Model for Self-Diffusion Coefficient

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MODEL FOR SELF-DIFFUSION COEFFICIENT

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In this study, we have relaxed one of the assumptions made in the model proposed by Tankeshwar, Singla and Pathak (1991, *J. Phys.: Condens. Matter* **3**, 3173). We have used a Debye spectrum of frequencies instead of a fixed frequency and have derived an analytical expression for the velocity auto-correlation function of the fluid. It is found that the use of the spectrum of frequencies rather than a single frequency does not improve the prediction of the model for the self-diffusion coefficient as has been judged by comparing the results with molecular dynamics data.

Keywords: Self-diffusion; liquid metals; Lennard Jones fluids; velocity auto-correlation function.

Recently, we have proposed [1] a model, hereafter referred as I, based on the idea [2] of separating the configuration space of many body system into vibration part and a stable packing part, for the calculation of velocity auto-correlation function (VACF) and hence for the self-diffusion coefficient. Our model was based on the following assumptions:

(i) Configuration space of many body system is divided into 'cells'. Each cell being associated with local minima on the potential energy hypersurface of the system.

(ii) The configuration of the system remains in one of these minimum performing almost harmonic motion until it finds a saddle point in potential energy surface and jumps to another cell with jumping frequency τ^{-1}. The effect of cell jump is to rearrange equilibrium position of particles in a particular subvolume V^* of the total volume V of the system.

(iii) Within the cell the liquid configuration executes harmonic oscillations about the local minima which are described by a 'fixed' frequency ω.

(iv) The waiting time distribution for cell jump affecting the contents of any V^* was assumed to be sech (t/τ).

(v) The motion of the system in a particular subvolume is uncorrelated before and after jump.

These assumptions have resulted in an expression for normalized velocity auto-correlation function given as:

$$C(t) = \frac{1}{N} \sum_{\omega} \operatorname{sech}(t/\tau) \cos(\omega t). \tag{1}$$

If the assumption (iii), that frequency of oscillation is same as that in Einstein model of solids, is applied we obtain an expression for VACF given as:

$$C(t) = \operatorname{sech}(t/\tau) \cos(\omega t). \tag{2}$$

This model has been found to yield very good results for the self-diffusion coefficients for one component fluids [1] like Lennard-Jones (LJ) fluids, Yukawa fluids, one component plasma and also recently for liquid alkali metals [3]. This was also extended to the multi-component fluids [4-6] where it has yielded ratio of self-diffusion coefficients of two species in good agreement with computer simulation data. In fact this form of $C(t)$ has also been used to study [7] shear viscosity and thermal conductivity in LJ fluids. Inspite of good success of the model for predicting the self-diffusion coefficients, there remains a point of interest that what would happen if the assumption (iii) is relaxed. This implies that frequency of oscillations are not fixed rather we have a spectrum of frequencies with some cut-off. In fact the original work by Zwanzig [8] and later by Mahanty [9] have used a Debye spectra for it. Therefore, the study of affect of Debye spectra, instead of a constant frequency picture as in I, is a motivation of the present work.

Employing the Debye spectrum in Eqn. (1) and converting the summation into an integral we get

$$C(t) = A \int_0^{\omega_D} \omega^2 \cos(\omega t) \operatorname{sech}(t/\tau) \, d\omega, \tag{3}$$

where

$$A = \frac{3}{\omega_D^3}.$$

Integrating Eqn. (3) over ω we obtain

$$C(t) = 3\left[\frac{\sin(\omega_D t)}{\omega_D t} + \frac{2\cos(\omega_D t)}{(\omega_D t)^2} - \frac{2\sin(\omega_D t)}{(\omega_D t)^3}\right]\text{sech}(t/\tau).$$

This expression is to be compared with Eqn. (2) obtained in I. Since, expression (4) represents the VACF of fluid state of matter, it is to satisfy its sum rules defined as:

$$C_{2n} = (-1)^n \left\langle \frac{d}{dt^n} v_{1x}(t) \frac{d}{dt^n} v_{1x}(t) \right\rangle_{t=0} \bigg/ (k_B T/M), \tag{5}$$

where $v_{1x}(t)$ is x component of velocity of the tagged particle 1, and k_B, T and M are Boltzmann constant, temperature and mass of the particle of the system. C_{2n} is called $2n$th sum rule of the VACF. Comparing the short time expansion of Eqn. (4) with the short time expansion of $C(t)$, given as:

$$C(t) = 1 - C_2 \frac{t^2}{2!} + C_4 \frac{t^4}{4!} \cdots, \tag{6}$$

we obtain

$$C_2 = 3\left(\frac{\omega_D^2}{5} + \frac{1}{3\tau^2}\right), \tag{7}$$

$$C_4 = 3\left(\frac{5}{3\tau^4} + \frac{6\omega_D^2}{5\tau^2} + \frac{\omega_D^4}{7}\right). \tag{8}$$

Equations (7) and (8) are solved for τ and ω_D and we obtain

$$\tau^{-2} = C_2 - \frac{3}{5}\omega_D^2, \tag{9}$$

$$\omega_D^2 = \frac{5}{6}\left[21C_2 - \left[336C_2^2 + 21C_4\right]^{1/2}\right]. \tag{10}$$

From Eqn. (10) it may be noted that ω_D is zero when $C_4 = 5C_2^2$. This condition is same as that obtained in our earlier work I. If ω_D is to be considered as some parameter then for $C_4 > 5C_2^2$ we can see that ω_D is imaginary and in that case Eqn. (4) can be written as:

$$C(t) = 3\left[\frac{\sinh(\omega_D t)}{\omega_D t} - \frac{2\,\cosh(\omega_D t)}{(\omega_D t)^2} + \frac{2\,\sinh(\omega_D t)}{(\omega_D t)^3}\right]\operatorname{sech}(t/\tau). \qquad (11)$$

It is noted that $C(t)$ from Eqn. (11) does not show any backscattering effect. Then the condition $C_4 < 5C_2^2$ predicts the existence of backscattering effect which is in accordance with the computer simulation data as has already been shown in I for LJ system.

The self diffusion coefficient 'D' can be obtained from Green-kubo relation given as:

$$D = \frac{k_B T}{M}\int_0^\infty C(t)\ dt. \qquad (12)$$

In order to see the difference in results obtained from Eqns. (4) and (2) we use our earlier results [10] for C_2 and C_4 for LJ fluids. Results obtained for self-diffusion coefficient $D^* = D(\varepsilon\sigma^2/M)^{1/2}$ by calculating the area under $C(t)$ obtained from Eqn. (4) are given in Table I, for various reduced temperatures $T^* = k_B T/\varepsilon$ and densities $n^* = n\sigma^3$; where ε and σ are two parameters of LJ fluid. Molecular dynamics (MD) results of Heyes [11,12] are given for comparison. The results for D^* obtained from Eqn. (2) are also given in brackets. It can be seen from Table I that results obtained using Eqns. (4) and (2) are very close to each other, except at high temperature and low densities. At low densities close to the critical density the Eqn. (4) seems to fail to describe the time evolution of $C(t)$. Results obtained from Eqn. (4) for time development of $C(t)$ are shown as full curve in Figure 1a and 1b for two thermodynamic states. Results obtained from Eqn. (2) are shown as dotted lines, whereas MD data [13, 14] are shown as solid circles for comparison. It is seen that results obtained from Eqns. (4) and (2) are quite similar.

We have also compared our results for self-diffusion coefficients of liquid alkali metals obtained using Eqns. (4) and (2). The value of C_2 and C_4 are used from the work of Ranganathan and Pathak [1], calculated by using the potential given by Price et al [15]. The results are compared in Table II, MD data [16] and experimental results [17, 18] are also given there. It is noted that Eqn. (4) overestimates the results by about $15 - 20\%$ from those obtained using Eqn. (2) and also from MD data. The time evolution of $C(t)$ is compared

TABLE I Values of the self-diffusion coefficients at different temperatures T^* and densities n^*. D^* represents our results and D^*_{MD} represents molecular dynamics data. The values in brackets are the results of I

T^*	n^*	D^*	D^*_{MD}
0.72	0.835	0.046 (.044)	0.031
0.72	0.848	0.044 (.042)	0.0269
1.06	0.679	0.11 (.11)	0.11
1.06	0.731	0.093 (.092)	0.091
1.06	0.821	0.068 (.067)	0.060
1.06	0.880	0.056 (.053)	0.042
1.06	0.910	0.050 (.047)	0.035
1.23	0.419	0.33 (.287)	0.33
1.28	0.600	0.175 (.174)	0.180
1.16	0.844	0.070 (.0680)	0.063
1.83	0.500	0.379 (.337)	0.390
1.81	0.600	0.244 (.239)	0.280
1.81	0.700	0.170 (.170)	0.170
1.90	0.801	0.126 (.125)	0.130
2.47	0.400	1.09 (.636)	0.611
2.48	0.500	0.54 (.448)	0.478
2.50	0.600	0.338 (.322)	0.38
2.56	0.743	0.20 (.20)	0.20
2.5	0.803	0.163 (.162)	0.180
3.46	0.500	0.79 (.599)	0.66
3.41	0.600	0.45 (.423)	0.43
3.50	0.700	0.314 (.311)	0.35
3.54	0.803	0.22 (.22)	0.20
4.49	0.500	1.04 (.738)	0.64
4.53	0.600	0.58 (.532)	0.56
4.45	0.700	0.385 (.379)	0.46
4.45	0.803	0.272 (.272)	0.31
6.00	0.500	1.90 (.969)	0.87
6.00	0.637	0.70 (.621)	0.63
6.00	0.818	0.35 (.355)	0.35
6.00	0.872	0.30 (.30)	0.30
10.00	0.600	1.77 (1.099)	1.0
10.00	0.700	0.94 (.819)	0.79
10.00	0.800	0.642 (.617)	0.63

in Figure 2 for Rb at its triple point. Results obtained from Eqn. (2) are shown as dotted lines, whereas MD data [16] is shown as solid circles. It is noted that results obtained from Eqns. (2) and (4) are qualitatively similar.

From the comparison of results obtained in the present work with results of I and the MD data, we conclude that the use of spectrum of frequencies rather than a single frequency does not improve the prediction of the model for the self-diffusion coefficient.
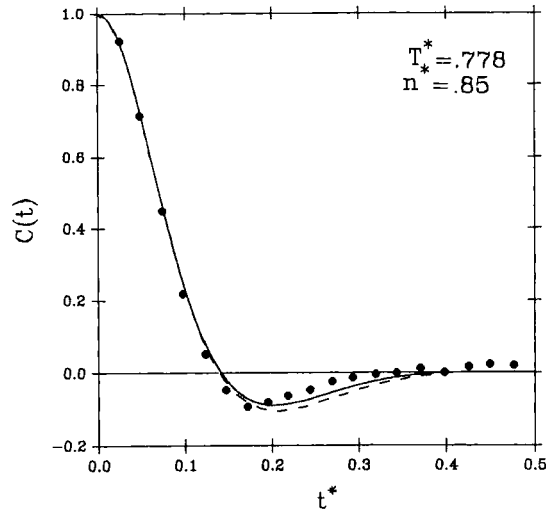
(a)
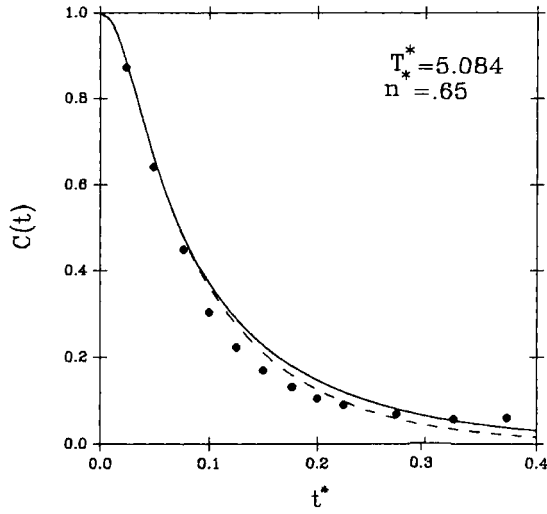
(b)

FIGURE 1   Velocity auto-correlation function $C(t)$ as a function of t^* for LJ fluids. $t^* = t/\tau$ and $\tau = (M\sigma^2/\varepsilon)^{1/2}$. Solid curve from Eqn. (4), broken curve is results of Eqn. (2) and full circles represents MD data. (a) for $T^* = .778$ and $n^* = .85$; (b) for $T^* = 5.084$ and $n^* = .65$.
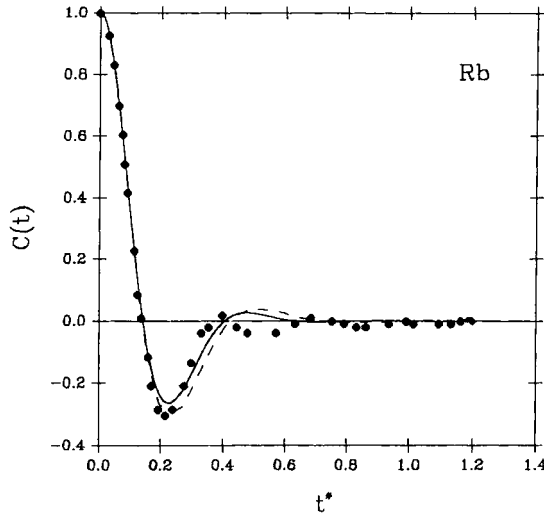
FIGURE 2   Velocity auto-correlation function $C(t)$ as a function of t^* for Rb. Solid curve is results obtained from Eqn. (4), broken curve represents results of Eqn. (2) and full circles denote MD data.

TABLE II   Diffusion coefficients D (in units of 10^{-5} cm^2 s^{-1}) for liquid alkali metals. D_0 represents our results (Eqn. 4) and D_p represents results (Eqn. 2) of Ranganathan and Pathak. D_{MD} and D_{expt} are molecular dynamics and experimental values

Metal	$n(\overset{\circ}{A}{}^{-3})$	$T(k)$	D_0	D_p	D_{MD}	D_{expt}
Na	0.0229	376	5.21	4.41	4.06	4.06 − 4.35
K	0.0128	343	4.50	3.78	3.58	3.52 − 3.72
Rb	0.0104	312	3.08	2.60	2.40	2.60
Cs	0.0083	302	2.65	2.22	2.11	2.16

Acknowledgements

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