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LETTER TO THE EDITOR

Quantum fluctuations of order parameters in structural phase transitions and the pressure dependence of transition temperatures

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Abstract. Low-temperature saturation of the temperature dependence of order parameters $Q(T)$ leads to highly nonlinear phase boundaries $T_c(x)$ in (T_c, x) space where x is a secondary field variable. A typical experimental parameter x is the external pressure p or an electric field E which couple with the square of the order parameter ($H_{coupling} = \gamma x Q^2$). The general characteristics of $T_c(x)$ are derived in mean field theory for ϕ^4 and ϕ^p models. It is shown that in several cases the function $T_c(x)$ can be found by direct inversion of the function $Q(T)$ with the parameter mapping $\gamma Q^{p-2} \to x$.

1. Introduction

Phase transitions in ferroelastics and related materials with long-ranging order parameter correlations were found to follow Landau-type behaviour over large temperature intervals. Indeed, hardly any deviation from the predicted temperature evolution of the order parameter between T_c and absolute zero temperature was observed in several systems, provided that theoretical predictions take proper account of quantum saturation at low temperatures [1–9].

The close correlation between Landau theory of displacive phase transitions and the more general theory of the statistical mechanics of a ϕ^4 model was pointed out previously [10–14]. Monte Carlo simulations using *ab initio* Hamiltonians also show very similar results as those derived analytically or self-consistently in mean-field theory. In all cases, the effect of quantum saturation in these order parameters became independent of temperature at sufficiently low temperatures. This is a fundamental physical feature because the third law of thermodynamics requires that the entropy changes, and hence order parameter changes, at absolute zero temperature are zero. A consequence of the order parameter saturation at low temperatures is a highly nonlinear dependence of the phase transition temperature T_c on the secondary control parameters x which couple with the order parameter Q via an interaction energy

$$H_{coupling} \propto x Q^2.$$

The effect of quantum saturation on phase diagrams was treated previously [3, 15–19] using a Landau-type energy expression for the order parameter in the displacive limit

$$G = \frac{1}{2} A\theta_s \left(\coth \frac{\theta_s}{T} - \coth \frac{\theta_s}{T_c} \right) Q^2 + \frac{B}{4} Q^4 + \frac{C}{6} Q^6 + \frac{A\theta_s k}{2} x Q^2$$

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which leads to the transition temperature $T_c\ (x)$ as

$$T_c(x) = \frac{\theta_s}{\coth^{-1}(\coth(\theta_s/T_c) - kx)}.$$

In this paper we argue that similar effects are predicted in self-consistent theory under more general conditions away from the displacive limit. We also show that the physical origin of the x-dependence of T_c is clearly seen in the local deformation of atomic potentials.

2. The model

The theoretical model and mean-field treatment in [1] is reformulated in order to make the various physical parameters intuitive. The model Hamiltonian is [1]

$$H = \sum_{\ell} \frac{1}{2m} p_\ell^2 + V(Q_\ell) + \frac{1}{4} \sum_{\ell,\ell'} \upsilon_{\ell\ell'}(Q_\ell - Q_{\ell'})^2$$

$$V(Q_\ell) = (-2Q_\ell^2 + Q_\ell^4)E_0$$

where m is the effective mass associated with the coordinates Q_ℓ, P_ℓ are the conjugate momenta and $V(Q_\ell)$ is the local potential. The type of transition is determined by the wavevector q_0 at which the Fourier transform of the interaction $\upsilon_{\ell\ell'}$ assumes its maximum value υ. In the context of this paper we consider $q_0 = 0$. The model Hamiltonian represents the classic ϕ^4 model, although extension to higher-order terms ϕ^6 [1] and ϕ^p [20–23] will be discussed later. The following parameters are now defined for convenience:

$$\upsilon = \sum_{\ell'} \upsilon_{\ell\ell'} \qquad \varepsilon_0 = \frac{E_0}{\upsilon}.$$

The parameter E_0 describes the nature of the transition $\varepsilon_0 \to 0$ in the displacive limit and $\varepsilon_0 \to \infty$ in the order–disorder (o/d) Ising limit. The quantum effects depend on the atomic mass with the saturation temperature [1–3]

$$\theta_s = \frac{1}{2}\frac{\hbar}{k_B}\left(\frac{\upsilon}{m}\right)^{1/2}.$$

In the Einstein quasi-harmonic approximation the variational equations for the thermodynamic limit of the ϕ^4 model are [1]

$$[(3\sigma - 1) + Q^2]Q = 0$$

$$m\Omega^2 = -4E_0 + \upsilon + \tfrac{1}{2}E_0(Q^2 + \sigma)$$

where Ω is the temperature-dependent Einstein frequency and σ is

$$\sigma = \langle \delta Q_\ell^2 \rangle = \frac{\hbar}{2m\Omega} \coth\left(\frac{\hbar\Omega}{2k_B T}\right).$$

The phase transition occurs at T_c when

$$\sigma(T_c) = \frac{k_B\theta_s}{\upsilon} \coth\left(\frac{\theta_s}{T_c}\right) = \frac{1}{3}$$

which is, here, independent of the displacive degree ε_0. Phase transitions are suppressed by quantum fluctuations if

$$\frac{k_B\theta_s}{\upsilon} > \frac{1}{3}.$$

The correction of the transition temperature due to quantum effects is

$$T_c = T_c^{(\theta_s=0)} \frac{3k_B\theta_s}{\operatorname{arcth}(3k_B\theta_s)}.$$

3. The effect of secondary fields

We now consider how T_c changes if a secondary field x is introduced into the local potential as a perturbation in the lowest order

$$U(Q_\ell) = -2E_0(1-\gamma x)Q_\ell^2 + E_0 Q_\ell^4.$$

The role of x is to change the value Q_0 at the ground state of the potential as

$$Q_{\ell 0}^2 = (1-\gamma x).$$

The effect of the changes in $Q_{\ell 0}$ is taken into account for the value of $\sigma(T_c)$. In the displacive limit the phase transition occurs at $\sigma_c = \frac{1}{3}Q_0^2 = \frac{1}{3}(1-\gamma x)$ in the units of our model. This leads to

$$\sigma_c(x) = \frac{k_B\theta_s}{v}\coth\left(\frac{\theta_s}{T_c(x)}\right) = \frac{1}{3}(1-\gamma x)$$

or

$$\coth\left(\frac{\theta_s}{T_c(x)}\right) = \coth\left(\frac{\theta_s}{T_c(x=0)}\right)(1-\gamma x)$$

or

$$\frac{T_c(x)}{T_c(x=0)} = \frac{\theta_s/T_c(x=0)}{\coth^{-1}\{[\coth(\theta_s/T_c(x=0))](1-\gamma x)\}}.$$

This result is equivalent to that found by Hayward and Salje [3] or by Gonzalo [4], but has been derived here in a much wider context. It is valid for all self-consistent solutions and is independent of the value of the degree of o/d as characterized by ε_0. The fundamental assumptions are the validity of the mean-field theory, the coupling to Einstein oscillators as dominant dynamical excitations and the x-dependence of the minimum position of the potential via $Q_0^2 \propto (1-\gamma x)$. Similar solutions can be found for other dynamical excitation spectra, for example a Debye phonon density of states.

It is important to note that under the same premises the square of the saturation value of the order parameter should follow a linear law $Q_s^2(x) = Q_s^2(0) - \gamma x$. This contrasts with the law proposed in [4].

In the case of tricritical phase transitions, the macroscopic Gibbs free energy was previously derived in the same approximation [1] and we conjecture the same for local potentials of the ϕ^p model:

$$V(Q_\ell) = \left(\frac{2}{p-2}\right)E_0\left[-\frac{p}{2}Q_\ell^2 + Q_\ell^p\right] + \frac{p}{p-2}E_0\gamma x Q_\ell^2$$

where $p = 6$ represents a 'tricritical' potential. Higher values of p are likely to occur in Slater systems with hydrogen ordering [20]. As a perturbation, the x-dependence of $V(Q_\ell)$ can again be limited to the quadratic term in Q_ℓ. The critical variance $\sigma_c(x)$ has the same x-dependence, but with different numerical prefactors. The critical temperature scales with x in the same way as in the ϕ^4 model. This is, of course, no longer true if the higher-order terms in the local potential are also x-dependent.

4. How to visualize the phase diagram $T_c(x)$ from the order parameter saturation $Q(T, \theta_s)$

A simple relationship exists between the temperature dependence of $Q(T, \theta_s)$ at constant values of x and the phase diagram $T_c(x)$. Let us first consider a displacive, second-order transition with

$$Q^2(T) = 1 - \frac{\coth(\theta_s/T)}{\coth((\theta_s/T_c(x=0)))}$$

for $x = 0$. Following the x-dependence of $T_c(x)$ we can write

$$\coth\left(\frac{\theta_s}{T_c(x)}\right) = (1 - Q^2_{x=0}(T_c(x)))\coth\frac{\theta_s}{T_c(x=0)} = \coth\left(\frac{\theta_s}{T_c(x=0)}\right)(1-\gamma x)$$

or

$$Q^2(T_c(x)) = \gamma x.$$

The last relationship means that the curve $Q^2(T)$ against T at a constant value of x is identical to the curve $T_c(x)$ against x if the abscissa and ordinate of the plot are interchanged and Q^2 is rescaled to Q^2/γ. This result is important for practical applications: if the order parameter is known over a wide temperature interval, including the saturation regime, and the system is displacive, then one can predict the phase diagram by simply inverting the plot. The role of the saturation is then the breaking down of the transition temperature near the critical value

$$x_c = \frac{\upsilon - 3k\theta_s}{\upsilon\gamma} = \frac{1}{\gamma}Q_s^2$$

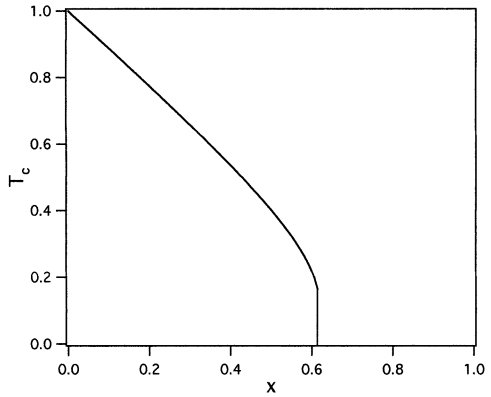
where Q_s is the saturation value of the order parameter in the absence of secondary fields. The relation between $T_c(x)$ and $Q^2(T)$ is shown graphically in figure 1.

Note that this rescaling approach allows the direct assessment of the displacive limit of the phase transition. The inverted and rescaled plot $T_c(x)$ corresponds to the plot of $Q^2(T)$ at $x = 0$ only if the system is in the displacive limit. By the same token, deviations between the two plots indicate that the transition deviates from the displacive limit.

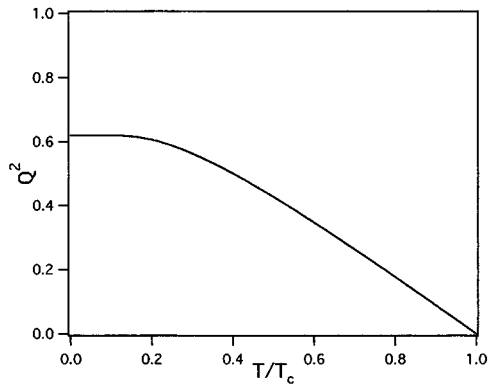
Similar conclusions can be reached for Q^p models. In this case the scaling exists between $Q^{p-2}(T, \theta_s)$ and $T_c(x)$. This means that a rather weak T-dependence of $Q(T)$ at $T \ll T_c$, as it is typical for tricritical and Slater systems, does not directly translate into a very abrupt breakdown of $T_c(x)$ near the critical value of x_c. As an example, in figure 3 of Hayward and Salje [3] the pressure dependence of the transition temperature was shown for KDP $< H_2PO_4$. A critical pressure is found near 1.7 GPa with a linear $T_c(P)$ dependence which extrapolates to 2.3 GPa at absolute zero ($T_c = 122 - (122/2.3)P$) (in kelvin). The equivalent order parameter dependence with $p = 16$ is then $Q \propto (P(T)/2.3)^{1/4}$ at $T > 30$ K which is compatible with the observed weak temperature dependence of Q at $T < 0.8T_c$ [20].

Although the direct inversion of $Q(T)$ to obtain $T_c(x)$ is valid (provided the value of p is known) for any ϕ^p model ($p \geqslant 4$), it is incorrect for transitions which are not in the displacive limit. Even in intermediate cases within the limits of the independent mode approximation, significant deviations are expected for $\varepsilon_0 \gg 0$. The ϕ^4 model, for example, gives a crossover to a tricritical behaviour at $\varepsilon_0 \to \frac{1}{8}$. The solutions of the self-consistency equations lead to a macroscopic 2-4-6 Gibbs free energy with a positive fourth-order term B depending on the value of ε_0 ($B = 1 - 8\varepsilon_0$). In such cases the scaling of $T_c(x)$ from $Q(T)$ requires the full solution of the Landau model and only works as long as the independent mode approximation is valid. For systems with higher degrees of o/d behaviour ($\varepsilon_0 > \frac{1}{8}$), we do not expect this approach to be a good approximation, although there seems to be no experimental data available which could test the applicability of our hypothesis in such cases. (e.g. an x-dependence of ε_0).

We finally comment on two aspects which were recently discussed in the case of 'nearly' displacive phase transitions in framework structures [21–29]. In all transitions, even those far away from the displacive limit, the function $T_c(x)$ is related to the behaviour of the quadratic term of the Landau-type free energy expansion. Only in the displacive limit do the other coefficients become temperature independent. Only in this case is rescaling between $T(x)$ and Q^{p-2} valid, while in all other cases we expect systematic deviations. The relevance of configurational entropy contributions can, in this case, simply be evaluated from, for example the comparison of the $T_c(p)$ phase boundary and the temperature evolution of the



(*a*)



(*b*)

Figure 1. The field dependence of the transition temperature (*a*) and temperature dependence of the square of the order parameter in the displacive limit of the ϕ^4 model (*b*). The two functions scale by simple inversion of the two axes of the plot. The scaling does not hold for o/d systems. In ϕ^p models the same scaling is valid for Q^{p-2} replacing Q^2 in this figure.

order parameter under constant pressure. The second aspect is that the quadratic coefficient of a general Landau potential results from the self-consistency equations and has the same temperature dependence for displacive and non-displacive phase transitions. That is the reason why the coth-expression for $T_c(x)$ is also valid out of the displacive limit as long as the dynamical excitations can be described in the Einstein approximation.

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