Self Diffusion in Isotopic Fluid

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SELF DIFFUSION IN ISOTOPIC FLUID

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Expressions for the second and fourth frequency sum rules of the velocity auto-correlation function have been obtained for an isotopic fluid. These expressions and Mori memory function formalism have been used to study the influence of the particle mass and mole fraction on the self diffusion coefficient. Our results confirm the weak mass dependence of the self diffusion. The influence of the mole fraction of the light particles on the self diffusion constant has been found to increase for the larger particle mass.

KEY WORDS: Isotopic mixture, Mori coefficients, self diffusion, mole fraction.

1 INTRODUCTION

In recent years a series of computer simulations[1–5] have been performed to investigate the mass dependence of the self diffusion coefficients in liquid mixture. In these studies Ar-Kr[6] and isotopic mixtures have been of interest because of the simplicity. These systems are simple in the sense that the isotopes interact through the mass in-dependent potential and show identical structures and mean forces over every particle. In these systems difference in the self diffusion originates only from the mass difference of the particles. In some of these studies the influence of the particle mass on the self diffusion have been studied[4] by taking only single heavy isotope in the system. The computer simulation studies have been found to be in agreement with the experimental observations of weak mass dependence of the diffusion constant. Various investigators[3,4,7] have tried to interpret the mass dependence of the self diffusion coefficient D by an empirical relation given by

$$\frac{D(m_2)}{D(m_1)} = \left(\frac{m_2}{m_1}\right)^{-\alpha},$$

(1)

where m_1 and m_2 are the atomic masses of the light (main component) and heavy particle (isotope) in an isotopic mixture. The value of α has been found to be varied (0.064 to 0.1). Nothing conclusive, at the present, can be said about the dependence of α on the mole fraction, density and temperature of the system.

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Theoretically, attempts[1,8,9,10] have been made to interpret the mass dependence of the self-diffusion coefficients. The kinetic theory prediction of α is 0.5 which is much higher than what has been predicted by experiments and computer molecular dynamics (MD) investigations. Perturbation theory[1] has also been found to be unsuccessful at liquid density and for higher mass differences. The other approach which has applied to investigate the mass dependence of the self diffusion coefficients is through the Mori's memory function formalism[11,12]. Toxvaerd[4] has made the MD calculation of the Mori coefficients (or sum rules) of the velocity auto correlation function. His analysis using mori coefficients and the gaussian memory has shown that the Mori formalism does not support the relation (1), however it predicts the weak mass dependence of the self diffusion. It has also been demonstrated by him that gaussian memory increases and dominates with increase of mass differences.

In the present work we have extended the work of the use of Mori formalism by deriving the explicit microscopic expressions of the sum rules of the velocity auto correlation function of an isotopic fluid mixture. The expressions are derived in Section 2. Our expressions are functions of masses m_1 and m_2 and mole fraction. These expressions are useful in studying the mole fraction dependence in addition to the mass dependence of the self diffusion. In Section 3, we present the expression for the self diffusion coefficient. The influence of the mole fraction and mass on Mori coefficients and self diffusion coefficient is given in Section 4. Our results for the Mori coefficients has been found to be in very good agreement with MD results of Toxvaerd. Our results confirm the weak mass dependence of the self diffusion coefficients. It has also been found that the influence of the mole fraction on self diffusion increases with increase in the mass difference. The conclusion is given in Section 5.

2 EXPRESSIONS FOR SUM RULES

We consider an N particle isotopic system with $N = N_l + N_h$ where N_l is the number of light particles of atomic mass m_1 and N_h is the number of heavy particles of atomic mass $m_2 = K m_1$ $(K > 1)$. The normalised velocity auto-correlation function (VACF) of such a system is defined as

$$V(t) = \langle v_{1x}(t)v_{1x}(0)\rangle/\langle v_{1x}^2\rangle, \tag{2}$$

where $v_{1x}(t)$ is the x cartesian component of the velocity of the particle with index 1 at time t. The particle with index 1 can be either light or heavy and will be under the interaction of all other particles in the system. In Eq. (2) angular brackets denote the ensemble averages. The short time expansion of the VACF is given by

$$V(t) = 1 - V_2(t^2/2!) + V_4(t^4/4!) + \cdots \tag{3}$$

where $-V_2$ and V_4 are the so-called frequency sum rules of the VACF. These sum rules will be depending upon the choice of the particle with index 1 to be heavy or

light one. The expression for $V_2(m_1)$ i.e., the second sum rule of VACF of the light particle in the isotopic mixture, is obtained to be

$$V_2(m_1) = \frac{n}{m_1} \int d\bar{r}_1 g(r_1) U_{1xx}, \qquad (4)$$

where $U_{1xx} = d^2 U(r_1)/d^2 r_{1x}$ i.e., second derivative of the pair potential $U(r_1)$, $g(r_1)$ is the static pair correlation function and n is the number density. The expression for $V_2(m_2)$ can be obtained from Eq. (4) by replacing m_1 by m_2. This implies that

$$m_1 V_2(m_1) = m_2 V_2(m_2). \qquad (5)$$

The expression for $V_4(m_1)$ can be obtained by assuming particle labelled as 1 to be of mass m_1 and all other particles having mass m_1 or m_2. The calculation of $V_4(m_1)$ is though simple, but tricky. Therefore, we state here some steps. We define $V_4(m_1)$ as

$$V_4(m_1) = \frac{\langle \ddot{v}_{1lx}(t) \ddot{v}_{1lx}(t) \rangle_{t=0}}{\langle v_{1lx}^2 \rangle} \qquad (6)$$

where $v_{1lx}(t)$ is double time derivative of $v_{1lx}(t)$. The subscript l on v represents that particle with index 1 is a light particle. Defining

$$\ddot{v}_{1lx} = -m_1^{-1} \sum_{j=1}^{N} \frac{d^2 U(r_{1lj})}{dr_{1lx} dr_{i\alpha}} \cdot v_{i\alpha}. \qquad (7)$$

From Eq. (7) it can be seen that the particle 1 is under the interaction of particles with index named as j and i which can be heavy or light ones. Substituting Eq. (7) in Eq. (6) and separating out the possible choices of the particles to be heavy or light, we finally obtain

$$V_4(m_1) = \frac{I_1}{m_1^2}\left[2C + (1-C)\left(1 + \frac{m_1}{m_2}\right)\right] + \frac{I_2}{m_1^2}[C^2 + (1-C)^2 + 2C(1-C)], \qquad (8)$$

where,

$$I_1 = n \int d\bar{r}_1 g(r_1) U_{1x\alpha}^2, \qquad (9)$$

and

$$I_2 = n^2 \iint d\bar{r}_1 d\bar{r}_2 g_3(\bar{r}_1, \bar{r}_2) U_{1x\alpha} U_{2x\alpha}. \qquad (10)$$

In obtaining Eq. (8) we have assumed that in an isotopic system particles interact via the same interaction potential. In above equations and in what follows C is the mole fraction of the light particles, $g_3(r_1, r_2)$ is static triplet correlation function and

$$U_{1x\alpha} = \frac{d^2 U(r_1)}{dr_{1x} dr_{1\alpha}}. \tag{11}$$

The subscript 2 on U in Eq. (10) implies that argument of the pair potential $U(r_1)$ is changed from r_1 to r_2.

Here it may be noted that the terms in Eq. (8) with C as multiplicator are due to the light-light particle interaction, whereas terms containing $(1 - C)$ appears as the result of light-heavy particle interactions. It may also be noted that Eq. (8) reduces to an expression of V_4 for an atomic (one component) system[13] when $m_1 = m_2$ or $C = 1$. The expression for $V_4(m_2)$ can be obtained by assuming the particle 1 as heavy particle and following the procedure used for obtaining Eq. (8). The expression thus obtained is given by

$$V_4(m_2) = \frac{I_1}{m_2^2} \left[2(1 - C) + C\left(1 + \frac{m_2}{m_1}\right)\right] + \frac{I_2}{m_2^2} \left[C^2 + (1 - C)^2 + 2C(1 - C)\right], \tag{12}$$

In this expression the terms containing $(1 - C)$ and C as multiplicator are due to heavy-heavy and heavy-light particle interaction, respectively.

Recently computer molecular dynamics calculation has been carried out[4] by assuming only one heavy particle present in the system. For such a system the terms in Eq. (11) which appears as a result of heavy-heavy particle interaction will vanish as there will be no other heavy particle in the mixture. Following this we obtain

$$V_4^s(m_2) = \frac{C}{m_2} I_1 \left(\frac{1}{m_1} + \frac{1}{m_2}\right) + \frac{C^2}{m_2^2} I_2 \tag{13}$$

The subscript s on $V_4(m_2)$ represents an isotopic system with single heavy particle. In Eq. (13)

$$nC = \frac{(N - 1)}{V} \approx \frac{N}{V},$$

where V is the volume of the system.

The expressions for the fourth frequency sum rule obtained above are new results. These expressions are purely microscopic and tractable. It is expected that these will be useful in studying the self diffusion in an isotopic system.

3 EXPRESSION FOR THE SELF DIFFUSION

The Green–Kubo expression for the self diffusion coefficient D is given by[11]

$$D = \frac{k_B T}{m} \int_0^\infty V(t)dt. \tag{14}$$

where, k_B and T are the Boltzmann constant and temperature, respectively.

The exact evaluation of the time correlation function $V(t)$ is not yet feasible except for very simple cases and for some models of the fluids. However, at the molecular level the time correlation function can be obtained using the generalised Langevin equation:

$$\frac{dV(t)}{dt} = - \int_0^t M_1(t - \tau)V(\tau)d\tau, \tag{15}$$

where $M_1(t)$ is the first order memory function or relaxation kernel. In order to calculate the VACF from Eq. (15), the fundamental theoretical quantity to be calculated in this formalism is the $M_1(t)$. Although we have a microscopic expression for the memory function, its calculation is not simple and amounts to a solution of a many body problem. Therefore, several phenomenological forms of the memory function have been proposed in the literature and an extensive review of this has been given by Boon and Yip[11]. In this work, we use a phenomenological form given by

$$M_1(t) = \delta_1 \exp\left(-\delta_2 \frac{t^2}{2}\right), \tag{16}$$

where δ_1 and δ_2 are called Mori coefficients appearing in the continued fraction representation of the Mori equation (15). These Mori Coefficients are related to the sum rules by the relations

$$\delta_1 = V_2$$

and

$$\delta_2 = \frac{V_4}{V_2} - V_2 \tag{17}$$

We have chosen the memory function to be gaussian because (1) it gives the exact short time behaviour of the correlation function and (2) it has been demonstrated by Toxvaerd that the gaussian memory increases and dominates as the isotopic mass is increased. The contribution of the gaussian memory to the self diffusion coefficient

is given by

$$D(m_2) = \frac{k_B T}{m_2 \delta_1(m_2)} \sqrt{\frac{2\delta_2(m_2)}{\pi}} \tag{18}$$

From the expression and Eq. (5) it is clear that the mass dependence solely comes from $\delta_2(m_2)$. In the next section we carry out the numerical calculation of the sum rules and the self diffusion coefficients with varying the mass of the isotope and the mole fraction.

4   CALCULATION AND RESULTS

In order to obtain the numerical estimates for the frequency sum rules from the expressions obtained in Section 2, we first perform the angular integration of the integrals appearing in Eqs. (4), (9) and (10). The method of angular integration is given in our earlier work[13,14]. The static pair contributions involve single integration, whereas the triplet contribution involves three dimensional integration. The inputs require for the numerical calculation of the resulting expressions are the interaction potential, the static pair and triplet correlation function. We use the Lennard-Jones (LJ) potential as the interaction potential. The static pair correlation function is calculated using the method Sung and Chandler[15] based on optimised cluster theory. This $g(r)$ has been in good agreement[16] with the molecular dynamics data. Due to a little information about the static triplet correlation function, we have used superposition approximation for it. Here it may be noted that this approximation has provided a good estimate for the triplet contribution to the V_4 as demonstrated in our earlier work on LJ system. The Gauss quadrature method have been used to compute the integrals. The accuracy of our numerical work is better than 5 percent. The values of $V_2(m_1)$, I_1 and I_2 at n^* ($= n\sigma^3$) = 0.75 and $T^* = (k_B T/\varepsilon) = 0.9$, where σ and ε are two parameters of the LJ potential having the dimension of length and energy, respectively, are obtained to be

$$(m_1\sigma^2/\varepsilon)V_2(m_1) = 225.14$$

$$(m_2\sigma^4/\varepsilon^2)I_1 = 83265.73$$

$$(m_2\sigma^4/\varepsilon^2)I_2 = 32054.37$$

We have chosen this particular thermodynamic state in order to compare our results with the available computer simulation results of Mori coefficients and the self diffusion coefficients for the isotopic system.

The numerical results obtained for the Mori coefficients $\delta_1(m_2)$ and $\delta_2(m_2)$ of the isotopic mixture having only one heavy particle are given in Table 1 for variable mass. The available computer molecular dynamics results of Toxvaerd for such a

Table 1 Mori coefficients for single heavy isotopic mixture for $T^* = 0.9$ and $n^* = 0.9$.

$K = \dfrac{m_2}{m_1}$	δ_1 (our)	δ_1 (MD)	$\delta_2(m_2)$	$\delta_2(m_2)$ (MD)	$D^*(m_2)$ (Eq. (1))	$D^*(m_2)$ (Eq. (18))
1.0	225.14	226.4 ± 7.8	656.94	659 ± 7.5	0.072	0.081
1.5			558.10	537 ± 9	0.071	0.073
2.0			510.67	498 ± 17	0.069	0.072
4.0			439.54	444 ± 20	0.0658	0.066
6.0			415.83		0.0641	0.065
8.0			403.97		0.063	0.064
10.0			396.86		0.062	0.0635
12.0			392.12		0.0613	0.0630
14.0			388.73		0.0607	0.0628
16.0			386.19	398 ± 40	0.0602	0.0621

system are also given there for comparison. From Table 1 it can be seen that our results are in very good agreement with the simulation results. This suggests that the use of superposition approximation for the static triplet correlation function does not make any significant differences in the values of the sum rules. This is in accordance with our earlier conclusion[17] for the LJ system.

To see the effect of mole fraction on the Mori coefficients and hence on self diffusion coefficients we have calculated $\delta_2(m_1)$ and $\delta_2(m_2)$ from Eqs. (8), (12) and (17) for mole fraction ranging from 0.5 to 0.9. The results obtained are plotted in Figure 1 for K $(= m_2/m_1) = 2,4$ and 16. From Figure 1 it can be seen that as the number of heavy
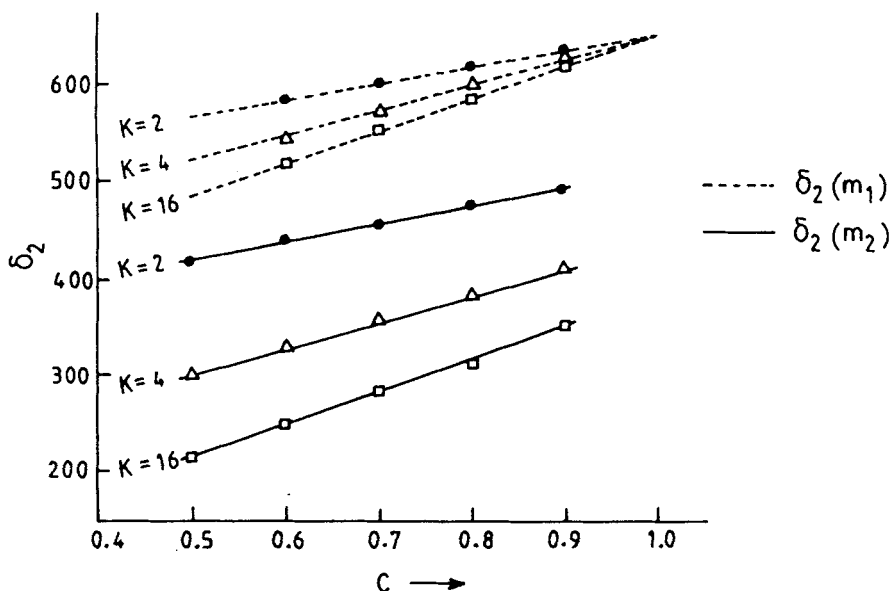
Figure 1 Variation of Mori coefficients with mole fraction, C for K $(= m_2/m_1) = 2$, 4 and 16.

particles in the mixture decreases the $\delta_2(m_1)$ as well as $\delta_2(m_2)$ increases linearly with the almost same slopes for a given mass ratio. From this and Eq. (18) it can be seen that the self diffusion coefficient increases, irrespective of whether it is of light or heavy particle, with the increase in percentage of light particles in the mixture. This is due to the fact that light particles provides less resistance to the movement of the particle (light or heavy) than the heavier particles.

The self diffusion coefficient of the isotopic fluid mixture is calculated from Eq. (18) using the values of the Mori coefficients from Table 1. The results obtained for $D^* = D(m/\varepsilon\sigma)^{0.5}$ are given in the same table for a system with only one heavy isotope. The results obtained from Eq. (1) by assuming $\alpha = 0.0641$ (see Ref. 4) are also given in Table 1. It can be seen from Table 1 that for a large mass ratio our results are in good agreement with that obtained from Eq. (1). This agrees with the earlier conclusion of Toxvaerd. Table 1 also demonstrates the weak mass dependence of the self diffusion coefficient.

In order to see the mole fraction dependence of the self diffusion coefficients, we have calculated $D(m_1)$ and $D(m_2)$ using Eq. (18) and the results of Mori coefficients plotted in Figure 1. The results obtained are given in Table 2. From Table 2, it can be seen that both $D(m_1)$ and $D(m_2)$ increases with increase in the mole fraction of the light particles i.e., C. This is an expected result as pointed out earlier. From the table it can also be seen that $D(m_1)/D(m_2)$ decreases with the increase in the percentage of the light particles in the mixture. This decrease is more for large mass ratio.

Table 2 Values of the self diffusion coefficients for different mole fraction C, and for different mass ratios, K.

K	C	$D^*(m_2)$	$D^*(m_1)$	$D^*(m_1)/D^*(m_2)$
1	1	—	0.081	
2	0.5	0.0654	0.0757	1.157
	0.6	0.0668	0.0770	1.153
	0.7	0.0682	0.0782	1.147
	0.8	0.0696	0.0794	1.141
	0.9	0.0710	0.0805	1.134
4	0.5	0.0555	0.0726	1.308
	0.6	0.0580	0.0745	1.285
	0.7	0.0603	0.0764	1.267
	0.8	0.0626	0.0782	1.249
	0.9	0.0649	0.0800	1.233
16	0.5	0.0467	0.0701	1.501
	0.6	0.503	0.0727	1.443
	0.7	0.0537	0.0750	1.396
	0.8	0.0569	0.0773	1.358
	0.9	0.0599	0.0795	1.327

5 SUMMARY AND CONCLUSION

In this paper, we have obtained the complete expressions for the second and fourth frequency sum rules of the velocity auto-correlation function of the isotopic fluid mixture. The expressions presented here are new and are useful in the study of the mass and mole fraction dependence of the self diffusion constant. The numerical results obtained have been compared with those obtained using computer simulation method. A very good agreement has been obtained. These results for the sum rules and the Mori memory function formalism have been used to study the mass and mole fraction dependence of the self diffusion coefficients. Our results confirm the weak mass dependence of the self diffusion. The influence of the mole fraction of the lighter particles on the self diffusion has been found to increase for larger mass ratio.

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