Role of attractive forces in self-diffusion in dense Lennard-Jones fluids*

Joseph Kushick† and Bruce J. Berne

Department of Chemistry, Columbia University, New York, New York 10027

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The Lennard-Jones potential is separated into a purely repulsive and a purely attractive part, V_R and V_A, respectively. The velocity correlation function (vcf) is computed by molecular dynamics separately for $(V_R + V_A)$ and for V_R in both isotropic and nematic liquids for several thermodynamic states. It is found that in dense fluids, the results for these two different potentials are in qualitative agreement. The role of the attractive force is discussed. This work is motivated by the recent success of perturbation theories in connection with the equilibrium properties of fluids.

INTRODUCTION

Recently Chandler, Weeks, and Anderson[1] have developed a perturbation theory of the structure and thermodynamic properties of simple liquids. This theory has been remarkably successful when tested against the pair correlation functions and thermodynamic properties determined on the basis of molecular dynamics computer experiments. The starting point for these considerations is the decomposition of the Lennard-Jones (12–6) potential

$$V(r) = 4\epsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right]$$

into a sum of a strong short range purely repulsive part

$$V_R(r) = V(r) + \epsilon \quad r/\sigma < 2^{1/6},$$
$$= 0 \quad r/\sigma > 2^{1/6},$$

and a weak longer range attractive part

$$V_A(r) = -\epsilon \quad r/\sigma < 2^{1/6},$$
$$= V(r) \quad r/\sigma > 2^{1/6}.$$

Investigation of static properties such as the pair correlation function has shown that substitution of $V_R(r)$ for $V(r)$ preserves many essential features of the system under study.

All of the previous work concerned itself with the equilibrium properties of fluids. The success of the perturbation theory in predicting the static properties of fluids should lead, in the near future, to successful perturbation theories of transport coefficients in which the transport coefficients for realistic potentials can be determined from those of model systems like hard sphere fluids.

The technique of molecular dynamics (in which the equations of motion of a many-body system are solved on a computer) has often been used to probe the static and dynamic properties of many-body systems.[2] The Lennard-Jones potential has often been assumed in such studies of monatomic

fluids. One major difficulty of the method is the large amount of computer time required for the calculations. Since the computer time required depends on the number of interactions suffered per molecule, which in turn depends on the cube of the range of the potential, it is of some importance to study the effect on molecular dynamics results of substitution of a short range interaction for the full Lennard-Jones potential. It is the purpose of this work to explore the effects of replacing $V(r)$ by $V_R(r)$ and to characterize the role played by the attractive forces in the decay of velocity correlations in dense fluids.

CALCULATIONS

A series of molecular dynamics simulations was carried out for 500 argon atoms in various thermodynamic states. The states studied are shown in Table I.

The first ten simulations listed in Table I consist of five consecutive pairs. Each of these five pairs consists of studies done at the same number density and approximately the same temperature on systems interacting first with the full (F) Lennard-Jones potential $V(r)$, and then with the truncated (R) Lennard-Jones potential $V_R(r)$. The range of the full L-J potential was 2.5σ. For each of these ten simulations, the normalized vcf, the corresponding memory function, and the self-diffusion coefficient were calculated.

For the remaining states in Table I; that is, for states with $\rho\sigma^3 < 0.75$, we performed molecular dynamics calculation only for systems interacting with $V_R(r)$. The vcf's so obtained were then compared with those corresponding to the full potential $V(r)$, by making use of an interpolation scheme presented by Levesque and Verlet.[3] These authors made a detailed study of self-diffusion in Lennard-Jones fluids. One of the byproducts of their studies is the parametric form for the memory function

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TABLE I. Molecular dynamics simulations of argon. ρ is the density, T the temperature, D the diffusion coefficient, $K(0)$ the initial value of the memory function, Δt the time increment used in the computation, and N the number of time steps in the trajectory. In the "Potential" column, F means the full $V(r)$ and R means $V_R(r)$. Results in brackets were obtained from Eqs. (1) and (2) rather than from dynamics. All quantities are expressed in L-J reduced units where m, σ, and ϵ are the units for mass, length, and energy respectively. In particular, our unit of time is $\tau = \sigma\sqrt{m/\epsilon}$. Since the reduced unit of time in Ref. 3 differs from that used by us, the results of that work must be converted in order to be compared with our results: $D_{present} = D_{Ref.\,3} \times \sqrt{48}$; $K(0)_{present} = K(0)_{Ref.\,3} \times 48$.

ρ	T	Potential	D	$K(0) \times 10^{-2}$	$\Delta t \times 10^3$	N
0.85	0.82	F	0.040	2.90	7.5	500
0.85	0.76	R	0.048	2.90	7.5	600
0.85	4.68	F	0.29	7.53	4.0	900
0.85	4.64	R	0.30	7.65	4.0	1230
0.81	0.74	F	0.044	2.47	7.5	600
0.81	0.74	R	0.055	2.54	7.5	600
0.75	0.96	F	0.084	2.27	7.5	460
0.75	0.91	R	0.093	2.21	7.5	600
0.75	5.13	F	0.39	6.30	4.0	500
0.75	5.10	R	0.41	6.32	2.0	600
0.65	1.42	F	[0.17]	[2.16]	⋯	⋯
0.65	1.42	R	0.20	2.09	5.0	600
0.65	5.09	F	[0.48]	[4.72]	⋯	⋯
0.65	5.09	R	0.53	4.47	2.0	600
0.30	1.58	F	[0.65]	[0.80]	⋯	⋯
0.30	1.58	R	0.70	0.57	5.0	760

$$K(t) = \Omega_0^2 \exp(-B_0 t^2/2) + A_0 t^4 \exp(-\alpha_0 t), \qquad (1)$$

where the quantities Ω_0^2, B_0, A_0, and α_0 are parameters which are tabulated in Ref. 3. When this parametric form for $K(t)$ is combined with the memory function equation[4] for the normalized vcf, $C(t)$; that is,

$$\partial C(t)/\partial t = -\int_0^t d\tau\, K(\tau) C(t-\tau), \qquad (2)$$

then $C(t)$ can be determined. Levesque and Verlet claim that this interpolation reproduces their computer generated vcf's to within 0.01. Thus we compare all of our simulations for $V_R(r)$ and for $\rho\sigma^3 < 0.75$ with the calculations of Levesque and Verlet on the full potential as embodied in their interpolation scheme. In our view, this procedure is not entirely trustworthy so that our comparisons between (F) and (R) for states with $\rho\sigma^3 < 0.75$ are not as accurate as those for $\rho\sigma^3 \geq 0.75$. The reason that we regard the interpolative scheme as less accurate is simple. We compared the interpolative scheme for the calculation of the (F) vcf's with our molecular dynamics computations of the (F) vcf's for states with $\rho\sigma^3 \geq 0.75$ and found that there were rather large discrepancies. The discrepancies were such that as the temperature was increased by a factor of 5 at a given density, the interpolated (F) vcf still de-

viated by a large amount from the simulated (R) vcf whereas the simulated (F) vcf differed very little from the simulated (R) vcf. On the basis of physical intuition we expect the differences between the (F) vcf's and the (R) vcf's to disappear as T is increased. We can only conclude from these observations that the interpolation procedure is not adequate for a comparison between (F) and (R) simulations. For those states ($\rho\sigma^3 \geq 0.75$) which are important in a discussion of perturbation theories we use the full dynamics for (F) and (R), whereas for the less interesting states ($\rho\sigma^3 < 0.75$), rather than recalculate the (F) results (which would involve us in enormous expense with perhaps somewhat smaller yield) we use the interpolation procedure.

To summarize: for the states $\rho\sigma^3 < 0.75$ we use the interpolative procedure for (F) and simulations for (R) whereas for $\rho\sigma^3 > 0.75$ we use simulations for both (F) and (R).

Figure 1 shows the various vcf's. The error bars were calculated from the Zwanzig–Ailawadi estimate of statistical error.[5] In Fig. 2 we show the normalized memory functions, which were calculated numerically from the vcf's,[6] except for the three cases where we used Eq. (1). The temperatures shown in these two figures are the temperatures of the $V_R(r)$ simulations.

The diffusion coefficients for the various states, obtained by integrating the vcf's, are listed in Table I. The vcf's were integrated in time until they began to exhibit a substantial level of noise, which in all cases did not occur until the functions had decayed very close to zero. Therefore, as is generally the case in molecular dynamics calculations, there is some inaccuracy in our determination of diffusion coefficients due to the arbitrariness in the cutoff point for integration. In addition, we attempted to "correct" for the temperature difference between members of each pair of simulations by using an empirical formula for D given in Ref. 3, but the results were inconclusive.

In addition to these calculations on systems composed of spherical particles, we performed molecular dynamics simulations of systems composed of ellipsoidal particles. With suitable values for the major to minor axis ratio, density, and temperature, these systems form ordered, nematic-like fluids. In one case, the particles interacted via an ordinary L-J potential which was modified to take account of the nonsphericity of the particles.[7] In another, only the repulsive part of the potential was used, in analogy to $V_R(r)$. These two simulations were carried out with a time increment of 0.005, and were continued for 600 time steps. The axial ratio was 3.5, the temperature was 0.75,
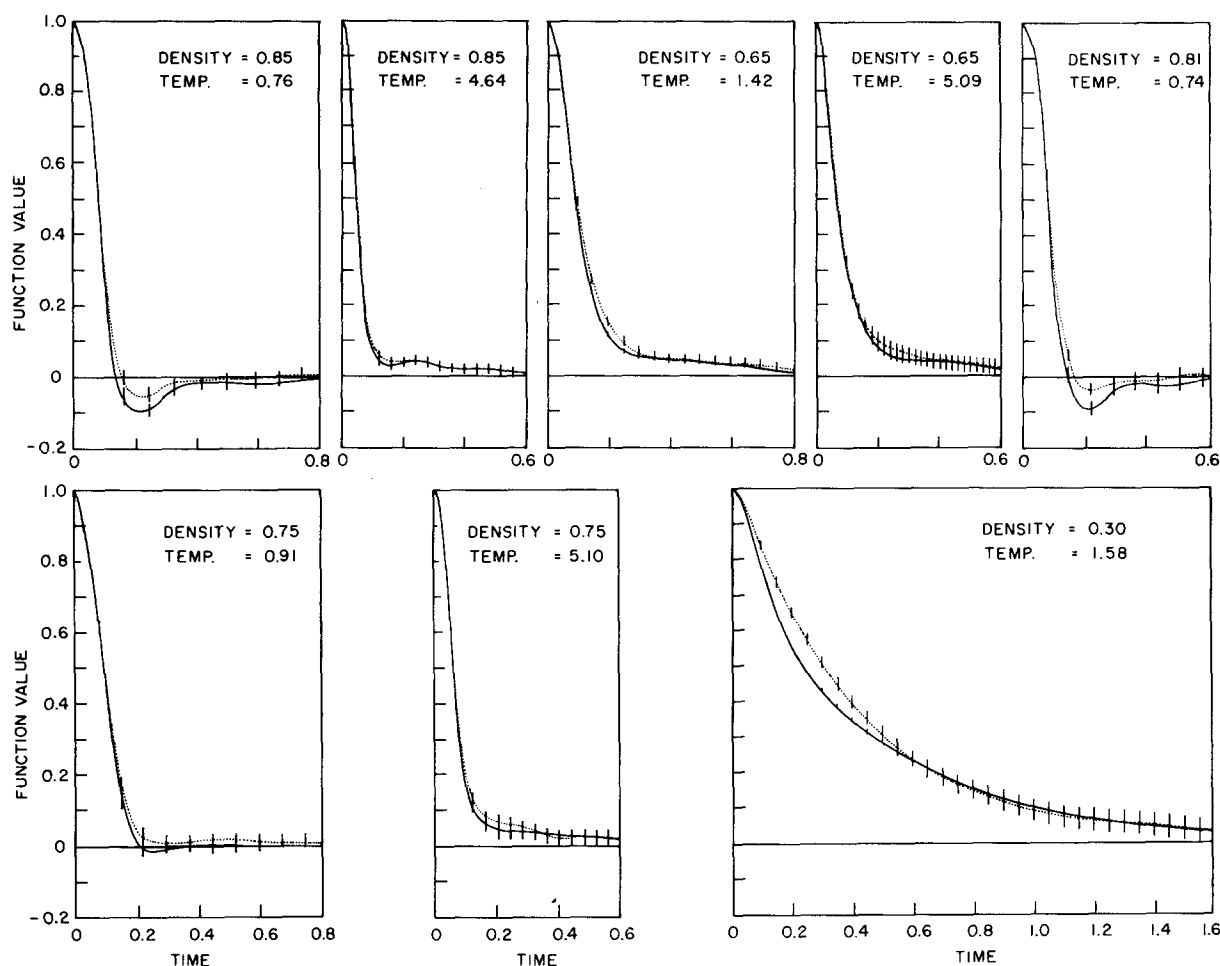
FIG. 1.   Normalized argon velocity correlation functions.   Solid line, full L-J potential; dotted line, repulsive part only.

and the density was 0.289 (in reduced units).   Figure 3 shows the velocity correlation functions (averaged for 300 time steps) calculated from these dynamics results, both perpendicular and parallel to the direction of preferential alignment, $\hat{n}$.

DISCUSSION

We find that for the high density systems there are no qualitative differences between the velocity correlation functions for the "truncated" and the "full" L-J potential.   However, there is a systematic tendency for the functions calculated from $V_R(r)$ to be higher valued than those calculated from $V(r)$.   In particular, $V_R(r)$ seems less likely to produce a pronounced negative region than $V(r)$.   It may be instructive to view $V_R(r)$ as intermediate in character between $V(r)$, in which the average molecule interacts simultaneously with a relatively large number of other molecules, and a hard sphere interaction which is truly binary.   Broadly speaking, a negative region in the velocity corre-

lation function occurs when there is a tendency for the average molecule to reverse the direction of its velocity within a characteristic time period.   When these velocity reversals occur coherently, that is with a narrow distribution of first collision times, the velocity correlation function should exhibit a substantial negative region.   We might then expect that velocity reversals should occur less coherently for a hard sphere fluid than for a Lennard-Jones fluid, and indeed, velocity correlation functions calculated for hard sphere fluids show less inclination to have negative regions than do functions for L-J fluids.[8]   In this light, the quantitative differences between the velocity decay for $V(r)$ and $V_R(r)$ appear physically reasonable.

Perturbation theory has been successfully applied to the calculation of the pair correlation function in Lennard-Jones fluids.   From this theory it is expected that the (F) and (R) potentials should give rise to very similar structures either
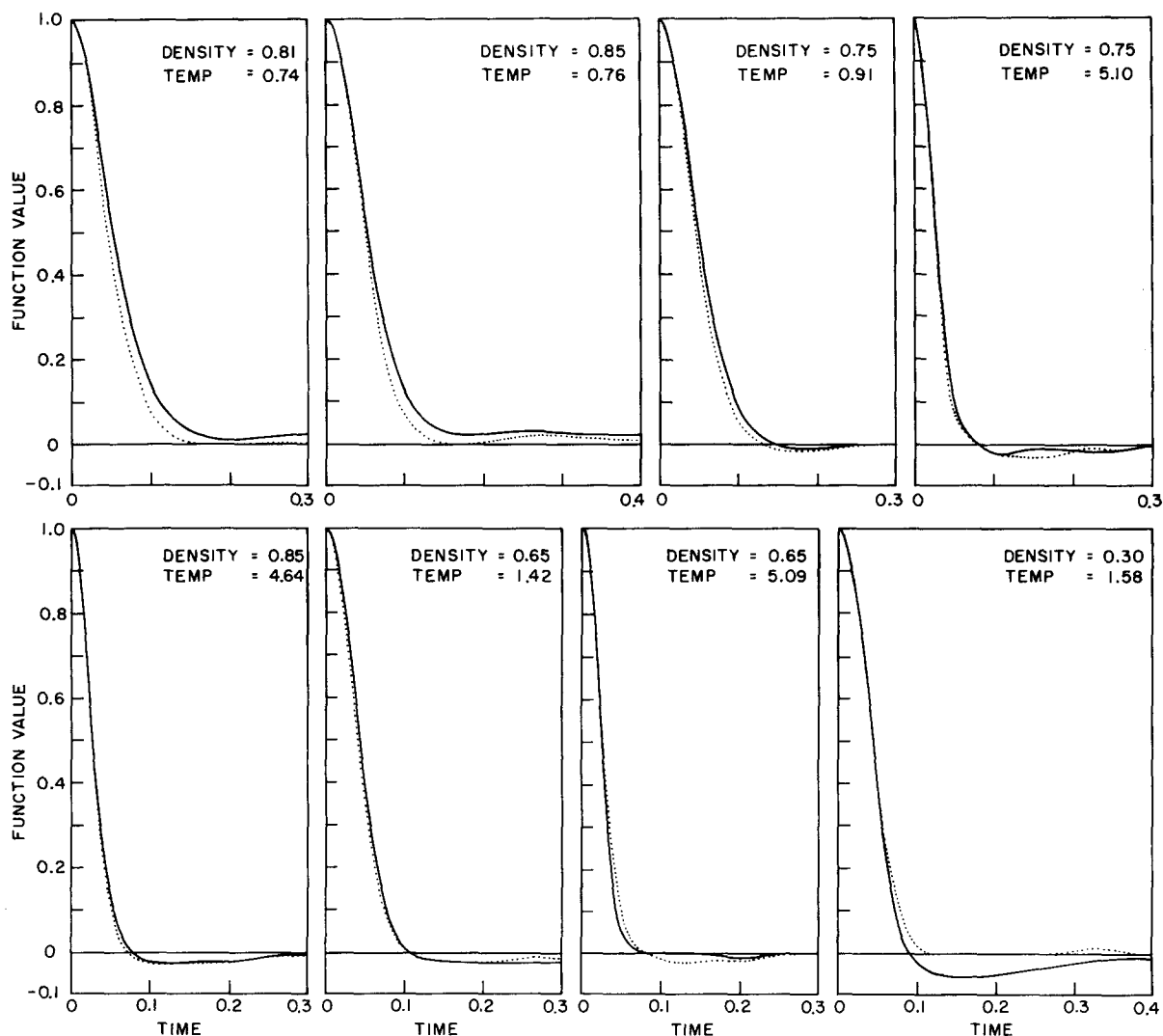
FIG. 2. Normalized memory functions for the vcf's of Fig. 1. Solid line, full L-J potential; dotted line, repulsive part only.
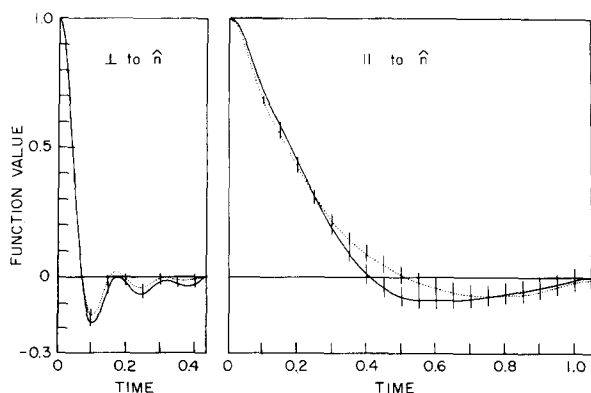

FIG. 3. Normalized vcf for nematic liquid crystal, ⊥ and ∥ to the director. Solid line, full L-J potential; dotted line, repulsive part only. The reduced unit of time is obtained from the molecular parameters in the modified L-J potentials.

when the density is such that the nearest neighbor distance is near the repulsive region of the pair potential, as in the case $\rho\sigma^3 \sim 0.85$, for any temperature or for temperatures that are sufficiently high that the attractive contribution is negligible for any density, as for example when $T \sim 4$ or 5). If self-diffusion were purely determined by this static structure then the vcf's and their corresponding diffusion coefficients should agree for (R) and (F) in all of these regions. From Fig. 1 we see that this is not the case. Although the vcf's agree at high temperature for (R) and (F) they do not agree at high density $(\rho\sigma^3 = 0.85)$. It thus behooves us to find a perturbation theory that accounts for this not entirely unexpected result.

The use of the truncated potential resulted in a substantial decrease in the cycle time; that is, the

computer time needed to advance the system through one time step. For example, in the run we conducted on 500 argon atoms with $\rho\sigma^3 = 0.81$ and $kT/\epsilon = 0.74$ the cycle time on our IBM 360/91 was 3.5 sec for the full L-J potential and 0.5 sec for the truncated L-J potential. This is an enormous saving of time. Since the results are qualitatively the same; that is there are no differences in the physical content of the two solutions, the truncated potential can be used to great advantage in otherwise very difficult computations such as those involved in the elucidation of long time tails. We are presently using this idea in our studies of nematic liquid crystals, where, for example, the full potential requires a cycle time of 66 sec and the truncated potential requires a cycle time of 8 sec. This is perhaps the most important feature of this calculation.

Note added in proof: It has recently come to our attention that P. Schofield has investigated the role of attractive forces in velocity relaxation, [Computer Phys. Comm. **5**, 17 (1973)].

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