

Molecular dynamics simulation of self-diffusion coefficients for liquid metals*

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The temperature-dependent coefficients of self-diffusion for liquid metals are simulated by molecular dynamics methods based on the embedded-atom-method (EAM) potential function. The simulated results show that a good inverse linear relation exists between the natural logarithm of self-diffusion coefficients and temperature, though the results in the literature vary somewhat, due to the employment of different potential functions. The estimated activation energy of liquid metals obtained by fitting the Arrhenius formula is close to the experimental data. The temperature-dependent shear-viscosities obtained from the Stokes–Einstein relation in conjunction with the results of molecular dynamics simulation are generally consistent with other values in the literature.

Keywords: molecular dynamics, self-diffusion coefficients, shear-viscosity, liquid metals

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1. Introduction

Diffusion is the transport of mass from one region to another at an atomic scale. Diffusivities in liquid metals are much higher than those in solid metals by a factor of 100 to 1000. The diffusivities of liquid metals, usually on the order of $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, are of great importance because the knowledge of diffusivities plays a key role in the design of metallurgical and solidification processes, such as those adopted by the casting industry.^[1–4] The transport properties of liquids together with structural thermodynamic information can provide an experimental basis for theories of the liquid state.^[5–8] Unfortunately, data exist mostly for solid metals, while the data for liquid metals are relatively scarce and subject to larger errors.^[9] At present, it would appear that experimental data for the self-diffusivities of liquid metals are available only for twelve or thirteen liquid metals.^[10] Kinetic theory such as the Chapman–Enskog method is usually used to describe the diffusion properties of liquids based on some semi-empirical modifications.^[11] These semi-empirical theories have been widely applied to real fluids at high temperatures and pressures.^[12] Of course, they are easily applicable to liquid metals. For a clear understanding of those phenomena related to diffusion, a study of self-diffusivities in liquid metals is of critical importance.

Molecular dynamics simulation is a powerful tool to predict structural thermodynamic and transport properties for various liquids.^[13–17] In this work, the coefficients of self-

diffusion for liquid metals are obtained by using the molecular dynamics (MD) method based on the embedded-atom-method (EAM) potential function. The simulated results show that self-diffusion increases with temperature and a good inverse linear relation exists between the natural logarithm of self-diffusion coefficients and temperature. By fitting the best simulated results to the Arrhenius formula, the activation energy of liquid metals is estimated. The temperature-dependent shear-viscosities calculated from the Stokes–Einstein relation in conjunction with the MD simulation results are generally consistent with other published values.

2. Computational details

The potential function plays an important role in the MD simulation, and different potential functions with the same form as EAM potential is employed in the current study. The functional form of the EAM potential is given by

$$E_{\text{tot}} = \frac{1}{2} \sum_{i \neq j} V(r_{ij}) + \sum_i F(\rho_i), \quad (1)$$

$$\rho_i = \sum_j \phi(r_{ij}), \quad (2)$$

where E_{tot} is the total energy, $V(r_{ij})$ the pair potential, $F(\rho_i)$ the embedding function, and $\phi(r_{ij})$ the electron density contribution from atom j to atom i . The total electron density ρ_i at an atom position i is calculated via the linear superposition of electron density contributions from neighboring atoms.

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The system was prepared in FCC configuration, using fully periodic boundary conditions on a super-cell size of $18a_0 \times 18a_0 \times 18a_0$ (where a_0 is the lattice constant). The initial velocities of the atoms are randomly assigned from a Gaussian distribution. The system was first equilibrated for 5×10^4 time steps with a time integration step of $dt = 1$ fs at various temperatures and a fixed pressure of 0 Pa, and then another 2×10^5 time steps were performed to collect the position and velocity of the atoms for computing the self-diffusion of liquid metals.

3. Results and discussion

Figure 1 presents the pair-correlation function $g(r)$ simulated for liquid Al using the first potential function by Mei *et al.*^[18] along with the X-ray scattering results.^[19] The agreement between the simulation and experiment is quite good.

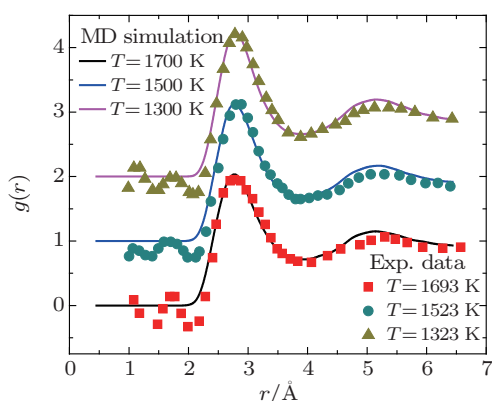


Fig. 1. (color online) Comparison of $g(r)$ for liquid Al at various temperatures.

The self-diffusion coefficients can be directly calculated from the long-time behavior of the mean-square displacement (MSD) of the atoms:

$$D = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle \sum_{i=1}^N [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \right\rangle, \quad (3)$$

where $\mathbf{r}_i(t)$ is the position vector of atom i at time t , N is the number of atoms, and $\langle \dots \rangle$ denotes the ensemble average.

Figure 2 shows the time profile of MSD at various temperatures from 1100 K to 2000 K based on the first potential function. It can be found that in the simulated range of temperatures the MSD varies linearly with time and the slope of the MSD increases notably with temperature, indicating that the system has been melted completely.

According to Eq. (3), the self-diffusion coefficients of liquid Al at various temperatures of 1100 K \sim 2000 K can be obtained, as shown in Fig. 3. The self-diffusion coefficients increase with temperature, which can be easily understood in that the atoms move more dramatically at higher temperatures than at lower temperatures. The simulated data are compared

with the self-diffusion coefficients reported from an extensive set of MD simulations using different potentials^[20] and the latest experimental data available, measured by quasi-elastic neutron scattering (QNS).^[23] The results of the present work are in good agreement with the results simulated by MKBA1 potential which is in turn close to the experimental data. Although the general linear trends of $\ln D$ and $1000/T$ all coincide, the self-diffusion coefficients simulated based on different potentials vary somewhat. The same situation occurs in the simulation of the heat capacity of liquid Al.^[24] To verify this point, another set of results based on the potential function by Ercolessi and Adams^[25] was obtained, and these are not as encouraging as the first ones. Hence, it can be concluded that the results based on the first potential function appear to work best overall in describing the mass transport properties of liquid Al.

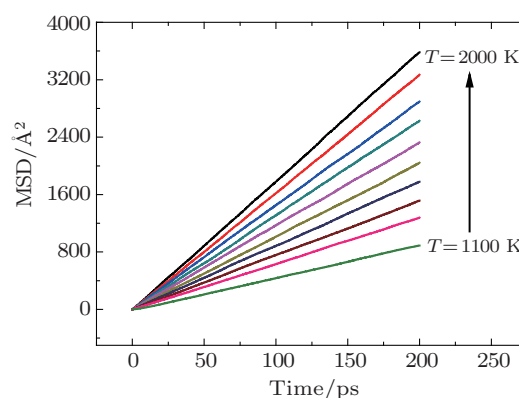


Fig. 2. (color online) MSD for liquid Al at temperature ranges from 1100 K to 2000 K with an interval of 100 K.

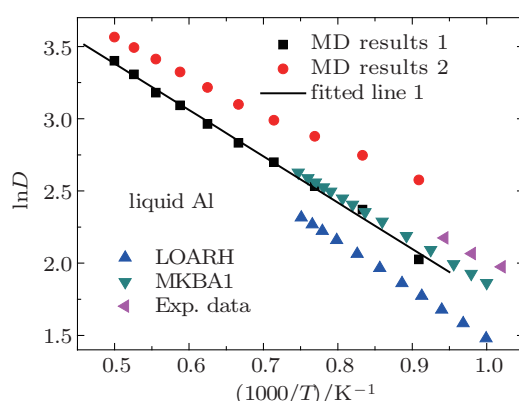


Fig. 3. (color online) Simulated coefficients of self-diffusion D ($10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$) for liquid Al. MD results 1 and MD results 2 denote our results based on the EAM potential from Ref. [18] and Ref. [25], respectively; fitted line 1 denotes the fitted line of results based on the EAM potential from Ref. [18]; LOARH and MKBA1 denote the results based on the potential function from Ref. [21] and Ref. [22], respectively.

In addition, the self-diffusion coefficients for liquid Cu at various temperatures were simulated, as shown in Fig. 4. It can be seen that the same general linear trend between $\ln D$ and $1/T$ exists for the liquid Cu, though the results based on the first potential function by Mishin *et al.*^[26] and the second

potential function by Zhou *et al.*^[27] varies obviously. The simulated results based on the first potential function are close to the experimental data^[1] at higher temperatures, while those based on the second potential function are close to the latest experimental data available measured by QNS^[28] at lower temperatures.

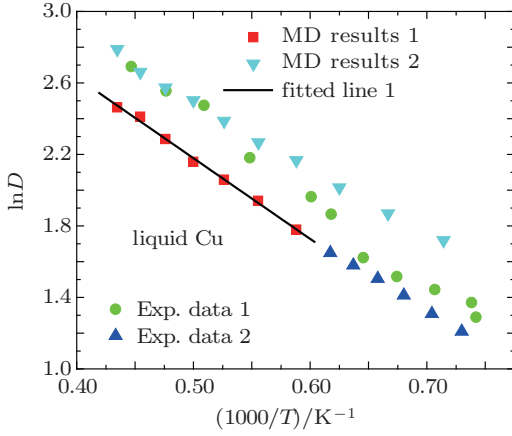


Fig. 4. (color online) Simulated coefficients of self-diffusion D ($10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$) for liquid Cu. MD results 1 and MD results 2 denote our results based on the EAM potential from Ref. [26] and Ref. [27], respectively; fitted line 1 denotes the fitted line of results based on the EAM potential from Ref. [26]; Exp. data 1 and Exp. data 2 denote the experimental results from Ref. [1] and Ref. [28], respectively.

The temperature dependence of the self-diffusion coefficients $D(T)$ has special interest since the activation energy is experimentally accessible. In order to compute the activation energy, the self-diffusion coefficients D at various T should be computed and the results be fitted to the Arrhenius form

$$D = D_0 \exp\left(-\frac{E}{k_B T}\right). \quad (4)$$

The self-diffusion coefficients of liquid Al over a wide range of temperatures (1100 K \sim 2000 K) are simulated with the results shown in Fig. 3, and the fitted relation of $\ln D = 4.9851 - 3.2076 \times 1000/T$ fits well to Eq. (4). So the activation energy $E = 276.81 \text{ meV}$ and $D_0 = 1.4621 \times 10^{-7} \text{ m}^2/\text{s}$, which are close to the experimental values of $E = 280 \text{ meV}$ and $D_0 = 1.7298 \times 10^{-7} \text{ m}^2/\text{s}$.^[23] For liquid Cu the fitted relation to the Arrhenius formula is $\ln D = 4.4371 - 4.5165 \times 1000/T$. Hence, the activation energy $E = 389.76 \text{ meV}$ and $D_0 = 0.8453 \times 10^{-7} \text{ m}^2/\text{s}$, which agrees well with the experimental data of $E = 337 \text{ meV}$ and $D_0 = 0.5870 \times 10^{-7} \text{ m}^2/\text{s}$.^[28] The potential function by Mei *et al.* for Al and that by Mishin *et al.* for Cu both fit well to the experimental data and Arrhenius formula, and they are valid for nearest neighbor interactions. Hence, it can be concluded that short-range interactions are dominant in the liquid metals.

In simple liquids, shear-viscosity η and the self-diffusivity D generally obey the Stokes–Einstein (SE) relation

$$D = \frac{k_B T}{4\pi\eta r}, \quad (5)$$

where η stands for the shear-viscosity, D the self-diffusion coefficients, k_B the Boltzmann constant, and r the radius of the moving atoms.

The temperature dependence of the shear-viscosities for liquid Al and Cu are hereby obtained by Eq. (5), as shown in Fig. 5. The radii of Al and Cu equaling 1.29 Å and 1.32 Å, respectively, were used in the calculation. The general tendency of shear-viscosities versus temperatures coincides with the experimental results, although the experimental values of shear-viscosities for liquid Al are scant, as shown in Fig. 5(a).^[29–31] The SE relation calculated in conjunction with the MD simulation results agrees well with the experimental data of shear-viscosities for liquid Cu, as shown in Fig. 5(b).^[32–34] Anyway, the calculated results of the current study work best overall in accounting for the temperature dependence of the shear-viscosities for liquid metals.

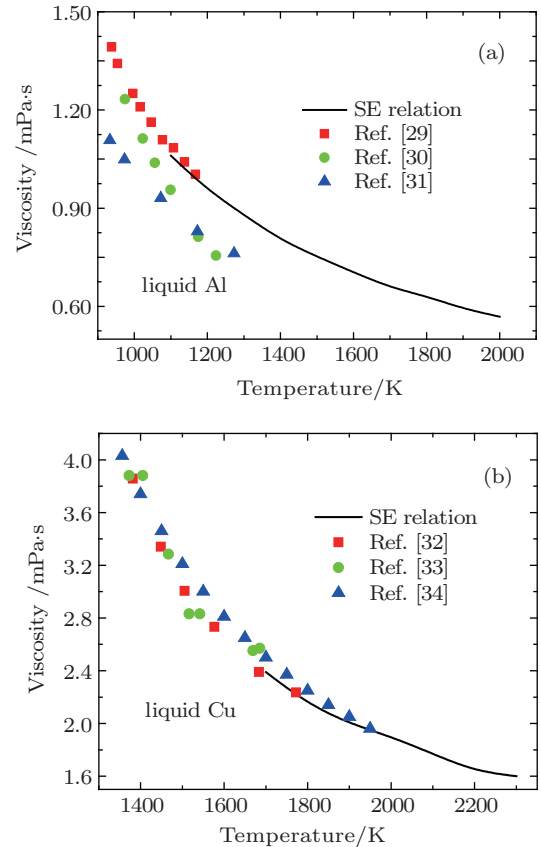


Fig. 5. (color online) Shear-viscosities of liquid metals at various temperatures. (a) liquid Al and (b) liquid Cu.

4. Conclusion

In conclusion, the temperature-dependent self-diffusion coefficients for liquid metals simulated by MD methods based on the EAM potential function have been presented. The simulated results show that the self-diffusion coefficients increase with temperature and that a good inverse linear relationship exists between the natural logarithm of self-diffusion coefficients and temperature, though results in the literature vary somewhat, due to the employment of different potential functions.

The estimated activation energy of liquid metals obtained by fitting the Arrhenius formula is close to the experimental data. The temperature-dependent shear-viscosities from the SE relation in conjunction with the MD simulation results are generally consistent with other values in the literature.

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