Critical phase transition point and optical modes

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The effect of the interaction between the moment and the optical modes on the change in nature of the phase transition is considered in the framework of scaling theory. It is shown that the contribution from a uniform polarization leads to the termination of the first-order phase-transition line. The behavior of a system near the critical point is studied.

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In a number of substances the first order phase transition curves terminate in critical or tri-critical points. Various models have been proposed to explain this. For instance, in the paper by Korotkikh and Nabutovskiĭ [1] the change from a first to a second order transition arises when one takes into account not only a uniform deformation[2] but also equilibrium impurities. Aharony[3] considered the interaction of fourth order in the moment. Bergman, Imry, and Gunther[4] explain the change in the nature of the transition by a large contribution from the fluctuating deformation modes (which apparently is a peculiar feature of the model considered). On the whole the change in the form of the transition in those papers is explained by the effect of "hidden" internal degrees of freedom.[5] As a result the point where the first order phase transition line terminates is a tri-critical point where the first order transition changes to a second order one with "renormalized" critical indices.

A different modification of the tri-critical behavior occurs in the case where there exists, apart from the uniform deformation, a mechanism which suppresses a first order transition and it appears also as a form effect. An example of this is the interaction considered in our paper of the order parameter with the long-wavelength optical modes and, in particular, with a uniform polarization. For a system with a ferromagnetic kind of order it leads to the appearance of a tri-critical point on the transition curve and subsequently to the smearing out of the second order transition, i.e., to the transformation of the tri-critical point into a simple critical one. The temperature behavior of the thermodynamic quantities on both sides of the transition turns out to be significantly asymmetric and has a rather complicated asymptotic behavior.

CHOICE OF MODEL

We consider a lattice with two atoms in a cell; let the moment $\boldsymbol{\sigma}$ be localized on one of them. We assume further that for rigidly fixed positions of all atoms in the system there occurs at a temperature T_c a second order transition which orders σ. The free energy for such a fixed system in a field can in the region of the transition in the framework of scaling theory be written as (see, e.g.,[6])

$$F=-T\ln\operatorname{Sp}\exp\Big\{-\frac{J}{T}\sum_l\xi_l+\mathbf{h}\sum_l\sigma_l\Big\}=-NT_cf(\tau,h). \qquad (1)$$

Here T is the temperature, $J\xi_l$ the local value of the energy operator in the l-th cell, and J corresponds to the exchange integral; the sum is over all N cells of the lattice; from dimensionality arguments we have $T_c = bJ$, where b is a constant of order unity, $\tau = (T/T_c) - 1$, $h = |\mathbf{h}|$ is the dimensionless field and f is the dimensionless function introduced in scaling theory which has a singularity in its derivatives as $\tau \to 0$ and $h \to 0$. The asymptotic behavior of the thermodynamic quantities is determined by the ratio of τ and h. Assuming for the sake of simplicity that the behavior is symmetric on both sides of the transition when $|\tau| \ll 1$, $h \ll 1$ we can write in the limit $|\tau| \gg h$ for any f the approximate equations:

$$c=(1+\tau)f_{\tau\tau}''=A_\tau|\tau|^{-\alpha};\quad \langle\sigma\rangle=\frac{f_h'}{1+\tau}=B_\tau(-\tau)^\beta,\quad \tau<0;$$
$$\chi=f_{hh}''/(1+\tau)=E_\tau|\tau|^{-\gamma}. \qquad (2a)$$

In the opposite limiting case $|\tau| \ll h$

$$c=A_hh^{-\epsilon},\quad \langle\sigma\rangle=B_hh^{1/\delta},\quad \chi=\delta^{-1}B_hh^{-\lambda}. \qquad (2b)$$

The lower indexes on f indicate here the arguments with respect to which the partial derivative has been taken; A_τ, A_h, B_τ, B_h, and E_τ are constants; α, β, γ, δ, λ, and ϵ are the critical indices of the scaling theory.

We turn to the consideration of an elastic lattice. We describe (as in[2]) the effect on the system of the moments of a uniform deformation and of the long-wavelength longitudinal acoustical modes by expanding J in terms of the local change of the volume up to the linear term. We introduce the interaction with the long-wavelength optical modes as a direct interaction between the local moment and the field induced by the relative motion of the sublattices: $D\boldsymbol{\sigma}_l\cdot\mathbf{w}_l$ (here $\mathbf{w}_l$ is the relative displacement vector and D the appropriate coefficient).1) The Hamiltonian of the total system without a field has the form

$$H=H_{el}+H_o+H_\sigma+H_{el\sigma}+H_{o\sigma},$$
$$H_{el}=\frac{K}{2}Nx^2+\sum_{\mathbf{k}}\frac{\lambda+\mu}{2}|\mathbf{k}\mathbf{u}_{\mathbf{k}}|^2,$$
$$H_o=\sum_{\mathbf{k},\nu}m[\omega_\nu^2+\delta_{\mathbf{k}0}(\omega_0^2-\omega_\nu^2)]|w_{\mathbf{k}}^\nu|^2; \qquad (3)$$
$$H_\sigma=J\sum_l\xi_l,\quad H_{el\sigma}=J'x\sum_l\xi_l+iJ'\sum_{\mathbf{k}}(\mathbf{k}\mathbf{u}_{\mathbf{k}})\xi_{-\mathbf{k}};$$
$$H_{o\sigma}=D\sum_{\mathbf{k},\nu}(\mathbf{e}_{\mathbf{k}}^\nu\boldsymbol{\sigma}_{-\mathbf{k}})w_{\mathbf{k}}^\nu,$$

where we have taken into account in H_{el} the contribution from the uniform deformation x and of the longitudinal acoustical modes; K is the compressibility, μ the shear modulus, $\lambda = K - \mu/3$, $\mathbf{u}_{\mathbf{k}}$ the Fourier transform of the relative displacement vector of the cells, H_0 the Hamiltonian of the unperturbed optical modes with an Einstein spectrum, considered for the sake of simplicity also to be an elastic one, in the high-temperature harmonic approximation; m the reduced mass of the cell, ν numbers the (longitudinal and degenerate transverse) modes, $\mathbf{e}_{\mathbf{k}}^\nu w_{\mathbf{k}}^\nu$ is the Fourier transform of the relative displacement vector, and $\mathbf{e}_{\mathbf{k}}^\nu$ the appropriate polarization vector.

The term with $\delta_{\mathbf{k}0}$ describes the fact that when all three dimensions of the sample are commensurable the characteristic frequencies of the optical oscillations with $\mathbf{k} = 0$ lie between $\omega_\parallel$ and $\omega_\perp$, are in the general case different and are functionals of the form.2) In that case there is for $\mathbf{k} = 0$ a degeneracy in energy of all three optical branches which is given by the expression

$$\omega_0^2={}^1/_3[\omega_\parallel^2+2\omega_\perp^2].$$

The Hamiltonians of the interaction with the acoustical and optical modes are denoted by $H_{el\sigma}$ and $H_{O\sigma}$ and J' is the derivative of J with respect to the cell volume.

THERMODYNAMIC POTENTIAL

The thermodynamic potential Φ of the system has for fixed pressure p the form

$$\Phi=-T\ln \operatorname{Sp}\exp\left\{-\frac{1}{T}[H+Npx]\right\}, \tag{4}$$

where the constant deformation x is determined from the condition that Φ be a minimum. Denoting the potential of the non-interacting vibrational modes by Φ_0 we can rewrite Φ as follows:

$$\Phi=\Phi_0+N\frac{K}{2}x^2+Npx-T\ln\operatorname{Sp}\left\{\exp\left(-\frac{J(x)}{T}\sum_l\xi_l\right)\right.$$
$$\left.\times\left\langle\exp\left(-\frac{1}{T}\left[iJ'\sum_{\mathbf{k}}(\mathbf{k}\mathbf{u}_{\mathbf{k}})\xi_{-\mathbf{k}}+D\sum_{\mathbf{k},\nu}(\mathbf{e}_{\mathbf{k}}^\nu\boldsymbol{\sigma}_{-\mathbf{k}})w_{\mathbf{k}}^\nu\right]\right)\right\rangle\right\}. \tag{5}$$

Here $J(x) = J + J'x$ and the angle brackets indicate averaging over the unperturbed vibrational modes. Using the harmonicity of the modes we can write the average in the form

$$\exp\left\{\frac{1}{2T^2}\left[(J')^2\sum_{\mathbf{k}}\langle|\mathbf{k}\mathbf{u}_{\mathbf{k}}|^2\rangle|\xi_{\mathbf{k}}|^2+D^2\sum_{\mathbf{k}\nu}|(\mathbf{e}_{\mathbf{k}}^\nu\boldsymbol{\sigma}_{-\mathbf{k}})|^2\rangle|w_{\mathbf{k}}^\nu|^2\rangle\right]\right\}$$
$$=\exp\left\{\frac{1}{2T}\left[\frac{(J')^2}{\lambda+\mu}\left(\sum_l\xi_l^2-\frac{1}{N}\left(\sum_l\xi_l\right)^2\right)\right.\right. \tag{6}$$
$$\left.\left.+z_1\sum_l\sigma_l^2-\frac{z}{N}\left(\sum_l\sigma_l\right)^2\right]\right\}$$

When changing to the last equation we used the explicit Gaussian form for the acoustical and optical averages, in the "optical" part we averaged over angles, the whole expression is written in the site representation, and

$$z_1=\frac{D^2}{3m}\left[\frac{1}{\omega_\parallel^2}+\frac{2}{\omega_\perp^2}\right],\quad z=z_1-\frac{D^2}{m\omega_0^2}.$$

In the spirit of scaling theory we assume[7,8] that the scalar local operators in all correlators behave in the region of scale invariance like the energy and in that sense can be replaced by some equivalent expression which is linear in the energy. A similar replacement for the operator

$$\frac{(J')^2}{\lambda+\mu}\sum_l\xi_l^2+z_1\sum_l\sigma_l^2$$

leads, when substituted in (5), to additive corrections to J and Φ_0 which are constant in the transition region and which in what follows we have included in the definition of these parameters.3)

The remaining terms can be transformed if we use the statistical identity:[8]

$$\left\langle\exp L\left(\frac{1}{N}\sum_l\eta_l\right)\right\rangle=\left\langle\exp\left[\frac{\partial L(\langle\eta\rangle)}{\partial\langle\eta\rangle}\frac{1}{N}\sum_l\eta_l\right]\right\rangle$$
$$\times\exp\left[L(\langle\eta\rangle)-\langle\eta\rangle\frac{\partial L(\langle\eta\rangle)}{\partial\langle\eta\rangle}\right], \tag{7}$$

where L is an arbitrary (differentiable) function and η_l an arbitrary local operator.

As a result we get for the thermodynamic potential the following expression:

$$\frac{\Phi}{N}=\frac{\Phi_0}{N}+\frac{K}{2}x^2+px-\frac{(J')^2}{2(\lambda+\mu)}\langle\xi\rangle^2+\frac{z}{2}\langle\sigma\rangle^2$$
$$-\frac{T}{N}\ln\operatorname{Sp}\exp\left\{-\frac{1}{T}\left[\left(J(x)+\frac{(J')^2\langle\xi\rangle}{\lambda+\mu}\right)\sum_l\xi_l-z\langle\sigma\rangle\sum_l\sigma_l\right]\right\} \tag{8}$$

where x is substituted from the condition $(\partial\Phi/\partial x)_{p,T} = 0$. The averages themselves are here defined over the ensemble given by the index of the exponent in the last term. The term with the average moment in that index leads to an additional interaction only in the case of ferromagnetic ordering (see[2]), in that case increasing the effective transition temperature. The expression for the logarithm in (8) is in form the same as expression (1). This enables us to introduce effective parameters τ and h which are determined by the following self-consistent set of equations:

$$T=T_c(1+\tau),\quad T_c=b\left(J-\frac{J'p}{K}-\frac{G}{b^2}\langle\xi\rangle\right),\quad G\equiv(bJ')^2\left[\frac{1}{K}-\frac{1}{\lambda+\mu}\right],$$
$$\langle\xi\rangle=b[(1+\tau)f_\tau'-f],\quad h=\frac{z}{T}\langle\sigma\rangle=\frac{z}{T}\frac{f_h'}{1+\tau}. \tag{9}$$

When $z/T \ll 1$ (the case to which we restrict ourselves in this paper) the averages can be expressed in terms of τ and h through the usual formulae of scaling theory. The thermodynamic potential finally takes the form

$$\frac{\Phi}{N}=\frac{\Phi_0}{N}-\frac{p^2}{2K}+\frac{G}{2b^2}\langle\xi\rangle^2+\frac{T^2h^2}{2z}-T_cf(\tau,h). \tag{10}$$

NATURE OF THE CRITICAL BEHAVIOR OF A SYSTEM

Equations (9) and (10) give the thermodynamics of the system in parametric form. For instance, we have for the specific heat, the thermal expansion coefficient, and for the inverse of the isothermal compressibility, and also for the derivatives with respect to the parameters the following asymptotic relations:

$$c_p=c_{p0}+T_c\frac{df_\tau'}{d\tau}\frac{d\tau}{dT},\quad \frac{1}{N}\left(\frac{\partial V}{\partial T}\right)_p=\frac{\partial T_c}{\partial p}\frac{df_\tau'}{d\tau}\frac{d\tau}{dT}, \tag{11}$$
$$\frac{1}{K_{\text{is}}}=\frac{3}{2\mu}\left[-1+\frac{\lambda+\mu}{K}T_c\frac{d\tau}{dT}\right];$$

$$\frac{df_\tau'}{d\tau}=f_{\tau\tau}''+f_{\tau h}''\frac{dh}{d\tau}; \tag{12}$$

$$\frac{dT}{d\tau}=T_c-G\frac{df_\tau'}{d\tau},\quad \frac{dh}{d\tau}=\frac{zf_{\tau h}''/T}{1-zf_{hh}''/T}. \tag{13}$$

We can at once split off some regions of characteristic temperature behavior of the thermodynamic quantities when we approach the singularity. Far from, above, and below the transition as long as $dT/d\tau \approx T_c$ the τ-asymptotic behavior holds where τ is linear in T. Later, with decreasing $|\tau|$ there appears a region with a non-linear dependence $\tau(T)$. When $\tau < 0$, $|\tau| \sim h^{1/\beta\delta}$, there occurs a transition from τ- to h-asymptotic behavior.

A characteristic peculiarity of the solution of the set (9) is that τ and h do not vanish simultaneously:

$$h=(zB_h/T_c)^{1/\lambda}\equiv h_c\ \text{when}\ \tau=0. \tag{14}$$

This is a reflection of the role of the term with the "field" in (8) as an additional interaction. Hence it follows immediately that the partial derivatives of f are bounded which may lead to a critical point.

Indeed, $h(\tau)$ is by virtue of its definition everywhere single-valued. Therefore, $dT/d\tau$ (and dT/dh) has, according to (13), a finite minimum value which because of the dependence $T_c(p)$ is a function of the pressure. The minimum of $dT/d\tau$ is determined by the condition for going over from the h- to the τ-asymptotic behavior when $\tau > 0$:

$$\tau_k=\Lambda h_k^{1/\beta\delta}, \tag{15}$$

where $\Lambda \sim 1$ is a parameter determined by the actual form of f. When $\min(dT/d\tau) < 0$ we have a second order phase transition. When the opposite inequality holds the singularity is smeared out. The condition

$$\min\frac{dT}{d\tau}=0$$

determines the critical point parameters p_0 and T_0.

Knowing the scaling asymptotic behavior (2) enables us to give only a qualitative description of the behavior in the transition region. For instance, using in (9) for the case $\tau > 0$ the simple interpolation formula

$$\langle\sigma\rangle\approx h\left(\frac{h^\lambda}{B_h}+\frac{\tau^\gamma}{E_\tau}\right)^{-1}, \tag{16}$$

we find easily

$$h^\lambda=\frac{h_c^\lambda}{1+\tau}-\frac{\gamma-1}{\beta}\left(\frac{\tau}{\Lambda}\right)^\gamma. \tag{17}$$

This expression is valid as long as $h \geq 0$. When the parameters change further we have, by virtue of (9), $h = 0$. We note that (17) describes the way in which h becomes zero when the corresponding τ lie outside the instability region (otherwise $h = 0$ already on the upper boundary with respect to τ of the discontinuity).

From (15) and (17) we determine the parameters of the extremum:

$$\left(\frac{h_k}{h_c}\right)^\lambda=\frac{\beta}{\beta\delta-1},\qquad T_k=T_c(1+\tau_k). \tag{18}$$

In the vicinity of the critical point T_k is the temperature of the second order transition below the critical point and the temperature of the maximum of the singularity above it. The transition characteristics can be expressed in terms of the deviation of the parameter T_c from the critical value:

$$T_c(p_0)=G\frac{\gamma-1}{\beta\delta-1}\tau_k^{-\alpha}\left[A_\tau+\frac{\beta\delta\gamma(\gamma-1)}{\beta\delta-1}\frac{B_h}{\Lambda^{2-\alpha}}\right]\sim G\left(\frac{z}{T_c}\right)^{-\alpha/\gamma}. \tag{19}$$

For the limiting value $(df'_\tau/d\tau)_{\rm lim}$ below the critical point, the temperature hysteresis and for the discontinuities in the entropy and the volume we get

$$\left(\frac{df_\tau'}{d\tau}\right)_{\rm lim}\approx\frac{T_c-3(T_c(p_0)-T_c)}{G}, \tag{20}$$

$$\Delta T\approx\left\{3\left[\frac{G}{2}\left|\left(\frac{d^3f_\tau'}{d\tau^3}\right)_k\right|\right]^{1/2}\right\}^{-1}4|T_c(p_0)-T_c|^{3/2}$$
$$\sim T_c\left(\frac{T_c}{G}\right)^{1/2}\left(\frac{z}{T_c}\right)^{(2+\alpha)/2\gamma}\left|\frac{T_c(p_0)-T_c}{T_c}\right|^{3/2}; \tag{21}$$

$$\Delta s\approx\frac{3T_c}{G}\frac{\Delta T}{T_c(p_0)-T_c},\qquad \Delta v=\frac{\partial T_c}{\partial p}\Delta s. \tag{22}$$

Above the critical point Eq. (21) determines the width over which the phase transition is smeared out.

We compare the results obtained with data on NH_4Cl. For this substance $G/T_c = 0.23$. If we put $z/T_c \sim 10^{-1}$ to 10^{-2}, we get from Eqs. (18) to (22) the temperature of the critical point $T_0 \approx T_c(p_0) \sim 10^2$ K, and also $\Delta s \sim 10^{-1}$ and $\Delta T/T_k \sim 10^{-3}$ for $p - p_0 \sim p_0$ which agrees with experiments.

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[1] In ionic crystals there appears an induced electric field as a result of the relative displacement of the sublattices. In ferroelectrics it interacts directly with the local dipole moment. Moreover, the effective interaction of this field with the "moment" can be introduced also for the case of orientation transitions where it is connected with the breaking of the symmetry of the field of the fixed surroundings.

[2] More exactly we consider samples with a shape which differs little from a spherical one which together with the degeneracy of the spectrum guarantees the non-vanishing of vector quantities when averaged over angles.

[3] In fact we assume that the possible renormalization of the critical behavior which is connected with such terms lies outside the range of values of the external parameters in which we are interested.

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