
Brief Reports

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Molecular-dynamics study of self-diffusion in liquid transition metals

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Molecular-dynamics simulations on liquid transition metals were performed with use of Johnson's analytic nearest-neighbor embedded-atom model. The coefficients of self-diffusion for Cu, Ag, Au, Ni, Pd, and Pt at their melting points were computed. The temperature dependence of the self-diffusivity for liquid copper has been studied with the value of the activation energy in good agreement with experiments.

Dynamical diffusion properties distinguish the liquid phase from the solid phase of a material. Atoms in a solid will not self-diffuse in the absence of defects. On the other hand, in the liquid the atoms will diffuse away from their original positions. Many properties of a material, such as the bond energy and force constants, directly affect the rate at which atoms will diffuse. Experimental data for the self-diffusivities of liquid metals are only available for twelve or thirteen liquid metals.¹ So it is quite interesting to simulate liquid transition metals and calculate the self-diffusivities using computer simulation methods.

The lower symmetry of liquids makes a band-structure approach difficult to handle. Empirical-pair-potential methods are computationally simple, but fail to give accurate self-diffusion constants.^{2,3} Car and Parrinello⁴ recently developed a first-principles liquid theory. This theory has been applied to calculate the activation energy for diffusion in liquid sodium⁵ and accurate results were obtained. It has not been applied yet to the transition metals because their narrow d bands are not adequately described by plane-wave basis sets. Moreover, computer limitations make this first-principles theory applicable only to small (typically 100 atoms) systems. For many calculations we need a theory that can handle a large number of atoms. This requires a model that is both accurate and computationally simple.

The embedded-atom method (EAM) proposed by Daw and Baskes⁶ provides such a computationally simple model. It is applicable to the transition metals as well as the simple metals. The wide application⁷ of this method shows that it is quite successful. To simplify the fitting

procedures of the EAM, Johnson⁸ developed an analytic EAM model for close-packed metals, which includes nearest-neighbor interactions only. This model, to our knowledge, has not been used to perform computer simulations. In fact, the simple analytic form of the EAM functions in the model make it just as easy to use as the pair-potential methods for molecular-dynamics (MD) simulations.

All EAM models are developed for the solid phase of metallic systems. Foiles⁹ made the application of the EAM to liquid transition metals and showed that the EAM also provides a realistic description of the energetics and structure properties of the liquid phase. For further study on the EAM and to provide a "computer experiment" on the self-diffusion of liquid transition metals, we have performed MD simulations on liquid Cu, Ag, Au, Ni, Pd, and Pt using Johnson's analytic model.⁸ We have calculated the diffusion coefficients of those six liquid metals and the activation energy for liquid Cu.

The details of our calculations are as follows. The simulations are performed by solving Newton's equations via the four-value Gear algorithm¹⁰ for a collection of particles (atoms) confined within a cubic cell with periodic boundary conditions. We have chosen the canonical ensemble, which has been realized by using Hoover's constant temperature technique¹¹ during the simulations. For a particular metal, the liquid phase near its melting point (T_m) was obtained first by heating a perfect crystal to a high temperature (approximately $T=4T_m$), after 5000 time steps (which, we found, is long enough for the crystal to be melted completely), and then gradually cooling down to the desired melting point. Once the liquid

TABLE I. Simulation results of the internal energy per atom and pressure for liquid metals at constant temperatures and atomic densities specified.

Liquid	T (K)	n (\AA^{-3})	P (kbar)	E (eV)	E^a (eV)
Cu	1349	0.0740	0.04	-3.08	-2.99
Ag	1227	0.0510	-0.16	-2.42	-2.33
Au	1330	0.0526	-0.11	-3.47	-3.38
Ni	1720	0.0764	-0.58	-3.80	-3.72
Pd	1818	0.0584	-1.24	-3.27	-3.18
Pt	2037	0.0578	-0.31	-5.04	-4.95

^aFrom Ref. 9.

phase was obtained, we performed a standard run, consisting of 2000 steps for equilibration, and then 10000 additional steps for the statistical average. All the simulations were performed with the particle number $N=256$. For a particular metal, the time step is $0.005t_u$, with the reduced unit $t_u=(mr_e^2/\phi_e)^{1/2}$, where m is the atomic mass of the metal, r_e is the nearest-neighbor distance of the atoms at zero temperature, and ϕ_e is the model parameter,⁸ which has the units of energy $t_u=2.70 \times 10^{-13}$ sec for Cu.

Table I lists the input temperatures and density, as well as the pressures and internal energies per atom computed for the liquid metals Cu, Ag, Au, Ni, Pd, and Pt. The temperature and density have been chosen to be close to the melting points of the metals. The pressures obtained here are very small compared to the typical 1-Mbar bulk moduli. The last column of the table lists the internal energies per atom computed by Foiles,⁹ which are about 0.09 eV higher than our results due to the different models used. Figure 1 presents the pair-correlation function

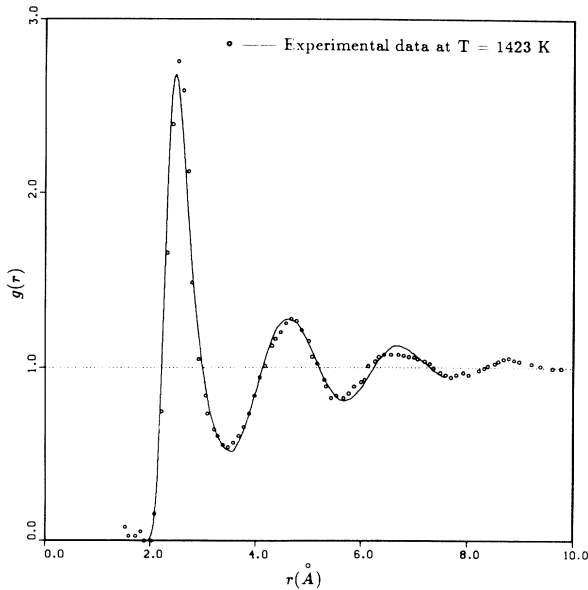


FIG. 1. Pair-correlation function $g(r)$ for liquid Cu at $T=1349$ K and $n=0.0740 \text{ \AA}^{-3}$. The solid line is the MD simulation result and the points are the experimental data (Ref. 1).

computed for liquid Cu along with the x-ray scattering results.¹ The agreement between the simulation and experiment is quite good.

The coefficient of self-diffusion D can be calculated from the long time behavior of the mean-square displacement of the atoms:

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

where $\langle \rangle$ represents the average over $t_{\max}=10000$ time origins and N particles. Our simulation results showed that the curves for the mean-square displacements plotted against time have the well-defined linear behavior at large times. This linearity characterizes the liquid structures. The coefficients of self-diffusion D computed by Eq. (1) are listed in Table II. There are few experimental data of self-diffusion available for liquid transition metals. Table II also lists both the experimental¹² and theoretical

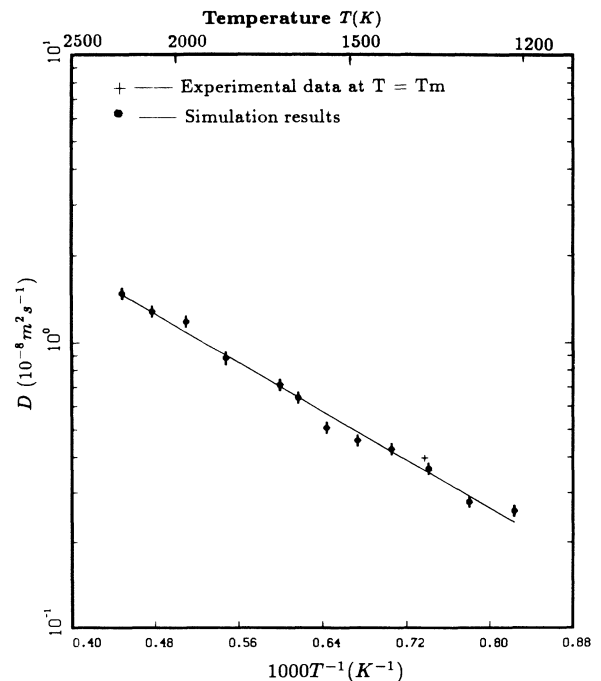


FIG. 2. The calculated coefficient of self-diffusion D as a function of inverse temperature T (K) for liquid Cu.

TABLE II. The coefficients of self-diffusion D for the liquid metals near their melting points. D is in units of $10^{-8} \text{ m}^2 \text{ sec}^{-1}$.

Liquid	Cu	Ag	Au	Ni	Pd	Pt
D	0.365 ± 0.007	0.302 ± 0.011	0.375 ± 0.012	0.385 ± 0.009	0.449 ± 0.007	0.287 ± 0.005
D^a	0.397	0.256				
D^b	0.340	0.277				

^aExperimental data (Ref. 12).

^bTheoretical data (Ref. 13).

data¹³ for Cu and Ag, which are comparable to our results. There are no experimental data for the other metals.

The temperature dependence of the self-diffusivity $D(T)$ has special interest since the activation energy is experimentally accessible. In order to compute the activation energy, we need to compute D at various T and fit the data to the Arrhenius form:

$$D(T) = D_0 \exp(-E_a/k_B T). \quad (2)$$

We simulated liquid Cu over a wide range of temperature (1200–2500 K) with the results shown in Fig. 2. The simulations were still performed in the canonical ensemble, but the constant-pressure constraint method due to Evans¹⁴ has been used to find the equilibrium density at each temperature. The data in Fig. 2 fit well to formula (2). Points with T below the melting temperature represent supercooled liquid states. From least-squares fitting we obtained $E_a = (40.4 \pm 1.1) \text{ kJ mol}^{-1}$ and $D_0 = (1.30 \pm 0.14) \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, which are close to the experimental values of $E_a = 40.6 \text{ kJ mol}^{-1}$ and $D_0 = 1.46 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. The agreement between the simulation results and the experimental data is remarkable for this simple EAM model valid only for nearest-

neighbor interactions. It suggests that the short-ranged interactions play the dominant role in the liquid metals. We have used canonical ensemble for all the calculations. The constant-pressure MD simulations¹⁵ tend to overestimate the values of self-diffusion constants due to large density fluctuation.

In conclusion, we have applied Johnson's EAM model to liquid transition metals using MD simulations. The results showed that even though this model contains only nearest-neighbor interactions, it provides a realistic description of the self-diffusion constants and the activation energy for liquid copper. The pair-correlation function of liquid Cu computed using the EAM is also in good agreement with x-ray scattering results. The calculated self-diffusion constants for liquid Ag, Au, Ni, Pd, and Pt provide useful data for the study of diffusion in liquid metals.

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¹T. Iida and R. I. L. Guthrie, *The Physical Properties of Liquid Metals* (Clarendon, Oxford, 1988), pp. 200 and 28.

²A. Paskin and A. Rahman, *Phys. Rev. Lett.* **16**, 300 (1966).

³R. S. Lewis and T. O. Callaway, *J. Chem. Phys.* **66**, 5083 (1977).

⁴R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).

⁵G. X. Qian, M. Weinert, G. W. Fernando, and J. W. Davenport, *Phys. Rev. Lett.* **64**, 1146 (1990).

⁶M. S. Daw and M. I. Baskes, *Phys. Rev. B* **29**, 6443 (1984).

⁷J. B. Adams and S. M. Foiles, *Phys. Rev. B* **41**, 3316 (1990), and the references within.

⁸R. A. Johnson, *Phys. Rev. B* **37**, 3924 (1988); **39**, 12 554 (1989).

⁹S. M. Foiles, *Phys. Rev. B* **32**, 3409 (1985).

¹⁰C. W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations* (Prentice-Hall, Englewood Cliffs, 1971).

¹¹W. G. Hoover, *Annu. Rev. Phys. Chem.* **34**, 103 (1983).

¹²J. Henderson and L. Yang, *Trans. Metall. Soc. AIME* **221**, 72 (1961); L. Yang, S. Kado, and G. Derge, *ibid.* **212**, 628 (1956).

¹³P. Protopapas, H. C. Andersen, and N. A. D. Parlee, *J. Chem. Phys.* **59**, 15 (1973).

¹⁴D. J. Evans and G. P. Morriss, *Chem. Phys.* **77**, 63 (1983).

¹⁵H. Häkkinen and M. Manninen, *J. Phys. Condens. Matter* **1**, 9765 (1989).