# Bifurcation behaviour in structural phase transitions with multi-well potentials

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**Abstract.** A model solid with a double-well potential at each site and intersite coupling $J$ is considered, where $J$ is sufficiently small that $kT_C$ is much less than the depth $kT_0$ of the well. The effect of the local breaking of symmetry that occurs around $T_0$ is investigated for a single site. Anomalies are particularly noticeable in the oscillation frequencies, mean squared displacement and heat capacity. There are examples of materials and computer simulations that display such behaviour.

## 1. Introduction

Many solids display structural phase transitions which can be modelled by an on-site double-well or multi-well potential (see, for example, Onodera 1970, Eisenriegler 1974, Bruce 1980, Janssen 1986, Benkert *et al* 1987, Benkert 1987). In such a potential $v(x)$ (figure 1) the system undergoes some sort of crossover or quasi-transition around a temperature $T = T_0$ where $kT_0$ is the characteristic well depth. For $T > T_0$ one may imagine a particle oscillating freely across the whole well, whereas when $T < T_0$ it oscillates temporarily in the right or left half of $v(x)$, i.e. a 'bifurcation' has already occurred. Thus at $T < T_0$ the system can be thought of as having locally already made the phase transition in a fluctuating sense.

The macroscopic phase transition at temperature $T_C$ is a cooperative phenomenon mediated by the intersite coupling, $J$, and quite separate from $T_0$ where, although there is a displacement at each site, the system average remains symmetrical. In order to focus on the behaviour around $T_0$, we assume that $T_C$ is small compared with $T_0$. Hence the thermodynamics of a single site are examined, and it should be noted that the precursors expected at $T = T_0$ are purely on-site effects which are quite different from the cooperative precursors of critical fluctuations around $T_C$.

Some examples are considered in section 3. The present purpose is to investigate this behaviour in more detail by computation. The Hamiltonian we envisage is

$$H = \sum_n v(x_n) - \sum_n \sum_m J_{nm} x_n x_m. \tag{1.1}$$

As already noted, the intersite coupling $J_{mn}$ has no direct connection with the depth of

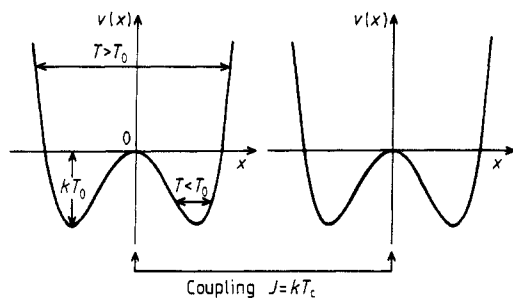§ Now at Physics Department, Massachusetts Institute of Technology, Cambridge MA 02139, USA.

**Figure 1.** The double-well potential in one dimension with the two tempeature regimes $T > T_0$ and $T < T_0$. The coupling $kT_C$ between sites is assumed small.

the well, and is neglected in this work. The only point relevant is that the intersite coupling is written in the form (1.1) so that it averages to zero in the high temperature disordered state, unlike the more customary form $J_{nm}(x_n - x_m)^2$ (Bruce 1980).

The simplest double-well potential is

$$v(x) = -\alpha x^2 + \beta x^4. \tag{1.2}$$

The minima are at $x_0$, given by $x_0 = \sqrt{(\alpha/2\beta)}$, and the characteristic well depth, or rather the height of the central barrier, is $kT_0 = \alpha^2/4\beta$. Hence the well can conveniently be rewritten as

$$v(x) = kT_0[1 - (x/x_0)^2]^2 - kT_0 \tag{1.3}$$

which defines the zero of energy.

We also need to consider the case of a negative coefficient $\alpha$ in equation (1.2); defining $x_0^2$ as $|\alpha|/2\beta$, then as before we have $\frac{1}{2}|\alpha|x_0^2 = \beta x_0^4 = kT_0$ and the well has the form

$$v(x) = kT_0[1 + (x/x_0)^2]^2 - kT_0. \tag{1.4}$$

Thus at $T_0$ there is again a crossover from predominantly parabolic to quartic form. A phase transition remains possible if the intersite coupling is sufficiently strong and again we consider the $J_{nm}$ such that $T_C \ll T_0$. Under such conditions one would also expect some kind of crossover behaviour at $T_0$ in the disordered phase in the single-well case (1.4). Of course the double (1.3) and single (1.4) wells correspond respectively to the usual order/disorder and displacive phase transitions (Onodera 1970, Bruce 1980), at least when $T_C < T_0$. It is therefore of interest to compare the behaviour at the quasi-transition in the two situations to see clearly the specific effects of the local bifuraction in the double-well case.

We emphasise again that the crossover behaviour we are discussing is entirely different from the more sophisticated type of crossover displayed (in principle) by all displacive transitions near $T_C$ (see, for example, Müller *et al* 1982, Baker *et al* 1982). The latter results from the growth of locally ordered regions as $T_C$ is approached from above. Such a region treated as a whole displays an Ising type of behaviour, where it is polarised in the positive or negative $x$ direction if the region is large enough, even if the single site is well in the soft mode regime $T > T_0$. The reason is easy to see. The total energy of an *ordered region*, including the $J_{nm}$, has a double-well form even in the displacive case, with a well depth proportional to the size of the region. Thus it tends increasingly to the Ising limit as the region grows. All of this depends on the growth of short range order, and is quite distinct from the behaviour we have discussed, which is concerned purely
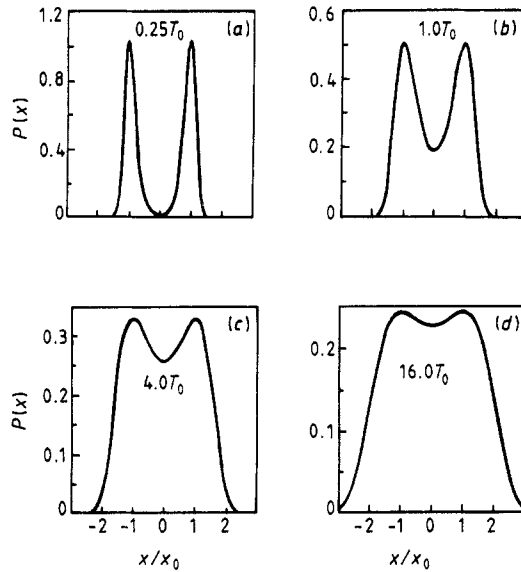
**Figure 2.** Boltzmann probability distributions for a particle in the double-well potential $v(x)$, $\alpha > 0$, (figure 1) at four temperatures: (a) $T = 0.25T_0$ with $\langle x^2 \rangle = 0.918x_0^2$; (b) $T = T_0$ with $\langle x^2 \rangle = 0.833x_0^2$; (c) $T = 4.0T_0$ with $\langle x^2 \rangle = 1.042x_0^2$; (d) $T = 16.0T_0$ with $\langle x^2 \rangle = 1.666x_0^2$.

with the well on a single site. In some situations it should be possible to distinguish experimentally between these two crossover effects if $T_C \ll T_0$ and if the dimension (presumably $d = 3$) is sufficiently greater than the critical dimensionality $d_C$ of the type of transition being observed.

## 2. Analysis

The Boltzmann probability distribution $\exp(-v/kT)$ over the double well is plotted (figure 2) for various temperatures. Note that at $T_0$ the distribution already demonstrates considerable splitting, and that the small dip in the centre persists for arbitrarily high temperatures.

Figure 3(a) shows the mean squared displacement $\langle x^2 \rangle$ as a function of $T$, related to the single-well susceptibility as usual by

$$\chi = \langle x^2 \rangle / kT. \tag{2.1}$$

The well-defined minimum in $\langle x^2 \rangle$ at $T \simeq 0.85T_0$ is really the most important physical effect. As one comes down from a high temperature the distribution clearly narrows, but widens again as the system decends into the regime of the two minima. Above $T_0$ the curve appears substantially linear over the range plotted, while at high temperatures it tends towards the limiting form

$$\langle x^2 \rangle \simeq (\Gamma(\tfrac{3}{4})/\Gamma(\tfrac{1}{4}))x_0^2 T^{1/2}. \tag{2.2}$$

In fact at $T \gg T_0$ the system is dominated by the $\beta x^4$ term in the potential and the limiting behaviour of all equilibrium quantities is expressible using gamma functions
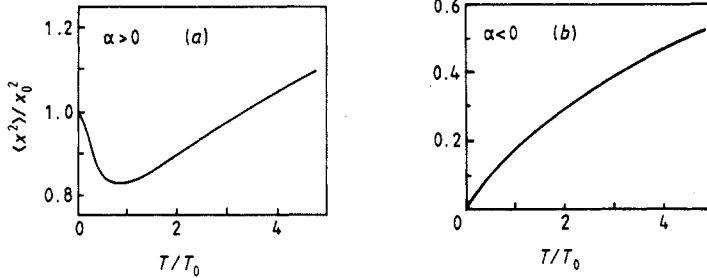
**Figure 3.** $\langle x^2 \rangle$ versus $T$ for $(a)$ the double well, $\alpha > 0$ (note the minimum at $0.85T_0$) and $(b)$ the single well, $\alpha < 0$.
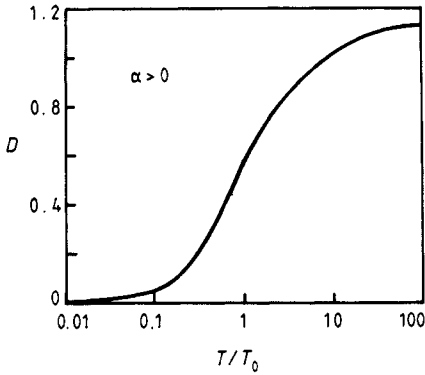


**Figure 4.** Variation of the quasi-order parameter $D$ (equation (2.3)) with temperature.

(Eisenriegler 1974). The low temperature limits are given by parabolae suitably fitted to the minima.

We have given thought to whether one may define a quasi-order parameter to describe the bifurcation. We choose the quantity (figure 4)

$$D = (\langle x^4 \rangle - \langle x^2 \rangle^2)/\langle x^2 \rangle^2. \tag{2.3}$$

which varies from zero to

$$(\Gamma(\tfrac{1}{4})/2\Gamma(\tfrac{3}{4}))^2 - 1 = 1.88. \tag{2.4}$$

As expected, there is a change in behaviour around $T = T_0$, but high and low temperature limits are approached rather slowly as shown by the logarithmic plot. An appropriate measure of bifurcation might therefore be $\psi$ given by

$$\psi^2 = 1 - D/1.188. \tag{2.5}$$

Thermodynamic quantities can be derived from the free energy

$$G(T) = -kT \ln \int \exp(-v(x)/kT) \, \mathrm{d}(x/x_0) \tag{2.6}$$

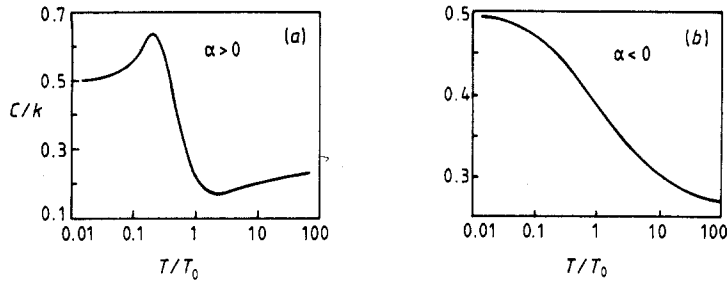The most striking manifestation of the double well is seen in the heat capacity $C(T)$

**Figure 5.** Heat capacity $C$ versus $T$ for the two cases. ($a$) The double well, $\alpha > 0$, illustrating maximum and minimum values during the crossover around $T_0$ from 'parabolic' to 'quartic' limits; ($b$) the single well, $\alpha < 0$.
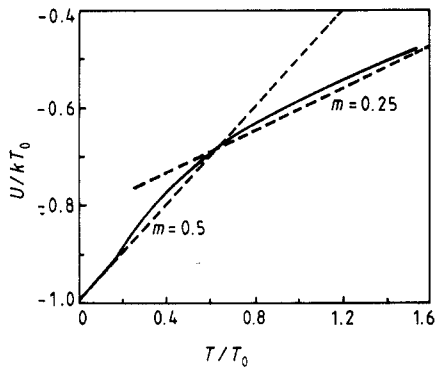


**Figure 6.** Internal energy $U$ versus $T$ for the double-well system. Notice how $U$ approaches both limits from above.

(figure 5($a$)). This demonstrates a pronounced anomaly during the crossover between the low temperature limiting value of $\frac{1}{2}k$ (characteristic of a parabolic potential) and the high temperature limit $\frac{1}{4}k$ (pure quartic). The implication is that the quasi-transition has the form illustrated in figure 6, where the internal energy $U(T)$ approaches the low $T$ limit of $\frac{1}{2}kT$ from above.

The peak in $C(T)$ arises as follows. At $T < T_0$ the particle oscillates mostly in the left or the right well which contains a cubic term in the potential when expanded around the minima $\pm x_0$. This is well known to increase the specific heat of all solids at high $T$ above the ideal value of Dulong and Petit. One can say that the well is effectively softened more on the low $|x|$ region than hardened on the high $|x|$ side because the particle spends more time in the former: a soft potential gives an enchanced $C(T)$ as one can see from $V \sim x^n$ with $n < 2$. Similarly, at $E > kT_0$ the potential (1.2) has steep sides somewhat like a square well, which has zero specific heat (aside from the kinetic energy which we have ignored in (2.6)). We therefore expect $C(T)$ to be below the high $T$ limit in figure 5($a$) for $T > T_0$.

For comparison the same results are shown for the single well (equation (1.7)) in figures 3($b$) and 5($b$). Naturally $\langle x^2 \rangle$ now has no minimum. Also the crossover has a smooth form with no extrema in $C(T)$, since there is a smooth transition in well shape from quartic ($T \gg T_0$) to quadratic form ($T \ll T_0$).
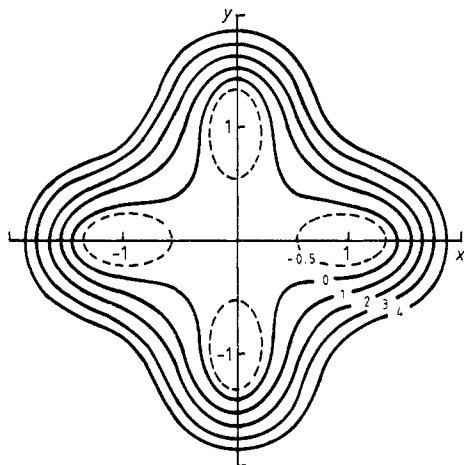
**Figure 7.** Contour plot of the single-site potential with multiple (four) wells at $(x, y) = (\pm 1, 0), (0, \pm 1)$ around a central maximum of height $kT_0$ used in the computer simulation of section 3. The form of the potential is given in equation (3.2). The contours are labelled in units of $kT_0$.
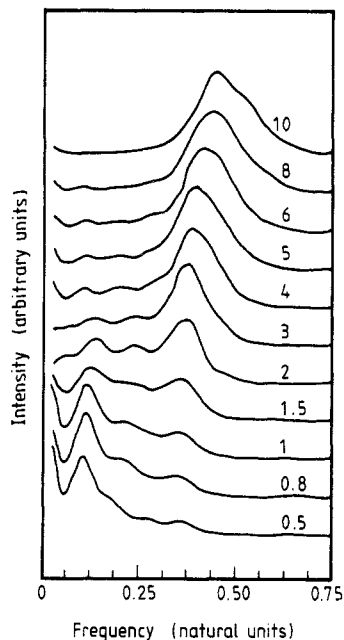


**Figure 8.** The power spectrum, equation (3.3), shown for a range of temperatures above and below $T_0$. Note that the central peak is not fully shown on these spectra. The spectra are labelled in units of $T/T_0$.

## 3. Computer simulation

We have carried out a computer simulation to give unequivocal evidence of the reality and observability of the quasi-transition at $T_0$. We have considered the lattice vibrations in a three-dimensional system with the following Hamiltonian:

$$H = \tfrac{1}{2} \sum_n (x_n^2 + y_n^2) + \sum_n V(x_n, y_n) - \sum_{\text{pairs}} J(x_n x_m + y_n y_m). \qquad (3.1)$$

The coupling, to nearest neighbours only, is weak and 'ferromagnetic'. The on-site potential

$$v(x, y) = \alpha(x^2 + y^2) + \beta(x^2 + y^2)^2 + \gamma x^2 y^2 \exp[-\delta(x^2 + y^2)] \qquad (3.2)$$

is two-dimensional and contains four wells (figure 7). The values of the model parameters are given in table 1, and were chosen so that $T_C \approx \tfrac{1}{3}T_0$ (where $T_0$ is the height of the central barrier in $v(x, y)$, i.e. where $kT_0 = \alpha^2/4\beta$), and so that the four wells were quite anisotropic. With our choice of parameters $kT_0 = 1$, and the minima in $v(x, y)$ lie at $(x, y) = (\pm 1, 0), (0, \pm 1)$. Here $x$ and $y$ represent the components of some two-dimensional variable of the entity at each site, and are not necessarily associated with displacements. Details of the method of the simulation are given in Giddy *et al* (1989).

**Table 1.** The values of the model parameters used in the computer simulation of section 3. See equations (3.1) and (3.2) for details.

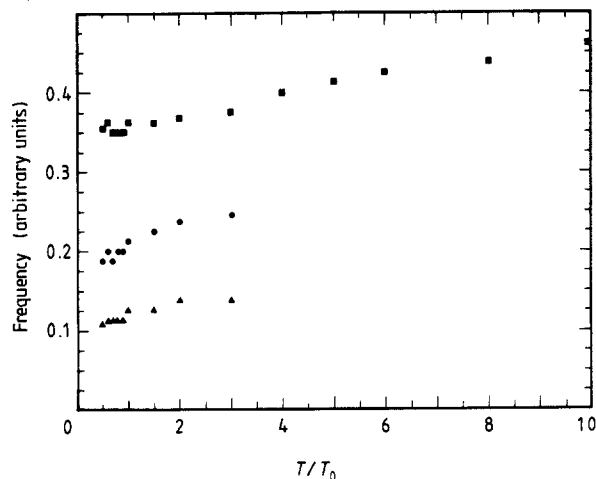| $\alpha$ | $\beta$ | $\gamma$ | $\delta$ | $J$ |
|---|---|---|---|---|
| $-2.0$ | $1.0$ | $20.87$ | $0.6711$ | $0.1$ |



**Figure 9.** Variation of frequency, $\omega(q = 0)$, of the peaks in figure 8 for the two-dimensional potential with multiple wells (figure 7) with $T_C \simeq \frac{1}{4}T_0$. The line dominating above $T_0$ (shown by ■) is doubly degenerate. The splitting of the double degeneracy around and below $T_0$ breaks only local symmetry.

The calculations were performed using 4096 unit cells on the AMT-DAP in Cambridge. In figure 8 we plot the power spectrum

$$S_{xx}(q, \omega) = \int \langle x(q, 0)x(-q, t)\rangle \exp(i\omega t) \, dt \tag{3.3}$$

for $q$ at the centre of the Brillouin zone over a range of temperatures above and below $T_0$. Note that as the temperature drops, the high temperature, high frequency mode decreases in intensity, and the two low temperature, low frequency modes increase. Figure 9 shows the evolution with temperature of the estimated positions of the peaks in $S_{xx}(q, \omega)$. At high $T \gg T_0$ there is a single twofold-degenerate frequency as expected from the symmetry: the particle oscillates over the whole region of the wells including the central maximum. This frequency softens as the temperature drops. Around and below $T_0$ but above $T_C$, some particles are confined in one or other of the four wells, and oscillations polarised in the two directions within each are no longer equivalent. Hence the frequency is split into two components, associated with 'longitudinal' and 'transverse' motions, with a central ($\omega = 0$) peak due to hopping between wells. Of the two low temperature modes that with the lower frequency is associated with the 'longitudinal' motion, and that with the higher frequency with the 'transverse' motion. Such local apparent breaking of symmetry defines $T_0$ rather than $T_C$. Of course overall fourfold

symmetry is retained in the sense that one obtains exactly the same data for the correlations $\langle x(q, 0)x(-q, t) \rangle$ and $\langle y(q, 0)y(-q, t) \rangle$ of displacements along the $x$ and $y$ directions. The quasi-transition at $T_0$ is not sharply defined: rather it is a smooth crossover from displacive to order–disorder behaviour.

## 4. Other examples

The clearest experimental case is that of lead phosphate $Pb_3(PO_4)_2$. These crystals possess a phase transition from a trigonal phase to a monoclinic phase at about 450 K. Salje and Wruck (1983) have established a local symmetry breaking by displacement of Pb ions into one of three equivalent wells in the trigonal crystal. An excess specific heat which cannot be explained by critical fluctuation is observed between $T_C$ and a temperature $T_3 > T_C$, where there is a change in the gradient of $C_p(T)$. This can be identified as a quasi-transition involving the three minima, with $T_3$ analogous to $T_0$ above. This local displacement of the lead atoms from the threefold axis, and their subsequent hopping between the macroscopically symmetrically equivalent sites is also apparent from the behaviour of the integrated intensities and linewidths of hard Raman bands above $T_C$ (Salje *et al* 1983). X-ray and neutron scattering experiments (Bismayer and Salje 1982) show diffuse super reflections above $T_C$ which are also explained by the quasi-transition.

Measurements of the dielectric constants in perovskite materials (Müller *et al* 1982) would appear to provide an example of the two crossover effects occurring nearly simultaneously. On coming down in temperature the phonon frequencies undergo a change in behaviour, which we ascribe as being probably the $T_0$ effect rather than the other crossover due to critical fluctuations, because the temperature at which it occurs is rather far out in the wings of the critical fluctuation peak in the measured dielectric constant.

Molecular dynamic simulation of the surface reconstruction of $W(001)$ has been carried out by Wang (1986). The mean squared displacements of surface atoms are seen to behave as $\langle x^2 \rangle$ above, and the surface energy is characteristic of the internal energy $U(T)$ for a quadruple well potential, i.e. similar to figure 6. In the phonon frequencies (Wang *et al* 1987), $T_C$ and $T_0$ are seen to be concurrent, which also demonstrates that the double well character may promote transition in view of (2.1) and the minimum in $\langle x^2 \rangle$ at $T_0$.

Kinetic studies of the ordering at phase transitions, i.e. variation of the order parameter $Q$ with time, confirm that the two regimes exist. Displacive processes are rapid, with $\ln(Q) \propto t$ as the system moves into the energy minimum, whereas order/disorder processes with multi-well potentials are characterised by $Q \propto \ln(t)$ (Salje 1988). Of course one cannot observe both types of behaviour on cooling in a single material because ordering must be associated with $T_C$. However shock heating an ordered sample to temperatures $T > T_C$ in the two ranges $T < T_0$ and $T > T_0$ allows the two distinct kinetic regimes to be observed during disordering. An example is albite (Carpenter and Salje 1989). In this case the distortion of the anion ring is described by a double-well potential, and is believed to be the primary order parameter, the preferential attachment of Si and Al to certain sites after distortion being a secondary phenomenon.

## Acknowledgments

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