Journal of Statistical Physics, Vol. 29, No. 3, 1982

Collective Modes of One-Dimensional Lennard–Jones Systems

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Received March 9, 1982

The density fluctuations of one-dimensional Lennard–Jones systems are investigated by molecular dynamics simulation. The full Lennard-Jones potential is compared to the repulsive Lennard–Jones potential. It is found that the behavior of the density fluctuations at small wave vectors is determined by the repulsive portion of the potential. The variation of the fluctuations with density is explained. It is shown that these systems do not display hydrodynamics.

KEY WORDS: Collective modes; one-dimensional molecular dynamics; Lennard–Jones.

1. INTRODUCTION

In a study by Bishop and Berne[1] of the density fluctuations of a high-density one-dimensional Lennard–Jones system, it was found that these fluctuations decayed like a damped cosine with frequency, ω_k, and lifetime, τ_k, such that the dispersion relation was very similar to that of a harmonic chain and τ_k went as $k^{-1/3}$ at small k. Their τ_k result was consistent with the t^{-3} asymptotic behavior of the velocity autocorrelation function.[2–5] Since hydrodynamics requires[6] $\tau_k \sim k^{-2}$, it was concluded that the one-dimensional Lennard–Jones system did not display a hydrodynamic decay. In this note, the density fluctuations are calculated for high and low densities and for the full (FLJ) and repulsive (RLJ) Lennard–Jones potentials. It is found that the propagating mode present at high densities disappears at lower densities. The existence of a diffusive mode for low-density systems is established. Its lifetime goes as $k^{-1/3}$. In addition, the

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0022-4715/82/1100-0623$03.00/0

density fluctuations are very similar for both the FLJ and RLJ. Thus, the repulsive portion of the potential is the major factor in determining the relaxation of the density fluctuations.

2. METHOD

Molecular dynamics calculations were done for both the FLJ and the RLJ. These have the form

$$\text{FLJ:}\quad U(x) = 4\left[(1/x)^{12} - (1/x)^{6}\right], \qquad x < 2.5$$
$$= 0, \qquad x > 2.5 \tag{1}$$

This is shifted by subtracting $U(2.5)$ for $x < 2.5$.

$$\text{RLJ:}\quad U(x) = 4\left[(1/x)^{12} - (1/x)^{6} + 1/4\right], \qquad x < 2^{1/6}$$
$$= 0, \qquad x > 2^{1/6} \tag{2}$$

where x is the molecular separation and all results are given in reduced units.[7] Starting with N particles ($N = 100$) one-dimensional number densities, ρ, of 0.65 and 0.935 were selected for study. The particles were initially placed on lattice sites and the velocities selected from a Maxwellian distribution by the Box–Muller[8] method. Newton's equations of motion were integrated by Verlet's[9] scheme with step size 0.005. Periodic boundary conditions were imposed and the minimum image convention was used for the potential.

A "box scheme" is not needed for one-dimensional calculations because of the small number of pair interactions which must be considered. The first 900 equilibration steps were discarded and the subsequent 12,000 equilibrium configurations used for later analysis. However, the potential energy per particle, U, the total energy per particle, E, and the pressure, P, were calculated concurrently with the trajectory. These are defined by

$$U = \frac{1}{2NN_0} \sum_{i \neq k}^{N} \sum_{j}^{N_0} U_j(|R_{ij}|) \tag{3}$$

$$E = U + \frac{1}{2NN_0} \sum_{i}^{N} \sum_{j}^{N_0} V_i^2(j) \tag{4}$$

and

$$P = \rho T\left[1 + \frac{1}{TNN_0} \sum_{i}^{N} \sum_{j}^{N_0} x_i(j) F_i(j)\right] \tag{5}$$

where N is the number of system particles, N_0 the number of time steps the data is averaged over $V_i^2(j), x_i(j)$, and $F_i(j)$ are the velocity squared, the

position, and the force, respectively, of the ith particle at the jth time step, ρ is the number density, and R_{ij} the relative distance between particles i and j. The temperature, T, is given by $T = 2(E - U)$.

3. RESULTS

The simulation results are presented in Table I. They may be compared to the data of Bishop, De Rosa, and Lalli,[7] who studied 1000 particles at the same densities. They used the Runga–Kutta–Gill technique to integrate Newton's equation and averaged over about 1400 steps of size 0.005. Since they did not shift their FLJ by $U(2,5)$, it is best to compare RLJ states. For a density of 0.65, they found $U = 0.048$, $E = 0.411$, $T = 0.725$, and $P = 1.40$ compared to our $U = 0.050 \pm 0.03$, $E = 0.415 \pm 0.001$, $T = 0.730$, and $P = 1.42 \pm 0.01$, whereas for a density of 0.935 they reported $U = 0.443$, $E = 0.803$, $T = 0.722$, and $P = 11.21$ compared to 0.441 ± 0.001, $E = 0.804 \pm 0.001$, $T = 0.726$, and $P = 11.18 \pm 0.01$. The agreement is excellent. By studying a smaller system, one can obtain more time steps for the same computer costs. Hence, collective properties such as the density fluctuations can be calculated more accurately.

The collective modes can be determined by calculating the density–density time autocorrelation funciton, $F(k,t)$:

$$F(k,t) = \frac{1}{N}\left\langle \sum_{j}^{N}\sum_{l}^{N} \exp\{ik[x_j(t) - x_l(0)]\}\right\rangle \tag{6}$$

where k is the wave vector and the $\langle\ \rangle$ indicates an ensemble (or time) average. The periodic boundary conditions for a line of length L fix the smallest wave vector, $k_{\min}$, as $2\pi/L$. Hence, one finds that for $\rho = 0.935$, $k_{\min} = 0.0588$ and for $\rho = 0.65$, $k_{\min} = 0.0408$. In general, the Fourier

Table I. The Simulation Results

ρ^a	Range^b	U^c	E^d	P^e	T^f
0.65	2.5	-0.493 ± 0.008	-0.105 ± 0.001	0.96 ± 0.04	0.776
0.65	$2^{1/6}$	0.050 ± 0.003	0.415 ± 0.001	1.42 ± 0.01	0.730
0.935	2.5	-0.561 ± 0.001	-0.187 ± 0.001	10.50 ± 0.06	0.748
0.935	$2^{1/6}$	0.441 ± 0.001	0.804 ± 0.001	11.18 ± 0.01	0.726

[a] ρ is the number density,
[b] range is the potential range,
[c] U is the average potential energy per particle,
[d] E is the average total energy per particle,
[e] P is the average pressure,
[f] T is the temperature.

transform of $F(k,t)$, the dynamic structure factor, $S(k,\omega)$, can have[6] a propagating mode and a diffusive mode as $k \to 0$ (e.g., the hydrodynamic regime).

In Figs. 1 and 2, $F(k,t)$ is plotted for $k = 7^* k_{\min}$. The results are very similar for both the FLJ and the RLJ systems. Note, however, that at $\rho = 0.935$ there is a long-lived oscillating mode but that at $\rho = 0.65$, there is just a damped mode. The Fourier transform of these functions contains a propagating mode and, perhaps, a small intensity diffusive mode, for $\rho = 0.935$ but only a diffusive mode for $\rho = 0.65$. The high-density results agree with the findings of Bishop and Berne.[1] The dispersion relation for this system has been determined by plotting the position of the $\omega \neq 0$ $S(k,\omega)$ peak vs. k. This is shown in Fig. 3. The behavior for both the FLJ and RLJ systems is similar. This is in agreement with the data of Haan, Mountain, Hsu, and Rahman[10] for three-dimensional systems. Hence, the repulsive part of the potential is the major factor in determining the small wave vector properties of the density fluctuations.

The different behavior of the modes as a function of density can be explained. At high density Bishop and Berne[1] found that the dispersion relationship was in close agreement with that expected for a one-dimensional harmonic lattice. This was consistent with the "solidlike" shape of the pair correlation function, $g(x)$, which they reported. Yoshida, Shobu, and Mori have made an exact, analytical calculation of $S(k,\omega)$ for a perfect, one-dimensional harmonic "liquid." They have shown that there is only a propagating mode for this system. Visscher[12] has demonstrated the relationship between the k dependence of the mode lifetime and the asymptotic time behavior of the velocity autocorrelation function, $\psi(t)$, e.g.,

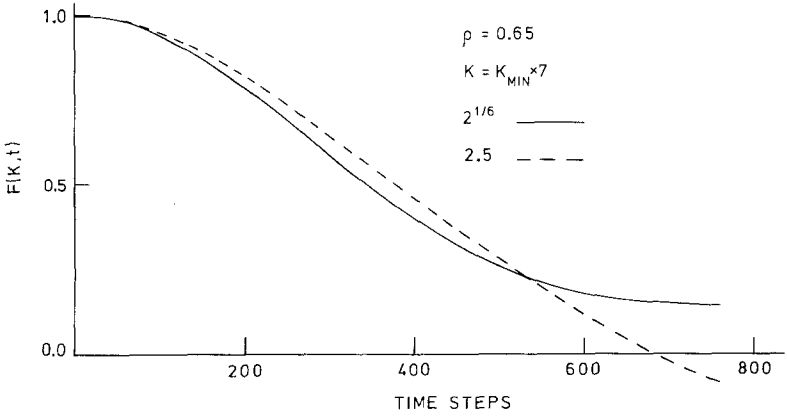

Fig. 1. The density autocorrelation function vs. time for $\rho = 0.65$ and for the RLJ and FLJ systems. Time steps are in number of steps of 0.005.

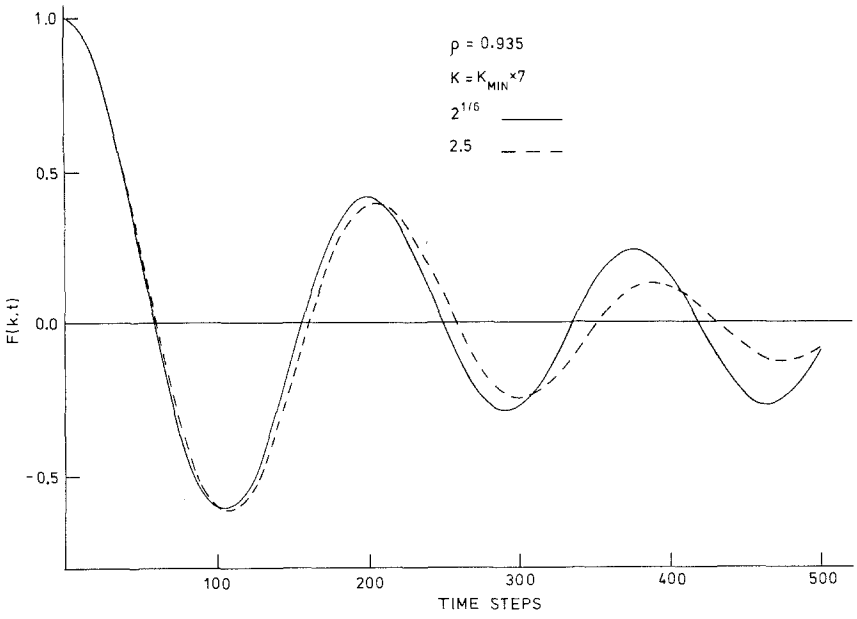

Fig. 2. The density autocorrelation function vs. time for $\rho = 0.935$ for the RLJ and FLJ systems. Time steps are in number of steps of 0.005.

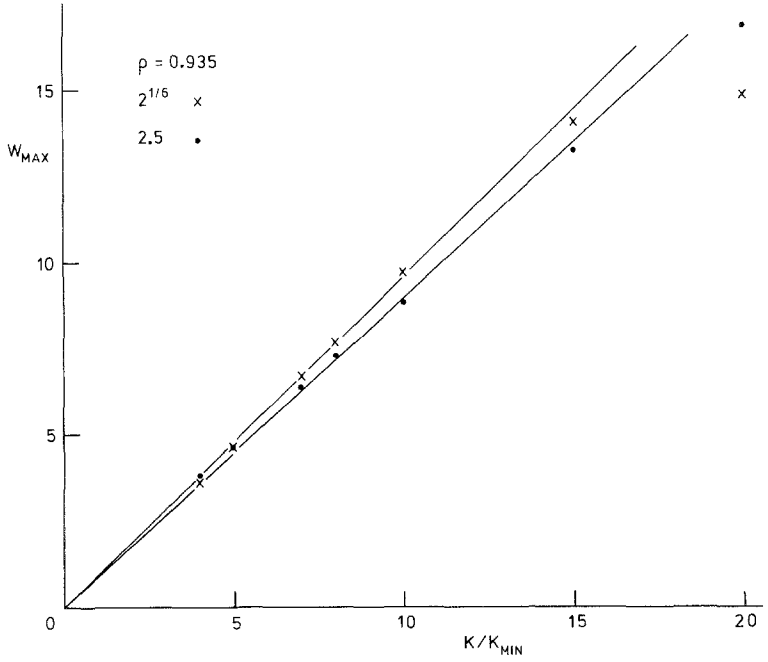

Fig. 3. The dispersion relation between the collective mode frequencies and the wave vector for $\rho = 0.935$ and for the RLJ and FLJ systems.

Table II. The Mode Lifetime Behavior for Small Wave Vector for the Diffusive Mode: The Product $\tau_k k^{1/3}$ as a Function of Wave Vector for $\rho = 0.65$ and for the RLJ and FLJ

$k/k_{\min}$	RLJ $\tau_k(k/k_{\min})^{1/3}$	FLJ $\tau_k(k/k_{\min})^{1/3}$
4	2.65	3.17
5	2.44	2.85
7	2.73	2.39
8	2.50	2.22
10	2.69	2.69

if $\psi(t) \to t^{-1/n}$ then $\tau_k \to k^{-n}$. Since Mazur and Montroll[13] have proven that $\psi(t) \to t^{-1/2}$ for this system, τ_k will go as k^{-2} and the perfect harmonic liquid will display hydrodynamics.

However, Bishop and Berne[1] found $\tau_k \to k^{-1/3}$ consistent with $\psi(t) \to t^{-3}$. It has been shown by Lebowitz, Percus, and Sykes,[14] that $F(k,t)$ for a one-dimensional system of hard rods does not display damped oscillatory behavior unless the velocity distribution contains some δ functions. Moreover, even for a δ-function distribution, there exists no single velocity (sound velocity) describing the propagation of a disturbance because each particle velocity is conserved.[15]

The $g(x)$ for $\rho = 0.65$ reported by Bishop, De Rosa, and Lalli[7] is "liquidlike" and, thus, it is not surprising that the one-dimensional harmonic lattice results are not at all applicable for this density. The data of Lebowitz, Percus, and Sykes[14] for $\rho = 0.50$ and a Maxwellian velocity distribution are similar to the $\rho = 0.65$ results. The lifetime of the modes have been calculated from the half-width of $S(k,\omega)$ at half-maximum. Table II demonstrates that $\tau_k \sim k^{-1/3}$, within the scatter of the data. Thus, the diffusive lifetimes do not agree with hydrodynamic predictions but are consistent with the $\psi \to t^{-3}$ decay.

4. CONCLUSION

One-dimensional Lennard–Jones systems do not display hydrodynamics because the lifetimes of the collective modes $\to k^{-1/3}$ instead of k^{-2}. This mirrors the behavior of $\psi(t)$ which $\to t^{-3}$ for these systems. The repulsive portion of the potential is the major factor in determining the short wave vector properties of the density fluctuations. This is in contrast to the influence of the attractive part of the potential on single particle motions[7] [e.g., $\psi(t)$].

ACKNOWLEDGMENT

This investigation is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.) supported by the Organisatie voor Zuiver-Wetenschappelijk Onderzoek (Z.W.O.).

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