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Instability and Phase Transition
in an Anharmonic Chain

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John S. Shier

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INSTABILITY AND PHASE TRANSITION IN AN ANHARMONIC CHAIN

by

John S. Shier

ABSTRACT

A simple anharmonic chain model is presented, and it is demonstrated how the anharmonic forces give rise to a low temperature instability and a phase transformation. Approximate expressions are given for the transition temperature and the interaction strength necessary to produce a phase transformation.

INTRODUCTION

It has long been appreciated that the anharmonic interactions between the atoms in a solid can give rise to lattice instability.¹⁻³ In particular, ferroelectric phase transformations are believed to arise because of anharmonic forces, and it is possible that the cubic-to-tetragonal phase transformation in certain intermetallic compounds having the beta-tungsten structure is also caused by anharmonicity.⁴⁻⁶

We have tried to find the simplest possible one-dimensional anharmonic chain model that exhibits qualitatively the same type of instability as that found in a solid. The model presented here illustrates in a simple way how anharmonic forces give rise to instability, and it is simple enough that one might hope to calculate its properties exactly.

We have chosen to examine a one-dimensional model because it represents the physical ideas in the simplest way. In reality, the exact solution of the system discussed here probably does not exhibit a phase transition. However, the obvious generalizations of this system to two and three dimensions probably do possess phase transitions.

THE MODEL

The Hamiltonian for a harmonic chain with nearest-neighbor interactions can be written as

$$H = \sum_{i=1}^N \left[\frac{1}{2} M \dot{x}_i^2 + 2\beta (x_i^2 - x_i x_{i+1}) \right], \quad (1)$$

where M is the mass of the atoms, x_i is the displacement of the i th atom from its equilibrium position, β is the force constant, and there are N atoms in the chain.

We will consider an anharmonic modification of the above Hamiltonian, in which the x_i^2 term is replaced by an anharmonic term,

$$H_{an} = \lim_{m \rightarrow \infty} \left\{ \sum_{i=1}^N \left[\frac{1}{2} M \dot{x}_i^2 + V_0 \left(\frac{x_i}{b} \right)^{2m} + \gamma x_i x_{i+1} \right] \right\}. \quad (2)$$

Here m is an integer, and γ is a nearest-neighbor force constant. We will also consider a cyclic system in which $x_{N+1} = x_1$.

Physically, Hamiltonian (2) represents a series of square wells of width $2b$, with the particles in neighboring wells coupled by an interaction quadratic in the displacements. The reasons for this choice will be discussed later.

The effect of the interaction term $\gamma x_i x_{i+1}$ is to push the particles to the edges of their potential wells. If γ is positive, the configuration of the system with lowest potential energy is one in which $x_i = (-1)^i b$; i.e., alternate particles are displaced to the edge of the well in opposite directions. When γ is negative, the configuration with lowest potential energy is $x_i = b$. These configurations are illustrated in Fig. 1.

The model is artificial in that the square-well part of the potential does not depend on the relative displacements of the particles. Physically it

Fig. 1. Configurations of the system having the lowest potential energy, for γ positive and negative.

might represent the situation in a diatomic chain containing, alternatively, two kinds of atoms with very different masses. Our Hamiltonian might then represent the motion of the light atoms anharmonically coupled to heavy nearest neighbors and coupled to the light second-nearest neighbors by an unstable harmonic interaction. It would thus represent an optical mode.

SELF-CONSISTENT FIELD APPROXIMATION

We begin by calculating the thermal-average displacement of a particle in a square well under the influence of a uniform external field (represented by a potential $-Fx$). We denote thermal averaging by $\langle \dots \rangle_T$, and k is the Boltzmann constant.

$$\langle x \rangle_T = \frac{\int_{-b}^b x e^{Fx/kT} dx}{\int_{-b}^b e^{Fx/kT} dx},$$

$$= \left[\coth \left(\frac{Fb}{kT} \right) - \frac{1}{\left(\frac{Fb}{kT} \right)} \right], \quad (3)$$

$$\xrightarrow{F \rightarrow 0} \frac{Fb^2}{3kT}. \quad (4)$$

These results are valid for the classical (high temperature) limit. It is evident that the weak-field response $\lim_{F \rightarrow 0} \langle x \rangle_T / F$ of the particle increases as $1/T$ at low temperatures; that is, the response becomes "softer." An increased response is not unique to a square well, but holds for any potential of the form x^{2m} , except for a harmonic potential ($m = 1$).

We will now show how this soft response gives rise to an instability and a phase transformation

at low temperatures, using a "self-consistent field" approximation, in analogy with the Weiss theory of ferromagnetism.⁷ We will consider the anharmonic chain in a uniform external field F_{ext} , and let the field due to the interaction with a neighboring particle be $-\gamma \langle x \rangle_T$. (This is the self-consistency condition in the present case; we require that the average displacement $\langle x \rangle_T$ of a particle be the same as the average displacements in the neighboring wells which "create" the self-consistent field $-\gamma [\langle x_{i+1} \rangle_T + \langle x_{i-1} \rangle_T]$ seen by the i^{th} particle.)

We define a polarizability α for a particle in a square well via

$$-\alpha = \lim_{F \rightarrow 0} \frac{\langle x \rangle_T}{F}, \quad (5)$$

which in the classical limit becomes

$$\alpha = \frac{C}{T}, \quad (6)$$

where $C = b^2/3k$ plays the role of a "Curie constant" in this case.

It is evident from Section 2 that if $\gamma > 0$ the particles tend to be displaced antiparallel in alternate wells. In setting up the self-consistency equations we therefore assign alternate wells to two different "sublattices" in which each particle in the same sublattice has the same average displacement. We then investigate the conditions under which this is a self-consistent solution.

The self-consistency conditions for the average displacements $\langle x_A \rangle_T$ and $\langle x_B \rangle_T$ of the two sublattices A and B are:

$$\langle x_A \rangle_T = \frac{C}{T} [F_{\text{ext.}} - 2\gamma \langle x_B \rangle_T],$$

and

$$\langle x_B \rangle_T = \frac{C}{T} [F_{\text{ext.}} - 2\gamma \langle x_A \rangle_T], \quad (7)$$

or, in matrix notation,

$$\begin{bmatrix} T & T_c \\ T_c & T \end{bmatrix} \begin{pmatrix} \langle x_A \rangle_T \\ \langle x_B \rangle_T \end{pmatrix} = CF_{\text{ext.}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad (8)$$

where

$$T_c = 2\gamma b^2/3k. \quad (9)$$

We wish to find conditions under which it is

possible to have a finite displacement when $F_{\text{ext.}} = 0$. Equations (8) then become a homogeneous linear system and have a solution if the determinant of coefficients vanishes. It is evident that this happens when $T = T_c$. The solution vectors are

$$\begin{pmatrix} \langle x_A \rangle_T \\ \langle x_B \rangle_T \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \text{ if } \gamma > 0, \text{ or} \\ \begin{pmatrix} 1 \\ 1 \end{pmatrix} \text{ if } \gamma < 0, \end{pmatrix} \quad (10)$$

so that adjacent particles are displaced parallel if $\gamma < 0$ or antiparallel if $\gamma > 0$. If we use Expression (3) instead of the weak-field limit (4), we see that in the limit $T \rightarrow 0$, the magnitude of the average displacement approaches b , the distance to the edge of the well.⁷

We have seen that at temperatures below T_c the particles can have nonzero average displacements even in the absence of an external field, while above T_c there is no self-consistent solution if $F_{\text{ext.}} = 0$. The average displacement $\langle x \rangle_T$ can thus be regarded as the order parameter of a phase transformation. If we use Expression (3) to evaluate the "spontaneous" displacement $\langle x \rangle_T$ as a function of temperature, we see that $\langle x \rangle_T$ varies continuously with temperature near T_c , which indicates that the phase transformation is of second order.

If Expression (3) were replaced by an exact quantum-mechanical expression valid at all temperatures, the spontaneous displacement $\langle x \rangle_T$ would approach a value less than b at absolute zero (its magnitude depending on the value of γb^2), and for sufficiently small γ no instability would take place. This stability occurs when the interaction energy is small compared to the zero-point energy of the particles, as we shall see in the next section.

QUANTUM-MECHANICAL TREATMENT

There are numerous ingenious calculations of the properties of an anharmonic chain, using Green's function techniques and various approximation schemes.^{8,9} None of these calculations yields a

phase transformation. The principal difficulty appears to arise because a phase transformation takes place only when the anharmonic interaction is strong, and, in this case, perturbation schemes starting from the harmonic part of the Hamiltonian give poor results. It has been pointed out by Cowley,³ that in cases where instability arises, the strictly harmonic part of the interaction may be repulsive, i.e., the strictly harmonic frequencies may include some imaginary frequencies.

In the present model we reverse the usual procedure by using an exactly soluble anharmonic Hamiltonian (the first two terms of (2)) as H_0 and by taking the perturbation V to be the harmonic part (the third term of (2) which in the absence of the square-well part of the potential represents a harmonic system with imaginary frequencies).

The Hamiltonian H_0 is simply the sum of Hamiltonians for N noninteracting infinite square wells. The energy eigenvalues for a particle in a square well are $E_n = n^2 E_0$, where $E_0 = \hbar^2 \pi^2 / 8mb^2$ and n is an integer. The matrix elements of the x operator are

$$M_{kn} = \frac{4b}{\pi^2} \left[\frac{\sin(k+n)\pi/2}{(k+n)^2} + \frac{\sin(k-n)\pi/2}{(k-n)^2} \right]. \quad (11)$$

In particular, $M_{12} = 32b/9\pi^2$. Note the parity selection rule that $M_{kn} = 0$ if $(k-n)$ is even, and that the matrix elements decrease rapidly in magnitude away from the main diagonal.

It is now easy to calculate the polarizability, α_0 , at absolute zero. Perturbation theory gives the following result.

$$\alpha_0 = 2 \sum_{n=1}^{\infty} \frac{M_{1n}^2}{E_n - E_1} = \frac{2}{E_0} \left(\frac{4b}{\pi^2} \right)^2 (0.2698) \\ = 0.08664 \, b^2 / E_0. \quad (12)$$

The perturbation series converges very rapidly in this case because of the wide spacing of the levels.

If we replace C/T by α_0 in Equations (7), we see that if $|2\gamma\alpha_0| < 1$, the determinant of coefficients does not vanish at any temperature; i.e., there is no phase transformation. This means that the criterion for existence of a phase transformation is

$$|2\gamma\alpha_0| > 1, \text{ or } |2\gamma b^2| > 11.54 E_0. \quad (13)$$

Since $2\gamma b^2$ is approximately the interaction energy per particle, and E_0 is approximately the zero-point energy, this is simply the requirement that the interaction energy be sufficiently greater than the zero-point energy.

The following scheme shows the first few energy levels of the unperturbed system described by the first two terms in Hamiltonian (2). The numbers below the levels give their degeneracy. All energies are given relative to the ground state energy.

$$E = 9E_0 \frac{N(N-1)(N-2)/6}{N}$$

$$\frac{E}{N} = 8E_0$$

$$E = 6E_0 \frac{N(N-1)/2}{N}$$

$$E = 3E_0 \frac{N}{N}$$

$$E = 0 \frac{1}{1}$$

We find approximate wave functions for the lowest levels of the system, using a scheme similar to the tight-binding approximation. This has the disadvantage that the states thus calculated are neither totally symmetric nor antisymmetric under permutation of the coordinates; i.e., they are neither boson nor fermion states. This is also true of tight-binding wave functions or spin waves.

We consider configurations where all of the particles are in the first (ground) square-well state, except the p^{th} particle, which is in the second square-well state. This configuration is labeled $|p2\rangle$. We then construct states $|q\rangle$ which are eigenstates of the translation operator

$$|q\rangle = \frac{1}{\sqrt{N}} \sum_{p=1}^N e^{ipqa} |p2\rangle \quad (14)$$

where q is the wave vector that labels the state, and a is the lattice constant.

We now calculate the matrix elements of the perturbation V (the last term of Hamiltonian (2))

between $|q\rangle$ and $|q'\rangle$. We need the relation

$$(p2|V|p'2) = M_{12}^2 \gamma [\delta_{p,p'+1} + \delta_{p,p'-1}]. \quad (15)$$

It then follows that

$$\begin{aligned} \langle q|V|q'\rangle &= \frac{1}{N} \sum_{pp'} e^{i(qp - q'p')a} (p2|V|p'2) \\ &= \frac{\gamma}{N} M_{12}^2 \sum_p [e^{i(q - q')pa + iq'a} \\ &\quad + e^{i(q - q')pa - iq'a}] \\ &= \frac{2\gamma}{N} M_{12}^2 \sum_p e^{i(q - q')pa} \cos(q'a). \end{aligned}$$

Since this lattice sum yields a delta function $N\delta_{qq'}$, we have thus diagonalized the Hamiltonian within the set of states chosen, yielding

$$E_q = 2\gamma b^2 (32/\pi^2)^2 \cos(qa) + 3E_0. \quad (16)$$

There are no matrix elements connecting the ground state and the states $|p2\rangle$, so the ground state energy remains the same in this approximation. The quantum-mechanical treatment gives the following energy levels:

We see that if $2\gamma b^2 (32/\pi^2)^2 > 3E_0$, the state with no excited particles is no longer the lowest state of the system, but at low temperatures the system condenses into the state with $q = \pi/a$. Likewise, for $2\gamma b^2 (32/\pi^2)^2 < 3E_0$, the state at $q = 0$ is the lowest state. This implies a new ground state of the system, in which the particle displacements

are correlated antiparallel or parallel, respectively. Note that in the former case the lattice period is now $2a$. The criterion for a phase transformation is $2\gamma b^2 > 23.12 E_0$, which is in satisfactory agreement with (13) in view of the approximation used.

Still another way to estimate the value of $\gamma b^2/E_0$ at which a phase transformation becomes possible is to seek the best ground state wave function of the form (which assumes we are dealing with Bose particles)

$$\Psi_{\text{trial}} = \prod_{i=1}^N f(x_i). \quad (17)$$

The variational problem then requires that we minimize the energy E given by

$$E = \frac{-\frac{\hbar^2}{2M} \int_{-b}^b f(x) f''(x) dx + \gamma \left[\int_{-b}^b x f^2(x) dx \right]^2}{\int_{-b}^b f^2(x) dx} \quad (18)$$

In general, minimizing E leads to a nonlinear eigenvalue problem. For the present purposes we will be content to use a trial function of the form ($0 \leq A \leq 1$),

$$f(x) = \frac{1}{\sqrt{b}} \left[\sqrt{A} \cos\left(\frac{\pi x}{2b}\right) + \sqrt{1-A} \sin\left(\pi \frac{x}{a}\right) \right], \quad (19)$$

which leads to

$$E = E_0(4 - 3A) + 4\gamma M_{12}^2 (A(1 - A)). \quad (20)$$

Examination of this expression shows that if $4\gamma M_{12}^2 > -3E_0$, E is always a minimum for $A = 1$; i.e., the wave function is always a symmetric cosine function. If $4\gamma M_{12}^2 < -3E_0$, the wave function that minimizes the energy contains an admixture of the antisymmetric sine function; i.e., the particle now has a mean displacement from the center of its well. This calculation gives a phase transform-

ation if $2\gamma b^2 < -11.54E_0$.

DISCUSSION

We have shown how anharmonic (nonlinear) forces in a chain can give rise to a low temperature instability and a phase transformation. The model presented is harder to solve than the one-dimensional Ising problem, but simple enough that one might hope to find an exact solution. It also differs from the Ising problem in that it has a time dependence and, in principle, calculable transport properties. The anharmonic chain model is easily generalized to two and three dimensions.

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