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## Shear viscosity of expanded rubidium

Saroj K Sharma<sup>†</sup> and K Tankeshwar<sup>‡</sup>

<sup>†</sup> Department of Physics, H P University, Shimla 171005, India

<sup>‡</sup> Department of Physics, Centre of Advanced Study in Physics, Panjab University, Chandigarh 160014, India

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**Abstract.** The zeroth, second and fourth frequency sum rules of the transverse stress auto-correlation function of Rb have been evaluated for six thermodynamic states along the liquid–vapour co-existence curve by using the Ashcroft pseudo-potential and the corresponding pair correlation function obtained by molecular dynamics simulation. The numerical results for the sum rules thus obtained and a model for the memory function appearing in the Mori formalism are used to calculate the shear viscosity. The results obtained have been used to compare with the experimental results and with those of Kahl and Kambayashi. It is found that our method provides almost quantitative explanation for the density and temperature dependence of the shear viscosity of expanded rubidium.

### 1. Introduction

Recently we have studied [1] density and temperature dependence of the velocity auto-correlation function and self-diffusion coefficient of expanded rubidium for six thermodynamic states using only the interaction potential as input. For the interaction potential we employed the Ashcroft pseudo-potential [2] with Ichimaru–Utsumi [3] screening. It was found that our model for the self-diffusion coefficient provided a explanation for its density and temperature dependence as judged by comparing our results with experimental/molecular dynamics [4] data. However, at present no similar study exists for predicting the shear viscosity of expanded metal. Therefore, in the present work we extend our work for the study of thermodynamic state dependence of the shear viscosity of expanded rubidium. For the calculation of shear viscosity we used the Green–Kubo relation which expresses it as a time integral of the transverse stress auto-correlation (TSC) function. The time evolution of the transverse stress auto-correlation has been studied using Mori’s memory function formalism [5]. For the memory function we have used a hyperbolic secant form which was proposed earlier [6]. The parameters of the potential have been related to the zeroth, second and fourth frequency sum rules of frequency spectrum of transverse stress auto-correlation function. The numerical results for these sum rules are obtained for six thermodynamics states of the expanded rubidium. The results obtained for the shear viscosity have been compared with experimental data [7] and the results of Kahl and Kambayashi [8]. It has been found that our method provides a good description of the variation of viscosity with density and temperature.

The paper is organized as follows. In the following section we present the theoretical formalism. Calculations and results are given in section 3. The paper is concluded with a summary in section 4.

## 2. Theoretical formalism

For a classical system the transverse stress variable is defined as

$$J_{xy}(t) = \sum_{i=1}^N [m v_{ix}(t) v_{iy}(t) + F_{iy} x_i(t)] \quad (1)$$

where  $v_{ix}(t)$  and  $x_i(t)$  are the  $x$  component of the velocity and the position of the  $i$ th particle, respectively, at time  $t$ .  $F_{iy}$  is the  $y$  component of the force on the  $i$ th particle. The short-time expansion of the TSC function, defined as

$$S(t) = \langle J_{xy}(t) J_{xy}(0) \rangle \quad (2)$$

is given by

$$S(t) = S_0 - S_2 \frac{t^2}{2!} + S_4 \frac{t^4}{4!} \dots \quad (3)$$

where  $S_0$ ,  $-S_2$  and  $S_4$  are called the zeroth, second and fourth frequency moments of the TSC function. The expressions for  $S_0$ ,  $S_2$  and  $S_4$  have already been given in the work of Tankeshwar *et al* [6]. These involve the interaction potential and static correlation function up to four particles. The Green–Kubo formula for the shear viscosity  $\eta$  is given by

$$\eta = \frac{1}{V k_B T} \int_0^\infty S(t) dt \quad (4)$$

where  $k_B$ ,  $V$  and  $T$  are the Boltzmann constant, volume and temperature of the system. For the calculation of the time evolution of the time correlation function,  $S(t)$ , for all time we express it in terms of the memory function using Mori's equation of motion which is given as

$$\frac{dS(t)}{dt} = - \int_0^t S(\tau) M(t - \tau) d\tau. \quad (5)$$

Defining the Fourier–Laplace transform as

$$\tilde{S}(\omega) = i \int_0^\infty \exp(-i\omega t) S(t) dt \quad (6)$$

we obtain from (5)

$$\tilde{S}(\omega) = - \frac{S(t=0)}{\omega + \tilde{M}(\omega)}. \quad (7)$$

Using (4) and (7), we obtain

$$\eta = \frac{i}{V k_B T} \frac{S_0}{\tilde{M}(0)}. \quad (8)$$

Thus the problem of calculating  $S(t)$  is now reduced to the evaluation of the memory function. Though there exists a microscopic expression for the MF in terms of the projection operator, its calculation based on the mode coupling approach [9] for any density and temperature is much more involved. In the present work we use a phenomenological form [10] for the memory function, proposed earlier [6], which is given as

$$M(t) = a \operatorname{sech}(bt). \quad (9)$$

This memory function behaves as Gaussian at small times and as simple exponential at long times. The parameters  $a$  and  $b$  are determined so that short-time properties are exactly satisfied. It is found that

$$a = \delta_1 = S_2/S_0 \quad (10a)$$

and

$$b^2 = \delta_2 = S_4/S_2 - S_2/S_0. \quad (10b)$$

The memory function given by (9) is a solution of a nonlinear equation given as

$$\frac{d^2 M(t)}{dt^2} - b^2 M(t) + \frac{2b^2}{a^2} M^3(t) = 0. \quad (11)$$

The above equation is derivable [11, 12] from the Mori equation of motion by employing two approximations for the higher-order memory function, though arguable. The merits and demerits of the memory function (9) have been studied in detail by Tankeshwar and Pathak [13] and Lee *et al* [14]. The analytical results [13] obtained for the time correlation function using the hyperbolic secant memory have demonstrated the effect of nonlinearity incorporated through (11). The above memory function has already been used [15] to study the time dependence of the stress auto-correlation function for Lennard-Jones fluids for various thermodynamic states. It was found that it provides a reasonable agreement with the simulation data for  $S(t)$  at short and intermediate times. The error introduced in estimating the shear viscosity due to long-time values of  $S(t)$  was not found to be significant except near the triple point of Lennard-Jones fluids.

Equations (7) and (9) provide an expression for the shear viscosity given as

$$\eta = \frac{2}{\pi} (n/k_B T) (S_0^2/S_2) (S_4/S_2 - S_2/S_0)^{1/2} \quad (12)$$

where  $n$  is the number density. On the other hand if we use a Gaussian model for  $M(t)$  we find that  $\eta$  is  $(\pi/2)^{1/2}$  times that given by (12). In order to calculate  $\eta$  from (12) we need to know  $S_0$ ,  $S_2$  and  $S_4$ . The numerical results for these and the shear viscosity are given in the next section.

**Table 1.** Temperature  $T$  and mass density  $\rho$  of six Rb states I–VI investigated in the present study.  $\sigma$  and  $\epsilon$  are the parameters of potentials.

State	$T$ (K)	$\rho$ (g cm <sup>-3</sup> )	$\sigma$ (Å <sup>0</sup> )	$\epsilon$ (ergs) $\times 10^{-12}$
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

### 3. Calculations and results

The numerical results for zeroth, second and fourth sum rules of the transverse stress auto-correlation function are obtained for six thermodynamic states of expanded Rb. These sum rules use the interaction potential, pair and triplet correlation function as inputs. For the interaction potential we have used the Ashcroft pseudo-potential with Ichimaru–Utsumi screening. The details of the evaluation of the potential and its derivatives are given in our earlier work [1] and also by Kahl and Kambayashi [8]. The thermodynamic states chosen in the present work, the values of  $\epsilon$ , the well depth of the potential, and  $\sigma$ , the position of the first zero of potential, are given in table 1. The corresponding pair correlation function is

taken from the work of Kahl and Kambayashi. For the triplet correlation function we have used a superposition approximation. This approximation does not introduce a significant error in the numerical values of total sum rules as has earlier been demonstrated [15]. In the present work we neglect the quadruplet contribution to the fourth sum rule as this is not important [6] in determining the shear viscosity of the system. The numerical integration involved in the evaluation of sum rules is done using the Gauss-quadrature method. The accuracy of our numerical results for sum rules is better than 5%. The results for these are given in table 2 where  $S_{nm}$  represents the  $m$ -body contribution to the  $n$ th frequency sum rule. From table 2 it is noted that the three-body contribution is quite appreciable. The ratio of the static triplet contribution to the pair contribution to the second and fourth sum rules increases as one moves from critical to triple point. This ratio ranges from about 15 to 60% and from 6 to 35% for the second and fourth sum rules, respectively.

**Table 2.** Values of the frequency moments of the TSC function for six thermodynamic states.  $S_{nm}$  represents the  $m$ -body contribution to the  $n$ th sum rule.

State	$S_0$ ( $\epsilon^2$ )	$S_{22}$ ( $\epsilon^3 m/\sigma^2$ )	$S_{23}$ ( $\epsilon^3 m/\sigma^2$ )	$S_{42} \times 10^{-3}$ ( $\epsilon^4 m/\sigma^4$ )	$S_{43} \times 10^{-3}$ ( $\epsilon m^2/\sigma^4$ )
I	9.2651	1541.8	-999.30	459.690	-166.590
II	9.5547	1611.5	-988.73	494.690	-167.750
III	16.784	2852.9	-770.63	1560.30	-184.730
IV	16.950	2995.6	-644.21	1700.30	-191.170
V	14.694	1692.7	-275.54	899.610	-55.237
VI	8.0106	744.28	-102.47	260.770	-14.293

**Table 3.** Shear viscosity,  $\eta$ , in centipoise for six thermodynamic states of Rb.  $\eta$  represents results obtained by using (11).  $\eta_{expt.}$  and  $\eta_{KK}$  are experimental and MD results, respectively.  $\eta_2$  represents shear viscosity obtained from (11) by including only the two-body contribution to the sum rules.

State	$\eta$	$\eta_2$	$\eta_{expt.}$	$\eta_{KK}$
I	0.484	0.112	0.476	0.607
II	0.412	0.1097	0.433	0.528
III	0.136	0.104	0.136	0.107
IV	0.0947	0.0821	0.112	0.115
V	0.103	0.0984	0.0996	0.102
VI	0.0561	0.0558	0.0870	0.0774

The shear viscosity of the expanded Rb is calculated from equation (12) by using the values of the sum rules from table 2. The results obtained are given in table 3. The experimental results as given in [8] are denoted by  $\eta_{expt.}$  and those of Kahl and Kambayashi,  $\eta_{KK}$ , are also given there for comparison. Here, it may be noted that Kahl and Kambayashi obtained these results by fitting a memory function to the MD simulation data of the transverse current-current correlation function. It can be seen from table 3 that our results are close to experimental values except near the critical point where our results are about 30% off. This may be due to the use of the model memory function.

In order to see the importance of the three-particle contribution to the sum rules in determining the shear viscosity, we have calculated it by taking into account only the two-body contribution to the sum rules. The results thus obtained for shear viscosity are

represented by  $\eta_2$  and are given in table 3. It can be seen from table 3 that the effect of the triplet contribution in determining the shear viscosity is quite significant near the triple point and it decreases with increasing temperature and decreasing density.

#### 4. Summary and conclusion

In this paper we have numerically evaluated zeroth, second and fourth frequency sum rules of the TSC function for expanded Rb for six thermodynamic states along the liquid–vapour co-existence curve using the Ashcroft pseudopotential with Ichimaru–Utsumi screening and the corresponding  $g(r)$ . These sum rules and a phenomenological form of the memory function within Mori–Zwanzig formalism have been used to study the state dependence of the shear viscosity of expanded Rb. The results obtained have been compared with experimental results and those of Kahl and Kambayashi. It is found that our results agree well with the experimental data except near the critical point. Here it may be noted that our work requires only the knowledge of the interaction potential.

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