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Strain-related fluctuations near tricritical points: first-order transitions for anisotropic fluctuations and coupling with a tracer order parameter

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Abstract. Fluctuations of order parameters Q near a tricritical point coupled with strain $e(\propto eQ^2)$ lead to fluctuation-induced first-order phase transitions. Anisotropic fluctuations with strong correlations along a 'hard' direction show a much reduced first-order behaviour. In the case of improper ferroelastics the fluctuation-related renormalizations become immeasurably small and a classic tricritical behaviour is expected.

Experimental observations of such fluctuations are facilitated if the fluctuating order parameter couples bi-quadratically with a second, non-critical order parameter which is used as tracer. The fluctuation-induced renormalization of the tracer order parameter is calculated.

1. Introduction

The theory of fluctuation corrections to Landau theory with elastic degrees of freedom predicts first-order phase transitions in solids for a great number of physical scenarios [1–6]. In case of the margins of the applicability of Landau theory, elastic coupling of the type λeQ^2 (where e is the strain, Q is the order parameter and λ is a coupling constant (e.g. in improper ferroelastic transitions) [7]) leads to stepwise transitions for short-range interactions for $d = 4$ and dipolar interactions for $d = 3$ but continuous transitions are possible for higher dimensions [8, 9]. Under pinned boundary conditions, for uniaxial dipolar systems of hexagonal and trigonal symmetry second-order transitions were predicted, whereas a stepwise behaviour is expected for other symmetries (unless the transition occurs at a uniaxial Lifshitz point) [10]. Experimentally, it appears that the first-order step of the transition can be smaller than the experimental resolution. The term 'weakly first-order' or 'almost second-order' transition is often employed to describe a situation where all experimental evidence shows a continuous phase transition although theory tells us that a small discontinuity should or could exist. Note, however, that in the case of a proper ferroelastic transition with coupling of the type λeQ the continuous transition is always possible and this is, indeed, what is often observed experimentally [7]. For a review of the experimental situation see [11, 12].

Whereas the first-order nature of improper ferroelastics and related materials may often justifiably be ignored, this is not the case for another marginal condition. Levanyuk *et al* [1] have shown that (nearly) tricritical systems with linear–quadratic strain coupling (i.e.

$\lambda e Q^2$) also become first-order when the fluctuations are properly accounted for. The origin of the first-order effect is not just the classic renormalization of the coefficients in the Landau potential (which depends on their initial values) but relates to the appearance of a fluctuation-induced third-order term $\propto |Q|^3$. In isotropic systems this term can be large and will always generate a first-order transition independent of the original form of the Landau potential (as long as the system is close to a tricritical point).

The advantage in focusing on tricritical systems is not only that such systems are surprisingly widespread amongst improper ferroelastic materials [7] but also that it is possible to treat the fluctuations in perturbation theory [1]. In fact, our perturbation theory is applicable only if the renormalized coefficient of the fourth-order term in the Landau potential of the homogeneous part of the order parameter is small compared with the equivalent coefficient of the inhomogeneous contribution to the free energy. This condition is not met in a case of an ordinary second-order phase transition. We will argue that the second condition for our approach is that for a phase transition close to (but not at) a tricritical point the shear modulus μ does not vanish.

Although the approach in [1] seems to describe the situation of the stepwise transition in NH_4Cl [13] (and possibly quartz [14, 15]) correctly, it is at variance with observations in improper ferroelastics. Tricritical behaviour (or very closely so) is observed in the $Pb_3(PO_4)_2$–$Pb_3(VO_4)_2$ system [16–19], in GMO [20], and other systems [7, 21–24]. We also find continuous transitions close to the tricritical point in co-elastic materials such as $CaCO_3$ and $NaNO_3$ (always within experimental resolution) [25–28]. We show in this paper that these observations can be explained if the anisotropic nature of fluctuations in these materials is included in the theory. We find that all fluctuation-induced effects scale as the inverse correlation volume and can be quite small for improper ferroelastic phase transitions.

The second question relates to the possibility of observing the fluctuations experimentally. Two main obstacles seem to exist. Firstly, it is always difficult in real materials to distinguish between intrinsic fluctuation effects and those generated by defects. Secondly, order parameter fluctuations above the transition point (as observed spectroscopically or via specific heat measurements) have to be subtracted from an (often ill-defined) baseline signal (see [7] for review). This latter problem may be overcome in the following situation. Let a material display two (or more) transitions. Two order parameters will then couple, most commonly as $Q_1^2 Q_2^2$. This coupling is compatible with all symmetry constraints [7]. Near the lower transition temperature the second-order parameter is non-zero. Its value will be modified by the first-order parameter and its fluctuations. It is possible, therefore, to investigate fluctuations of the critical order parameter via the tracer of a non-critical order parameter. We will show that these effects should be experimentally observable.

2. Anisotropic order parameter fluctuations and the first-order nature of the phase transition

The effective Hamiltonian has the form of the usual Landau potential. Following closely the nomenclature in [1] we write

$$\phi(Q, u) = \int [\varphi(Q) + \varphi(Q, u)] \, dv \tag{1}$$

with

$$\varphi(Q) = \tfrac{1}{2} A Q^2 + \tfrac{1}{4} B Q^4 + \tfrac{1}{6} C Q^6 + \tfrac{1}{2} D_{\parallel} (\nabla Q)_{11}^2 + \tfrac{1}{2} D_{\perp} (\nabla Q)_{\perp}^2 \tag{2}$$

$$\varphi(Q, u) = r Q^2 u_{11} + \tfrac{1}{2} K u_{11}^2 + \mu (u_{ik} - \tfrac{1}{3} u_{11} \delta_{ik})^2 \tag{3}$$

where Q is the order parameter, u_{ik} is the strain tensor and r is the coupling constant. The Ginzburg energy coefficient D is anisotropic with $D_\parallel$ along the unique direction (e.g. the direction of the intersection of ferroelastic twin planes) and $D_\perp$ in the plane perpendicular to the unique direction. Strictly speaking, we should also consider the elastic energy to be fully anisotropic. This effect would probably enhance the reduction of the fluctuations which we wish to describe and does not lead to a fundamentally different physical picture. We abstain from a full treatment of the anisotropy of the elastic constants in this paper because it leads to unnecessarily complicated expressions for the free energy without contributing much to our physical understanding. Some aspects of the effect of anisotropic elastic behaviour have previously been discussed in [10]; here we restrict ourselves to the most simple approach. Integrating out the elastic degrees of freedom leads to the renormalized uniform expression of the free energy F_0 which still has the usual Landau form with $\tilde{B} = B - 2r^2/K$. The non-uniform part, on the other hand, becomes

$$F_h = \tfrac{1}{2}\left[\sum_{k\neq 0}(A + 3B_1 Q_0^2 + 5CQ_0^4 + D_\parallel k_z^2 + D_\perp(k_x^2 + k_y^2)\right] Q_k Q_{-k} \tag{4}$$

with $B_1 = B - \frac{2}{3}r^2/K - \frac{4}{3}r^2/\lambda$ and $\lambda = K + \frac{4}{3}\mu$. The applicability of our approach is constrained by the condition [1] $\tilde{B}/B_1 < 2/3$. Note that this condition is violated for $r = 0$ (no strain coupling) or $\mu = 0$ (vanishing shear modulus). The expression (4) is for $D_\parallel = D_\perp$ identical with the result in [1] (their equation (8)). In the case of an (almost) tricritical phase transition we find the fourth-order term in F_0 to disappear ($\tilde{B} = 0$). The equivalent term in F_h is B_1 which is always greater than $\tilde{B}$ due to the elastic interaction, i.e. $B_1 > 0$. We now evaluate the free energy expression of ϕ related to F_h. Within perturbation theory one finds

$$\Delta\phi = -T \log \int \exp\left(-\frac{F_h}{T}\right) \Pi_k \, \mathrm{d}Q_k. \tag{5}$$

Here we made use of the Gaussian character of the fluctuations (as an essential approximation).

Replacing the summation by an integration leads to

$$\Delta\phi = \frac{VT}{12\pi^2} k_m^3 \left[\ln(\alpha + D_\parallel)\frac{k_m^2}{T}\right] + 2\left[\frac{(\alpha + D_\perp)^{3/2}}{D_\perp\sqrt{D_\parallel - D_\perp}} \tan^{-1}\sqrt{\frac{D_\parallel - D_\perp}{\alpha + D_\perp}} - \frac{(\alpha)^{3/2}}{(D_\parallel D_\perp^2)^{1/2}} \tan^{-1}\sqrt{\frac{D_\parallel}{\alpha}}\right] \tag{6}$$

where k_m is the relevant zone boundary wavevector and

$$\alpha = (A + 3B_1 Q_0^2 + 5CQ_0^4)/k_m^2. \tag{7}$$

Two limiting cases can be obtained without further calculations. In case of $D_\parallel = D_\perp = D$, we recover the result for the isotropic behaviour:

$$\Delta\phi \approx \frac{VT}{12\pi^2} k_m^3 \left[3\frac{\alpha}{D} - \pi\frac{\alpha^{3/2}}{D} + \text{constant}\right] \qquad \text{for } \frac{\alpha}{D} \ll 1. \tag{8}$$

The term linear in α renormalizes the Landau potential by changing the transition temperature without modifications to the form of the Landau potential. The term proportional to $\alpha^{3/2}$ is the origin of the first-order step discussed by Levanyuk *et al.* For $\alpha \propto Q_0^2$ this term leads to a fluctuation-induced third-order term $|Q_0|^3$ which is not part of the original static Landau potential. Our result is, of course, identical to that in [1].

Let us now consider the other extreme case, namely the most anisotropic fluctuations such as we would expect to occur in improper ferroelastics. In this case we consider, as the mildest effect, $D_\parallel \to \infty$, whereas $D_\perp$ remains finite:

$$\Delta\phi = \frac{VT}{12\pi^2}k_m^3\left\{\frac{\alpha}{D_\parallel} + \frac{3\alpha\pi}{2D_\perp^{1/2}(D_\parallel - D_\perp)^{1/2}} - \pi\left(\frac{\alpha^3}{D_\parallel D_\perp^2}\right)^{1/2} + \text{constant}\right\}. \tag{9}$$

The α-dependent part of this expression becomes zero for $D_\parallel \to \infty$, so no fluctuation corrections occur in this case. The most relevant last term disappears as the inverse correlation volume

$$\propto \left(\sqrt{D_\parallel D_\perp^2}\right)^{-1}$$

showing that any large correlations will annihilate the fluctuation corrections. The crux of the matter is that one direction is sufficient for the suppression of the fluctuation correction altogether.

For intermediate cases, it is easy to show that the power-law expansion of $\Delta\phi$ remains as

$$\Delta\phi = A^*\left(\frac{\alpha D}{D_\perp}\right) + B^*\left(\frac{\alpha D}{D_\perp}\right)^{3/2} + C^*\left(\frac{\alpha D}{D_\perp}\right)^2 \tag{10}$$

with $B^* = -\pi\sqrt{D_\perp/D_\parallel}$. The values of A^* and C^* depend on the regime $D_\parallel \leqslant 2D_\perp$ or $D_\parallel \gg D_\perp$. For the latter we find in the lowest-order approximation that all coefficients A^*, B^* and C^* are of the same order of magnitude. This shows that the fluctuation correction decreases for $D_\parallel \gg D_\perp$ as $(D_\perp/D_\parallel)^{1/2}$ without major changes of the functional form of $\Delta\phi$ for $\alpha/D_\perp \ll 1$. The results of numerical calculations are shown in figure 1.

3. Detection of fluctuations by a tracer order parameter

Two interacting order parameters show a multitude of equilibrium configurations [7, 29–32] and domain structures which are characterized by chiral domain walls [31–35]. It has been shown that small variations of one order parameter can lead to substantial variations of the other [7], whereby this effect is amplified if the two critical temperatures are not too different. The analytical treatment and the experimental observations are reviewed in detail in [7] with further discussions in [32, 24, 18, 20–22]. In the context of the present discussion it is sufficient to consider a system of two order parameters, Q_1 and Q_2, with each subsystem described by the equations (1)–(3). The coefficients of the subsystem of Q_1 are dentoed by a subscript 1 and those of Q_2 with a subscript 2. The two subsystems are coupled via an additional energy $\frac{1}{2}B^*Q_1^2Q_2^2$. As the strain couples with each order parameter separately, we can treat each subsystem in exactly the same way as before. The uniform part of F becomes after elimination of the strain coordinates

$$F_0 = \tfrac{1}{2}A_1Q_1^2 + \tfrac{1}{4}\tilde{B}_1Q_1^4 + \tfrac{1}{2}A_2Q_2^2 + \tfrac{1}{4}\tilde{B}_2Q_2^4 + \tfrac{1}{2}B'Q_1^2Q_2^2 \tag{11}$$

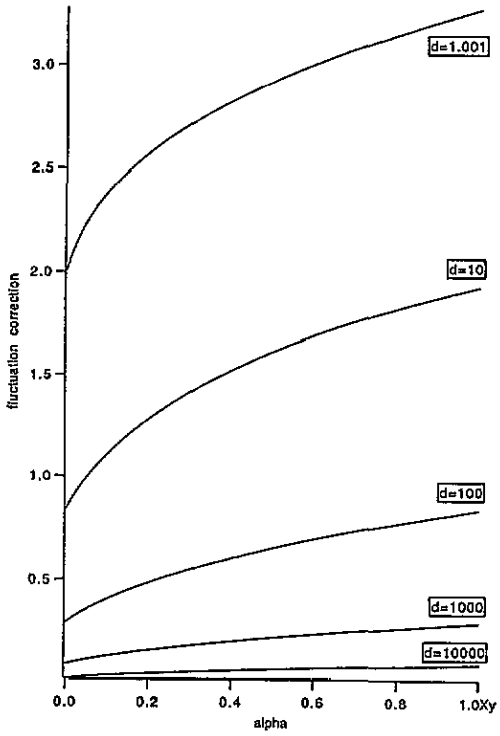

Figure 1. The functional form of the fluctuation correction in equation (6) for varying anisotropy parameter $d = D_{\parallel}/D_{\perp}$. Fluctuation-induced first-order transitions ($\propto Q^3$) are due to the curvature for small values of α. The curvature and the fluctuation correction disappear for highly anisotropic systems.

where $\tilde{B}_1 = B_1 - 2r_i^2/K$ and B' contains all coupling terms (direct and via strain [7]). This expression is similar to the case of a two-component order parameter except that all coefficients are indexed with respect to one of the two order parameters. Using the same formalism as in the case of one order parameter, one finds that the relevant fluctuation-related part of the free energy is

$$\Delta\phi \propto \frac{T}{2}\sum_k \log(\alpha_1^*\alpha_2^* - \alpha_3^{*2}) \tag{12}$$

where

$$\alpha_1^* = (A_1 + D_1k^2) + (\tilde{B}_1 + 2\hat{B}_1)Q_{10}^2 + B'Q_{20}^2 \tag{13}$$

$$\alpha_2^* = (A_2 + D_2k^2) + (\tilde{B}_2 + 2\hat{B}_2)Q_{20}^2 + B'Q_{10}^2 \tag{14}$$

$$\alpha_3^* = 2B'Q_{10}Q_{20}. \tag{15}$$

The index 0 indicates again the value of the uniform part of the order parameter. We consider now a situation in which the order parameter $Q_{10} \neq 0$ is well below its transition temperature. The uniform part of the second order parameter shall be zero, i.e. we envisage a structural state with $Q_{10} \neq 0$ and $Q_{20} = 0$ which is phase I in the nomenclature

of [7]. Cooling such a system often leads to structural phase transition to a phase III with $Q_{10} \neq 0$, $Q_{20} \neq 0$. At temperatures slightly above this transition point we expect $D_1k^2 \gg D_2k^2 \gg A_2$, so all thermodynamic fluctuations stem from Q_2 but not from $Q_1 = Q_{10}$. The fluctuations of Q_2 will modify the value of Q_{10}, however, because both order parameters are coupled. With $Q_{20} = 0$ we obtain after integration of equation (12)

$$\alpha_3 = 0 \tag{16}$$

$$\alpha_1 = \frac{A_1 + (\tilde{B}_1^1 + 2\hat{B}_1^1)Q_{10}^2}{k_m^2} \approx \text{constant} \tag{17}$$

$$\alpha_2 = \frac{A_2 + B'Q_{10}^2}{k_m^2}. \tag{18}$$

We now consider the behaviour at $A_2 \geqslant 0$ (i.e. slightly above the transition point of Q_2). The relevant part of ϕ is then in order Q_{10}^2:

$$\Delta\phi = \frac{VT}{12\pi^2}k_m^3\left[\ln\left(1 + \frac{A_2 + B'Q_{10}^2}{D_2k_m^2} + \cdots\right) + 2\left(\frac{A_2 + B'Q_{10}^2}{D_2k_m^2}\right)\right.$$
$$\left. - 2\left(\frac{A_2 + B'Q_{10}^2}{D_2k_m^2}\right)^{3/2}\tan^{-1}\left(\frac{D_2k_m^2}{A_2 + B'Q_{10}^2}\right)^{1/2} + \text{constant}\right]. \tag{19}$$

This term can induce some 'anomalous' behaviour in the temperature dependence of Q_{10} near the transition point of Q_2. In the case of weak coupling the $\tan^{-1}$-term can be approximated by $\pi/2$. In this case we find two corrections for Q_{10}. The first correction is a term quadratic in Q_{10} and proportional to B'. This term is positive for competitive interaction and reduces the order parameter Q_{10} in the fluctuation regime. The second term is proportional to $|Q_{10}|^3$ and is negative in the limit of weak coupling. This term will enhance Q_{10}, thereby partly compensating the effect of the first term. Although this partial compensation reduces the effect, the amplitude of ΔQ_{10} will remain relatively large, i.e. in the same order as in the case of the uniform coupling. Note also that the numerical values for the various parameters can be determined in the low-temperature phase with $Q_{10} \neq 0$, $Q_{20} \neq 0$, so the fluctuation correction can be calibrated.

4. Conclusion

The size of the fluctuation-induced first-order step depends sensitively on the numerical values of $D_\parallel$, $D_\perp$ and r. Levanyuk *et al* [1] show that the relevant dimensionless parameter is

$$g \approx \frac{T}{4\pi}\frac{\mu\pi^2}{K\lambda}\frac{1}{(A'T_0D^3)^{1/2}}.$$

This coefficient was roughly estimated to be a few 10^{-3} in NH_4Cl and this was enough to get a rather large step. For other materials the strain coupling may be weaker ($u_\parallel \approx 10^{-3}$ for $Q_0 = 1$) [7] and the correlation constant D larger ($Dk_m^2 \geqslant 100A'T_0$) [33, 34]. The step is then found to be well below the experimental level of detection.

The fluctuation-induced stepwise behaviour may also not occur (within experimental resolution) in most improper ferroelastics with tricritical phase transitions [7]. At temperatures slightly below the observed (i.e. renormalized) transition point, they form characteristic domain structures. These domain structures consist of tweed and stripes (i.e. walls) perpendicular to two soft directions. The junctions between the walls define the third, hard direction along which no domain structures seem to exist [7]. Careful experimental observations give no evidence for fluctuations along the hard direction indicating $D_\perp/D_\parallel \to 0$. Fluctuation corrections become irrelevant for such materials. The same argument also applies (and even to a greater extent) to proper ferroelectric or ferroelastic transitions, since the long-range character of the interactions induces a singular correlation energy ($\propto (Dk^2 + D'(k/k)^2)$ for the dipolar case). This is roughly equivalent to an infinite $D_\parallel$ in our calculations.

We have also shown that in the case of coupled order parameters the fluctuations of one order parameter renormalize the value of the uniform part of the second order parameter. As it is experimentally easier to measure such uniform order parameters with a high degree of resolution rather than to measure fluctuations, it might be possible to quantify fluctuations using a second order parameter as a tracer. We hope that this idea may stimulate experimental work which could test the validity of our idea.

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