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A Molecular Dynamics Study of Expanded Liquid Rubidium

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CONTENTS

ABSTRACT

Molecular dynamics calculations for expanded liquid rubidium are reported. Effective interatomic pair potentials estimated from low-angle structure factors have been used in this study. Results for the radial distribution function, the structure factor, the mean-square displacement, the velocity autocorrelation function and the self-diffusion constant are given and discussed. Finally, the effective pair potential for 1900°K is discussed in comparison with those derived from nearly-free-electron linear response theory.

1. INTRODUCTION

The concept of effective interatomic pair potentials $v_{eff}(r)$ between screened ions offers the basis for calculations of structural, thermodynamic and transport properties of liquid metals. The theoretical approach for determining $v_{eff}(r)$ in liquid metals is to use the electron theory of metals within the framework of pseudopotential perturbation theory and of linear screening theory /1–3/. This method has been successfully applied to simple (s-p bonded) metals. The $v_{eff}(r)$ thus evaluated, however, are sensitive to the approximations employed in the electronic screening calculation and also to the choice of the form factors of bare pseudopotentials /4–7/.

On the other hand, the direct determination of $v_{eff}(r)$ from the measured structure factor $a(k)$ of a liquid is also possible. This approach has been of continuing interest since the pioneering works of March and co-workers /8, 9/, but it is now generally accepted that it might not be feasible to obtain a unique $v_{eff}(r)$ from the observed $a(k)$ data /10, 11/. This is partly because any liquid theory which relates $a(k)$ to $v_{eff}(r)$ contains some approximations and partly because very high precision scattering data are required over a wide range of momentum transfer k. In spite of the shortcomings mentioned above, this approach still provides one with enough information on $v_{eff}(r)$ in liquid metals. An inversion scheme that has been proposed by the present authors /12, 13/ appears to be competitive in accuracy with those used hitherto and to be worth noting. This scheme is based on the phonon model /14/ combining features of the mean spherical approximation suggested by Hayter *et al.* /15/. The method has been applied to liquid sodium and potassium near their melting points /12/ and to expanded liquid rubidium for temperatures up to 1900°K and pressures up to 122 bar near saturation conditions /13/. It has been shown that the $v_{eff}(r)$ thus obtained can reproduce the observed $a(k)$ very well within the accuracy of the Percus-Yevick (PY) approximation /13/.

The purpose of the present paper is as follows: firstly, to confirm the structural results reported in the previous work /13/ using a molecular dynamics (MD) simulation; secondly, to calculate the self-diffusion constant from two routes of the velocity autocorrelation function and the mean square displacement; thirdly, to comment on the interatomic pair potentials for 1900°K derived from nearly-free-electron linear response theory. All calculations in this paper are made using the same $v_{eff}(r)$ previously reported /13/ and the present paper may be viewed as an extension of the earlier work.

2. MOLECULAR DYNAMICS CALCULATIONS

2.1. Computational Procedure

The MD procedure used here has been well documented in the literature /5, 16–21/. Briefly, the classical equations of motion have been solved for N = 216 particles enclosed in a cubic box with periodic boundary conditions. The side L of the basic box is determined by $MN/L^3 = \rho$, where M is the mass of a ribidium atom (1.419×10^{-22} g) and ρ is the mass density. The values of L for the five states investigated are given in Table 1. The interaction between particles was set at zero for distances greater than L/2 and the step of integration over time was chosen to be equal to $\Delta t = 5 \times 10^{-15}$ s. Then, the systems were annealed for over more than 1600 time steps.

TABLE 1
Values of L for the five thermodynamic states

T (°K)	350	900	1400	1800	1900
L (Å)	27.6	29.3	31.6	34.8	36.3

2.2. Structural Properties

The pair distribution function g(r) is computed over the next 800 time steps for $r \leqslant L/2$ by the definition:

$$g(r) = (L^3/N)\frac{\langle n(r)\rangle}{4\pi r^2 \Delta r} \qquad (1)$$

where $\langle n(r)\rangle$ is the mean number of particles situated at a distance between r and r + Δr from an arbitrarily chosen centred particle with Δr = 0.02Å. The g(r) provided by these runs have typical differences of 3% for the first peak becoming of the order of 2% at larger distances. In Fig. 1 the g(r) thus computed are displayed together with those from the PY equation. The overall agreement between the two sets of the g(r) is very good, although there exist small disagreements in the first- and second-peak regions for the 900°K case.

On the other hand, $a(k)$ can be calculated simply and with good accuracy from the Fourier transform of g(r) when the g(r) data is available for a wide range of r. The calculated $a(k)$ for the four states are shown in Fig. 2 together with those from the PY equation. As can be seen from the figure, the PY $a(k)$ are well reproduced by the MD calculations except for a small disagreement in the vicinity of the first peak of the 900°K case. Computer simulation is known not to be so reliable at very low k, because the finite range for the values of the g(r) prevents us from obtaining reliable results in this region. Unfortunately, the PY $a(k)$ are also unstable in the region of interest. However, the present authors maintain the view, from the present MD calculations, that the $v_{eff}(r)$ reported in /13/ is well accepted for discussing the structural features of liquid metals.

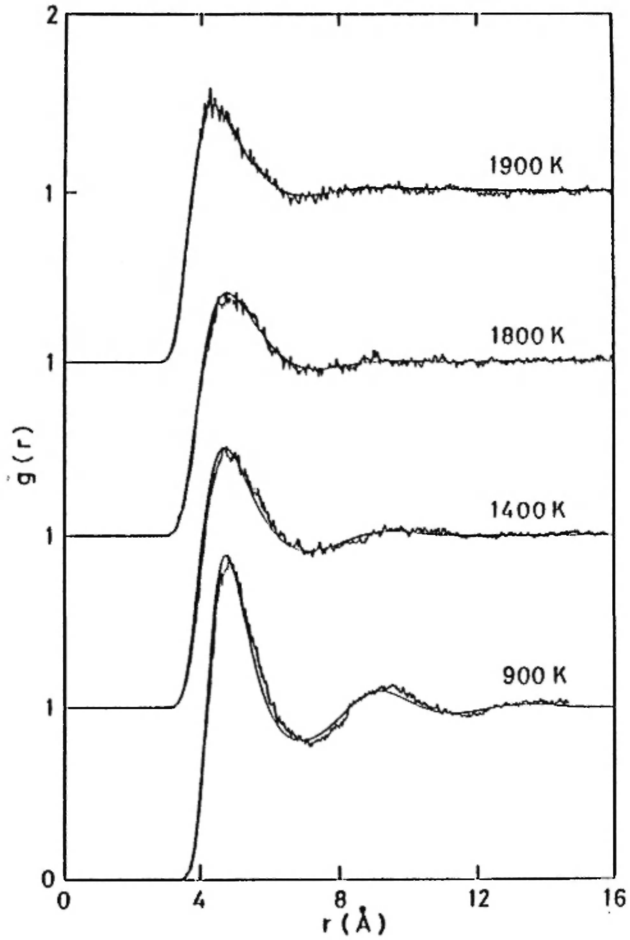

Fig. 1. Pair distribution functions of expanded liquid rubidium calculated using the $v_{eff}(r)$ reported in /13/: ——, PY approximation; , MD results.

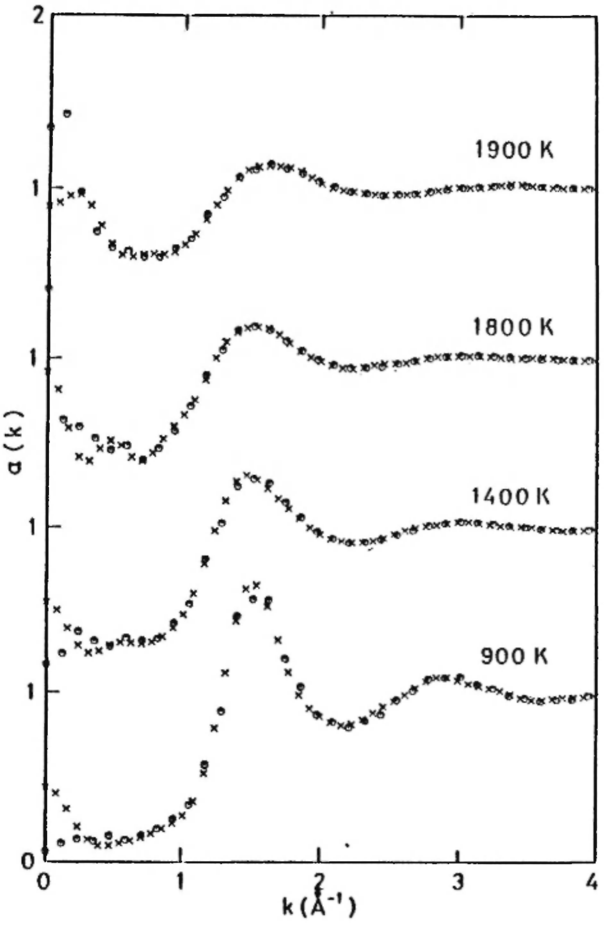

Fig. 2. Comparison of structure factors calculated by the Fourier transform of the g(r) shown in Fig. 1 with those from PY approximation: xxx, MD results; OOO, PY approximation.

Since a noteworthy sensitivity to $v_{eff}(r)$ can be seen in the atomic transport properties in liquid metals /22/, we have worked out self-diffusion constant D in order to re-examine the credibility of those potentials.

2.3. Self-Diffusion Constant

The mean square displacement $r^2(t)$ is defined as:

$$r^2(t) = \frac{1}{N} \langle \sum_{i=1}^{N} | \vec{r}_i(t) - \vec{r}_i(0) |^2 \rangle \qquad (2)$$

where $\vec{r}_i(t)$ is the position of particle i at time t. The results for $r^2(t)$ are drawn in Fig. 3. The following quadratic relation is obtained for values of t less than about 2.0×10^{-13} s for all the cases presently studied:

$$r^2(t) = (3k_B T/M) t^2 \qquad (3)$$

A linear evolution of $r^2(t) = 6Dt$ + constant is also obtained for t greater than about 7.5×10^{-13} s for 350°K, but this switching time over to the linear evolution appears to get gradually longer with increasing temperature (i.e., 8.0×10^{-13} s for 900°K, 9.0 . 10^{-13} s for 1400°K, 11.0×10^{-13} s for 1800°K and 12.0×10^{-13} s for 1900°K, respectively). Incidentally, we have calculated the $v_{eff}(r)$ for 350°K for comparison with the observed diffusion constant given in Table 2. The $r^2(t)$ for 350°K is quite similar in behaviour to that of Gonzàlez Miranda and Torra /19/ for liquid sodium at 373°K, and Gonzalez Miranda /21/ for liquid potassium at 340°K. Over the time range between 2.0×10^{-13} s and 7.5×10^{-13} s, however, the $r^2(t)$ functions for higher temperatures show different behaviour from that for 350°K. This is attributed, in the authors opinion, to the sensitivity of the diffusive processes to $v_{eff}(r)$. The values of D have been estimated from the linear part of the $r^2(t)$ by a least-squares fit to a straight line.

An alternative description of the diffusive behaviour can be made by the velocity autocorrelation function $\Psi(t)$ which is defined as:

$$\Psi(t) = \frac{1}{N} \langle \sum_{i=1}^{N} \vec{v}_i(0) \cdot \vec{v}_i(t) \rangle \qquad (4)$$

where $\vec{v}_i(t)$ is the velocity of particle i at time t. The calculated results for the five states are drawn in Fig. 4.

TABLE 2

Self-diffusion constant $D(10^{-5}\,cm^2 s^{-1})$ of liquid rubidium: MSD; from the mean square displacement, VA; from the velocity autocorrelation function.

T (°K)		350	900	1400	1800	1900
D	MSD	2.53	19.4	47.9	87.6	125
	VA	2.50	20.0	49.8	91.2	133
	Experiment*	2.70 (2.60)				

* taken from /23/.

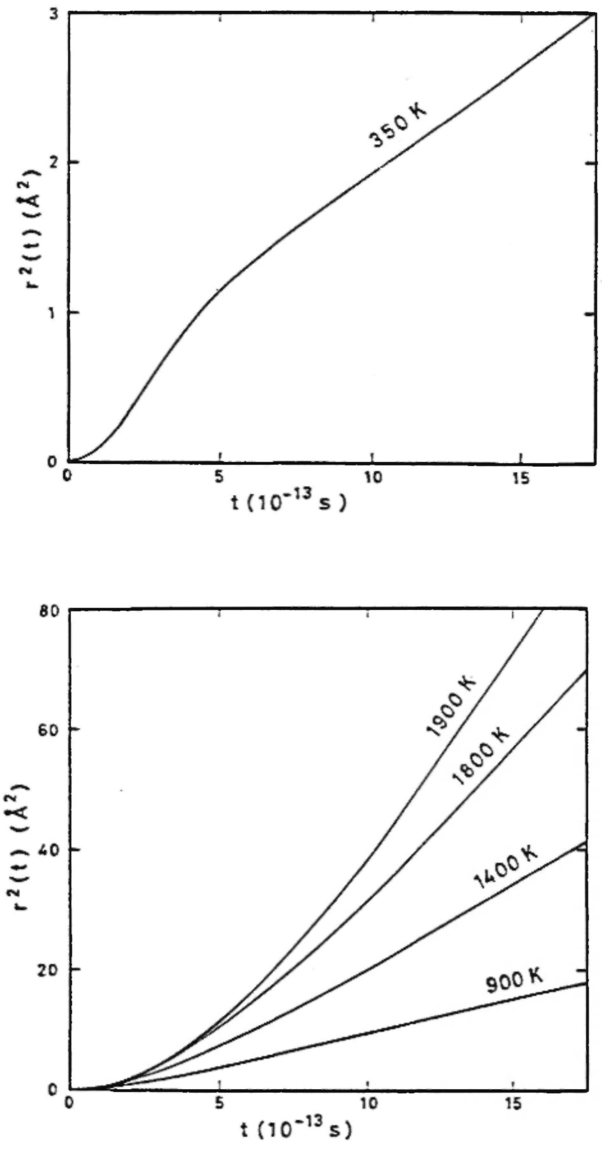

Fig. 3. Mean square displacement as a function of time for expanded liquid rubidium.

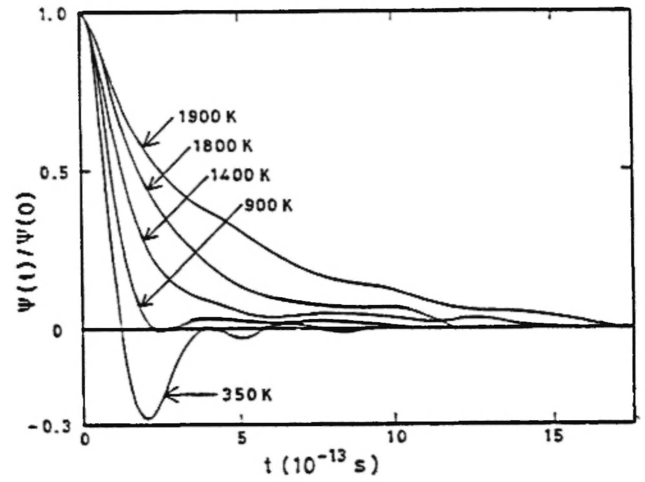

Fig. 4. Normalised velocity autocorrelation functions for expanded liquid rubidium.

All the $\Psi(t)$ functions show much the same behaviour as those for liquid potassium and sodium /20, 21/. The $\Psi(t)$ function is related to the diffusion constant D through the following equation:

$$D = \frac{1}{3} \int_0^\infty \Psi(t)\, dt \qquad (5)$$

The values of D computed from this equation are also given in Table 2. The agreement between both sets of the calculated values of D seems to be satisfactory in view of the rather small size of the computer 'experiment'.

Tanaka /5/ has computed the self-diffusion constants, with N = 864 particles, for expanded liquid rubidium using the optimised Heine-Abarenkov pseudopotential method proposed by Shaw to describe the effective pair potential. His mean square displacement results are in excellent agreement with those from the velocity autocorrelation function for the six states studied. This confirms that his MD computations were done at a reasonable level. The present results appear to be systematically smaller than his results, although there are differences in the thermodynamic states studied. However, it is worth mentioning that the present values of D for 350°K are consistent with both Rahman's value ($D = 2.41 \times 10^{-5}$ cm^2 s^{-1}) /16, 17/ and the observed ones taken from a recent compilation /23/. We found, incidentally, that the change of D along the saturated vapour-pressure curve cannot be described by the Arrhenius-type or the empirical formulae suggested in /23/.

3. DISCUSSION

The observed $a(k)$ of expanded liquid rubidium can be quite well understood through the PY equation using the $v_{eff}(r)$ reported in /13/. This was confirmed by the present MD calculations. As has been pointed out /13/, the $v_{eff}(r)$ for 1900°K is obviously different from those obtained by Tanaka /5/ and McLaughlin and Young /24/ based on the nearly-free-electron linear response theory. For comparison, these three $v_{eff}(r)$ for 1900°K are shown in Fig. 5. The depth of Tanaka's minimum is almost half that of McLaughlin and Young's, but the position of the minima do not show a significant difference. On the contrary, the major disagreement of our $v_{eff}(r)$ with theirs lies in the size of the core, ours being too small, although the depth of the minimum is almost between the two.

As far as the long-wavelength density fluctuations are concerned, the work of McLaughlin and Young is the most successful among the theoretical works /5, 24, 25/ reported so far. Here we would like to reexamine this in terms of the PY equation. Following McLaughlin and Young, we take Ashcroft empty-core pseudopotential and Geldart-Vosko screening /26/ using their density-dependent core radius $r_c = 2.10 a_0 + 0.07 r_s$ where a_0 is the Bohr radius and r_s is the electron separation parameter. With these interatomic pair potentials the corresponding structure factors are calculated through the PY equation. Results are shown in Fig. 6 compared to the experimental data. As Fig. 6 shows, the experimental $a(k)$ are quite

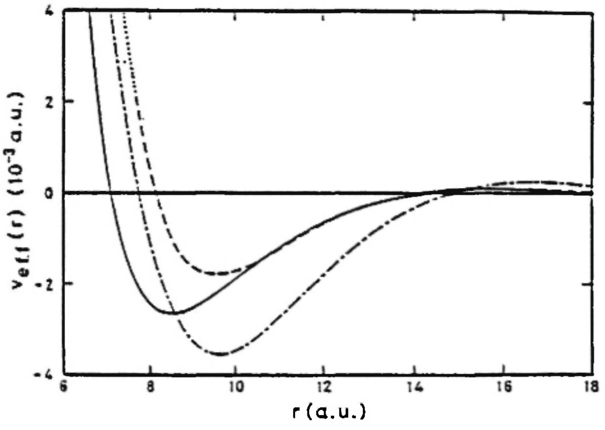

Fig. 5. Comparison of effective pair potentials for 1900°K; ———, Present work; – – – –, Tanaka /5/; —·—·—, McLaughlin and Young /24/.

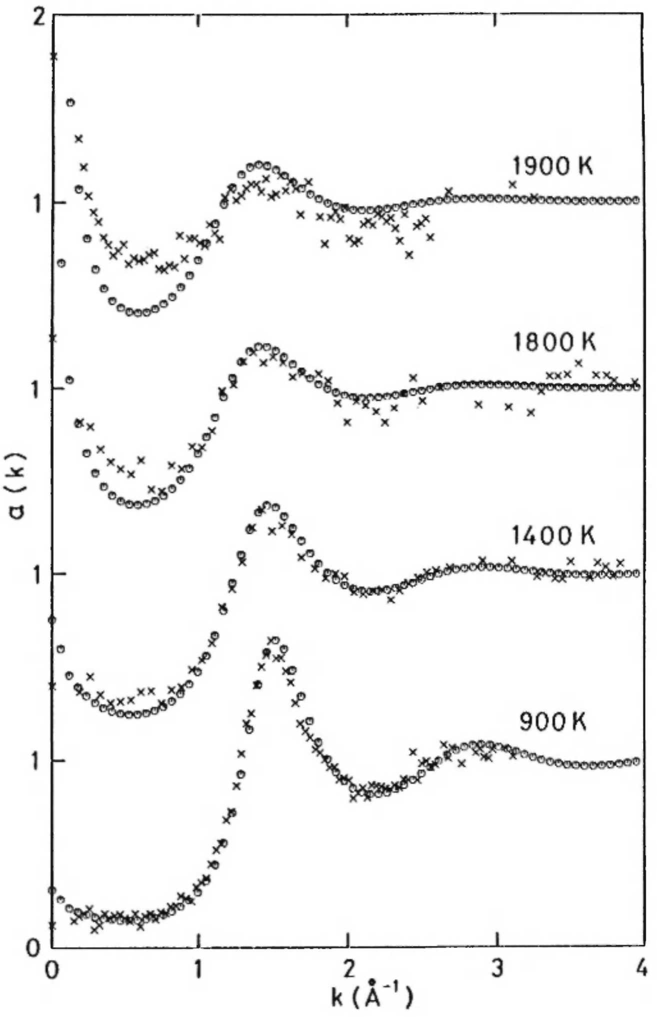

Fig. 6. Structure factors of expanded liquid rubidium calculated using Ashcroft pseudopotential and Geldart-Vosko screening function: ooo, PY approximation, xxx, experiment /27/.

well described by their pseudopotentials for the three cases up to 1800°K. For 1900°K, however, the description of the region around $0.5\,\text{Å}^{-1}$ is not better than that of /13/ [see also Fig. 2 (1900°K)]. The calculated $a(k)$ in very low k are generally more stable than those in Fig. 1 of /13/. This is because the interatomic pair potentials derived by Ashcroft pseudopotential with Geldart-Vosko screening have no clear-long-range oscillatory part. The interatomic pair potential for this case corresponds to the one shown in Fig. 5.

For densities near double the critical density and conditions near the saturation curve, characteristic changes have been observed for both the electrical and magnetic properties /28/, marking the onset of a transition from metallic to nonmetallic states. This strongly influences the nature of the electronic states and, apparently, requires a transformation of the interatomic interaction. The $v_{eff}(r)$ for 1900°K reported in /13/ is consistent with this observation. The core size is about 3.75 Å and is very similar to that of fluid Kr (3.60 Å) described by the Lennard-Jones potential /29/, although the softness of the repulsive part and the depth of the minimum are different from those of fluid Kr.

4. CONCLUSIONS

We have reported the MD results for expanded liquid rubidium using the effective interionic pair potential $v_{eff}(r)$ obtained from low-angle structure factors. The following points are of interest:

(1) The conclusion given in /13/ based on the PY approximation has been confirmed by the present MD study.

(2) The values of the diffusion constant computed in this work are consistent with those calculated from the interatomic pair potentials derived from nearly-free-electron linear response theory.

(3) The $v_{eff}(r)$ for 1900°K appears to be more credible in the light of the available experimental evidence than those obtained so far from pseudopotential theory.

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