PHYSICAL REVIEW A VOLUME 15, NUMBER 3 MARCH 1977

Radial distribution function of liquid potassium

R. D. Murphy

Department of Physics, University of Missouri—Kansas City, Kansas City, Missouri 64110

(Received 19 August 1976)

The radial distribution function and static structure factor of liquid potassium at temperatures of 338 and 408 K have been calculated by a Monte Carlo method using a realistic ion-ion potential. The agreement between the calculated liquid structure factor and recent x-ray diffraction measurements is excellent.

I. INTRODUCTION AND FORMULATION

The results presented here are similar to those for sodium presented in a previous paper.[1] The essential feature of the present paper is the calculation of the radial distribution function, $g(r)$, for potassium by a Monte Carlo method using a realistic interionic potential. The Fourier transform of $g(r)$ gives the liquid structure factor, $S(k)$, which turns out to be in very good agreement with x-ray diffraction measurements[2] made at two temperatures, 338 and 408 K.

We consider a system of N potassium ions in volume V at temperature T, and denote by $\rho \equiv N/V$ the number density. A convenient scale factor for lengths and wave vectors is $a = (2/\rho)^{1/3}$; thus the Fermi wave vector k_F is given by $k_F a = (6\pi^2)^{1/3}$. For potassium, $a = 5.40$ Å at $T = 338$ K and $a = 5.44$ Å at $T = 408$ K.

We assume that the effective ion-ion interaction is a two-body, central, volume-dependent interaction $v_{\text{eff}}(r, a)$. Then the radial distribution function is defined by

$$g(r_{12}) = N(N-1)\rho^{-2}\frac{\int P_N\, d\vec{r}_3 \cdots d\vec{r}_N}{\int P_N\, d\vec{r}_1 \cdots d\vec{r}_N}\,,$$

where

$$P_N \equiv \exp\Big[-\beta \sum_{i<j} v_{\text{eff}}(r_{ij})\Big]\,,$$

$$\beta = (k_B T)^{-1}\,,$$

$$r_{ij} \equiv |\vec{r}_i - \vec{r}_j|\,.$$

The liquid structure factor $S(k)$ is

$$S(k) = 1 + \rho \int e^{i\vec{k}\cdot\vec{r}}\,(g(r) - 1)\, d^3 r\,.$$

The form of $v_{\text{eff}}(r, a)$ used here is, as before,[1] based on the work of Duesbery and Taylor[3] and Basinski *et al.*[4] For convenience, we write this effective interaction in the form $\phi(r/a)$. The small difference in a at the two temperatures leads to slightly different interactions, which are tabulated in Table I. For $r/a \geqslant 3$, we found the following asymptotic form adequate:

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

For both temperatures, it was sufficient to use $A = -0.003\,76$ eV and $B = -0.0209$ eV. As in sodium, the expected term proportional to $r^{-3}\cos(2k_F r)$ is again essentially absent.[4]

II. COMPUTATIONAL METHODS AND RESULTS

The evaluation of the radial distribution function $g(r)$ was done by the usual Monte Carlo method using a system of 432 particles with nearest-image periodic boundary conditions. The "computer experiment" was done for the same temperatures as the x-ray diffraction experiment,[2] namely 338 and 408 K, using the $\phi(r/a)$ appropriate to the density at each temperature. As in the previous work,[1] it was necessary to be certain that the system was in a fluid, rather than a bcc solid, phase, during the configurations over which various thermal averages were being evaluated. In order to do this, the "interaction energy"

$$U_0 \equiv \tfrac{1}{2} N\rho \int d^3 r\, \phi(r/a) g(r)$$

and the quantities

$$\Delta_i = \sum_{j=1}^{N} \cos\vec{Q}_i \cdot \vec{r}_j\,,$$

where $\vec{Q}_i$ are the three smallest lattice vectors in the (fcc) reciprocal lattice, were monitored. If the system is in thermal equilibrium, U_0 should be fairly stable; if the system is a fluid, the Δ_i should oscillate about zero with amplitude $\sim\sqrt{N}$, whereas if the system is a solid, the Δ_i should be $\sim N$.

In an initial run started from the bcc lattice sites, the system failed to "melt" even after 226 000 configurations. So a new run, beginning with the particles at random locations in the box, was made. In this run, the first 216 000 configurations were discarded and the averages were made over the next 302 400 configurations. The final positions of this run at 408 K were used as the initial positions for the run at 338 K; this run consisted to 21 600 equilibrating configurations, which

TABLE I. Potential and radial distribution function at the two temperatures.

r/a	$T=338$ K, $\phi(r/a)$ (eV)	$a=5.40$ Å $g(r/a)$	$T=408$ K, $\phi(r/a)$ (eV)	$a=5.44$ Å $g(r/a)$
$\leqslant 0.48$	0.896	0.0	0.863	0.0
0.525	0.588	0.0	0.562	0.0
0.575	0.347	0.0	0.328	0.0
0.625	0.186	$0.455(10^{-2})$	0.172	0.0174
0.675	0.0809	0.0899	0.0718	0.176
0.725	0.0170	0.617	0.0112	0.788
0.775	-0.0180	1.655	-0.0211	1.717
0.825	-0.0331	2.420	-0.0344	2.272
0.875	-0.0356	2.384	-0.0357	2.159
0.925	-0.0313	1.856	-0.0307	1.721
0.975	-0.0239	1.332	-0.0230	1.315
1.025	-0.0157	0.952	-0.0149	0.974
1.075	$-0.008\,28$	0.705	$-0.007\,49$	0.774
1.125	$-0.002\,21$	0.579	$-0.001\,61$	0.656
1.175	0.002 09	0.544	0.002 46	0.603
1.225	0.004 59	0.561	0.004 74	0.624
1.275	0.005 58	0.638	0.005 54	0.672
1.325	0.005 47	0.751	0.005 29	0.770
1.375	0.004 67	0.889	0.004 40	0.894
1.425	0.003 49	1.040	0.003 19	1.026
1.475	0.002 18	1.176	0.001 87	1.140
1.525	$9.27(10^{-4})$	1.258	$6.64(10^{-3})$	1.217
1.575	$-1.07(10^{-4})$	1.294	$-2.94(10^{-4})$	1.244
1.625	$-8.25(10^{-4})$	1.272	$-9.32(10^{-4})$	1.214
1.675	$-1.21(10^{-3})$	1.191	$-1.26(10^{-3})$	1.163
1.725	$-1.32(10^{-3})$	1.097	$-1.32(10^{-3})$	1.086
1.775	$-1.21(10^{-3})$	0.990	$-1.19(10^{-3})$	0.998
1.825	$-9.65(10^{-4})$	0.901	$-9.16(10^{-4})$	0.927
1.875	$-6.40(10^{-4})$	0.837	$-5.66(10^{-4})$	0.880
1.925	$-2.92(10^{-4})$	0.808	$-1.99(10^{-4})$	0.858
1.975	$1.18(10^{-5})$	0.822	$1.15(10^{-4})$	0.862
2.025	$2.42(10^{-4})$	0.866	$3.36(10^{-4})$	0.893
2.075	$3.85(10^{-4})$	0.926	$4.57(10^{-4})$	0.932
2.125	$4.48(10^{-4})$	0.992	$4.94(10^{-4})$	0.990
2.175	$4.46(10^{-4})$	1.059	$4.71(10^{-4})$	1.038
2.225	$3.94(10^{-4})$	1.101	$4.00(10^{-4})$	1.072
2.275	$2.96(10^{-4})$	1.120	$2.92(10^{-4})$	1.084
2.325	$1.75(10^{-4})$	1.116	$1.65(10^{-4})$	1.086
2.375	$4.88(10^{-5})$	1.094	$4.18(10^{-5})$	1.074
2.425	$-5.73(10^{-5})$	1.053	$-6.30(10^{-5})$	1.046
2.475	$-1.32(10^{-4})$	1.010	$-1.32(10^{-4})$	1.021
2.525	$-1.72(10^{-4})$	0.972	$-1.73(10^{-4})$	0.986
2.575	$-1.85(10^{-4})$	0.944	$-1.85(10^{-4})$	0.966
2.625	$-1.71(10^{-4})$	0.927	$-1.66(10^{-4})$	0.949
2.675	$-1.34(10^{-4})$	0.924	$-1.25(10^{-4})$	0.942
2.725	$-8.15(10^{-5})$	0.931	$-6.78(10^{-5})$	0.946
2.775	$-2.77(10^{-5})$	0.952	$-0.87(10^{-5})$	0.961
2.825	$2.02(10^{-5})$	0.982	$4.08(10^{-5})$	0.982
2.875	$5.47(10^{-5})$	1.009	$7.51(10^{-5})$	1.002
2.925	$7.80(10^{-5})$	1.033	$9.37(10^{-5})$	1.017
2.975	$9.07(10^{-5})$	1.049	$1.01(10^{-4})$	1.032

TABLE II. Values of the parameters in the asymptotic fit to $g(r)$.

	C	αa	γa	r_0/a
$T=338$ K $a=5.40$ Å	1.3863	0.692 01	8.7430	2.3116
$T=408$ K $a=5.44$ Å	1.4708	0.849 47	8.6511	2.3226

were discarded, followed by 302 400 configurations over which the various averages were performed. In both runs, the configurations over which thermal averages were taken appeared to be those of fluids in equilibrium. The results for $g(r)$ are listed in Table I for the region $(0 \leqslant r/a \leqslant 3)$ to which their validity is limited by the nearest-image periodic boundary convention.

In order to evaluate the liquid structure factor $S(k)$, it is not sufficient simply to set $g(r)=1$ for $r/a > 3$ because the oscillations in $g(r)$ are not sufficiently damped to be neglected. Of the numerous possible methods of obtaining an estimate of $g(r)$ in the "tail" region $r/a > 3$, the simplest method, which proved to be satisfactory, was to assume that $g(r)$ followed the theoretical[5] asymptotic form:

$$g(r) - 1 \to C(a/r)\exp(-\alpha r)\cos[\gamma(r-r_0)],$$

with the quantities C, α, γ, and r_0 chosen by a nonlinear least-squares fit to the region $1.5 \leqslant r/a \leqslant 3$. The values of these parameters are contained in Table II. The asymptotic form is a good fit, and it was used for r/a to the right of the last zero of the function $g(r)-1$, thereby insuring continuity of the integrand in the Fourier transform.

The $S(k)$ thus computed are compared with experiment[2] in Fig. 1 (for $T=338$ K) and Fig. 2 (for $T=408$ K). The agreement is within the 2% error one might expect from the combined experimental

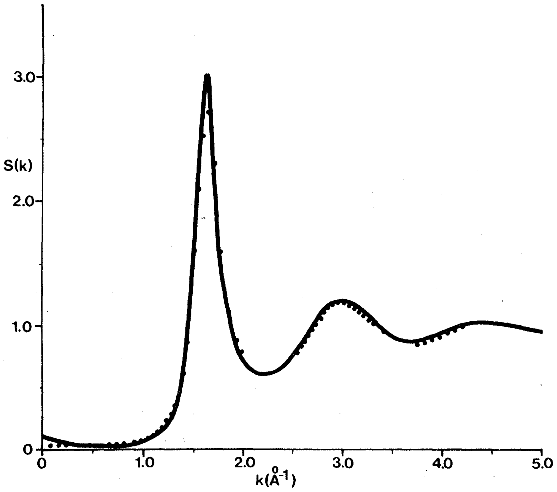

FIG. 1. Experimental (• • •) and theoretical (——) liquid structure factors, $S(k)$, for $T=338$ K.

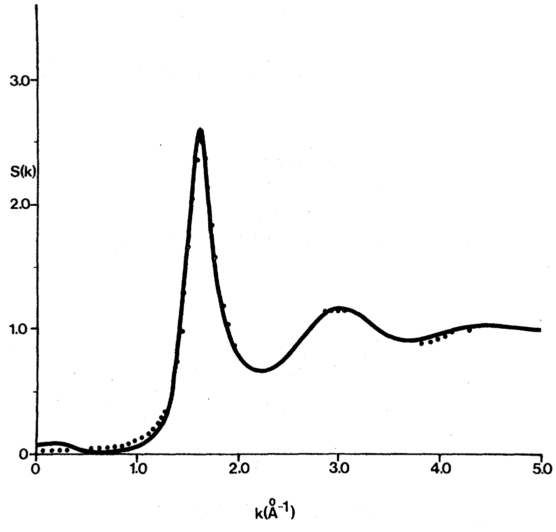

FIG. 2. Experimental (• • •) and theoretical (——) liquid structure factors, $S(k)$, for $T = 408$ K.

uncertainty and the Monte Carlo statistics except in two places: near $k = 0$, where a small spurious oscillation occurs, evidently the result of the fact that the tail correction is not perfect, and just at the first maximum, which in both cases is a few percent too high (3.04 vs the experimental 2.73 at 338 K and 2.62 vs the experimental 2.51 at 408 K).

III. DISCUSSION

The results presented here are, as before in the case of sodium,[1] zero-parameter calculations, both in the construction of the potential and in the Monte Carlo calculation of $g(r)$. The detailed agreement between theory and experiment in both cases suggests that the potential is a reasonably accurate one. In the case of potassium, further evidence for the validity of the potential is afforded by the calculations[6-8] of a number of thermodynamic properties of potassium using this interionic potential or a refinement of it. Investigations over a wider range of temperature and pressure would be most interesting, as would be attempts to see if calculations of this nature are accurate enough to distinguish among various proposed forms of the electron-gas screening function.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge with thanks useful discussions with Dr. M. L. Klein, Dr. R. O. Watts, and especially Dr. Roger Taylor, who also supplied the interionic potential used here; the assistance of W. Lotko with the Fourier transform; a grant of machine time from the University of Missouri Computer Network; and support from the National Research Council of Canada for a portion of the work done while the author was at Memorial University of Newfoundland.

---

[1] R. D. Murphy and M. L. Klein, Phys. Rev. A 8, 2640 (1973).

[2] A. J. Greenfield, J. Wellendorf, and N. Wiser, Phys. Rev. A 4, 1607 (1971).

[3] M. S. Duesbery and R. Taylor, Phys. Lett. 30A, 496 (1969).

[4] Z. S. Basinski, M. S. Duesbery, A. P. Pogany, R. Taylor, and Y. P. Varshni, Can. J. Phys. 48, 1480 (1970).

[5] I. Z. Fisher, *Statistical Theory of Liquids* (U. of Chicago Press, Chicago, 1964), p. 140.

[6] S. S. Cohen and M. L. Klein, Phys. Rev. B 12, 2984 (1975).

[7] R. C. Shukla and R. Taylor, Phys. Rev. B 9, 4116 (1974).

[8] M. S. Duesbery, R. Taylor, and H. R. Glyde, Phys. Rev. B 8, 1372 (1973).