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Anharmonic oscillator model for first order structural phase transition

AVINASH KHARE and S N BEHERA
Institute of Physics, A/105, Saheed Nagar, Bhubaneswar 751 007, India

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Abstract. Exact solutions for the motion of a classical anharmonic oscillator in the potential $V(\phi)=B\phi^2-|A|\phi^4+C\phi^6$ are obtained in (1 + 1) dimensions. Instanton-like solutions in (imaginary time) which takes the particle from one maximum of the potential to the other are obtained in addition to the usual oscillatory solutions. The energy dependence of the frequencies of oscillation is discussed in detail. This can be used as a model for the first order structural phase transition in the mean field approximation. The high and low temperature behaviour of the static susceptibility is obtained. Finally, a qualitative explanation is offered for the observed central peak in ferroelectrics like $SrTiO_3$.

Keywords. Structural phase transition; anharmonic oscillator; soft mode; central peak.

1. Introduction

In recent years the study of structural phase transitions in ferroelectric crystals has attracted lot of attention. It is well known that such a transition is associated with soft phonon modes whose frequency decreases as the temperature approaches the critical value (T_c) from above (Lines and Glass 1977). Another puzzling feature associated with this transition is the development of a central peak near zero frequency in the dynamic structure function whose width is negligible, and the strength increases as T_c is approached. In order to understand the soft mode behaviour one takes recourse to two different models namely the order-disorder and the displacive phase transitions (Bruce 1978). Even though some understanding of the soft mode concept is achieved (Lines and Glass 1977), till recently no proper understanding of the central peak has emerged (Krumhansl ad Schrieffer 1975).

One-dimensional model calculations have proved to be greatly useful in dealing with the problem of structural phase transitions, as it provides a non-perturbative approach for strongly anharmonic systems, in spite of the fact that it does not show a phase transition at finite temperature. One of the first such studies was due to Onedora (1970), who studied the dynamics and thermodynamics of classical anharmonic oscillators, moving in the potential

$$V(\phi) = B\phi^2 + A\phi^4, \qquad A > 0. \tag{1}$$

This potential develops a double-well character for $B<0$, and simulates a second order phase transition at $B=0$. Taking into account the coupling between the oscil-

lators within a mean field approximation, he could calculate the susceptibilities of the system from the knowledge of the dynamics of a single oscillator. This model could account for the soft mode behaviour. However, the weakness of this model lies in its mean field approximation. The next significant development was the work of Krumhansl and Schrieffer (1975) who considered the corresponding (1+1)-dimensional classical field theory problem which admits non-perturbative (Kink) solutions which they identified to be domain walls. Their major contribution is the realisation of the fact that both phonon and domain wall-like excitations determine the low temperature behaviour of the system. The model shows a central peak-like phenomena which occurs only below T_c in terms of the parameters of the potential, in contradiction with the experimental observation of the same at $T \geqslant T_c$. However, this being a one-dimensional model, strictly speaking the transition occurs only at $T=0$, and in that sense the central peak does appear above T_c. Similar results were also obtained by Varma (1976), Halperin and Varma (1976) and Aubry (1976). Further evidence in support of the existence of the domain walls or clusters came from the molecular dynamics calculations (Schneider and Stoll 1975, 1976) in one- and two-dimensions and quantum mechanical calculations (Bishop *et al* 1976). Recently Bruce *et al* (1979) have calculated the distribution function for two-and three-dimensions using renormalisation group techniques which further confirms the existence of domain walls in systems undergoing structural phase transitions. Thus it is clear that domain wall solutions do play an important role in structural phase transitions and that there may exist a relation between these and the observed central peak.

All the theories mentioned above have considered models exhibiting second-order phase transitions (ϕ^4-field theories). It is well known that for this transition the soft mode frequency goes to zero at the transition temperature. However, a careful analysis of the experimental data on $SrTiO_3$ (Shapiro *et al* 1972) indicates that the phonon frequency remains finite as $T \to T_c$. Qualitatively similar behaviour has also been observed in a number of other perovskites (see Halperin and Varma 1976 for references) and a variety of other materials. This suggests that the transitions are of first order (Lines and Glass 1977) rather than second. Hence, it may be worthwhile to consider a model exhibiting first-order phase transition and examine whether it can explain the observed soft mode and central peak behaviour. This is the task to which we address ourselves in this paper.

We consider the one-dimensional model potential

$$V(\phi) = B\phi^2 + A\phi^4 + C\phi^6; \quad C > 0, \tag{2}$$

which is essentially the free energy expansion in the case of the structural phase transition problems. This model corresponds to a first order phase transition if

$$B > 0, \quad A < 0, \tag{3a}$$

and

$$0 < a \; (\equiv 9BC/2|A|^2) < 3/2. \tag{3b}$$

The last condition follows from the consideration of the extrema of equation (2), i.e. only in this case the potential has three minima, (which are essential for a first-order phase transition in contrast to the second-order case of equation (1) where there are only two minima) at

$$\phi=0, \tag{4a}$$

$$\phi^2_{\min}/\phi_0^2=\frac{1}{2}\left[1+\left(1-\frac{2a}{3}\right)^{1/2}\right], \tag{4b}$$

with $\phi_0^2=2\,|A|\,/\,3C$. At the phase transition point ($a=9/8$) all the three minima are degenerate. The potential for different values of a is plotted in figure 1. The positions of the maxima in this figure are at

$$\phi^2_{\max}/\phi_0^2=\frac{1}{2}\left[1-\left(1-\frac{2a}{3}\right)^{1/2}\right]. \tag{5}$$

The value of the potential at these extremum points are ($\phi\neq 0$)

$$V^{\max}_{\min}/V_0=\frac{1}{2}\left[(a-1)\pm\left(1-\frac{2a}{3}\right)^{3/2}\right], \tag{6a}$$

$$V_0=4\,|A|^3/27C^2. \tag{6b}$$

Further, as can be seen from figure 1 at $a=3/2$ there is only one minimum at $\phi=0$ and a point of inflation at $\phi^2=|A|/3C$. It is worth noting that as a decreases from 9/8 to 0, the order parameter ϕ_0 increases from $(|A|/2C)^{1/2}$ to the maximum value of $(2|A|/3C)^{1/2}$; with further decrease of a from 0 to $-\infty$, ϕ_0 decreases and asymptoti-

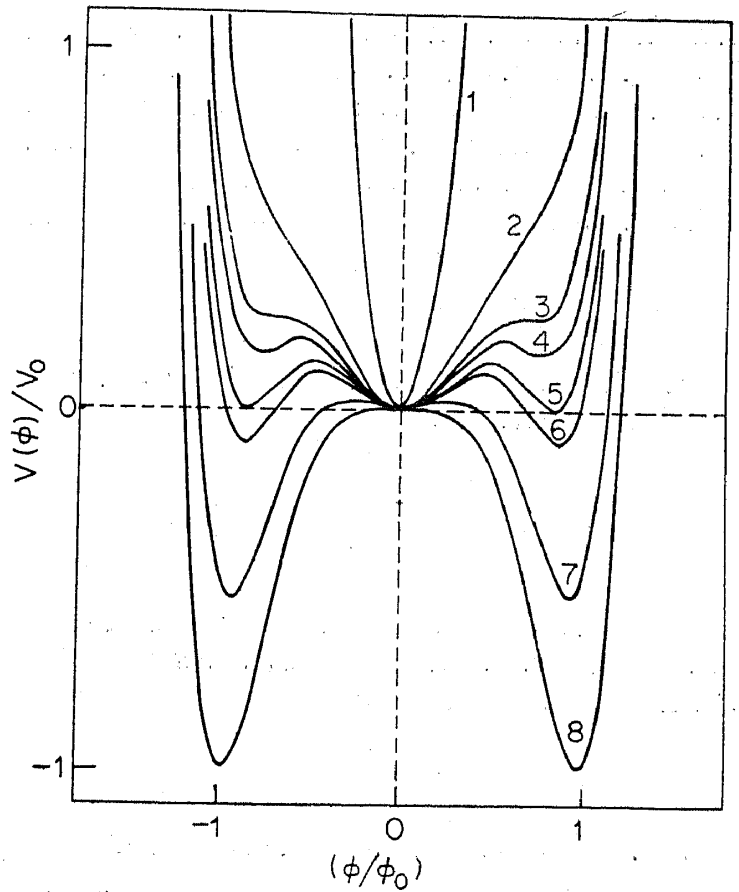

Figure 1. The plot of the potential $(V(\phi)/V_0)$ as a function of (ϕ/ϕ_0) for different values of the parameter a: (1) 10, (2) 2, (3) 1.5, (4) 1.35, (5) 1.125, (6) 1, (7) 0.5 and (8) 0.

cally approaches its starting value of $(|A|/2C)^{1/2}$. For $A > 0$ one always has a second-order phase transition, the transition taking place at $B = 0$.

In this paper we shall show that this model system (equation (2)), under different conditions, can account for both the order-disorder and the displacive transitions. For the order-disorder transition it is essential to have the solution of the classical anharmonic oscillator problem characterised by equation (2). This is done in § 2, where we show that the exact solutions are the Weirstrass' functions (Abramowitz and Stegun 1965). We also obtain the explicit energy dependence of the classical frequencies and discuss its relevance to the central peak phenomena in § 3. Further the low and high temperature behaviour of the polarisability is calculated in the mean field approximation following Onedora (1970) in § 4.

In the concluding § 5, we summarise the results obtained in this paper; and present a qualitative picture of the central peak. The next paper in this series is devoted to a detailed discussion of the dynamics and thermodynamics of the corresponding classical ϕ^6-field theory (Behera and Khare 1979a).

In carrying out the calculations below, the energy and length are measured in units of $V_0 = 4|A|^3/27C^2$ and $\phi_0 = (2|A|/3C)^{1/2}$ respectively wherever explicit mention of these is not made.

2. Structural phase transition

The model we have in mind is the one where at every lattice site the particle experiences an on-site potential given by equation (2). For the order-disorder transition it is necessary that the on site well-depths are made larger compared to the intersite coupling. The intersite coupling which will be assumed to be quadratic in $\phi(\sim\gamma\phi_i\phi_j)$ can therefore be treated in the mean-field approximation. Following Onedora (1970) it can be shown that the dynamic susceptibility of such a system can be written as

$$\chi(\omega) = \frac{f(\omega)}{[1 - \gamma f(\omega)]}, \tag{7}$$

where $f(\omega)$ represents the classical dynamic polarisability of non-interacting anharmonic oscillators. The imaginary part of $f(\omega)$ is given by

$$\mathrm{Im}\, f(\omega) = \frac{\omega}{2k_B T}\int_{-\infty}^{\infty} \exp(i\omega t) \langle \phi(0)\phi(t) \rangle_0 \, dt, \tag{8}$$

where the average $\langle \ \rangle_0$ has to be taken with respect to the non-interacting system. It is thus clear that for the evaluation of the dynamical susceptibility the solution of the single anharmonic oscillator is necessary.

2.1. *Solution of the single anharmonic oscillator*

Consider a classical particle of mass M moving in the potential given by equation (2). The equation of motion is

$$M\ddot{\phi} + 2B\phi + 4A\phi^3 + 6C\phi^5 = 0. \tag{9}$$

Integrating this equation one obtains the energy E of the system as

$$E = \frac{M}{2}\dot{\phi}^2 + B\phi^2 + A\phi^4 + C\phi^6, \tag{10}$$

which when further integrated gives

$$t = (\tfrac{1}{2}M)^{\frac{1}{2}} \int \frac{d\phi}{[E - B\phi^2 - A\phi^4 - C\phi^6]^{1/2}}. \tag{11}$$

We should consider the cases (a) $E>0$ and (b) $E<0$ separately since the solutions are going to be different in the two cases.

(a) $E > 0$

In this case equation (11) can be reduced to the form

$$\left(\frac{1}{\phi^2} - \frac{aC}{2|A|\epsilon}\right)$$

$$-(2\epsilon V_0/M)^{1/2}\, t = \int \frac{d\eta}{(4\eta^3 - g_2\eta - g_3)^{1/2}}, \tag{12}$$

where
$$g_2 = \frac{3C^2}{|A|^2}\left(\frac{a^2}{\epsilon^2} + \frac{9A}{|A|\epsilon}\right), \tag{13a}$$

$$g_3 = \frac{C^3}{|A|^3}\left(\frac{a^3}{\epsilon^3} + \frac{27aA}{2|A|\epsilon^2} + \frac{27}{\epsilon}\right), \tag{13b}$$

where $\epsilon = E/V_0$ with a and V_0 given by (3b) and (6b). A useful quantity which characterises the motion of the particle is

$$\Delta = g_2^3 - 27g_3^2, \tag{14a}$$

$$= \frac{16|A|^3}{V_0^3\epsilon^4}\left[-4\epsilon^2 + \frac{4A}{|A|}\epsilon(1-a) + \frac{a^2}{3}\left(1 - \frac{8a}{9}\right)\right]. \tag{14b}$$

Equation (12) is a standard integral which can be expressed in terms of Weirstrass' functions as follows

$$1/\phi^2(t) = \frac{aC}{2|A|\epsilon} + \wp\,[-(2\epsilon V_0/M)^{1/2}\, t;\ g_2;\ g_3]. \tag{15}$$

It follows from the properties of the Weirstrass' functions that as $t \to 0$, $\phi \to 0$. However if one chooses the boundary condition that at $t=0$, $\phi=\phi_{\min}$ (which could be one of the minima of the potential, figure 1) then the solution takes the form

$$1/\phi^2(t) = \frac{aC}{2|A|\epsilon} + \left[\wp\,(-2\epsilon V_0/M)^{1/2}\, t + \wp^{-1}\left(\phi_{\min}^{-2} - \frac{aC}{2|A|\epsilon}\right); g_2; g_3\right]. \tag{16}$$

It can be shown that in the limit of $C \to 0$ (and $A > 0$) these solutions reduce to the Jacobi elliptic functions as obtained by Onedora (1970).

These solutions (equations (15) and (16)) take different forms depending on whether $\Delta > 0$, $\Delta < 0$ or $\Delta = 0$. From here onwards we shall only consider $A < 0$ which is relevant to the case of first-order phase transition. It can be seen from (14) that

(i) $a > 3/2$, $\Delta < 0$,

(ii) $a = 3/2$, $\Delta < 0$ for $\epsilon > 0$ ($\epsilon \neq V_{\text{inflation}}$),

(iii) $9/8 < a < 3/2$, $\Delta < 0$ for $0 < \epsilon < V_{\text{loc. min}}$ and $\epsilon > V_{\max}$; $\Delta > 0$ for $V_{\text{loc. min}} < \epsilon < V_{\max}$

(iv) $a = 9/8$ $\Delta > 0$ for $V_{\min} < \epsilon < V_{\max}$ and $\Delta < 0$ for $\epsilon > V_{\max}$

(v) $a < 9/8$, $\Delta > 0$ for $V_{\min} < \epsilon < V_{\max}$ and $\Delta < 0$ for $\epsilon > V_{\max}$

(vi) $\Delta = 0$ at $\epsilon = V_{\max}^{\min}$ for all a.

For $\Delta \gtrless 0$, the solutions (equation (15)) can be expressed in terms of Jacobi elliptic functions (see Abramowitz and Stegun 1965). For example in the case of $\Delta > 0$

$$\phi(t) = \frac{Sn(-y^{1/4} z t \mid k)}{\left[y^{1/2} + \left(\frac{aC}{2 \mid A \mid \epsilon} + e_3\right) Sn^2 (-y^{1/4} zt \mid k)\right]^{1/2}}, \tag{17}$$

where $$e_3 = -\tfrac{1}{2}(k+1)\ [g_2/3(k^2-k+1)]^{1/2} \tag{18a}$$

$$z = (2 \epsilon V_0/M)^{1/2} \tag{18b}$$

and y is the real root of the cubic equation.

$$y^3 - \frac{3}{2} g_2 y^2 + \frac{9}{16} g_2^2 y - \frac{\Delta}{16} = 0. \tag{19}$$

The parameter $0 < k < 1$ is a measure of the degree of anharmonicity and is given by

$$k = \tfrac{1}{2}\{1 \pm [3(g_2 - y)/y]^{1/2}\} \tag{20}$$

Equation (17) is an oscillatory solution, with frequency

$$\omega/\omega_0 = \pi y^{1/4}\ [\epsilon \mid A \mid /6aC]^{1/2}\ K(k), \tag{21}$$

where the Sn function has a period of $4K(k)$, $K(k)$ being the normal elliptic integral of the first kind, given by

$$K(k) = \int_0^{\pi/2} (1 - k \sin^2\theta)^{-1/2}\, d\theta, \tag{22}$$

and ω_0 is the harmonic frequency

$$\omega_0 = (2B/M)^{1/2}. \tag{23}$$

Similarly for $\Delta < 0$, the solution (equation (15)) takes the form

$$\phi(t) = \frac{Sn(-y_1^{1/4}\, zt|k)}{\left[y_1^{1/2}\, Cd^2(-y_1^{1/4}\, zt\,|\,k) + \left(e_2 + \frac{ac}{2|A|\varepsilon}\right) Sn^2(-y_1^{1/4}\, zt\,|\,k)\right]^{1/2}}, \tag{24}$$

where $$e_2 = \left[\frac{g_2(1-2k)^2}{3(16k^2-16k+1)}\right]^{1/2}, \tag{25}$$

and y_1 is the real root of the cubic equation

$$y_1^3 - \frac{3}{4} g_2\, y_1^2 + \frac{\Delta}{16} = 0. \tag{26}$$

For this case the parameter k is given by

$$k = \frac{1}{2}\left[1 - \frac{\sqrt{3}}{2}\left(1 + \frac{g_2}{4y_1}\right)^{1/2}\right], \tag{27}$$

and its allowed values lie in the range $0 < k < \frac{1}{2}$. The frequency of oscillation is now given by

$$\omega/\omega_0 = \pi(\epsilon\,|A|\,/\,6aC)^{1/2}\, y_1^{1/4}/K(k). \tag{28}$$

Finally let us consider the case $\Delta = 0$. For $a < 3/2$, $\Delta = 0$ is possible if either (i) $g_2 > 0$, $g_3 < 0$ or (ii) $g_2 > 0$, $g_3 > 0$. The former holds at $\epsilon = V_{\max}$ and the latter at $\epsilon = V_{\min}$. For case (i) the solution is given by (Abramowitz and Stegun 1965)

$$1/\phi^2(t) = \frac{aC}{2|A|\epsilon} + (g_2/12)^{1/2} + \frac{3(g_2/12)^{1/2}}{\sinh^2(\sqrt{3}\,(g_2/12)^{1/4}\, zt)} \tag{29a}$$

$$\equiv \frac{aC}{2|A|\epsilon} + \wp. \tag{29b}$$

Note that unlike the solutions given by (17) and (24) this solution is not oscillatory. It has the property that as $t \to 0$, $\phi(t) \to 0$, while as $t \to \pm\infty$, $\phi(\pm\infty) = \pm\phi_{\max}$ as given by (5). Thus as t goes from $-\infty$ to $+\infty$ the solution (equation (29)) takes the particle from one hill top of the potential to the other i.e. it is an instanton solution in imaginary time (for a review see Jackiw 1977). One could also write

down solutions with the boundary condition that initially the particle is not at $\phi=0$, but at one of the other minima ($\phi_{\min}$), which using (16) can be written as,

$$(1/\phi^2(t)) = \frac{aC}{|A|\epsilon} - \frac{1}{\phi^2_{\min.}} - (g_2/12)^{1/2} + \tfrac{1}{4}\left\{[4\wp^3 - g_2\wp - g_3]^{1/2} - \left[4\left(\phi^{-2}_{\min} - \frac{aC}{2|A|\epsilon}\right)^3 - g_2\left(\phi^{-2}_{\min} - \frac{aC}{2|A|\epsilon} - g_3\right) - g_3\right]^{1/2}\right\}^2 \times \left[\wp - \left(\phi^{-2}_{\min} - \frac{aC}{2|A|\epsilon}\right)\right]^{-2}, \tag{30}$$

where $\wp$ is defined by (29b). As $t \to \pm\infty$ equation (30) takes the particle from $\phi_{\min}$ to the hill top. It may be interesting to note here that in the corresponding field theory case such solutions (kink) take the particle from one potential minimum to the other as x goes from $-\infty$ to $+\infty$ (Behera and Khare 1979a).

For the case (ii) the solution is given by

$$\phi^{-2}(t) = \frac{aC}{2|A|\epsilon} - (g_2/12)^{1/2} + \frac{3(g_2/12)^{1/2}}{\sin^2(\sqrt{3}(g_2/12)^{1/4} zt)} \tag{31}$$

In contrast to the case (i) these are oscillatory solutions oscillating around $\phi=0$. There exist similar solutions around the local minima too.

At $a=3/2$, $\triangle=0$ corresponds to $g_2=g_3=0$ ($\epsilon=1/4$) and gives rise to the interesting solution

$$(1/\phi^2(t) = (3C|A|) + (2M/V_0 t^2). \tag{32}$$

This solution has the property that at $t = 0$, $\phi(0) = 0$ while as $t \to \pm\infty$, $\phi = \pm(|A|3C)^{1/2}$ which is the point of inflation of the potential. Hence (32) represents a sticking solution.

(b) $E < 0$

In this case equation (11) can be reduced to the form

$$-\left(\phi^{-2} + \frac{aC}{2|A||\epsilon|}\right)$$

$$(2|\epsilon|V_0|M)^{1/2}t = \int \frac{d\eta}{[4\eta^3 - g_2'\eta - g_3']^{1/2}} \tag{33}$$

where $$g_2' = \frac{3C^2}{|A|^2}\left(\frac{a^2}{|\epsilon|^2} + \frac{9}{|\epsilon|}\right), \tag{34a}$$

$$g_3 = \frac{C^3}{|A|^3}\left(\frac{a^3}{|\epsilon|^3} + \frac{27}{2}\frac{a}{|\epsilon|^2} + \frac{27}{|\epsilon|}\right), \tag{34b}$$

and the parameter Δ' becomes

$$\Delta' = \frac{16\,|A|^3}{V_0^3\,|\epsilon|^4}\left[-4|\epsilon|^2 + 4|\epsilon|(1-a) + \frac{a^2}{3}\left(1-\frac{8}{9}a\right)\right]. \tag{35}$$

As $|\epsilon|<1$, always $\Delta'>0$. The solutions of (33) are again Weirstrass' functions and for the initial condition that at $t=0$, $\phi=\phi_{\min}$. these are given by

$$\frac{1}{\phi^2(t)} = -\frac{aC}{2\,|A|\,|\epsilon|} - \wp\,(2\,|\epsilon|\,V_0/M)^{1/2}\,t + \wp^{-1}\left(\left(-\phi_{\min}^{-2}\cdot\frac{aC}{2\,|A|\,|\epsilon|}\right);\, g_2;\, g_3\right). \tag{36}$$

Following the procedure of the $E>0$ and $\Delta>0$ case the solutions (equation (36)) can be expressed in terms of Jacobi elliptic functions, and it can be shown that the frequency is given by

$$(\omega/\omega_0) = \pi y_2^{1/4}\,(|\epsilon|\,|A|/6aC)^{1/2}/K(k), \tag{37}$$

where y_2 is the real root of the cubic equation

$$y_2^3 - \frac{3}{2}g_2' y_2^2 + \frac{9}{16}g_2'^2\,y_2 - \frac{\Delta'}{16} = 0, \tag{38}$$

and

$$k = \tfrac{1}{2}[1 \pm [3(g_2' - y_2)/y_2]^{1/2}] \tag{39}$$

with $0<k<1$.

In the special case of $a=0$ (i.e., $B=0$) the frequency expressions (equations (28) and (37)) are invalid. It can be shown that for this case

$$(\omega/\omega_0) = \pi y_2^{1/4}\,(|\epsilon|\,|A|/6C)^{1/2}/K(k),\ \epsilon<0, \tag{40a}$$

$$\pi y_1^{1/4}(2|\epsilon|\,|A|/3C)^{1/2}/K(k),\ \epsilon<0, \tag{40b}$$

3. Discussion of results

The energy dependence of the parameter k, which measures the degree of anharmonicity, ($k=0$ being the harmonic limit) is numerically calculated using (20), (27) and (39). The results are shown in figure 2 for the particular cases of $a=1{\cdot}35$, $1{\cdot}125$ and 1 which correspond to points above, at and below the phase transition respectively. It can be seen that k has two allowed values for $\Delta>0$, which are complementary to each other such that $k_1+k_2=1$. However, for $\Delta<0$ it has only one value which lies between 0 and $\frac{1}{2}$. As $\epsilon\to\infty$, $k\to\frac{1}{2}(1-\sqrt{3}/2)$ irrespective of the value of a. Below the phase transition $0<a\leqslant 9/8$, k has two branches

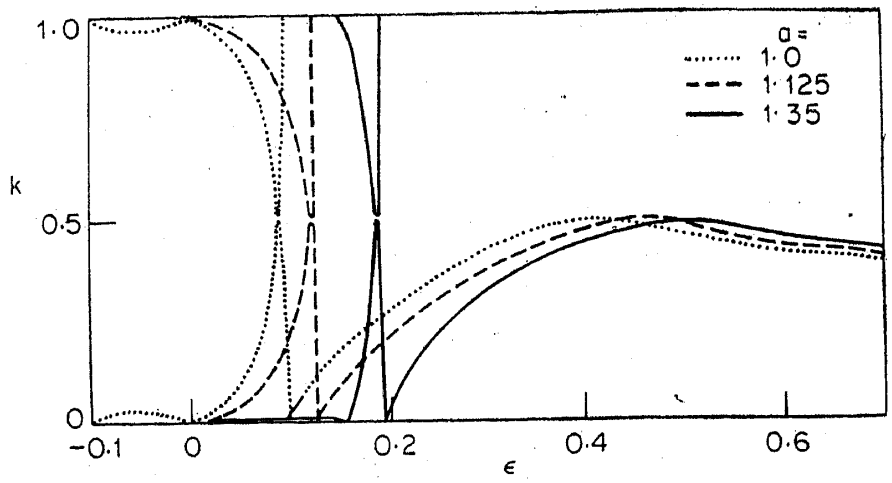

Figure 2. The degree of anharmonicity as measured by k plotted as a function of energy ϵ; for different values of a.

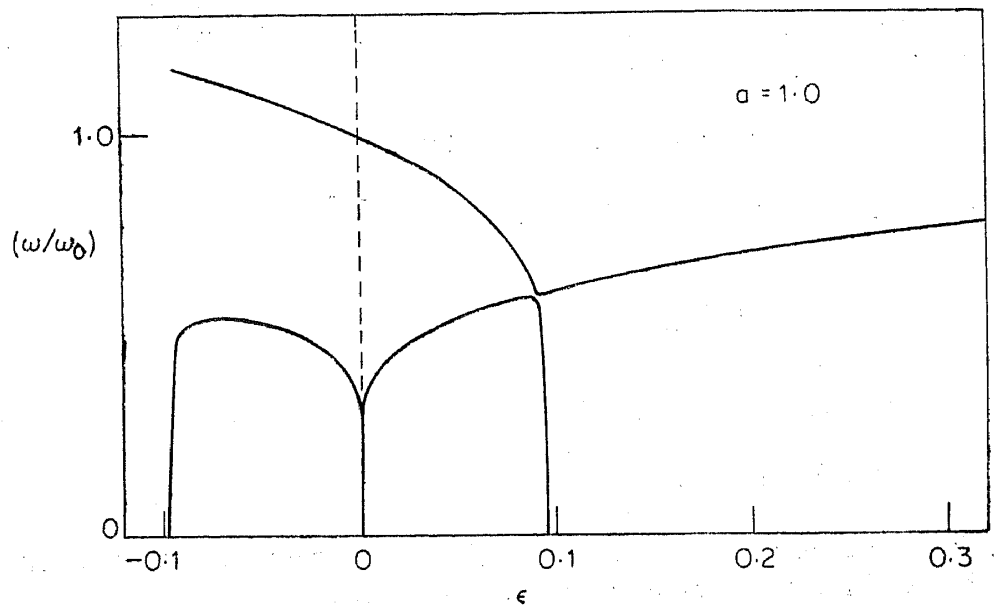

Figure 3. The frequency (ω/ω_0) versus energy (ϵ) for $a = 1.0$.

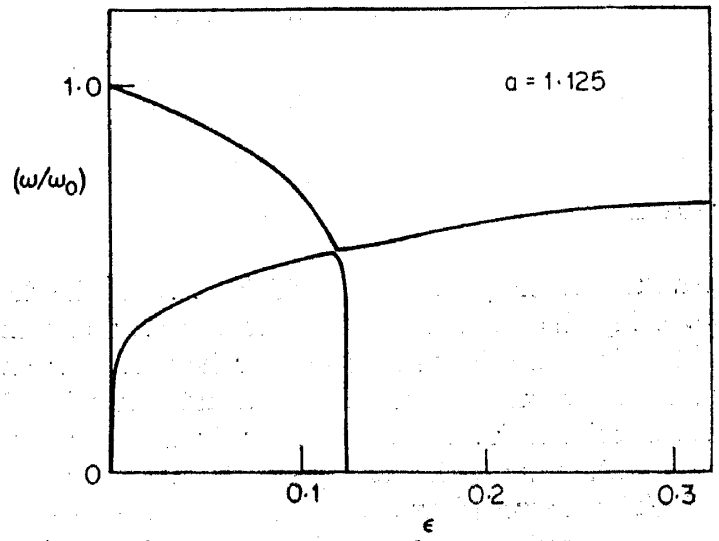

Figure 4. The frequency versus energy for $a_c = 1.125$

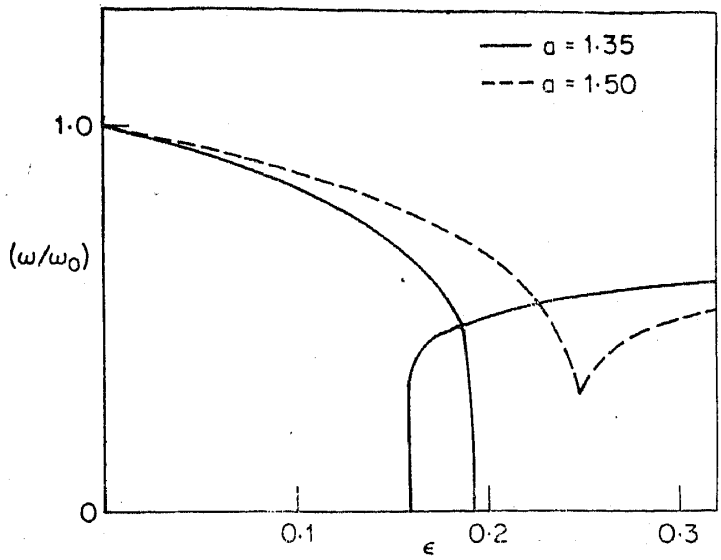

Figure 5. The frequency versus energy for $a = 1.35$ and 1.5

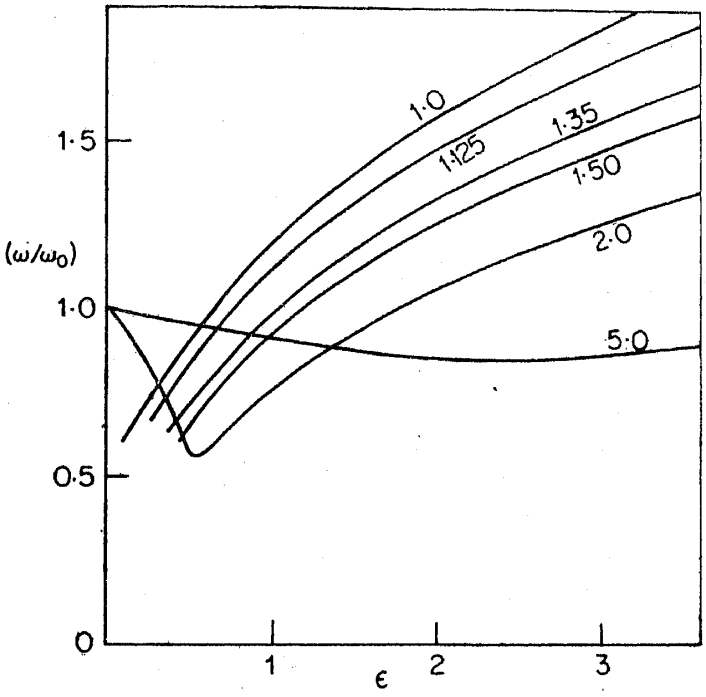

Figure 6. The frequency versus energy showing the high energy behaviour for $a = 1$, 1.125, 1.35, 1.5, 2 and 5

for $V_{\min} \leqslant \epsilon \leqslant V_{\max}$ and only one branch above $V_{\max}$. On the other hand above the phase transition $(9/8 < a < 3/2)$ k has only one branch for $0 < \epsilon < V$ local min and $\epsilon > V_{\max}$ but two branches for $V_{\text{local min}} < \epsilon < V_{\max}$. Hence there will be corresponding number of branches for the frequencies as well (as a function of ϵ). Figures 3 to 6 show the energy-dependence of the frequencies as calculated from (21), (28) and (37). The general features of the energy-dependence of the frequencies at $V_{\min}$, $V_{\text{local min}}$ and $V_{\max}$, where $\Delta = 0$ can be inferred from the above equations (i) for $0 < a < 9/8$, it is clear from (19) that at $\epsilon = V_{\min}$ $\Delta = 0$ and $y = (3/4)g_2$ and hence from (20) it follows that $k = 0$ and 1. Since the period $K(k = 1) = \infty$ and $K(k = 0) = \pi/2$, using (13a) it follows that the corresponding

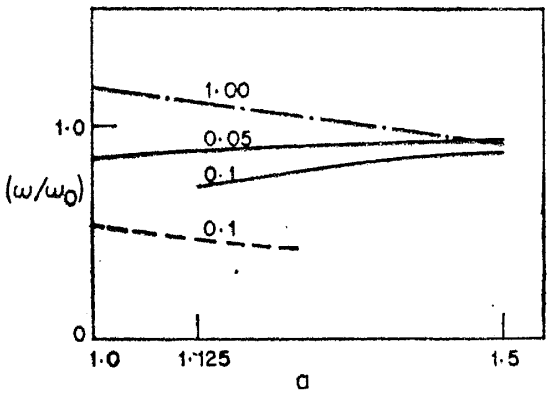

Figure 7. The frequency versus a for $\epsilon = 0{\cdot}05$, $\epsilon = 0{\cdot}1$ and $\epsilon = 1{\cdot}0$

frequencies will be 0 and $(1+9\,|\,V_{\min}|\,/a^2)^{1/4}$ respectively. A similar analysis for $\epsilon = V_{\text{local min}} = 0$ indicates that the two frequencies are 0 and 1 respectively. On the other hand at $\epsilon = V_{\max}$, depending on whether this point is approached from below or above, the frequencies are 0 and $(1-9\,V_{\max}/a^2)^{1/4}$ for the former and $(1-9\,V_{\max}/a^2)^{1/4}$ for the latter. Thus the continuity of the frequencies in one of the branches is maintained. This behaviour of frequency curves is depicted for the sample case of $a=1$ in figure 3. (ii) At the phase transition point (i.e. $a=9/8$), the variation of the frequencies with ϵ is given in figure 4. The behaviour is the same as discussed in case (i) except for the fact that in this case all the three minima in the potential (see figure 1) are degenerate, as a result there are no local minima. (iii) Above the phase transition point (i.e. $9/8 < a < 3/2$), there is a single branch of frequency for $0 < \epsilon < V_{\text{local min}}$ its value at $\epsilon = 0$ (the absolute minimum) being 1, and at $\epsilon = V_{\text{local min}}$ being $(1-9\,V_{\text{loc. min}}/a^2)^{1/4}$. On the other hand for $V_{\text{loc. min}} < \epsilon < V_{\max}$, there are two frequency branches and the frequencies are again given by 0 and $(1-9\epsilon/a^2)^{1/4}$ at $\epsilon = V_{\text{loc. min}}$ as well as $V_{\max}$. Thus again the continuity of the frequencies is maintained. Figure 5 shows these curves for $a=1{\cdot}35$ and $1{\cdot}5$. It is worth noting that for $a=1{\cdot}5$, there is a single branch of frequency for the entire range of ϵ, and it shows a dip at the point of inflation of the potential curve (figure 1). This feature persists even for $a > 3/2$ as can be seen from figure 6. The dip in frequency is clearly marked for the curve corresponding to $a=2$, but becomes more shallow for $a=5$. As ϵ further increases the frequency increases monotonically and asymptotically approaches $\approx 1{\cdot}5\ \epsilon^{1/3}/a^{1/2}$.

It is interesting to follow the variation of the frequency for a given energy as a function of the potential parameter a, which in the present model is equivalent to following the frequency through the phase transition. From figure 7 we see that for $\epsilon < 0{\cdot}25$ (see figure 5) there are two frequency branches. For the higher frequency branch the mode corresponding to say $\epsilon = 0{\cdot}1$ softens as one approaches a_c ($=1{\cdot}125$ the critical value) from above with a non-vanishing value at a_c, which further decreases as one goes below a_c. This is the expected soft mode behaviour for a first-order phase transition. On the other hand for the low frequency branch the mode corresponding to $\epsilon = 0{\cdot}1$ hardens with decreasing a. It is interesting to note that a similar behaviour has been anticipated earlier (see Bruce 1978). For $\epsilon \geqslant 0{\cdot}25$ (say $\epsilon = 1$) the mode frequency always increases as a approaches a_c from above and continues to do so even below a_c.

Yet another interesting feature which emerges from figures 3, 4 and 5 is that for $a < 3/2$ even at finite energies there are zero frequency vibrations. As one approaches

a_c from above the energies corresponding to the zero frequency modes decrease. This is to be contrasted with the second order phase transition (Onedora 1970) where the zero frequency modes exist only at $\epsilon = 0$. Its relation to the central peak is further discussed in the concluding section.

4. Calculation of static susceptibility

Making use of the results of the previous section the static and dynamic susceptibilities of the system can be evaluated by using equations (7) and (8). In this paper, however, we will restrict ourselves to the low and high temperature dependence of the static susceptibility only. It can be obtained (Onedora 1970) from equation (7) by putting $\omega=0$, i.e.

$$\chi(0) = (f(0)/[1 - \gamma f(0)]), \tag{41}$$

where $$f(0) = \langle\phi^2\rangle_0/k_B T. \tag{42}$$

For our problem $\langle\phi^2\rangle_0$ is given by

$$\langle\phi^2\rangle_0 = Z^{-1} \int_{-\infty}^{\infty} d\phi\, \phi^2 \exp\,[-\beta V(\phi)], \tag{43}$$

where the classical partition function Z is

$$Z = \int_{-\infty}^{\infty} d\phi \exp\,[-\beta V(\phi)], \tag{44}$$

with $V(\phi)$ given by equation (2). Unfortunately these integrals cannot be evaluated exactly; but one can nevertheless obtain the high and low temperature behaviour of $\chi(0)$.

In the limit of large temperatures (44) and (43) can be approximated by

$$Z \cong (C\beta)^{-1/6} \int_{-\infty}^{\infty} dy \exp\,(-y^6)\,[1 - BC^{-1/3}\,\beta^{2/3}\,y^2 + |A|\,C^{-2/3}\,\beta^{1/3}\,y^4 + \ldots], \tag{45}$$

and

$$\langle\phi^2\rangle_0 \cong Z^{-1}\,(C\beta)^{-1/2} \int_{-\infty}^{\infty} dy\, y^2 \exp\,(-y^6)\,[1 - BC^{-1/3}\,\beta^{2/3}\,y^2 + |A|\,C^{-2/3}\,\beta^{1/3}\,y^4 + \ldots.]. \tag{46}$$

Equations (45) and (46) when evaluated gives

$$f(0) \cong T^{-2/3}\,(Ck_B^2)^{-1/3}\,[\Gamma(\tfrac{1}{2})/\Gamma(\tfrac{1}{6})] \times \left[1 - \frac{(6\,\Gamma(\tfrac{1}{2})\,\Gamma(\tfrac{5}{6}) - \Gamma^2(\tfrac{1}{6}))}{6\,\Gamma(\tfrac{1}{2})\,\Gamma(\tfrac{1}{6})} |A|\,C^{-2/3}\,k_B^{-1/3}\,T^{-1/3} + \ldots.\right]. \tag{47}$$

It is interesting to note that in contrast with the case of second-order phase transition, where

$$f(0) \xrightarrow[T \gg 1]{} T^{-1/2}$$

(Onedora 1970) in the present case the dependence is $T^{-2/3}$.

In the low temperature ($T \ll 1$) limit, equations (44) and (43) can be approximated by

$$Z \cong (B\beta)^{-1/2} \int_{-\infty}^{\infty} dy \exp(-y^2) [1 + |A| B^{-2} \beta^{-1} y^4 - CB^{-2} \beta^{-2} y^6 + \ldots], \quad (48)$$

and

$$\langle \phi^2 \rangle_0 \cong Z^{-1} (B\beta)^{-3/2} \int_{-\infty}^{\infty} dy\, y^2 \exp(-y^2) [1 + |A| B^{-2} \beta^{-1} y^4 - CB^{-3} \beta^{-2} y^6 + \ldots.]. \quad (49)$$

On evaluating these integrals $f(0)$ becomes

$$f(0) = (2B)^{-1} [1 + 3|A| B^{-2} k_B T + \ldots], \quad (50)$$

Thus in the low temperature limit the leading term in $f(0)$ is temperature-independent, which is also the case for the second order transition (Onedora 1970).

One can also calculate the transition temperatures (T_c) and its γ dependence from (41) following Onedora (1970).

5. Conclusions

We summarise below, the main results of the present paper, and using these a qualitative explanation of the central peak phenomenon is proposed. Exact solutions have been obtained for the motion of an anharmonic oscillator in the ϕ^6 potential. In addition to the usual oscillatory solutions, we also obtain instanton-like solutions which take the particle from one maximum to the other as time t goes from $-\infty$ to $+\infty$. In the limit of $t \to ix$ these solutions go over to the domain wall (kink) solution of the corresponding classical field theory (Behera and Khare 1979 b). The energy-dependence of the frequencies of oscillations corresponding to various solutions is studied in detail. It is shown that for a given energy there is a single frequency for $a > 3/2$ but there can be two frequencies branches for $0 \leqslant a < 3/2$ in certain energy ranges. It was further shown that for $\epsilon < 0{\cdot}25$, there exists a mode whose frequency softens with decreasing potential parameter a, attains a nonvanishing value at a_c, and decreases further below a_c showing typically a first-order phase transition. However, simultaneously, there exists another low frequency mode which hardens. Finally, the low and high temperature behaviour of the static susceptibility of the system is calculated, within the mean field approximation. We would like to emphasise one feature of the frequency-energy curves (figures 3, 4 and 5). It can be seen that for $9/8 < a < 3/2$, there appears zero frequency vibrations at $\epsilon = V_{\max} (\neq 0)$ and also at $\epsilon = V_{\text{loc. min}} (\neq 0)$. On the other hand for $0 < a < 9/8$, the zero frequency vibration

occurs at $\epsilon = V_{max} (\neq 0)$ and at $\epsilon = V_{min}$ (of course there are also zero frequency modes at zero energy for $0 \leqslant a < 3/2$ but these are not relevant for the discussion to follow). Since $\epsilon = V_{max}$ is an unstable point for the particle the zero frequency modes associated with these will not carry any physical significance. On the other hand the zero frequency mode at $\epsilon = V_{min}$ which appears below the phase transition ($a < a_c$) will be masked by the appearance of the Bragg peak and hence will be difficult to observe. Thus the only observable zero frequency mode will be for $9/8 < a < 3/2$ corresponding to the metastable position of the particle at the local minima. We believe that this will correspond to the observed central peak. As $a \to a_c$ from above the value of $\epsilon (= V_{loc\ min})$ decreases; while the barrier which the particle sitting at the local minima sees increases. Thus as $a \to a_c$ from above, the number of particles at the local minima will increase, which in turn will increase the strength of the central peak; and ultimately at $a = a_c$, the central peak will have a large strength. This provides a qualitative explanation of the central peak phenomena observed in ferroelectrics. This picture is further corraborated by a study of the corresponding classical field theory (Behera and Khare 1979b). It is interesting to note that a similar picture has also been proposed by Bruce (1978) from altogether different considerations.

The present calculation being a mean-field one will reflect all the limitations of the approach, when the statistical mechanics of the system is carried through in detail. In particular, it will not provide a satisfactory description of the critical phenomena associated with structural phase transitions. Hence we calculate the statistical mechanics of the system, not in the present model, but for the ϕ^6-field theory which is done in the following paper (Behera and Khare 1979a).

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