What do Landau free energies really look like for structural phase transitions?

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Abstract. Landau free-energy expansions are commonly used to describe systems undergoing structural phase transitions. The Landau free energy of a model solid with an anharmonic potential (often a double well) at each site and mean-field-like inter-site coupling has been calculated both analytically and from molecular dynamics simulation.

The calculated free-energy function is not well described by a simple polynomial in the order parameter. This result is not due to critical fluctuations in the Ginzburg interval. If, however, such a polynomial is used the coefficient of the fourth-order term is found to be highly temperature dependent. For a certain range of model parameters this coefficient is small relative to that of the second-order term.

These observations help to explain the occurrence of 'non-critical, non-standard' values of the exponent β in the variation of the order parameter, $\bar{x}$, with temperature:

$$\bar{x} \propto (T_c - T)^\beta.$$

More importantly they also help to explain why so many natural systems behave in a tricritical-type manner, with $\beta \simeq \frac{1}{4}$.

1. Introduction

This is the first of three papers, hereafter called I, II (Normand *et al* 1989) and III (Giddy *et al* 1989), concerning a theoretical and computational study of an idealised soft-mode phase transition. The total energy of the system is

$$V = \sum_n v(x_n) - \sum_{\text{pairs}} J_{mn} x_m x_n \tag{1.1}$$

where

$$v(x) = a_1 x^2 + a_2 x^4 \tag{1.2}$$

and the first sum is taken over the N sites. Here x can be some variable of an entity, for example the intra-molecular twist angle of a biphenyl molecule (Benkert *et al* 1987), of which there is one per site. The N sites are taken on a simple cubic lattice. The value of a_1 is often negative, which implies an on-site double well (figure 1). A phase transition is, however, still possible for weak positive a_1, provided the coupling between sites is
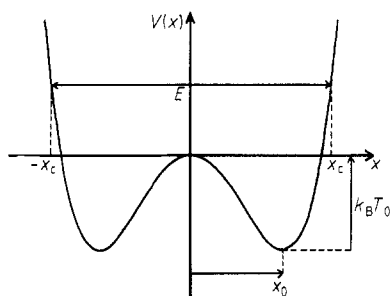
Figure 1. The on-site potential $v(x)$ (equation (1.2)) with a_1 negative. The height of the central maximum is kT_0 and the minima are at $\pm x_0$. An entity with energy E would oscillate classically between $\pm x_c$.
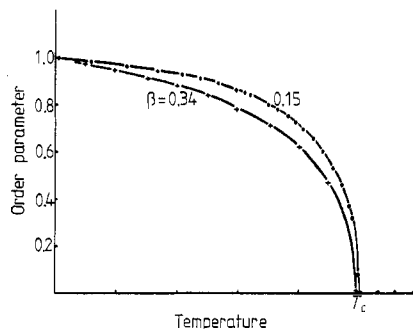
Figure 2. Order parameter, $\bar{x}$, against temperature, T, as measured from MDS for two sets of model parameters. The on-site potential was a double well (a_1 negative) for the upper curve and a single well (a_1 positive) for the lower. Note the rather low values of the exponent β, and the wide temperature range over which equation (1.6) holds. The lines are drawn as a guide to the eye.

strong enough. We choose the signs of J_{mn} such that the phase transition always occurs at $k = 0$ (zone centre), so our order parameter is

$$\bar{x} \equiv \langle x_n \rangle = \frac{1}{N} \sum x_n \tag{1.3}$$

for a system of N entities. Note that the coupling is taken in the form $J_{mn}x_m x_n$ rather than $\frac{1}{2}J_{mn}(x_m - x_n)^2$ because the former averages to zero in the high-temperature disordered state; in any case x_n is not necessarily an acoustic displacement. For some purposes it is more convenient to write

$$v(x) = kT_0\{[1 - (x/x_0)^2]^2 - 1\} \qquad \text{if } a_1 < 0 \tag{1.4a}$$

$$v(x) = kT_0\{[1 + (x/x_0)^2]^2 - 1\} \qquad \text{if } a_1 > 0 \tag{1.4b}$$

with $x_0^2 = |a_1|/2a_2$ and $kT_0 = a_1^2/4a_2$.

The study of structural phase transitions has moved from general phenomenological theory, such as Landau free-energy expansions (Landau and Lifshitz 1958), to a quantitative understanding of the macroscopic phenomena in terms of the microscopic interatomic forces. The detailed study of the incommensurate phases of biphenyl is a good example (Benkert et al 1987, Benkert and Heine 1987a, b, Benkert 1987). We therefore want to develop the connection between microscopic models of the inter-atomic potentials, such as equation (1.1), and the macroscopic phenomena. The motivation for our work is that several aspects of the structural phase transitions arising from equation (1.1) appear to have never been clarified, although our model system has been extensively studied by Blinc and Zeks (1974), Bruce (1980), Schneider and Stoll (1980), and others.

The present paper essentially poses the question, what does the Landau free energy really look like? The theory of phase transitions has traditionally been written mostly in terms of the susceptibility or phonon frequencies. However, the experimental phenomena, including coupling to different fields and strains etc, are usually described in terms of the Landau free-energy expansion $G_L(\bar{x}, T)$. We therefore want to develop the theory of G_L.

Following Landau, it is fashionable to write down expansions of the form:

$$G_L(\bar{x}, T) = G_0(T) + a(T - T_c)\bar{x}^2 + b\bar{x}^4 + c\bar{x}^6 + \ldots \tag{1.5}$$

We are, however, not aware of any explicitly calculated curves of G_L for our model (equation (1.1)). This is not an idle question because pathologies are not uncommon and we want to understand them. There are surprisingly many systems that behave more or less 'tricritically', i.e. the usual $\bar{x}^4$ term in G_L (equation (1.5)) seems to be quite small. If the terms beyond $b\bar{x}^4$ in equation (1.5) can be neglected and b is independent of T, then the build up of the order parameter $\bar{x}$ below T_c is given by the standard Landau law

$$\bar{x}(T) = \text{constant} \times (T_c - T)^\beta \tag{1.6}$$

with the standard exponent $\beta = \frac{1}{2}$. However in the so-called tricritical situation the $b\bar{x}^4$ term is absent from equation (1.5), so $c\bar{x}^6$ dominates and $\beta = \frac{1}{4}$. Some recently investigated examples include calcite (Dove and Powell 1989, Redfern *et al* 1989), anorthite (Redfern *et al* 1988) and sodium nitrate (Reeder *et al* 1988). The point is that there has been no apparent reason why the $b\bar{x}^4$ term in equation (1.5) should be zero or very small in these and many other materials. A similar behaviour is shown in figure 2, generated from our model by molecular dynamics simulation (MDS), where curves for two sets of model parameters are shown. We note that equation (1.6) with $\beta = 0.15$ and 0.34 fits the curves well over the temperature range from $T = 0$ to $0.75T_c$. We shall refer to these values of β that are significantly less than $\beta = \frac{1}{2}$ as non-critical, non-standard exponents. Note that for the deep-well limit of our model (the Ising model) fitting equation (1.6) does not result in a constant value for β over a wide range of temperature. In fact β increases from a rather low value (<0.15) as the temperature decreases. The point about figure 2 is that it shows that our model (equation (1.1)) is relevant to the question of why such low values of β occur. Note that we are *not* concerned with the region of critical fluctuations close to T_c but with the broad variation of $\bar{x}(T)$ over a wide range of T. In any case the Ginzburg interval of critical fluctuations is very narrow for the materials mentioned above and below (Ginzburg *et al* 1987). Of course $\bar{x}(T)$ is not expected to follow a precise power law: equation (1.6) is merely a convenient form of approximation. For some values of the parameters in equations (1.1) and (1.2), particularly negative a_1, the coefficient b in equation (1.5) is indeed small; it is also strongly temperature dependent, and a polynomial like equation (1.5) is not a good representation of the shape of $G_L(\bar{x}, T)$. There is another side to the matter of low non-critical non-standard exponents: there are other materials where equation (1.6) with $\beta = \frac{1}{2}$ represents $\bar{x}(T)$ over a surprisingly wide range of T, e.g. calcium-rich plagioclase (Redfern *et al* 1988), arsenic pentoxide (Redfern and Salje 1988). Note that these, and the other systems mentioned above, all have important elastic energy contributions to the free energy. This 'standard' behaviour with $\beta = \frac{1}{2}$ also needs explaining because the simple form (equation (1.5)) with constant coefficients was only intended originally as an expansion near $T = T_c$. In general one would expect the coefficients to depend on T and for the higher-order terms $c\bar{x}^6$ etc to become important as $\bar{x}(T)$ increases at low T. We shall show that such 'standard' behaviour can also be given by our model (equation (1.1)) with appropriate values of the parameters. Thus as well as explaining the low values of β, our work allows one to infer from an observed β some information about the microscopic parameters a_1, a_2 and J. A second pathology concerns the soft-mode phonon frequencies. The slopes of ω^2 versus T above and below T_c should have a ratio of $1:2$ according to the renormalised phonon theory but preliminary computer simulations showed ratios differing significantly from $1:2$. Indeed it was these unusual

ratios that prompted our investigation. We shall not pursue this point further because it is not purely a matter of free energy, although we believe that the main effect comes from the equilibrium $\bar{x}(T)$ that the system is oscillating about and hence is related to equation (1.6).

Such then are the pathologies to be explained, particularly the low non-critical, non-standard exponents β. Three possible explanations come to mind. Firstly, that the behaviour is due to critical fluctuations: we shall show conclusively that this is not so. Secondly, one could have strong temperature dependence of the coefficient b in equation (1.5). Thirdly, one can have important terms higher than $b\bar{x}^4$ in equation (1.5). We shall show that both the latter points apply, and that they depend strongly on the nature of the system, i.e. whether $v(x)$ represents a single well ($a_1 > 0$) or a double well ($a_1 < 0$).

Let us write the Landau free energy per entity of the system (equation (1.1)) as

$$G_{\mathrm{L}}(\bar{x}, T) \simeq g_{\mathrm{L}}(\bar{x}, T) - \tfrac{1}{2}J\bar{x}^2 \tag{1.7a}$$

where

$$J = \sum_{\text{neighbours}} J_{mn}. \tag{1.7b}$$

Here g_{L} is the Landau free energy for a single entity and the last term in equation (1.7a) is the mean-field approximation for the coupling between them. This form follows from the Bogoliubov inequality (Falk 1970) with the set of wells (equation (1.2)) as the unperturbed Hamiltonian and the coupling between them in equation (1.1) as the perturbation. We know that this approach overestimates T_{c} by a factor of 1.32–1.52 (Bruce (1980), p 122), but apart from that we find from MDS (§ 3) that it gives a good representation of the general variation of G_{L} with $\bar{x}$.

We can further write

$$g_{\mathrm{L}}(\bar{x}, T) = g_0(T) + \tfrac{1}{2}(\chi_0(T))^{-1}\bar{x}^2 + g_{\mathrm{h}}(\bar{x}, T) \tag{1.8}$$

where χ_0 is the susceptibility of a single entity and g_{h} represents all the higher-order terms. We have calculated g_{h} directly (§ 2) and from MDS (§ 3); typical results are shown in figure 3. The first point is that g_{h} really has two regions,

$$g_{\mathrm{h}} \simeq b(T)\bar{x}^4 \qquad |\bar{x}| < x_{\mathrm{c}} \tag{1.9a}$$

where b is small, and then

$$g_{\mathrm{h}} \simeq a_2\bar{x}^4 \qquad |\bar{x}| > x_{\mathrm{c}} \tag{1.9b}$$

when $\bar{x}$ is large. Note that equation (1.9a) applies at any given temperature, the 'constant' b being temperature dependent. This latter effect contributes to the value of β, particularly near T_{c}. Secondly, the coefficient for large $\bar{x}$ is just a_2 of the bare potential (equation (1.2)). Thirdly, the crossover x_{c} occurs around the classical turning point of the motion, where $v(x_{\mathrm{c}}) = E$ (figure 1), i.e. the entity would oscillate classically between $-x_{\mathrm{c}}$ and $+x_{\mathrm{c}}$ if it had energy E, where

$$x_c = \pm\{[a_1^2 + 4a_2E)^{1/2} - a_1]/2a_2\}^{1/2}. \tag{1.10}$$

This form of g_{h} is easy to understand qualitatively. Remember that $g_{\mathrm{L}}(\bar{x}, T)$ is the free energy of one entity if the order parameter is artificially constrained to some value $\bar{x}$ by an external force. For small external force the 'centre of gravity' of the motion is easily pulled to one side or the other within the classical turning points, but if we apply a very
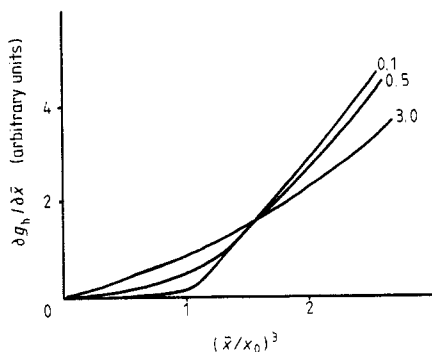
Figure 3. The derivative of the higher-order terms, $\partial g_h/\partial \bar{x}$, in the single-site Landau free energy (equation (1.8)) against order parameter to the third power calculated analytically for three temperatures. Labels are T/T_0. Note the non-linearity and the change in regime around $\bar{x} = x_0$ from a rather small gradient to a gradient $\sim a_2$ in equation (1.2) in the low-temperature curve.
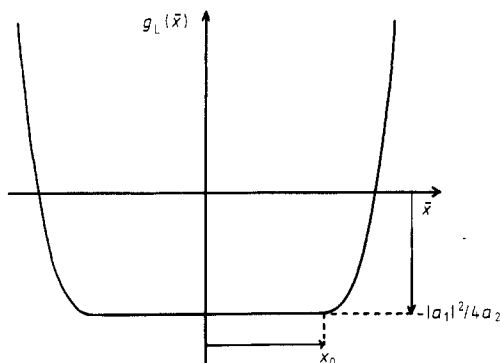
Figure 4. The single-site free energy, g_L, at $T = 0$ for an on-site double well (a_1 negative) as a function of order parameter, $\bar{x}$. The form is given in equation (1.11). Note the flat bottom between $\pm x_0$.

large force, we can pull it beyond these up the slope of the bare $v(x)$ curve beyond x_c. Moreover in the region of low $\bar{x}$ the coefficient $b(T)$ depends strongly on T.

The qualitative form and understanding of figure 3 given above is our principal conclusion. We can push this a bit further by considering two limiting cases. Let $a_1 < 0$ so that as $T \to 0$ the $g_L(\bar{x}, T)$ does *not* tend to $v(x)$. Rather we have

$$g_L(\bar{x}, T = 0) = v(x) \qquad \text{for } |\bar{x}| > x_0 \qquad (1.11a)$$

$$g_L(\bar{x}, T = 0) = -|a_1|^2/4a_2 = v(x_0) \qquad \text{for } |\bar{x}| < x_0 \qquad (1.11b)$$

as shown in figure 4. The reason for the flat bottom (equation $(1.11b)$) is that at $T = 0$ the entities are distributed between the two lowest-energy states at $x = \pm x_0$ in whatever ratio is needed to give $\langle x \rangle = \bar{x}$. Such a behaviour of the free energy is well known in other contexts (Binder 1986). In consequence, $g_L(\bar{x}, T = 0)$ has a power series expansion with all coefficients equal to zero, and this power series ceases to represent $g_L(\bar{x}, T = 0)$ beyond $|\bar{x}| = x_0$. Thus we expect that $b(T) \to 0$ as $T \to 0$ and that no simple polynomial expression will represent $g_L(\bar{x}, T)$ at any T beyond the change in regime around $\bar{x} = x_c$ in equation (1.9).

We turn now to the case for $a_1 > 0$. The energy at $T = 0$ is

$$V = (a_1 - \tfrac{1}{2}J)x^2 + a_2 x^4 \qquad (1.12)$$

and we must have $J/2 > a_1$ for there to be a phase transition. However, if $J/2$ is only slightly larger than a_1, say $a_1 < J/2 < 2a_1$, then we have at $T = 0$

$$(\bar{x}(T = 0))^2 = (\tfrac{1}{2}J - a_1)/2a_2 < x_0^2. \qquad (1.13)$$

It follows that $\bar{x}(T)$, for all temperatures between zero and T_c, lies inside the range $|\bar{x}(T)| < x_0$ where the well $v(x)$ is only slightly perturbed from parabolic. We might therefore expect $\bar{x}(T)$ to have a simple behaviour again in such a case, as we shall discuss later.

Our results shed an interesting light on the theory of the lock-in behaviour of incommensurate phases. By suitable choice of J_{mn} an incommensurate phase can be produced. A lock-in transition to $q = rg/s$ (where r and s are integers, and g is the first reciprocal-lattice vector) has traditionally been described by a term $b_s \bar{x}^s$ in G_L where s is large. Parlinski and Michel (1984) have pointed out that from the point of view of renormalised phonon theory, such high powers arising from quadratic and quartic $v(x)$ seems implausible. We now see from figure 3 that a polynomial is really rather inappropriate to express the rapid rise of $g_h(\bar{x})$ for $\bar{x} > x_c$. Rather, the rapid rise of $g_h(\bar{x})$ results in a squaring up of the shape of the modulation, and it is therefore more appropriate to discuss the lock-in in terms of the formation and interaction of solitons via other terms in the Landau expansion (Heine 1989).

We want to emphasise two points. Firstly, as already mentioned, we do not seek to describe the Ginzburg region of critical fluctuations close to T_c. Secondly, we assume that such critical fluctuations are an additional effect on top of a smooth free-energy function (which we associate with the Landau function) above and below T_c. Is it conceptually valid to divide the free energy that way, i.e. to think of a *single* smooth function valid *above* and *below* T_c? We believe that the answer is yes, because in the presence of an external field there is a smooth continuous transition. Also the theory of the partition function in complex temperature space suggests an analytic continuation between $T \gtrless T_c$ (Derrida *et al* 1983). Another reason is that the approximation (equation (1.7)) derives from the Bogoliubov inequality: being a variational principle, it cannot be far wrong. The existence of a Landau free-energy function in this sense is inherent in our work. This point that the Landau free energy is valid over a range of $\bar{x}$ and T is also particularly important in the theory of time-dependent processes and kinetics (Salje 1988), and in order also to be able to relate the behaviour at temperatures above and below T_c.

2. Analytic calculations

The quantity g_L in equation (1.7) is given by

$$g_L = U - TS = \int v(x)p(x)\,\mathrm{d}x + kT \int p(x)\ln(p(x))\,\mathrm{d}x \tag{2.1}$$

where $p(x)$ is the probability distribution and $v(x)$ is the on-site potential (equation (1.2)). The g_L (equation (2.1)) is minimised using the constraints

$$\int p(x)\,\mathrm{d}x - 1 = 0 \tag{2.2}$$

$$\int xp(x)\,\mathrm{d}x - \bar{x} = 0. \tag{2.3}$$

The second constraint represents the fact that the Landau free energy is not just the free energy at some temperature T: it is the notional free energy when the order parameter is constrained to some predetermined value $\bar{x}$.
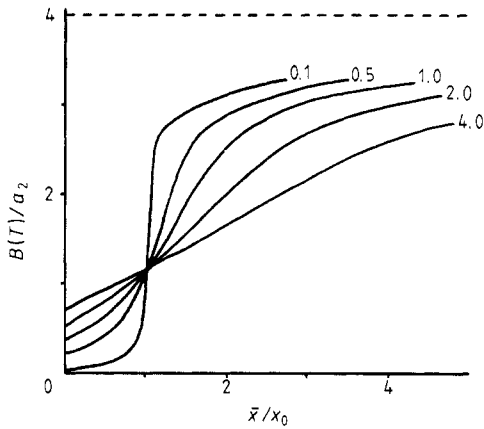
Figure 5. The derivative $B(T)$ (equation (2.6)) against order parameter, $\bar{x}$, for a double well (a_1 negative) for a range of temperatures. Labels are T/T_0. Note the change in regime around $\bar{x} \simeq x_0$ and the rather low value of $B(T)$ below $\bar{x} \simeq x_0$. Note also that $B(T) \to 4a_2$ as $\bar{x} \to \infty$.
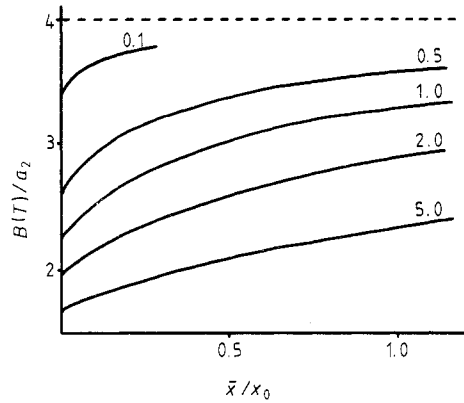
Figure 6. The derivative $B(T)$ (equation (2.6)) against order parameter, $\bar{x}$, for a single well (a_1 positive) for a range of temperatures. Labels are T/T_0. Note that $B(T) \to 4a_2$ as $T \to 0$.

Thus we minimise the quantity

$$L(p(x)) = g_L - \mu \left(\int p(x)\,dx - 1 \right) - F\left(\int xp(x)\,dx - \bar{x} \right) \qquad (2.4)$$

where μ and F are the Lagrange multipliers. This gives the probability distribution

$$p(x) = \exp\left(\frac{-v + Fx}{kT} \right) \bigg/ \int \exp\left(\frac{-v + Fx}{kT} \right) dx \qquad (2.5)$$

where F is still to be determined by substituting equation (2.5) into equation (2.3). This defines F as a function of x which is inserted into equation (2.5). The latter can then be used to calculate g_L from equation (2.1). Similarly $\chi_0^{-1} = kT/\langle x^2 \rangle$ and $g_0(T) = g_L(\bar{x} = 0)$ can be calculated. Finally g_h (equation (1.8)) can be calculated as a function of order parameter for a range of temperatures.

A typical result for $g_h(\bar{x}, T)$ for a double well ($a_1 < 0$) is shown in figure 3. The shape of the curve $g_h(\bar{x}, T)$ can conveniently be indicated by the derivative

$$B(\bar{x}, T) = \partial^2 g_h / \partial \bar{x}^3\, \partial \bar{x} \qquad (2.6)$$

shown in figure 5 (double well, $a_1 < 0$) and figure 6 (single well, $a_1 > 0$). Note that $B(T)$ tends to $b(T)$ (equation (1.9a)) as $\bar{x} \to 0$, and to $4a_2$ as $\bar{x} \to \infty$ for all T in accordance with our previous discussion. Figure 5 shows the change in character around $x_c \simeq x_0$. Figure 5 also shows that $B(T) \to 0$ as $T \to 0$ as expected (§ 1). On the other hand in figure 6 the function $B(T) \to 4a_2$ as $T \to 0$ (§ 1).

Figure 7 shows the variation of the order parameter with temperature, for a value of J that is small relative to kT_0, the height of the central maximum of the on-site potential (equation (1.2), figure 1). This was calculated from $g_L(\bar{x}, T)$ and equation (1.7a) by numerically solving the equation

$$J\bar{x} = \partial g_L / \partial \bar{x}. \qquad (2.7)$$

Equation (1.6) was fitted to the results and the value of the exponent β is given. Note
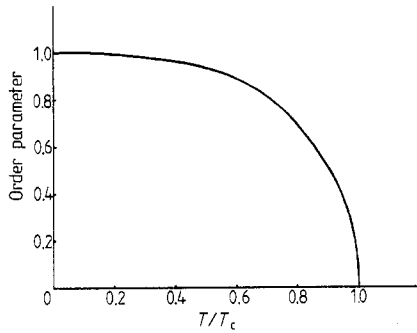
Figure 7. Order parameter, $\bar{x}$, against temperature, T, as calculated analytically for a double well (a_1 negative) for a low value of the inter-site coupling, J, relative to the height of the central maximum of the on-site potential. Note that equation (1.6) with $\beta = 0.37$ holds over a wide range of temperature and that the value of β is rather low.
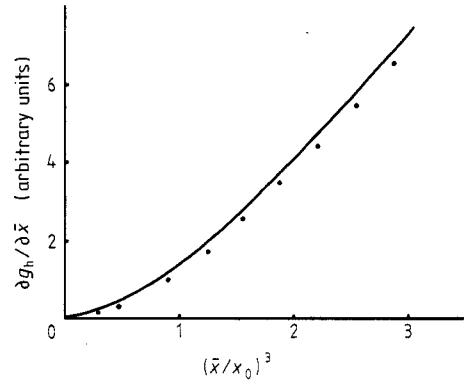
Figure 8. The derivative $\mathrm{d}g_h/\mathrm{d}\bar{x}$ (equation (3.2)) as calculated analytically (§ 2) (full curve) and as measured from MDS (§ 3) (full circles) plotted against the order parameter cubed. Note the similarity between the curves, especially at low values of the order parameter.

that the fit is good over a wide range of T and that the value of β is small. Choosing other parameters for the model (equation (1.1)) results in a wide range of non-critical, non-standard exponents β, and that apparent tricritical behaviour is probably to be explained in this way. On the other hand exponents near the standard value of $\beta = \frac{1}{2}$ are also obtained with a value of J that is large relative to kT_0 (figure 1).

3. Molecular dynamics simulation

The purpose of doing some MDS runs on our model (equation (1.1)) is to show that the pathologies mentioned in § 1 are not due to critical fluctuations. So far our calculations in § 2 have been carried out using G_L (equation (1.7)) which includes the effect of the couplings J_{mn} only in a mean-field approximation, i.e. one that excludes critical fluctuations. We want to show that this does not invalidate our conclusions concerning the shape of $g_L(\bar{x}, T)$. The MDS calculations were performed using the Distributed Array of Processors (DAP) at Queen Mary College with a sample of size $16 \times 16 \times 16$ entities arranged on a simple cubic lattice. The algorithm due to Beeman (1976) was used and Born–von Karman periodic boundary conditions applied. The J_{mn} were chosen as $J/6$ to each of the nearest neighbours and zero otherwise.

The results for $\bar{x}(T)$ for two sets of parameters are shown in figure 2. Equation (1.6) is again fitted to the results, and values of the exponent β calculated. These are found to be non-critical, non-standard and small, namely $\beta = 0.34$ and 0.15.

In order to focus on $G_L(\bar{x}, T)$ directly, we carried out some further MDS runs in a somewhat unusual way. We want to obtain information about $G_L(\bar{x}, T)$ as a function of $\bar{x}$ at some constant T. We therefore ordered the system progressively by increasing J at fixed temperature, giving $\bar{x}(J, T = \text{constant})$. The system first starts to order at some J_c

given by the vanishing of the second-order term in G_L. Thus we can rewrite equation (1.7a) as

$$G_L = G_0 + \tfrac{1}{2}(J_c - J)\bar{x}^2 + g_h(\bar{x}, T) \tag{3.1}$$

The equilibrium $\partial G_L/\partial \bar{x} = 0$ is given by

$$\partial g_h/\partial \bar{x} = (J - J_c)\bar{x}. \tag{3.2}$$

The results calculated from § 2 are shown in figure 8. Of course they involve the mean-field approximation of equation (1.7a) and the question is how to compare them with the proper results from MDS. We believe the right-hand side of equation (3.2), with the $\bar{x}(J, T)$ from MDS, in a sense still repressnts the resistance of the system to increasing order under increasing internal force $J - J_c$. Thus figure 8 also shows the right-hand side of equation (3.2) evaluated with the J_c and $\bar{x}(J, T)$ from MDS. The two curves are remarkably similar.

From the similarities found within figure 8, we conclude that the picture of $G_L(\bar{x}, T)$ developed in § 1 and § 2 is semi-quantitatively correct. There are various inadequacies in the approximation (equation (1.7a))—for example, the effect on T_c of short-range order in the high-temperature phase. But the effects of critical flucatuations would show in discrepancies in the shape of figure 8 *around T_c only* (i.e. at low values of the order parameter). These are not noticeable on the scale drawn here. We therefore conclude that critical fluctuations are not the origin of the non-standard exponents β in equation (1.6) discussed in § 1 and § 2—indeed that critical fluctuations are irrelevant to the story we have presented.

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