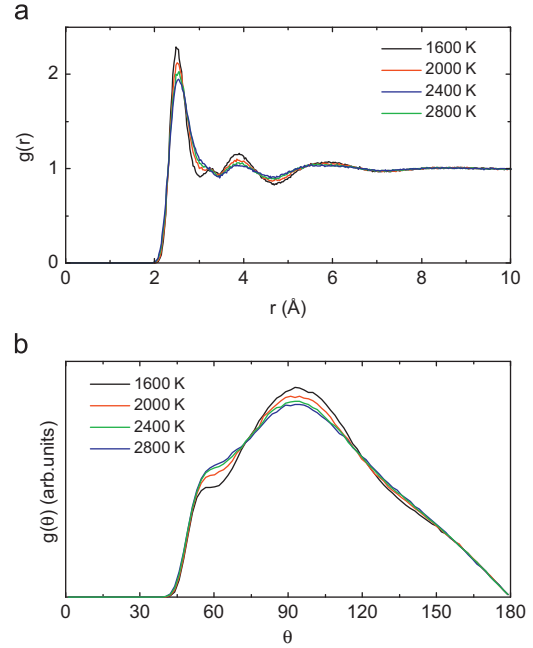


Fig. 4. (a) The pair distribution function $g(r)$ and (b) the angle distribution function $g(\theta, r_m)$ for l -Si at four temperatures.

hard-sphere-like fluid. As shown in Fig. 4(a), the pair distribution function $g(r)$ has a distinct shoulder on the immediate right-hand side of the first peak at 1600 K, which evolves into a plateau with increasing temperature. It is thought that this shoulder is probably a residue of angular (covalent bonding) interactions in l -Si and l -Ge [25,26]. In addition to the $g(r)$, bond angle distributions provide valuable information on the local structural units and their connectivity in the liquid. In liquid simple metals, the angle distribution function $g(\theta, r_m)$ peaks at around $\theta \approx 60^\circ$ and 120° , which are close to those expected for a local icosahedra arrangement. The $g(\theta, r_m)$ of l -Si and l -Ge are plotted in Fig. 4(b), where we see two maxima at 60° and about 90 – 110° . The former corresponds to contribution from metallic bonds, while the latter represents the covalent-bond nature favoring the tetrahedral symmetry. The two-peak structure of $g(\theta, r_m)$ clearly shows that the bonding in l -Si and l -Ge is a mixture of covalent and metallic bonds [27,28]. In addition, from Fig. 4(b), we can observe significant changes in the distribution of the bond angles according to the increase of temperature. The former peak becomes higher with increasing temperature but the latter becomes lower. The behavior of $g(\theta, r_m)$ and $g(r)$ indicates that (i) the bonding in l -Si and l -Ge is a mixture of covalent and metallic bonds, (ii) the degree of metallic nature in the l -Si and l -Ge increases as temperatures increases, and (iii) covalent bonds still exist at temperature as high as 2800 K. We note that an analogous breakdown of Rosenfeld scaling for silica was associated with significant departures from the Gaussian diffusive behavior [29,30]. Fig. 5 shows the mean square displacement (MSD) as a function of time for several temperatures. Using a logarithmic scale in both axes, inflexion point can be observed on the MSD plots, and the inflexion point is marked by arrow in the figure. The inset shows a closeup of the area, where the transition between logarithmic and diffusional motion takes places. But there is no evidence of a well-defined plateau region, a characterization of local caging effects, which can be seen in the case of liquid silica.

The features of the shoulder on the immediate right-hand side of the first peak of $g(r)$ and the two-peak structure of $g(\theta, r_m)$ give solid illustrations of the deviation from hard-sphere-like structure. But it is difficult to quantitatively analyze the deviation

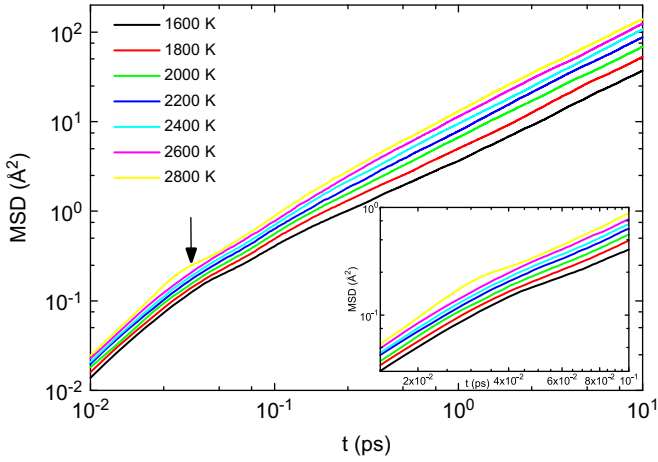


Fig. 5. Mean square displacements (MSDs) for liquid silicon at several temperatures. The inset shows a closeup of the area, where the transition between logarithmic and diffusional motion takes place, and the inflexion point is marked by an arrow in the figure.

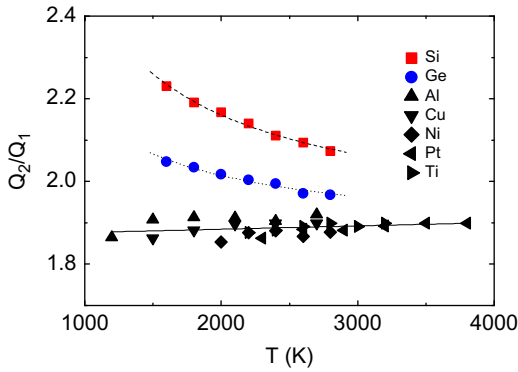


Fig. 6. The temperature dependence of the ratio between Q_1 and Q_2 of liquid Al, Cu, Ni, Pt, Ti and Si as well as Ge. Q_1 indicates the wave vector of the first peak of structure factor, $S(Q)$, and Q_2 indicates that of the second peak. Lines are guides to the eyes.

using their temperature dependence. According to the criterion of the classification of the structure of liquid melts, proposed by Waseda [25,31], the ratio of the positions of the second and first peaks of the structure factor Q_2/Q_1 reflects the structure of liquids in the following way. For isotropic liquids, Q_2/Q_1 typically takes a value of 1.86. As the anisotropy of the local structures increases, this quantity increases. In Fig. 6, we plotted this quantity of several simple liquid metals, *l*-Si and *l*-Ge against temperature. The static structure factor is calculated from the Fourier transform of $g(r)$. We find that the values of Q_2/Q_1 for liquid Al, Cu, Ni, Pt and Ti are very close to 1.86 and remain to be unchanged even at high temperatures, which indicates that their local structures are isotropic. On the other hand, different temperature dependence of the values of Q_2/Q_1 was observed for *l*-Si and *l*-Ge. For *l*-Si and *l*-Ge, Q_2/Q_1 at low temperature has highly anisotropic values of 2.23 and 2.07, respectively, and decreases as temperature increases. In other words, at fixed temperatures, *l*-Si is more anisotropy than *l*-Ge and they become closer to isotropic liquids upon increasing temperature. However, this does not mean that anisotropy completely disappears at high temperature, because the values of Q_2/Q_1 for *l*-Si and *l*-Ge are still much larger than isotropic value 1.86 even at the highest temperature investigated. Generally speaking, it is expected that metallic bonds are isotropic and covalent bonds are anisotropic. Thus, it is natural to assume that isotropic structures originate from metallic bonds,

while anisotropic structures originate from covalent bonds. In this respect, the behavior of Q_2/Q_1 in Fig. 6 indicates that as temperature increases, the system becomes more metallic, although the covalent bonds persist even at temperature as high as 2800 K, the highest temperature investigated. Above all, we can get the conclusion that the deviation of the value of Q_2/Q_1 from the value 1.86 may be a key parameter to describe the deviation of local structures of liquid from hard-sphere-like structure.

Although the structures of *l*-Si and *l*-Ge cannot be modeled with a simple hard-sphere model, Ashcroft et al. [26] proved that they could be obtained assuming the existence of transient clusters with fast atomic exchange. The first maximum of $S(Q)$ reflects intercluster correlation, while the shoulder on the high- Q side of the first peak and the remaining oscillations in $S(Q)$ are due to the atom-atom contribution. From the viewpoint of the cluster model, one can expect that the diffusion must result from a superposition of the single atom- and cluster-translational motion in the liquid contains covalent structures. The latter is derived from the microscopic cage effect (covalently bound atoms in clusters are oscillating around their equilibrium positions), and this contribution seem to be subject to relatively slow diffusion while the single atom motion is more rapidly. In other words, the collision frequency (or mean free path) in the liquid contains covalent structures will be smaller (or larger) than that directly calculated by Enskog theory which was developed for hard-sphere systems under otherwise equal conditions, and the collision frequency (or mean free path) become smaller (or larger) as the ratio of the covalent part increases. As mentioned above, Q_2/Q_1 can be used to reflect the structure of liquids. For hard-sphere-like liquid it takes the value of 1.86, and this quantity increases as the anisotropy of the local structures increases. This suggests that one can establish a quantity to represent the anisotropy of the local structures and use this quantity to modify the reduction parameters of the diffusion coefficient in Eqs. (3) and (5) in the following way:

$$D_{R0}^M = D_{R0} \left(\frac{1.86}{Q_2/Q_1} \right)^n, \quad (15)$$

$$D_{D0}^M = D_{D0} \left(\frac{1.86}{Q_2/Q_1} \right)^n, \quad (16)$$

where 1.86 is a typical value of Q_2/Q_1 of hard-sphere-like liquid, n is the positive integer. Therefore, the diffusion coefficients can be scaled by the simple modified reduction parameters via

$$D_R^M = \frac{D}{D_{R0}^M} = \frac{D}{D_{R0}} \left(\frac{Q_2/Q_1}{1.86} \right)^n, \quad (17)$$

$$D_D^M = \frac{D}{D_{D0}^M} = \frac{D}{D_{D0}} \left(\frac{Q_2/Q_1}{1.86} \right)^n. \quad (18)$$

We have chosen $n=2$ in this work, and the choice of the value of n may be related to the fact that the coordination number of simple liquid metals is twice as much as that in *l*-Si and *l*-Ge. The new scaled diffusion coefficients D_R^M and D_D^M are plotted in Fig. 7. From this figure, we find that, based on the two different choices of the modified reduction parameters defined by Eqs. (15) and (16), the scaling laws of diffusion coefficient hold well not only for the simple liquid metals but also for *l*-Si and *l*-Ge.

4. Conclusion

In this work, molecular simulations of a series of melts are used to study the scaling laws of diffusion coefficients proposed by Rosenfeld and Dzугutov. Simulation results show that the failure of the scaling laws in application of *l*-Si and *l*-Ge is closely

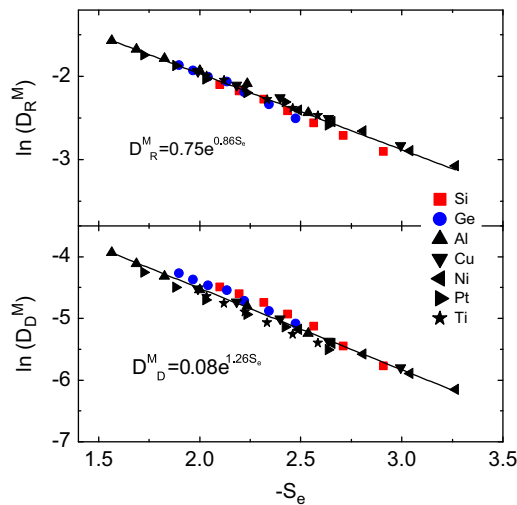


Fig. 7. The modified reduced diffusion coefficients as a function of the excess entropy S_e . D_R^M and D_D^M are scaled by Eqs. (17) and (18), respectively. Entropy is expressed in units of k_B . The solid lines, being the best fit to the data of all the studied system, represent the present scaling law of equations given in the figure.

related to that fact that the excess entropy cannot be calculated approximately in terms of the two-body contribution and the original reduction parameters are no longer appropriate for *l*-Si and *l*-Ge, which is itself tied to the fact that the structure of *l*-Si and *l*-Ge strongly differs from that in the hard-sphere-like liquids. Moreover, the pair distribution function $g(r)$, the angle distribution function $g(\theta, r_m)$, and the ratio between the positions of the second and the first peak in the structure factor Q_2/Q_1 are used to study the local structural change of *l*-Si and *l*-Ge induced by increasing temperature. We find that (i) *l*-Si and *l*-Ge become closer to hard-sphere-like liquids as temperature increases, (ii) Q_2/Q_1 is a direct measure of the structural deviation from hard-sphere-like case. Based on the temperature dependence of Q_2/Q_1 , we construct modified reduction parameters of the diffusion coefficient. Furthermore, we show that the modified Rosenfeld scaling law and the modified Dzугutov scaling law are appropriate for all the studied systems, while the original scaling laws fail to describe the diffusivity of *l*-Si and *l*-Ge. However, we also identify some limitations of the approach. For example, the final scaling suggested by us in Eqs. (15) and (16) is somewhat arbitrary in the way the exponent n is chosen. The present work may also be informative to develop generalized excess entropy scaling law of diffusion coefficient in future.

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