A simple model for the calculation of self-diffusion

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Abstract. We propose a simple model for the calculation of the self-diffusion coefficient of classical fluids. The model is based on the idea of separating the configurational space of a fluid system into a vibrational part and a structural part. There is no adjustable parameter in the model and the only input required is the interatomic potential. Using the model we have calculated the self-diffusion coefficients of the Lennard-Jones fluid, the one component plasma and the Yukawa fluid. The predicted results have been compared with recent computer simulation data and a good agreement has been achieved.

1. Introduction

It is well known that dynamical and transport properties of a physical system are embodied in time correlation functions. The exact calculation of the time correlation functions is not feasible because this amounts to solving the complicated many body problem. Time correlation functions do not reflect the details of atomic trajectories because they are ensemble averages. Therefore, it seems intuitively plausible to treat the system using a simplified description of atomic motion. Jumps models (Springer 1972) for the calculation of the diffusion constant are examples of such simplified descriptions (Martin and Yip 1968, Isbiester and McQuarrie 1972). In the present work, we propose a simple model for the calculation of self-diffusion coefficients of the classical system based on the extension of some ideas of Stillinger and Weber (1983). Using this model we have calculated the self-diffusion coefficients of Lennard-Jones (LJ) fluids, one component plasma (OCP) and Yukawa fluids. The predicted results have been compared with recent computer simulation data and a good agreement has been achieved.

In section 2, we propose the model for the calculation of self-diffusion coefficients. Calculation and results are given in section 3.

2. Model

For an identical N particle system, the self-diffusion coefficient 'D' is given by the Green–Kubo expression (Boon and Yip 1980)

$$D = \int_0^\infty V(t) \, dt \qquad V(t) = \frac{1}{3N} \sum_i \langle v_i(t) \cdot v_i(0) \rangle. \tag{1}$$

The exact calculation of the time development of the velocity auto-correlation function

(VACF), $V(t)$, is not yet feasible except for in simple cases of atomic motion. For example, in dilute gases $V(t)$ can be calculated using the binary collision approximation (McQuarrie 1976) whereas in crystalline solids only the vibrational (harmonic) motion is sufficient to calculate $V(t)$. These two ideal cases have little in common. Attempts to extend either case to an intermediate state, i.e. dense fluids (liquids and dense gases), usually result in a model of liquid diffusion which must be classified as solid like or gas like rather than an appropriate hybrid of the two. Recently, Zwanzig (1983) and Mahanty (1985) have used the idea of separating the configuration space of a many body system into a vibrational part and stable packing part. Using similar arguments we propose a model for the calculation of $V(t)$ and hence for the self-diffusion coefficients. Our model is based on the following assumptions:

(i) The configuration space of a many body system is divided into a number of cells. Each cell is characterized by a fixed configuration associated with local minima on the potential energy hypersurface of the system.

(ii) The system jumps between the cells with a certain jump frequency τ^{-1}. The effect of the cell jump is to rearrange the equilibrium position of particles in a particular subvolume V^* of the total volume V of the system.

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

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

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

Our model differs from the models of Zwanzig (1983) and of Mahanty (1985) with respect to the assumptions (iii) and (iv). Our choice of the waiting time distribution is such that it provides more jumps at small times than at large times during the diffusion process. On the other hand our third assumption will make the calculation of the frequency ω and time period of the jump τ very simple. This enables us to make numerical predictions of the self-diffusion coefficients of the fluids as demonstrated below.

Within our assumptions (i) and (iii), the sum over particles in equation (1) becomes the sum over normal modes. The time dependence of the normal mode contribution in equation (1) is proportional to $\cos(\omega t)$ until the motion in volume V^* is interrupted by a cell jump. The factor sech(t/τ) takes care of the interruption. This results in an expression for the VACF:

$$V(t) = (k_B T/m)\,\text{sech}(t/\tau)\cos(\omega t). \tag{2}$$

The power spectrum of the VACF defined as

$$\tilde{V}(\omega_1) = \int_0^\infty \cos(\omega_1 t) V(t)\,\mathrm{d}t \tag{3}$$

is obtained to be

$$\tilde{V}(\omega_1) = (k_B T/m)\pi\tau\left(\frac{\cosh[(\pi/2)\omega_1\tau]\cosh[(\pi/2)\tau\omega]}{\cosh(\pi\tau\omega_1) + \cosh(\pi\tau\omega)}\right). \tag{4}$$

The self-diffusion coefficient D is obtained to be

$$D = \bar{V}(0) = (k_B T/m)(\pi/2)\tau \, \text{sech}(\pi\omega\tau/2). \tag{5}$$

It is clear from equation (5) that $\omega\tau \gg 1$ corresponds to solid like behaviour and in this limit we obtain

$$D \to (k_B T/m)\pi \exp[-(\pi/2)\omega\tau]. \tag{6}$$

In order to make explicit predictions for D we estimate ω and τ from the short time property of the normalized VACF given by

$$(m/k_B T) \, V(t) = 1 - V_2 \, t^2/2! + V_4 \, t^4/4! - V_6 \, t^6/6! + \dots \tag{7}$$

where $-V_2$, V_4 and $-V_6$ are the second-, fourth- and sixth-frequency sum rules of the spectral function of the VACF. Comparing the short time expansion of equation (2) with equation (7) we obtain

$$\tau^{-2} = \delta_2/4 \qquad \omega^2 = (4\delta_1 - \delta_2)/4$$

where $\delta_1 = V_2$ and $\delta_2 = (V_4/V_2 - V_2)$ are called Mori coefficients. From our earlier work (Tankeshwar *et al* 1987, 1990) we note that, for the LJ fluids, V_4 increases with increase in temperature and V_2 approaches a constant value at high temperature. Consequently, ω^2 becomes negative beyond the temperature and density at which $V_4/V_2^2 = 5$ (or $4\delta_1 = \delta_2$) and τ remains positive. Then the form of $V(t)$ is given as

$$V(t) = (k_B T/m) \cosh(\omega' t)/\cosh(t/\tau) \tag{8}$$

where $\omega'^2 = (\delta_2 - 4\delta_1)/4$.

For the power spectrum this provided

$$\bar{V}(\omega_1) = (k_B T/m)\pi\tau \left(\frac{\cos[(\pi/2)\tau\omega] \cosh[(\pi/2)\omega_1\tau]}{\cosh(\pi\tau\omega) + \cos(\pi\tau\omega_1)} \right). \tag{9}$$

Equation (9) implies that for $4\delta_1 \leq \delta_2$, the VACF ceases to oscillate and decays monotonically in time. For large times the form of $V(t)$ is

$$V(t) = (k_B T/m) \exp[-t(1/\tau - \omega')] \tag{10}$$

as one would expect for high temperature dilute gases. From equation (10) it can easily be seen that $\omega'\tau = 1$ or $4\delta_1/\delta_2 = 0$ corresponds to the case for an ideal gas with an infinite diffusion constant.

3. Calculation and results

In order to calculate the self-diffusion coefficient from equation (5) we require δ_1 and δ_2 as inputs. The general expressions for these are given by Tankeshwar *et al* (1987). The calculation of δ_1 involves only the static pair correlation function $g(r)$, whereas δ_2 involves $g(r)$ and the static triplet correlation function, $g_3(r, r')$ in addition to the interatomic potential. In the absence of any knowledge of the triplet correlation function, we have used a superposition approximation for it. Here it may be noted that this approximation has provided a good estimate of the triplet contribution to V_4 as demonstrated in our earlier works (Tankeshwar *et al* 1990, Singla *et al* 1990). We therefore use
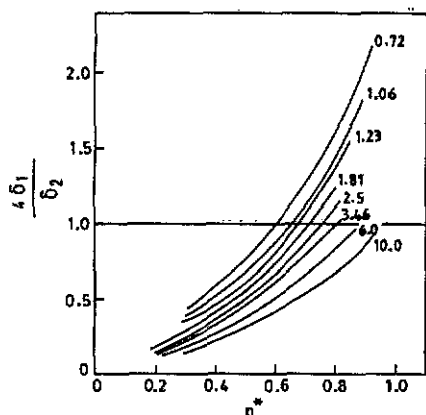
Figure 1. Variation in $4\delta_1/\delta_2$ of the LJ fluids with density n^* for various temperatures, T^*, indicated along each curve.
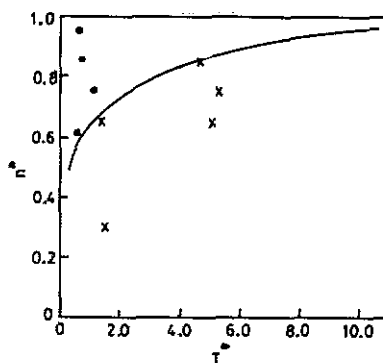
Figure 2. The plot of n^* against T^* for which $4\delta_1 = \delta_2$.

the same procedure for the calculation of V_2 and V_4. In the next subsection we present the results for the self-diffusion coefficients of LJ fluids, OCP and Yukawa fluids, separately.

3.1. Lennard-Jones fluids

For the LJ fluids the numerical results of δ_1 and δ_2 have already been given in our earlier works (Tankeshwar *et al* 1987, 1990) for wide ranges of densities and temperatures. In figure 1 we have plotted $4\delta_1/\delta_2$ as a function density $n^*(= n\sigma^3)$ for various $T^*(= k_B T/\varepsilon)$, σ and ε being the parameters of the LJ potential. For $4\delta_1 = \delta_2$, $V(t)$ ceases to oscillate, and therefore the horizontal line in figure 1 separates the phase of oscillatory behaviour of the VACF from that of monotonic decay of the function. From figure 1, we obtain n^* and T^* at which $4\delta_1/\delta_2 = 1$. These n^* and T^* are plotted in figure 2. The (n^*, T^*) points above the line in figure 2 correspond to thermodynamic states for which our model predicts back scattering or a negative minima in the decay of the VACF. On the other hand, (n^*, T^*) below the line correspond to a dilute system in which the VACF decays monotonically. The full circles and crosses in figure 2 represent the molecular dynamics (MD) (Kushick and Berne 1973, Levesque and Verlet 1970, Lee and Chung 1986) (n^*, T^*) states where the VACF does and does not show the back-scattering effect, respectively. Therefore, from figure (2) we find that the predictions of our model for the existence of a back-scattering effect in the Lennard-Jones system is in accordance with the computer simulation results.

   In order to have an explicit picture of the time evolution and power spectrum of the VACF of Lennard-Jones fluids we have plotted these in figures 3 and 4, respectively. The normalized $V(t)$ calculated from equation (2) for five thermodynamics states are shown as full curves whereas the MD results (Kushick and Berne 1973, Lee and Chung 1986) are shown as full circles in figure 3. It can be seen from figure 3, that a satisfactory agreement is obtained for a good span of time. However, our model does not predict the good agreement at long times. The long time behaviour of the calculated $V(t)$ is clearly reflected in the small ω_1 behaviour of $\tilde{V}(\omega_1)$ in figure 4 where the agreement is not satisfactory. However, our results for $V(\omega_1)$ are comparable to the earlier existing
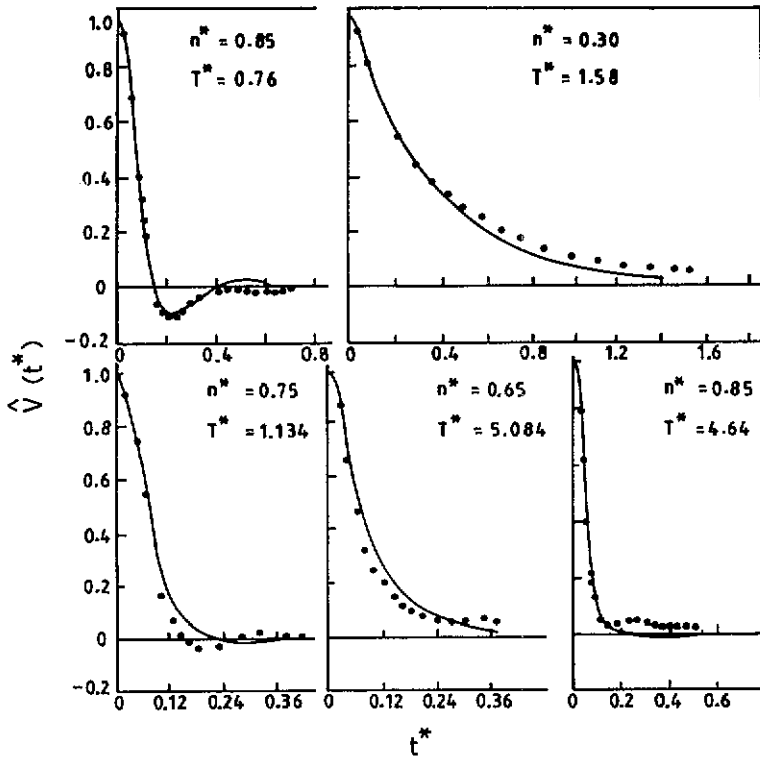
Figure 3. Variation in the normalized VACF $\hat{V}(t)$ with time $t^* = t(\varepsilon/m\sigma^2)^{1/2}$ obtained for five thermodynamic states of the LJ fluids: full curve—results obtained from equation (2); full circles—MD results (Kushick and Berne 1973, Lee and Chung 1986).
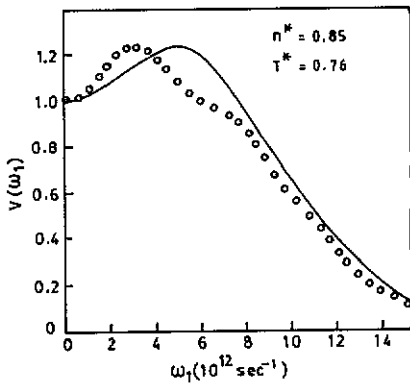

Figure 4. Normalized power spectrum of VACF for liquid argon at its triple point: full curves—results obtained from equation (4); empty circles—simulation results (Rahman 1964).

models (Berne *et al* 1966, Rahman *et al* 1962, Sears 1969). Overall, we find that our model is satisfactory for $V(t)$.

The results for the diffusion coefficients $D^* = D(m\varepsilon/\sigma^2)^{1/2}$ are obtained from equation (3) and D^*n^* are plotted in figure 5 as a function of density for six isotherms. The MD results of Heyes (1983, 1988) are also shown there. For a dilute gas D^*n^* is almost constant. With increasing density the particles will be arrested in the cages formed
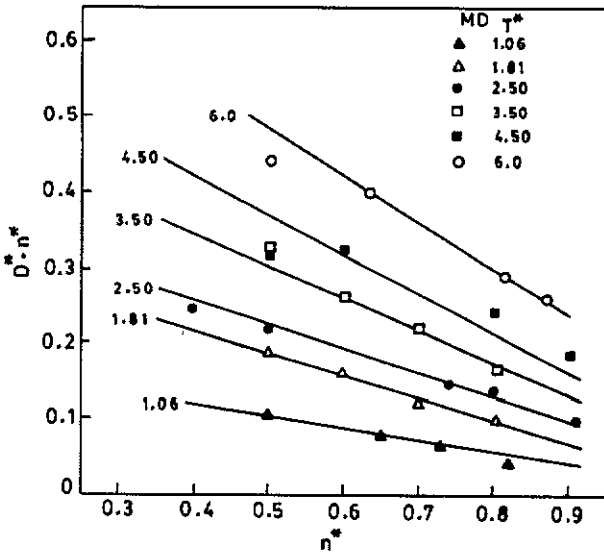
Figure 5. Variation in the diffusion coefficients of LJ fluids with density at various temperatures. Our results.
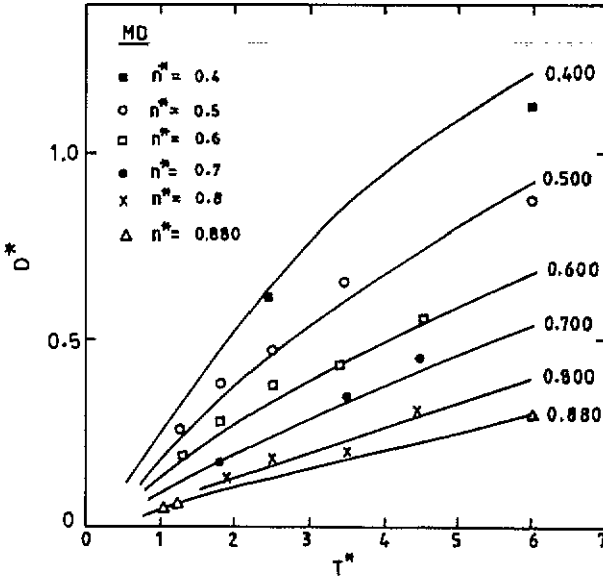

Figure 6. Variation in diffusion coefficients of LJ fluids with temperature. Our results.

by their neighbouring particles and this results in a decrease in D^*n^* with increasing density as can be seen from figure 3. The temperature dependence of the diffusion constant is presented in figure 6 for five densities along with the corresponding computer simulation data (Heyes 1983, 1988). It can be seen from figures 5 and 6 that the agreement

Table 1. Values of the sum rules V_2 and V_4 and the self-diffusion coefficients D^* of the Yukawa fluid ($D^* = 2\pi D/V_2 a^2$).

ξ	Γ	V_2 (in units of $\varepsilon n\, m^{-1}$)	V_4 (in units of $\varepsilon^2 n\, a^{-3} m^{-2}$)	D^*	D^*_{MD}
3.19	280	1.394	3.718	0.588	0.692
	4552	9.384×10^{-2}	0.18415	0.677	0.615
7.14	3764	9.802×10^{-2}	0.21288	0.892	1.039
	2769	6.340×10^{-2}	0.00867	1.770	1.924
	38520	7.015×10^{-3}	0.1168×10^{-3}	1.400	1.192
10.10	29137	8.414×10^{-3}	0.5999×10^{-3}	1.978	2.001
	23120	8.676×10^{-3}	0.2102×10^{-3}	2.497	2.616

is satisfactory over the entire fluid range. Our model also provides a good description of the density and temperature dependence of the self-diffusion coefficient.

3.2. Yukawa fluids

The fluid system of the particles interacting via Yukawa or screened Coulomb potentials provides a model for dense ionic plasmas in a polarizable electron background, where the screening is treated within the Thomas–Fermi approximation, or for charged stabilized colloidal dispersions where the screened Coulomb potential provides the interaction between the electron double layers surrounding the colloidal particles. The interaction potential for the Yukawa fluids is given as

$$\phi(r) = (\varepsilon/r) \exp(-Kr). \tag{11}$$

where ε has the dimensions of charge squared and K is the reciprocal of the screening length. We write equation (11) in a more convenient form as

$$\beta\phi(x) = (\Gamma/x) \exp(-\xi x) \tag{12}$$

where $\beta = (k_B T)^{-1}, x = r/a$ and $\xi = Ka; a = (1/n)^{1/3}$ is the ion sphere radius and n is the number density. The numerical results of V_2 and V_4 for the Yukawa fluid have been calculated using the molecular dynamics data for $g(r)$ of Robbins *et al* (1987). The numerical results for these are given in table 1.

The time evolution of the normalized VACF $\bar{V}(t)$ of the Yukawa fluid is calculated from equation (2) using the values of V_2 and V_4 from table 1 for different values of ξ and Γ. The results obtained are presented as full curves in figure 7 for two typical values of ξ and Γ. The recent computer simulation results of Robbins *et al* (1987) are shown as full circles. From figure 7 it can easily be seen that the initial decay of the VACF is very well demonstrated by our model up until a time $\frac{1}{3}\tau_E$ where τ_E is related to the Einstein frequency $\omega_E (= \sqrt{V_2})$ as $\tau_E = 2\pi/\omega_E$. For times greater than $\frac{1}{3}\tau_E$, our results predict a minimum whose position is in agreement with simulation data, although the amplitude of the oscillation is overestimated. It can also be seen that our theory shows enhancement of oscillations in $V(t)$ as the screening parameter ξ decreases in agreement with simulation results. For times greater than τ_E, the oscillations are found to be damped. The oscillations die out for $t \simeq 2\tau_E$. On comparing the time period of oscillation with $V(t)$, we have found that our theory overestimates it.

The results obtained for the coefficient of self-diffusion $D^* (= D(2\pi/\omega_E a^2))$ from equation (6) along with the MD results of Robbins *et al* (1987) are given in table 1. It can
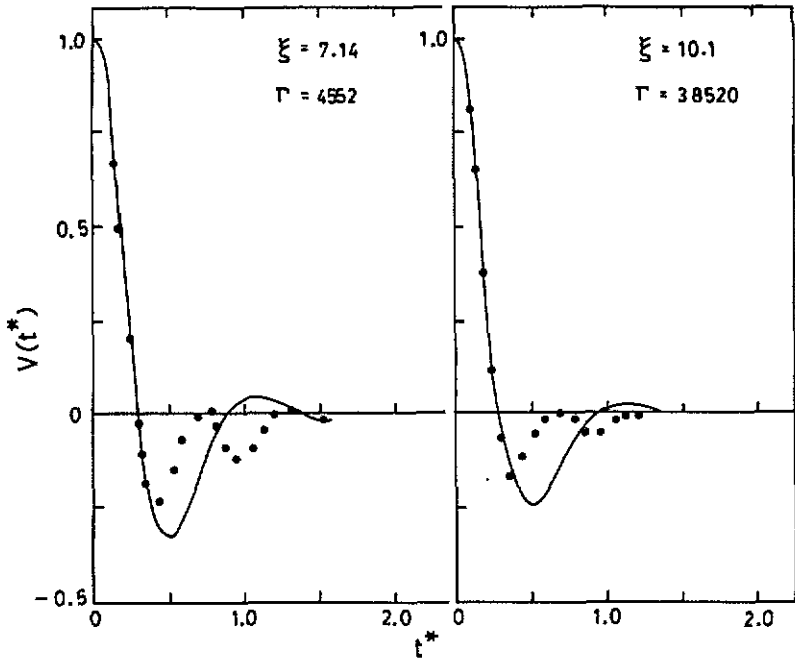
Figure 7. Variation of the normalized VACF $V(t^*)$ with $t^* = t/\tau_E$ obtained for two values of ξ and Γ: full curves—our results obtained from equation (2); full circles—MD results of Robbins *et al* (1987).

be seen from table 1 that our model provides a good estimate for the self-diffusion coefficient of Yukawa fluids for various ξ and Γ.

From the results plotted in figure 7 for $V(t)$ it can be seen that the time evolution of the VAC function is not very satisfactory. However, the area under the curve, i.e. the self-diffusion is quite satisfactory for most of the thermodynamic states.

3.3. One-component plasma

In the study of charged fluid dynamics, the OCP of point charges interacting through repulsive Coulomb potential, immersed in a uniform background of positive charges, has been the simplest system. This system is characterized by a single parameter $\Gamma = e^2/r_0 k_B T$; e and r_0 are electron charge and ion-sphere radius. The expressions for δ_1 and δ_2 (or V_2 and V_4) are already known (Singh *et al* 1979). The numerical results for δ_1 and δ_2 obtained using computer simulation data of $g(r)$ (Brush *et al* 1966, Hansen *et al* 1975) are plotted in figure 8 as a function of Γ. From figure 8 it can easily be seen that δ_1 is constant for all Γ, whereas δ_2 decreases with increasing Γ. From this and equation (6), it can easily be seen that the Γ dependence of self-diffusion is solely determined by δ_2. We also find that δ_2 decreases rapidly with increasing Γ in the low Γ regime, whereas for large Γ δ_2 decreases slowly. The self-diffusion coefficient $D^* = D/\omega_p r_0^2$ where ω_p is the plasma frequency, calculated from equation (6) for the OCP system and plotted in figure 9 as a function of Γ. The MD results of Hansen *et al* (1975) are represented by full circles. It can be seen from figure 9 that our model explains well the Γ dependence of the self-diffusion coefficient. However, the results for the time evolution of $V(t)$ are not
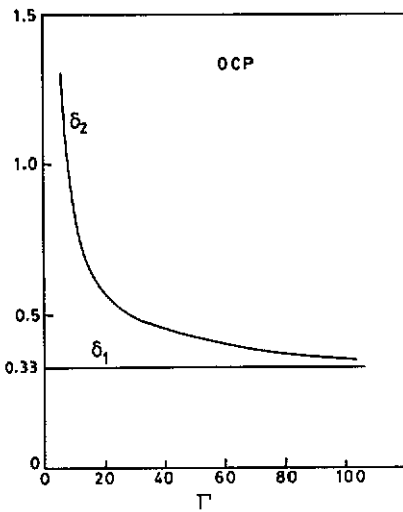
Figure 8. Variations in δ_1 and δ_2 of OCP with Γ.
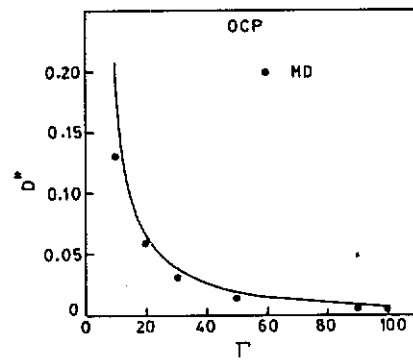
Figure 9. Variation in the self-diffusion coefficient of OCP with Γ.

satisfactory for the OCP system. The agreement is only qualitatively similar to the earlier plotted results for the Yukawa fluid.

4. Conclusion

It is found that our model consistently predicts the value of the self-diffusion coefficients in agreement with simulation results for LJ fluids, Yukawa fluids and OCP. We also found that the prediction of our model for the existence of back-scattering effects for the Lennard-Jones fluids is in accordance with the available simulation data. Our model also simulates satisfactory time behaviour of the VACF of Lennard-Jones fluids. However, results for the VACF of the Yukawa and OCP are not satisfactory. It may be that the waiting-time distribution is more complicated for Yukawa fluids and OCP, and different from that for the LJ fluids. Here it may be noted that our model gives $D = 0$ for the solid phase. For this case, $V_4 = V_2^2$ and hence the jump frequency is zero and the particle will be localized in local potential wells, implying no diffusion.

We have also investigated the use of the Gaussian and exponential models for the waiting-time distribution. It is found that results are very sensitive to the choice of this distribution. This is also noted by Mahanty (1985). In our theory the best results are obtained using $\operatorname{sech}(t/\tau)$ as the waiting-time distribution.

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