

Ab initio calculation of density dependence of liquid-Na properties

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We have performed *ab initio* quantum-mechanical calculations of the Hellmann-Feynman forces in liquid Na, which were used in a molecular-dynamics simulation without recourse to Car-Parrinello methods. The diffusion coefficient (D) and pressure (P) were obtained as a function of the temperature (T) and volume (V). Three simple formulas relating D to T , D to V , and P to V were found to be obeyed.

Qian, Weinert, Fernando, and Davenport¹ (QWFD) have performed a first-principles calculation of the activation energy for diffusion in liquid Na, obtaining excellent agreement with experiment. Their calculations were performed at a density close to the experimental density of liquid Na at its melting temperature, even though they noted that the density they calculated for the solid is 43% greater than the experimental value at 5 K. If this discrepancy extrapolates to the liquid, we estimate their calculations were performed at negative pressures between -30 and -20 kbar, depending on temperature.

Our calculation mimics QWFD in that we have 54 atoms per cubic supercell, expand the Kohn-Sham orbitals with a Fermi-Dirac occupancy at the Γ point in the Brillouin zone (BZ) in plane waves up to $G^2=12$ Ry, and use a fully nonlocal pseudopotential² with s nonlocality. It differs in that we use the Wigner correlation functional and in that our pseudopotential is one we recently developed³ based on Hartree-Fock exchange with the core electrons, resulting in a density (in the solid) 8% smaller than the 5-K experimental value. Rather than use the Car-Parrinello⁴ method (CPM), we perform a complete quantum-mechanical electronic-structure calculation (using an iterative technique⁵) after each

molecular-dynamics (MD) time step,⁶ obtaining both the Hellmann-Feynman forces and the pressure $P=(\text{Tr}\bar{\sigma}+m\langle v^2\rangle)/3V$, where $\bar{\sigma}$ is the stress tensor and V the volume per atom. The starting potential for each time step is calculated from the converged charge density of the previous time step plus the *difference* between a superposition of atomic charge densities at the current and previous times. After 3 iterations, requiring 110 Cray YMP seconds, the forces are within 2% of their converged values⁷ and P within 0.1%. These errors are smaller than those introduced by the one-point sample of the BZ. It is the electrons and not the ions which control the time step Δt in the CPM; thus QWFD took $\Delta t=1.2\times 10^{16}$ sec, 10 times shorter than our $\Delta t=50t_{\text{a.u.}}$,⁸ which is still quite a bit smaller than the $\Delta t=10^{-14}$ sec used in classical MD simulations by Rahman.⁹ Thus our procedure is computationally more efficient than the CPM. QWFD used a microcanonical ensemble, obtaining the temperature from $m\langle v^2\rangle=3kT$, whereas we fixed T with the Nose¹⁰ thermostat.

The pair-distribution functions $g(r)=V\langle\sum_i'\delta(|\mathbf{r}_i-\mathbf{r}_j|-r)/4\pi r^2\rangle$ shown in Fig. 1(a) for fixed V and different T are quite similar to QWFD's. The $g(r)$ in Fig. 1(b) with fixed T have their peaks increase, and the whole curve

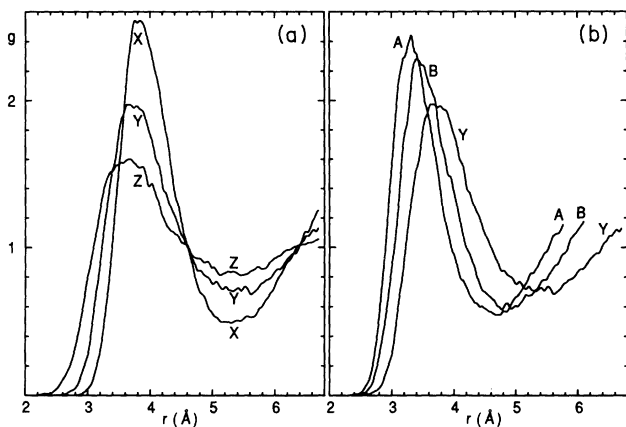


FIG. 1. Pair-distribution function $g(r)$ for the following temperatures and atomic volumes: A (700 K, 29.8054 \AA^3), B (700 K, 35.3096 \AA^3), Y (700 K, 46.8597 \AA^3), X (400 K, 46.8597 \AA^3), and Z (1400 K, 46.8597 \AA^3).

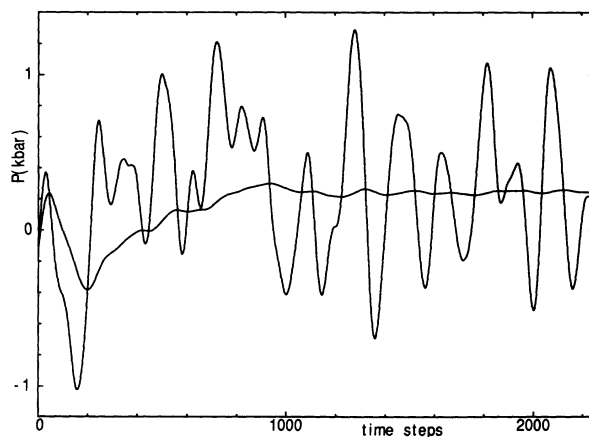


FIG. 2. Pressure and its running average at each of 2250 time steps for $T=700$ K and $V=46.8597 \text{ \AA}^3$. The small rapidly varying kinetic contribution has been averaged.

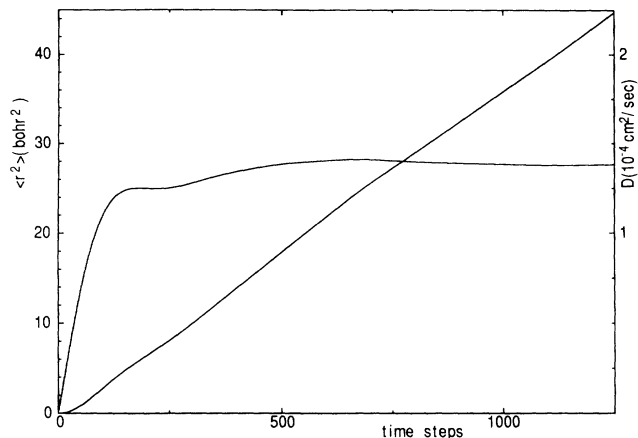


FIG. 3. $\langle r^2 \rangle$ and coefficient of self-diffusion at each of 1250 time steps for $T=700$ K and $V=46.8597 \text{ \AA}^3$.

compress with increasing P , as observed experimentally.¹¹

Figure 2 displays the pressure and its running average calculated for $T=700$ K and $V=46.8597 \text{ \AA}^3/\text{atom}$. Several hundred time steps during which the system was approaching equilibrium have been discarded. Figure 3 displays $\langle r^2 \rangle$ averaged over the 54 atoms in the supercell and over 1000 different initial times (i.e., each of the first 1000 time steps in Fig. 2 were used to start Fig. 3), as well as a running estimate of the diffusion constant, defined to be

$$D(T) = \lim_{t \rightarrow \infty} [\langle r^2(T, t) \rangle / 6t]. \quad (1)$$

For smaller T or V , the number of time steps discarded and the number of initial times needed in the r^2 average was larger. In Table I we list D , P , and $\langle E \rangle$, the energy per atom, for six different combinations of T and V .

The Birch¹² equation of state is

$$P = 1.5B[(V_0/V)^{7/3} - (V_0/V)^{5/3}] + P_0, \quad (2)$$

where B is the isothermal bulk modulus. Taking P_0 and V_0 from the first row of Table I, we fitted the other two (P, V) at 700 K in Fig. 4, almost exactly with $B(700 \text{ K}) = 41\,200$ bars, which compares well with the experimental value¹³ of $B(700 \text{ K}) = 38\,616$ bars. The mean free path for an ideal gas is well known to be $\lambda = V/4\pi\sqrt{2}r_0^2$, where r_0 is the scattering radius. We subtract an excluded

TABLE I. Pressure, average energy per atom, and coefficient of self-diffusion calculated at six different temperatures and volumes.

T (K)	V ($\text{\AA}^3/\text{atom}$)	P (bars)	$\langle E \rangle$ (eV)	D ($10^{-5}\text{cm}^2/\text{sec}$)
700	46.8597	246	-6.080 13	13.82
700	35.3096	20 864	-6.072 24	7.668
700	29.8054	46 343	-5.994 23	4.954
400	46.8597	-3407	-6.170 19	3.238
1400	46.8597	6305	-5.914 33	32.60
1400	29.8054	55 183	-5.806 23	16.20

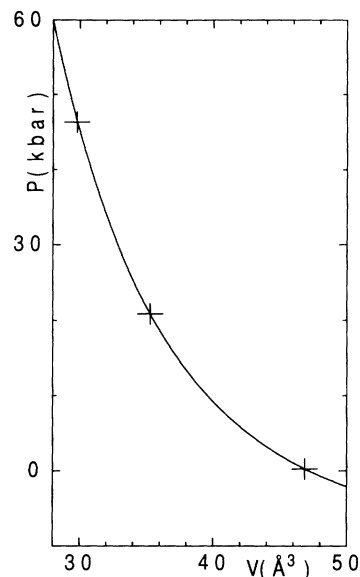


FIG. 4. Pressure at three volumes at $T=700$ K fitted with Eq. (2).

volume $4\pi r_0^3/3$ from V , note that the square of the distance a particle diffuses per second is λ^2 times the number of λ 's per sec, $\langle v \rangle / \lambda$, and obtain

$$D = (kT/m\pi^3)^{1/2}(V - 4\pi r_0^3/3)/6r_0^2. \quad (3)$$

Equation (3) with a single parameter $r_0=1.69 \text{ \AA}$ fits $D(V)$ at 700 K almost perfectly, as seen in Fig. 5. At 1400 K, $r_0=1.3138 \text{ \AA}$ (1.3465 \AA) is required to satisfy (3) at $V=46.8597 \text{ \AA}^3$ (29.8054 \AA^3). These radii may be compared with our pseudopotential cutoff radius of 0.8996 \AA , the standard ionic radius of 0.97 \AA , and the Wigner-Seitz radii at the three densities at which we have calculated,

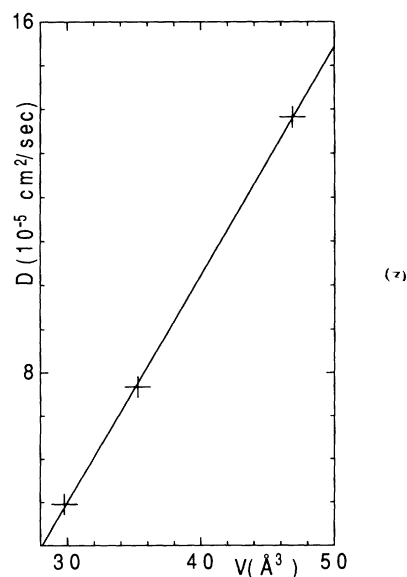


FIG. 5. Diffusion coefficient D at three volumes at $T=700$ K fitted with Eq. (3).

2.2365, 2.0352, and 1.9234 Å. There are no hard cores in these calculations; the interactions between the ions are strictly a Coulomb repulsion screened by the electron gas. We think it is quite remarkable that the scattering of these ions can be described by the simplest kinetic theory, assuming a soft core with a single effective radius for both the excluded volume and scattering cross section. The effective radius is some measure of the distance of closest approach of the ions and therefore decreases with increasing temperature, but over a large range of Wigner-Seitz radii varies by no more than the uncertainties in the calculated diffusion constants. In Fig. 6 the self-diffusivity is least-squares fit to the Arrhenius form at two densities:

$$D(T) = D_0 \exp(-E_a/kT), \quad (4)$$

with $D_0 = 84.6 \times 10^{-5} \text{ cm}^2/\text{sec}$ and $E_a = 0.112 \text{ eV}$ at "normal" density; QWFD obtained $D_0 = 84 \times 10^{-5} \text{ cm}^2/\text{sec}$ and $E_a = 0.099 \text{ eV}$. At high density we expect the averaging to be interminable at 400 K; hence D was calculated only at 700 and 1400 K, resulting in $D_0 = 52.8 \times 10^{-5} \text{ cm}^2/\text{sec}$ and $E_a = 0.143 \text{ eV}$. Using the same two points at normal density gives $D_0 = 76.9 \times 10^{-5} \text{ cm}^2/\text{sec}$ and $E_a = 0.104 \text{ eV}$. Thus we conclude that D_0 and E_a are strongly dependent on V and hence P , but if one has a pseudopotential which cannot give $P(V)$ correctly, one should calculate D as a function of V rather than P .

We attempted to calculate $C_V = (\langle E^2 \rangle - \langle E \rangle^2)/kT^2$, but the Nose thermostat, which was said¹⁰ to give all thermodynamic averages correctly, fails for the square of the kinetic energy K . Although the numerical average of $K = 3(N-1)kT/2N$ to five significant figures ($N=54$), $K(t)$ oscillates about its average with a period and amplitude which depends on the thermostat mass parameter. It should be obvious that in the limit that this parameter approaches zero the coupling between the kinetic energy of the system, the thermostat becomes infinitely tight, and the kinetic energy has no fluctuations. Thus the Nose thermostat with a reasonable mass parameter appears to be adequate for most averages, but not for fluctuations. In the very-large-mass-parameter limit, we assume it would also give fluctuations correctly, but would require an inordinately long integration time to achieve ergodicity. We therefore fit $\langle E(T) \rangle$ at normal density to obtain $C_V = (8.526 - 2.920 \times 10^{-3}T) \text{ cal}/(\text{mol K})$. This gives, with experimental values¹³ in parentheses, at 400 K, $C_V = 7.358(7.030)$; at 700 K, $C_V = 6.482(5.739)$; and

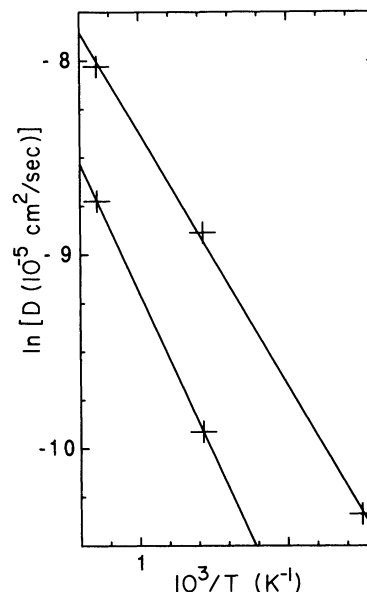


FIG. 6. $\ln D$ fit with Eq. (4) at three temperatures for $V = 46.8597 \text{ \AA}^3$ and at two temperatures for $V = 29.8054 \text{ \AA}^3$.

at 1400 K, $C_V = 4.438(4.851)$. The comparison between the calculated C_V and experiment should not be taken too seriously. The experimental values are at atmospheric pressure, whereas the calculated ones are at fixed density. Also, a three-point fit to the internal energy is not adequate for determining C_V over a 1000° range. We also fitted $P(T)$ to obtain $(\partial P/\partial T)_V = (16.051 - 7.042 \times 10^{-3}T) \text{ bar/K}$. The volume coefficient of thermal expansion $\alpha = (\partial P/\partial T)_V/B$. Using our calculated value of B at 700 K, $\alpha_{700} = 2.574 \times 10^{-4} \text{ K}^{-1}$, in excellent agreement with the experimental¹² $\alpha_{700} = 2.666 \times 10^{-4} \text{ K}^{-1}$. Finally, we note that $C_P - C_V = VT\alpha^2 B = 1.288 \text{ cal/mol}$ at 700 K. This compares to $C_P - C_V = 1.24 \text{ cal/mol}$ obtained from the tabulated values.¹³ As far as we know, quantum-mechanical molecular-dynamics calculations of $C_P - C_V$ or α have not previously been performed for any liquid.¹⁴

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