Molecular-dynamics study of a phase transition in a system of interacting anharmonic oscillators

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The molecular-dynamics tenchnique is applied to the study of a classical system of anharmonic oscillators interacting via a nearest-neighbor coupling plus a coupling which is infinitely long range in character. Such a system undergoes a second-order phase transition at a finite temperature which depends upon the strength of the long-range coupling. The overall features of the transition are seen to be fairly well described by the self-consistent phonon approximation and evidence is found that the system as a whole fluctuates between a displaced and an undisplaced phase in the vicinity of the transition.

I. INTRODUCTION

There has been considerable interest of late in the study of interacting anharmonic oscillators as prototypes of displacive and order-disorder ferroelectrics.[1-10] These models have been treated by the molecular-field approximation,[1,2,7] the self-consistent phonon approximation,[5,8] the mean-field approximation,[3,7,11] transfer-matrix techniques,[9,10,12] and numerical simulation[9,13] by the molecular-dynamics (MD) method. There was no long-range interaction in the last, which precluded a phase transition in one dimension (1D). The present work[14] is concerned with the MD treatment of a 1D classical system of interacting oscillators in the presence of an infinitely-long-range interaction, which permits a second-order phase transition at finite temperature. The MD results, which are in principle exact, will be compared with those obtained from an approximate technique—the self-consistent phonon approximation.

In the model to be considered, the interaction potential has the form

$$V=\sum_l \tfrac{1}{4}[(u_l^2+1)^2-1]+\frac{S}{2}\sum_l (u_{l+1}-u_l)^2 - \frac{1}{4}\sum_{l,l'}\chi(ll')\,u_l u_{l'}. \quad (1)$$

Here u_l represents the displacement of each particle from its equilibrium position in the 1D linear array. S is a short-range nearest-neighbor coupling constant, whereas $\chi(l\,l')$ represents an all-neighbor coupling constant which is long range in nature. Specifically, we choose $\chi(l\,l')$ to be infinitely long range and infinitely weak in character; i.e.,

$$\chi(l\,l')=(1/N)\chi, \quad N\to\infty \quad (2)$$

where N is the number of particles and χ is a constant. Equation (1) represents an interaction which consists of a set of local anharmonic quartic potentials together with a harmonic potential which has been divided into a short- and a long-range part. The ansatz (2) has the effect of replacing the Hamiltonian (1) by

$$V=\sum_l \tfrac{1}{4}[(u_l^2+1)^2-1]+\frac{S}{2}\sum_l (u_{l+1}-u_l)^2 - \frac{\chi\bar{u}}{2}\sum_l u_l + N\frac{\chi\bar{u}^2}{4}, \quad (3)$$

where $\bar{u}(t)=N^{-1}\sum u_l(t)$. The order parameter is then $\langle\bar{u}(0)\rangle$, the ensemble average of $\bar{u}$. In replacing (1) by (3), we have effectively treated the long-range interaction in a molecular-field approximation while leaving the short-range correlations intact. Each quartic anharmonic potential well in Eq. (3) possesses a single minimum and hence is applicable to purely displacive phase transitions.

II. MOLECULAR DYNAMICS

Assuming the interaction (3), the equation of motion for the displacement, u_l, takes the form

$$\ddot{u}_l=-u_l^3-u_l-S(u_l-u_{l-1})+S(u_{l+1}-u_l)+\tfrac{1}{2}\chi\bar{u}. \quad (4)$$

Here the mass of each particle has been chosen equal to 1 and a dimensionless time unit has been used. A phase transition ($\langle\bar{u}\rangle\neq 0$) is only possible when a displaced solution is stable at zero temperature. According to Eq. (4) this requires $\chi>2$.

The equations of motion were solved numerically using a standard molecular-dynamics technique.[15] A system of 1000 particles was considered, and the displacements of the particles were determined at 200 000 time steps with a time-step size of 0.1

in order to achieve reliable statistics. The system was aged for 10 000 time steps initially in order to eliminate nonrandom initial conditions. Periodic boundary conditions were applied to the linear chain. The two quantities of prime importance which were evaluated using the MD technique were, firstly, $\langle \bar{u} \rangle$ and, secondly, the space-time Fourier transform $S(q, \omega)$ of the displacement-displacement correlation function $\langle u_l(t) u_0(0) \rangle$. In computing the $S(q, \omega)$ some smoothing in ω has been carried out employing a numerical technique described elsewhere.[16]

III. SELF-CONSISTENT PHONON APPROXIMATION

The details of the application of the self-consistent phonon approximation (SPA) to the treatment of a system of coupled anharmonic oscillators are given in Ref. 8. The model considered here differs somewhat from that treated in Ref. 8 owing to the presence of the nearest-neighbor coupling in (3). However, the formalism is identical. In the SPA one constructs a displaced oscillator trial density matrix which is quasiharmonic in form and which depends on a set of variational force constants. A free energy is then constructed from the interaction (3) and the trial density matrix. This free energy is subsequently minimized with respect to the trial force constants and the mean displacement $\langle \bar{u} \rangle$, thus yielding a set of self-consistent equations for the optical phonon frequency ω_q and $\langle \bar{u} \rangle$. Omitting the details of the calculation, we merely present the results. We find that the minimization procedure yields two solutions, an undisplaced solution with

$$\begin{aligned} &\langle \bar{u} \rangle = 0, \quad \langle u^2 \rangle = \frac{1}{N} \sum_q{}' \frac{T}{\omega_q^2}, \\ &\omega_0^2 = 3\langle u^2 \rangle + 1 - \tfrac{1}{2}\chi, \\ &\omega_{q\neq 0}^2 = \omega_0^2 + \tfrac{1}{2}\chi + 2S(1 - \cos q), \end{aligned} \tag{5}$$

and a displaced solution with

$$\begin{aligned} &\langle \bar{u} \rangle^2 = \tfrac{1}{2}\chi - 3\langle u^2 \rangle - 1, \\ &\langle u^2 \rangle = \frac{1}{N} \sum_q{}' \frac{T}{\omega_q^2}, \\ &\omega_0^2 = 3\langle u^2 \rangle + 3\langle \bar{u} \rangle^2 + 1 - \tfrac{1}{2}\chi, \\ &\omega_{q\neq 0}^2 = \omega_0^2 + \tfrac{1}{2}\chi + 2S(1 - \cos q). \end{aligned} \tag{6}$$

The above equations may be solved self-consistently for ω_0^2 or $\langle u^2 \rangle$. The details are given in Ref. 8. In both (5) and (6), the high-temperature (classical) approximation has been used for $\langle u^2 \rangle$. From (6) we see that since $\langle u^2 \rangle = 0$ at $T = 0$, the requirement that $\langle \bar{u} \rangle > 0$ at $T = 0$ requires $\chi > 2$, as we deduced previously.

A significant feature of (5) and (6) is the fact that a finite gap exists between ω_0^2 and ω_q^2 evaluated at the smallest nonzero wave vector. Indeed,

$$(\lim_{q \to 0} \omega_q^2) - \omega_0^2 = \tfrac{1}{2}\chi. \tag{7}$$

This is basically because the spatial Fourier transform of an interaction, which is independent of particle indices, vanishes identically except for $q = 0$. As we shall see in Sec. IV, ω_0 is to be identified with the soft mode which vanishes at the second-order transition temperature.

At the second-order transition temperature, both the order parameter $\langle \bar{u} \rangle$ and the soft-mode frequency ω_0 vanish. Thus setting $\langle \bar{u} \rangle = 0 = \omega_0^2$ in (6) we immediately obtain an expression for the SPA transition temperature,

$$T_c = (\chi - 2)\left(3 \frac{1}{N} \sum_q{}' [\chi + 4S(1 - \cos q)]\right)^{-1}. \tag{8}$$

For the particular case which we treat in Sec. IV, this expression has been evaluated numerically.

IV. RESULTS AND DISCUSSION

In utilizing the MD technique and the SPA in the treatment of our model system, we have employed the set of parameters $S = \frac{1}{4}$ and $\chi = 4$. This choice assures that a transition occurs at finite temperature and that the SPA transition is second order.

The results of our calculations for $\langle \bar{u} \rangle$ are summarized in Fig. 1. The SPA transition temperature as calculated from (8) is $T_c = 0.820$. In the

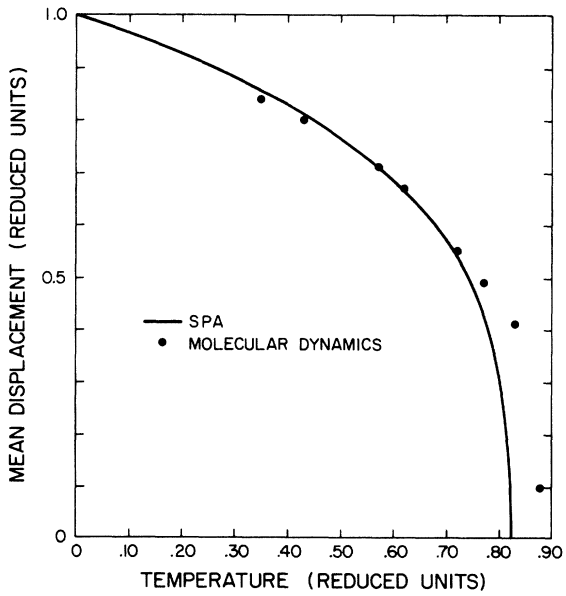

FIG. 1. Temperature dependence of the mean displacement as predicted by the SPA and the MD treatments of the system of coupled oscillators.

MD simulation it was found that there are two difficulties in establishing the transition temperature. First, the MD temperature is determined statistically from the mean kinetic energy and one expects fluctuations in this quantity. Second, near the transition temperature the decay time is large enough so that $\langle \bar{u} \rangle$ will not vanish for a finite-length run even when it should. We found $\langle \bar{u} \rangle \neq 0$ in runs for which there was an obvious long-time decay in $\langle u(t)u(0) \rangle$. From the MD data of Fig. 1, the extrapolated transition temperature is approximately 0.90; however, this is misleading. Examination of the correlation function showed that the transition obviously occurred between the two points at 0.83 and 0.87. For the most part, the agreement between the MD data points and the SPA curve is quite good. We did not carry out MD simulations below $T \approx 0.30$, because we know that the order parameter must approach the saturation value of unity at $T = 0$ and the general low-temperature trend is toward that.

The MD simulation yields plots of $S(q, \omega)$ as functions of q and ω and as a function of T. In Figs. 2(a)–2(d), we summarize some of our results for $S(0, \omega)$. The choice of temperatures is such that two temperatures lie below the transition and two above. The narrow central peak which appears in Figs. 2(a) and 2(b) is an indication that

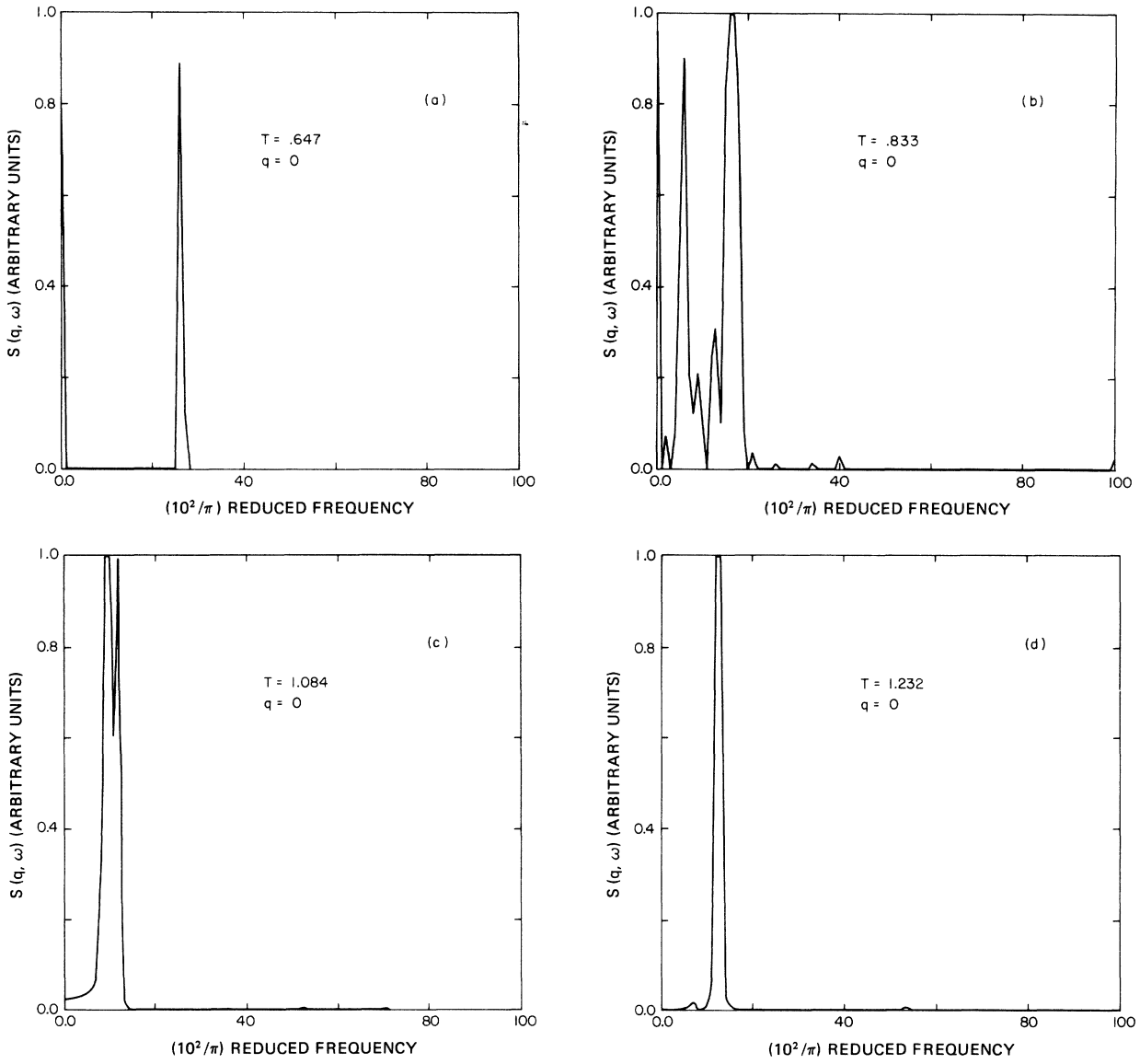

FIG. 2. (a)–(d) Plot of $S(q = 0, \omega)$ vs ω at the four temperatures $T = 0.647$, 0.833, 1.084, and 1.232.

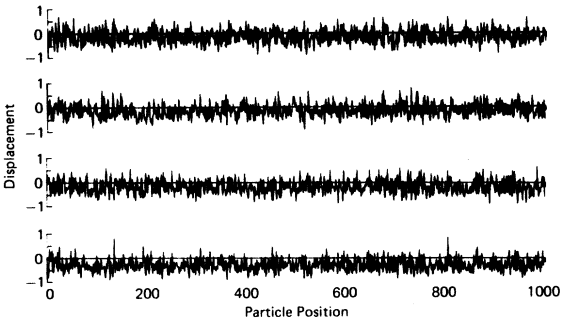

FIG. 3. Particle displacements at 1000 lattice sites for $T = 0.833$, and four different time steps.

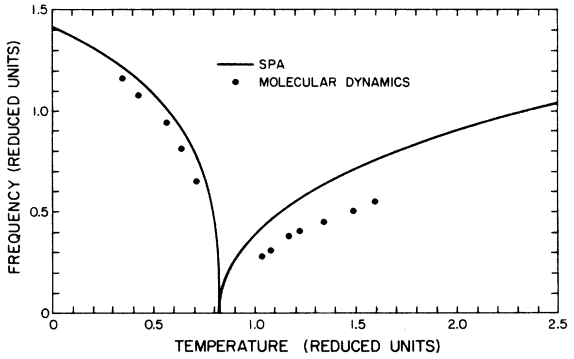

FIG. 4. Temperature dependence of the soft-mode frequency ω_0 as predicted by the SPA and MD treatments of the system of coupled oscillators.

the phase transition has occurred.

At the lowest temperature ($T = 0.647$) and at the highest temperature ($T = 1.232$), the results in Figs. 2(a)–2(d) are unambiguous. The resonances at these two temperatures are well defined and the positions of these resonances may be identified with the $q = 0$ soft-mode frequency. In the region just below the transition ($T = 0.833$), however, a double peak structure appears. This same effect, although less dramatic, is apparent just above the transition ($T = 1.084$). We postulate that the two-peak structures arise from the fact that in the region near the transition the system is fluctuating between a displaced state and an undisplaced state. The times when $\bar{u}$ is oscillating with small amplitude about a displaced minimum give rise to the higher of the two peaks in Fig. 2(b), whereas the times when the system is oscillating with larger amplitude about $\bar{u} = 0$ give rise to the lower of the two peaks.

In partial support of our speculative explanation of this two-peak structure we have plotted out the actual displacements of the 1000-particle system at four time steps in Fig. 3. It is clear that the lower figure corresponds to a displaced state, while $\bar{u} \approx 0$ for the upper figure. Further evidence is the fact that the calculated rms value of $\bar{u}$ is typically an order of magnitude larger than $\langle \bar{u} \rangle$ in the vicinity of the phase transition. Thus, because the phase transition is driven by a long-range interaction, the system as a whole fluctuates between alternate states rather than breaking up into the domains which have been studied in Refs. 9, 10, 13, and 17. In these models each particle moves in a double well potential obtained by changing $u_i^2 + 1$ to $u_i^2 - 1$ in (1) and setting $\chi = 0$. Then the tendency toward a phase transition is driven by the double minima. We attempted to treat such a model with $\chi \neq 0$, but found the transition to occur over such a narrow temperature range that we could not obtain meaningful numerical results for any property of interest.

In Fig. 4, we present the results of a determination of the "soft" optical phonon frequency as a function of temperature. The solid line denotes the SPA calculation, whereas the solid dots represent the results of the MD determination of the phonon frequency as the peak of $S(q = 0, \omega)$. There are no MD data points between $T = 0.75$ and $T = 1.0$ owing to the difficulty of unambiguously identifying the resonance in the region where $S(0, \omega)$ develops a multipeak structure. It is apparent, however, that over the temperature region considered the agreement between the MD calculation and the SPA calculation is reasonably good, at least when contrasted to the predictions of the traditional harmonic approximation, where ω_0 would be a constant independent of temperature. Of course, the SPA is incapable of reproducing the multipeak structure in $S(0, \omega)$ near the phase transition, since within the context of the SPA $S(0, \omega)$ is represented by a δ function at the soft-mode frequency.

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