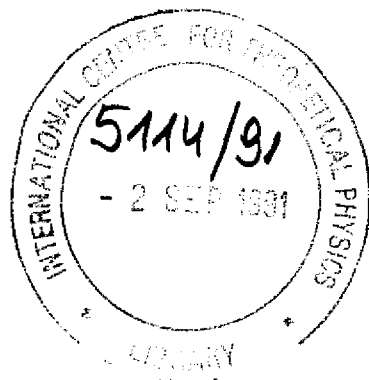


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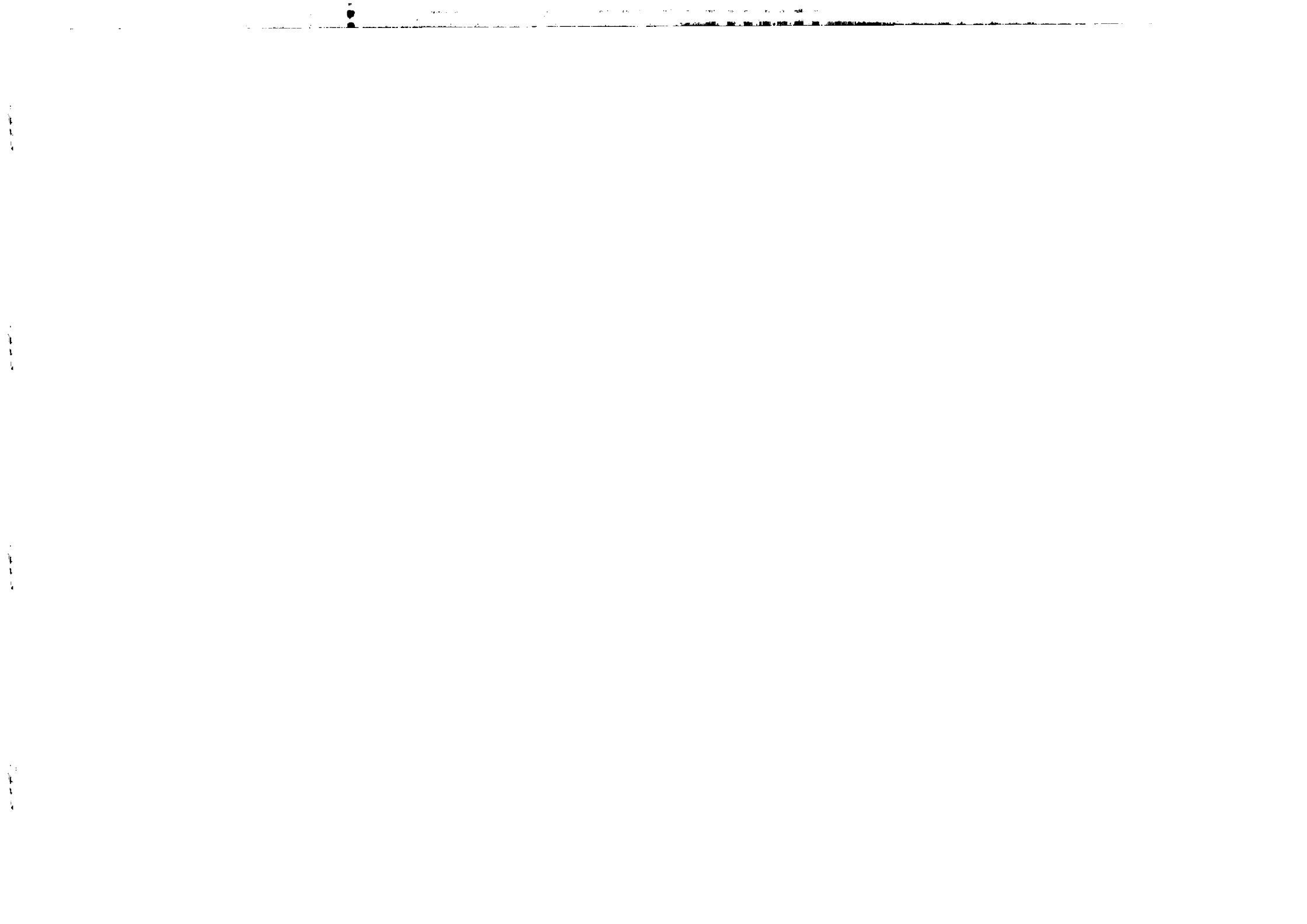


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TRACER DIFFUSION IN A SIMPLE LIQUID

K. Tankeshwar* and F. Ould-Kaddour**

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ABSTRACT

A simple model is used to calculate the tracer diffusion in a Lennard-Jones tracer-solvent system. The influence of the size ratio between tracer and solvent, and of their mass ratio on the tracer diffusivity is investigated. The adopted model, proposed by Tankeshwar et al., is based on the idea, put forward by Zwanzig, of separating the configurational space of fluid system into a vibrational part and a structural part. The results offer an interpretation of the molecular dynamics data showing a positive deviation from Stokes-Einstein behaviour for small size of the tracer. The deviation is explicitly related to the length parameter of tracer-solvent interaction. The calculated values of the tracer diffusion coefficients for a large range of its size and mass values are quite satisfactory as judged by comparison with simulation results.

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1. INTRODUCTION

In binary fluid mixtures and molten salts the two species have generally different diffusivity. This difference in the diffusivity can be attributed to the size ratio between the two species, their mass ratio, and to the interaction between them. From experiments on real systems it is difficult to investigate the separate influence of these parameters as they are changed simultaneously. Molecular dynamics (MD) simulation, on the other hand allows a systematic investigation of the way each of them affects the diffusivity. Recently, one of us has performed an extensive MD simulation for a tracer - solvent system[1] to investigate the influence of the size ratio between tracer and solvent molecules, their mass ratio on a small tracer diffusivity. The system was made of 100 solvent molecules and 8 solute molecules interacting through Lennard-Jones potentials. The main features of the MD runs for the influence of size ratio on tracer diffusion is a strong positive deviation from the Stokes-Einstein (SE) relation, which provides the following relation[1] for the the tracer diffusion

$$\frac{D_2}{D_1} = \frac{\sigma_1}{\sigma_2}, \quad (1)$$

where D and σ are the diffusion coefficient and molecular diameter. The subscripts 1 and 2 represent, respectively the solvent and solute molecules. It has been found that D_2 increases as the tracer size decreases then levels off at a size independent value. This levelling off takes place for a size ratio σ_1/σ_2 between 5 and 10; so for $\sigma_2 < 0.1\sigma_1$ the tracer behaves essentially as a pointlike particle in the external potential created by the solvent molecules. On the other hand, for the mass dependence of the diffusion constant, it has been found that D_2 increases considerably when the mass of the tracer is very small compared to the solvent molecule's mass. The enhancement in D_2 increases with decrease in the size ratio. This behaviour is contrary to the earlier prediction [2] of the weak mass dependence of the diffusion constant. The aim of the present work is to investigate theoretically the influence of the size and mass of the small tracer on its diffusivity.

As is well known, the self-diffusion coefficient is a macroscopic manifestation of the autocorrelations of the single particle velocity in time. Much progress in understanding the dynamics of dense gases and liquids has been based on the Mori-Zwanzig formalism, using phenomenological Ansatzes and mode-coupling approximations for the memory functions. The approach is extensively discussed by Boon and Yip[3] and by Hansen and McDonald[4]. This line of approach has been followed[5,6] in theoretical work on the mass dependence of the self diffusion coefficient of an isotope in a LJ system with satisfactory results as judged by comparison with computer simulation data; in particular, when the mass of the tracer was higher than that of the solvent molecule's mass. However, no similar studies have as yet been reported on the tracer self-diffusion constant for sufficiently small size and mass of the tracer molecules. Therefore, reasons for the large deviation of the tracer diffusivity from the SE relation is not yet understood.

In the computer simulation runs for the tracer diffusion, it has been suggested that for small tracer the diffusion processes involve the jumping motion in a locally nearly frozen environment. Models of liquid-state diffusion through jumping processes have also been developed for simple liquids. The model which we use in the present work belongs to this class, since it invokes a combination of vibrational and jumping motions of the particles. It derives from an idea of Stillinger and Weber[7], as developed and exploited by Zwanzig[8] and Mohanty[9] to derive transport coefficients in cold dense fluids directly from the Green-Kubo time correlation formulas. The general picture has been clearly stated in the work of Zwanzig [8]. The model assumes that the configuration space of the many-body system is divided into "cells", each cell being associated with a local minimum on the potential energy hypersurface. Some of these minima correspond to almost crystalline configurations, while others correspond to liquid-like configurations. The configuration of the melt remains in one of these minima, performing approximate harmonic vibrations about it, until it finds a saddle point in the potential energy surface and jumps to another cell. The effects of a cell jump are (i) to rearrange the equilibrium positions of the particles in some subvolume V^* and (ii) to interrupt the oscillations within it, so that the motions in V^* before and after the jump are uncorrelated. Similar ideas have been used by Tankeshwar, Singla and Pathak

[10] to develop a simple model for the calculation of self-diffusion of classical fluids. The model when applied to LJ fluids, one-component plasma and Yukawa fluids, provides good results for the diffusion constant over large ranges of values of system temperature and density, as judged from the comparison with simulation results. Recently, the model has been extended to be applied to the two component molten salt system by Tankeshwar and Tosi [11], and was found to predict successfully the right ratios of self-diffusion coefficients of the two ionic species in superionic conductor and normal melts.

The main result of our application of the above model to a tracer-solvent system is to explicitly relate the difference in self-diffusion coefficients of the tracer of different sizes to the 'partial tracer-solvent' liquid structure factor. The levelling of the tracer diffusion constant at very small sizes is found to appear as a result of its dependence on the tracer-solvent diameter, $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ and not solely on the tracer diameter σ_2 . Our numerical calculations involve the use of pair potential and of pair distribution functions obtained from MD simulations, so that the pair potentials are in fact the essential input. Our calculations are successful in predicting the ratio of self-diffusion coefficients for the tracer of different sizes and masses in agreement with simulation results.

The layout of the paper is briefly as follows. In section 2 we develop the model to be used in the calculation of self-diffusion coefficients. The results are presented and discussed in section 3. Section 4 gives a short summary and some concluding remarks.

2. THEORY

We consider a solvent-solute system consisting of N_1 solvent molecules with mass m_1 and diameter σ_1 and N_2 solute molecules with mass m_2 and diameter σ_2 , in a volume V . The self-diffusion coefficients D_1 and D_2 are given by the Green-Kubo formulas

$$D_1 = \frac{k_B T}{m_1} \int_0^\infty C_1(t) dt \quad (2a)$$

and

$$D_2 = \frac{k_B T}{m_2} \int_0^\infty C_2(t) dt, \quad (2b)$$

where $C_1(t)$ and $C_2(t)$ are the VACF's of solvent and solute molecules. These are, respectively, given by

$$C_1(t) = \frac{1}{N_1} \sum_{i=1}^{N_1} \langle \mathbf{v}_i^{(1)}(t) \cdot \mathbf{v}_i^{(1)}(0) \rangle / \langle (v_i^{(1)})^2 \rangle, \quad (3a)$$

and

$$C_2(t) = \frac{1}{N_2} \sum_{i=1}^{N_2} \langle \mathbf{v}_i^{(2)}(t) \cdot \mathbf{v}_i^{(2)}(0) \rangle / \langle (v_i^{(2)})^2 \rangle, \quad (3b)$$

where $\mathbf{v}_i^{(1)}(t)$ and $\mathbf{v}_i^{(2)}(t)$ are the velocities of the i th solvent and solute molecule at time t , respectively. The angular brackets in eqns.(3) represent the ensemble average.

The realization of Zwanzig's model recalled in section 1 introduces a spectrum of oscillation frequencies to reduce the sum over coordinates in eqn (3) to a sum over normal modes localised in the various subvolumes V^* and having a time dependence of the form $\cos(\omega t)$. One also introduces a waiting time distribution for cell jumps destroying coherence in any subvolume V^* , that we take of the form [10] $\text{sech}(\frac{t}{\tau})$. With these approximation we obtain, in general, for the velocity auto correlation function:

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

We approximate the frequency spectrum by Einstein frequencies ω_1 and ω_2 for solvent and solute molecules, respectively, and correspondingly introduce jumping frequencies τ_1^{-1} and τ_2^{-1} . With this approximations we obtain

$$C_1(t) = \cos(\omega_1 t) \text{sech}\left(\frac{t}{\tau_1}\right) \quad (4a)$$

and

$$C_2(t) = \cos(\omega_2 t) \text{sech}\left(\frac{t}{\tau_2}\right). \quad (4b)$$

Substituting eqns (4) in eqns (2) we obtain expressions for the self diffusion constants given by

$$D_1 = \frac{k_B T}{m_1} \frac{\pi}{2} \tau_1 \text{sech}\left(\frac{\pi}{2} \omega_1 \tau_1\right) \quad (5a)$$

$$D_2 = \frac{k_B T}{m_2} \frac{\pi}{2} \tau_2 \text{sech}\left(\frac{\pi}{2} \omega_2 \tau_2\right). \quad (5b)$$

An advantage of using the same frequencies for all the solvent or solutes molecules is that the parameters $\omega_{1,2}$ and $\tau_{1,2}$ can be estimated from the microscopic sum rules satisfied by the VACF. On comparing the short-time expansion of eqns (4) with the exact short-time expansion of the VACF for solvent and solute molecules, given by

$$C(t) = 1 - C_2(t^2/2!) + C_4(t^4/4!) + \dots, \quad (6)$$

we obtain the following relations

$$\tau_1^{-2} = \frac{C_4^{(1)} - (C_2^{(1)})^2}{4C_2^{(1)}} \quad (7)$$

and

$$\omega_1^2 = \frac{5(C_2^{(1)})^2 - C_4^{(1)}}{4C_2^{(1)}}, \quad (8)$$

where superscript 1 in brackets represents the solvent system. Similar expressions relate ω_2 and τ_2 to the coefficients $C_2^{(2)}$ and $C_4^{(2)}$ in the short-time expansion of $C_2(t)$. As can be seen from eqns (5)-(8), if $C_4 = C_2^2$ then $D = 0$, implying perfect crystalline behaviour. On the other hand, for $C_4 > 5C_2^2$ diffusion is gas-like and no backscattering process is present.

In order to calculate the self-diffusion constants from eqns (5a) and (5b) we need expressions for the sum rules C_2 and C_4 . These are given by the following:

$$C_2^{(1)} = \frac{n_1}{m_1} \int d\mathbf{r} g_{11}(\mathbf{r}) U_{xx}^{11} + \frac{n_2}{m_1} \int d\mathbf{r} g_{12}(\mathbf{r}) U_{xx}^{12} \quad (9)$$

and

$$C_4^{(1)} = \frac{2n_1}{m_1^2} \int d\mathbf{r} g_{11}(\mathbf{r}) (U_{xx}^{11})^2 + \frac{n_2}{m_1} \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \int d\mathbf{r} g_{12}(\mathbf{r}) (U_{xx}^{12})^2 \quad (10)$$

where $C_{4(2)}$ represents the two body contribution to the fourth sum rule. The derivation of the triplet contribution to this sum rule and its simplified form are given in the Appendix. In eqns (9) and (10) n_1 and n_2 are the number density of the solvent and

solute molecules, $g_{11}(r)$ and $g_{12}(r)$ are the partial solvent-solvent and solvent-solute radial distribution functions, $U^{11}(r)$ and $U^{12}(r)$ are the the corresponding pair potentials and the notation

$$U_{\alpha\beta} = \frac{d}{dr_\beta} \left(\frac{dU(r)}{dr_\alpha} \right) \quad (11)$$

has been used, with the convention of summation over repeated Cartesian index α . The second and fourth sum rules for the solute, $C_2^{(2)}$ and $C_4^{(2)}$, follow by interchanging the indices 1 and 2 in eqns (9) and (10). Clearly, each sum rule contains a contribution from like particles and a contribution from unlike particles. The expression (9) and (10) are general and are applicable to any binary system of any partial concentration. However, in the present case we are interested in a system of infinitely dilute solution, where tracer molecules interact very weakly with each other than with the solvent molecules. For such a system the above equations reduce to

$$C_2^{(1)} = \frac{n_1}{m_1} \int dr g_{11}(r) U_{xx}^{11}, \quad (12)$$

$$C_{4(2)}^{(1)} = \frac{2n_1}{m_1^2} \int dr g_{11}(r) (U_{x\alpha}^{11})^2, \quad (13)$$

and

$$C_2^{(2)} = \frac{n_1}{m_2} \int dr g_{12}(r) U_{xx}^{12} \quad (14)$$

$$C_{4(2)}^{(2)} = \frac{n_1}{m_2} \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \int dr g_{12}(r) (U_{x\alpha}^{12})^2. \quad (15)$$

From the above expressions for $C_2^{(2)}$ and $C_{4(2)}^{(2)}$ one finds that these sum rules and hence ω_2 and τ_2 are implicitly related to the solute-solvent diameter $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ through the solvent-solute interaction and $g_{12}(r)$. In the next section we proceed to evaluate these sum rules and hence the self-diffusion coefficients.

3. CALCULATION AND RESULTS

The inputs for the numerical calculation of the frequency sum rules of the VACF are the interatomic potentials and the partial radial distribution functions. We have used the LJ potential adopted by Ould-Kaddour and Barrat [1] in their (MD) work, together with the structure factors that they obtained by simulation. The calculated values of the sum rules for the tracer are given in table 1, for various sizes and mass ratios. The LJ interaction energy ϵ was kept constant for all molecules, and the units of energy, length and mass were respectively ϵ , σ_1 and m_1 . The thermodynamical state of the system is therefore specified by the reduced temperature $T^* = \frac{k_B T}{\epsilon}$ and reduced density $n^* = n\sigma_1^3$.

In the first two sets of data in table 1, The tracer mass is varied for two fixed size ratios $\sigma_2/\sigma_1 = 0.5$ and $\sigma_2/\sigma_1 = 0.1$. The thermodynamic state of the pure solvent was chosen to be near the triple point ($T^* = 0.75, n^* = 0.85$). When reducing the tracer size the total density had to be increased slightly, in order to keep the solvent-solvent radial distribution function and the solvent diffusion coefficient constant. In the third set of data, the tracer size is decreased keeping it mass equal to the solvent mass. The pure solvent was chosen to be a supercritical fluid ($T^* = 2.75, n^* = 0.7$). As stated earlier the total density was slightly increased. The results of $C_4^{(2)}$ includes the triplet contribution which is discussed in the Appendix. From table 1, it can be seen that both C_2 and C_4 are functions of size and mass. The mass dependence of $C_2^{(2)}$ and $C_4^{(2)}$ for a fixed size of tracer can be approximately derived from eqns (14) and (15), yielding the following relations:

$$m_2 C_2^{(2)}(\sigma_2, m_2) = m_1 C_2^{(2)}(\sigma_2, m_1), \quad (16)$$

and

$$m_2 C_{4(2)}^{(2)}(\sigma_2, m_2) = 1/2 m_1 (1 + m_1/m_2) C_{4(2)}^{(2)}(\sigma_2, m_1). \quad (17)$$

On the other hand for a fixed mass the size dependence of $C_2^{(2)}$ and $C_4^{(2)}$ are found to obey the following relations:

$$C_2^{(2)}(\sigma_2, m_2) = (\sigma_{12}/\sigma_1) C_2^{(2)}(\sigma_1, m_2), \quad (18)$$

and

$$C_4^{(2)}(\sigma_2, m_2) = (\sigma_1/\sigma_{12}) C_4^{(2)}(\sigma_1, m_2). \quad (19)$$

The two latter expressions show that for a sufficiently small tracer size $C_2^{(2)}$ and $C_4^{(2)}$ will become almost size independent as $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ acquires almost a constant value for sufficiently small value of σ_2 compared to σ_1 . Therefore, one finds that the sum rules coefficients are explicitly dependent on σ_{12} and hence will be the self-diffusion constant.

The tracer self-diffusion coefficient D_2 is calculated from eqn (5b), using the numerical values for the sum rules from table 1. The mass dependence of the self diffusion is plotted in figures (1) and (2), together with the simulation data, for the two different size ratios studied. From fig. (1) and (2) it can be seen that the ratio $D_2(m_2)/D_2(m_1)$ start to increase rapidly with decreasing m_2 which is in agreement with simulation results. This increase is found to be more pronounced for diameter ratio 0.1 than for 0.5, which is also in agreement with the simulation results. In our model this fact is related to the relative increase in jumping frequencies for the two diameter ratios. Overall, we find that our results are in better agreement with the simulation data for the tracer size 0.1 than for 0.5. The results of our model start departing from the simulation results for the size ratio equal to 0.5 when the mass of the tracer is lower than 30 percent of that of solvent particles. However, for very small mass ratio, our model predict a sharp increase in the diffusion constant. The departure of our results from the simulation data may indicate the limitations of our model in which highly correlated motions are not fully accounted for.

The results for the size dependence of $D_2(\sigma_2)$ are given in figure (3). The computer simulation results and the prediction of SE relation (eqn. (1)) are also given in the figure for comparison. From fig. 3 it can be seen that our model explains the levelling of the ratio D_2/D_1 for diameter ratio σ_2/σ_1 less than 0.1 in agreement with the simulation results. This saturation effect takes place in our model as a result of the levelling off in the jumping frequency below a size ratio of 0.1, as can be seen from table 1. As has been stated earlier the sum rules coefficients $C_2^{(2)}$ and $C_4^{(2)}$ and hence jumping frequencies are related to σ_{12} which itself levels off. Therefore, in order to have an empirical relation between ratios D_2/D_1 and σ_{12}/σ_1 , we have plotted $\log(D_2/D_1)$ vs $\log(\sigma_1/\sigma_{12})$ in fig. (4). The data

points in fig. 4 lies almost on a straight line which yields the relation

$$\frac{D_2}{D_1} = \left(\frac{\sigma_1}{\sigma_{12}}\right)^{2.88}. \quad (20)$$

The above empirical relation may be useful in further investigations and in modification of the Stokes-Einstein relation for the tracer diffusion.

4. SUMMARY AND CONCLUDING REMARKS

We have used a simple model for the diffusional dynamics in tracer-solvent system and related its vibrational and jumping frequency parameters to sum rules describing the short-time behaviour of velocity autocorrelations, in order to derive expressions for the self-diffusion coefficients of the two species which explicitly contain pair potentials and pair distribution functions. These expressions have allowed us to study the separate effects of the mass and size of the tracer molecule on its diffusivity. The numerical values that we have obtained are quite satisfactory for the ratio of tracer diffusivity of very different sizes and masses. In our model the difference in the self diffusivity of the tracer of the different sizes and masses arises due to the difference in jumping frequencies which are related to tracer-solvent liquid structure. The levelling off the diffusivity for a very small size of tracer takes place due to its dependence on the solvent-solute diameter σ_{12} . This levelling off is contradictory to the predictions of the SE relation (eqn(1)). Therefore, we expect that our work will be useful in understanding and in modification of the SE relation in views of the simulation results[1].

ACKNOWLEDGEMENTS

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APPENDIX

The triplet contribution to the fourth sum rule $C_4^{(1)}$ is obtained from

$$C_{4(3)}^{(1)} = \frac{1}{m_1^2} \sum_{j \neq k \neq 1} \left\langle \frac{d^2 U(r_{1j})}{dr_{1z} dr_{1\alpha}} \frac{d^2 U(r_{1k})}{dr_{1z} dr_{1\alpha}} \right\rangle, \quad (A.1)$$

where the particle 1 is taken to be a solvent particle, while particles j and k may be of either species. Separating out the various choices of particles j and k and writing the averages in terms of distribution functions, we obtain

$$\begin{aligned} C_{4(3)}^{(1)} &= \frac{n_1^2}{m_1^2} \int \int dr_1 dr_2 g_3(r_1, r_2) U_{1z\alpha}^{11} U_{2z\alpha}^{11} \\ &+ \frac{n_2^2}{m_1^2} \int \int dr_1 dr_2 g_3(r_1, r_2) U_{1z\alpha}^{12} U_{2z\alpha}^{12} \\ &+ \frac{2n_1 n_2}{m_1^2} \int \int dr_1 dr_2 g_3(r_1, r_2) U_{1z\alpha}^{11} U_{2z\alpha}^{12}, \end{aligned} \quad (A.2)$$

where $g_3(r_1, r_2)$ are the respective triplet distribution functions and $U_{1z\alpha} = \frac{d^2 U(r_1)}{dr_{1z} dr_{1\alpha}}$, $U_{2z\alpha} = \frac{d^2 U(r_2)}{dr_{2z} dr_{2\alpha}}$. The expression for $C_{4(3)}^{(2)}$ is obtained from eqn (A.2) by interchanging 1 and 2 in the superscripts.

The integrals in eqn(A.2) can only be evaluated by using an approximate closure for the triplet correlation functions. However, a simple decoupling approximation on eqn (A.1), which amounts to neglecting the correlations between particles j and k , has been suggested in earlier work for static quadruplet correlation function in simple Lennard-Jones fluids [12]. Using similar ideas we approximate eqn (A.1) as

$$C_{4(3)}^{(1)} = \frac{1}{2m_1^2} \sum_{j \neq 1} \left\langle \frac{d^2 U(r_{1j})}{dr_{1z} dr_{1\alpha}} \right\rangle \sum_{k \neq 1} \left\langle \frac{d^2 U(r_{1k})}{dr_{1z} dr_{1\alpha}} \right\rangle. \quad (A.3)$$

Separating out the possible choices of the particles j and k to solute or solvent particles, we obtain

$$C_{4(3)}^{(1)} = \frac{1}{2} (C_2^{(1)})^2. \quad (A.4)$$

We use eqn (A.4) to estimate the triplet correlation contribution to the fourth sum rule.

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Table 1 : Sum rules coefficients $C_2^{(2)}$ and $C_4^{(2)}$ of the VACF for tracer molecules as a function of size ratio σ_2/σ_1 , and mass ratio m_2/m_1 . Also given is the jumping frequency from subvolumes τ^{-1} .

T^*	n^*	σ_2/σ_1	m_2/m_1	$C_2^{(2)}$	$10^{-5} * C_4^{(2)}$	τ^{-1}
0.75	0.90	1.0	1.0	296.65	2.47	11.63
0.75	0.90	0.5	1.0	244.89	4.27	19.23
0.75	0.90	0.5	0.7	349.84	7.50	23.26
0.75	0.90	0.5	0.5	480.36	12.59	23.26
0.75	0.90	0.5	0.4	612.23	19.25	23.26
0.75	0.90	0.5	0.3	816.30	32.02	23.26
0.75	0.90	0.5	0.1	2406.5	254.8	45.45
0.75	0.90	0.5	0.05	4793.8	943.7	62.50
0.75	0.92	0.1	1.0	150.45	5.52	29.41
0.75	0.92	0.1	0.7	204.09	9.0	32.26
0.75	0.92	0.1	0.5	286.28	15.60	35.71
0.75	0.92	0.1	0.4	362.57	23.03	38.46
0.75	0.92	0.1	0.25	575.20	51.38	45.45
0.75	0.92	0.1	0.1	1497.10	297.1	66.66
0.75	0.92	0.1	0.05	3129.40	1353.0	100.0
2.75	0.70	1.0	1.0	403.99	9.01	21.28
2.75	0.768	0.15	1.0	231.72	23.69	50.0
2.75	0.770	0.10	1.0	228.04	28.6	55.55
2.75	0.771	0.08	1.0	222.55	29.5	57.14
2.75	0.775	0.05	1.0	202.81	25.2	55.55

Figure Captions

Fig. 1. Tracer diffusion coefficients as a function of mass ratio for a size ratio $\frac{\sigma_2}{\sigma_1} = 0.5$. The system temperature and density are $T^* = 0.75$, $n^* = 0.9$: Solid circles, MD results; solid triangles, theoretical work; - - -, Stokes-Einstein behaviour (eqn (1)).

Fig. 2. Same as fig. 1, but for smaller size ratio $\frac{\sigma_2}{\sigma_1} = 0.1$.

Fig. 3 The ratio of tracer over solvent diffusion coefficients $\frac{D_2}{D_1}$ as a function of inverse size ratio, for equal masses. The thermodynamic state of the pure solvent is $T^* = 2.75$ and $n^* = 0.7$, the density is increased from 0.70 to 0.77 as the tracer size is decreases: Solid circles, MD results; solid triangles, theoretical results; - - - SE behaviour eqn. (1)

Fig. 4. Variation of $\log(D_2/D_1)$ with $\log(\sigma_1/\sigma_{12})$ for the thermodynamic state of the system same as that of figure 3. The dotted line corresponds to eqn (20).

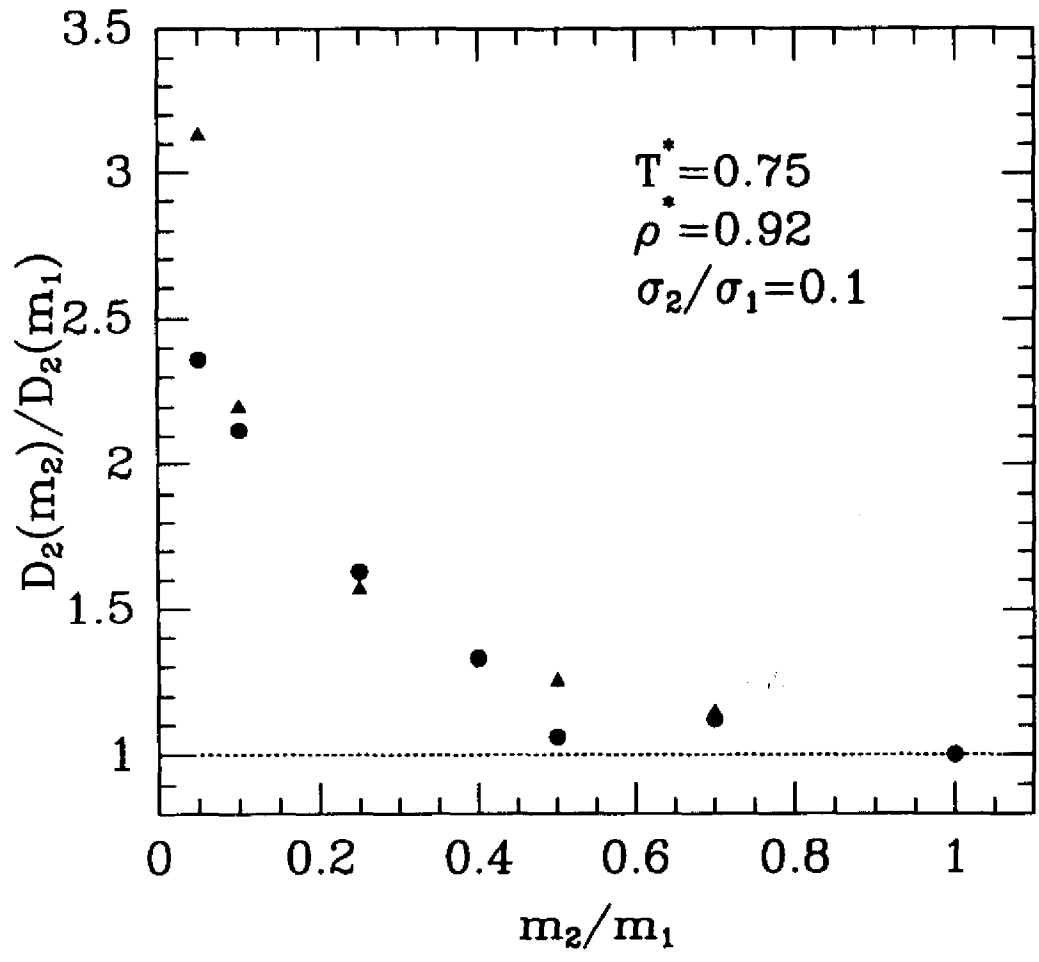


Fig.1

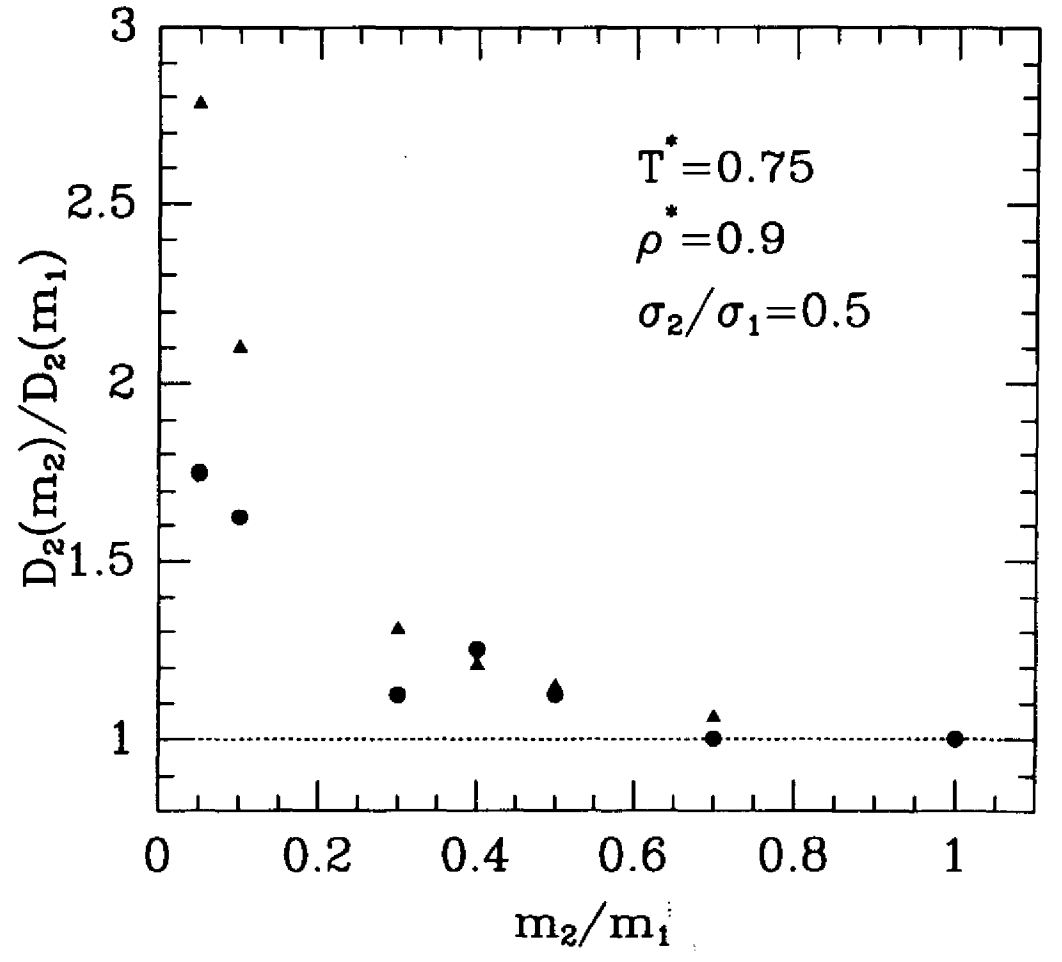


Fig.2

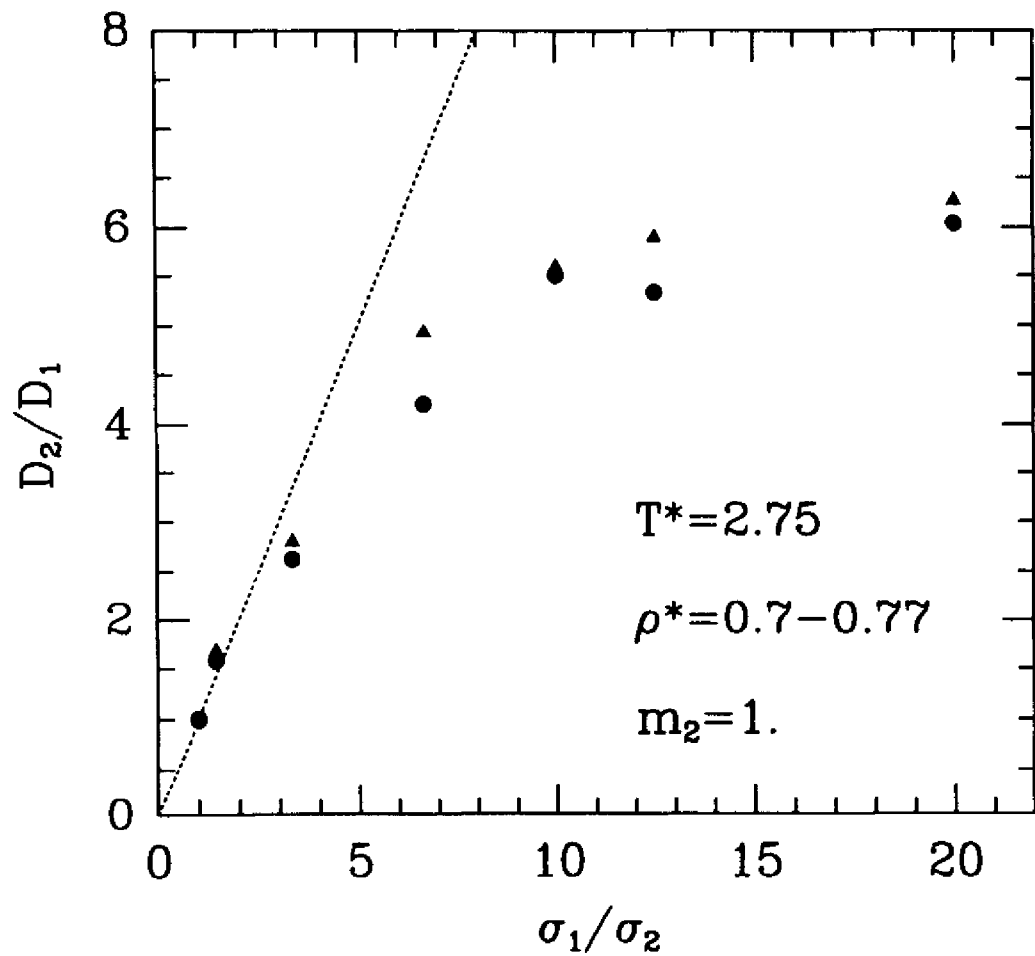


Fig.3

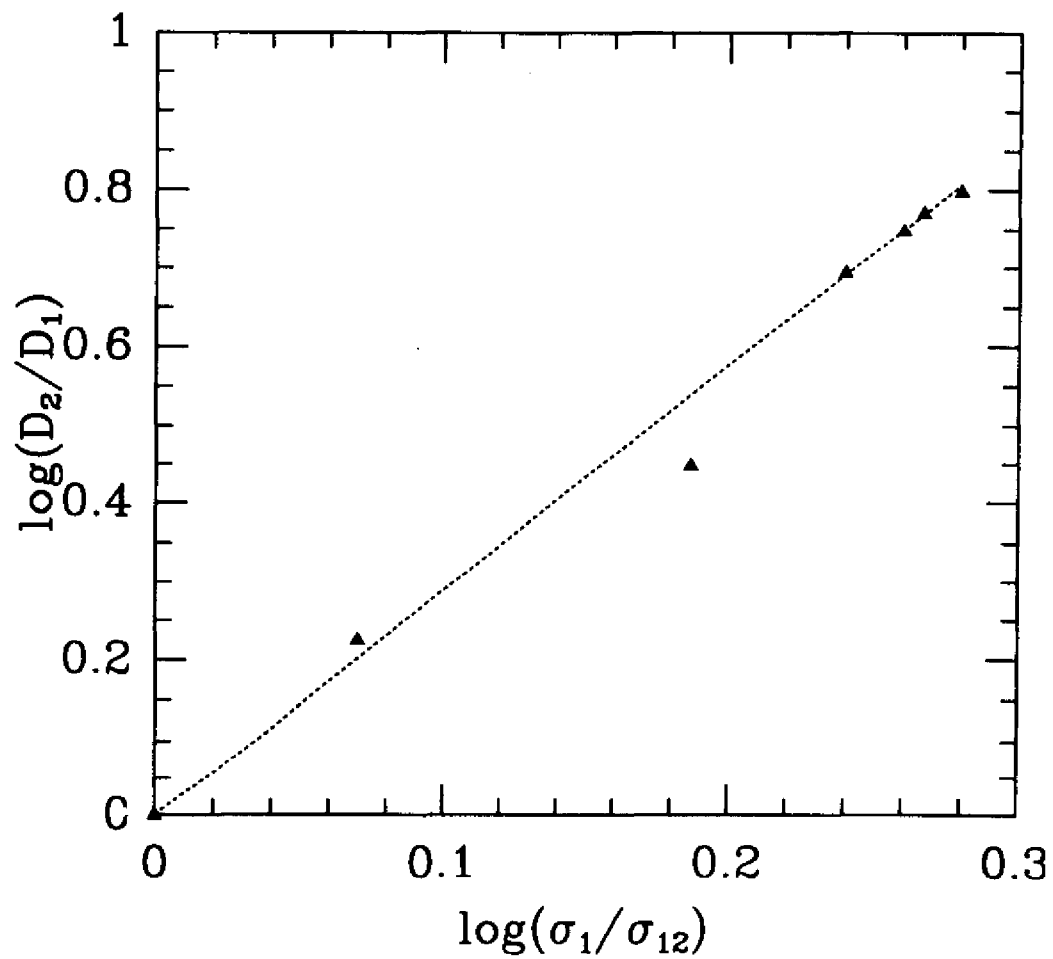


Fig.4

