MOLECULAR DYNAMICS SIMULATION OF A MODEL
FOR (ONE-DIMENSIONAL) STRUCTURAL PHASE TRANSITIONS*

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ABSTRACT

Molecular dynamics computer simulations have been carried out for a structurally unstable 1-D lattice, having a double well local potential and nearest neighbor coupling. The results show pronounced domain structure at low temperature - a feature that is not to be found in mean field or anharmonic phonon perturbation theories. Quantitative comparison is made with the analysis of Krumhansl and Schrieffer, which predicts this behavior.

Recently, there has been considerable interest¹⁻³ in the statistical mechanics and quantum field theory of one-dimensional fields described by the Hamiltonian

$$H = \sum_i \frac{p_i^2}{2m} + \sum_i \left(\frac{A}{2} u_i^2 + \frac{B}{4} u_i^4 + C \frac{(u_{i+1} - u_i)^2}{2} \right) \quad (1)$$

where u_i and p_i are field displacement from equilibrium and momentum at the i -th location. While A may be temperature dependent, there are already regimes of interest for which $A < 0$ and $B > 0$, corresponding to a double well potential. This model may be related to ferroelectric systems² and, under certain conditions, to structural transitions of the so-called Peierls type in pseudo one-dimensional materials.

If the parameter C which determines the coupling of the field between neighboring sites is sufficiently large so that the intersite strain energy exceeds the depth of the potential wells, then large amplitude finite temperature excitations with the displacement field varying slowly between adjacent sites may be expected. In this "displacive" regime it is possible, making a 1-D continuum approximation, to 1) do the formal statistical mechanics (classical) exactly by means of a functional integral calculation of the partition function, and 2) construct various exact solutions of the nonlinear classical equations of motion and substantially identify them with the results of the "exact" functional integral calculation at low temperatures. The details of this procedure have been given by Krumhansl and Schrieffer² (K-S) for the one-dimensional chain; extensions to coupled arrays of chains have been carried through more recently⁴ using earlier results.⁵

The main physical results of K-S are:

1) At low temperature, not only are there phonon-like excitations about the potential minima, but there are also important excitations (which we call

domain walls) for which the displacement (order parameter) changes from one potential minimum to the other through a region of well-defined characteristic thickness dependent on the parameters of the Hamiltonian. The displacement pattern associated with one domain wall is

$$u = u_0 \tanh \left(\frac{x - v_D t}{\sqrt{2} \xi} \right). \quad (2)$$

This pattern moves with speed $v_D < c_0$, the speed of sound in the model

$$(c_0^2 = Cl^2/m, \text{ with lattice spacing } l) \text{ and } \xi \text{ is a length: } \xi = \xi_0 (1 - v^2/c_0^2)^{1/2}, \\ \xi_0 = l(C/|A|)^{1/2}.$$

2) For small v_D one may associate with such a domain wall a formation energy (potential) E_{DP} and kinetic energy $(m_D^* v_D^2/2)$.⁶ At low temperature there are few such walls so that they are separated on the average by distances much larger than ξ . In this case they can be considered as a 1-D gas of weakly interacting quasi-particles. In higher approximation these interact with each other, as well as with the phonon-like states. K-S showed that their statistical mechanics substantially reproduces the nonfree phonon part of the functional integral result.

The literature of nonlinear field problems in other contexts contains similar ideas. For example, Goldstone and Jackiw³ liken the phonons to meson fields and domain walls to heavy baryons. Also, Varma⁷ calls attention to relations with the subject of solitons.

All of the above discussion deals with the problem from the formal side. Another fruitful approach to studying phase transitions has been the use of computer simulation, which has been developed for various models.⁸ In particular, we report here on studies which show directly the main physical features postulated above for the behavior of the displacement field at various temperatures.

Equal time "snapshots" of the linear chain were obtained from a computer simulation using the molecular dynamics technique (the direct solution of Newton's equation of motion for a classical system). The potential in (1) was put in a convenient computational form:

$$v = \frac{1}{4} \sum_i (\bar{u}_i^2 - 1)^2 + \frac{1}{2} \bar{C} \sum_i (\bar{u}_{i+1} - \bar{u}_i)^2 \quad (3)$$

where $\bar{u} = u/u_0$, $u_0 = (|A|/B)^{1/2}$, $\bar{C} = C/|A|$. The depth of the double well minima are now $\frac{1}{4}$, occurring at $\bar{u}_i = \pm 1$. Time $\bar{t}$, energy and temperature $\bar{T}$ are expressed in units $\bar{t} = (|A|/m)^{1/2} t$, $\bar{T} = k_B T/A^2$. Then the equations of motion are

$$\frac{d^2 \bar{u}_i}{d\bar{t}^2} = \bar{u}_i^3 + (1 - 2\bar{C}) \bar{u}_i + \bar{C}(\bar{u}_{i+1} + \bar{u}_{i-1}) \quad (4)$$

and the system's temperature is given by $\bar{T} = \langle \bar{u}_i^2 \rangle$ where $\langle \cdot \rangle$ denotes the ensemble average which, according to the philosophy of molecular dynamics, is obtained from the time average. (4) was solved using the Verlet⁹ central difference algorithm:

$$\bar{u}_i(\bar{t} + \delta) = 2\bar{u}_i(\bar{t}) - \bar{u}_i(\bar{t} - \delta) + \delta^2 \ddot{\bar{u}}_i(\bar{t}) \quad (5)$$

This proved to have good long-term stability for our system. A step size $\delta = 0.2$ was used. The molecular dynamics run was started with the initial positions and velocities distributed so as to approximate a typical configuration, and the system was run for at least 5,000 time steps before any of the plots were drawn, in an effort to eliminate any initial bias. Other mechanical details of the calculation will be described elsewhere.¹⁰

While the data can be processed in various ways, it is useful here to show plots of the particle displacements along the chain as a series of snapshots in time, and for various temperatures.

In Fig. 1 the displacements are plotted for $\bar{T} = 0.117$ and $\bar{C} = 1$ at $\bar{t} = 0, 100$, and 200 time steps. This temperature is such that the mean energy per particle is well below the height of the potential hump. Excitations of domain-like character are immediately apparent. Moreover, evolution with time is evident. The mean displacement is small (i.e., there is no long-range order) but the mean square displacement is not. The following features may be checked against K-S theory (with an appropriate interpretation):

- a) The domain wall thickness (transition from $\bar{u} \approx -1$ to $\approx +1$) is computed from theory as $\Delta = 2/2 \xi = 2/2 \bar{C}^{1/2} \ell = 3\ell$. This is a good agreement with the present computer results, even though the continuum model is not strictly valid in this regime; however, we have shown that the continuum solution (2) is a good approximation even for such thin walls.¹²
- b) The r.m.s domain wall speed is readily computed in the low temperature approximation of K-S as $\langle \bar{v}_D^2 \rangle = \left(\frac{3}{2\sqrt{2}} \right) \bar{C}^{1/2} \bar{T} \ell^2$. With $\bar{T} = 0.117$ and $\bar{C} = 1$, we find that the mean domain wall motion per time step should be $\approx 0.07\ell$. This is consistent with the displacements observed in the 200 time steps of Fig. 1. Further, the maximum speed $\bar{c}_0$ should be 0.2ℓ per time step. All observed speeds are indeed less than this value.
- c) The concentration of domain walls has proven an extremely sensitive test of the K-S theory. With the assumptions that the concentration was low enough and the domain walls were noninteracting, K-S deduced the concentration

$$\langle n_w \rangle = \Delta^{-1} \exp (-E_{DP}/k_B T), \quad (6)$$

where E_{DP} is a domain wall potential energy (temperature independent). The "bare" E_{DP} at $T = 0$ is given by K-S; with the present parameters $E_{DP}^B = \frac{2}{3} \sqrt{2}$. However, it can be expected that the domain wall and other solutions of (1) will mix together at $T > 0$ to some degree. Indeed, double domain wall and other excitations are known solutions as well as a continuum of scattering

states.^{3,11} In particular, the latter represent a dressing of the domain walls, so that E_{DP} in (6) should be viewed as a renormalized quantity. Calculation of E_{DP}^R is not trivial; since the exact scattering states are available, progress will be possible. However, as a first approximation we have attempted to extract E_{DP}^R indirectly from the static correlation function $\langle u(0) u(x) \rangle$, as follows.

At low temperatures (here $\bar{T} \leq 0.15$ ⁴) the exact functional integral result gives²

$$\langle \bar{u}(0) \bar{u}(x) \rangle = (\bar{u}_0(\bar{T}))^2 e^{-\frac{x}{\lambda(\bar{T})}}, \quad (7)$$

where $\bar{u}_0(\bar{T})$ is weakly temperature dependent⁴ ($\approx 0.95 \bar{u}_0$ at $\bar{T} = 0.117$) and the correlation length is

$$\lambda_{\text{exact}}(\bar{T}) = \bar{\epsilon}_0 / \bar{\epsilon}_{10} \quad (8)$$

with $\bar{\epsilon}_{10}$ taken from numerical solutions of the functional integral.⁴ Assuming noninteracting dressed domain walls, we find from K-S that

$$\lambda_D(\bar{T}) = \frac{1}{2} \Delta e^{E_{DP}^R / k_B T} = (2 \langle n_w \rangle)^{-1} \quad (9)$$

from (6). Our approximation is to equate λ_{exact} with λ_D , whence $\langle n_w \rangle = (\bar{\epsilon}_{10} / 2\bar{T})$ per unit length, independently of Δ . To assess the importance of the phonon dressing we have computed E_{DP}^R from (8) and (9) and compared this with E_{DP}^B . We find that for $\bar{T} \leq 0.25$, $E_{DP}^B / E_{DP}^R \approx 1 + 3/2 \bar{T}$. We have verified numerically that $E_{DP}^B = E_{DP}^R$ at $T = 0$, in agreement with the view of K-S in that limit.

The most important conclusion is that phonon dressing is nearly always significant. Since E_{DP} enters (6) in an exponential, $\langle n_w \rangle$ is extremely sensitive to the dressing. Thus, with $\bar{T} = 0.117$, E_{DP}^B in (6) suggests only ~ 1 wall

per 10^4 particles, whereas E_{DP}^R predicts ~ 2 walls per 10^3 particles. On the average, the computer results indicate ~ 8 per 10^3 particles. In view of the sensitivity of $\langle n_w \rangle$ to E_{DP} and the absence of an exact assessment of phonon effects, we view this as satisfactory agreement with the principal features of our model.¹²

For higher temperatures and displacement, some plots are given in Fig. 2 for $\bar{T} = 0.19, 0.26$, and 1.68 . It will be seen that the density of domain walls increases with temperature, but when $\bar{T} = 1.68$ the domain walls disappear. Of course, by then $(E_{DP}^R/k_B T) \ll 1$ and the walls are completely destroyed by thermal fluctuations.⁴ We have computed the expected density of walls; at $\bar{T} = 0.19$ and 0.26 we compute ~ 25 and 60 walls per 10^3 particles respectively, compared with observed values of ~ 15 and 30 . Refinements will be necessary to compare accurately with the higher temperature computer results, but we believe the main trends are clear.

A more detailed examination of the time evolution data (for example, over longer time periods than shown in Fig. 1) has revealed that the domain walls do not carry out free translation between collisions with other walls. Rather, isolated walls appear to undergo Brownian-like motion, presumably driven by the gas of phonons. As is well known,^{3,11} in the continuum limit small amplitude phonons are not reflected by domain walls but simply suffer a phase shift on passing through a wall. Thus, the observed diffusive wall motion may be a result of effects nonlinear in the phonon amplitudes, as well as possible discrete lattice effects. These effects will be studied separately by decreasing $\bar{T}$ and by increasing $\bar{C}$ respectively. We note that the domain wall mechanism² for the central peak in the dynamic structure factor will persist even though diffusive wall motion occurs. The primary effect is to reduce the peak width relative to that given by the model of freely translating walls.

We have discussed here mainly the domain structure, a principal feature of the 1-D K-S model, which the computer simulations bring out so much more clearly than low order correlation functions can. Such domains are lost in any mean field models. There is evidence for some of the other excitations expected of nonlinear wave modes,^{3,7} particularly at the higher temperatures. There would seem to be no serious difficulty in extending the simulations to 2-D, and to compare with B-K.⁴ Phase transitions are to be expected, but, no doubt, other interesting features of nonlinear waves in 2-D and 3-D will appear.

REFERENCES

- * This work has been supported by the Energy Research and Development Administration under contract number AT(11-1)-3161, Technical Report number C00-3161-34.
- † Andrew D. White Professor-at-Large; permanent address: Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19174.
- 1. D. J. Scalapino, M. Sears, and R. A. Ferrell, Phys. Rev. B 6, 3409 (1972).
- 2. J. A. Krumhansl and J. R. Schrieffer, Phys. Rev. B (1975).
- 3. J. Goldstone and R. Jackiw, Phys. Rev. (to be published).
- 4. A. R. Bishop and J. A. Krumhansl, preprint (1975).
- 5. J. Lajzerowicz and P. Pfeuty, J. de Physique (Suppl.), 32, C5a-193 (1971);
B. Stoeckly and D. J. Scalapino, Phys. Rev. B 11, 205 (1975).
- 6. Note that the continuum field's equation of motion has a Lorentz "relativistically" invariant form with the harmonic sound speed c_0 taking the role of the speed of light. Thus, ξ scales with a Lorentz contraction factor and the total energy of a domain wall exhibits the corresponding relativistic speed dependence:
$$E_{DT}(v) = \frac{2}{3} \sqrt{2} (\xi_0/l) (A^2/B) / (1 - v^2/c_0^2)^{\frac{1}{2}}.$$

 E_{DP} is taken as $E_{DT}(0)$ and, to $O(v^2/c_0^2)$, m_D^* arises purely from E_{DK} as in K-S. Phonon renormalization of E_{DP} is discussed in the text.
- 7. C. M. Varma, preprint (1975).
- 8. T. Schneider and E. Stoll, Phys. Rev. Lett. 31, 1254 (1973), and references;
S. Aubry and R. Pick, presented at "International Conference on Ferroelectricity," Edinburgh (1973).

9. L. Verlet, Phys. Rev. 159, 98 (1967).
10. T. R. Koehler and P. A. Lee, to be published.
11. J. Rubinstein, J. Math. Phys. 11, 258 (1970).
12. We have computed the discrete lattice displacements numerically and find them to be very well represented by the continuum solution (2), even for these thin walls. However, other properties can be more sensitive; e.g., E_{DP}^B (see text) is increased by approximately 25% from its continuum value in the present case. The use of an effective Hamiltonian^{1,2} in the exact functional integral results may well be suspect for such thin walls.⁴

FIGURE CAPTIONS

Fig. 1: Displacements at 1,000 lattice sites for $\bar{T} = 0.117$; $\bar{t} = 0, 100, 200$.

Fig. 2: Displacements at 1,000 lattice sites for $\bar{T} = 0.117, 0.19, 0.26, 1.68$.

FIG. 1. DISPLACEMENTS AT 1000 LITHIC SITES FOR
 $\bar{T} = 0.117$; $\bar{t} = 0, 100, 200$.

FIG. 2 DISPLACEMENTS AT 1000 LATTICE POINTS. $\bar{T} = 0.117, 0.19, 0.26, 1.68$