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Mass dependence of self-diffusion in isotopic fluids

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Abstract. By using Mori memory function formalism we have derived a simple relation for the mass dependence of self-diffusion of a particle in an isotopic fluid. It has been shown that the self-diffusion coefficient of a massive particle for a very large mass ratio (≥ 25) has a unique value at a given density and temperature which is $1/\sqrt{2}$ times the self-diffusion coefficient of the fluid. The prediction of the formula has been supported by the recent molecular dynamics data on Lennard-Jones fluids. We have also studied the effect of density and temperature on the mass-dependent self-diffusion coefficient. It is found that the ratio of self-diffusion coefficient of the heavy particle to that of the fluid is weakly dependent on thermodynamic state of the fluid.

1. Introduction

In recent years there has been considerable interest shown in studying the effect of variation in mass and/or size of particles on the transport coefficients of binary fluid mixtures. Such investigations have been possible only due to computer simulation and theoretical studies in which these parameters can be changed independently of each other. Very recently, molecular dynamics (MD) simulations has been performed by Nuevo, Morales and Heyes [1] in order to study the mass dependence of the self-diffusion coefficient of a single heavy particle in a fluid, for mass ratios ranging from 1 to 50 for Lennard-Jones (LJ) and Weeks–Chandler–Anderson (WCA) fluids. They showed that the self-diffusion coefficient of a Brownian particle with mass ratio more than 25 reaches a thermodynamic limit depending neither on its mass nor on the number of particles of solvent. For smaller mass ratios their results confirm the weak dependence of the self-diffusion observed in previous findings by computer simulation [2–5] and from theory [6, 7]. This weak dependence of the self-diffusion is contrary to the prediction of dilute-gas results where it is known that it varies as the square root of the mass. The computer simulation carried out [5] for an equimolar system of LJ isotopes led to the relation

$$\frac{D(m_B)}{D(m)} = \left(\frac{m_B}{m}\right)^{-\mu} \quad (1)$$

where m and m_B are the masses of the solvent and of the species whose mass is varied. $D(m)$ represents the self-diffusion coefficient of the species with mass m . The exponent μ has been found to vary from 0.06 to 0.1. Although from MD simulations [3] and theory [6] within the Mori memory function formalism one can predict the weak mass

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dependence of the self-diffusion, relation (1) has been found to be valid only roughly. These studies are based on the evaluation of Mori's coefficients (or frequency sum rules) for the velocity autocorrelation function by using a Gaussian form of the memory function. Mori's coefficients were evaluated using MD simulations and by deriving microscopic expressions for them. The analytical expressions have the advantage that one can derive a relation for the mass dependence of the self-diffusion coefficient from them. Finding such a relation is very much desired, especially in the context of the recent findings of a unique value for the self-diffusion of massive Brownian particles, and this thus forms one of the aims of the present work.

In the past all the studies [1, 3, 6] of the mass dependence of the self-diffusion coefficient of a single heavy particle in a fluid have been made for only one thermodynamic state; therefore its dependence is not known as a function of density and temperature. In the present work, by using our theoretical procedure, we study it for different densities and temperatures. It is found that the ratio of self-diffusion coefficients of a heavy particle to that of the fluid is weakly dependent on density and temperature, and the variation is found to be at most of the order of 10% for the densities and temperatures investigated here. Here, it may be noted that in real fluid mixtures/colloidal solutions, the mass, size and interaction energies of lone Brownian particles change simultaneously. So, our work is useful only in predicting the mass dependence of the self-diffusion of a particle. However, the theory can easily be extended for studying the effects of all other parameters affecting the self-diffusion of the particle.

The organization of the paper is as follows. In section 2 we present the theory. In section 3 the calculation and results are presented. The work is concluded in the last section.

2. Theory

The Green-Kubo expression which relates [8] the self-diffusion coefficient to the normalized velocity autocorrelation function $\phi(t)$ is given as

$$D = \frac{k_B T}{m} \int_0^{\infty} \phi(t) dt \quad (2)$$

where k_B , T and m are the Boltzmann constant, temperature and mass of the system, respectively. Exact calculation of $\phi(t)$ is not yet possible as that involves the solution of a complicated many-body problem. However, it is shown by Mori [9] at the microscopic level that $\phi(t)$ satisfies the equation

$$\frac{d\phi(t)}{dt} + \int_0^t M(t-\tau)\phi(\tau) d\tau = 0 \quad (3)$$

where $M(t)$ is a memory function involving the Liouville and projection operators, and plays a key role in the study of the dynamics of fluids. The microscopic calculation of the memory function is now possible by using mode-coupling theory [10] combined with microscopic evaluation [11] of the binary collision contribution to the memory function. On the other hand one can propose phenomenological forms for the memory function preserving a number of properties of the time correlation functions. Such a procedure [12] has been exploited by many workers to study transport [13-16] and dynamical properties [13, 17] of the fluid. In fact very recently we have provided a theoretical basis for such an approach by deriving [18] a hyperbolic secant memory function from the Mori equation of motion. Other forms of the memory functions which have been frequently used in the literature are the Gaussian and a simple exponential. All these phenomenological forms of the memory

function can in general be written in the form

$$M(t) = K_1 F(\sqrt{K_2 t}) \quad (4)$$

where $F(x)$ is some functional form of the memory function (say Gaussian), and K_1 and K_2 are Mori coefficients of first and second order. These Mori coefficients are related to the frequency sum rules of the velocity autocorrelation function by

$$K_1 = V_2 \quad (5a)$$

$$K_2 = V_4/V_2 - V_2 \quad (5b)$$

where V_2 and V_4 are second- and fourth-order sum rules of the normalized velocity autocorrelation function. Taking the Laplace transform of equation (3) and using equation (2) we obtain

$$D = \frac{k_B T}{m} \frac{1}{\tilde{M}(0)} \quad (6)$$

where $\tilde{M}(0)$ is the zero-frequency Laplace transform of the memory function. Using equation (4) for the memory function we obtain

$$D = C \frac{k_B T}{m} \frac{\sqrt{K_2}}{K_1} \quad (7)$$

where

$$C^{-1} = \int_0^\infty F(x) dx. \quad (8)$$

For a two-component system in which the two species differ only in their masses, implying that they interact via the same intercalation potential, the Mori coefficients will be functions of only the masses for a given density and temperature. Therefore, we write

$$D(m) = C \frac{k_B T}{m} \frac{\sqrt{K_2(m)}}{K_1(m)} \quad (9)$$

and

$$D(m_B) = C \frac{k_B T}{m_B} \frac{\sqrt{K_2(m_B)}}{K_1(m_B)}. \quad (10)$$

These provide the ratio of self-diffusion coefficients as

$$\frac{D(m)}{D(m_B)} = \frac{m_B}{m} \frac{K_1(m_B)}{K_1(m)} \sqrt{\frac{K_2(m)}{K_2(m_B)}} \quad (11)$$

which is independent of C and hence does not depend on the functional form of the memory function. From equation (11) we also see that mass dependence of the self-diffusion coefficient depends only on the mass dependence of the Mori coefficients or frequency sum rules. The expressions for the sum rules for a system having only one heavy particle have already been derived by us [6] and these are given as

$$V_2(m) = \frac{n}{m} \int dr g(r) U_{xx} \quad (12)$$

$$V_2(m_B) = \frac{n}{m_B} \int dr g(r) U_{xx} = \frac{m}{m_B} V_2(m) \quad (13)$$

$$V_4(m) = 2I_1 + \frac{V_2^2(m)}{2} \quad (14)$$

$$V_4(m_B) = \frac{I_1 m}{m_B} \left(1 + \frac{m}{m_B}\right) + \frac{V_2^2(m_B)}{2} \quad (15)$$

where

$$I_1 = \frac{n}{m^2} \int dr g(r) U_{x\alpha}^2 \quad (16)$$

and

$$U_{x\alpha} = \frac{\partial^2 U(r)}{\partial r_x \partial r_\alpha} \quad (17)$$

where α runs over x , y and z coordinates. In the above equations $g(r)$, $U(r)$ and n are the static pair correlation function, interatomic potential and number density of the fluid, respectively. While deriving these sum rules it is assumed that particles interact via mass-independent interaction potentials. The second term in equations (14) and (15) represents the three-body contribution expressed in terms of the two-body contribution by using a low-order decoupling approximation [7]. The exact expression for the triplet contribution to the fourth sum rule is given in the appendix. Using the above equations in equations (5) and (11) we obtain a relation for the mass dependence of the self-diffusion coefficients of the two species:

$$\frac{D(m)}{D(m_B)} = \sqrt{\frac{2I_1/V_2(m) - \frac{1}{2}V_2(m)}{(I_1/V_2(m))(1 + m/m_B) - (m/2m_B)V_2(m)}} \quad (18)$$

Neglecting the second part of the numerator and denominator (small compared with the first term), we obtain

$$\frac{D(m_B)}{D(m)} = \sqrt{\frac{(1 + m/m_B)}{2}} = \sqrt{\frac{K_2(m)}{K_2(m_B)}} \quad (19)$$

In the limiting cases where m approaches m_B we find $D(m) = D(m_B)$, and when m_B is very large we find that $D(m_B) = D(m)/\sqrt{2}$. This implies that however large the mass of the massive Brownian particle, the diffusion has a unique value for a given density and temperature of the fluid. This is a new and important result. The result is independent of the dimensionality of the system and of the nature of the interaction potential.

3. Calculations and results

In order to study the mass dependence of the self-diffusion of a system at various densities and temperatures using the expression derived in the above section, we need to evaluate only V_2 and I_1 for a given density and temperature. The results for these can be obtained from our earlier work [14] in which we have presented the results for the sum rules of the velocity autocorrelation (VAC) function for Kr fluid. In table 1, we now present results for V_2 and I_1 for LJ fluids in reduced units for various n^* ($=n\sigma^3$) and T^* ($=K_B T/\epsilon$), where σ and ϵ are two parameters for LJ fluids. These results are useful as one can calculate self-diffusion coefficients for any mass ratio using equation (16). Before studying the mass dependence of self-diffusion we would like to test the approximations used in deriving equation (17). An approximation used in describing the three-body contribution to V_4 is tested by calculating it using the Kirkwood superposition approximation and comparing the results in table 1 with the approximation used in the present work. It can be seen from the table that a reasonably good agreement is achieved for all the densities and temperatures investigated here. Here, it may be noted that the use of the superposition approximation

Table 1. Values of the integrals V_2 and I_1 in units of $\epsilon/m\sigma^2$ and $(\epsilon/m\sigma^2)^2$, respectively, for various densities and temperatures. V_{43} is the triplet contribution obtained using the superposition approximation.

T^*	n^*	V_2	I_1	V_{43}	$V_2^2/2$
0.90	0.75	225.14	83 265.00	32 054.37	25 344.10
1.23	0.20	53.90	24 087.37	1647.00	1452.65
1.23	0.30	80.21	36 028.12	3705.75	3216.80
1.23	0.42	111.01	50 439.37	6588.00	6161.63
1.26	0.50	136.68	63 821.24	9882.00	9340.34
1.28	0.60	179.03	86 261.61	17 705.25	16 025.51
1.20	0.70	228.44	108 496.10	30 469.49	26 091.77
1.16	0.84	345.86	173 346.70	78 644.23	59 810.99
1.81	0.20	55.18	33 145.87	1647.00	1522.65
1.81	0.30	119.99	73 497.36	7411.50	7199.24
1.83	0.50	162.99	102 525.70	13 587.75	13 282.23
1.83	0.60	216.89	138 142.10	24 704.99	23 519.98
1.81	0.70	290.04	191 257.80	46 527.74	42 061.07
1.90	0.80	402.33	290 283.70	95 114.23	80 935.41
2.57	0.20	62.24	50 439.37	2058.75	1937.08
2.47	0.40	139.89	112 407.70	9882.00	9784.00
2.48	0.50	192.50	158 523.70	18 940.50	18 528.75
2.50	0.60	261.16	222 139.10	35 410.49	34 102.98
2.56	0.74	179.67	369 133.80	88 937.98	16 140.60
2.50	0.80	473.56	437 072.50	128 054.20	112 128.60
3.46	0.50	234.21	255 902.60	27 175.49	27 427.69
4.50	0.50	273.35	361 928.20	36 645.74	37 361.36

makes no difference to the result for the sum rules of the VAC function, as judged [15] by the comparison with computer simulation results.

In order to test the approximation used in deriving equation (17) from equation (16), we plot $(D(m)/D(m_B))\sqrt{2/(1+m/m_B)}$ against m_B/m in figures 1, 2 and 3 for a various densities at temperatures $T^* = 1.23, 1.84$ and 2.5 , respectively. In these figures the horizontal line represents the prediction of equation (17) whereas all the other symbols represent results obtained using equation (16). Thus in the figures we have shown the deviation of the results for equation (16) from those for equation (17), and also the dependence of the mass dependence of the self-diffusion coefficient on the density and temperature of the fluid. It is seen from the figures that for all the thermodynamic states the deviation from 1 increases with the increase in mass, and it becomes almost constant for mass ratios greater than 25. This could easily be seen to follow from equation (16) by noting that the second part in the denominator becomes negligible with increase in mass ratio whereas the numerator is independent of the mass of the Brownian particle. It can also be seen from the figures that the deviation of the results for equation (16) from those for equation (17) increases with the increase in density and decrease in temperature. However, for all the densities, temperatures and mass ratios studied here this deviation is not more than 10%. Thus we are led to conclude that the mass dependence of self-diffusion is weakly dependent on the thermodynamic state and deviates slightly from that predicted from equation (17).

In figure 4 we represent the results on the ratio of the self-diffusion coefficient of the Brownian particles to that of the fluid as a function of the mass ratios at $T^* = 0.9$ and $n^* = 0.75$ where MD simulations have been performed. In figure 4 the solid line

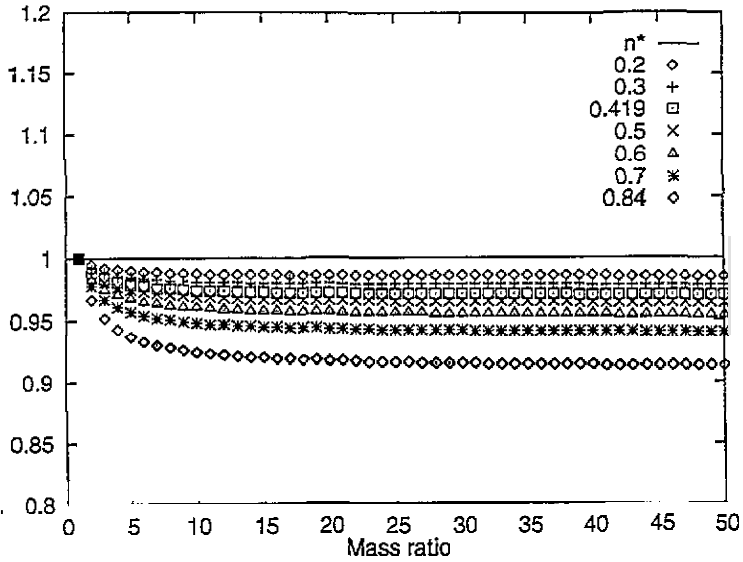


Figure 1. The variation of $(D(m)/D(m_B))\sqrt{2/(1+m/m_B)}$ with m_B/m for $T^*=1.23$. The solid line represents the predictions from equation (17). All other symbols represent results obtained using equation (16) at the various densities given in the figure.

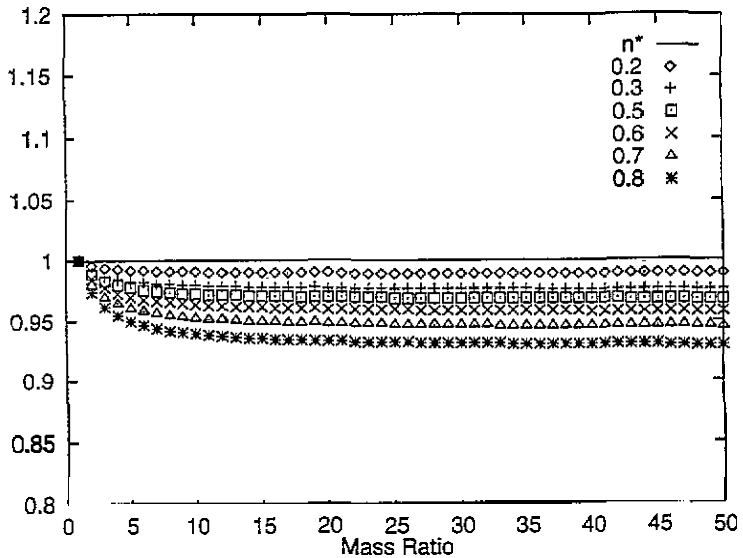


Figure 2. As figure 1 but at $T^* = 1.84$.

represents the prediction from equation (17), whereas squares represent results obtained using equation (16). The MD results obtained using Mori's approach are represented by the diamond-shaped symbols whereas MD results obtained using the mean square displacement (MSD) method are represented by crosses. It can be seen from figure 4 that the prediction of equation (16) agrees well with the MD simulation results obtained using Mori's approach. However, MD results obtained by using the MSD method deviate more from the prediction of theory. But here it must be noted that the MD simulations for the LJ system are for a

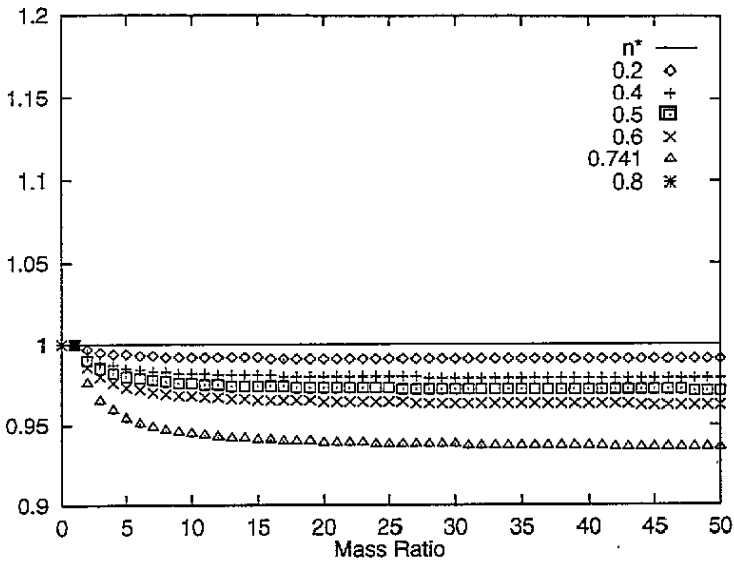


Figure 3. As figure 1 but at $T^* = 2.5$.

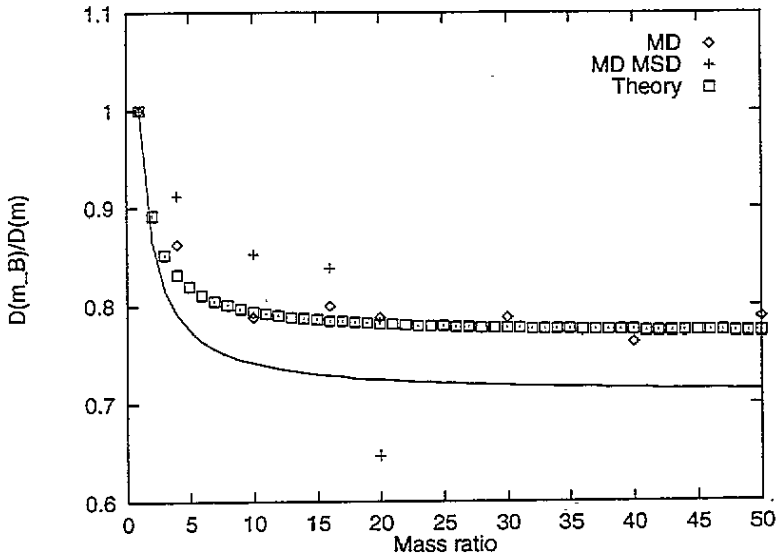


Figure 4. The variation of $D(m_B)/D(m)$ with m_B/m for $T^* = 0.9$ and $n^* = 0.75$. The solid line represents the prediction from equation (17) whereas squares represent the results obtained using equation (16). The MD MSD results are shown as crosses.

small size ($N = 256$) of system and involve uncertainties as has been pointed out by Nuevo *et al* [1]. For example the value of the reduced self-diffusion coefficient of the WCA fluid for $m_B/m = 10$ changes [1] from 0.060 to 0.085 when the number of particles in the system is changed from 108 to 2916. Thus we see that the reasons for the deviations of MD MSD results from the present results may lie in the simulations of the small-size systems. Such a size dependence of Mori's coefficients has been found to be very weak.

4. Summary and conclusions

By using Mori's memory function formalism we have derived a simple relation for the mass dependence of the self-diffusion coefficient of a heavy particle in a fluid. We have found that for a mass ratio greater than 25 the self-diffusion coefficient of a heavy particle becomes almost constant. This agrees with the prediction of recent MD simulations. We have also studied the density and temperature dependences of the mass-dependent self-diffusion coefficients. It is noted that the ratio of the self-diffusion coefficient of a heavy particle to that of the fluid is weakly dependent on the thermodynamic state whatever the mass of the heavy particle.

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Appendix

The triplet contribution to the fourth sum rule of the VAC function for a particle with mass m is given by

$$V_{43} = \frac{n^2}{m^2} \int \int d\mathbf{r} d\mathbf{r}_1 g_3(\mathbf{r}, \mathbf{r}_1) U_{x\alpha} U_{1x\alpha} \quad (\text{A1})$$

where $g_3(\mathbf{r}, \mathbf{r}_1)$ is the static triplet correlation function. The subscript 1 on U implies that the argument of the potential is changed from r to r_1 . The expression for the triplet contribution to the fourth sum rule for a heavy particle can be obtained from equation (A1) by replacing m by m_B . For the evaluation of V_{43} we have used a superposition approximation given by

$$g_3(\mathbf{r}, \mathbf{r}_1) = g(r)g(r_1)g(|\mathbf{r} - \mathbf{r}_1|). \quad (\text{A2})$$

The rest of the details for the numerical calculations are in [14].

References

- [1] Nuevo M J, Morales J J and Heyes D M 1995 *Phys. Rev. E* **51** 2026
- [2] Alder B J, Alley W E and Dymond J H 1974 *J. Chem. Phys.* **61** 1415
- [3] Toxvered S 1985 *Mol. Phys.* **56** 1017
- [4] Kaddour F O and Barrat J L 1992 *Phys. Rev. A* **45** 2308
- [5] Bearman R J and Jolly D L 1981 *Mol. Phys.* **44** 665
- [6] Tankeshwar K 1991 *Phys. Chem. Liq.* **24** 21
- [7] Tankeshwar K and Kaddour F O 1992 *J. Phys.: Condens. Matter* **4** 3349
- [8] Hansen J P and McDonald I R 1986 *Theory of Simple Liquids* (London: Academic)
- [9] Mori H 1965 *Prog. Theor. Phys.* **33** 423
- [10] Gotze W and Lucke M 1976 *Phys. Rev. B* **13** 3825; 1975 *Phys. Rev. A* **11** 2173
- [11] Pathak K N, Ranganathan S and Johnson R E 1994 *Phys. Rev. E* **50** 1135
- [12] Martin P C and Yip S 1968 *Phys. Rev.* **170** 151
- [13] Boon J P and Yip S 1980 *Molecular Hydrodynamics* (New York: McGraw-Hill)
- [14] Tankeshwar K, Pathak K N and Ranganathan S 1987 *J. Phys. C: Solid State Phys.* **20** 5749
- [15] Tankeshwar K, Pathak K N and Ranganathan S 1990 *J. Phys.: Condens. Matter* **2** 5891
- [16] Heyes D M and Powles J G 1990 *Mol. Phys.* **71** 781
- [17] Tankeshwar K, Dubey G S and Pathak K N 1988 *J. Phys. C: Solid State Phys.* **21** L811
- [18] Tankeshwar K and Pathak K N 1995 *J. Phys.: Condens. Matter* **7** 5729