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Phenomenological order parameter and local parameters fluctuation far beyond the critical region of the continuous phase transition

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ABSTRACT

In the framework of an extended phenomenological approach to phase transitions, we show that existing nonlinear relation between local critical atomic parameters and phenomenological order parameter induces the corresponding nonlinear temperature scaling transformation, and find the explicit form for such a transformation. The theoretically predicted uniform function reproduces well the experimentally observed behavior of order parameters in different systems.

1. Introduction

It is well established in the literature that, despite the fact that the phenomenological Landau theory of phase transitions [1,2] deals with various types of variational free energy, it predicts, in fact, a single set of the critical point exponents ($\alpha=0$, $\beta=1/2$, $\gamma=1$ and $\delta=3$) and thus belongs to the single "mean field" universal class [3]. In what follows we use the terminology of the theory of *critical phenomena* for the *phenomenological theory*, although the latter does not treat critical phenomena properly. The phenomenological theory characterizes a system by the critical exponents both outside and within the critical region, where temperature behavior of a general function $f(t)$ can be approximated by a simple power function $f(t)=At^{\lambda}$, with λ as a critical point exponent, and $t=|T\text{-}T_C|/T_C$ as a dimensionless variable to measure the temperature difference with the critical temperature T_C. A considerable body of experimental data indicates that the real systems show regular deviation from the behavior predicted in the framework of the Landau phenomenological theory, and different universality classes were found experimentally in such systems. It is convenient to consider such a discrepancy as caused by two main reasons: (i) the phenomenological theory neglects critical fluctuations, i.e. one assumes that the order parameter can be characterized by a single value at any temperature, and (ii) the above theory uses the dimensionality for the fluctuation space lower than the marginal dimensionality ($d<d*$) (see, for example, [4–6]). These reasons both relate to the *critical* fluctuations and are valid in the critical region. However, the existence of background hetero- and homophase fluctuations [7,8] was not considered in the analysis of the above discrepancies. Here we highlight yet another reason for the divergence of the phenomenological calculations and the corresponding experimental data. Specifically, a transcendental relation between a phenomenological order parameter and the corresponding local atomic variables along with the nonlinear temperature scaling transformation result in a deviation of the experimental values for the critical exponents from those predicted by the Landau theory. We show how the nonlinear transformation parameters depend on the fluctuation properties of the real systems *far beyond* the critical region.

2. Microscopic and macroscopic order parameters

2.1. Order parameter space

The Landau theory uses the increment $\delta\rho(\mathbf{r})$ of the probability density, expressing the difference between the initial density in high-symmetry parent phase, $\rho_0(\mathbf{r})$, and the final low-symmetry

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phase, $\rho_d(\boldsymbol{r})$, expanded as a function of the basis functions of an irreducible representation (IR) τ_{kj} of the space group G_0 of the parent phase [1,2]. This expansion has the form:

$$\delta\rho(\mathrm{r}) = \rho_d(\mathrm{r}) - \rho_0(\mathrm{r}) = \sum_{k,j,i} \eta^i_{kj}\varphi^i_{kj}(\mathrm{r}) \tag{1}$$

The wave vector $\boldsymbol{k}$, located in the first Brillouin zone, characterizes the translational symmetry of the basis functions $\varphi^i_{kj}(\boldsymbol{r})$, which are the *linear* combinations of the local atomic functions, associated with the crystalline structure. The index j labels the representations τ_{kj} of G_0, and the index i ($i=1,\ldots,n$) runs over the distinct basis functions spanning the n-dimensional IR τ_{kj}. For a given j, the set of scalar coefficients η^i_{kj} defines the *order parameter* (OP), which describes the total distortion of the initial structure at the transition. Usually a single irreducible OP breaks the symmetry in a phase transition, so we only keep index i in Eq. (1).

The linear coupling between η_j and $\varphi_j(\boldsymbol{r})$ in Eq. (1) allows choosing either of these two quantities as a forming basis of the relevant IR. As a consequence, the non-equilibrium thermodynamic potential, associated with the transition, $\Phi_L(T,p,\delta\rho)$, can be considered as a function of the η_i instead of the $\varphi_i(\boldsymbol{r})$. The OP components define the order parameter space ε_n that is irreducible invariant space by the group G_0. The $\delta\rho$ variation of the probability density, associated with a phase transition, can be considered as a vector in the representation ε_n-space, and the components of $\eta = \{\eta_i^{eq}\}$ invariant vector, in the basis of this space, are the values of the OP that minimize the thermodynamic potential (for details see [9–11] and references therein).

Naturally, we consider the symmetry identity of η_i and $\varphi_i(\boldsymbol{r})$ as a general property which is also valid for the more general renormalization group approach. Indeed, a linear *projection operator* of a space group induces basis functions for the relevant IR in the form of the linear combinations of local atomic functions. The latter are linked to the phase transition mechanism and were selected as a result of a *regular* renormalization transformation, separating critical and non-critical variables [6,12,13]. The integral over the non-critical variables gives the equilibrium part of the free energy Φ_0, and unintegrated part forms the variational free energy (Landau potential) $\Phi_L(\delta\rho)$.

The crystal geometry analysis of the different displacive type structural phase transitions, in particular, martensitic transformations, shows that there exists a transcendental functional relation between the value of the phenomenological OP η_i and the magnitude of local atomic shifts, or the periodic character of its distortions [11,14–16]. Same type of non-linear periodic dependence was obtained for η_i as a function of probability density variation for the segregation type phase transitions [17]. One can conclude thus that the order-parameter space, denoted hereafter σ_n, in general case (i.e. for the full range of the OP variation), conceptually differs from the order-parameter space ε_n used earlier in the description of continuous phase transitions. While ε_n is a n-dimensional *vectorial* space, σ_n is a n-dimensional closed *functional* space *with boundary*, whose structure depends on the type of the variational parameters that identify the transition mechanism [11].

2.2. Phenomenological order parameter and essential variational parameters

We derive the general form of the function $\eta_i(\xi_j)$, where the set of η_i is a long-range phenomenological order parameter and ξ_j represent variational local atomic parameters, i.e. short-range order parameters (variation of probability for the segregation or disorder-order transformation, magnitude of atomic displacements for displacive type transitions etc.), by considering the problem in the functional order-parameter space σ_n.

One makes use of the usual scheme for calculating $\eta(\xi)$ by finding the solution of the Euler's variational equation $\{\delta\Phi/\delta\eta(\xi)\}=0$ that minimizes the free energy functional. The appropriate choice for the latter in the case of continuous phase transition is the classical Landau–Ginzburg functional

$$\Phi(\eta) = \int_{V_\xi} d\xi\left\{a_1\eta(\xi)^2 + a_2\eta(\xi)^4 + g\left(\frac{d\eta}{d\xi}\right)^2\right\} \tag{2}$$

where the integral is over a volume in the *OP space*. For the sake of simplicity we treat a single-component or effective OP, while the conjugate external field is neglected. The coefficient a_1 is conveniently assumed to be a regular function of thermodynamic variables (the temperature, pressure, etc.) and the remaining coefficients are regarded as temperature- and pressure-independent parameters. The corresponding Euler's equation takes the form:

$$\frac{\delta\Phi}{\delta\eta(\xi)} = a_1\eta(\xi) + 2a_2\eta(\xi)^3 + g\frac{d^2\eta}{d\xi^2} = 0 \tag{3}$$

The boundary conditions are $\eta(0)=0$ and $\eta'(0)=1$. The first condition indicates a coincidence of the origin points for the variables η and ξ. The second one ensures their identical behavior close to T_C, i.e. it justifies the change of variables $\xi\to\eta$ in the Landau theory. The differential Eq. (3) has exact general solution expressed as

$$\eta = \eta_0 \cdot sn[\mu(\xi - \xi_0), k] \tag{4}$$

In the above equation $\mathrm{sn}[\mu(\xi-\xi_0),\kappa]=\mathrm{sn}u$ is the elliptic sine of Jacobi, and μ and ξ_0 are the arbitrary constants [18]. With the applied boundary conditions, $\mu=1$ and $\xi_0=0$. The parameter $\kappa=\sqrt{(a_2/|g|)}$ is the *modulus* of the elliptic integral of the first kind

$$u = F(\xi,\kappa) = \int_0^\xi \frac{d\xi}{\sqrt{1-\kappa^2\sin^2\xi}} \tag{5}$$

The phase diagram of this system can be obtained by minimizing the Landau potential

$$\Phi_L(\eta) = a_1\eta^2 + a_2\eta^4 \tag{6}$$

where the OP η has the form of Eq. (4). The minimization of Φ_L with respect to the actual variational parameter ξ is expressed by $\frac{\partial\Phi_L}{\partial\xi} = \frac{\partial\Phi_L}{\partial\eta}\cdot\frac{\partial\eta}{\partial\xi}$, giving the equation of state

$$\eta\eta'\left\{a_1 + 2a_2\eta^2\right\} = snu\cdot cnu\cdot dnu\left\{a_1 + 2a_2 sn^2u\right\} = 0 \tag{7}$$

where $\mathrm{cn}u=\sqrt{1-\mathrm{sn}^2 u}$ and $\mathrm{dn}u=\sqrt{(1-\mathrm{k}^2\ \sin^2\xi)}$. Eq. (7) yields three possible stable states: (i) The parent phase *I* for $\mathrm{sn}u=0$ (origin of the space σ); (ii) The limit, non-Landau, phase *II*, given by $\mathrm{cn}u=0$ ($\mathrm{sn}u=1$) (boundary of the space σ), corresponding to the fixed values η_0 of the OP; (iii)'"Landau'" phase corresponding to the standard minimization of Φ_L with respect to the OP η, whose value $\eta_2=-a_1/2a_2$ varies between 0 and η_0 (interior of the space σ). The function $\mathrm{dn}u$ has zeros only if $\kappa=1$, however, even in this case $\mathrm{dn}u$ vanishes simultaneously with $\mathrm{cn}u$ and no different solution of Eq. (7) exists.

The stability condition has the form:

$$\frac{\partial^2\Phi_L}{\partial\eta^2}\left(\frac{\partial\eta}{\partial\xi}\right)^2 + \frac{\partial\Phi_L}{\partial\eta}\frac{\partial^2\eta}{\partial\xi^2} \geq 0 \tag{8}$$

The resulting phase diagram in the plane of thermodynamic parameters (a_1,a_2) is shown in Fig. 1(a). The second-order phase transition line $a_1=0$ separates parent *I* and Landau *III* phases. The stability regions of Landau *III* and limit *II* phases adjoin along the