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Computer study of the collective modes of a one dimensional disordered chain*

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It is found, on the basis of molecular dynamics experiments, that the density fluctuation of wavenumber k, in a one dimensional disordered chain of Lennard-Jones rods, decays like a damped cosine with frequency ω_k and lifetime τ_k such that the dispersion relation $\omega = \omega_k$ is very similar to that of an harmonic chain and that τ_k goes as $k^{-1/3}$ at small k. This latter observation is shown to be consistent with the conjecture that the single particle velocity autocorrelation function behaves asymptotically as t^{-3}. It is concluded that the Lennard-Jones chain does not display a hydrodynamic decay.

Neutron scattering experiments[1] have demonstrated the existence of collective modes in liquids. These collective modes have also been found in computer experiments[2] which probe the same molecular regime as the neutron scattering experiments but provide much more detailed information. The modes can be examined by observing the density-density autocorrelation function, $F(k,t)$, as the wave vector, k, approaches the hydrodynamic limit ($k \to 0$). Recently, it has been shown 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.[3] 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.[4] Thus, the existence of collective modes for one dimensional disordered system is still an open question. In this note we investigate the collective modes of a one dimensional Lennard-Jones argon fluid via the method of molecular dynamics.

If the position of particle j is $x_j(t)$ at time t, the Fourier transform of the particle density, $n(k,t)$, at time t is

$$n(k,t) = (1/\sqrt{N}) \sum_{j=1}^{N} e^{ikx_j(t)} \tag{1}$$

where N is the number of particles in the system.

The corresponding time autocorrelation function is

$$F(k,t) = \langle n(k,t) n^*(k,0) \rangle \tag{2}$$

where the * denotes the complex conjugate and $\langle\,\rangle$ indicates an ensemble average.

Newton's equations of motion for 100 particles (at reduced density 0.935) interacting through a pairwise additive Lennard-Jones (12–6) potential ($\epsilon/k = 119.8$ °K, $\sigma = 3.405$ Å, $m = 6.63 \times 10^{-23}$g) were

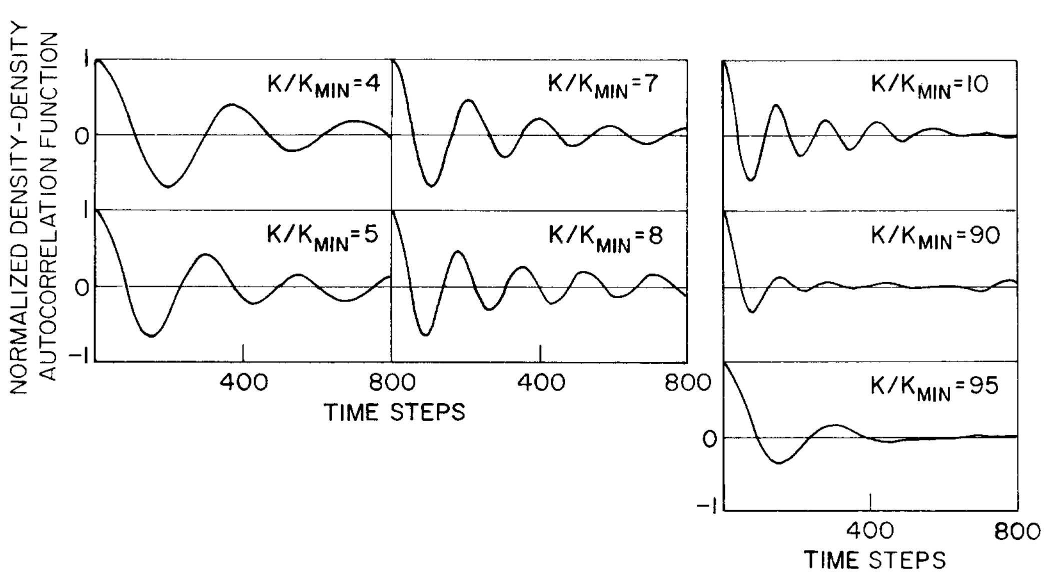

FIG. 1. The normalized density–density autocorrelation function for various wavevectors. Each time step is 1×10^{-14} sec. $K_{\min} = 1.725 \times 10^{-2}$ Å^{-1}.

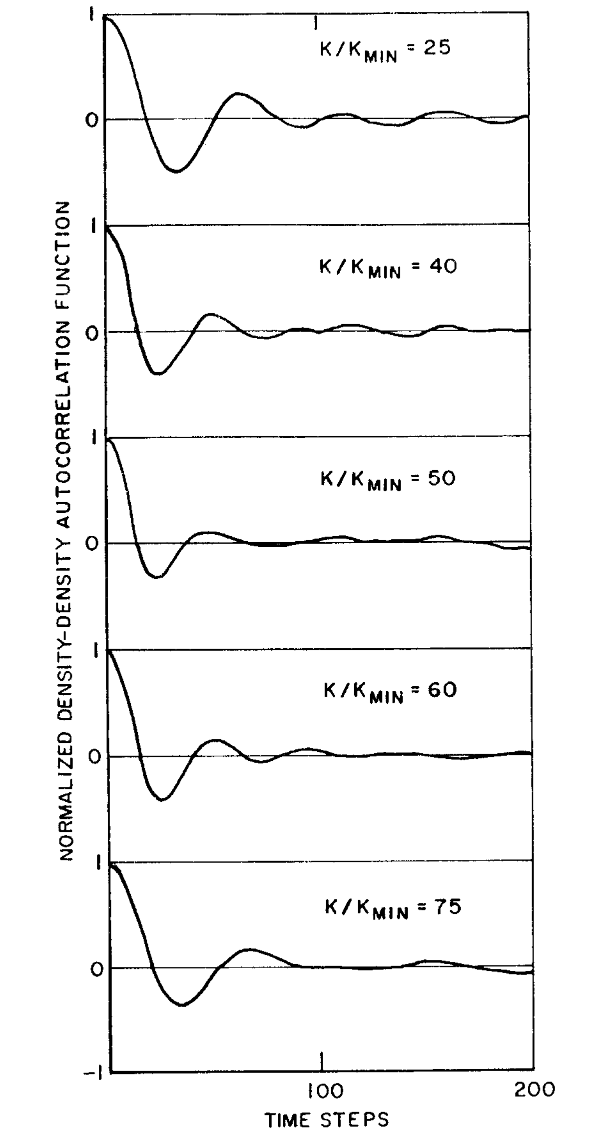

FIG. 2. The normalized density–density autocorrelation function for various wavevectors. Each time step is 1×10^{-14} sec. $K_{\min}=1.725\times10^{-2}$ Å^{-1}.

integrated by the Runga–Kutta–Gill algorithm with a step size of 1×10^{-14} sec and with periodic boundary conditions. The periodic boundary conditions for a line of length L fix the smallest wave vector, $K_{\min}$, as $2\pi/L$. For N equals 100, $K_{\min}$ equals 1.725×10^{-2} Å^{-1}. The particle velocities were selected from a Maxwellian distribution at a temperature of 85.3 °K. After 89 equilibration steps, 13 000 equilibrium steps were generated and placed on nine-track magnetic tape.

$F(k,t)$ was calculated from the stored position values by replacing the ensemble average in Eq. (2) by a time average over the 13 000 steps. The machine values of $F(k,t)$ for a variety of k's are presented in Figs. 1 and 2. Note that at low k values the functions have a long-lived oscillatory mode whereas at intermediate and high k values the mode is quickly damped. The Fourier transform of $F(k,t)$, the dynamic structure factor $S(k,\omega)$, reveals the existence of a propagating mode although the existence of a diffusive mode is an open question because of numerical difficulties in the Fourier transform around $\omega=0$ (see Figs. 3 and 4). A dispersion relation for this system can be determined by plotting the position of the $\omega\neq0$ $S(k,\omega)$ peak vs. k. This is shown in Fig. 5. A propagation speed can be determined from these frequencies: $c_s=\omega/k$. The low k values ($k\leq 10\mathrm{K}_{\min}$) can be fit by a straight line with slope 2.51×10^5 cm/sec. It is interesting to note that the Lennard-Jones data can be represented by the dispersion relation for a one dimensional harmonic lattice[5]

$$\omega_n=(4C/M)^{1/2}\,|\sin(k_n a/2)| \tag{3}$$

where C is the force constant, M the particle mass, k_n the nth wavevector, and a the lattice spacing L/N. In our case k_n equals $2\pi n/aN$ so that equation 3 becomes

$$\omega_n=A\,|\sin(\pi n/N)| \tag{4}$$

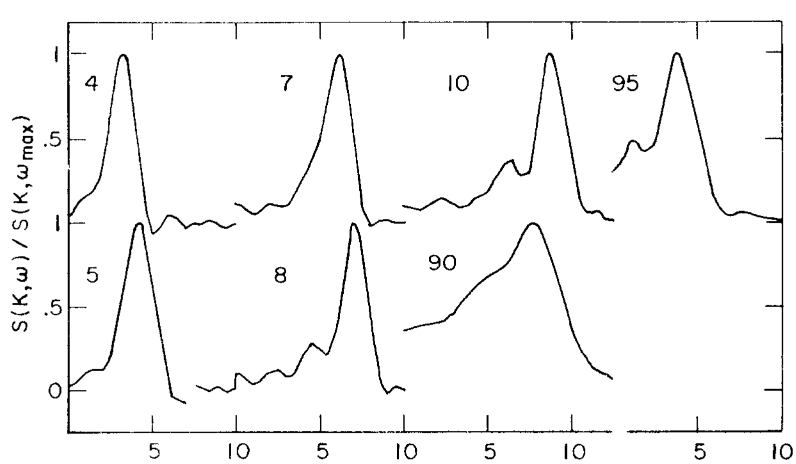

FIG. 3. The dynamic structure factor for various wavevectors. Each frequency step is 4.64×10^{11} sec^{-1}. $S(k,w)$ is normalized by dividing by the maximum height.

Equation (4) fits the date points when $A = 120\times 10^{11}$ sec^{-1}. The group velocity of the one dimensional lattice is given by

$$V_g = \partial\omega/\partial k = (AL/2N)\cos \pi n/N \quad . \qquad (5)$$

This equals 2.18×10^5 cm/sec for our conditions when $k\to 0$.

The lifetimes, τ_k, of the collective modes are

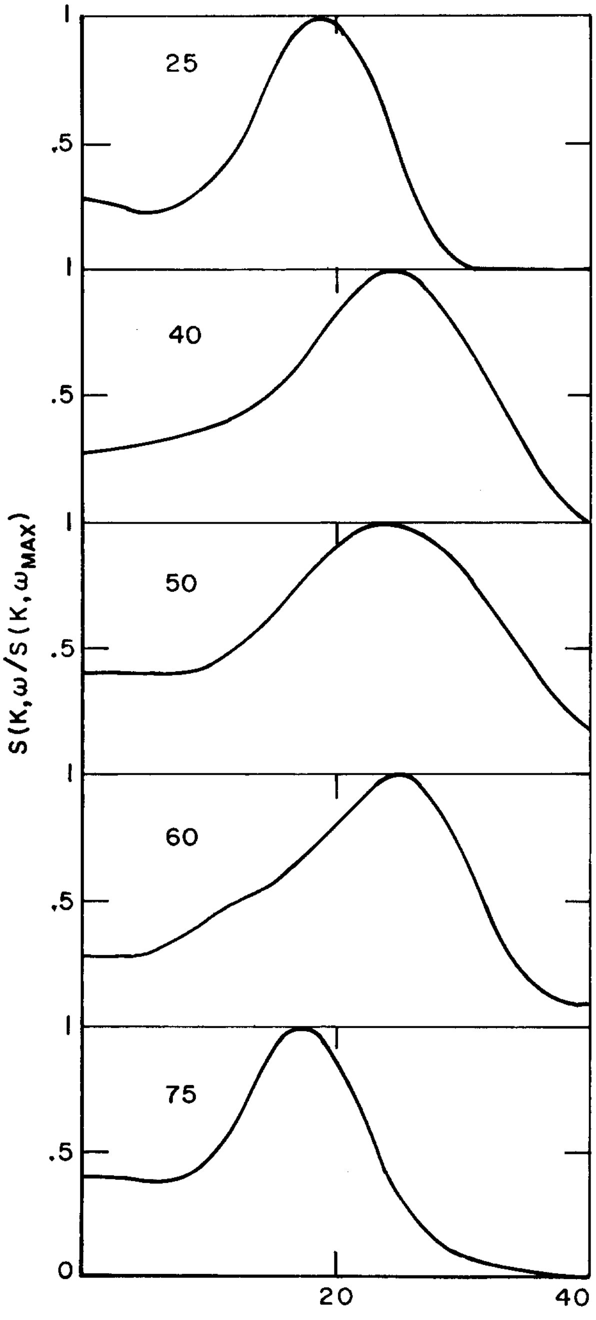

FIG. 4. The dynamic structure factor for various wavevectors. Each frequency step is 4.64×10^{11} sec^{-1}. $S(k,w)$ is normalized by dividing by the maximum height.

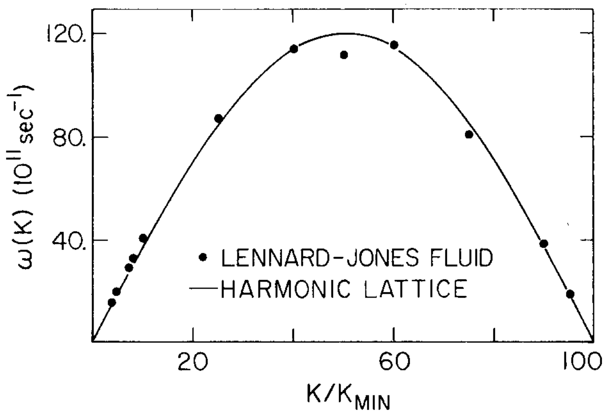

FIG. 5. The dispersion relation between the collective mode frequencies and the wavevector. $K_{min} = 1.725\times 10^{-2}$ Å^{-1}. Note that K/K_{min} equals 50 corresponds to π/a for the lattice.

calculated from the halfwidth of $S(k,\omega)$ at half maximum. These times are listed in the table and in Fig. 6. From the table it should be noted that $k^2\tau_k$ is not a constant for small values of k as would be expected from hydrodynamics. What then is the behavior of τ_k at small values of k? To this end we offer the following partially corroborated conjecture.

Conjecture: The single particle velocity autocorrelation function, (v.c.f.) $\langle v(0)v(t)\rangle$, decays asymptotically as t^{-3}.

This conjecture springs from the analytical solution of the one dimensional hard-rod system where it has been shown[6] that $|\langle v(0)v(t)\rangle|_{t\to\infty}\to t^{-3}$. There is no evidence that this conjecture is valid for an arbitrary disordered one dimensional system. But if, the asymptotic time dependence of the v.c.f. in a fluid is purely determined by dimensionality, as appears to be the case in two and three dimensions,[7] it is reasonable to make this conjecture.

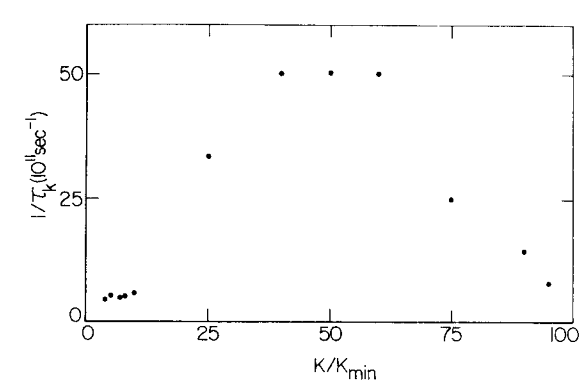

FIG. 6. The half width at half maximum $(1/\tau_k)$ of $S(k,\omega)$ for various wavevectors. $K_{min} = 1.725\times 10^{-2}$ Å^{-1}.

TABLE I. The lifetimes of the collective modes and the product $\tau_k k^{1/3}$ as a function of wavevector.

$k/k_{\min}$	$\tau_k(10^{-12})$	$\tau_k(k/k_{\min})^{1/3}$
4	2.3	3.7
5	2.0	3.4
7	2.1	4.0
8	2.0	4.0
10	1.8	3.9
25	0.3	0.9
40	0.2	0.7
50	0.2	0.7
60	0.2	0.8
75	0.4	1.7
90	0.7	3.1
95	1.3	5.9

Now this conjecture can be used to infer the k dependence of τ_k. To this end we expand the v.c.f. in terms of the normal modes of the fluid.[8] This gives

$$\langle v(0)v(t)\rangle = \sum_k \langle |v_k|^2\rangle e^{-t/\tau_k} e^{i\omega_k t} \tag{6}$$

where τ_k and ω_k are the lifetime and frequency of the kth mode. By equipartition $\langle |v_k|^2\rangle = k_B T/m$. The asymptotic time dependence of Eq. (6) is determined by the small wave number components so that ω_k and τ_k can be replaced by their small k limits. At small k we have established that $\omega_k = ck$. Unfortunately we can only surmize that at small k τ_k is given by some inverse power law, $\tau_k = Ak^{-n}$ where A and n are constants. Eq. (6) now becomes

$$\langle v(0)v(t)\rangle \sim \int_0^\infty dk\, e^{-k^n t/A} e^{ickt} \tag{7}$$

If n is a fractional power as we surmize, then for sufficiently small k, we can replace e^{ickt} by unity giving

$$\langle v(0)v(t)\rangle \underset{t\to\infty}{\longrightarrow} (1/n)\Gamma(1/n)A^{1/n}t^{-1/n} \tag{8}$$

where $\Gamma(x)$ is the gamma function of argument x.

In order to retrieve the conjectured asymptotic time dependence of t^{-3}, n must be a fractional power $n=1/3$, and correspondingly

$$\tau_k \underset{k\to 0}{\longrightarrow} k^{-1/3} \tag{9}$$

We thus infer that $k^{1/3}\tau_k$ should be a constant in the small k limit. This product is listed in Table I. It should be noted that this product is constant for $k \le 10K_{\min}$ within the scatter of the data. This observation supports our conjecture that $\langle v(0)v(t)\rangle \sim t^{-3}$ for one dimensional fluids. Perhaps more importantly, Eq. (9) is in marked contradiction with the predictions of ordinary hydrodynamics according to which $\tau_{k_{k\to 0}} \to k^{-2}$. This indicates that a longitudinal viscosity does not exist in the one dimensional fluid. Although our data is insufficient for the purposes of determining whether $S(k,\omega)$ contains a central band (or Rayleigh band) with a width determined by the thermal diffusivity, we conjecture that if such a band exists at all in a one dimensional system, it will not be described by hydrodynamics.

The one dimensional fluid described here has certain features in common with the one dimensional harmonic chain, in that there exist collective modes with a single sound speed, and in addition the dispersion relation $\omega = \omega_k$ in the two systems is quite similar. Nevertheless there are major differences. First the harmonic chain has $\tau_k = \infty$ whereas our system has $\tau_k = \sim 10^{-12}$ sec. Similar behavior was found by Kim and Nelkin[9] when they investigated the difference between an ordered one dimensional har-

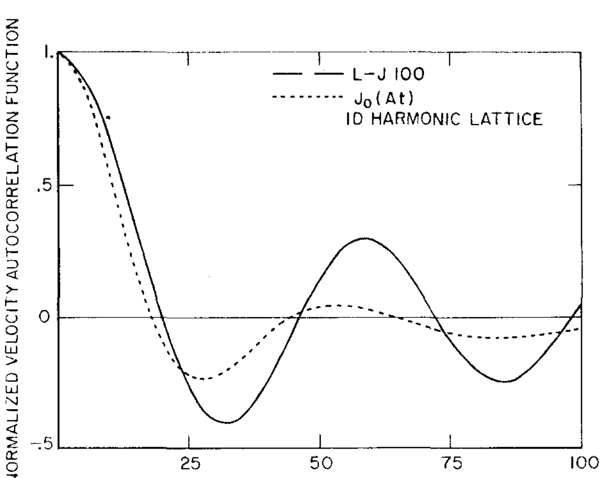

FIG. 7. The normalized velocity autocorrelation function for the L-J fluid and the 1D harmonic lattice. Each time step is 1×10^{-14} sec. $A = 120\times10^{11}$ sec^{-1}.

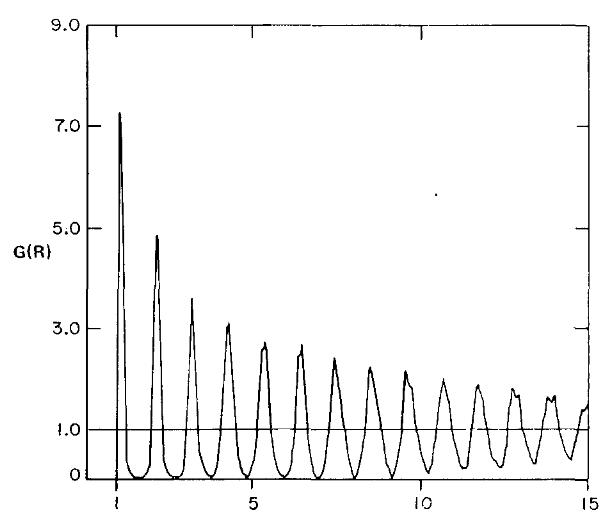

FIG. 8. The pair correlation function as a function of separation. R is in reduced units (x/σ).

monic solid and a disordered one in which the particles had random equilibrium positions. The collective modes of the disordered system had finite lifetimes and the $S(k\omega)$ peak positions were close to the harmonic results. Second, it should be noted from Fig. 7 that the single particle velocity autocorrelation function $\langle v(0)v(t)\rangle$ for the Lennard-Jones system is considerably different from that in a one dimensional harmonic lattice.[10] It has a shallower minimum and no well defined frequency. Thus we are presented with two observations: (a) the fluid looks "solid like" with respect to its collective properties but (b) fluid-like with respect to its single particle properties. It can be conjectured that collective motion involves the long range order observed (see Fig. 8) in the fluid which is strikingly solid like whereas the velocity autocorrelation function mirrors large relative local fluctuations and anharmonic effects should be important. It should not be difficult to pin this argument down.

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