Radial Distribution Function of Liquid Sodium[†]

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The radial distribution function and static structure factor of liquid sodium at temperatures of 100 and 200 °C have been calculated by a Monte Carlo method using a realistic ion-ion potential. The calculated structure factor is in excellent agreement with recent x-ray-diffraction measurements.

I. INTRODUCTION

The properties of the liquid alkali metals, e.g., sodium, are of great interest both because of their engineering applications and because of their fundamental importance, since they are simple metals. Their simplicity is a consequence of the fact that the Fermi surface of the conduction electrons in the solid phase is nearly spherical and is completely contained inside the first Brillouin zone. Hence, the alkali metals are comparatively tractable theoretically, and it appears reasonable that an effective ion-ion interaction derived from calculations on the solid phases might be useful for the liquid phases.

The structure of a liquid metal is crucial in determining its electrical and thermodynamic properties, and thus is an important test of theoretical ideas. For sodium and potassium, this structure is now accurately known from recently reported x-ray-diffraction measurements.[1] The aim of this paper is to show by a first-principles calculation that fairly detailed agreement between theory and experiment can be obtained in the case of sodium. In essence, we have calculated a theoretical liquid-structure factor from the Fourier transform of the radial distribution function, which we obtained by a Monte Carlo method using a realistic ion-ion interaction. Our results are in substantially better agreement with experiment than previous calculations.

II. FORMULATION

We consider a system of N sodium ions in volume V at temperature T. We let $\rho = N/V$, the number density, and we introduce the quantity $a = (2/\rho)^{1/3}$, which is the lattice constant for the (bcc) solid phase and is a convenient measure of the density in the liquid. The Fermi momentum $\vec{P}_F$ of the N conduction electrons is then given by $P_F \equiv \hbar k_F = \hbar (3\pi^2 \rho)^{1/3}$.

The basic theoretical picture of metallic sodium is that the 3s conduction electrons form a Fermi gas which screens the Coulomb interactions between the ions, producing a volume-dependent interaction potential, $v_{eff}(r, a)$, between the ion cores. Presumably v_{eff} is repulsive at short distances and of a damped oscillatory nature (the Friedel oscillations) at large distances. We assume that the effective ion-ion interaction is a two-body central interaction; then the radial distribution function $g(r, a)$ depends only on r, the magnitude of the interparticle separation (and, of course, on the volume and temperature). The radial distribution function is defined by

$$g(r_{12}, a) = N(N-1)\rho^{-2} \int d\vec{r}_3 \cdots d\vec{r}_N$$

$$\times \exp\left(-\beta \sum_{i<j} v_{eff}(r_{ij}, a)\right)$$

$$\times \left[\int d\vec{r}_1 \cdots d\vec{r}_N \right.$$

$$\left. \times \exp\left(-\beta \sum_{i<j} v_{eff}(r_{ij}, a)\right)\right]^{-1}, \quad (1)$$

where $r_{ij} \equiv |\vec{r}_i - \vec{r}_j|$ and $\beta = (kT)^{-1}$. The liquid-structure factor $S(k)$ is

$$S(k) = 1 + \rho \int d\vec{r} \, [g(r) - 1] \, e^{i\vec{k}\cdot\vec{r}}. \quad (2)$$

Schiff[2] has noted that there is some question as to whether the use of (1) is justified in the case of a liquid metal, i.e., whether a liquid metal can be treated as a fictitious classical fluid, described by Boltzmann statistics, interacting via the pair potential v_{eff}. We feel that in at least one important way such a treatment may not be justified, namely, that the solidification point of the fictitious classical fluid may not be at all related to the solidification point of the real liquid metal. This is due to the fact that in a real metal contributions to the free energy of both the liquid and solid phases from the volume-dependent terms arising from the kinetic, correlation, and band-

structure energy of the conduction electrons are much larger than the contribution from the effective ion-ion interaction.[3,4] For example, sodium undergoes a volume change ~3% on melting, which changes the Fermi energy of the election by ~2% or ~0.06 eV, while the maximum depth of the effective ion-ion interaction is ~0.03 eV. The solidification of the fictitious fluid, on the other hand, is governed entirely by v_{eff}. It therefore seems quite possible that there could be a difference in melting points, and that it could cause some difficulty in the usual Monte Carlo or molecular-dynamics calculations done for temperatures between the two melting points. As discussed in Sec. IV, however, we feel that the results presented in this paper are not subject to this difficulty, i.e., that the configuration over which we averaged $g(r)$ were liquidlike configurations.

III. ION-ION INTERACTION

A very simple but useful model of the effective ion-ion interaction is due to Ashcroft and Lekner,[5] who assume a hard-sphere potential and calculate $S(k)$ from the analytic solution of the Percus-Yevick equation for this potential; the hard-sphere diameter can be chosen to fit either the first peak in the experimental $S(k)$ or the compressibility sum rule. The qualitative success of this model is due to the fact that much of the structure of liquids is simply an excluded-volume effect. However, Greenfield *et al.*[6] have shown that even if an additional parameter, the packing fraction, is introduced into this model, no choice of hard-sphere radius and packing fraction will lead to detailed quantitative agreement with the experimental $S(k)$ for sodium and potassium.

More realistic forms of the potential were used in Monte Carlo and molecular-dynamics calculations by Schiff.[2] These forms consisted of a soft-core repulsion at short distances plus an oscillatory term proportional to $r^{-3}\cos 2k_F r$ asymptotically. One of the forms used by Schiff, the LRO2 with parameters appropriate to sodium, was treated by a perturbation method by Wehling *et al.*,[7] who found good agreement between their results for $S(k)$ and those of Schiff, but only fair agreement with experiment, due presumably to the inaccuracy of the LRO2 potential.

The ion-ion potential we have selected is essentially that proposed by Duesbery and Taylor[8] and Basinski *et al.*[9] This potential, which is volume dependent, contains no adjustable parameters: It is obtained by doing a one-orthogonalized-plane-wave (OPW) calculation of the ion-electron matrix element and using the electron-gas screening function of Geldart and Taylor.[10] Calculations of the

elastic constants[9] and phonon frequencies[11] of sodium using this form of v_{eff} have yielded good agreement with experiment.

It is convenient to write this effective interaction in the form $\phi(r/a)$, and the choice $a = 4.37$ Å is sufficiently accurate (to ~0.5%) for liquid sodium in the temperature range (100–200 °C) of present interest. We took $\phi(r/a) = 1.15$ eV for $0 \leqslant r/a \leqslant 0.48$; for $0.48 < r/a \leqslant 3$ we used a table of numbers, a portion of which is listed in Table I; for $3 < r/a$, we used the fit

$$\phi(r/a) = \frac{A\cos(2k_F r) + B\sin(2k_F r)}{(r/a)^5},$$

with $A = -0.00722$ eV and $B = -0.018699$ eV, which is a reasonably accurate fit for $1 \lesssim r/a \leqslant 6$. The asymptotic form one would expect, a term proportional to $r^{-3}\cos(2k_F r)$, enters with such a small coefficient[9] (because the ion-electron matrix element is very close to zero at $2k_F$) that it can be neglected for the region $0 \leqslant r/a \leqslant 6$ of interest to us.

IV. COMPUTATIONAL METHODS AND RESULTS

Our method was the usual Monte Carlo (MC) method of evaluating the radial distribution function $g(r)$ by using a small system with periodic boundary conditions and averaging over a large number of configurations generated with probability proportional to the Boltzmann factor $\exp[-\beta \sum_{i<j} \phi(r_{ij}/a)]$. The temperatures were the same as those in the experiments,[1] namely, 100 and 200 °C. The results reported here are based on systems of 128 particles. To determine whether the system was fluid or solid, we monitored the behavior of the interaction energy of the fictitious substance, $U_0 \equiv \frac{1}{2}N\rho \int d\vec{r}\, g(r)\phi(r/a)$, and the quantities $\Delta_i \equiv \sum_{j=1}^{N}\cos(\vec{Q}_i \cdot \vec{r}_j)$, where the $\vec{r}_j$ are the coordinates of the particles and $\vec{Q}_i$ are the three smallest lattice vectors in the (fcc) lattice reciprocal to the (bcc) direct lattice of solid sodium. For a bcc solid, the Δ_i should be about N; for a fluid they should oscillate with amplitude $\sim\sqrt{N}$ about zero.[12]

For the system at 200 °C, we placed the particles initially at the sites of a bcc lattice. After ignoring the first 12 800 configurations, we generated another 128 000 configurations during which U_0 drifted upward and then approximately stabilized and the Δ_i decreased and began to oscillate about zero with amplitude ~30. We then concluded that the system was a fluid and obtained the $g_{\text{MC}}(r)$ listed in Table I by averaging over an additional 256 000 configurations, during which U_0 was reasonably stable and the Δ_i continued to oscillate.

For the system at 100 °C, we again attempted to

start at the bcc lattice sites, again ignoring the first 12 800 configurations; after another 128 000 configurations during which U_0 was stable, the Δ_i were between 85 and 100, implying that the system had remained solid. As might be expected, the $g(r)$ thus computed had a great deal of structure and the $S(k)$ calculated from it had a solidlike appearance. We therefore made a new run of 384 000 configurations at 100 °C, beginning from the fluidlike positions that the system at 200 °C had after 384 000 configurations. This time the system apparently remained a fluid, since U_0 was stable and the Δ_i again oscillated with amplitude ~30. The resulting g_{MC} (r), which is listed in Table I, showed much less structure than the solidlike run. In another run, a system of 54 particles at 100 °C started from the bcc lattice sites failed to melt even after 540 000 configurations. The long equilibration time between phases had been noted many times previously, e.g., in recent molecular-dynamics calculations of rubidium near its melting point.[13]

The nearest-image periodic-boundary conditions limit the validity of g_{MC} (r) for the 128-particle system to $r/a \lesssim 2$. However, a liquid metal has much more long-ranged oscillations in $g(r)$ than does an insulating fluid, and these oscillations are not sufficiently damped at $r/a = 2$ to permit truncation of the Fourier transform. In order to take these oscillations into account at least approximately, we solved the Percus-Yevick (PY) equation,

using the potential $\phi(r/a)$, by an iterative method similar to that of Broyles.[14] We obtained the solution g_{PY} for $r/a \lesssim 6$ at temperatures as low as 30 °C.

As can be seen from Table I, g_{PY} is in moderately good agreement with g_{MC} for $r/a \lesssim 2$. Although the oscillations in g_{PY} for $1 \lesssim r/a \lesssim 2$ are more damped than those in g_{MC}, it is reasonable to compute a theoretical $S(k)$ by Fourier transforming:

$$g_T(r) = g_{MC} \quad (0 \leqslant r/a < 2)$$
$$= g_{PY} \quad (2 \leqslant r/a \leqslant 6)$$
$$= 1 - \beta\phi(r/a) \quad (6 < r/a).$$

The form for the region $r/a > 6$, which leads to sine and cosine integrals in $S(k)$, is the asymptotic form according to the arguments of Enderby et al.[15] It appeared to us that g_{PY} was approaching this theoretical asymptotic form only very slowly, if at all, and that it would reach it only when $g(r)$ -1 was too small to test the prediction numerically. In practice, the contribution to $S(k)$ from the region $r/a > 6$ was negligible ($\sim 10^{-4}$).

Our calculated $S(k)$ are compared with the results of Greenfield et al.[1] in Fig. 1 (for $T = 100$ °C) and Fig. 2 (for $T = 200$ °C). The agreement is quite good and is within the combined experimental and Monte Carlo statistical error (each ~1%) for much of the range. In addition, the locations of all the maxima and minima except the first are
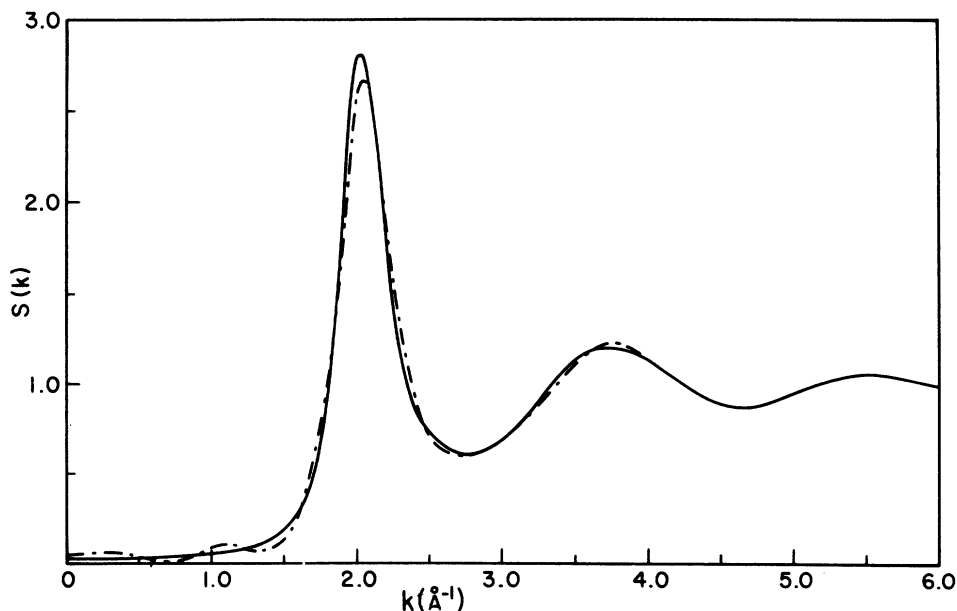

FIG. 1. Comparison of experimental (solid line) and theoretical (dashed line) liquid-structure factors at 100°C.

TABLE I. Interionic potential and the Monte Carlo and Percus-Yevick radial distribution functions at the two temperatures; $a = 4.37$ Å.

$\dfrac{r}{a}$	$\phi\left(\dfrac{r}{a}\right)$ (eV)	$T = 100°\text{C}$		$T = 200°\text{C}$	
		$g_{\text{MC}}\left(\dfrac{r}{a}\right)$	$g_{\text{PY}}\left(\dfrac{r}{a}\right)$	$g_{\text{MC}}\left(\dfrac{r}{a}\right)$	$g_{\text{PY}}\left(\dfrac{r}{a}\right)$
0.485	1.057	0.0	$<10^{-14}$	0.0	$<10^{-11}$
0.525	0.697	0.0	$2.74\ (10^{-9})$	0.0	$2.49\ (10^{-6})$
0.575	0.415	0.0	$1.38\ (10^{-5})$	$1.57\ (10^{-4})$	$1.99\ (10^{-4})$
0.625	0.227	0.0220	$3.72\ (10^{-3})$	0.0131	0.0158
0.675	0.106	0.104	0.120	0.195	0.235
0.725	$3.29\ (10^{-2})$	0.682	0.861	0.873	1.066
0.775	$-7.42\ (10^{-3})$	1.819	2.136	1.864	2.103
0.825	$-2.58\ (10^{-2})$	2.510	2.627	2.318	2.396
0.875	$-3.07\ (10^{-2})$	2.318	2.137	2.144	1.982
0.925	$-2.79\ (10^{-2})$	1.765	1.453	1.672	1.427
0.975	$-2.15\ (10^{-2})$	1.227	0.992	1.231	1.024
1.025	$-1.41\ (10^{-2})$	0.866	0.758	0.906	0.799
1.075	$-7.32\ (10^{-3})$	0.675	0.661	0.724	0.694
1.125	$-1.99\ (10^{-3})$	0.574	0.637	0.613	0.662
1.175	$1.71\ (10^{-3})$	0.544	0.653	0.582	0.674
1.225	$3.82\ (10^{-3})$	0.576	0.798	0.609	0.716
1.275	$4.59\ (10^{-3})$	0.653	0.765	0.686	0.782
1.325	$4.38\ (10^{-3})$	0.791	0.852	0.795	0.866
1.375	$3.58\ (10^{-3})$	0.938	0.954	0.939	0.964
1.425	$2.48\ (10^{-3})$	1.087	1.065	1.072	1.069
1.475	$1.34\ (10^{-3})$	1.207	1.172	1.180	1.163
1.525	$3.54\ (10^{-4})$	1.266	1.248	1.246	1.221
1.575	$-3.81\ (10^{-4})$	1.288	1.261	1.252	1.223
1.625	$-8.54\ (10^{-4})$	1.232	1.203	1.223	1.170
1.675	$-1.07\ (10^{-3})$	1.163	1.100	1.153	1.084
1.725	$-1.07\ (10^{-3})$	1.060	0.993	1.062	0.997
1.775	$-8.89\ (10^{-4})$	0.956	0.913	0.964	0.929
1.825	$-6.08\ (10^{-4})$	0.873	0.870	0.886	0.891
1.875	$-2.98\ (10^{-4})$	0.832	0.862	0.843	0.882
1.925	$-1.1\ (10^{-5})$	0.820	0.879	0.829	0.894
1.975	$1.78\ (10^{-4})$	0.838	0.911	0.850	0.921
2.00	$3.04\ (10^{-4})$		0.923		0.933
2.10	$4.55\ (10^{-4})$		1.010		1.008
2.20	$3.47\ (10^{-4})$		1.074		1.062
2.30	$1.33\ (10^{-4})$		1.081		1.066
2.40	$-3.9\ (10^{-5})$		1.030		1.024
2.50	$-1.38\ (10^{-4})$		0.968		0.975
2.60	$-1.22\ (10^{-4})$		0.944		0.956
2.70	$-2.8\ (10^{-5})$		0.964		0.971
2.80	$5.4\ (10^{-5})$		1.001		1.000
2.90	$8.4\ (10^{-5})$		1.029		1.022
3.0	$7.2\ (10^{-5})$		1.032		1.025

essentially exact. We believe that most of the discrepancy near the first peak is due to the tail correction from g_{PY}, since the first peak in the $S(k)$ calculated from g_{PY} alone is quite a bit too low and similarly displaced to the right. The oscillations in the theoretical $S(k)$ for small k also arise from g_{PY}. It appears likely that were it not for these truncation difficulties, essentially exact agreement between theory and experiment could be obtained.

V. DISCUSSION

The results we have presented are zero-parameter calculations, both in the construction of the ion-ion potential and in the Monte Carlo calculation of $g(r)$. It is most encouraging that they appear to account essentially quantitatively for the structure of liquid sodium.

Our results tend to support the conclusion drawn by Schiff[2] that it is difficult to see clearly
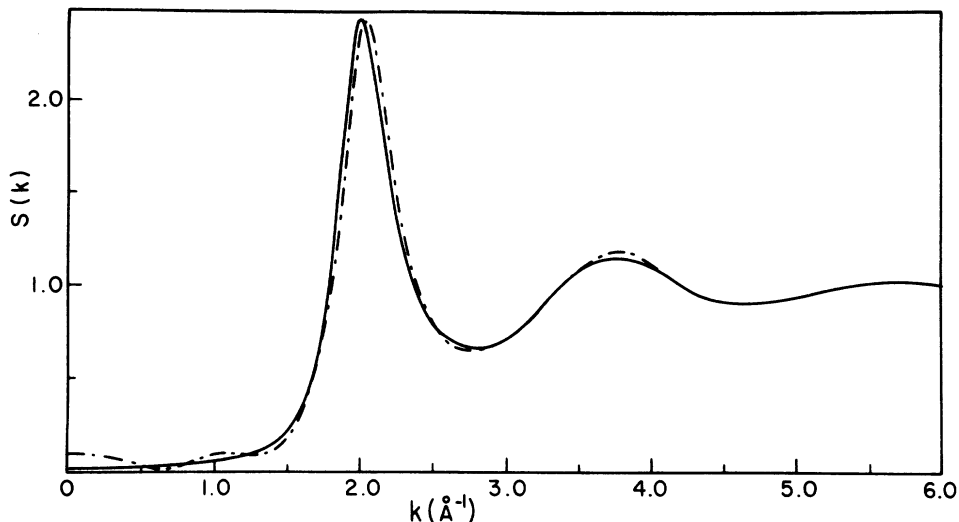
FIG. 2. Comparison of experimental (solid line) and theoretical (dashed line) liquid-structure factors at 200°C.

the effect on the structure of the liquid of the predicted term proportional to $r^{-3}\cos(2k_F r)$: The ion-ion interaction we have used does not contain this term, yet it accounts for the structure quite well.

It is, of course, possible to predict more or less the same structure for a liquid from different potentials. Because of this fact, it can be asserted only that our results, taken with other calculations[9,11] on the solid phase of sodium, tend to suggest that the effective ion-ion potential we have used is reasonably accurate. It cannot be asserted that our results prove that the potential we have used is correct, and the aim of this paper has been the considerably more limited one

of showing that *some* realistic potential would reproduce the structure correctly. Considerable additional information could be gained from theoretical and experimental studies over a wider range of temperature and pressure.

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