Molecular Dynamics Simulations of One-Dimensional Lennard-Jones Systems

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One-dimensional Lennard-Jones systems are investigated by molecular dynamics simulations. The full Lennard-Jones potential is compared to the repulsive Lennard-Jones potential. It is found that the pair correlation function and the normalized velocity autocorrelation function agree at high densities and high temperature. However, the diffusion coefficient indicates that the attractive potential introduces additional correlations into particle dynamics which are not reflected in the statics. These results are in agreement with three-dimensional studies.

KEY WORDS: Perturbation theory; one dimensional; molecular dynamics; Lennard-Jones.

INTRODUCTION

Recently, perturbation theories[1] have been developed which describe the liquid state. Properties of complex systems can now be obtained by a suitable perturbation from a simple reference system. The manner in which the reference system is selected forms the basis of the various perturbation theories. In the Weeks–Chandler–Anderson theory[2] the intermolecular potential is split into a purely repulsive and a purely attractive part. The purely repulsive system is taken as the reference system. By simulating both model systems with the full (repulsions and attractions) potential and systems with only the repulsive potential, the roles of repulsions and attractions in determining thermodynamic and transport properties can be assessed. In this note we report on our molecular dynamics calculations of one-dimensional Lennard-Jones systems.

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MODEL

The full Lennard-Jones (FLJ) potential has the form

$$U(X) = 4\left[(1/X)^{12} - (1/X)^6\right], \qquad X \leqslant 2.5$$
$$= 0 \qquad\qquad\qquad\qquad X > 2.5 \qquad (1)$$

whereas the repulsive Lennard-Jones (RLJ) potential has the form

$$U(X) = 4\left[(1/X)^{12} - (1/X)^6 + 1/4\right], \qquad X \leqslant 2^{1/6}$$
$$= 0 \qquad\qquad\qquad\qquad\qquad X > 2^{1/6} \qquad (2)$$

Here X is the molecular separation. All results will be given in the usual reduced units. Lengths are measured in units of σ, velocity in units of $(\epsilon/m)^{\frac{1}{2}}$, and time in units of $\sigma(m/\epsilon)^{\frac{1}{2}}$, where σ is the length of a particle, m is the mass of a particle, and ϵ is the well depth of the potential.

The initial particle configuration is specified as follows: starting with N particles ($N = 1000$) one-dimensional number densities, ρ, of 0.935, 0.72, and 0.65 were selected for study. The particles were initially placed on lattice sites with spacing $1/\rho$. The particle velocities were selected from a Maxwellian distribution by the Box–Muller method.[3] Newton's equations of motion were integrated by the Runge–Kutta–Gill method using a step size of 0.005. Periodic boundary conditions are imposed on the equations of motion. This means that if X_i is the position of particle i in the line, there are two periodic images at $X_i \pm L$ where L is the length of the basic cell. L is determined by fixing the number density N/L. A given particle interacts with all particles and images within the potential range. However, because the potential range is limited to 2.5, particles can only interact with at most their third nearest neighbor. A "box scheme" is not needed for one-dimensional calculations because of the small number of pair interactions which must be considered.

RESULTS

Initial relaxation to the equilibrium phase was determined by following the temperature fluctuations. After an appropriate number of equilibrium steps (see Table I) data were stored on magnetic tape for subsequent analysis. Haus and Raveche[4] have investigated the relaxation behavior of one-dimensional hard rods. They found that the approach of a dynamic property such as the pressure to the exact equilibrium value was not a sufficient indicator of structural relaxation. One needs to follow the relaxation of the singlet distribution function and the order parameter $f(t)$

Table I.   The Results for All the Systems[a]

ρ	Range	NONEQ	EQ	U	E	T	P	D
0.65	2.5	154	1400	− 0.441	− 0.053	0.775	0.873	0.144
0.65	$2^{1/6}$	89	1400	0.048	0.411	0.725	1.40	0.177
0.65	2.5	77	1400	− 0.109	2.40	5.02	7.89	0.464
0.65	$2^{1/6}$	77	1400	0.419	2.95	5.06	8.50	0.478
0.72	2.5	105	1400	− 0.549	− 0.151	0.796	1.28	0.117
0.72	$2^{1/6}$	89	1400	0.070	0.440	0.738	2.01	0.136
0.935	2.5	106	1400	− 0.599	− 0.235	0.727	10.41	0.030
0.935	$2^{1/6}$	81	1400	0.443	0.803	0.722	11.21	0.031

[a] ρ is the number density, range is the potential range, NONEQ is the number of time steps needed for temperature relaxation, EQ is the number of additional steps obtained, U is the average potential energy per particle, E is the average total energy per particle, T is the average temperature, P is the average pressure, and D is the diffusion coefficient.

defined as

$$f(t) = \frac{1}{N} \sum_{i}^{N} \cos\left[2\pi\rho X_i(t)\right] \tag{3}$$

where ρ is the number density, N is the number of system particles, and $X_i(t)$ is the position of particle i at time t. In the initial periodic lattice $f(t)$ is equal to 1; in a random array $f(t)$ will fluctuate about zero. One finds that at low densities $f(t)$ rapidly decays to zero. However, at the very high density of 0.935 there is still some residual order. The singlet distribution function, $g_1(x)$, is defined so that $g_1(x)dx$ is the probability that any one of the N particles will be found at a distance between X and $X + \Delta X$ ($\Delta X = 0.01$) from the position X_l^0 on the initially ordered array. It is calculated from

$$g_1(X) = \frac{1}{N_0 M N \rho} \sum_{m}^{M} \sum_{l}^{N_0} \sum_{k}^{N} n\left(X_l^0 - X_k^m\right) \tag{4}$$

where $n(X_l^0 - X_k^m)$ is the number of particles a distance X away from the initial periodic lattice sites. This quantity is averaged over all particles N, all lattice sites N_0, and all time steps M. A random array is expected to have $g_1(X) \rightarrow 1$. One notes that this prediction is approached as the number of time steps used is increased. However, there is still some residual order and it is more pronounced at the higher density. Similar results were obtained by Haus and Raveche[4] for hard rod systems. Structural relaxation required 1000 additional time steps; all these as well as the velocity equilibration steps were discarded for the reported calculations.

In the Table I we present the results for our studies. The temperature, T, is obtained by averaging over time steps:

$$T = \frac{1}{MN} \sum_m^M \sum_i^N V_i^2(m) \tag{5}$$

where $V_i^2(m)$ is the square of the velocity of particle i at time m. The pressure, P, is determined via the virial theorem:

$$P = \rho \left[T + \frac{1}{MN} \sum_m^M \sum_i^N X_i(m) F_i(m) \right] \tag{6}$$

where $X_i(m)$ and $F_i(m)$ are the position and total force on particle i at time m, respectively.

The phase space trajectories allow one to evaluate any function of coordinates and momenta. The pair correlation function, $g(X)$, describes the local structure of the system. In general, $g(X)$ is calculated from the
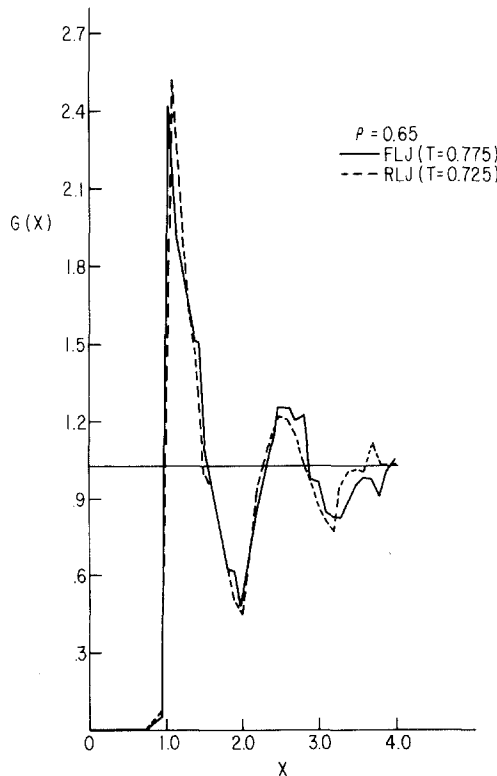

Fig. 1. The pair correlation function for RLJ and FLJ; $\rho = 0.65$.

operational definition

$$g(X) = \frac{\langle n(X) \rangle}{\rho 2 \Delta X} \tag{7}$$

where $\langle n(X) \rangle$ is the average number of pairs having separations between X and $X + \Delta X$. We have set $\Delta X = 0.01$ in our calculations and have averaged over 200 time origins as well as over 1000 particles. In Figs. 1 and 2, $g(X)$ is graphed for two different densities. The results for the FLJ and the RLJ are in closest agreement at higher densities. Systems with densities of 0.935, 0.72, and 0.65 have approximate nearest-neighbor distances of 1.07, 1.39, and 1.54, respectively. The range of the repulsive potential is $2^{1/6} \approx 1.12$. Hence, the higher density states have their nearest-neighbor distance near the repulsive region in the potential and it is expected that the $g(X)$ of the RLJ systems would be an excellent representation for the FLJ systems under these conditions. Such results have also been obtained for three-dimensional systems by Schofield[5] and Chen and Rahman.[6]

The relaxation of the normalized velocity autocorrelation function (NVAF), $\psi(t)$, provides information about particle motions. The NVAF is
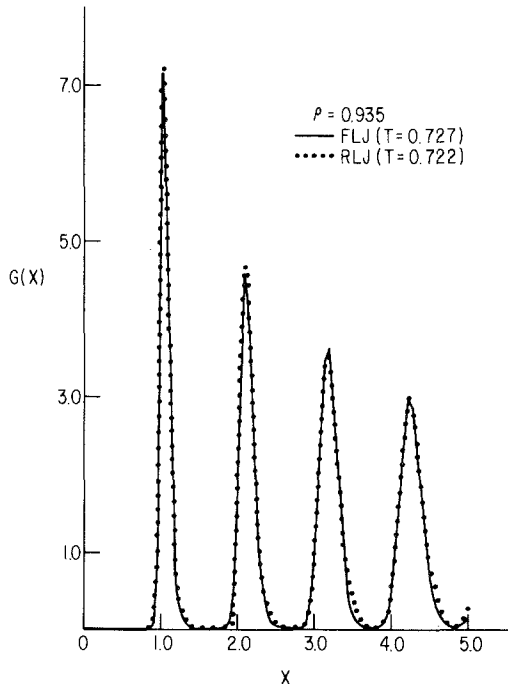

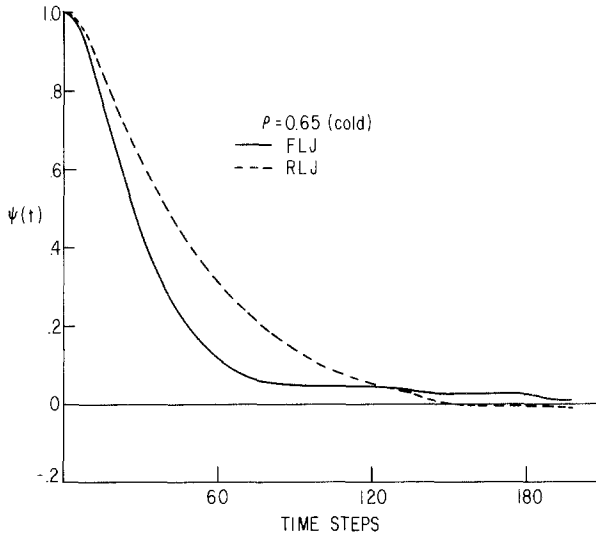Fig. 2. The pair correlation function for RLJ and FLJ: $\rho = 0.935$.

Fig. 3.   The normalized velocity autocorrelation function for RLJ and FLJ; $\rho = 0.65$.

determined from the data by

$$\psi(t) = \frac{\sum_m^M \sum_i^N V_i(t + m) V_i(m)}{\sum_m^M \sum_i^N V_i^2(m)} \tag{8}$$

where $V_i(m)$ is the velocity of particle i at time m. We have averaged over all particles (1000) and over 200 time origins of data. The results are compared in Figs. 3 and 4 for different densities. In all cases, the NVAF for the RLJ systems are more positive than those for the FLJ systems. In addition, the higher the density or the higher the temperature, the closer the NVAFs are. The diffusion coefficient, D, has been calculated by a Simpson integration of the NVAF,

$$D = \langle V^2 \rangle \int_0^{t_c} \psi(t)\, dt \tag{9}$$

The upper limit of the integral was selected to be the region where $\psi(t)$ becomes mostly noise. The D's are in the table. D for the RLJ is greater than that of the FLJ reflecting the NVAF results. Such conclusions were also obtained for three-dimensional systems by Kushick and Berne,[7] Schofield,[5] and Chen and Rahman.[6]

CONCLUSIONS

Our studies of one-dimensional Lennard-Jones systems parallel those of others on three dimensional systems. A RLJ potential predicts approxi-
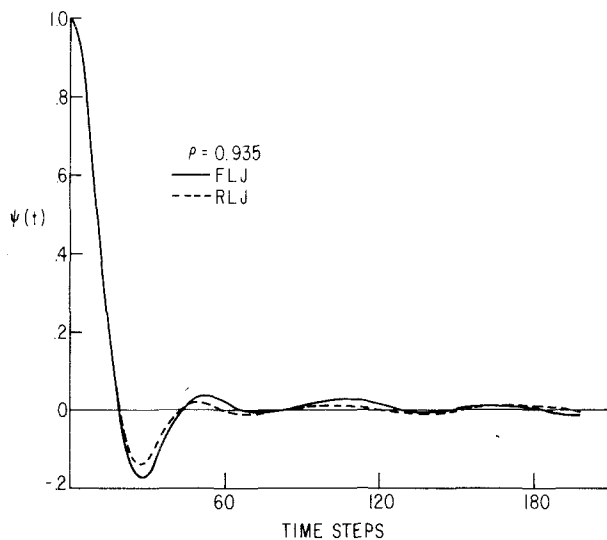
Fig. 4.   The normalized velocity autocorrelation function for RLJ and FLJ; $\rho = 0.935$.

mately the same $g(X)$ and NVAF at high densities and temperatures. However, D of the RLJ is greater than that of the FLJ, which indicates that the attractive part of the potential introduces additional correlations into the particle dynamics, which is not mirrored in the static properties. We are currently examining a number of theoretical models in order to elucidate these effects.

ACKNOWLEDGMENTS

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