

**MASTER**

DYNAMICS AND STATISTICAL MECHANICS OF A ONE-DIMENSIONAL  
MODEL HAMILTONIAN FOR STRUCTURAL PHASE TRANSITIONS\*

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Dynamics and Statistical Mechanics of a One-Dimensional  
Model Hamiltonian for Structural Phase Transitions\*

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Abstract

We have studied thermodynamic and some dynamic properties of a one-dimensional model system whose displacement field Hamiltonian is strongly anharmonic, and is representative of those used to study displacive phase transitions. By studying the classical equations of motion, we find important solutions (domain walls) which cannot be represented effectively by the usual phonon perturbation expansions. The thermodynamic properties of this system can be calculated exactly by functional integral methods. No Hartree or decoupling approximations are made nor is a temperature dependence of the Hamiltonian introduced artificially. At low temperature, the thermodynamic behavior agrees with that found from a phenomenological model in which both phonons and domain walls are included as elementary excitations. We then show that equal time correlation functions calculated by both functional integral and phenomenological methods agree, and that the dynamic correlation functions (calculated only phenomenologically) exhibit a spectrum with both phonon peaks and a central peak due to domain wall motion.

## I. Introduction

In recent years, there has been considerable interest in systems in which structural phase transitions apparently take place due to the instability of some lattice displacement pattern, which takes the system from some stable high temperature phase to a different low temperature lattice configuration. The dynamics of such systems is frequently characterized by a vibrational mode whose frequency decreases rapidly near the critical temperature, as though the restoring force for that displacement pattern softens, thus "soft modes". The history of this viewpoint is generally well known,<sup>1,2,3</sup> particularly in the study of ferroelectrics, though many other systems show the behavior in some form or other. Peierls instabilities would share some of the features, although significant changes in the electronic properties occur simultaneously with the lattice distortion, and the coupled problem is more complex.

While it is likely that such displacive transitions are at least accompanied by soft modes, the theoretical interpretation is not altogether satisfactory since formal analyses to date are all based on anharmonic phonon perturbation theory, using some set of self-consistent high temperature lattice phonons as a basis. But at the transition temperature, the displacements relative to that lattice become large and no perturbation scheme is expected to be satisfactory.

Computer simulations<sup>4,5,6</sup> have been carried out to shed light on these matters; and, indeed, are very informative. In addition to showing features which are expected as some order parameter develops a nonzero value, there are two other interesting features: the appearance of clusters of locally ordered regions, and the development of a "central peak" near  $\omega = 0$  in the dynamic response function  $S(q_0, \omega)$ . The "central peak" which accompanies the soft mode experimentally<sup>2</sup> has received a variety of interpretations,<sup>2,7,8</sup> which also remain somewhat open to question.

We thought that it might serve a useful purpose to see whether one could approach these problems from other than a perturbation or mode-mode coupling point of view, and the work here is a first step in that direction.

To date, the development has been restricted to a one-dimensional model, for which there cannot really be a phase transition for finite range interactions. On the other hand, we have been able to treat strong nonlinearity in some detail, making contact with an exact (in principle) calculation of the equilibrium statistical mechanics using functional integral methods. Several interesting features appear in the results, principally of an interpretive nature. The most important result potentially is that the Fourier (phonon) representation commonly used in perturbation calculations is inadequate to discuss one important type of excitation that can occur in highly nonlinear systems, and which we refer to as "domain walls". These were postulated by Takahashi<sup>9</sup> some time ago on phenomenological grounds, and now appear to us to be a natural consequence of strong anharmonicity in the statistical mechanics of this model system.

The plan of the paper is as follows: In Section II, we present the model Hamiltonian, and discuss the solutions of the resulting equation of motion for the displacement field; from the small amplitude phonon modes to some limiting large displacement patterns, including time dependent solutions. In Section III, we use the functional integral method to calculate the partition function for this Hamiltonian, adapting and extending the work of Sears, Scalapino, and Ferrell,<sup>10</sup> including the calculation of correlation functions. In Section IV, we do the statistical mechanics of a random array of domain walls on a background of small amplitude phonons, and we can make a complete identification with the functional integral result in the low temperature regime. In Section V, we show that static correlation functions can be calculated either way, and that one is led to a model for dynamic correlations which can yield a "central peak"

in an appropriate scattering function - because of the motion of domains - not because of coupling to entropy fluctuations or hydrodynamic modes. Conclusions and discussion are contained in Section VI.

## II. Model and Excitations of the System

A standard model Hamiltonian for a system which might undergo a displacive phase transition<sup>4,5,6</sup> assumes that the Hamiltonian is of the form

$$H_0 = \sum_i \left\{ \left( \frac{A u_i^2}{2} + \frac{B u_i^4}{4} \right) + \sum_j C_{ij} \frac{(u_i - u_j)^2}{2} \right\} + \sum_i m_i \frac{\dot{u}_i^2}{2} \quad (1)$$

Here  $i, j$  indicate lattice sites;  $A, B, C_{ij}$  are potential coefficients;  $u_i, \dot{u}_i$  are displacements and velocity of the displacing ion with respect to some heavy ion or reference lattice. Typically,  $A$  might be determined by attractive interactions of the mobile ion with the reference lattice,  $B$  by short range repulsion of those near ions, and  $C_{ij}$  by interactions between the displacing atoms. In the situations where this is presumed to represent a lattice which is unstable against a displacive transition,  $A$  is negative;  $B$ , positive; and  $C_{ij}$  are positive. This Hamiltonian is a tremendous oversimplification of any real three-dimensional system, particularly of symmetry restrictions and long range forces, which are important in real ferroelectrics. None the less, we find that even in one dimension there are results which are interesting and nontrivial.

Before proceeding with the analysis, we note two approximations which are often made in discussing the finite temperature behavior of the model system:

(1) Hartree approximation:  $(u_i^2)^2 = u_i^2 \langle u_i^2 \rangle_T$  usually  $\langle u_i^2 \rangle_T \approx |A| (T/T_0)$  in the high temperature region. This yields a psuedo-harmonic Hamiltonian<sup>1,2,10</sup>

(also derivable by low order anharmonic phonon perturbation theory) with

$A^* = |A| (T/T_0 - 1)$ . This describes a stable lattice for  $T > T_0$ , and vice versa

below  $T_0$ . Many studies have been made with this effective Hamiltonian as a

point of departure, but the approximate nature of its basis should not be forgotten.

(2) Mean field approximation: Onedera<sup>11</sup> has studied the statistical mechanics of this system with the approximation  $u_j = \langle u \rangle_T$  in  $\sum_j C_{ij} (u_i - u_j)^2/2$ . This suppresses all dynamic information which depends on the details of inter-ion displacements, and amounts to a collection of anharmonic oscillators coupled only by their mean thermal displacements. Thus, no phonons are considered, and interparticle fluctuation effects are certainly omitted.

We have tried to avoid either of these approximations; and particularly in contrast to the analysis in reference 10, we take  $A \equiv -|A|$  to be independent of temperature, as in the original Hamiltonian, thus not putting in the critical behavior artificially. We do not attempt to employ renormalization methods to obtain an effective Hamiltonian.

The one approximation we will make is to assume that the Hamiltonian (1) can be replaced by a continuum representation

$$H \approx \int \frac{dx}{\ell} \left\{ \frac{p(x)^2}{2m} + \frac{A}{2} u(x)^2 + \frac{B}{4} u(x)^4 + \frac{mc_0^2}{2} \left( \frac{du}{dx} \right)^2 \right\} \quad (2)$$

where  $\ell$  is the lattice spacing and  $x_j = j\ell \equiv x$  locates an element (ion) in the continuum representation. This approximation limits us to displacement fields which do not change radically over a lattice spacing. In the above,  $c_0$  is the velocity of low amplitude sound waves (phonons) which would occur if  $A$  and  $B$  were negligible (i.e., only interaction between displacing ions are important). We now proceed with the analysis.

Taking  $A = -|A|$ ,  $B > 0$ , the "on-site" potential is a double well potential with minima at (see Figure 1)

$$u = \pm u_0 = \pm \left( \frac{|A|}{B} \right)^{1/2} \quad (3a)$$

$$v(\pm u_0) = -\frac{1}{4} \frac{|A|^2}{B} \quad (3b)$$

$$v(u \pm u_0) = -\frac{1}{4} \frac{|A|^2}{B} + 2|A| \frac{(u \pm u_0)^2}{2} + \dots \quad (3c)$$



Two different physical regimes of the parameters occur under the names of "order-disorder" or "displacive" systems. If the depth of the wells is so great that an intersite energy  $mc_o^2 (2u_o/l)^2$ , which is the interaction energy between nearest neighbors displaced to opposite wells, is not great enough to lift the particle over the barrier, then only large thermal fluctuations at individual sites can do it. Effectively, one has a collection of weakly coupled anharmonic oscillators, randomly displaced to  $u \approx \pm u_o$ , as one expects in a disordered system. This "order-disorder" regime occurs for

$$\frac{1}{2} \frac{|A|^2}{B} \gg \frac{4 mc_o^2 u_o^2}{l^2} \quad (4)$$

In the opposite limit to this inequality, there is strong intersite interaction and extended lattice modes determine the physics. Here the system is said to undergo "displacive" transitions and

$$\frac{1}{2} \frac{|A|^2}{B} \ll \frac{4 mc_o^2 u_o^2}{l^2} \quad (5)$$

We will be concerned entirely with the displacive case, that being more relevant to the soft mode situation.

Applications are generally at high temperature, and no essentially quantum effects are involved. Therefore, we first consider the classical equations of motion and their solutions; then in the next section, the classical statistical mechanics of the system.

The equation of motion for the displacement field  $u(x)$  which follows from (2) is

$$m \ddot{u} + A u + B u^3 - mc_o^2 u'' = 0 \quad (6)$$

We note that quite generally, if  $u = f(x - vt)$ , then  $f$  must obey

$$m(v^2 - c_o^2) f'' + A f + B f^3 = 0 \quad (7)$$

Introduce the dimensionless variables

$$\frac{n(c_o^2 - v^2)}{|A|} = \xi^2 \quad (\text{length squared}) \quad (8a)$$

$$\frac{f}{u_o} = \eta \quad (8b)$$

$$\frac{x - vt}{\xi} = s \quad (8c)$$

The dimensionless form of the equation is

$$\frac{d^2 \eta}{ds^2} + \eta - \eta^3 = 0 \quad (9)$$

Both static and time dependent solutions may be constructed from the solutions of (9). We discuss first the limiting forms of solutions:

A. Small amplitude,  $\eta^3 \ll \eta \ll 1$ .

Solutions of  $\eta'' + \eta = 0$  are of the form

$$\eta = \alpha \sin (s + \theta) \quad (10)$$

where  $\alpha$  is amplitude and  $\theta$  = phase. Substituting physical variables

$$u = \alpha u_o \sin \left[ \frac{x - vt}{\xi} + \theta \right] \quad (11)$$

which is simply a phonon with wave number  $q = \xi^{-1}$ , frequency  $(v/\xi)$ , and phase velocity  $v$  (which is  $q$  dependent) that satisfies the equation

$$v^2 q^2 = c_o^2 q^2 - \frac{|A|}{m} = \omega_q^2 \quad (12)$$

which is also a dispersion relation. Of course, since  $A$  is negative, the frequency  $\omega_q$  will only be real for finite  $q \geq (|A|/mc_o^2)^{\frac{1}{2}}$ . These phonons are small amplitude oscillations about  $u = u_o$ .

Another set of small amplitude oscillations can occur if all particles are displaced and lowered in energy to the bottom of one of the wells. Then  $\eta = 1 + \gamma$ , where  $\gamma$  is a small dimensionless displacement. To terms linear in  $\gamma$ , the equation of motion is

$$\gamma'' - 2\gamma + O(\gamma^2) = 0$$

With a slight revision in the definition (8a) the solutions are small oscillations about  $\pm u_0$  of the form

$$u = \pm u_0 + \alpha u_0 \sin(qx - \omega_q t + \theta) \quad (13)$$

with the dispersion relation

$$c_0^2 q^2 + \frac{2|A|}{m} = \omega_q^2 \quad (14)$$

instead of (12). The frequencies are real for (all)  $q \geq 0$ . It should be noted that for  $N$  particles, this state is very much lower in energy ( $NA^2/4B$ ) than the configuration vibrating about  $u \approx 0$ .

In the cases above, the nonlinear term  $\eta^3$  has been omitted or linearized about  $\eta = 1$ . Thus, the modes found can be superimposed in lowest order calculation of the partition function. But, of course, as soon as the nonlinear terms are considered, the phonon modes are coupled to each other; and the thermodynamics is quite nontrivial. For the most part, Green's function decoupling approximations, or perturbation methods, have been the only methods applied to the interacting phonon system. However, we proceed somewhat beyond those formulations in the present case.

To do so, we now look at the solutions of (9) in another regime, which we call the large amplitude strong anharmonic regime.

B. large amplitude regime,  $\eta^3 \approx \eta \approx \pm 1$ .

The equation (9) is formally identical to that governing the order parameter in Ginzburg-Landau theory for a 1-D superconductor. One type of solution,

for which  $\eta$  is not small, is  $\eta = +1$  or  $-1$  for all  $s$ . This is mostly an uninteresting solution, the order parameter constant throughout the system; but it is the lowest energy state since all particles are at rest at the bottom of a potential well. The small oscillations in the second case above are one kind of low energy excitation above this lowest energy state.

But there are other, intrinsically nonlinear, field patterns which are also important in the low lying excitation spectrum. More important, they cannot be represented by any reasonable order of perturbation theory based on phonons. Such field patterns are well known in type II superconductors. For example, one simple particular solution of (9) is

$$\eta = \tanh \left( \frac{s}{\sqrt{2}} \right) \quad (15)$$

This corresponds to a family of solutions in physical variables

$$u = u_0 \tanh \left( \frac{x - vt}{\sqrt{2} \xi} \right) \quad (16)$$

where  $\xi$  is defined in (8a). In this pattern, the displacement is constant at  $-u_0$  over nearly all the semi-infinite region  $(x - vt) < 0$ ; it is  $+u_0$  for  $(x - vt) > 0$ . The transition takes place through a "domain wall" of approximate thickness  $2/\sqrt{2} \xi$ , and the wall moves with a velocity  $v$ . From the definition (8a)  $\xi = (m/|A|)^{1/2} (c_0^2 - v^2)^{1/2}$  it is seen that  $c_0$  is the upper limit on the drift velocity (perhaps more precisely that  $\xi$  must not be less than a lattice constant).

The excitation energy required to produce this pattern is localized in the domain wall; it will be calculated in detail in Section IV. But it is apparent that this kind of excitation is quite the converse of phonon excitations where the energy is distributed throughout the lattice. In one sense, phonons are independent in  $q$ -space while these domain walls are independent in  $r$ -space,

their interaction falling off exponentially when separated by more than a wall thickness. There is, however, the all important difference that the small amplitude solutions above were approximate solutions of (9), while (15) is an exact solution.

This last observation prompted us to see whether we could connect the two types of solutions. This has been partly possible, as follows, in terms of elliptic functions. Equation (9) may be converted by quadrature into an implicit integral relation between  $\eta$  and  $s$ . Let  $\sigma = (s/\sqrt{2})$  and

$$\frac{a^2}{b^2} = 1 + \left[ 1 - \left( \frac{d\eta}{d\sigma} \right)^2_{\eta=0} \right]^{\frac{1}{2}} \quad (17)$$

then

$$\left( \frac{d\eta}{d\sigma} \right)^2 = (a^2 - \eta^2)(b^2 - \eta^2) \quad (18)$$

and  $\sigma$  is found from the elliptic integral

$$\sigma = \int_0^{\eta} \frac{dy}{\sqrt{(a^2 - y^2)(b^2 - y^2)}} \quad (19)$$

the notation being standard.<sup>12</sup> This is an elliptic integral of the first kind, and generates the family of solutions

$$\eta = a \operatorname{sn}(b\sigma) \quad (20)$$

where  $\operatorname{sn}(b\sigma)$  is the "elliptic sine function". For  $b\sigma = 0$ , i.e.,  $s = \frac{x - vt}{\xi} = 0$ ,

$\eta = 0$ , and  $\operatorname{sn}$  is an odd function of its argument. With a modest amount of algebra, it is easy to find the "small amplitude" and "large amplitude" limits.

Equation (20) may be written out in further detail:

$$\eta = \left[ 1 - \sqrt{1 - 2 \left( \frac{d\eta}{ds} \right)^2_{\eta=0}} \right] \operatorname{sn} \left[ \left( 1 + \sqrt{1 - 2 \left( \frac{d\eta}{ds} \right)^2_{\eta=0}} \right)^{\frac{1}{2}} \frac{s}{\sqrt{2}} \right] \quad (21)$$

The elliptic sine is periodic in  $4K$  where  $K$  is the complete elliptic integral of modulus  $k$

$$k = \frac{a}{b} = \left[ \frac{1 - 1 - 2 \left( \frac{d\eta}{ds} \right)_{\eta=0}^2}{1 + 1 - 2 \left( \frac{d\eta}{ds} \right)_{\eta=0}^2} \right]^{\frac{1}{2}} \quad (22)$$

The small amplitude solutions are found in the limit  $(d\eta/ds)_{\eta=0} \ll 1$ , where  $k \approx 0$ , and  $4K \approx 2\pi$ . We recover (10)

$$\eta = a \sin s.$$

But for large amplitude,  $K \rightarrow 1$  then  $K \rightarrow \infty$  and the period of the solution becomes very long (and not related to any renormalized fundamental period). In fact, if  $(d\eta/ds)_{\eta=0} = (2)^{\frac{1}{2}}$  then one finds that (21) approaches

$$\eta = \tanh (s/2)$$

and we recover the domain wall solution above. In all of the above, the phase  $\theta$ , a choice of origin, has not been explicitly written in; but because the Hamiltonian is translationally invariant, it is clear that this freedom exists. Also, since  $s = \frac{x - vt}{\xi}$ , a whole family of stationary and moving fields is included in (21).

It would be nice, now given various dynamic solutions of the equation of motion, to proceed to express the Hamiltonian using them as a basis, then do the statistical mechanics. This is what is usually done with phonons, because a harmonic Hamiltonian separates in mode space. Unfortunately, as is obvious from the nature of nonlinear systems, it is absolutely impossible to do the same superposition by simply adding two solutions for the displacement field. Indeed, the whole subject of nonlinear oscillations in extended systems is

extremely complex; and we must admit to having been unable to carry forward a rigorous program to connect these exact solutions of the equation of motion to an evaluation of such thermodynamic quantities as the partition function.

On the other hand, we believe that the analysis above suggests certain features which should be included in a proper phenomenological discussion of the statistical mechanics - at least in the low temperature region where low energy excitations dominate. Specifically, we believe that one will see two different patterns in the displacement field; one, small amplitude oscillation motions about the potential minima  $u \approx \pm u_0$ ; and then the other, occasional "domain walls" where the displacement flips from one minimum to the opposite over a region of length  $\approx 2/2 \xi$ .

There will be a thermal mixture of these two kinds of excitation. It is apparent that phonons (extended) and walls (localized) interact weakly; and if the density of walls is low, they interact weakly with each other. Can one go from one language to the other in a systematic way? Again, the complex physics of nonlinear oscillations in extended systems (e.g., laser oscillations) often seems to allow the pumping of energy from a number of weakly excited extended modes, via the nonlinearity, into a local pulse or shock; and our conclusion is that this happens here.

To test these ideas, one must resort either to experiment or to some related theoretical calculation which can be carried out exactly. It is not possible to find a real system which is accurately represented in nature by our model Hamiltonian. Computer simulations<sup>4,5,6</sup> are of considerable use in a quantitative way, and we will comment on them in the concluding discussion. However, a formally exact solution for the thermodynamic quantities would be much more useful for calibration purposes. Fortunately, using functional integral methods<sup>10,13</sup> it is possible to evaluate the partition function for this one-dimensional model exactly - conditional on a knowledge of solutions of a

one-dimensional anharmonic oscillator Schrödinger-like equation - which can be solved numerically if necessary.

We carry out that exact calculation in the next section (III), and then compare it in Section IV with the phenomenological thermodynamic behavior deduced from a mixture of phonons and domain walls.

### III. Equilibrium Thermodynamics of the One-Dimensional Model: "Exact"

The classical partition function follows from the Hamiltonian (2) as a functional integral in the field variables  $u(x)$ ,  $p(x)$

$$Z = \int [\delta(u) \delta(p)] \exp [-\beta H(p, u)] \quad (23)$$

Scalapino, Sears, and Ferrell,<sup>10</sup> and Kac and Helfand<sup>13</sup> have shown how this expression may be evaluated in terms of the eigenfunctions of transfer integral operators. We have followed SSF generally, except in two respects: (1) We do not put an explicit temperature dependence into  $A$ , e.g.,  $a(T - T_0)$ , which in a sense puts in the phase transition "by hand", but take  $A = -|A|$  constant; (2) instead of solving the anharmonic oscillator Schrödinger equation numerically to determine the eigenvalues of the transfer operator, we studied the lowest states in a formal (WKB approximation) way; this preserves subtle interpretive features that can be easily lost in numerical studies.

In the classical approximation, for the given Hamiltonian, the momentum and field displacement integrations for  $Z$  factor completely.  $Z = Z_p Z_u$ , with  $Z_p = (2\pi m k_B T)^{N/2}$  as usual for  $N$  particles. We are left with the potential energy term  $Z_u [V(\{u\})]$  to compute. Dividing  $x$  into stations  $x_i$  separated by  $\ell$ , one writes the partition function, for nearest neighbor interactions, as

$$Z_u = \int \prod_i \left[ du_i e^{-\beta f(u_i, u_{i-1})} \right] \quad (24)$$

where  $f(u_i, u_{i-1})$  is that part of the potential depending on  $u_i$  and  $u_{i-1}$ .



The integral may be evaluated exactly in the limit of a large system using the eigenfunctions and eigenvalues of the transfer integral operator

$$\int du_{i-1} e^{-\beta f(u_i, u_{i-1})} \psi_n(u_{i-1}) = e^{-\beta \epsilon_n} \psi_n(u_i) \quad (25)$$

The  $\psi_n$  are distribution functions for the field amplitude  $u$ , which are not only useful to compute  $Z$ , but also to compute expectation values of various quantities, assuming that their properties are such that the  $\psi_n$  form a complete set, i.e.,

$$\delta(u - v) = \sum_n \psi_n(u) \psi_n^*(v) \quad (26)$$

Thus, supposing at first that at  $x_1$ ,  $u_1 = v$ , then the integral  $Z_u$  can be rewritten

$$Z_u = \sum_n \psi_n^*(v) \int \prod_i du_i e^{-\beta f(u_i, u_{i-1})} \psi_n(u_1) \quad (27a)$$

$$= \sum_n \psi_n^*(v) \psi_n(u_{N+1}) \left( \prod_{i=1}^N e^{-\beta \epsilon_n} \right) \quad (27b)$$

Next, integrating over all possible initial and final displacements  $v$ ,  $u_{N+1}$ , and replacing  $N$  by  $(L/\ell)$  yields

$$Z_u = \sum_n e^{-\frac{L}{\ell} \beta \epsilon_n} \quad (28)$$

Obviously, as  $L \rightarrow \infty$ ,  $Z_u$  is dominated by the lowest eigenvalue  $\epsilon_0$

$$Z_u \approx e^{-\frac{L}{\ell} \beta \epsilon_0} \quad (29)$$

This procedure and calculations of moments or correlation functions are discussed further in the references cited.

The burden is now transferred to finding solutions of the transfer operator equation. These are found<sup>10</sup> from the solutions of an equation which is Schrödinger-like (of course, quantum mechanics is not really involved). Applying the method of SSF, we find the effective oscillator equation, in which  $\hbar = 1$ ,

$$\left[ s_0 + \frac{A}{2} u^2 + \frac{B}{4} u^4 - \frac{\ell^2}{2\beta^2 m c_0^2} \frac{d^2}{du^2} \right] \Psi_n(u) = \epsilon_n \Psi_n(u) \quad (30)$$

where  $s_0$  is a zero of energy from normalizing certain integrals and plays little role in the thermodynamics. Note one important difference between (30) and SSF (2.23); we maintain the strong temperature dependence of an effective mass  $m^*$  on temperature, as defined by

$$\frac{\ell^2}{2\beta^2 m c_0^2} \frac{d^2}{du^2} = \frac{1}{2m^*} \frac{d^2}{du^2}$$

$$\text{or } m^* = m(c_0^2 / \ell^2 K_B^{-2} T^2).$$

A variety of results were obtained by SSF from numerical evaluation of the solutions of their version of (30). More insight can be gained, at least for the low temperature region, by an interpretive examination of the low energy solutions of (30), as a function of temperature. The potential is shown in Figures 1a, 1b, 1c, with an indication of the way in which the energy levels might be distributed for low, intermediate, and high temperature. For low temperature, the effective mass  $m^*$  is large and the eigenvalues begin near the bottoms of the wells, split into pairs by "tunneling" - in the sense of this effective Schrödinger equation. At high temperature,  $m^*$  may become so small that the lowest eigenstate  $\epsilon_0$  lies well above the potential hump. This does not provide an exact criterion for obtaining a true phase transition, but it does suggest that below some intermediate temperature the thermal distribution

is such as to find the displacement pretty much near  $\pm u_0$ , while well above this temperature the displacements range over the whole region in the lowest eigenfunction  $\Psi_0(u)$ .

An examination of computer solutions would provide further detail, if done with high precision. However, in the lower temperature regime, approximate solutions can be constructed, as for standard quantum mechanical double well problems. To a first approximation we have harmonic oscillator states in each well, for which the (doubly degenerate) spectrum

$$E_n \approx (n + \frac{1}{2}) \left( \frac{2|A|}{m} \right)^{\frac{1}{2}} \quad (31a)$$

$$\approx (n + \frac{1}{2}) \frac{\ell K_B T}{c_0} \left( \frac{2|A|}{m} \right)^{\frac{1}{2}} \quad (31b)$$

The potential near the minima is  $V_{u_0} \approx (2|A|)(u - u_0)^2/2$ . This double degeneracy is split by tunneling

$$E_{n,s} \approx E_n \pm t_n \quad (32)$$

where  $t_n$  is the matrix element connecting the  $n^{\text{th}}$  states in opposite wells. Taking the lowest states,  $n = 0$ , as lying on either side of a potential hump of height  $(A^2/4B)$  and average width  $u_0$ , a WKB approximation yields

$$t_0 \approx \frac{E_0}{2} e^{-\frac{u_0}{K_B T} \sqrt{\frac{A^2}{B} \frac{mc_0^2}{2\ell^2}}} = \frac{E_0}{2} e^{-u_0 \sqrt{\frac{A^2}{2B} n^*}} \quad (33)$$

Thus, the two lowest levels have eigenvalues (from (31a) with  $n = 0$ )

$$\begin{aligned} \epsilon_{o,s} &= \frac{1}{2} \left( \frac{2A}{m^*} \right)^{\frac{1}{2}} \left( 1 - \frac{1}{2} e^{-u_o \sqrt{\frac{A^2}{2B} m^*}} \right) \\ \epsilon_{o,a} &= \frac{1}{2} \left( \frac{2A}{m^*} \right)^{\frac{1}{2}} \left( 1 + \frac{1}{2} e^{-u_o \sqrt{\frac{A^2}{2B} m^*}} \right) \end{aligned} \quad (34)$$

with

$$\Psi_{o,s} = \frac{1}{\sqrt{2}} \left[ \Psi_o(u - u_o) \pm \Psi_o(u + u_o) \right] \quad (35)$$

where  $\Psi_o(u)$  is the  $n = 0$  harmonic oscillator state.

For low temperature, but finite, the "tunneling" splitting of the lowest oscillator level as given by (33) may be very small, but upon taking the thermodynamic limit  $(L/\ell) = N \rightarrow \infty$  only the lower of the pair of states survives. We have the series of equations using (29), (31b), (32),

$$\begin{aligned} Z_u &= \exp \left[ -\frac{L}{\ell} \beta (s_o + E_o - t_o) \right] \\ F &= -K_B T / n \left[ Z_p Z_u \right] = F_p + F_u \end{aligned} \quad (34)$$

$$F_p = -\frac{NK_B T}{2} \ln(2\pi M K T) \quad (35)$$

$$F_u = NK_B T \left[ \frac{\ell}{2c_o} \left( \frac{2|A|}{m} \right)^{\frac{1}{2}} + \frac{s_o - t_o}{KT} \right] \quad (36)$$

Upon substituting and collecting terms after some algebra

$$F = F_{osc} + F_{tunn} \quad (37)$$

$$F_{osc} = NK_B T \left[ \frac{\ell}{2c_o} \left( \frac{2|A|}{m} \right)^{\frac{1}{2}} + \log \left( \frac{c_o}{2\pi K_B T \ell} \right) \right] \quad (38a)$$

$$F_{\text{tunn}} = -Nk_B T \frac{\ell}{4c_0} \left( \frac{2|A|}{\pi} \right)^{\frac{1}{2}} e^{-\frac{2u_0}{k_B T} \left( \frac{A_n^2 c^2}{2B\ell^2} \right)^{\frac{1}{2}}} \quad (38b)$$

The terms in (38a) are shown in Appendix I to be the free energy of the phonons specified by (13) and (14). What is  $F_{\text{tunn}}$ ? We show in the next section that it is just equal to the free energy of a thermodynamic distribution of domain walls, together with the phonons. Thus, this detailed functional integral calculation shows that two qualitatively distinct low energy excitations are present, particularly at low temperature.

#### IV. Statistical Mechanics of Domain Walls

Let us assume the viewpoint that the domain walls can be considered as weakly interacting elementary excitations if, say at low temperature, they are distributed at random in low concentration along the one-dimensional model system. We then compute the thermodynamic properties, and compare the result with the exact calculation in the preceding section, to see whether this view is plausible.

The point is that if separated by much more than a wall thickness, the strain and kinetic energy fields do not interfere between domain walls. Actually, there are some interesting kinematic restrictions, in that domain walls of the same sign cannot be adjacent to each other nor pass through each other while walls of opposite sign can pass through each other and annihilate. For the present, we assume that the density of walls is so low that these finer details will contribute only an "excluded volume" type of correction to an otherwise dilute gas.

To proceed, we need the excitation energy associated with the wall, which from (1) comprises kinetic and potential energy terms. These are to be evaluated for the field given by (15) and (16). The potential energy, relative to

the lowest energy where  $u = \pm u_0$  is given by

$$E_{DP} = \int \frac{dx}{\ell} \left\{ \frac{A}{2} (u^2 - u_0^2) + \frac{B}{4} (u^4 - u_0^4) + \frac{mc_0^2}{2} \left( \frac{du}{dx} \right)^2 \right\} \quad (39)$$

and the kinetic energy by

$$E_{DK} = \int \frac{dx}{\ell} \left\{ \frac{m}{2} \dot{u}^2 \right\} \quad (40)$$

with  $u = u_0 \tanh [(x - vt)/2\xi]$ . These integrals could be evaluated numerically; but for interpretive reasons, we approximate so that they can be evaluated formally, as follows: (a) replace  $\tanh y$  by  $y$  if  $|y| < 1$ , and by  $\pm 1$  otherwise, (b) considering only low energy excitations, we assume that the slow moving walls,  $v^2 \ll c_0^2$ , dominate; then  $\xi \approx \xi_0$  independent of  $v$ . With these approximations

$$E_{DP} \approx 2/2 \frac{\xi_0}{\ell} \frac{A^2}{2B} \left( 1 - \frac{7}{60} \right) \quad (41)$$

$$E_{DK} \approx \frac{m}{2} \left( \frac{2/2 \xi_0}{\ell} \right) \left( \frac{u_0^2}{2 \xi_0} \right) v_D^2 = \frac{m_D^*}{2} v_D^2 \quad (42)$$

The factor (7/60) from integrations will be neglected. Each of these expressions is easily interpreted, defining  $\Delta = 2/2 \xi_0$  as the thickness of a domain wall. The number of particles in a wall is  $(2/2 \xi_0/\ell)$ , with mean potential energy approximately  $(A^2/2B)$  (relative to the ground state). Similarly, the kinetic energy may be associated with a kinetic effective mass of the domain wall  $m_D^*$  given by

$$m_D^* = m \left( \frac{2/2 \xi_0}{\ell} \right) \left( \frac{u_0^2}{2 \xi_0} \right) \quad (43)$$

The statistical problem is then that of a "gas" of "quasi particles" having the above potential and kinetic energy, distributed in a one-dimensional volume.

The partition function is that found for placing these particles on a line. So that they may be considered distinguishable, we divide the line into  $n_s$  segments having thickness of a domain wall  $\Delta = 2/2 \xi$ , then  $n_s = (L/\Delta)$ . The partition function is then

$$Z_D = \left[ \sum_{n_w} \left( \int \frac{dv_D}{B} e^{-\frac{\beta \hbar^2}{2} v_D^2} \right)^{n_w} \frac{n_s!}{n_w! (n_s - n_w)!} e^{-\beta n_w E_{DP}} \right] \quad (44)$$

where B is an appropriate phase space normalization. In the approximation that Z is dominated by the most probable  $n_w$ , which if  $e^{-\beta E_{DP}} \ll 1$  is also the average  $\bar{n}_w = n_s e^{-\beta E_{DP}}$ , then the expression can be evaluated to yield

$$Z_D \approx Z_{DK} Z_{DP} \approx \left( \frac{2\pi K_B T}{B^2 \hbar^2} \right)^{\frac{\bar{n}_w}{2}} e^{+\bar{n}_w} \quad (45)$$

The same result can be obtained more elegantly using a grand canonical distribution. From (45) the free energy is

$$F_D = -KT \log Z_D = -K_B T \bar{n}_w \left[ 1 + \frac{1}{2} \log \left( \frac{2\pi K_B T}{B^2 \hbar^2} \right) \right] \quad (46)$$

$$F_D = -NKT \left( \frac{l}{2/2 \xi_0} \right) \left( 1 + \frac{1}{2} \log \frac{2\pi K_B T}{B^2 \hbar^2} \right) e^{-\frac{E_{DP}}{KT}} \quad (47)$$

We now compare this with the "tunneling contribution" to free energy found from the exact functional integral calculation as given by (38b). Inserting the definitions for  $\xi_0$ ,  $E_{DP}$  from (41) [but neglecting (7/60) compared to unity], and  $u_0$ , we find that (38b) may be rewritten

$$F_{tunn} = -NK_B T \left( \frac{l}{2/2 \xi_0} \right) e^{-\frac{E_{DP}}{K_B T}} \quad (48)$$

Remarkably, except for a prefactor of the order of unity,  $F_D \equiv F_{\text{tunn}}$ . Thus, a qualitatively important part of the exact free energy is associated with the excitation of domain walls.

We take this agreement between the phenomenological statistical mechanical model and the exact calculation as confirmation of the proposal in Section I that when nonlinearity plays an important role, both phonon and localized domain wall excitations are to be found in the thermodynamic behavior. Of course, the phonon free energy varies slowly (linearly) with  $T$  in this classical approximation, while the free energy and concentration of domain walls drops rapidly (exponentially) with decreasing temperature. However, as we will see in the next section, a number of experimental quantities can depend strongly on the presence of domain walls.

## V. Applications of the Phenomenological Model

### A. Equal-Time Correlation Functions - Low Temperature

As discussed by SSF,<sup>10</sup> the two point equal-time correlation function may be written

$$\langle u(0) u(x) \rangle = \sum_n e^{-\beta(\epsilon_n - \epsilon_0)(x/L)} |\langle 0 | u | n \rangle|^2 \quad (49)$$

where again the  $\epsilon_n$  and states  $|n\rangle$  are those of the eigenfunctions of the transfer integral operator defined for the functional integral in Section III. If we include higher oscillator states in the sum, we can find the correlation function characteristic of phonons about  $\pm u_0$ . But a much larger displacement is associated with a jump from  $-u_0$  to  $+u_0$ ; at low temperature, the sum (49) is then dominated by the lowest pair of tunneling states. It is straightforward using (33) and (35) to find then that



$$\begin{aligned} \langle u(0) u(x) \rangle &\approx u_0^2 e^{-2\beta t_0(x/l)} \\ &\approx u_0^2 e^{-\frac{x}{\lambda_c}} \end{aligned} \quad (50)$$

where the correlation length is found from (33) to be

$$\lambda_c = \sqrt{2} \xi_0 e^{\frac{E_{DP}}{KT}} \quad (51)$$

in the low temperature region where the tunneling approximation holds. At higher temperature, when the lowest eigenstates of (30) are above the saddle point between wells, one expects an algebraic dependence of  $\lambda_c$  on temperature. Thus, below some intermediate temperature, the correlation length begins to increase dramatically (exponentially); but, of course, does not ever become infinite for any finite temperature, for a one-dimensional system. So much for the functional integral result for the equal time displacement-displacement correlation function.

Can the phenomenological domain wall model be used to calculate this correlation function? Consider the following model: At  $x = 0$ ,  $u \approx u_0$ , except for small phonon oscillations, but between  $x = 0$  and a finite value of  $x$ , there may be  $n_w(x)$  domain walls. At each wall  $u = \pm u_0$  flips to  $\mp u_0$ . Thus, the correlation function

$$u(x) u(0) \approx u_0^2 (-1)^{n_w(x)} \quad (52)$$

At low density of domain walls, a Poisson distribution should apply, and

$$\text{Pr}(n_w(x)) = \frac{(\bar{n}_w)^{n_w}}{n_w!} e^{-\bar{n}_w} \quad (53)$$

where  $\bar{n}_w(x) = (x/\Delta) e^{-\beta E_{DP}}$  from (44). The average value of the correlation

function is

$$\langle u(x) u(0) \rangle = u_0^2 \langle (-1)^{n_w(x)} \rangle \quad (54)$$

and

$$\begin{aligned} \langle (-1)^{n_w(x)} \rangle &= (-1)^0 \cdot e^{-\bar{n}_w} + (-1)^1 \bar{n}_w e^{-\bar{n}_w} \\ &\quad + (-1)^2 \frac{(\bar{n}_w)^2}{2!} e^{-\bar{n}_w} + \dots \\ \langle (-1)^{n_w(x)} \rangle &\approx e^{-2\bar{n}_w} \end{aligned} \quad (55)$$

whence, where  $\Delta = 2/2 \xi_0$ ,

$$\langle u(x) u(0) \rangle = u_0^2 \exp \left[ -\frac{2x}{\Delta} e^{-\beta E_{DP}} \right] \quad (56)$$

$$\langle u(x) u(0) \rangle = u_0^2 e^{-\frac{x}{\lambda_c}} \quad (57)$$

with  $\lambda_c$  being identically the same correlation length given by (51) from the functional integral calculation.

This result is one more indication that the domain wall model is both formally and practically valid for obtaining information about thermodynamic averages in the low temperature regime.

#### B. Dynamic Correlation Functions

For scattering experiments in which some probe excites a displacement  $u(0, 0)$  which in turn induces emission proportional to  $u(x, t)$ , a relevant quantity is

$$\langle u(0, 0) u(x, t) \rangle \quad (58)$$

and its Fourier transform  $S(q, \omega)$

$$S(q, \omega) = \frac{1}{(2\pi)^2} \iint dx dt e^{i(qx - \omega t)} \langle u(0, 0) u(x, t) \rangle \quad (59)$$

This correlation function description is an idealized model of real photon or neutron scattering.

We have not yet been able to make an exact calculation of this dynamic quantity in the spirit of the functional integral for equilibrium quantities. Therefore, we now rely completely on the domain wall model (again for low temperature).

Considering a particular point  $x$ , then the phenomenological picture we have is that for a while  $u(x, t)$  is approximately  $+u_0 + \alpha \cos \omega_0 t$ , then along comes a domain wall flipping the displacement to  $-u_0 + \alpha' \cos \omega_0 t$ , and so on. Here,  $\alpha \cos \omega_0 t$  is a small amplitude oscillation with  $\omega_0 \approx (2|A|/m)^{1/2}$ . These domain walls have random spacings and random velocities, according to the distribution discussed in Section IV. Some important features of the frequency spectrum can be found as follows: Assume that over a correlation length  $\lambda_c$ , we can approximate  $\langle u(0, 0) u(x, t) \rangle$  by  $\langle u(0, 0) u(0, t) \rangle$ , then

$$S(q, \omega) \propto \frac{\sigma_\lambda(q)}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle u(0, 0) u(0, t) \rangle \quad (60)$$

with  $\sigma_\lambda(q)$  an approximate spatial transform over a correlation length. But by the convolution theorem, the  $\omega$ -transform of the correlation function is just the power spectrum  $\langle u(0, \omega) u^*(0, \omega) \rangle$ , where

$$u(0, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} u(0, t) \quad (61)$$

This Fourier transform in our model becomes

$$\begin{aligned}
 u(0, \omega) = \sum_i \left\{ \frac{e^{-i\omega t_i}}{2\pi} (\pm u_0) \left[ \frac{e^{-i\omega(t_{i+1} - t_i)} - 1}{-i\omega} \right] \right. \\
 + \frac{\alpha_i}{2\pi} e^{-i(\omega - \omega_0)t_i} \left[ \frac{e^{-i(\omega - \omega_0)(t_{i+1} - t_i)} - 1}{-i(\omega - \omega_0)} \right] \\
 \left. + \frac{\alpha_i}{2\pi} e^{+i(\omega + \omega_0)t_i} \left[ \frac{e^{-i(\omega + \omega_0)(t_{i+1} - t_i)} - 1}{-i(\omega + \omega_0)} \right] \right\} \quad (62)
 \end{aligned}$$

where the  $t_i$  are the random arrival times of the domain walls. As usual, the average of the sum of random phased terms in  $u(0, \omega)$  is negligible, but not so for  $\langle u(0, \omega) u^*(0, \omega) \rangle = X(\omega)$  which is found to be

$$\begin{aligned}
 X(\omega) = \frac{u_0^2}{\pi^2} \langle \frac{[\sin \omega(t_i - t_{i+1})]^2}{\omega^2} \rangle_{D.W.} \\
 + \langle \frac{\alpha_i^2}{\pi^2} \frac{[\sin (\omega - \omega_0)(t_i - t_{i+1})]^2}{(\omega - \omega_0)^2} \rangle_{D.W.} \\
 + \langle \frac{\alpha_i^2}{\pi^2} \frac{[\sin (\omega + \omega_0)(t_i - t_{i+1})]^2}{(\omega + \omega_0)^2} \rangle_{D.W.} \quad (63)
 \end{aligned}$$

The average is to be carried out over the distribution of arrival intervals

$(t_{i+1} - t_i)$  domain walls. This distribution is calculated as follows:

(1) At  $x = 0$ , walls move in from right and left.

(2) The number reaching  $x = 0$  from one side between  $0$  and  $t$  and having velocity  $v$  is the number lying in the interval  $l = vt$ . Thus

$$N > (t) = \int_0^\infty vt \bar{n}_w(v) dv \quad (64)$$

where  $\bar{n}_w(v)$  is the average number of walls per unit length having velocity  $v$ .

From Section IV

$$\bar{n}_w(v) = \frac{1}{\Delta} e^{-\beta E_{DP}} e^{-\frac{\beta m_D^* v^2}{2}} \quad (65)$$

The number arriving from both sides between 0 and  $t$  is

$$N(t) = \frac{2t}{\Delta} e^{-\beta E_{DP}} \int_0^\infty v e^{-\frac{\beta m_D^* v^2}{2}} dv = \frac{t}{t_D} \quad (66)$$

where

$$t_D^{-1} = \frac{2}{\beta \Delta m_D^*} e^{-\beta E_{DP}} \quad (67)$$

(3) The probability  $P(t)$  that no domain wall has yet reached  $x = 0$  up to time  $t$  obeys

$$\frac{dp}{dt} = -\frac{dn}{dt} = -\frac{1}{t_D}$$

whence

$$P(t) = \frac{1}{t_D} e^{-\frac{t}{t_D}} \quad (68)$$

and this is the probability distribution to be used for the intervals in (63).

We then must calculate quantities like

$$\int_0^\infty \frac{dt}{t_D} e^{-\frac{t}{t_D}} \frac{\sin^2 \omega t}{\omega^2} = \frac{2 t_D}{1 + 4 \omega^2 t_D^2}$$

From (63), in the spirit of (60), we find

$$S(q, \omega) \propto \frac{2\sigma_\lambda(q)}{\pi^2} \left\{ u_0^2 \frac{t_D}{1 + 4\omega^2 t_D^2} + \bar{\alpha}^2 \left[ \frac{t_D}{1 + 4(\omega - \omega_0)^2 t_D^2} + \frac{t_D}{1 + 4(\omega + \omega_0)^2 t_D^2} \right] \right\} \quad (69)$$

Here  $\bar{\alpha}^2$  is a mean square thermal amplitude of the phonons with frequency  $\omega_0$  (as specified by  $q$ ).

We see that the spectral function contains not only the expected peaks at the phonon frequency  $\omega_0$ , but also a "central peak" whose height increases exponentially with inverse temperature as  $t_D$  increases. This central peak is a manifestation of the strongly nonlinear domain wall type of displacement field, not of coupling to entropy or hydrodynamic modes.

It is tempting to say that this "central peak" is that seen in computer simulation experiments,<sup>4,5</sup> or in real neutron scattering experiments. However, we can only say that it is provocative, for at least two reasons: First, this is a one-dimensional model and a real phase transition cannot occur; second, the analysis here would really only apply in the low temperature regime where it would be difficult to separate from any Bragg peak at the same  $q$ ; the extent to which the features would survive at and above a transition is uncertain.

We hope to extend the model to a two-dimensional system, so that closer comparison with computer experiments and real transitions can be carried out.

## VI. Summary and Discussion

We have studied thermodynamic and some dynamic properties of a one-dimensional model system whose displacement field Hamiltonian is strongly anharmonic, and is representative of those used to study displacive phase

transitions. By studying the classical equations of motion, we find important solutions (domain walls) which cannot be represented effectively by the usual phonon perturbation expansions. The thermodynamic properties of this system can be calculated exactly by functional integral methods. No Hartree or decoupling approximations are made nor is a temperature dependence of the Hamiltonian introduced artificially. At low temperature, the thermodynamic behavior agrees with that found from a phenomenological model in which both phonons and domain walls are included as elementary excitations. We then show that equal time correlation functions calculated by both functional integral and phenomenological methods agree, and that the dynamic correlation functions (calculated only phenomenologically) exhibit a spectrum with both phonon peaks and a central peak due to domain wall motion.

Much remains to be done to examine the extent to which the ideas discussed here apply to real systems, and how they relate to or are in contradiction with conventional theories. None the less, it seems that such features as clusters (i.e., regions bounded by domain walls) which appear in computer simulations of model systems, the "central peak", and the consistency of exact and phenomenological thermodynamic calculations is encouraging. However, we also must note that the lack of any general methodology for discussing the finite temperature behavior of extended nonlinear systems presents a formidable obstacle to the possible extension to higher dimensional systems, or to do exact dynamics at finite temperature.

Finally, we record a few speculative ideas, which may be worth further development. First, if these domain walls are present in the low temperature phases of pseudo one-dimensional crystals which have undergone Peierls transitions, the Peierls energy gap in those walls could go to zero, the material becoming locally metallic. One could then have a distribution of conducting sheets (walls) in an insulating matrix; the low frequency

electrical properties and optical properties would not be simply related, as in a homogeneous medium. Second, there is the question of whether a soft mode going to zero frequency is the exact condition for a structural phase transition. This question cannot be answered properly until adequate dynamic extensions of the analysis here can be made. On the other hand, the functional integral analysis is suggestive that there is a temperature range in which the collective dynamic behavior will change from that of oscillations in either of two wells to that of a single nonlinear oscillator, whose period becomes very long in the transition region. In our model, this would occur in the region of Figure 1(b), when the effective mass  $m^* = m(c_0^2/\ell^2 K_B T^2)$  is such that the lowest eigenvalue of (30) lies near the saddle point of the potential. Thus, while it is not certain that a phase transition will occur exactly at the temperature where the soft mode frequency goes to zero, it is very likely to be nearby.

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# Appendix

## Phonon Free Energy for Vibrations in Well

The dispersion relation (14) is

$$\omega_q^2 = c_o^2 q^2 + 2 \frac{|A|}{m} \quad (A.1)$$

The density of states in q-space is  $(L/\pi)$ , whence the density of states in  $\omega$  is

$$\frac{dn}{d\omega} = \frac{L}{\pi c_o} \frac{\omega}{\sqrt{\omega^2 - 2 \frac{|A|}{m}}} \quad (A.2)$$

It may be rewritten in terms of  $N = (L/\ell)$ , and a Debye normalization

$$\begin{aligned} \int_{\omega_{\min}}^{\omega_{\max}} d\omega \left( \frac{dn}{d\omega} \right) &= N \\ \omega_{\min} &= \left( \frac{2|A|}{m} \right)^{\frac{1}{2}} \end{aligned} \quad (A.3)$$

leads to

$$\frac{dn}{d\omega} = N \frac{\ell}{\pi c_o} \frac{\omega}{\sqrt{\omega^2 - 2 \frac{|A|}{m}}} \quad (A.4)$$

and

$$\omega_{\max}^2 = \frac{2|A|}{m} + \frac{\pi^2 c_o^2}{\ell^2} \quad (A.5)$$

The free energy per oscillator is  $F(\omega) = K_B T \log [1 - e^{-\frac{\hbar\omega}{K_B T}}] \rightarrow K_B T \log (\hbar\omega/K_B T)$  in the classical limit  $KT \gg \hbar\omega$ . The total free energy is then

$$F_{\text{vib}} = K_B T \int_{\omega_{\min}}^{\omega_{\max}} d\omega \left( \frac{dn}{d\omega} \right) \log \left( \frac{\hbar\omega}{K_B T} \right) \quad (A.6)$$

Substituting from above, after some tedious algebra, we find

$$F_{\text{vib}} = NK_B T \left[ \left( \frac{2|A|}{n} \right)^{\frac{1}{2}} \left( \frac{\ell}{nc_o} \right)^{\sec^{-1} \left( 1 + \frac{n \pi^2 c_o^2}{2|A| \ell^2} \right)} \right. \\ \left. + \log \left( \frac{\hbar \left( \frac{2|A|}{n} \right) + \left( \frac{\pi^2 c_o^2}{\ell^2} \right)}{K_B T e} \right) \right] \quad (\text{A.7})$$

In the limit  $\ell \rightarrow 0$ , which is in the spirit of the functional integral method used,  $\left( \frac{\pi c_o}{\ell} \right)^2 \gg \frac{2|A|}{n}$  and  $\sec^{-1} \rightarrow \frac{\pi}{2}$  so

$$F_{\text{vib}} = NK_B T \left[ \frac{\ell}{2c_o} \left( \frac{2|A|}{n} \right)^{\frac{1}{2}} + \log \left( \frac{\hbar}{e} \frac{\pi c_o}{K_B T} \right) \right] \quad (\text{A.8})$$

The first term identifies with the lowest oscillator level in the functional integral. While the logarithmic term is given by (35) and the  $s_o$  term of (34) when  $\hbar = 1$ ,

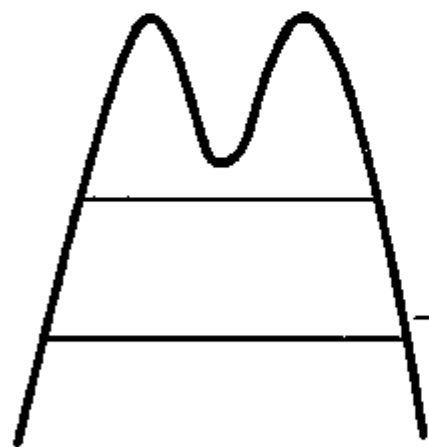
$$-K_B T [\log Z_p - N\beta s_o] = NK_B T \log \left( \frac{c_o}{2\pi K_B T \ell} \right) \quad (\text{A.9})$$

Figure Captions

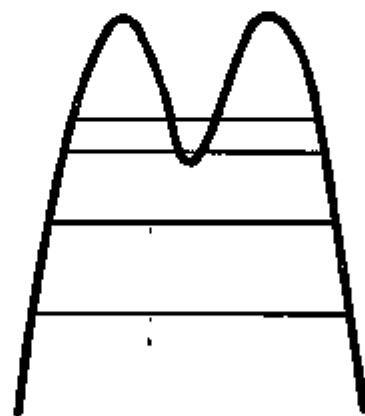
Figure 1: Eigenvalue spectrum (schematic) of the transfer operator, from equation (30), for temperature dependent effective mass

$m^* = m(c_0^2 / \ell^2 \kappa_B^2 T^2)$ : (a) low temperature,  $m^*$  large, (b) intermediate temperature, (c) high temperature,  $m^*$  small.

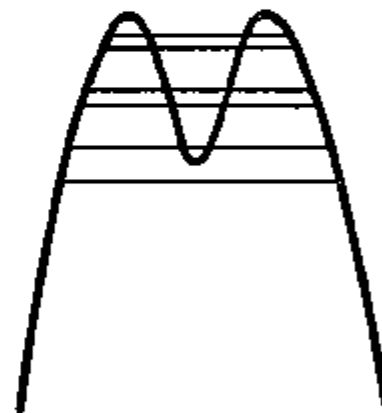
(c)



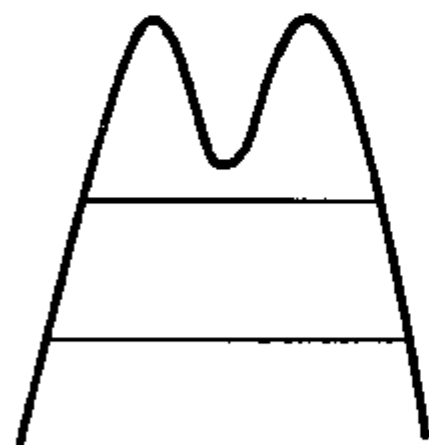
(q)



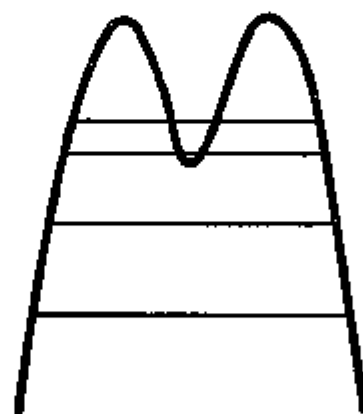
(o)



(c)



(q)



(D)

