First-Principles Calculation of the Activation Energy for Diffusion in Liquid Sodium

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We have performed the first calculation of the activation energy for self-diffusion in a liquid metal which contains no adjustable parameters. The calculation uses the local-density-functional theory combined with the Car-Parrinello technique for molecular-dynamics simulation. The coefficient of self-diffusion agrees well with the experimental value and fits the form $D=D_0\exp(-E_a/k_BT)$, with $E_a=0.099$ eV, $D_0=0.84\times10^{-3}$ cm^2/sec, compared to the most recent experimental values of $E_a=0.096$ eV, $D_0=0.86\times10^{-3}$ cm^2/sec.

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One of the most obvious effects of temperature is the change of phase from solid to liquid. While the difference between a liquid and a solid is clear in everyday life, on a microscopic level the distinction is more subtle. Static properties such as pair-correlation functions cannot distinguish between amorphous solids and liquids; dynamical diffusion properties are necessary to make the distinction. At low temperature in the absence of defects, the atoms in a solid will not self-diffuse, while in a liquid the atoms will diffuse away from their original positions. Many properties of the material affect the rate (at a given temperature) at which atoms will diffuse. Some obvious examples include the degree of directional, covalent, ionic or metallic bonding, and the force constants of the solid. All of these terms contribute in some complicated manner to the activation energy for self-diffusion, which is an experimentally accessible measure of the temperature dependence of diffusion.

Until recently there has been no first-principles theory of liquids and amorphous solids which has the same level of rigor which we are accustomed to in crystalline solids. However, in a pioneering paper[1] Car and Parrinello (CP) showed that it was feasible to perform molecular-dynamics simulations of liquids by solving the electronic structure within the local-density approximation (LDA). The forces on the individual ions are then determined via the Hellmann-Feynman theorem.[2] This eliminates the need for empirical pair (or three-body, four-body, etc.) potentials and opens the way to first-principles molecular dynamics.

There are many possible applications of such a theory. We focus here on the activation energy for self-diffusion because of its intrinsic interest as a measure of the local bonding, it clearly involves dynamics and temperature-dependent effects, and it provides a good test for the underlying LDA and the validity of the Born-Oppenheimer approximation which separates the ionic and electronic degrees of freedom.

The CP technique has been applied so far to a number of *s-p* bonded materials such as Si,[1,3] SiO$_2$,[4] C,[5] Se,[6] As,[7] GaAs,[8] and to finite-sized metallic clusters.[9] However, there have been no applications to ordinary metals in the liquid phase. The purpose of this Letter is to present our results for liquid sodium. We chose sodium because (1) it is a prototype free-electron metal which has been studied previously by empirical pair potentials; (2) there exist neutron[10] and x-ray-scattering[11,12] data for the pair-correlation function as well as measurements of the coefficient of self-diffusion;[13-15] and (3) the crystalline structure and its static properties at zero temperature have been studied extensively using the LDA and a nonlocal pseudopotential.[16] The discrepancy between LDA calculations and the experimental bandwidth has also been addressed by adding a nonlocal self-energy to the local-density results.[17]

The details of our calculations are as follows. The supercell of our actual simulation contains 54 sodium atoms with periodic boundary conditions. The ions are initially held at their perfect bcc lattice positions with lattice constant $a=4.357$ Å. This corresponds to a density close to the experimental density of the liquid at its melting temperature (0.927 g/cm^3) and is 4.5% smaller than the equilibrium density at 293 K. The Kohn-Sham orbitals are expanded in a plane-wave basis with energy $(k+G)^2$ up to $E_{\text{pw}}=12$ Ry that leads to 5614 plane waves at the Γ sampling point in the first Brillouin zone. The parametrized form of Perdew and Zunger[18] for the exchange-correlation functional and a fully nonlocal pseudopotential[4,19] with s nonlocality are used. With the atoms at their crystalline positions and varying the density a lattice constant of 3.77 Å (uncorrected for the zero-point motion) was obtained. This is reasonably close to the experimental value of 4.23 Å. Similar contractions have been found for alkali metals by Woodward and coworkers.[20] The calculation of Dacorogna and Cohen[16] yielded 3.98 Å by using a partial core correction. Our calculated bulk modulus of 110 kbar compares well with 106 kbar obtained by Dacorogna and Cohen.[16] During the molecular-dynamics simulation, a constant time step $\Delta t=1.2\times10^{-16}$ sec was used in updating both ionic positions and electronic wave functions via the Verlet algorithm.[21] The electronic fictitious mass was chosen to be

100 a.u. These choices ensure an accurate integration of the equations of motion and guarantee energy conservation to better than five significant features over an observation time of several thousand time steps. In a typical (constant-volume) molecular-dynamics run the system is first equilibrated at a given temperature, and then observed for another ~1 psec in order to gather statistics. Although this time is short compared to traditional molecular-dynamics simulations, the statistics, as shown below, are adequate for a determination of the diffusion constants.

A problem in simulating a liquid metal via the Car-Parrinello technique occurs when the occupancy of states at the Fermi level changes. These changes result in the electrons leaving the Born-Oppenheimer surface and thus violating one of the basic assumptions of the method. While this effect is difficult to include consistently in the fictitious Lagrangian formulation, we have presented elsewhere[22] a general solution that is conceptually simple and computationally tractable. A closely related question concerns the choice of supercell size and k-point sampling. For certain supercells and k-point samplings, the single-particle spectrum can have a pseudogap, which in our case is ~0.8 eV. Thus, as discussed previously,[22] the finite supercell and k-point sampling approximation makes the density of states less accurate than *integral* properties such as electron density, Hellmann-Feynman forces, and elastic properties which should be reasonable, and therefore the trajectories of the ions should be accurate.

As an indication of the reasonableness of our results, Fig. 1 shows the calculated pair distribution function (PDF) of liquid Na at 420 and 1402 K compared to the x-ray-diffraction measurement.[12] The prominent peak is softened as the temperature goes up, as expected since the ions have larger displacements. The calculated PDF agrees well with both the x-ray- and the neutron-scattering data.[10]

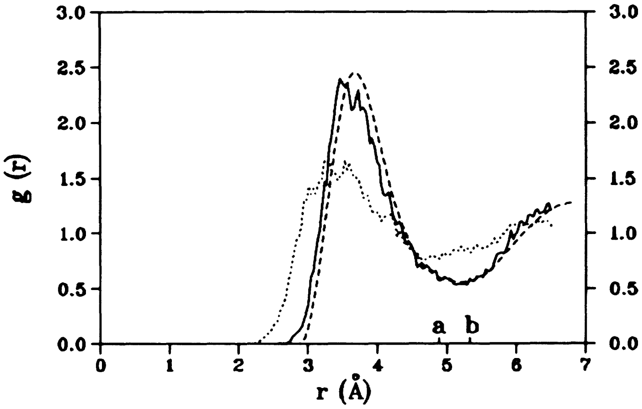

FIG. 1. The calculated pair distribution function $g(r)$ at 420 K (solid line) and 1402 K (dotted line), and the x-ray measured $g(r)$ at 373 K (Ref. 12, dashed line) are shown. Points a and b mark the calculated interatomic distances which correspond to the coordination number twelve and fourteen, respectively, at $T=420$ K.

Changes in the coordination number give a measure of how the local structure of the liquid differs from that of the crystal. In the bcc structure, the nearest-neighbor shell contains eight atoms, and only slightly farther away is the second shell containing another six. With a small amount of disorder, the distinction between first and second neighbors fades, and thus one can consider the bcc structure to have a near-neighbor shell of fourteen atoms. On the other hand, the fcc structure has a well resolved first shell coordination number of twelve. Thus to identify the liquid as either bcc-like or fcc-like, it is necessary to determine whether the coordination number is twelve or fourteen. From Fig. 1, however, the values of the radial distances, a and b, corresponding to coordination numbers twelve and fourteen, respectively, are located at the bottom of a broad minimum, making a unique identification of the structure difficult. Likewise the calculated angular distribution (Fig. 2) also supports the above conclusion. In order to understand the evolution of the angular distribution function when the system changes from ideal (fcc or bcc) crystalline order to a liquid, we consider the effect of randomly displacing atoms on the angular distribution function. In Fig. 2 we show the effects of random (uncorrelated) displacements from the ideal bcc or fcc structures on the angular distribution functions. When these random displacements are small, the two lattice structures can be easily distinguished from one another while for larger displacements, the differences in the angular distribution function for the bcc and the fcc disappear. The latter case

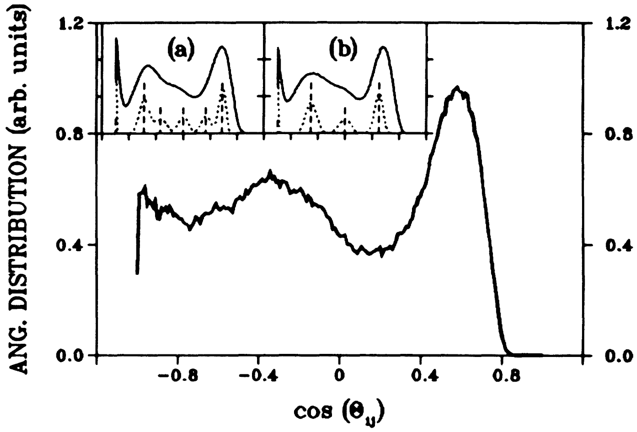

FIG. 2. The calculated angular distribution function for liquid sodium at the average temperature of 420 K. (a) The angular distribution function for an ideal bcc lattice (dashed line), for a bcc lattice with small (dotted line) and large (solid line, scaled by a factor of 4.17 for clarity) random displacement of atoms from their ideal positions. (b) Same as in (a) for an fcc lattice.

closely resembles the *actual* angular distribution calculated for the liquid after equilibration, apart from the actual distribution having fewer small-angle pairs due to core-core repulsion. The local order is neither bcc- or fcc-like, but rather a combination. This lack of local order reflects the small energy difference between the crystalline bcc and fcc phases [$\sim 10^{-3}$ eV (Ref. 16)] and the lack of directional bonding (weakly correlated ionic displacements) in a free-electron-like material such as Na. This behavior is in contrast to that found for liquid arsenic where an obvious order was identified.[7]

The long-time behavior of the mean-square displacement of the atoms differentiates a liquid from a solid. For an N atom unit cell, the mean-square displacement as a function of time t and temperature T is given by

$$\langle r^2(t,T)\rangle = \frac{1}{N}\sum_{i=1}^{N}\langle \mathbf{r}_i(t,T) - \mathbf{r}_i(0,T)\rangle^2 . \tag{1}$$

The coefficient of self-diffusion D can be evaluated as

$$D(T) = \frac{1}{6}\lim_{t\to\infty}\frac{d\langle r^2(t,T)\rangle}{dt} . \tag{2}$$

Figure 3(a) shows curves of $\langle r^2(t,T)\rangle$ for Na below the melting temperature (T_m) and at four temperatures above, in the units of d^2, where d is the nearest-neighbor distance of a bcc Na structure at its liquid density at the melting temperature (i.e., $d = 3.77$ Å). $\langle r^2(t,T)\rangle$ was computed by averaging over positions along the trajectory, but no other smoothing was performed. The curve for $T < T_m$ shows no diffusion, demonstrating that the atoms remain localized about a site. (Since there are no voids or defects in our cells, we cannot compare to the measured solid self-diffusion.) The linearity of these curves for $T > T_m$ at large t indicates that these systems are indeed in the liquid state and that the observation times of the simulations are long enough. The increase in slope as the temperature is raised indicates an increase in its diffusion coefficient, as expected. The quantitative comparison of the coefficient of self-diffusion with experimental measurements[13-15] and previous calculations with empirical pair potentials[23,24] is shown in an Arrhenius plot in Fig. 3. Over a wide range of temperatures (400–1400 K), the results of our calculation are in good agreement with experiment and better than any of the previous pair-potential calculations. Note that two different values of D were obtained by Paskin and Rahman[23] using two different potentials both of which yielded good pair distribution functions. The self-diffusivity $D(T)$ is usually fitted to the Arrhenius form

$$D(T) = D_0 \exp(-E_a/k_B T) . \tag{3}$$

The values of D_0 (in units of 10^{-3} cm^2/sec) and E_a (in units of eV/atom) obtained from the least-squares fitting the present calculations are $D_0 = 0.84(\pm 0.06)$, $E_a = 0.099(\pm 0.004)$, compared against the experimental values of $D_0 = 1.10$, $E_a = 0.105$ (Ref. 13), $D_0 = 0.92$, $E_a = 0.102$ (Ref. 14), and $D_0 = 0.86(\pm 0.09)$, $E_a = 0.096(\pm 0.004)$ (Ref. 15). Our results are in excellent agreement with the values obtained from the most recent experiment.[15] We are not aware of any previous theoretical results for these values. The activation energy is much larger than the structural energy differences among the hcp, bcc, and fcc phases of crystalline sodium which is $\sim 10^{-3}$ eV/atom,[16] consistent with the uncorrelated nature of the angular distribution functions and nondirectional nature of the bonding.

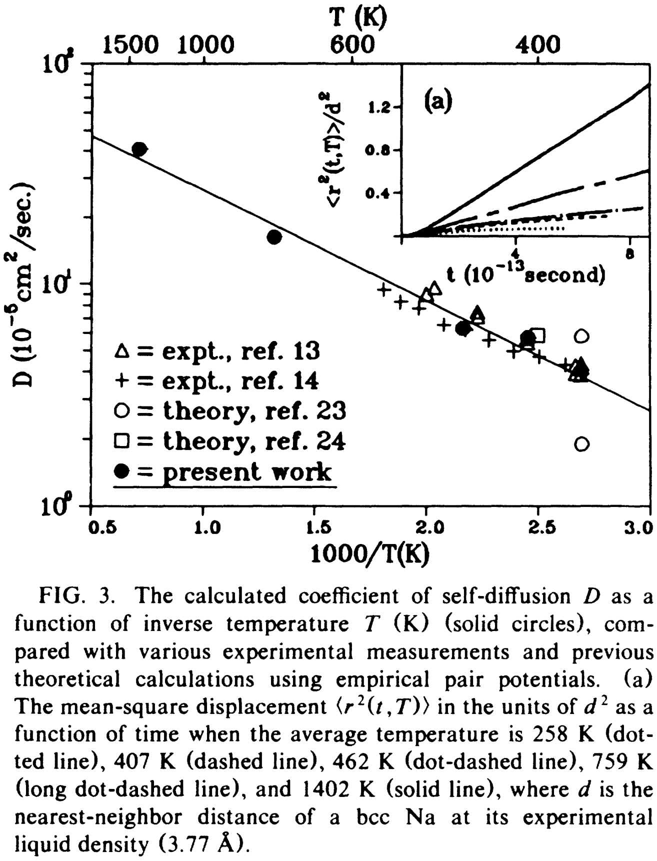

FIG. 3. The calculated coefficient of self-diffusion D as a function of inverse temperature T (K) (solid circles), compared with various experimental measurements and previous theoretical calculations using empirical pair potentials. (a) The mean-square displacement $\langle r^2(t,T)\rangle$ in the units of d^2 as a function of time when the average temperature is 258 K (dotted line), 407 K (dashed line), 462 K (dot-dashed line), 759 K (long dot-dashed line), and 1402 K (solid line), where d is the nearest-neighbor distance of a bcc Na at its experimental liquid density (3.77 Å).

In conclusion, we have studied the temperature dependence of diffusion properties of liquid sodium using first-principles molecular dynamics and the local-density approximation. The pair distribution function is in good agreement with x-ray- and neutron-scattering results. The local coordination is intermediate between fcc and bcc, consistent with the fact that the energy difference between these phases in the solid is very small. Finally, we have computed the coefficient of self-diffusion as a function of temperature and found Arrhenius behavior with an activation energy of ~ 0.1 eV in good agreement with experiment.

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