

Analysis of the role of attractive forces in self-diffusion of a simple fluid

By JOHN E. STRAUB

Department of Chemistry, Boston University, Boston, Massachusetts 02215, USA

(Received 5 December 1991; accepted 2 January 1992)

The role of the attractive force in self-diffusion of atoms in a Lennard-Jones fluid is explored through molecular dynamics simulation. Expressions for the self-diffusion coefficient in terms of the memory function and the random force autocorrelation function are used to develop simple approximations which separate the contribution of attractive and repulsive forces to self-diffusion. A result of the analysis is the definition of an effective hard-sphere radius for dynamic properties. The expression describing the effect of the attractive interactions on the rate of self-diffusion in a fluid at low density is found to predict successfully the dependence at much higher densities and $k_B T \geq \varepsilon$.

1. Introduction

The role of attractive forces in equilibrium properties of gases and liquids is now well appreciated. This is largely due to the enormous success of the van der Waals and similar theories of real gases and modern statistical mechanical perturbation theories of liquids such as the WCA theory of Weeks, Chandler and Andersen [1, 2]. A great deal is also known about the role of attractive interactions in dynamic properties such as self-diffusion of atoms in gases [3]. Consider a gas of atoms interacting with a Sutherland potential $V(r)$ where

$$\begin{aligned} V(r) &= \infty, & r < \sigma, \\ &= -\varepsilon(\sigma/r)^v, & r > \sigma \end{aligned}$$

and σ is the separation of the potential minimum whose depth is ε . The ratio of the self-diffusion coefficient for the Sutherland potential to that of a hard sphere of radius σ is [3]

$$\frac{D}{D_{\text{HS}}} = \frac{1}{1 + \varepsilon S(v)/k_B T}.$$

The Sutherland coefficient $S(v)$ which would correspond to a Lennard-Jones fluid is $S(v = 6) = 0.1667$ [3].

Since the time of Boltzmann it has often been argued that in an isotropic fluid the attractive forces on a particle have a negligible influence on self-diffusion (see Introduction of [4]). Recently, Speedy *et al.* presented an analysis of the temperature dependence of the coefficient of self-diffusion of a simple fluid [4]. They interpreted their data as obeying the empirical function

$$D = D_{\text{HS}}(\sigma_B) \exp(-\varepsilon/2k_B T),$$

where D is the diffusion coefficient for a Lennard-Jones fluid, $D_{\text{HS}}(\sigma_B)$ is the hard-sphere diffusion coefficient using an effective radius σ_B , ε is the well depth of the

Lennard-Jones potential, and $k_B T$ is the thermal energy. This expression is intriguing, since it is of the Arrhenius form which appears in models of diffusion in liquids and solids where diffusion is thought to occur on a potential surface of many minima and barriers [5]. The characteristic time for diffusion takes on the form of an activated process such as would result from transition state theory. The formula above suggests that the attractive interaction well-depth of the Lennard-Jones potential deepens the well minima relative to the barrier height, thereby slowing diffusion. This could arise from having more nearest neighbors at a distance close to a minimum in the potential energy surface of the fluid as opposed to the transition state.

Nearly twenty years ago, Kushick and Berne explored the relationship between the self-diffusion of atoms in a Lennard-Jones fluid and those in a WCA fluid, where atoms interact with the repulsive portion of the Lennard-Jones force only [6]. Speedy *et al.* report that the data of Kushick and Berne may be represented by the formula [4]

$$D = D_{\text{WCA}}(1 - 0.14\epsilon/k_B T).$$

Here, D_{WCA} is the diffusion coefficient of a WCA fluid serving as a reference system for the Lennard-Jones fluid. They observe that the effect of the attractive interaction is smaller when the reference system is the WCA soft-sphere system than when the hard-sphere reference system is employed. Therefore, the WCA fluid dynamics more closely approximate the Lennard-Jones fluid dynamics than do those of a hard-sphere fluid. Interestingly, the coefficient 0.14 is within 20% of the Sovine coefficient for the Sutherland potential (described above).

In this work, we examine the role of the attractive force in dynamics of a simple fluid using both numerical simulation and analytical approximation in several forms. Our goal is to describe the Lennard-Jones diffusion coefficient in terms of separate contributions from the repulsive and attractive forces. We demonstrate that the functional form of D/D_{WCA} for gases is valid for fluids at high density and moderate to high temperatures.

2. Background

We present four commonly used expressions for the diffusion coefficient. Each expression is consistent with the other and has its own benefits. One expression is superior for numerical determination of the diffusion coefficient; other expressions lend themselves to simple approximations which will help us dissect the influence and effect of the attractive force on self-diffusion in a simple fluid. There are many treatises which present lucid and detailed discussions of these formulae [7–9]. Here we simply present the results used in our analysis.

Perhaps the best known relation expresses the diffusion coefficient in terms of the asymptotic slope of the atomic mean-square displacement

$$\lim_{t \rightarrow \infty} \langle \Delta r(t)^2 \rangle \sim 6Dt. \quad (1)$$

From this form it is straightforward to express the diffusion coefficient in terms of the velocity autocorrelation function [7]

$$D = \frac{1}{3} \lim_{s \rightarrow 0} \int_0^{\infty} e^{-st} \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$$

where \mathbf{v} is the velocity vector of the Lennard-Jones atom and m is the mass. The limit of the integral is recognizable as the zero-frequency limit of the Laplace transform

$\tilde{C}(s)$ of the velocity autocorrelation function $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$ normalized by its zero-time value $\langle v^2 \rangle = 3k_B T/m$. This leads to the more compact form

$$D = \frac{k_B T}{m} \lim_{s \rightarrow 0} \tilde{C}(s). \quad (2)$$

In most cases it is difficult to determine the long time behavior of the velocity autocorrelation function accurately. This leads to uncertainties in the application of equation (2) which are avoided using equation (1) [10].

A third relation results from expressing the memory function in terms of the random force autocorrelation function. The dynamics of the velocity of an atom in our simple fluid may be described in terms of the well-known generalized Langevin equation

$$\frac{d\mathbf{v}(t)}{dt} = - \int_0^t d\tau K(\tau) \mathbf{v}(t - \tau) + \mathbf{F}(t),$$

where the memory function is related to the random force by the second fluctuation-dissipation theorem

$$K(t) = \frac{1}{3mk_B T} \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle.$$

We have made use of the fact that the fluid is isotropic and the three Cartesian components of the velocity are equivalent. Here $\mathbf{F}(t) = e^{iQ_L t} \mathbf{F}(0)$, where $\mathbf{F}(0) = m\dot{\mathbf{v}}(0)$. Note the time propagator is not e^{iLt} but the projected propagator where $Q = 1 - P$ and $P = (1/mk_B T)(\dots, m\mathbf{v})m\mathbf{v}$ is the projection operator which projects onto the momentum vector $m\mathbf{v}$. Defining the time integral over the force autocorrelation function as the zero-frequency friction

$$\zeta_0 = \frac{1}{3k_B T} \int_0^\infty dt \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle \quad (3a)$$

we arrive at

$$D = \frac{k_B T}{\zeta_0} \quad (3b)$$

which is the familiar Einstein relation.

A final expression for the diffusion coefficient results from relating the force autocorrelation function to the memory function $K(t)$ through the fluctuation-dissipation relation given above. Taking the Laplace transform of the relation and inserting in equation (3a, b) we find

$$D = \frac{k_B T}{m} \lim_{s \rightarrow 0} \frac{1}{K(s)} \quad (4)$$

for the diffusion coefficient as a function of the zero-frequency value of the memory function.

3. Methods

In the following sections we use several formulations of the diffusion coefficient to explore the role of the attractive force in the self-diffusion of atoms in a simple fluid. From molecular dynamics simulation we determine the diffusion coefficient for a

Lennard-Jones fluid and a WCA reference system where only the repulsive portion of the Lennard-Jones force is used. We use these data to determine the ratio D/D_{WCA} of the Lennard-Jones self-diffusion coefficient D normalized by D_{WCA} for the WCA fluid as a function of temperature. The random force autocorrelation function is calculated and used to separate the attractive and repulsive forces in a straightforward way. Finally, the memory function is taken as a starting point for equilibrium moment expansions of the memory function, where WCA perturbation theory is used to divide the equilibrium averages into contributions from the repulsive and attractive forces.

3.1. Numerical simulations

The Lennard-Jones interaction potential is

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (5)$$

with diameter σ and well depth ε . $(m\sigma^2/\varepsilon)^{1/2}$ is the unit of time and ρ is the number density. We carried out a series of simulations of a Lennard-Jones fluid for six temperatures ranging from 0.75 to 4.0 at five densities ranging from 0.30 to 1.05. For each calculation, the time step employed was 0.001 time units using a velocity Verlet algorithm [10]. All calculations were performed on a Stardent 3030 computer. The 512 atom system at density $\rho\sigma^3 = 0.75$ and temperature $k_B T/\varepsilon = 0.75$ required approximately 0.24 s per time step using the full Lennard-Jones potential with a cutoff of 2.5σ . As noted by Kushick and Berne, the WCA system requires approximately one-seventh the integration time required for integration using the full potential [6].

3.2. The random force autocorrelation function

The zero-frequency friction is defined in terms of the autocorrelation function of the random force

$$\zeta_0 = \frac{1}{3k_B T} \int_0^\infty dt \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle. \quad (6)$$

We separate the force $\mathbf{F}(0)$ into the repulsive and attractive contributions in the spirit of WCA theory as

$$\left. \begin{aligned} v_0(r) &= v(r) + \varepsilon & r < r_m \\ &= 0 & r > r_m, \\ v_1(r) &= -\varepsilon & r < r_m \\ &= v(r) & r > r_m, \end{aligned} \right\} \quad (7)$$

where r_m is the minimum energy position $r_m = 2^{1/6}\sigma$. An alternative is the method of Barker and Henderson (BH), where the potential energy is separated into attractive (negative) and repulsive (positive) regions. However, we are interested in dynamics, where the force and not the energy is important, and so we follow the WCA prescription.

The repulsive force is responsible for short-time collisional dynamics and for the short-time behavior of the memory function of the random force autocorrelation function. In the context of vibrational relaxation, Schweizer and Chandler have discussed the approximation where the force autocorrelation is divided into repulsive–repulsive and attractive–attractive terms, neglecting the crossterms [11]. However, as our results show, this approximation fails for our force autocorrelation function of

a single atom in a simple fluid. The crossterms are often substantial. As such, we write the force autocorrelation function as

$$\begin{aligned} \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle &= \langle \Delta \mathbf{F}_R(0) \cdot \Delta \mathbf{F}_R(t) \rangle \\ &+ \langle \Delta \mathbf{F}_R(0) \cdot \Delta \mathbf{F}_A(t) \rangle + \langle \Delta \mathbf{F}_A(0) \cdot \Delta \mathbf{F}_R(t) \rangle \\ &+ \langle \Delta \mathbf{F}_A(0) \cdot \Delta \mathbf{F}_A(t) \rangle. \end{aligned} \quad (8)$$

Collecting the last three terms into a single attractive correction term allows us to define the zero-frequency friction as

$$\zeta_0 = \zeta_R + \zeta_A, \quad (9)$$

where we have divided the contributions ζ_R arising from the repulsive–repulsive force correlation and the attractive correction ζ_A . Similarly, we may define the zero-frequency friction ζ_{WCA} for the WCA system which undergoes dynamics with the repulsive force only as the time-integral of

$$\langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle = \langle \Delta \mathbf{F}_{\text{WCA}}(0) \cdot \Delta \mathbf{F}_{\text{WCA}}(t) \rangle. \quad (10)$$

The propagator for the Lennard-Jones fluid is defined in terms of the Liouvillian $L = L_0 + L_1$, where the flow due to the inertial and repulsive force is

$$iL_0 = \sum_{j=1}^N \mathbf{v}_j \cdot \frac{\partial}{\partial \mathbf{R}_j} + \frac{1}{2} \sum_i^N \sum_{j \geq i}^N \mathbf{F}_{Rij} \cdot \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) \quad (11)$$

and the contribution of the attractive force is contained in

$$iL_1 = \frac{1}{2} \sum_i^N \sum_{j \geq i}^N \mathbf{F}_{Aij} \cdot \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right). \quad (12)$$

The Liouvillian L_0 describes the flow under the repulsive force only, that is, for the WCA reference system; L_1 describes the contribution of the attractive forces and will be proportional to the well depth ε . Intuitively we know that the contribution of L_1 will be negligible when $\varepsilon/k_B T \ll 1$.

For simplicity we rewrite the components of the force autocorrelation functions as

$$\langle \Delta \mathbf{F}_\alpha e^{iQ L t} \Delta \mathbf{F}_\beta \rangle = \langle \Delta \mathbf{F}_\alpha \Delta \mathbf{F}_\beta \rangle f_{\alpha\beta}(t), \quad (13)$$

where $F_{\alpha,\beta}$ denote the repulsive or attractive forces ($\alpha, \beta = R$ or A). For the WCA fluid

$$\langle \Delta \mathbf{F}_{\text{WCA}} e^{iQ L_0 t} \Delta \mathbf{F}_{\text{WCA}} \rangle = \langle \Delta \mathbf{F}_{\text{WCA}}^2 \rangle f_{\text{WCA}}(t). \quad (14)$$

Both of these equations express the force autocorrelation function in terms of the initial value (the *equilibrium* mean-square force) and an unspecified *dynamic* function of time describing the relaxation of the specific contribution to the random force. The zero-frequency friction can be expressed in terms of the mean-square force and the time-integral over the relaxation functions—the relaxation time of the force. Using the above equations we find a simple formula for the ratio of the self-diffusion coefficient of the Lennard-Jones system to that of the WCA system

$$\frac{D}{D_{\text{WCA}}} = \frac{\zeta_{\text{WCA}}}{\zeta_R + \zeta_A}. \quad (15)$$

Calculation of the time-dependence of the individual random force autocorre-

lation functions is complicated by the fact that the force is propagated by e^{iQLt} rather than the simple Hamiltonian flow described by e^{iLt} . However, there is a useful approximation that may be employed. A method for the calculation of memory functions has recently been presented where the coordinate of interest may be harmonically constrained and the effect of the constraint later removed [12]. It has been shown [13] that for such a constrained system the zero-frequency friction ζ_0 calculated from the random force autocorrelation function will be identical to that calculated from the force autocorrelation function under Hamiltonian flow, or that

$$\zeta_0 = \frac{1}{3k_B T} \int_0^\infty dt \langle \mathbf{F}(0) \cdot e^{iQLt} \cdot \mathbf{F}(0) \rangle = \frac{1}{3k_B T} \int_0^\infty dt \langle \mathbf{F}(0) \cdot e^{iLt} \cdot \mathbf{F}(0) \rangle. \quad (16)$$

Additionally, if we imagine increasing the constraining force constant to infinity, and the underlying memory function remains unchanged after subtracting the effect of the constraining force constant, then the random force autocorrelation function for the unconstrained system is identical to that when the atom is fixed. This result can be proved only for a harmonic bath [14]. Nevertheless, equation (16) provides a useful means of calculating the desired zero-frequency friction. To do so we constrain the atom rigidly, calculate the separate contributions to the force autocorrelation function from the Hamiltonian flow (normal dynamics at constant energy), and from these correlation functions determine the zero-frequency friction. The diffusion constant may then be calculated using equation (3b).

We note that equation (15) suggests a definition of the optimal effective hard-sphere reference system as one where

$$\zeta_R = \zeta_{HS}. \quad (17)$$

That is, the radius of particles in the hard-sphere fluid could be varied until $\zeta_R = \zeta_{HS}$. In this way, the repulsive force contribution to the Lennard-Jones dynamics is equaled by that of the hard-sphere reference system, and the contribution of the attractive force is treated as a correction to the reference system. This is a dynamic criterion for choosing an effective hard-sphere radius, and can be compared with choices of effective hard-sphere radii entertained by Speedy and co-workers [4]. Using this definition of the optimal hard-sphere reference system, equation (15) reduces to

$$\frac{D}{D_{HS}} = \left[1 + \frac{\langle \Delta F_A^2 \rangle \tau_A}{\langle \Delta F_R^2 \rangle \tau_R} \right]^{-1}, \quad (18)$$

where we have replaced the zero-frequency value of each force relaxation function with its characteristic time constant.

3.3. Equilibrium moment expansions of the memory function

Equilibrium moment expansion of the memory function has been explored in detail by many workers [9]. Here we employ two well-known approximations for the memory function $K(t)$ to derive approximate expressions for the diffusion coefficient in terms of separate contributions from the repulsive and attractive forces.

3.3.1. The exponential memory function

A useful approximation to the velocity autocorrelation function for a simple fluid

is the exponential model of Berne *et al.*, where the diffusion coefficient is simply [9]

$$D = \frac{k_B T}{3m\Omega_0^2 \tau} \tag{19}$$

Ω_0 is the generalized ‘Einstein frequency’ which is calculated from the mean-square force acting on the atom

$$\Omega_0^2 = \frac{1}{3mk_B T} \langle |\mathbf{F}|^2 \rangle = \frac{1}{3m} \langle \nabla^2 V \rangle, \tag{20}$$

where the force is $\mathbf{F} = -\nabla V(r)$ and $V(r)$ is the Lennard-Jones interaction potential. The relaxation time τ must be determined using computer simulation, fits to the experimental diffusion constant, or simple models.

We can use the exponential model to determine a form for D based on the reference system diffusion constant D_{WCA} . Following WCA theory we divide the interaction potential into a short-range repulsive part $v_0(r)$ and a long-range attractive interaction $v_1(r)$. Separating Ω_0^2 into two contributions

$$\begin{aligned} \Omega_0^2 &= \frac{1}{3m} [\langle \nabla^2 v_0 \rangle + \langle \nabla^2 v_1 \rangle] \\ &= \Omega_R^2 + \Delta\Omega^2. \end{aligned} \tag{21}$$

The first term is the repulsive force contribution to the mean-square force and the second is the correction for the contribution of the attractive force. The diffusion constant can now be written

$$\frac{D}{D_{WCA}} = \frac{\Omega_{WCA} \tau_{WCA}}{(\Omega_R^2 + \Delta\Omega^2) \tau}, \tag{22}$$

where the diffusion constant for the WCA reference system is

$$D_{WCA} = \frac{k_B T}{3m\Omega_{WCA}^2 \tau_{WCA}} \tag{23}$$

Note that if we define an optimal effective hard-sphere reference system by the criterion

$$\Omega_R^2 \tau = \Omega_{HS}^2 \tau_{HS} \tag{24}$$

then we may write

$$\frac{D}{D_{HS}} = \left[1 + \frac{\Delta\Omega^2 \tau}{\Omega_R^2 \tau_R} \right]^{-1}. \tag{25}$$

This criterion is equivalent to $\zeta_R = \zeta_{HS}$ (see previous section) within the exponential memory approximation when $\Omega_0^2 \tau = \zeta_0/3m$. It is expected that $\tau \neq \tau_R$, and the difference in the relaxation time also plays an important role. We next examine the Gaussian memory model, which provides an approximation for τ/τ_R .

3.3.2. The Gaussian memory function

The simplest approximation to the memory function which has the correct behavior at short times is the Gaussian memory [15]. The memory is determined entirely by the mean-square values of the velocity v , the acceleration a , and its time derivative \dot{a} as

$$K(t) = \frac{\langle a^2 \rangle}{\langle v^2 \rangle} \exp \left[-\frac{t^2}{2} \left(\frac{\langle \dot{a}^2 \rangle}{\langle a^2 \rangle} - \frac{\langle a^2 \rangle}{\langle v^2 \rangle} \right) \right]. \tag{26}$$

While this functional form does not lend itself to a simple separation of the contributions of attractive and repulsive forces, it is straightforward to determine the averages for a Lennard-Jones system and the WCA reference system numerically. This allows us to analyze separately the effects of the attractive interaction on the initial value of the memory, and the relaxation time

$$\tau_{\text{Gauss}} = \frac{\sqrt{\pi} \langle a^2 \rangle}{2 \langle v^2 \rangle} \left[\frac{\langle \dot{a}^2 \rangle}{\langle a^2 \rangle} - \frac{\langle a^2 \rangle}{\langle v^2 \rangle} \right]^{-1/2}, \quad (27)$$

which is determined entirely by the equilibrium moments.

4. Results

Diffusion constants were calculated from the atomic mean-square displacements for both the Lennard-Jones and WCA fluids using equation (1). We simulated 512 atoms using periodic boundary conditions and a time step of 0.001 Lennard-Jones units. Each system was equilibrated for 50 time units and then propagated for 150 time units to calculate averages of the mean-square displacement, radial distribution functions, and moments of the velocity, acceleration, and the time-derivative of the acceleration. The results are presented in table 1.

The dependence of the diffusion constant for the Lennard-Jones fluid normalized by that of the corresponding WCA system is shown in figure 1 for five densities and a wide range of temperature. Although the uncertainty in these data is small, so is the deviation of D from D_{WCA} and even a small uncertainty results in a sizeable scatter in D/D_{WCA} versus the temperature. However, there is a consistent downward slope in these data which is well described by the proposed functional dependence on temperature.

The equilibrium moment expansions were evaluated using data from the simulations described above. The absolute diffusion constant was calculated for the Lennard-Jones and WCA systems and for the Gaussian model; the reduced diffusion constant D/D_{WCA} was calculated for both the exponential and Gaussian model (where the relaxation time of the exponential model was taken to be independent of the attractive interaction). In figure 1 we compare the predictions of the Gaussian memory model for the reduced diffusion constant as a function of temperature with the simulation results. Data for the exponential memory model are nearly identical to the predictions of the Gaussian model over the full range of density and temperature.

The force autocorrelation functions were calculated for the force exerted on a single fixed atom surrounded by 124 fluid bath atoms. Each system was equilibrated for 50 time units followed by calculation of the force correlation functions over a 300 time unit trajectory. For simulations of the Lennard-Jones fluid the separate contributions to the force autocorrelation were calculated. For simulations employing the WCA repulsive force, we calculated the repulsive–repulsive, attractive–attractive and cross terms *as if the full force was present*. This can be thought of as a calculation of the full force autocorrelation function using the reduced propagator $e^{iL_0 t}$ (see equations (13) and (14)). As expected, the absolute diffusion constants were accurately predicted by the force autocorrelation function, but not to the degree needed to calculate the ratio D/D_{WCA} accurately. Therefore, the reduced diffusion constant was calculated using

$$\frac{D}{D_{\text{WCA}}} = \frac{\zeta_{\text{R}}}{\zeta_{\text{R}} + \zeta_{\text{A}}}, \quad (28)$$

where ζ_{R} and ζ_{A} were taken from the simulation of the Lennard-Jones fluid *or* that of

Table 1. Simulation data for diffusion coefficients in the Lennard-Jones and WCA simple fluids. All numbers are given in Lennard-Jones reduced units.

ρ	T	D	$\langle v^2 \rangle$	D_R	$\langle v^2 \rangle_R$
0.30	0.75	0.1843	2.298	0.4729	2.250
	1.00	0.4194	2.980	0.5438	2.999
	1.25	0.5743	3.720	0.6826	3.752
	1.50	0.6493	4.507	0.7512	4.499
	2.00	0.8480	5.991	0.9062	6.003
	3.00	1.0792	8.992	1.1039	9.001
	4.00	1.4251	11.989	1.4389	11.998
0.65	0.75	0.0986	2.260	0.1272	2.251
	1.00	0.1322	2.997	0.1549	2.997
	1.25	0.1622	3.754	0.1839	3.746
	1.50	0.1932	4.496	0.2088	4.511
	2.00	0.2539	6.002	0.2546	6.003
	3.00	0.3905	9.003	0.3967	9.003
	4.00	0.4823	11.986	0.4566	12.025
0.85	0.75	0.0329	2.261	0.0438	2.253
	1.00	0.0497	3.000	0.0639	3.003
	1.25	0.0658	3.743	0.0805	3.752
	1.50	0.0843	4.506	0.0930	4.507
	2.00	0.1210	6.004	0.1247	5.992
	3.00	0.1958	8.981	0.1948	9.018
	4.00	0.2416	12.009	0.2621	12.001
0.95	0.75	0.0130	2.260	0.0207	2.256
	1.00	0.0248	2.999	0.0311	3.005
	1.25	0.0339	3.741	0.0442	3.757
	1.50	0.0476	4.500	0.0565	4.501
	2.00	0.0697	5.994	0.0831	5.998
	3.00	0.1193	8.978	0.1337	8.982
	4.00	0.1709	12.014	0.1788	11.977
1.05	0.75	0.0006	2.739	0.0004	2.680
	1.00	0.0024	3.295	0.0112	2.996
	1.25	0.0160	3.746	0.0197	3.744
	1.50	0.0231	4.519	0.0280	4.496
	2.00	0.0425	6.007	0.0446	5.998
	3.00	0.0740	9.015	0.0884	8.978
	4.00	0.1320	12.012	0.1268	12.001

the WCA fluid. The zero-frequency friction constants were determined by integrating the force autocorrelation function through 2 time units. The exact value of the upper limit of the integration did not significantly affect the ratio D/D_{WCA} . The resulting reduced diffusion constants are displayed as a function of temperature in figure 1.

5. Discussion

Previous discussions of the role of attractive interactions in self-diffusion have searched for an appropriate effective hard-sphere reference system. We have used the WCA reference system as the most natural one for describing the role of attractive interactions since it is simply the Lennard-Jones potential in the absence of the attractive force.

The equilibrium moment expansions provide a clear means of analysing the

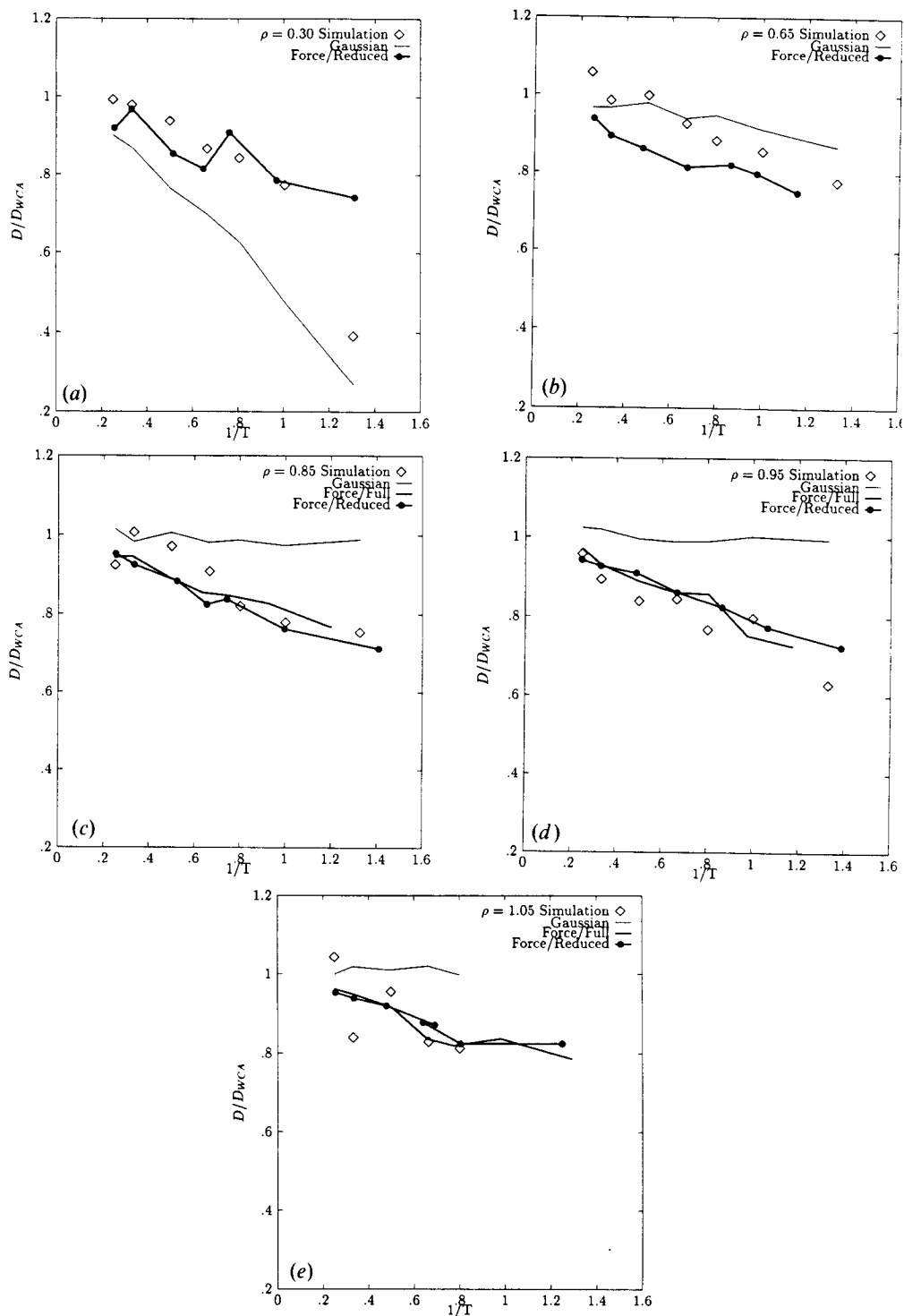


Figure 1. The ratio of the Lennard-Jones and WCA fluid diffusion coefficients is examined from simulation, the Gaussian memory model, and the force autocorrelation functions using the full or reduced propagator at densities of (a) 0.30, (b) 0.65, (c) 0.85, (d) 0.95 and (e) 1.05.

contribution of the attractive force where the moments of the velocity or acceleration are calculated directly for the Lennard-Jones or WCA systems. We find the exponential and Gaussian models predict a nearly identical dependence of the reduced diffusion constant on temperature at all densities. The zero-time value of the memory function is influenced by the presence of the attractive force (at least at some densities). However, the relaxation time predicted by the Gaussian memory is found to be independent of the attractive interactions. The moment expansions show a strong temperature dependence (through the mean-square force) for D/D_{WCA} at a density of 0.30, a weaker dependence at 0.65, and only a very weak dependence at higher densities (see figure 1 (b)).

It is well known that the long-time decay of the memory function due to hydrodynamic forces is not well described by the Gaussian memory. As a result, the temperature dependence of D/D_{WCA} predicted by the moment expansion models is too weak. This implies, not surprisingly, that an understanding of the effect of the attractive interactions on longer time relaxation of the bath is necessary for a complete description of the system dynamics.

The force autocorrelation functions provide a reasonably accurate estimate of the absolute diffusion constant for the fluid. Remember, these functions were calculated for an impurity in a bath of only 124 atoms. The small system size was used to generate the extended trajectories necessary for calculations of the force autocorrelation function for the single fixed atom (impurity). The reduced diffusion constant was calculated using equation (28) and the zero-frequency friction values ζ_{R} and ζ_{A} . For densities 0.75 and above, calculation of ζ_{R} and ζ_{A} using the full propagator or the reduced propagator gives nearly identical results.

At densities of 0.65 and 0.30, the results of the full propagator predict that $D_{\text{WCA}} < D$. This is due to the presence of significant negative crossterms contributing to an overall negative ζ_{A} . As a result, $\zeta < \zeta_{\text{R}}$ leading to the (erroneous) prediction that $D > D_{\text{WCA}}$. At these densities the approximation $\zeta_{\text{WCA}} \simeq \zeta_{\text{R}}$ is poor and one must use equation (15).

The force autocorrelation function decomposition provides an accurate dissection of the influence of attractive interactions on self-diffusion. Most interesting is the fact that the simulation data are well described by the functional form predicted by kinetic theory for low density fluids with the Sutherland [3] or square-well potentials [16, 17]

$$\frac{D}{D_{\text{WCA}}} = \frac{1}{1 + \alpha \epsilon / k_{\text{B}} T} \tag{29}$$

The constant α appears to be fairly independent of density [18].

We can argue why we expect α to be independent of temperature for the range of temperature and densities we have studied. Assuming that for our WCA reference system $\Omega_{\text{HS}}^2 \tau_{\text{WCA}} \simeq \Omega_{\text{R}}^2 \tau$ (see equations (17) and (24) and the surrounding discussion) we arrive at equation (25) with a definition of α

$$\alpha \frac{\epsilon}{k_{\text{B}} T} = \frac{\Delta \Omega^2 \tau}{\Omega_{\text{R}}^2 \tau_{\text{R}}} \tag{30}$$

For our purposes, we assume the WCA system dynamics are similar to those of a hard-sphere system which can be described approximately by Enskog theory or an empirical equation which provides accurate dependence at all densities [4]. Using the WCA theory decomposition of equation (7), the contribution to α from the ratio of

Table 2. Results for the coefficient α from simulation and theory.

Method	α
Sutherland model [3]	0.167
Hard sphere [4]	0.4
Kushick and Berne [4]	0.14
Simulation data	0.23
Force correlation/full propagator	0.19
Force correlation/WCA propagator	0.26

the mean-square forces is

$$\frac{\Delta\Omega^2}{\Omega_{HS}^2} \propto \frac{\varepsilon}{k_B T} \int_{r_{\min}}^{\infty} dr r^2 g(r; T) \nabla^2 v_1(r). \quad (31)$$

The proportionality constant is density dependent but independent of temperature; temperature dependence enters solely through the radial distribution function for the structure of the Lennard-Jones fluid $g(r; \rho, T)$. Additional temperature dependence may enter α through the ratio of the relaxation times τ/τ_R . However, our simulation data indicate that, for a particular density as a function of temperature, the ratio of relaxation times is roughly a constant

$$\tau/\tau_R = \text{constant} \geq 1. \quad (32)$$

The result is that, over the range of temperatures studied, the dominant contribution is the effect of the attractive interaction on the mean-square force as a function of density and temperature. It is through this ratio that the linear dependence of the correction term on $\varepsilon/k_B T$ enters. Higher-order dependence enters through the temperature dependence of the radial distribution function or the ratio of relaxation times. In particular, in supercooled liquids and glasses diffusion occurs by way of activated transitions. It is in this regime that we expect to find an Arrhenius (or Vogel-Fulcher [19] or Bässler-Zwanzig [20]) form for the decreased diffusion as the temperature is lowered. At higher temperatures, such as those examined in this study, the mechanism for diffusion is not activated, the diffusion constant is seen to vary as $D \sim T$, and the reduction in diffusion due to the presence of attractive forces follows the form of equation (29) seen in gases rather than the Arrhenius form, even at high densities. It is possible that the presence of attractive forces manifests itself through the Arrhenius form at lower temperatures in viscous liquids where the shear relaxation time $\geq 10^{-9}$ s [21], and this would be interesting to examine.

From our simulation data, the constant α when taken to be density independent is $\alpha = 0.23$. As we noted in the introduction, for a Sutherland potential one finds $\alpha = S(\nu = 6) = 0.1667$. For a collection of data, Speedy *et al.* found $\alpha_{HS} = 0.4$ for a Lennard-Jones system using an effective hard-sphere references, and $\alpha_{WCA} = 0.14$ using a WCA reference system and the data of Kushick and Berne [4]. The prediction of the force autocorrelation decomposition, using the full propagator, is $\alpha = 0.19$ (taking data for $\rho > 0.65$) and, using the WCA propagator, is $\alpha = 0.26$. These results, summarized in table 2, provide a consistent picture of the magnitude of the reduction in the self-diffusion coefficient due to the presence of attractive interactions.

In summary, our analysis indicates that attractive forces do have a significant effect on the rate of self-diffusion in a simple fluid. The functional form predicted by

kinetic theory for low density fluids and gases is accurate even at high density for a Lennard-Jones fluid if the reference system is taken to be the WCA fluid. This result suggests that the differences between the dynamic properties of WCA or hard-sphere fluids at low density can be used to predict accurately the behaviour of fluids at much higher densities for temperatures $T \geq \epsilon/k_B$.

Helpful comments on this manuscript by R. J. Speedy are gratefully acknowledged.

References

- [1] MCQUARRIE, D. A., 1975, *Statistical Mechanics* (Harper and Row).
- [2] The recent study of Ben-Amotz and Herschbach of fluid properties along the 'Zeno line' (the states for which the compressibility factor is unity) provides an example of the impressive nature of the balance between excluded volume and attractive interactions that define the imperfect fluid (BEN-AMOTZ, D., and HERSCHBACH, D. R., 1990, *Isr. J. Chem.*, **30**, 59). They have shown a strong correlation between the slope of the Zeno line (which spans states from the Boyle point to deep in the liquid region) and that of the law of rectilinear diameters $((\rho_L + \rho_v)/2 \propto T$ in the liquid-vapour coexistence region). They point out the implication that the equilibrium properties of fluids at low density determine the behavior of fluids at much higher densities.
- [3] HIRSCHFELDER, J. O., CURTISS, C. F., and BIRD, R. B., 1954, *Molecular Theory of Gases and Liquids* (Wiley).
- [4] SPEEDY, R. J., PRIELMEIER, F. X., VARDAG, T., LANG, E. W., and LÜDEMANN, H.-D., 1989, *Molec. Phys.*, **66**, 577.
- [5] JOST, W., 1960, *Diffusion in Solids, Liquids, Gases* (Academic Press).
- [6] KUSHICK, J., and BERNE, B. J., 1973, *J. chem. Phys.*, **59**, 3732.
- [7] BERNE, B. J., and PECORA, R., 1976, *Dynamic Light Scattering* (Wiley).
- [8] FORSTER, D., 1975, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions*, (Benjamin Cummings).
- [9] HANSEN, J. P., and McDONALD, I. R., 1986, *Theory of Simple Liquids* (Academic Press).
- [10] ALLEN, M. P., and TILDESLEY, D. J., 1990, *Computer Simulation of Liquids* (Oxford University Press).
- [11] SCHWEIZER, K. S., and CHANDLER, D., 1982, *J. chem. Phys.*, **76**, 2296. Stated loosely, for most fluid states the timescale for the decay of the repulsive force correlation will be approximately $\tau_R \cong 0.1$ to 0.3 ps. The timescale for changes in the attractive force will be the time required for an atom to diffuse approximately an atomic radius. Assuming that this time will be approximately $\tau_A \cong \sigma^2/D$ where D is the self-diffusion coefficient and taking $D \cong 5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} = 0.5 \text{ \AA}^2 \text{ ps}$ we find $\tau_A \cong 20$ ps. According to this argument, the expected separation of timescales $\tau_A/\tau_R \cong 10$ – 20 is substantial.
- [12] STRAUB, J. E., BORKOVEC, M., and BERNE, B. J., 1987, *J. phys. Chem.*, **91**, 4995; STRAUB, J. E., BORKOVEC, M., and BERNE, B. J., 1988, *J. chem. Phys.*, **89**, 4833.
- [13] BERNE, B. J., TUCKERMAN, M. E., STRAUB, J. E., and BUG, A. L. R., 1990, *J. chem. Phys.*, **93**, 5084; For the study of the friction on a diatomic molecule in a simple fluid, the results indicated that the approximation of fixing the vibrational coordinate agreed well with the friction calculated using a flexible bond. However, analysis of the temperature dependence indicated that the bath was not effectively harmonic.
- [14] DEUTCH, J. M., and SILBEY, R., 1971, *Phys. Rev. A*, **3**, 2049.
- [15] HARP, G. D., and BERNE, B. J., 1970, *Phys. Rev. A*, **2**, 975.
- [16] ALLEY, W. E., and ALDER, B. J., 1975, *J. chem. Phys.*, **63**, 3764.
- [17] KORLIPARA, R. K., STELL, G., and KARKHECK, J., 1989, *J. chem. Phys.*, **90**, 5687.
- [18] This functional form results from the fact that in the Chapman-Enskog approximation the diffusion coefficient takes the form $D \cong 1/\Omega_{12}^{(1,1)}$ where $\Omega_{SW} = \Omega_{12}^{(1,1)}$ for the square-well potential and $\Omega_{HS} = \Omega_{12}^{(1,1)}$ for the hard-sphere potential. The collision integral takes the approximate form [17] $\Omega_{SW}/\Omega_{HS} = 1 + \text{constant}(\epsilon/k_B T)$, which leads to the result $D_{SW}/D_{HS} = 1/(1 + \text{constant}(\epsilon/k_B T))$.
- [19] VOGEL, H., 1921, *Z. Phys.*, **22**, 645; FULCHER, G. S., 1925, *J. Am. Ceram. Soc.*, **8**, 339.
- [20] BÄSSLER, H., 1987, *Phys. Rev. Lett.*, **58**, 767; ZWANZIG, R., 1988, *Proc. natn. Acad. Sci. U.S.A.*, **85**, 2029.
- [21] GOLDSTEIN, M., 1969, *J. chem. Phys.*, **51**, 3728.