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Self-diffusion coefficients of expanded rubidium

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Abstract. The second-order and fourth-order frequency sum rules of the velocity autocorrelation function (VACF) of Rb have been evaluated for six thermodynamic states along the liquid–vapour coexistence curve by using the Ashcroft pseudopotential and corresponding pair distribution function obtained by molecular dynamics (MD) simulation. These sum rules and a model for the self-diffusion coefficient have been used to study the time evolution of the VACF and self-diffusion coefficients. The results obtained have been compared with MD simulation data. It is found that our model provides the first semiquantitative explanation for the density and temperature dependences of the VACF and self-diffusion coefficients of expanded Rb.

1. Introduction

During recent years the situation pertaining to the study of static and dynamic properties of the liquid metals (especially the alkali metals) has changed considerably. One important development has been made by Hensel and co-workers [1–4] who performed neutron scattering experiments on Rb and Cs from their melting points to the critical point. The thermodynamic states chosen in the experiments are along the liquid–vapour coexistence curve. This critical region is of particular interest as the metal Rb (or Cs) undergoes a metal–non-metal transition. From the experimental results on the static structure factor $S(q)$, one finds that the numbers of nearest neighbours are almost the same whereas the nearest-neighbour distance increases with increase in temperature. At low and intermediate temperatures the dynamical structure factor $S(q, \omega)$ shows a collective density excitation peak whereas at temperatures near the critical temperature the side peak broadens. Theoretically, the main difficulty in studying the properties of expanded liquid metal is the non-availability of the appropriate density- and temperature-dependent interaction potential. The density and temperature dependences of the interaction potential arise owing to the change in electronic properties in the course of the variation in density.

Recently, Kahl and Kambayashi [5] and Kahl [6] have performed molecular dynamics (MD) simulation studies of expanded Rb for six thermodynamic states using the local pseudopotential proposed by Ashcroft [7] and the Ichimaru–Utsumi [8] expression for exchange–correlation. This potential has been found to be quite successful up to intermediate temperatures as has been judged by comparing the MD results [5] with the experimental results [1, 2]. The deviations at the highest temperature are attributed to the interatomic effective potential. The MD simulation [5, 6] studies have investigated the static structure factor $S(q)$, the dynamical structure factor and the single-particle space–time correlation

functions. In the present work, we shall be concentrating only on the theoretical evaluation of the velocity autocorrelation function (VACF) and the self-diffusion coefficient of expanded Rb. Our motivation is to study the effect of the density and temperature dependences of time evolution of the VACF and self-diffusion coefficient. First of all we examine the state dependence of the short-time properties of the VACF, namely the frequency sum rules. We then use these in a model proposed by Tankeshwar *et al* [9] to study the time development of the VACF and self-diffusion coefficient. This model has already been used [10] to study the diffusion in liquid alkali metals, but only near the triple point, and has provided very good agreement with experimental and simulation data. This model has also been applied [11–13] to study the self-diffusion in multicomponent systems, where it has provided the ratio of the self-diffusion coefficients of different species in agreement with MD simulation data. From the present study of Rb we found that our model offers an interpretation of the variation in the diffusion coefficient with the density and temperature as has been judged by comparing our results with the simulation data of Kahl [6].

The paper is organized as follows. In section 2 we present the theoretical formalism. Calculations and results are given in section 3. We conclude the work in section 4.

2. Theoretical formalism

The normalized VACF $C(t)$ is defined as

$$C(t) = \langle v_{1x}(t)v_{1x}(0) \rangle / \langle v_{1x}^2(0) \rangle \quad (1)$$

where $v_{1x}(t)$ is the velocity of particle 1 at any time t . The Green–Kubo formula [14] relates $C(t)$ to the self-diffusion coefficient D , which is given as

$$D = \frac{k_B T}{M} \int_0^\infty C(t) dt. \quad (2)$$

The exact calculation of $C(t)$ is a complicated task as it amounts to solution of a many-body problem except for a simplified description of atomic motion. One approach to study the time evolution of $C(t)$ is based on writing it in terms of the memory function by using the Mori equation of motion [15]. This approach, however, only reduces the problem of calculation of the VACF to the calculation of the appropriate memory function but has advantages as one can develop theoretical [16] and phenomenological [17] models for the calculation of the memory function. The other way in which some physical consideration of the system is taken into account is used to calculate the VACF directly. One such model has been proposed recently by Tankeshwar *et al* [9]. This is based on separating [18] the configuration of the many-body system into a vibrational part and a stable packing part. The configuration space of the many-body system is considered to consist of a number of cells characterized by some fixed configuration determined by the local minima in the potential energy hypersurface of the system. The particle jumps from one cell to the other with a jump frequency τ^{-1} . The effect of the cell jump is to rearrange the equilibrium position of the particles after the cell jump. Within the cell, particles execute harmonic oscillations with a fixed frequency ω . The waiting-time distribution for cell jumps is assumed to be given by $\text{sech}(t/\tau)$. This provides an expression [9] for the VACF given as

$$C(t) = \text{sech}(t/\tau) \cos(\omega t). \quad (3)$$

Using equations (2) and (3) we obtain

$$D = \frac{\pi}{2} \tau \frac{k_B T}{M} \text{sech}\left(\frac{\pi}{2} \omega \tau\right). \quad (4)$$

The two parameters ω and τ are determined by taking the Taylor series expansion of equation (3) and comparing the coefficients of t^{2n} with the short-time expansion of $C(t)$ given as

$$C(t) = 1 - C_2 \frac{t^2}{2!} + C_4 \frac{t^4}{4!} - \dots \quad (5)$$

We find that

$$\begin{aligned} \tau^{-2} &= \frac{\delta_2}{4} \\ \omega^2 &= \frac{4\delta_1 - \delta_2}{4} \end{aligned} \quad (6)$$

with

$$\begin{aligned} \delta_2 &= \frac{C_4}{C_2} - C_2 \\ \delta_1 &= C_2. \end{aligned} \quad (7)$$

C_2 and C_4 are the second-order and fourth-order sum rules of the VACF. Expressions for these are known [19] and are given in appendix A. These involve the pair potential and static correlation function up to three particles.

From equation (6) it can be seen that ω is zero for $4\delta_1 = \delta_2$. This implies that, for $4\delta_1 > \delta_2$, $C(t)$ shows a negative region as can be seen from equation (3). However, for $4\delta_1 < \delta_2$, ω^2 is negative; then equation (3) reduces to

$$C(t) = \text{sech}(t/\tau) \cosh(\omega t) \quad (8)$$

which for a long time behaves as $\exp(-1/\tau + \omega)t$, representing a slow decay of $C(t)$ corresponding to a dilute gas. The expression for D is then given by

$$D = \frac{\pi}{2} \tau \frac{k_B T}{M} \sec\left(\frac{\pi}{2} \omega \tau\right). \quad (9)$$

In the next section we present the calculation of sum rules of the VACF, the time evolution of the VACF and the self-diffusion coefficients of expanded Rb.

3. Calculations and results

The calculation of the frequency sum rules given by equations (A1) and (A2) requires a pair potential, a static pair correlation function and a triplet correlation function as input. For the pair potential we use the pseudopotential proposed by Ashcroft. The expression for the effective interatomic potential is given as

$$\phi(r) = \frac{Z^2}{r} + \frac{1}{(2\pi)^3} \int \frac{q^2}{4\pi} \left(\frac{1}{\varepsilon(q)} - 1 \right) |v(q)|^2 \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{q} \quad (10)$$

where $v(q)$ is the Fourier transform of $v(r)$ given as

$$v(r) = \begin{cases} 0 \\ -\frac{Z}{r} \end{cases} \quad \text{for } \begin{cases} r < r_c \\ r > r_c. \end{cases} \quad (11)$$

We use the Ichimaru-Utsumi [8] form of the dielectric function. For Rb we have used $r_c = 2.47$ au. This procedure of evaluation of the potential is the same as that employed in the MD simulation by Kahl and Kambayashi [5]. In table 1 we present the densities and temperatures for which we have calculated the potential. The well depth ε of the

Table 1. Temperature T and mass density ρ of the six Rb states I–VI investigated in the present study. σ and ε are the parameters of the potentials.

State	T (K)	ρ (g cm ⁻³)	σ (Å)	ε ($\times 10^{-12}$ erg)
I	350	1.460	4.197 862	0.075 198 52
II	373	1.440	4.196 285	0.075 672 48
III	1073	1.130	4.107 260	0.087 710 05
IV	1373	0.980	4.041 256	0.098 709 86
V	1673	0.830	3.950 153	0.116 712 9
VI	1873	0.640	3.765 076	0.161 359 0

Table 2. Values of the second-order (C_2) and fourth-order (C_4) sum rules of the VACF in units of $\varepsilon/m\sigma^2$ and $(\varepsilon/m\sigma^2)^2$, respectively. C_{42} and C_{43} are the pair and triplet contributions to the fourth-order sum rule.

State	C_2	$C_{42} \times 10^{-2}$	$C_{43} \times 10^{-2}$
I	120.55	216.03	109.30
II	117.13	215.73	100.07
III	72.293	175.09	72.572
IV	60.462	159.95	14.400
V	39.743	84.332	6.2043
VI	23.884	38.279	1.8460

potential and the distance σ where $\phi(r)$ becomes zero is also given. The first and second derivatives of the potential $\phi(r)$ are determined by taking the derivative of equation (10) with respect to r analytically and then performing the integration numerically. For the static pair correlation function $g(r)$ we have used the MD simulation data of Kahl and Kambayashi [5]. The triplet contribution to the sum rules is evaluated using the Kirkwood superposition approximation. Here, it may be noted that the use of the superposition approximation does not introduce a significant error in the numerical results of total sum rules as has been demonstrated earlier [19]. The numerical integration in equations (A1) and (A2) is done by using the Gauss-quadrature method. The accuracy of our numerical results for the sum rules is better than 5%. The results are given in table 2, where C_{42} and C_{43} represent two- and three-body contributions, respectively, to the fourth-order sum rule of the VACF. It can be seen from table 2 that, near the melting point, C_{43} is about 50% of C_{42} whereas, at the highest temperature, it reduces to only 5%. This implies that higher-order correlation effects are important at high densities and low temperatures. It is also noted from table 2 that C_2 , i.e. the Einstein frequency, decreases as we go towards the critical point.

The values of the sum rules from table 2 are used to calculate the time evolution of the VACF $C(t)$ by using equation (3) or (8) and equations (6) and (7). The results obtained for $C(t)$ are shown in figure 1 as solid curves for six thermodynamics states. The MD results of Kahl [6] are shown by open circles for comparison. From figure 1 it can be seen that our results are in reasonable agreement with the MD data and qualitatively all important features of $C(t)$ are reproduced. It is noted that for states IV–VI our model does not predict any negative region in the time development of $C(t)$. At low temperatures corresponding to states I and II the tagged particle is trapped in a cage formed by its neighbouring atoms, which results in a negative region in $C(t)$. At high temperatures the cages become large and finally disappear and then the particle can move freely. This is evident from our

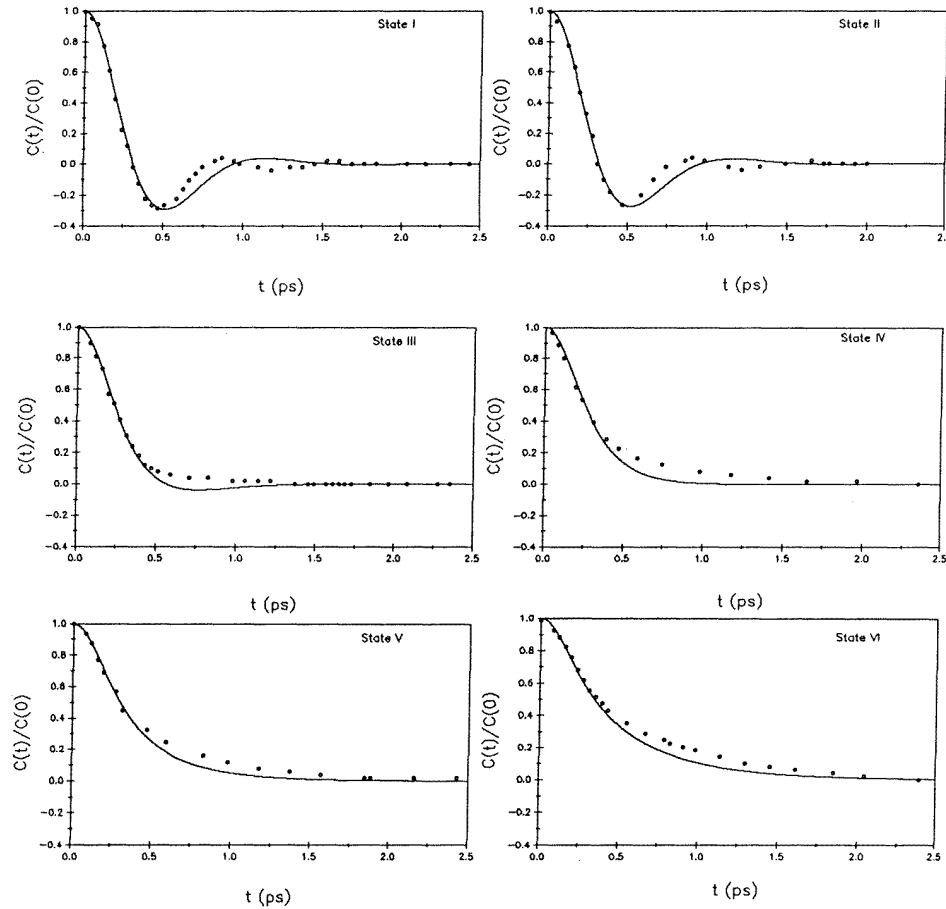


Figure 1. Variation of the normalized velocity auto-correlation function $C(t)/C(0)$ with time (ps) for six thermodynamic states. Full lines are our theoretical results. The dots are MD data of Kahl [6].

model as in this case ω^2 is imaginary; then the oscillatory motion of the particle in the cell is no longer present and the particle moves only in a translatory manner. However, our results on $C(t)$ are not in very good agreement with the MD data for all the thermodynamic states investigated here; it provides important information about the density and temperature dependences of the VACF which is one motivation for the present work.

The values of the self-diffusion coefficient for the six thermodynamics states are calculated from equation (4) or (9). The results are given in table 3 together with the MD results and experimental data given in [6]. From table 3 it can be seen that near the melting point the agreement with MD data is very good. The deviation of our results from the MD data increases as we go from state I to VI where it is about 30%. Here, it may be noted that the self-diffusion coefficient for state VI is about 30 times that for state I. Thus, as the same procedure is used to calculate the self-diffusion coefficient for all the states, it can be said that the agreement of our results with the MD data is reasonably good. Overall, it is gratifying to see that our model is successful in explaining the density and temperature dependences of the self-diffusion coefficient of expanded Rb.

Table 3. Diffusion coefficient D for six thermodynamic states of Rb. D_{our} , D_{MD} and D_{expt} are the results obtained in present work, in the MD simulation and in experiments, respectively.

State	D_{our} ($10^{-8} \text{ m}^2 \text{ s}^{-1}$)	D_{MD} ($10^{-8} \text{ m}^2 \text{ s}^{-1}$)	D_{expt} ($10^{-8} \text{ m}^2 \text{ s}^{-1}$)
I	0.302	0.298	0.352 ± 0.014
II	0.345	0.454	0.418 ± 0.020
III	2.421	3.429	3.661 ± 1.8
IV	3.944	5.675	6.047 ± 4.4
V	6.279	8.483	9.346 ± 8.4
VI	8.664	12.303	14.18 ± 14.7

4. Summary and conclusion

In this paper we have evaluated the second-order and fourth-order frequency sum rules of the VACF for expanded Rb at six thermodynamic states along the liquid–vapour coexistence curve using the Ashcroft pseudopotential and the corresponding $g(r)$. These sum rules and the model proposed earlier by Tankeshwar *et al* [9] were used to study the VACF and self-diffusion coefficient. The results obtained are compared with the MD predictions of Kahl [6]. It is found that our results are in reasonably good agreement with the MD data. Our model uses only the interatomic potential as the input as $g(r)$ can be generated using integral equation methods. Our work provides a first step towards the development of a theory which can predict the transport coefficient of fluid metal at any thermodynamic state.

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Appendix A

Expressions for second-order and fourth-order sum rules of the VACF are given as

$$C_2 = \frac{4\pi n}{3m} \int_0^\infty dr r^2 g(r) \left(\frac{2}{r} u_1 + u_2 \right) \quad (\text{A1})$$

$$C_4 = \frac{8\pi n}{3m^2} \int_0^\infty dr r^2 g(r) \left(\frac{2}{r^2} u_1^2 + u_2^2 \right) + \frac{8\pi^2 n^2}{3m^2} \int_0^\infty \int_0^\infty dr dr' r^2 r'^2 \int_{-1}^{+1} d\mu g_3(r, r') \\ \times \left(\mu^2 u_2 u_2' + \frac{1 + \mu^2}{rr'} u_1 u_1' + \frac{2(1 - \mu^2)}{r'} u_2 u_1' \right). \quad (\text{A2})$$

In equations (A1) and (A2), $u_1 = \partial\phi(r)/\partial r$ and $u_2 = \partial^2\phi(r)/\partial r^2$. The primes in equation (A2) represent the fact that the argument of potential $\phi(r)$ is changed to r' . $g(r)$ and $g_3(r, r')$ are the static pair and triplet correlation functions, respectively. n and m are the number density and mass, respectively.

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