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Self-diffusion in an isotopic fluid

Raman Sharma and K. Tankeshwar
Centre of Advanced Study in Physics, Department of Physics, Panjab University, Chandigarh 160014, India

K. C. Sharma
Department of Physics, Himachal Pradesh University, Shimla 171005, India

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An expression for the sixth-frequency sum rule of the velocity correlation function is derived for a two-component system. This, along with lower-order frequency sum rules and Mori's memory-function formalism, have been used to study the mass dependence of self-diffusion in an isotopic Lennard-Jones fluid. The effect of inclusion of the sixth-frequency sum rule on the mass dependence of a self-diffusion coefficient of a single heavy particle in a fluid has been studied explicitly. It is found that the ratio of the self-diffusion coefficient of a heavy particle to that of a fluid particle is not affected by the inclusion of the sixth-order sum rule. It is also found that for very high mass ratios the self-diffusion coefficients of a heavy particle can have a minimum value which is $1/\surd 2$ times the self-diffusion coefficient of fluid particles. The mole fraction dependence and thermodynamic state dependence of the mass dependence of self-diffusion of a heavy particle in the host fluid are also studied. [S1063-651X(98)15812-9]

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I. INTRODUCTION

In recent years there has been a keen interest to study independently the effect of variation in mass, size, and interaction between the particles of a binary fluid on transport phenomena. Such investigations have been possible only due to computer simulations and theoretical studies in which these parameters can be varied independent of each other. For this purpose Lennard-Jones fluids are found to be the most suitable systems because of their simplicity. The mass dependence of the self-diffusion coefficient in a binary fluid mixture has been studied through computer simulations [1–6]. The computer simulations have shown a weak mass dependence of the self-diffusion coefficient, which is in agreement with the experimental observations. Theoretical attempts [4–10] made within Mori's memory-function formalism have also proven weak mass dependence of the self-diffusion coefficient. In one such attempt, it was argued [10] that the weak mass dependence of the self-diffusion coefficient comes from the higher-order Mori coefficients (related to sum rules). Therefore, knowledge of higher-order sum rules is very much desirable. However, the expressions for the sum rules of the velocity autocorrelation (VAC) function for a two-component system are presently known up to fourth order only. There exist some estimates of the higher-order sum rules obtained from computer simulations [5,11] but they are not sufficient to study the effect of higher-order sum rules on the mass dependence of the self-diffusion coefficient. In the present work, we derive an analytical expression for the sixth-frequency sum rule of the VAC function for a two-component system, in general, in which interactions, size of particles, and masses of the particles may be varied independently. This expression for the sum rule, within Mori's memory-function formalism [12], has been used to study the mass dependence of the self-diffusion coefficient in an isotopic fluid. It is found that the inclusion of the sixth sum rule does not alter the qualitative conclusion drawn [7] earlier using sum rules up to fourth order. Thus, it is confirmed that the mass dependence comes only from the lower-order Mori coefficients. We have also studied the concentration and thermodynamic state dependence of the mass dependence of the self-diffusion coefficient.

The paper is organized as follows. Expressions for the frequency sum rules of the VAC function as a function of mass and concentration are derived in Sec. II, and an expression for the self-diffusion coefficient is given in Sec. III. In Sec. IV, an analytical result for the mass dependence of the self-diffusion coefficient is obtained. Results obtained for Mori's coefficients and the self-diffusion coefficient as a function of mass, concentration, temperature, and density are discussed in Sec. V. Finally, the work is concluded in Sec. VI.

II. FREQUENCY SUM RULES

We consider an isotopic fluid with $N=N_1+N_2$ number of particles, where N_1 is the number of light particles of atomic mass m_l and N_2 is the number of heavy particles of atomic mass m_h, such that $m_h/m_l>1$. Expressions for the normalized velocity autocorrelation functions for such a system are given as

$$C(t,m_l)=\frac{1}{N_1}\sum_{i=1}^{N_1}\frac{\langle v_{ix}(t)v_{ix}(0)\rangle}{k_BT/m_l} \tag{1}$$

and

$$C(t,m_h)=\frac{1}{N_2}\sum_{i=1}^{N_2}\frac{\langle v_{ix}(t)v_{ix}(0)\rangle}{k_BT/m_h}, \tag{2}$$

where $v_{ix}(t)$ is the x Cartesian component of the velocity of the ith particle at a time t. Angular brackets in the above equations represent the ensemble average. The short time expansion of the VAC function is

$$C(t,m)=1-C_2(m)\,\frac{t^2}{2!}+C_4(m)\,\frac{t^4}{4!}-C_6(m)\,\frac{t^6}{6!}+\cdots, \tag{3}$$

where the coefficients $C_2(m)$, $C_4(m)$, and $C_6(m)$ are second-, fourth-, and sixth-frequency sum rules of the VAC function of the species of mass m, respectively. In the present work we will use Mori's memory-function formalism and short time properties of the VAC function to study the effect of variation in the mass and concentration of particles on the self-diffusion coefficient. Therefore, first of all we will examine some of the exact properties, namely the frequency sum rules of the VAC functions for an isotopic fluid. Expressions for the second and fourth sum rules have already been derived [7,8] and are given as

$$C_2(m_l)=\frac{n}{m_l}\int d\mathbf{r}_1 g(r_1)U_{1xx} \tag{4}$$

and

$$C_4(m_l)=\frac{I_1}{m_l^2}\left[2c+(1-c)\left(1+\frac{m_l}{m_h}\right)\right]+\frac{I_2}{m_l^2}\,[c^2+(1-c)^2+2c(1-c)], \tag{5}$$

where I_1 and I_2 are integrals involving pair distribution functions $g(r)$ and pair potential $U(r)$, given as

$$I_1=n_l\int d\mathbf{r}_1 g(r_1)(U_{1x\alpha})^2 \tag{6}$$

and

$$I_2=n_l^2\int\int d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1,\mathbf{r}_2)U_{1x\alpha}U_{2x\alpha}. \tag{7}$$

In these equations n_l and $c(=N_1/N)$ are the number density and mole fraction of light particles and we have used the notation

$$U_{1\alpha\beta}=\frac{d^2U(r_1)}{dr_{1\alpha}dr_{1\beta}}. \tag{8}$$

r_α and r_β are Cartesian components of $\mathbf{r}$. The subscript 2 on U in Eq. (7) implies that the argument of the pair potential, $U(r_1)$, is changed from r_1 to r_2. In Eq. (7), $g_3(\mathbf{r}_1,\mathbf{r}_2)$ represents the static triplet correlation function. In the derivation of these frequency sum rules, it is assumed that the particles of the system interact via the same interaction potential so as to represent an isotopic fluid. Here it may be noted that the terms in Eq. (5) with c or c^2 as the multiplicator are due to interaction between light-light particles, and the terms involving $(1-c)$ or $(1-c)^2$ as the multiplicator are due to interaction between light-heavy particles. Expressions for $C_2(m_h)$ and $C_4(m_h)$ can be obtained from Eqs. (4) and (5) by interchanging m_l by m_h, c by $(1-c)$, and replacing n_l by n_h.

In the present work we have derived an expression for the sixth-frequency sum rule of the VAC function for a two-component system which at present is not available in the literature. By definition, the sixth sum rule is given as

$$C_6=\frac{1}{N_i}\sum_{i=1}^{N_i}\frac{\langle v'''_{ilx}(t)v'''_{ilx}(t)\rangle_{t=0}}{\langle(v_{ilx})^2\rangle}, \tag{9}$$

where $v'''_{ilx}(t)$ is the triple time derivative of the x component of the velocity of the ith light particle and is given as

$$v'''_{1lx}(t)=\sum_{j,k}\frac{-1}{m_l}\left[\frac{\partial^3U(r)}{\partial r_{1lx}\partial r_{j\alpha}\partial r_{k\beta}}\,v_{j\alpha}v_{k\beta}+\frac{\partial^2U(r)}{\partial r_{1x}\partial r_{k\alpha}}\left(-\frac{1}{m_l}\right)\frac{\partial U(r)}{\partial r_{k\alpha}}\right]. \tag{10}$$

From the above equation it can be seen that the tagged particle is under the interaction of particles with index j and k, which can be heavy or light ones. Using Eq. (10) in Eq. (9), and after some lengthy but simple algebra, we get

$$\begin{aligned}C_6(m_l)=\frac{1}{m_l}\biggl(&n_l\int d\mathbf{r}\;g(r)\biggl\{k_BT\biggl[\frac{12c}{m_l^2}+\frac{3(1-c)}{m_l^2}+(1-c)\biggl(\frac{3}{m_h^2}+\frac{6}{m_lm_h}\biggr)\biggr](U^{ll}_{1x\alpha\beta})^2+\frac{4c}{m_l^2}\,U^{ll}_{1x\alpha}U^{ll}_{1x\beta}U^{ll}_{1\alpha\beta}\\&+(1-c)\biggl(\frac{1}{m_l^2}+\frac{1}{m_h^2}+\frac{2}{m_lm_h}\biggr)U^{lh}_{1x\alpha}U^{lh}_{1x\beta}U^{lh}_{1\alpha\beta}\biggr\}+\frac{k_BT}{m_l^2}\,n_l^2\int\int d\mathbf{r}_1d\mathbf{r}_2g_3(\mathbf{r}_1,\mathbf{r}_2)\\&\times\biggl\{[6c(1-c)U^{ll}_{1x\alpha\beta}U^{lh}_{2x\alpha\beta}+3c^2U^{ll}_{1x\alpha\beta}U^{ll}_{2x\alpha\beta}+3(1-c)^2U^{lh}_{1x\alpha\beta}U^{lh}_{2x\alpha\beta}]+\frac{c^2}{m_l^2}\,(2U^{ll}_{1x\alpha}U^{ll}_{1x\beta}U^{ll}_{2\alpha\beta}\\&+4U^{ll}_{1x\alpha}U^{ll}_{2x\beta}U^{ll}_{1\alpha\beta})+(1-c)^2\biggl[\biggl(\frac{1}{m_l^2}+\frac{1}{m_h^2}\biggr)U^{lh}_{1x\alpha}U^{lh}_{1x\beta}U^{lh}_{2\alpha\beta}+2\biggl(\frac{1}{m_l^2}+\frac{1}{m_lm_h}\biggr)U^{lh}_{1x\alpha}U^{lh}_{2x\beta}U^{lh}_{1\alpha\beta}\biggr]\\&+c(1-c)\biggl[\biggl(\frac{1}{m_l^2}+\frac{1}{m_h^2}\biggr)(U^{lh}_{1x\alpha}U^{lh}_{1x\beta}U^{ll}_{2\alpha\beta}+U^{ll}_{1x\alpha}U^{ll}_{1x\beta}U^{lh}_{2\alpha\beta})+\frac{4}{m_l^2}\,U^{ll}_{1x\alpha}U^{lh}_{2x\beta}U^{ll}_{1\alpha\beta}\\&+2\biggl(\frac{1}{m_l^2}+\frac{1}{m_lm_h}\biggr)U^{lh}_{1x\alpha}U^{ll}_{2x\beta}U^{lh}_{1\alpha\beta}\biggr]-\biggl[\frac{c^2}{m_l^2}\,U^{ll}_{1x\alpha}U^{ll}_{2x\beta}U^{ll}_{12\alpha\beta}+\frac{(1-c)^2}{m_h^2}\,U^{lh}_{1x\alpha}U^{lh}_{2x\beta}U^{hh}_{12\alpha\beta}\end{aligned}$$

$$+\frac{c(1-c)}{m_l m_h}\,(U^{ll}_{1x\alpha}U^{lh}_{2x\beta}U^{lh}_{12\alpha\beta}+U^{lh}_{1x\alpha}U^{ll}_{2x\beta}U^{ll}_{12\alpha\beta})\bigg]\bigg]\bigg\}+\frac{1}{m_l^2}\,n_l^3\int\int\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 g_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$$

$$\times[c^3U^{ll}_{1x\alpha}U^{ll}_{2x\beta}U^{ll}_{3\alpha\beta}+c^2(1-c)(U^{ll}_{1x\alpha}U^{ll}_{2x\beta}U^{lh}_{3\alpha\beta}+U^{ll}_{1x\alpha}U^{lh}_{2x\beta}U^{ll}_{3\alpha\beta}+U^{lh}_{1x\alpha}U^{ll}_{2x\beta}U^{ll}_{3\alpha\beta})$$

$$+c(1-c)^2(U^{ll}_{1x\alpha}U^{lh}_{2x\beta}U^{lh}_{3\alpha\beta}+U^{lh}_{1x\alpha}U^{ll}_{2x\beta}U^{lh}_{3\alpha\beta}+U^{lh}_{1x\alpha}U^{lh}_{2x\beta}U^{ll}_{3\alpha\beta})+(1-c)^3U^{lh}_{1x\alpha}U^{lh}_{2x\beta}U^{lh}_{3\alpha\beta}]\bigg). \tag{11}$$

In deriving Eq. (11), the interactions between the two species are assumed to be different, therefore it represents a general expression for any two-component system. In the last term of Eq. (11), $g_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ is the static quadruplet correlation function. Subscripts 2, 12, and 3 on U represent that the argument of the potential $U(r_1)$ is changed to r_2, r_{12} $(=|\mathbf{r}_1-\mathbf{r}_2|)$, and r_3, respectively. The superscripts on U denote whether the interaction involved is between light-light (*ll*), heavy-heavy (*hh*), or light-heavy (*lh*) particles. The expression for C_6 involves a derivative of the potential up to third order and static correlation functions up to four particles. Therefore, it contains more correlation effects and anharmonicity of atomic motion than C_2 and C_4. For $c=1$ and $m_l=m_h$ from Eq. (11) one recovers an expression, obtained by Bansal and Pathak [13], for a one-component system.

For the present case of an isotopic liquid, the expression for C_6 as a function of mass becomes

$$C_6(m_l)=\frac{1}{m_l^3}\bigg\{k_BT\bigg(12c+3(1-c)+\frac{3(1-c)}{K^2}+\frac{6(1-c)}{K}\bigg)J_1+\bigg(4c+(1-c)\bigg[1+\frac{1}{K^2}+\frac{2}{K}\bigg]\bigg)J_2+k_BT[6c(1-c)+3c^2$$

$$+3(1-c)^2]J_3+\bigg[2c^2+\frac{(1-c)^2}{K^2}+(1-c)^2+2c(1-c)\bigg(1+\frac{1}{K^2}\bigg)\bigg]J_4+\bigg[4c^2+2(1-c)^2\bigg(1+\frac{1}{K}\bigg)$$

$$+2c(1-c)\bigg(3+\frac{1}{K}\bigg)\bigg]J_5-\bigg[c^2+\frac{2c(1-c)}{K}+\frac{(1-c)^2}{K^2}\bigg]J_6+\frac{1}{m_l^2}\,[(1-c)^3+3c^2(1-c)+3c(1-c)^2+c^3]J_7\bigg\}, \tag{12}$$

where $K=m_h/m_l$ and the integrals J_1, J_2, J_3, J_4, J_5, J_6, and J_7 are defined as

$$J_1=n_l\int d\mathbf{r}\; g(r)(U_{1x\alpha\beta})^2, \tag{13}$$

$$J_2=n_l\int d\mathbf{r}\; g(r)U_{1x\alpha}U_{1x\beta}U_{1\alpha\beta}, \tag{14}$$

$$J_3=n_l^2\int\int d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1,\mathbf{r}_2)U_{1x\alpha\beta}U_{2x\alpha\beta}, \tag{15}$$

$$J_4=n_l^2\int\int d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1,\mathbf{r}_2)U_{1x\alpha}U_{1x\beta}U_{2\alpha\beta}, \tag{16}$$

$$J_5=n_l^2\int\int d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1,\mathbf{r}_2)U_{1x\alpha}U_{2x\beta}U_{1\alpha\beta}, \tag{17}$$

$$J_6=n_l^2\int\int d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1,\mathbf{r}_2)U_{1x\alpha}U_{2x\beta}U_{12\alpha\beta}, \tag{18}$$

$$J_7=n_l^3\int\int\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 g_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)U_{1x\alpha}U_{2x\beta}U_{3\alpha\beta}. \tag{19}$$

In the same manner, the expression for the sixth-frequency sum rule of the second particle, i.e., $C_6(m_h)$, can be obtained by interchanging m_l by m_h, c by $(1-c)$, and n_l by n_h.

III. THE EXPRESSION FOR THE DIFFUSION COEFFICIENT

The general Green-Kubo expression [14] for the self-diffusion coefficient D is given as

$$D=\frac{k_BT}{m}\int_0^\infty C(t)dt, \tag{20}$$

where k_B and T are the Boltzmann constant and the temperature of the system, respectively. The exact evaluation of the VAC function $C(t)$ is not feasible except for simple cases and for some models of the fluids. However, at the molecular level the time correlation function can be obtained using Mori's equation,

$$\frac{dC(t)}{dt}+\int_0^\infty C(t-t')M_1(t')dt'=0, \tag{21}$$

where $M_1(t)$ is the first-order memory function. From the method of derivation of Eq. (21), it follows that $M_1(t)$ follows a similar equation. This provides a continued fraction representation for $\tilde{C}(\omega)$ given as

$$\tilde{C}(\omega)=-\frac{C(0)}{\omega+\tilde{M}_1(\omega)}, \tag{22}$$

with

$$\tilde{M}_n(\omega) = -\frac{\delta_n}{\omega + \tilde{M}_{n+1}(\omega)}, \quad n = 1,2,3,\ldots, \tag{23}$$

where $\tilde{C}(\omega)$ is the Fourier-Laplace transform of $C(t)$ and is defined as

$$\tilde{C}(\omega) = \iota \int_0^\infty e^{(\iota\omega t)} C(t)\,dt. \tag{24}$$

In Eq. (23), $\delta_n = M_n(0)$ are initial values of the nth stage of the memory function $M_n(t)$ and are called Mori coefficients. These Mori coefficients are directly related to the frequency sum rules of the VAC function and expressions for a few of them are given as

$$\delta_1 = C_2, \tag{25}$$

$$\delta_2 = \frac{C_4}{C_2} - C_2, \tag{26}$$

and

$$\delta_3 = \frac{C_6/C_2 - (C_4/C_2)^2}{\delta_2}. \tag{27}$$

The frequency spectrum $f(\omega)$ of the time correlation function (TCF), $C(t)$, is defined as

$$f(\omega) = 2\tilde{C}''(\omega) = 2\int_0^\infty \cos(\omega t) C(t)\,dt, \tag{28}$$

where $\tilde{C}''(\omega)$ is the imaginary part of $\tilde{C}(\omega)$. The time evolution of $C(t)$ can be determined from

$$C(t) = \frac{1}{\pi}\int_0^\infty \cos(\omega t) f(\omega)\,d\omega. \tag{29}$$

In order to calculate $\tilde{C}''(\omega)$ and hence $C(t)$, it is necessary to truncate the hierarchy of Eq. (22). The expression for D as obtained from Eqs. (20) and (28) is

$$D = \frac{k_B T}{m} C''(0) = \frac{k_B T}{2m} f(0). \tag{30}$$

It is difficult to deal with the higher-order memory function, therefore we restrict ourselves to the first- or second-stage memory function. Presently, we truncate the hierarchy of a continued fraction at the second stage. The expression thus obtained for the frequency spectrum is given as

$$f(\omega) = \frac{2\delta_1 \tilde{M}_2''(\omega)}{[\omega^2 - \delta_1 + \omega \tilde{M}_2'(\omega)]^2 + [\omega \tilde{M}_2''(\omega)]^2}. \tag{31}$$

To calculate $f(\omega)$ and hence $C(t)$, it is necessary to have a workable expression for the memory function. Although we have a microscopic expression for the memory function, its calculation is not simple as it amounts to a solution of a many-body problem. Therefore, several phenomenological forms [15] of the memory function have been proposed in the literature [14]. Here, we use the phenomenological form of the memory function given by

$$M_2(t) = a\ \exp(-b^2 t^2/2). \tag{32}$$

The parameters a and b can be determined by requiring that the first two coefficients in the expansion of the above equation and that of the exact memory function are the same. This implies that $a = \delta_2$ and $b = \sqrt{\delta_3}$. Using Eqs. (32), (31), and (29) in Eq. (30) we obtain

$$D = \frac{k_B T}{m}\left(\frac{\pi}{2}\right)^{1/2} \frac{\delta_2}{\delta_1\sqrt{\delta_3}}. \tag{33}$$

This expression will be used, for the first time, to study the mass dependence of the self-diffusion coefficient in an isotopic fluid. In an earlier study, the Mori coefficients up to second order were used and the expression used to calculate the self-diffusion coefficient was

$$D = \frac{k_B T}{m}\left(\frac{2}{\pi}\right)^{1/2} \frac{\sqrt{\delta_2}}{\delta_1}. \tag{34}$$

IV. ANALYTICAL EXPRESSION FOR MASS DEPENDENCE

For a two-component system where two species differ only in their masses and interact via the same potential, it becomes desirable to study the mass dependence of the self-diffusion coefficient of two species analytically. In such cases the Mori coefficients can be written as a function of masses, and expression (33) of the diffusion coefficient may be rewritten as

$$D(m_i) = \frac{k_B T}{m_i}\left(\frac{\pi}{2}\right)^{1/2} \frac{\delta_2(m_i)}{\delta_1(m_i)\sqrt{\delta_3(m_i)}}, \tag{35}$$

where m_i may be the mass of light or heavy particles. This gives the ratio of the self-diffusion coefficients of the particles of mass m_h and m_l as

$$\frac{D(m_h)}{D(m_l)} = \frac{m_l}{m_h}\frac{\delta_1(m_l)\delta_2(m_h)}{\delta_1(m_h)\delta_2(m_l)}\left(\frac{\delta_3(m_l)}{\delta_3(m_h)}\right)^{1/2}. \tag{36}$$

From the above equation it is obvious that the ratio of the two diffusion coefficients is independent of the functional form of the memory function. We assume that the system under consideration consists of only one heavy particle in the host fluid or that the concentration of heavy particles is so small that one can neglect their interaction. For such a system, expressions for the sum rules are to be modified. The expression for the second frequency sum rule of such a system is the same as that given by Eq. (4). From Eqs. (5) and (12) with $(1-c)=0$ and assuming that only two-body terms are taken into account, we obtain expressions for the fourth and sixth sum rules:

$$C_4(m_l) = \frac{2I_1}{m_l^2} \tag{37}$$

and

$$C_6(m_l)=\frac{1}{m_l^3}\,(12k_BTJ_1+4J_2). \tag{38}$$

Similar expressions for $C_4(m_h)$ and $C_6(m_h)$ are obtained:

$$C_4(m_h)=\frac{I_1(1+K)}{m_l^2K^2} \tag{39}$$

and

$$C_6(m_h)=\frac{1}{m_l^3K}\,(3J_1k_BT+J_2)(1+1/K)^2. \tag{40}$$

In writing the above two equations, we have again taken only the two-body contribution into account. Using these equations and Eq. (27), we found that

$$\frac{\delta_3(m_h)}{\delta_3(m_l)}=\frac{\delta_2(m_l)}{\delta_2(m_h)}\left(\frac{1+K}{2K}\right)^2. \tag{41}$$

This is an approximate solution based on truncation of all three-body and higher-body terms. The deviations of this result from those obtained including higher-order contributions is expected to be small, as is demonstrated in the next section. Using this value of $\delta_3(m_l)/\delta_3(m_h)$, and noting that $m_l\delta_1(m_l)=m_h\delta_1(m_h)$, Eq. (36) becomes

$$\frac{D(m_h)}{D(m_l)}=\left(\frac{\delta_2(m_h)}{\delta_2(m_l)}\right)^{3/2}\left(\frac{2K}{1+K}\right). \tag{42}$$

This expression has been obtained using sum rules up to sixth order, however the sixth sum rule does not appear in the final expression (42). This is an important result as it proves that the mass dependence of the self-diffusion coefficient is solely determined by lower-order sum rules. However, this expression is not the same as that derived earlier by using the sum rules up to fourth order. The expression obtained in that case is

$$\frac{D(m_h)}{D(m_l)}=\left(\frac{\delta_2(m_h)}{\delta_2(m_l)}\right)^{1/2}. \tag{43}$$

Now, if we use the approximation employed and tested in an earlier work [7], which is given as

$$\frac{\delta_2(m_h)}{\delta_2(m_l)}=\left(\frac{1+K}{2K}\right), \tag{44}$$

both the equations, i.e., Eqs. (42) and (43), yield

$$\frac{D(m_h)}{D(m_l)}=\left(\frac{1+K}{2K}\right)^{1/2}=\sqrt{1/2}\left(1+\frac{m_l}{m_h}\right)^{1/2}. \tag{45}$$

Thus the two expressions finally provide the same result.

From Eq. (45) it is clear that for $m_l=m_h$, $D(m_l)=D(m_h)$. It may be noted that for $m_h\gg m_l$, the diffusion coefficient of heavy particles becomes $D(m_h)=D(m_l)/\sqrt{2}$. Hence $D(m_l)/\sqrt{2}$ could be thought of as the minimum value of the self-diffusion coefficient that a heavy particle can have in the host fluid.

In the next section we have evaluated numerically the frequency sum rules and hence the self-diffusion coefficient for an isotopic fluid with varying mass and mole fraction of the isotopes.

V. RESULTS AND DISCUSSION

To calculate the self-diffusion coefficient of a particle in a fluid, we need to evaluate expressions of frequency sum rules numerically. For such a purpose, pair potential and static correlation functions are required as inputs. In the present work the calculations are done for an isotopic fluid by assuming that all particles of the fluid are interacting via the same Lennard-Jones pair potential. The calculations are performed at $T^*=0.90$ and $n^*=0.75$, with $T^*=k_BT/\epsilon$ and $n^*=n\sigma^3$ as the reduced temperature and density, respectively. ϵ and σ are the parameters of the Lennard-Jones potential. The static pair correlation function, $g(r)$, is obtained using the method of Sung and Chandler [16] based on the optimized cluster theory. The static pair correlation function $g(r)$ thus obtained is found to be in good agreement with the MD data. The triplet correlation function involved in the expressions of the frequency sum rules is approximated by using a superposition approximation [17] and the quadruplet correlation function involved in the sixth-frequency sum rule is approximated (see the Appendix) to the pair correlation function by using a decoupling approximation [18]. The numerical integration involved in the expressions of the frequency sum rules has been performed using the Gauss quadrature method.

A. Mori's coefficients

First-, second-, and third-order Mori coefficients, i.e., δ_1, δ_2, and δ_3, have been determined from Eqs. (25), (26), and (27). The calculated values of Mori's coefficients, i.e., $\delta_1(m_h)$, $\delta_2(m_h)$, and $\delta_3(m_h)$, along with MD data for heavy particles are given in Table I. Our values of $\delta_1(m_h)$, $\delta_2(m_h)$, and $\delta_3(m_h)$ are found to be in good agreement with the MD data [4,5,11], as evidenced by their values given in Table I. From Table I it can be seen that the ratio $m_h\delta_1(m_h)/m_l$ is independent of the value of (m_h/m_l) as predicted in [5]. It is found that, initially, the increase in mass ratio (m_h/m_l) results in a decrease of $\delta_2(m_h)$ and $\delta_3(m_h)$. However, when the ratio of the masses of the heavy to light particles is high, $\delta_2(m_h)$ and $\delta_3(m_h)$ become almost independent of the mass of the particle. Since the self-diffusion coefficient directly depends on these coefficients, the larger mass ratio diffusion coefficient should depend weakly upon the mass of the particle. In order to check the validity of Eq. (41), we have calculated $\delta_3(m_h)$ from this equation by using our numerical values of $\delta_2(m_l)$, $\delta_2(m_h)$, and $\delta_3(m_l)$. The results obtained are given in Table I, in parentheses, for mass ratios 4 and 16. The values of $\delta_3(m_h)$ predicted from Eq. (41) are close to simulation values and, which implies that the effect of the inclusion of the three-body contribution in the sum rules is quite small. This implies that a binary collision approximation may be sufficient to study the mass dependence in an isotopic system.

TABLE I. Values of Mori's coefficients, in units of $\epsilon/(m\sigma^2)$ for different values of m_h/m_l. MD represents molecular-dynamics data [4,5,11]. The values of $\delta_3(m_h)$ given in parentheses are predictions of Eq. (41).

$\frac{m_h}{m_l}$	$\delta_1(m_h)$	$\delta_2(m_h)$	$\delta_3(m_h)$	$\delta_1(m_h)$ MD	$\delta_2(m_h)$ MD	$\delta_3(m_h)$ MD
1	224.369	660.460	2238.890	231.90	684.80	2145±76
4	56.092	443.520	1340.300 (1302.340)	56.70	466.0	1240±30
10	22.437	400.135	1177.787	22.50	398.5	
16	14.023	389.288	1138.679 (1072.030)	14.5	417.9	1080±95
20	11.220	385.672	1125.799	11.2	396.8	
30	7.4789	380.852	1108.752	7.5	391.0	
40	5.610	378.441	1100.284	5.7	386.2	
50	4.480	376.995	1095.222	4.5	390.9	

B. Self-diffusion coefficient

Self-diffusion coefficients of light particles and heavy particles are calculated from Eqs. (33) and (34) using the numerical values of the Mori coefficients given in Table I. The values of $D^*(m_h)=D\sigma(\epsilon/m_h)^{1/2}$ so obtained are reported in Table II and MD data are also given there for comparison. Calculated values of the self-diffusion coefficients are found to be in good agreement with MD data. From Table II we can see that inclusion of higher-order Mori coefficients results in a decrease in the value of the self-diffusion coefficient of heavy particles. This may be due to the presence of more correlation effects, which comes through δ_3. To see the effect of the inclusion of the third-order Mori coefficient on the diffusion coefficient, we have plotted the ratio of two diffusion coefficient, i.e., $D^*(m_h)/D^*(m_l)$, in Fig. 1. The solid line represents the results of Eq. (33) and the dashed line represents the results of Eq. (34). At initial stages, the ratio of the diffusion coefficient $D^*(m_h)/D^*(m_l)$ decreases with the mass ratio and after, say, $m_h/m_l=25$ it becomes almost independent of the mass ratio. To compare our results with computer simulation data, we have also plotted MSD (mean-square displacement) MD data and MD data in Fig. 1. Solid circles represent MSD MD data and solid square represent MD data, respectively. From Fig. 1 it can be seen that the results of Eq. (33) that involve δ_3 are closer to MD data than the results of Eq. (34). Further, the inclusion of δ_3 does not affect the earlier prediction [7] that the self-diffusion coefficient of very heavy particles (for mass ratio $\geqslant 25$) has a value which cannot be less than $\sqrt{1/2}$ times the self-diffusion coefficient of the fluid particle at a given temperature and density. This can be understood from Eq. (45), where we have shown analytically that for $m_h \gg m_l$ the self-diffusion coefficient of heavy particles is $\sqrt{1/2}$ times the self-diffusion coefficient of light particles.

TABLE II. Self-diffusion coefficient of heavy particle for different values of m_h/m_l. $D_2^*(m_h)$ represents the results of Eq. (34) and $D_1^*(m_h)$ are results of Eq. (33). MD1 [4] and MD2 [5,11] represent molecular dynamics data.

$\frac{m_h}{m_l}$	$D^*(m_h)$ MD1	$D^*(m_h)$ MD2	$D_2^*(m_h)$	$D_1^*(m_h)$
1	0.0810	0.072	0.0822	0.0701
4	0.0683	0.066	0.0674	0.0609
10	0.0637		0.0640	0.0586
16	0.0633	0.060	0.0631	0.058
20	0.0639		0.0628	0.0578
30	0.0631		0.0624	0.0575
40	0.0619		0.0622	0.0573
50	0.0631		0.06214	0.05726

C. Effect of concentration on mass dependence of diffusion coefficient

The effect of concentration on the mass dependence of the diffusion coefficients of light and heavy particles is analyzed

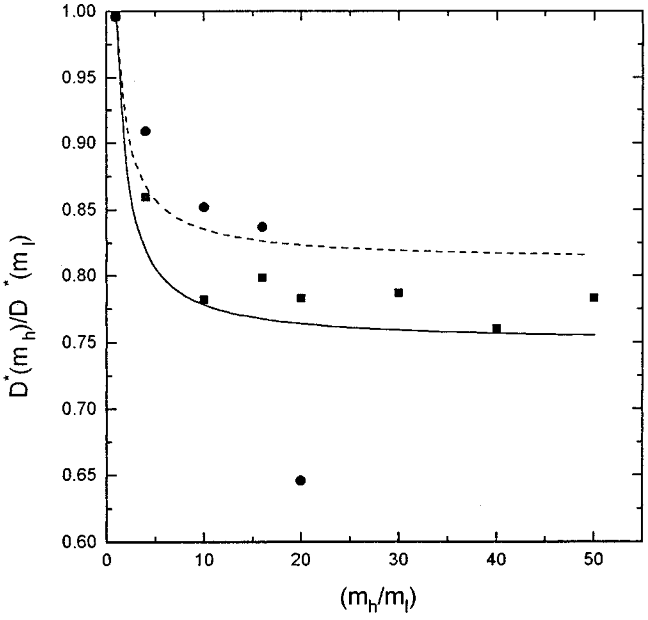

FIG. 1. Variation of diffusion ratio $[D^*(m_h)/D^*(m_l)]$ with mass ratio (m_h/m_l) for $T^*=90$ and $n^*=0.75$. (a) Solid line is the result of Eq. (33) and dashed line is the result of Eq. (34). Solid circles and solid squares represent MD MSD and MD data, respectively.

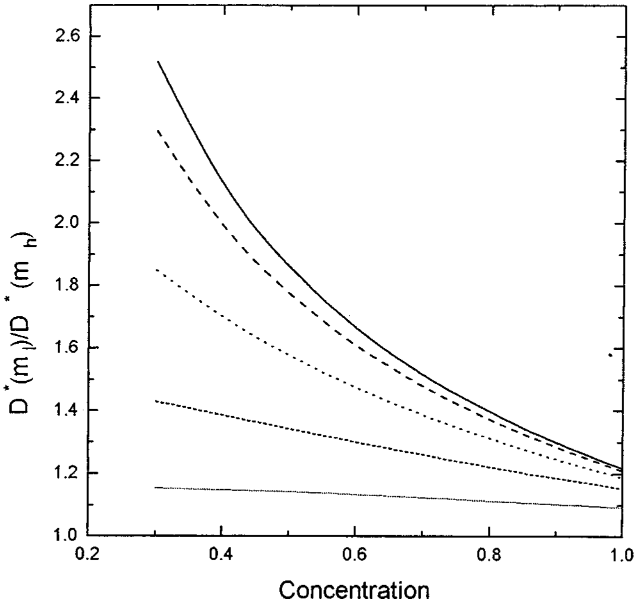

FIG. 2. Variation of diffusion $[D^*(m_l)/D^*(m_h)]$ with concentration c of the fluid for different mass ratio (K). Solid line for $K=24$; dashed line for $K=16$; dotted line for $K=8$; short dashed line for $K=4$; short dotted line for $K=2$.

by varying the concentration of light particles. Self-diffusion coefficients of light and heavy particles are obtained from Eq. (33) for different values of c, which is the concentration of light particles. Results obtained are reported in Table III. Results corresponding to $c \sim 1$ are for a system which has only one heavy particle in the fluid so that the interaction between the heavy-heavy particles is zero. From Table III it can be seen that the self-diffusion coefficient of both particles increases with an increase in the mole fraction of light particles in the system. This may be because light particles provide less resistance to the movement of other particles (light or heavy) than do the heavier particles. From Table III it can also be seen that for larger mass ratio the diffusion coefficient of heavy particles is more influenced by the concentration as compared to the diffusion coefficient of light particles. To show explicitly the effect of concentration on the mass dependence of the self-diffusion coefficient, we have plotted the ratio of the self-diffusion coefficient of a light particle to that of a heavy particle, i.e., $D^*(m_l)/D^*(m_h)$, as a function of concentration of light particles for different mass ratios in Fig. 2. The curves from bottom to top in the figure correspond to $m_h/m_l=2$, 4, 8, 16, and 24, respectively. From Fig. 2 it can be seen that the diffusion ratio decreases as the concentration of light particles increases. This decrease is greater for larger mass ratio. This shows that an increase in the diffusion coefficient of heavy particles with an increase in the concentration of light particles is greater compared to the diffusion of light particles. The above study shows a considerable effect of a mole fraction on the mass dependence of a diffusion coefficient.

D. Effect of density and temperature on mass dependence of diffusion coefficient

The effect of temperature and density on the mass dependence of self-diffusion is also studied. First, the temperature of the system is kept constant, i.e., $T^*=1.23$, and the density is varied from $n^*=0.20-0.80$, in a step of 0.10, while the mass ratio $m_h/m_l=2$ is also fixed. Results obtained for the self-diffusion coefficients and their ratios are reported in Table IV. The diffusion ratio decreases by about 4.5% in going from $n^*=0.20$ to 0.80 for the results obtained from Eq. (33) and this decrease is about 1.6% for the results obtained from Eq. (34). This shows a weak density dependence of the mass dependence of the self-diffusion coefficient. Here, it may be noted that even at low density ($n^*=0.2$) the ratio of the self-diffusion coefficients is far from the classical gas limiting result of $(m_h/m_l)^{1/2}$. The reason for this departure is that our system contains only one heavy particle. In the second case, the density is kept constant, i.e., $n^*=0.50$, and the temperature is varied from $T^*=0.90-4.50$ for a fixed mass ratio, i.e., $m_h/m_l=2$. The self-diffusion coefficients and their ratio obtained so far are given in Table V. The increase in the diffusion ratio is found to increase by 1.35% in going from $T^*=0.9$ to 4.5 for the results obtained from Eq. (33), and for the results from Eq. (34) this increase is about 0.52%. This shows that the mass dependence of the diffusion coefficient on temperature is very weak or negligible. Thus it is found that the inclusion of δ_3 in the calculations does not change the conclusion that the effect of density and temperature on the mass dependence of diffusion is almost negligible, as is evident from Eq. (45).

TABLE III. Self-diffusion coefficients of light and heavy particles for different value of concentration of light particles and for different values of mass ratio K $(=m_h/m_l)$.

	Mass ratio							
	$K=2$		$K=8$		$K=16$		$K=24$	
Concentration	$D^*(m_l)$	$D^*(m_h)$	$D^*(m_l)$	$D^*(m_h)$	$D^*(m_l)$	$D^*(m_h)$	$D^*(m_l)$	$D^*(m_h)$
0.3	0.060	0.052	0.050	0.027	0.048	0.021	0.048	0.019
0.4	0.61	0.054	0.053	0.031	0.051	0.025	0.051	0.024
0.5	0.063	0.055	0.056	0.035	0.054	0.030	0.054	0.029
0.6	0.064	0.057	0.058	0.040	0.057	0.035	0.057	0.034
0.7	0.065	0.058	0.061	0.044	0.060	0.041	0.060	0.040
0.8	0.067	0.060	0.064	0.050	0.063	0.046	0.063	0.045
0.9	0.068	0.062	0.067	0.054	0.067	0.052	0.066	0.051
~1.0	0.070	0.064	0.070	0.060	0.070	0.058	0.070	0.057

TABLE IV. Values of self-diffusion coefficients of light and heavy particles for different values of n^* at $T^*=1.23$ for $m_h/m_l=2$.

n^*	$D_2^*(m_l)$	$D_1^*(m_l)$	$D_2^*(m_h)$	$D_1^*(m_h)$	$\frac{D_2^*(m_l)}{D_2^*(m_h)}$	$\frac{D_1^*(m_l)}{D_1^*(m_h)}$
0.20	0.532	0.476	0.462	0.417	1.149	1.140
0.30	0.357	0.316	0.311	0.279	1.146	1.132
0.40	0.270	0.236	0.236	0.210	1.143	1.124
0.50	0.210	0.181	0.184	0.162	1.140	1.116
0.80	0.094	0.079	0.083	0.073	1.130	1.088

VI. SUMMARY AND CONCLUSIONS

In the present paper we have studied the mass dependence of the self-diffusion coefficient of heavy particles in an isotopic fluid. In this study we have used third-order Mori coefficient δ_3, which was not included in the earlier study. Determination of δ_3 requires frequency sum rules of VAC function up to sixth order, hence we derived an expression for the sixth sum rule of the VAC function for a two-component system. The static pair correlation function $g(r)$ required for calculations is obtained by using Sung and Chandler's method based upon optimized cluster theory. The frequency sum rules, up to sixth order, are numerically evaluated for an isotropic fluid in which all particles are interacting via the same LJ potential and the numerical values of the sum rules so obtained are used to evaluate the Mori coefficients. Self-diffusion coefficient of heavy and light particles are evaluated within Mori's memory-function formalism using the Gaussian memory function. The mole fraction and thermodynamic state dependence of the mass dependence of the self-diffusion coefficient are also studied.

Our values of the Mori coefficients and the self-diffusion coefficient, for a system consisting of a single heavy particle in the fluid of light particles, are found to be in good agreement with MD results. It has also been found that the ratio of the self-diffusion coefficients of a heavy particle to those of a light particle assumes a constant value after mass ratio $\geqslant 25$ at any density and temperature, which is in agreement with earlier predictions and supported by the MD simulations. Thus it is concluded that higher-order sum rules have no significant effect on the mass dependence of the self-diffusion coefficient. It is also found that the mole fraction of the light particles has a significant effect on the mass dependence of the self-diffusion coefficient, whereas the density and temperature dependence of mass dependence is very weak.

TABLE V. Values of self-diffusion coefficients of light and heavy particles for different values of T^* with $n^*=0.50$ for $m_h/m_l=2$.

T^*	$D_2^*(m_l)$	$D_1^*(m_l)$	$D_2^*(m_h)$	$D_1^*(m_h)$	$\frac{D_2^*(m_l)}{D_2^*(m_h)}$	$\frac{D_1^*(m_l)}{D_1^*(m_h)}$
0.90	0.143	0.130	0.125	0.117	1.138	1.111
1.23	0.210	0.181	0.184	0.162	1.140	1.116
1.90	0.320	0.270	0.280	0.241	1.142	1.120
2.50	0.409	0.340	0.358	0.303	1.143	1.122
3.46	0.540	0.431	0.472	0.394	1.144	1.125
4.50	0.673	0.546	0.588	0.484	1.144	1.126

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APPENDIX

Since very little information is available about the quadruplet correlation function, we simplify it using the low-order decoupling approximation as given below. The expression for the quadruplet contribution to C_6 is

$$C_{64}=\frac{n^3}{m^3}\int\int\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 g_4(r_1,r_2,r_3)U_{1x\alpha}U_{2x\beta}U_{3\alpha\beta}. \tag{A1}$$

This can be equivalently written as

$$C_{64}=\frac{1}{m^3}\sum_{k\neq l\neq m\neq 1}\left\langle\frac{\partial^2 U_{1k}}{\partial r_{1x}\partial r_{1\alpha}}\frac{\partial^2 U_{1l}}{\partial r_{1x}\partial r_{1\beta}}\frac{\partial^2 U_{1m}}{\partial r_{1\alpha}\partial r_{1\beta}}\right\rangle. \tag{A2}$$

Since there is no direct coupling between the atoms labeled by *k*, *l*, and *m*, we approximate Eq. (A2) as

$$C_{64}=\frac{1}{m_l^3}\sum_{k,l,m}\left\langle\frac{\partial^2 U_{1k}}{\partial r_{1x}^2}\right\rangle\left\langle\frac{\partial^2 U_{1l}}{\partial r_{1x}^2}\right\rangle\left\langle\frac{\partial^2 U_{1m}}{\partial r_{1x}^2}\right\rangle. \tag{A3}$$

It may be noted that once the correlation between *k*, *l*, and *m* is neglected, only $\alpha=\beta=x$ contributes in Eq. (A3). Finally, Eq. (A3) can be written as

$$C_{64}=\left(\frac{1}{m^3}\sum_{k\neq 1}\left\langle\frac{\partial^2 U_{1k}}{\partial r_{1x}^2}\right\rangle\right)^3=(C_2)^3. \tag{A4}$$

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