Jaynes' information theory formalism and critical phenomena in crystals with defects

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Abstract. We represent the general approach to the description of influence of defects on critical behaviors of system. The structure of the crystal with defects is represented as graph. Results of possible ways to determine a distribution function of defects are discussed. The phenomenological theory of phase transitions in crystals with defects with any distribution of defects is presented. It is shown, that temperature dependences of thermodynamic functions essentially depend on a concrete kind of distribution of defects.

Key Words: Phase transition, order parameter, defects, Jaynes' information theory formalism and Tsallis entropy, Beck-Cohen superstatistics, growth process, critical behaviors.

INTRODUCTION

Research influence of defects on physical properties of crystals near to phase transitions is an actual problem of statistical physics [1, 2]. Basically theoretical approaches consider one domain crystals with homogeneous distribution of defects in structure [1]. However growth leads to inhomogeneous distributions of defects in crystals [1].

At approach to critical temperature the correlation length grows, and in the point of phase transition becomes infinite. It leads singularity of thermodynamic functions. Originally was considered, that defects or completely destroy long-order fluctuations, that is singularity of thermodynamic functions smooth out, or make only shift of a critical point, but do not influence on critical behaviour, that is critical indexes remain same, as well as in ideal system. Then it has been understood, there is intermediate situation when close enough to a critical point is possible is established a critical regime which is described by new universal critical indexes [3].

The ideal crystal represents regular geometrical graph. Nodes the graph are atoms, and edges - chemical connections between atoms of structure. Introduction of defects in structure of a crystal leads to occurrence of additional connections (edges), and network turns a spatial network. Depending on a concrete kind of density distribution function of defects in structure regular graph turns to a spatial network with the certain of distribution function chemical connections. Thus, strictly speaking, symmetry of this structure should be determined by symmetry the graph.

Near to a point of phase transition due to of occurrence of large distance correlations at presence of defects it is necessary to expect formation a fractal spatial network [4, 5].

In this work we investigated the influence of defects on the critical behaviour of system near the phase transition.

NONEXTENSIVE ASPECTS FOR STOCHASTIC NETWORKS IN CRYSTALS

Using a maximum entropy principle, we can define a distribution function on a network formed in a crystal at presence of defects. Entropy of considered fractal systems we shall present in the form

$$S_q = \frac{1 - \int_0^\infty p^q(k)dk}{q-1} \tag{1}$$

where q denotes the entropic index an $p(x)$ the probability distribution of the state x [6].

Natural constraints in the maximization of (1) are

$$\int_0^\infty p(k)dk = 1, \tag{2}$$

corresponding to normalization, and

$$\int_0^\infty kp(k)dk = k_0 . \tag{3}$$

From the variational problem for (1) under the above constraints, one obtains

$$\frac{1}{1-q} qP^{q-1}(k) - \alpha - \beta k = 0 . \tag{4}$$

where α and β are Lagrange parameters. From the equation (4) follows that

$$P(k) = \left[\frac{1-q}{q}(\alpha + \beta k)\right]^{\frac{1}{1-q}} \tag{5}$$

Multiplying equation (4) on $p(q)$ and integrating on k from 0 up to ∞ one obtain

$$\frac{q}{1-q}\int_0^\infty p^q(k)dk - \alpha - \beta k_0 = 0 , \tag{6}$$

where we used the equations (2) and (3).

Let us denote be

$$\chi_q = \int_0^\infty p^q(k)dk , \tag{7}$$

then parameter of α is defined by

$$\alpha = \frac{q}{1-q}\chi_q - \beta k_0 . \tag{8}$$

Then after substitution (8) in (5) one obtain

$$P(k) = \chi_q^{\frac{1}{1-q}} \left[1 - \frac{1-q}{q}\frac{\beta}{\chi_q}(k_0 - k)\right]^{\frac{1}{1-q}} . \tag{9}$$

Using equation (2), one gets

$$P(k) = \frac{\left[1 - \frac{1-q}{q}\frac{\beta}{\chi_q}(k_0 - k)\right]^{\frac{1}{1-q}}}{Z_q} \tag{10}$$

where it is introduced notation $Z_q = \chi_q^{\frac{1}{1-q}}$ and

$$Z_q = \int_0^\infty \left[1 - \frac{1-q}{q}\frac{\beta}{\chi_q}\left(k_0 - k\right)\right]^{\frac{1}{q-1}} dk \tag{11}$$

Equation (10) may be rewritten as

$$P(k) = \frac{\left[1 + \frac{1-q}{q}\frac{\beta}{\xi\chi_q}k\right]^{\frac{1}{q-1}}}{\int_0^\infty dk\left[1 + \frac{1-q}{q}\frac{\beta}{\xi\chi_q}k\right]^{\frac{1}{q-1}}} \tag{12}$$

with

$$\xi = 1 - \frac{1-q}{q}\frac{\beta}{\chi_q}k_0 .$$

The integral (3) is easily evaluated

$$\int_0^\infty dk\left[1 + (1-q)\frac{k}{k_0(2q-1)}\right]^{\frac{1}{q-1}} = \frac{k_0(2q-1)}{q}, \tag{13}$$

and we obtains

$$\frac{\beta}{q\chi_q\xi} = \frac{1}{k_0(2q-1)} . \tag{14}$$

Then from equations (12) one gets

$$P(k) = \frac{q}{k_0(2q-1)}\left[1 + \frac{1-q}{q}\frac{\beta}{\xi\chi_q}k\right]^{\frac{1}{q-1}} . \tag{15}$$

The moments of distribution (15) is easily calculated. For example

$$\int_0^\infty k^2 p(k)dk = \frac{2k_0^2(2q-1)}{3q-2}, \tag{16}$$

$$\int_0^\infty k^4 p(k)dk = \frac{24k_0^4(2q-1)^3}{(3q-2)(4q-3)(5q-4)} . \tag{17}$$

GROWTH OF A CRYSTAL WITH DEFECTS AND NONEXTENSIVE STATISTICS

Let the basic matrix of a crystal grows as close-packed structure, for example, in the form of a cubic lattice with space group of symmetry O_h^5 . We assume that when the crystal grows, be going on a growth of defects of the structure of crystals. Generally placing of defect in the certain point of space inside of a crystal depends on the concrete mechanism formation of chemical connections. Concretely placing of defects depends on a kind and type and of the nearest environment of defects. In this sense emptiness where placing of the defects can be energetically favorable or on the contrary. As result crystal with defects formed some network, symmetry of which is defined by symmetry corresponding graph.

In fact we consider the following general problem. In each instant nee defects have be distributed in emptiness of close –packed structure. It is possible to assume, that distribution of chemical connections occurs as follows.

At each moment of time the new urn (emptiness) in which with the certain probability m spheres (defects) it is placed [7]. The distribution of chemical connections it is possible to define as follows. The probability, which a new sphere gets in the given urn, is proportional to the following characteristic of a urn: $A = A_0 + k_s$ which we shall name a energy advantage of a urn. It is obvious, that all urns are born with initial advantage $A \geq 0$ which then grows with k_s. Distribution $p(k,s,t)$ of connectivity k of site s at the time t $(t = 1,2,...)$ can be defined as follows. At the moment t the network contains t the node connected by $m(t-1)$ connections. The general advantage of a network at moment t is $A_\Sigma = (m + A)t$. We shall assume, that probability, that new connection linked with node s is equal $\frac{A_s}{A_\Sigma}$. Then probability for the node s to get precisely l new connections from m incoming connections is

$$\mathrm{P}_s^{(ml)} = \binom{m}{l}\left(\frac{A_s}{A_\Sigma}\right)^l\left(1 - \frac{A_s}{A_\Sigma}\right)^{m-l} \tag{21}$$

Hence, the connectivity distribution of a site obeys the following master equation:

$$p(k,s,t) = \sum_{l=0}^{m} \mathrm{P}_s^{(ml)} p(k-l,s,t) \tag{22}$$

Often, it is convenient to proceed in a slightly different way. Let us introduce the average degree of an individual node s at time t: $\bar{k}(s,t) = \int_0^\infty kp(k,s,t)dk$. Using master equation (22) it is easy to introduce equation for $\bar{k}(s,t)$ [7]. A namely, we consider equation evolution for $\bar{k}(s,t)$ in the form

$$\frac{\partial \bar{k}(s,t)}{\partial t} = \frac{f_p\left[\bar{k}(s,t)\right]}{\int_0^t du f_p(k(s,t))} \tag{23}$$

Let us search for the solution of equation (23) in the scaling form $\bar{k}(s,t) = \kappa(\xi)$, where $\frac{s}{t} = \xi$. Then

$$-\frac{\partial \kappa(\xi)}{\partial \ln \xi} = \frac{f_p[\kappa(\xi)]}{\int_0^1 d\varsigma f_p[\kappa(\varsigma)]} \tag{24}$$

Now suppose that

$$f_p[\kappa(\xi)] = f_0 + f_1\kappa(\xi), \tag{25}$$

where f_0 and f_1 are constant. Then we obtain

$$-\frac{\partial\kappa(\xi)}{\partial\ln\xi}=\frac{f_0+f_1\kappa(\xi)}{\int_0^1 d\varsigma f_p[\kappa(\varsigma)]} \tag{26}$$

It is clear that $\int_0^1 d\varsigma f_p[\kappa(\varsigma)] = f_0 + f_1 c$, where $c=\int_0^1 d\varsigma\kappa(\varsigma)$. Then, it is easy to prove that the solution of equation (26) has the form

$$s=t\left[\frac{f_0+f_1k(\xi)}{f_0+f_1}\right]^{-\frac{f_0+f_1c}{f_1}} \tag{27}$$

Probability function is defined as

$$P(k,t)=\frac{1}{t}\int_0^t ds\delta\left(k-\bar{k}(s,t)\right)=-\frac{1}{t}\left(\frac{\partial\bar{k}(s,t)}{\partial s}\right)_{[s=s(k,t)]} \tag{28}$$

where $s(k,t)$ is solution of equation $k=\bar{k}(s,t)$.

Inserting equations (27) into expression for (28) we obtain the distribution function

$$P(k)=\frac{\left[1-\frac{(1-q)}{\beta}k\right]^{\frac{1}{q-1}}}{\int_0^\infty dk\left[1-\frac{(1-q)}{\beta}k\right]^{\frac{1}{q-1}}} \tag{29}$$

where $\beta=-q(1+c)+c$. The obtained result means, that a growth process o with the competing mechanism leads to distribution of defects in structure described by Tsallis distribution.

CONSTRUCTING A STATISTICAL MECHANICS FOR BECK-COHEN SUPERSTATISTICS

Beck and Cohen constructed of stochastic differential equations with fluctuating friction forces that generate a dynamical correctly described by Tsallis statistics [8].
Let some quantity β distribution according to gamma-distribution

$$f(\beta)=\frac{1}{\Gamma\left(\frac{n}{2}\right)}\left\{\frac{n}{2\beta_0}\right\}^{\frac{n}{2}}\beta^{\frac{n}{2}-1}e^{\left\{-\frac{n\phi}{2\beta_0}\right\}} \tag{30}$$

Now assume that the time scale on which β fluctuates in much larger than the typical scale of order γ^{-1} that the Langevin system

$$\dot{u}=-\lambda u+\sigma l(t)$$

needs to reach equilibrium. In this case, one obtain for the conditional probability $p(u|\beta)$ (i.e. the probability of u given same value of β),

$$p(u|\beta)=\sqrt{\frac{\beta}{2\pi}}e^{\left\{-\frac{1}{2}\beta u^2\right\}} \quad (31)$$

for the joint probability $p(u,\beta)$ (i.e. the probability to observe both a certain value of u and a certain value of β)

$$p(u,\beta)=p(u|\beta)f(\beta) \quad (32)$$

and for the marginal probability $p(u)$ (i.e. the probability to observe a certain value of u no matter what β is),

$$p(u)=\int p(u|\beta)f(\beta)d\beta \quad (33)$$

The integral is easily evaluated and one obtain

$$p(u)=\frac{\Gamma\left(\frac{n}{2}+\frac{1}{2}\right)}{\Gamma\left(\frac{n}{2}\right)}\left(\frac{\beta_0}{\pi n}\right)^{\frac{1}{2}}\frac{1}{\left(1+\frac{\beta_0}{n}u^2\right)^{\frac{n}{2}+\frac{1}{2}}} \quad (34)$$

Hence the stochastic differential equations with gamma-distributed $\beta=\frac{\gamma}{\sigma^2}$ generates the generalized canonical distributions of nonextensive statistical mechanics

$$p(u)\sim\frac{1}{\left[1+\frac{1}{2}\tilde{\beta}(q-1)u^2\right]^{\frac{1}{q-1}}} \quad (35)$$

provided the following identification are made

$$q=1+\frac{2}{n+1}, \quad (36)$$

$$\tilde{\beta}=\frac{2}{3-q}\beta_0. \quad (37)$$

In [6] the C. Tsallis and A. M. Soza present an entropic functional and associated constraint which lead precisely to $p(u)$. This means that both the maximum энтропии principle and Beck-Cohen the superstatistics are equivalent and both are capable to generate the various types of statistics which can be describe distribution of considered quantities in various systems.

PHASE TRANSITIONS IN CRYSTALS WITH DEFECTS

Let's discuss a problem of phase transitions in crystals with defects. Free energy functional of crystal, necessary for the analysis of features of thermodynamic functions near to phase transition, constructed by from invariants of irreducible representation of space group of symmetry of high symmetry phase of a crystal. At presence of defects the free energy functional is not only function of the order parameter η, but also depends on the variable ψ describing a measure of disorder, introduced by presence of defects in crystal. We assume, that $\psi=k\eta$, where k — chemical connectivity of defect in a crystal.

Free energy functional can be represented as [9]

$$F[x,E]=-E\eta+\int_0^{\infty}P(k)f(\eta,k\eta)dk \qquad (38)$$

Here E is a field conjugated with η. We assume that free energy functional is a smooth function of η and $\psi=k\eta$ and can be represented a series in power of both η and $\psi=k\eta$

$$F[\eta,E]=-E\eta+\int_0^{\infty}P(k)\sum_{m,l}f_{ml}\eta^m\psi^l dk \qquad (39)$$

where f_{ml} are functions of temperature and pressure.

Free energy functional $F[\eta,E]$ is a singular function and can be presented as the sum of two contributions

$$F[\eta,E]=-E\eta+\Phi_f(\eta,\psi)+\Lambda_s(\eta,\psi) \qquad (40)$$

where $\Phi_f(\eta,\psi)$ and $\Lambda_s(\eta,\psi)$ are finite and singular contributions, respectively.

Origins singularity contributions are connected with divergence of the moments of distribution $P(k)$. For concreteness, we consider one dimensional irreducible representation (not being identical representation) space group O_h^5. In this case, the integer basis consists of one invariant η^2, and expansion of free energy contains integer degrees of the order parameter only.

From expressions (18), (19), (20) follows, that at values of the entropic index $q=\frac{2}{3}$, $q=\frac{3}{4}$ and $q=\frac{4}{5}$ the moments of distribution $P(k)$ of the second, third and fourth orders are diverges. Near to these values singular contributions can be calculated as follows.

For the determined singular contribution near the $q=\frac{3}{4}$ let us consider free energy functional in the form

$$F[\eta,0]=f_2\eta^2+\varphi(\eta)\eta^4+f_{04}\int_m^{\infty}dkP(k)\Lambda(\eta,\eta k) \qquad (41)$$

where m is a smallest degree in $P(k)$. Smooth function $\varphi(x)$ is determined by the convergent moments $\langle k^l\rangle$ with $l\leq 3$.

We can put $G(x,y)\approx G(0,y)$ and considering the integral over a variable $\psi=k\eta$, one can show that the region $m\eta\leq y\leq b$ gives a leading contribution. As results we obtain

$$F[\eta,E]=-E\eta+f_2\eta^2+\varphi(\eta)\eta^4+A\eta^4\ln\left(1+\frac{1-q}{2q-1}\frac{b}{k_0\eta}\right) \qquad (42)$$

if $q=\frac{3}{4}$ and

$$F[\eta,E]=-E\eta+f_2\eta^2+\varphi(\eta)\eta^4+B\left[1+\frac{1-q}{2q-1}\frac{b}{k_0}\eta\right]^{\frac{1}{q-1}-1}. \qquad (43)$$

in the case $\frac{2}{3} < \gamma < \frac{3}{4}$, where b is a model parameter.

Temperature dependence of the order parameter is defined by equation $\frac{\partial F[\eta, 0]}{\partial \eta} = 0$.

From expressions (42) and (43) we find $\eta \sim \frac{\tau^{\frac{1}{2}}}{\left(\ln \tau^{-1}\right)^{\frac{1}{2}}}$ and $\eta \sim \tau^{\frac{q-1}{4-3q}}$, respectively. It is necessary to notice that in the case ideal crystals we have $\eta \sim \tau^{\frac{1}{2}}$, where $\tau \sim (T - T_c)$, T_c is a critical temperature.

SUMMARY

In an ideal crystal the structure is defined by one of 230 space groups. The knowledge of space groups of symmetry high symmetry and low symmetry phases allows to define symmetry of the order parameter and to construct of the free energy functional. Using the free energy functional we can calculate temperature dependences of thermodynamic functions near the critical point.

The structure of a crystal with defects can be presented as graph, and in principle, symmetry of this structure is defined by symmetry of the corresponding graph. At the probability description of this structure it is possible to define of the distribution function of defects in structure. Particularly it can be made, using a maximum entropy principle or methods of Becк-Cohen superstatistics.

Free energy functional of such system depends on the order parameter and a measure of the disorder, contributed by defects. For calculation of temperature dependences of thermodynamic functions averaging under the disorder is necessary. If there are divergence moments of distribution, free energy functional of system contains finite and singular parts. Arising singularity in the free energy functional due to defects in crystal structure results an essential deviation of behaviour of thermodynamic functions near critical point.

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