

The Landau free energy of the three-dimensional Φ^4 model in wide temperature intervals

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 585

(<http://iopscience.iop.org/0953-8984/7/3/013>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.179

The article was downloaded on 13/05/2010 at 11:45

Please note that [terms and conditions apply](#).

The Landau free energy of the three-dimensional Φ^4 model in wide temperature intervals

S Radescu†, I Etxebarria‡ and J M Pérez-Mato§

† Departamento de Física Fundamental, Universidad de la Laguna, Tenerife, Spain

‡ Laboratoire Leon Brillouin, Centre d'Etudes Nucléaires Saclay, 91191 Gif-sur-Yvette Cédex, France

§ Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, Bilbao, Spain

Received 14 July 1994, in final form 14 September 1994

Abstract. The range of validity of Landau free-energy potentials with the usual approximation of constant coefficients for terms higher than quadratic has recently been questioned (*J. Phys.: Condens. Matter* 1 (1989) 8327). The frequent observation in real systems, within large temperature intervals, clearly outside any possible critical region, of power laws of the type $|T_c - T|^b$ for the order parameter has also been pointed out as an indication that certain simple general features in phase transitions, not related at all to critical phenomena, are beyond the usual approximations included in a Landau free-energy expansion. In particular, the value of the exponent b has been proposed to be related to the displacive and order–disorder degree of the system. In order to elucidate these questions, the temperature dependence of the Landau free energy corresponding to the three-dimensional Φ^4 model has been investigated using a straightforward Monte Carlo method. Different model parameters have been considered, ranging from typical displacive parameters to those approaching a pure order–disorder system. Following its formal definition, the Landau free energy at each temperature has been directly derived from the order parameter distribution in a Metropolis statistical sample. In contrast with other numerical methods used in previous literature, no approximation is introduced in the calculation, except inherent to the numerical method employed. It is shown that the temperature dependence of the Landau potential coefficients follows smooth simple laws that are outside the usual assumptions in Landau theory and can be related to the order–disorder degree of the system. The quadratic coefficient in the Landau potential exhibits a linear temperature dependence in large temperature intervals but shows a marked change in slope about the transition temperature. The quartic coefficient is shown to depend on temperature as strongly as the quadratic coefficient having a minimum around the transition point. The strong temperature dependence of this quartic coefficient is responsible for the ‘non-classical’ behaviour of the order parameter, which can be described by a power law.

1. Introduction

In the last few years, several questions on the limits of Landau theory for describing structural phase transitions outside the critical region have been raised. On the one hand, it has been pointed out that the order parameter of many compounds follows in extremely large temperature intervals power laws with the classical exponent 0.5 expected from mean-field theory or a Landau free energy restricted up to fourth-order terms [1–3]. These temperature intervals, which in many cases are larger than 0.5 in reduced temperature units surpass any reasonable value that one would expect for a theory restricted in principle to the proximity of the transition. On the other hand, the temperature behaviour of the

order parameter in many other systems follows in equally large temperature intervals non-classical power laws with exponents close to 0.25–0.3 [1, 4]. This is usually considered as an indication of the closeness of the system to a tricritical point, the behaviour of the order parameter being explained in terms of extended Landau free energies with sixth-order terms of magnitude comparable with the small fourth-order term, while keeping the Landau approximations for the temperature dependences of the coefficients in the Landau polynomial (all coefficients are constant, except the linear dependence of the quadratic coefficient) [5]. In both cases, the power laws observed cannot be considered as critical phenomena; they extend up to temperature quite outside any possible critical region and are observed using a coarse temperature scale. The main questions are then as follows. Why in many systems does the Landau approximation seem to work so well in temperature intervals so unexpectedly large? Is there any fundamental explanation for the fact that so many real systems seem to have their phase transition close to a tricritical point? Do they exist for the behaviour of systems exhibiting structural phase transitions when considered in large temperature intervals general laws that are beyond the usual Landau approximation? Is the commonly accepted extension of Landau theory made by including additional higher-order terms in the Landau polynomial with temperature-independent coefficients justified?

In order to clarify these points, Giddy *et al* [1, 4] recently investigated the Landau free energy of the microscopic Φ^4 model. This model essentially consists of a lattice of local continuous variables under the influence of local double wells and harmonic couplings with the neighbouring sites. It is commonly considered as a prototypical microscopic classical model containing the essential physics involved in structural phase transitions, where the local order parameter is a continuous variable instead of being a discrete spin. It has been widely used in the microscopic description of structural phase transitions and, in particular, ferroelectrics. According to [1, 4], the model exhibits wide temperature-range power laws for the order parameter with non-classical exponent values, ranging from 0.5 to 0.15 as the model parameters were varied from the displacive to the order–disorder limit. Using analytical approximations and molecular dynamics for the Φ^4 model, it was reported that the Landau free energy of the system is poorly described by the usual polynomials restricted up to fourth- or sixth-order terms. If such a description was forced, the fourth-order coefficient was strongly temperature (and order parameter) dependent and especially small in the case of model parameters approaching the order–disorder limit. The results suggested that some of the regularities observed in real systems mentioned above are beyond Landau predictions and are strongly correlated with the displacive/order–disorder degree of the microscopic mechanism of the transition.

In this paper, we present a direct Monte Carlo determination of the Landau free energy of the three-dimensional Φ^4 model, with parameters ranging from typical displacive parameters to those close to a pure order–disorder mechanism. The method is straightforward; it uses the formal statistical definition of the Landau free energy as an incomplete thermodynamic potential. Hence, no approximation is introduced in the calculation except for that inherent to the numerical method employed. The function obtained has been fitted to the usual power expansion. Direct unambiguous evidence for some of the points claimed in the references above has been obtained. In addition, very peculiar wide temperature-range behaviours of the Landau free-energy polynomial coefficients that are strongly dependent on the order–disorder degree of the model have been ascertained.

2. Method and results

The Landau free energy $F_L(Q)$, independently of its eventual functional form, can be defined

as an 'incomplete' thermodynamic potential where the order parameter is restricted to have an arbitrary value Q . Hence, in statistical terms, the Landau free energy can be expressed as [6, 7]

$$F_L(Q) = -k_B T \ln[Z(Q)] \tag{1}$$

where $Z(Q)$ is an incomplete partition function where all degrees of freedom have been integrated except that corresponding to the order parameter, which is fixed to the value Q . Thus, the total partition function of the system is obtained by integrating $Z(Q)$. On the other hand, the thermal probability distribution of Q is related to the incomplete partition function:

$$P(Q) = \frac{Z(Q)}{Z} \tag{2}$$

From (1) and (2), it is then obvious that

$$\Delta F_L = F_L(Q) - F = -k_B T \ln[P(Q)] \tag{3}$$

where $F = -k_B T \ln Z$ is the equilibrium free energy of the system. Hence, as F is Q independent, the Q -dependent part of the Landau free energy can be derived from the probability distribution of Q , and this latter is directly accessible from a standard Monte Carlo calculation.

Despite its radical simplicity, this way of looking at the probability distribution of the order parameter has been seldom considered when studying phase transitions. We are only aware of an application to a discotic liquid crystal [8, 9] and, to our knowledge, it has not been used in the analysis of the Φ^4 model. Certain numerical studies in the context of renormalization group theory have used similar expressions when deriving 'coarse-grained Hamiltonians' corresponding to the Kadanoff transformation [10–12] but their relevance in the framework of the Landau theory was not considered and they did not include large-cell calculations. Conversely, the direct relation of the Landau free energy with statistical magnitudes as expressed by (3) is usually overseen in phenomenological analyses based on Landau theory.

The Hamiltonian of the Φ^4 model can be expressed in the form [13]

$$H = \sum_i V(x_i) + \frac{1}{2} \sum_i \sum_j^{NN} C(x_j - x_i)^2 \tag{4}$$

with the on-site potential $V(x_i)$ given by

$$V(x_i) = E_0(x_i^2 - 1)^2 \tag{5}$$

E_0 represents the energy barrier between the two local wells for the site variable x . We only consider the next-nearest-neighbour interaction given by the coupling constant C . The units of the local variable x are normalized so that ± 1 corresponds to the minima of the on-site potential. The order parameter is defined as $Q = (1/N) \sum_i x_i$, where N is the number of cells in the lattice. Q can be interpreted as a collective degree of freedom associated with the homogeneous component of the Fourier spectrum of the x configurations. For any parameter values $E_0, C > 0$, there exists a phase transition temperature below which $\langle Q \rangle \neq 0$. Only one parameter is numerically relevant, the other being fixed by the chosen energy units.

Indeed, the ratio C/E_0 can be taken as a single model parameter, or equivalently energy units can be chosen so that $E_0 = 1$. The limits $C/E_0 \rightarrow \infty$ and $C/E_0 \rightarrow 0$ can be considered to represent the ideal pure displacive and pure order–disorder mechanisms, respectively [13]. When both energies are of the same order of magnitude, we are in a typical intermediate case. According to mean-field theory, the transition is directly proportional to the elastic parameter: $k_B T_c = 4C$ and $12C$ in the displacive and order–disorder limits, respectively. More exact relations have been obtained for the two limits [13, 14]:

$$\begin{aligned} \text{displacive limit } k_B T_c &= 2.6C \\ \text{order–disorder limit } k_B T_c &= 9.1C. \end{aligned} \tag{6}$$

The thermal probability distribution $P(Q)$ at different temperatures was obtained using the Metropolis algorithm [15] in a supercell $10 \times 10 \times 10$, using 2×10^7 Monte Carlo steps after a previous thermalization process of 5×10^5 steps. As the probability distribution should be symmetrical with respect to $Q = 0$, the final set of configurations was doubled by associating each configuration having a certain value Q for the order parameter, with both $+Q$ and $-Q$. Then, the per-site ‘Landau function’ f_L in E_0 energy units, defined as $f_L(Q) = (1/NE_0) \Delta F_L(Q)$, was calculated by applying equation (3). Figure 1 shows a pair of examples, above and below the phase transition temperature, of the resulting distribution $P(Q)$ for the case $C/E_0 = 1$ and the corresponding $f_L(Q)$. In figure 2, the form obtained for $f_L(Q)$ at several temperatures is depicted for the same C/E_0 -value. In the figure, one can nicely see the qualitative behaviour predicted by the Landau theory for the temperature variation of the Landau free energy.

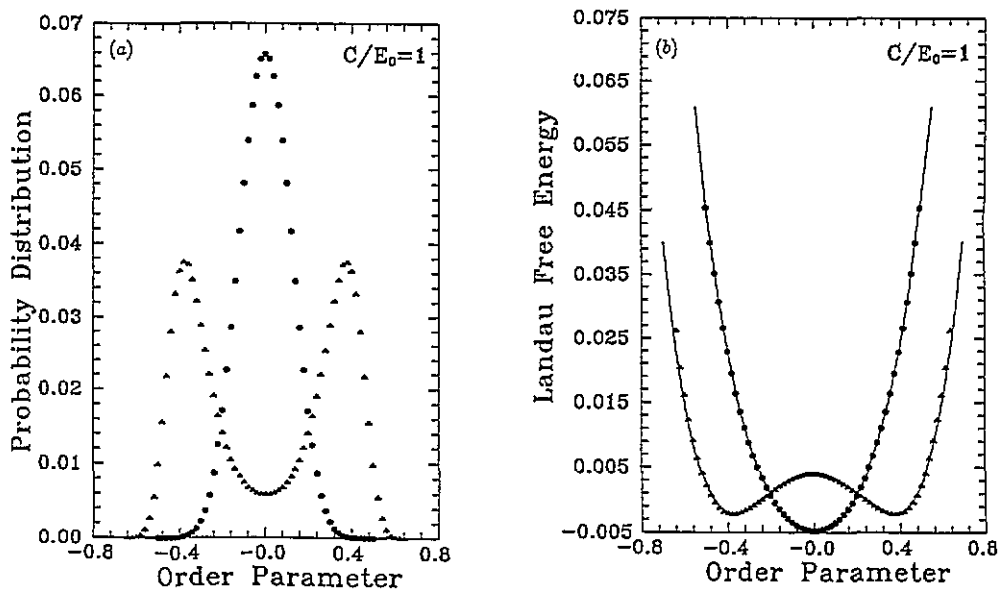


Figure 1. (a) Probability distribution of the order parameter Q and (b) corresponding Landau free energy per site according to (3) for $k_B T = 4E_0$ (\bullet) and $3.3E_0$ (\blacktriangle) in the case $C/E_0 = 1$: (b) resulting fits with a polynomial up to fourth-order term.

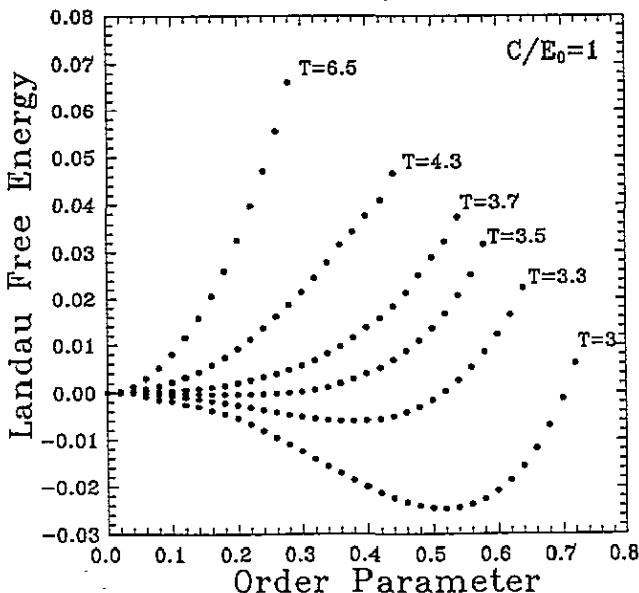


Figure 2. Monte Carlo Landau free energy f_L for $C/E_0 = 1$ for several temperatures, above and below the transition point. The functions have been arbitrarily translated along the vertical axis so that they all coincide at the origin.

The functions $f_L(Q)$ were fitted to the usual polynomial form

$$f_L(T, Q) = f_0 + A Q^2 + B Q^4 + \dots \tag{7}$$

The fitting was done with a weighting scheme that took into account the increasing statistical error of the points for large f_L -values. This proved to be essential for obtaining consistent results. Figure 1(b) shows some of these fits. Except for points very close to the transition temperature (see figures 3 and 4) where sixth-order terms were necessary, the function was in general well represented by a polynomial up to the fourth order. However, both the coefficient A and the coefficient B were in general temperature dependent. Their values as a function of the reduced temperature are depicted in figures 3 and 4, respectively, for all cases investigated ($C/E_0 = 0.1, 1, 10$). Well above the phase transition, the form of the function f_L becomes essentially parabolic and could be well described by the form (7) truncated at the quadratic term. At these temperatures it was senseless determining the coefficient B . This, however, should not be taken as an indication that B becomes zero; instead, it is related to the fact that, as the system moves away at high temperatures from the phase transition region, the hardening of the coefficient A makes the Landau free energy stiffer and a smaller range of Q -values is visited in the Monte Carlo runs (figure 5); the $f_L(Q)$ obtained is then limited to a Q -range where the effect of the B -term becomes negligible. Similarly, far below the phase transition, the statistics to determine the wings of the Landau function become very poor, as only a small parabolic region in the proximity of the deep minima is considered in the simulation. The truncation of the polynomial (7) up to fourth order was clearly a poorer approximation for the case $C/E_0 = 0.1$ where the inclusion of sixth-order terms was necessary in a larger region (in reduced temperature) around T_c , and even an eighth-order term seems to be present close to T_c .

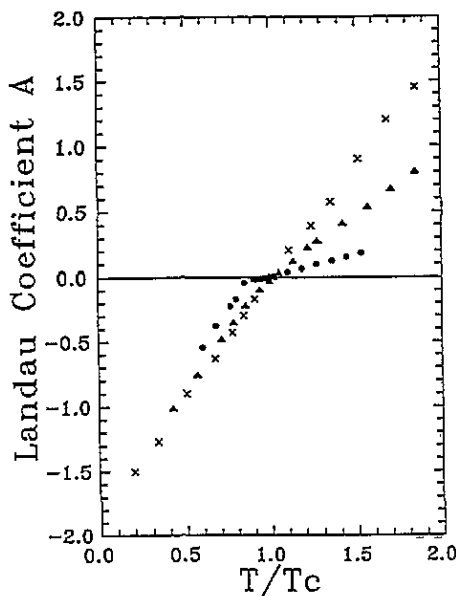


Figure 3. Temperature dependence of the quadratic Landau coefficient (A in equation (7)) for the three cases studied: \bullet , $C/E_0 = 0.1$; \blacktriangle , $C/E_0 = 1$; \times , $C/E_0 = 10$.

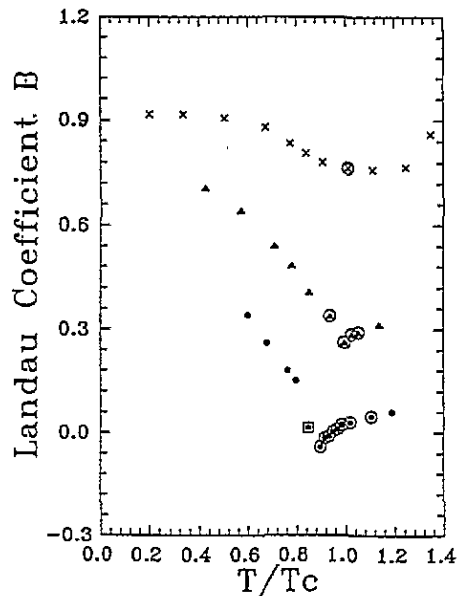


Figure 4. Temperature dependence of the quartic Landau coefficient (B in equation (7)) for the three cases studied. The symbols are the same as in figure 3. The points which required the inclusion of a sixth- and an eighth-order term in the fitted polynomial are indicated by an additional circle and square, respectively.

The size of the supercell used had to be a compromise between the necessity of a small sample to make statistical fluctuations sufficiently probable and sufficiently large to minimize finite-size effects. By observing the convergence of the values obtained for A and B for different supercell sizes, we could estimate that their errors in the $10 \times 10 \times 10$ calculation were less than 0.05. The transition temperatures obtained were $k_B T_c / E_0 = 0.589, 3.52$ and 29.7 for $C/E_0 = 0.1, 1$ and 10 , respectively. Their difference from the values predicted (see equation (6)) for the displacive and order-disorder limits indicates more the deviation of the system from these limits rather than a finite-size effect; similar coarse simulations done for $C/E_0 = 0.01$ and 100 yielded transition temperatures $k_B T_c / E_0$ of 0.098 and 276 , respectively, in accordance with the two limiting temperatures in (6). Obviously, finite-size effects can be very important very close to the phase transition where large-scale fluctuations take place, but we should stress that this region, which is small on the temperature scale considered in figures 3 and 4 [5], is outside the scope of the present study. The relative small size of the supercell was also favourable to avoiding, in the Monte Carlo sampling, the presence of configurations where the coexistence of 'macroscopic' domains having opposite values of the order parameter could spoil the calculated probability distribution which, by definition, should correspond to a single domain.

3. Discussion

According to its definition (1), as T goes to zero, the Landau free energy per cell for a certain value of Q must become equal to the mechanical energy of the configuration

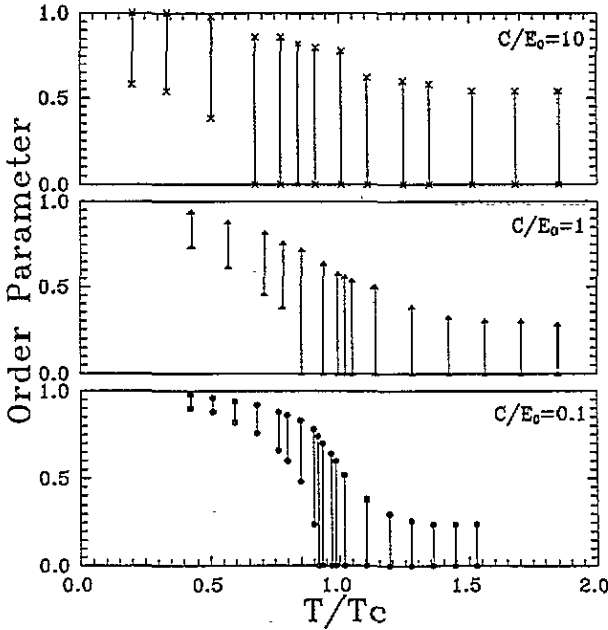


Figure 5. Temperature variation of the range of the order parameter considered in the Metropolis runs in the three cases studied. At each temperature, the relevant interval is indicated with a full line.

of minimal energy within the set of those having this Q -value. As stressed above, the Landau free energy is a thermodynamic function associated with the bulk material as a single-domain, i.e. surface or interphase (domain walls) energetics are not considered, and, for systems presenting several macroscopic or pseudo-macroscopic domains with different Q -values, a Landau function can be associated, separately, with the bulk of each domain. Therefore, disregarding polydomain configurations, the configuration of lowest energy, for a fixed value of Q , is the homogeneous configuration with $x_i = Q$ for all i , which has no energy contribution from the elastic term in (4). Accordingly, as T goes to zero, the Landau free energy per cell must approach the local potential $V(x)$, while the free energy F becomes equal to the minimum of $V(x)$ (zero in our case). Consequently, considering (5) and (7), we should expect that $f_0(0) = 1$, $A(0) = -2$ and $B(0) = 1$ (in E_0 units). The temperature dependence of the coefficients in figures 3 and 4 is in accordance with this expected low-temperature limit, which differs from that assumed in [1].

According to figure 4, the temperature variation in the coefficient B strongly depends on the model parameters. In all cases it has a minimum close to the transition temperature, but this minimum becomes much deeper for systems approaching the order-disorder limit. The existence of a minimum in $B(T)$ at the transition point represents a surprising additional support of the hypothesis in the Landau theory of a constant B in a region close to the transition point. This approximation is usually justified as a zeroth-order approximation for a function which is expected to be weakly temperature dependent [6]. However, the coefficient B exhibits in general a strong temperature dependence when compared with $A(T)$. It is the presence of the minimum that justifies a constant B approximation in the neighbourhood of the transition. The tendency of B to have small values at the transition point would explain the frequent observation of systems close to tricritical behaviour, which

should be related to the order–disorder character of the microscopic mechanism involved in the transition. The quite discontinuous behaviour of the coefficient B at points around its minimum is probably due to uncertainties because of the fitting problems mentioned above. On decreasing the temperature, the largest discontinuity typically happens at the temperature where the origin of Q becomes unaccessible in the Monte Carlo simulations, and the fit is reduced to polynomials up to fourth-order terms.

Independently of the system parameters, according to figure 3, the variation in $A(T)$ with temperature is approximately linear in large temperature intervals, above and below the phase transition. However, the slope of this linear relation changes around the transition temperature; this change tends to zero in the displacive limit and increases for systems approaching the order–disorder limit. In the case closer to the order–disorder limit, the change in slope is centred at a temperature somehow lower than T_c . It can be clearly seen in the figures that, obviously, when one limits the observation to a small temperature interval around the phase transition where the coefficient B can be considered to be approximately constant, a constant linear variation in $A(T)$ common to temperatures above and below the transition is a good approximation. This ‘Landau interval’, where the Landau hypothesis for the polynomial coefficients is valid, would extend in the displacive limit to the whole temperature range of the distorted phase and decreases rapidly for systems approaching the order–disorder regime, as expected from general arguments [7]. The important point is that even outside this interval the temperature variation in the coefficient A is also approximately linear. This means, for instance, that the order parameter susceptibility when considered in large temperature intervals should follow a Curie law, but the well known Landau-theory-predicted 0.5 slope ratio for the inverse of the susceptibility above and below the transition is substituted by a smaller ratio, as the system becomes closer to the order–disorder limit.

In the Landau approximation, the thermal equilibrium value of the order parameter can be identified with that minimizing the Landau free energy [6]. The temperature dependence in the distorted phase of this spontaneous equilibrium order parameter for the three cases investigated is shown in figure 6. For the cases $C/E_0 = 10$ and 1, their temperature variation could be fitted to a power law $|T - T_c|^b$ in the whole temperature range of the low-temperature phase with $b = 0.47$ and 0.33, respectively (we use b to avoid confusion with the critical index β). In the case closer to the order–disorder limit, however, a fit in the whole range was not possible and a fit limited to an interval around the transition yielded a value $b = 0.26$. In accordance with Giddy *et al* [1,4], the exponent b , starting from 0.5, decreases as the system deviates from the displacive limit. Values of the order of 0.3 are obtained for C/E_0 -values of the order of unity. However, the observed deviation from the Landau prediction for a polynomial truncated up to fourth order cannot be considered to be the result of the relevance of a constant sixth-order term, as usually assumed [7], but is essentially a consequence of the important temperature variation of the fourth-order coefficient. In the case closer to the order–disorder limit ($C/E_0 = 0.1$) the function $Q(T)$ is nearly step like near the phase transition, indicating the very small value of B and its tendency to become a first-order transition.

Within the Landau approximation, the free-energy difference between the distorted and the non-distorted phase at each temperature is given by $F_L(Q_0) - F_L(0)$, where Q_0 is the order parameter value at the Landau free-energy minimum. In figure 7, the temperature variation in this quantity (per cell) is shown. In contrast with the important differences for other quantities discussed above, the behaviour of this free-energy difference is very similar in the three cases investigated. The accuracy of the method is, however, not sufficient to analyse differences in the first and second derivatives corresponding to the transition entropies and specific heats.

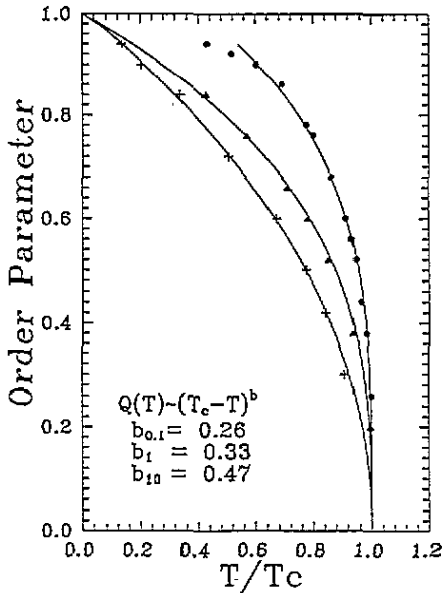


Figure 6. Temperature variation of the order parameter in the three cases studied, with their fit to a power law $|T - T_c|^b$. The symbols are the same as in figure 3.

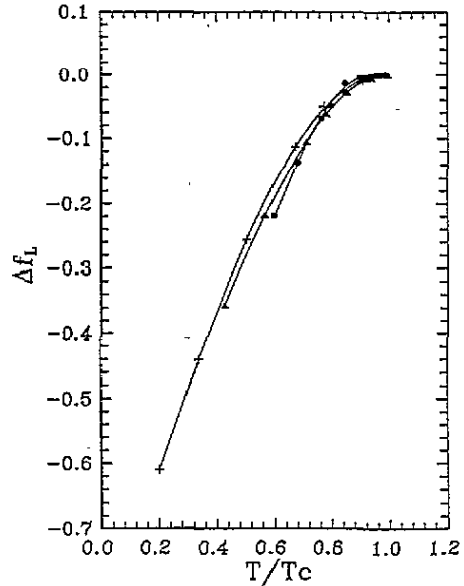


Figure 7. Temperature variation of the per-site free-energy difference between the distorted and the non-distorted phase calculated as indicated in the text. The symbols are the same as in figure 3.

4. Concluding remarks

It should be stressed that the simple Monte Carlo method employed explores only a small range of Q -values around the equilibrium value, and therefore at each temperature only a small portion of the Landau free energy is accessible. In general, the fitted polynomials only represent with confidence the Landau potential in the Q -interval visited by the Monte Carlo method. This is not critical at temperatures around the phase transition where the large fluctuations in Q make the Landau function observable in a wide interval around $Q = 0$ (see figure 5). At lower temperatures, however, the minima of the function are so pronounced that only values of the function around these off-centre values are obtained and the polynomial fit becomes ambiguous. Typically, the region accessible in these cases is limited to a parabolic region around the minimum; the function is then fully determined by the position of these minima and their curvature, and it can always be represented by a polynomial truncated up to fourth order; lacking additional information, any fit with higher-order terms would have no meaning. However, there is no guarantee that the polynomial so obtained is valid around the origin, or in other Q -intervals not considered. We checked this fact by performing Monte Carlo calculations analogous to those above, but with an applied external field E conjugate to the order parameter. According to its definition, the only change in the Landau free energy is the addition of a term $-QE$ and a change in f_0 . However, both coefficients A and B of the fitted polynomial suffered a significant variation, while keeping the general qualitative behaviour with temperature. This must be related to the important variation in the interval of Q that is examined when the field is applied. One can then state that A and B are Q dependent [1], and the values reported above refer only to the Q -interval around the equilibrium value. Alternatively, one could describe the situation by means of Landau expansions with Q -independent coefficients including

sixth- and higher-order terms, but then the values of the coefficients cannot be determined from the samplings obtained. In any case, a description in terms of Q -dependent Landau coefficients is probably more adequate when dealing with large values of Q . In this respect, it is interesting to see, for instance, the analytical limit of the Landau free energy for large Q -values at any temperature. In terms of Fourier components, the energy (4) can be written in the form [13]

$$\begin{aligned} \frac{H}{N} \simeq & 1 - 2Q^2 + Q^4 + \frac{1}{N} \sum_k \omega^2(k) |Q_k|^2 + \frac{1}{N^2} \sum_{k_1, k_2, k_3, k_4} Q_{k_1} Q_{k_2} Q_{k_3} Q_{k_4} \Delta(k_1 + k_2 + k_3 + k_4) \\ & + \frac{1}{N^{3/2}} 4Q \sum_{k_1, k_2, k_3} Q_{k_1} Q_{k_2} Q_{k_3} \Delta(k_1 + k_2 + k_3) + \frac{1}{N} 6Q^2 \sum_k |Q_k|^2 \end{aligned} \quad (8)$$

where the sums are limited to non-zero k -values and $\Delta(k)$ is unity for k a reciprocal-lattice vector and zero otherwise. In the limit of large Q we can neglect quartic, cubic and quadratic terms in the Fourier components except the term proportional to Q^2 , and we can approximate the Landau free energy by

$$\frac{F_L}{N} \simeq 1 - 2Q^2 + Q^4 - \frac{k_B T}{N} \ln \left[\int \prod_k dQ_k \exp \left(\frac{-6Q^2}{k_B T} \sum_k |Q_k|^2 \right) \right] \quad (9)$$

which yields

$$\frac{F_L}{N} \simeq 1 - 2Q^2 + Q^4 - k_B T \ln \left(\frac{\pi k_B T}{6Q^2} \right). \quad (10)$$

When the physically relevant Q -values are restricted by a certain field to a small interval around a non-zero value Q_0 , the logarithm in (10) can be expanded and the function (10) can be well represented by a polynomial of type (7) restricted up to fourth order, with $A = -2 + 2k_B T/Q_0^2$ and $B = 1 - k_B T/2Q_0^4$. Hence, as could be expected, at any temperature, the wings of the Landau free energy coincide with those of the local potential function $V(x)$ at sufficiently high values of the order parameter, irrespective of the polynomial form valid for values of Q close to zero. Although quite academic, because of the physical irrelevance of the function at such high values of the order parameter, this limit evidences the drawbacks of an extension of the Landau expansion to higher-order terms for describing the Landau free energy in regions far apart from the origin.

In practical terms and translated into real systems, the observed Q -dependence of the Landau coefficients implies that their experimental values can depend on the Q -interval visited by the system during the experiment and, therefore, are in general not 'transportable'.

The final question is what can be taken as model independent in the results above. Obviously, the zero-temperature limits of the coefficients A and B depend on the model on-site potential and they should have an important influence in their temperature behaviour far below the transition temperature. However, some of the trends observed in their temperature behaviour are probably general. In [9], for instance, where a discotic liquid crystal was simulated, the very small value obtained for the fourth-order coefficient was also stressed. Hence, we conjecture that the minimum observed in the fourth-order coefficient is a quite general property, and the same may happen with the change in slope observed for the quadratic coefficient. Similar investigations in different microscopic models are necessary for obtaining a final answer. Also, more complex Monte Carlo techniques such as umbrella sampling should be used to obtain information on more extended intervals of the order parameter space, so that the ' Q -dependence' of the Landau coefficients can be investigated.

What becomes clear is that one should refrain from extending Landau potentials by including higher-order terms with temperature-constant coefficients, when correcting the simplest Landau behaviour for temperature intervals far from the transition point.

Acknowledgments

The collaboration of M Aguado in the preliminary stages of this work is gratefully acknowledged. This work has been partially supported by the Spanish DGICYT (project PB91-0554).

References

- [1] Giddy A P, Dove M T and Heine V 1989 *J. Phys.: Condens. Matter* **1** 8327
Heine V, Chen X, Dattagupta S, Dove M T, Evans A, Giddy A P, Makais S, Padlewski S, Salje E and Tautz F S 1992 *Ferroelectrics* **128** 255
- [2] Salje E K, Wruck B and Thomas H 1991 *Z. Phys. B* **82** 399
- [3] Sollich P, Heine V and Dove M T 1994 *J. Phys.: Condens. Matter* **6** 3171
- [4] Giddy A P, Dove M T and Heine V 1990 *Ferroelectrics* **104** 331
- [5] Ginzburg V L, Levanyuk A P and Sobyenin A A 1987 *Ferroelectrics* **73** 171
- [6] Landau L D and Lifshitz E M 1980 *Statistical Physics* (Oxford: Pergamon)
- [7] Strukov B A and Levanyuk A P 1993 *Physical Principles of Ferroelectric Phenomena in Crystals* (Moscow: Nauka) (in Russian)
- [8] Ciccotti G, Frenkel D and MacDonald I R 1990 *Simulation of Liquids and Solids: Molecular Dynamics and Monte Carlo Methods in Statistical Mechanics* (Amsterdam: North-Holland)
- [9] Eppenga R and Frenkel D 1984 *Mol. Phys.* **52** 1303
- [10] Kaski K, Binder K and Gunton J D 1984 *Phys. Rev. B* **29** 3996
- [11] Milchev A, Heermann D W and Binder K 1986 *J. Stat. Phys.* **44** 749
- [12] Newlove S A and Bruce A D 1985 *J. Phys. A: Math. Gen.* **18** 589
- [13] Bruce A D 1980 *Adv. Phys.* **29** 111
- [14] Oppermann R and Thomas H 1975 *Z. Phys. B* **22** 387
- [15] Binder K 1979 *Monte Carlo Methods in Statistical Physics* (Berlin: Springer)