STUDY OF THERMODYNAMIC PROPERTIES OF THE LIEB FERROELECTRIC MODEL AT THE VICINITY OF A CRITICAL POINT

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The critical properties of the exactly solvable two-dimensional Lieb ferroelectric model are examined on the basis of the thermodynamic method of investigation of the critical states in one-component systems. The behavior of the complete set of characteristics of the stability upon the approach of a system to a critical point is analyzed, and the type of a critical behavior by the thermodynamic classification is determined. When $T \to T_c^-$ and $T \to T_c^+$, the second and fourth type of a critical behavior are realized, respectively. The violation of the scaling law hypothesis in the model ($\alpha' \neq \alpha$) is explained just by the realization of different types of critical behavior in the vicinity of a critical point. The existence of a new type of the critical point is established, in which three lines of the phase equilibrium converge.

As is known, the problem of phase transitions and the critical state is one of the most actual problems in the physics of condensed systems.

In the critical state, a system is under extremal conditions (on the thermodynamic stability boundary), and, in this case, there is a maximal development of fluctuations, which results in an anomaly in the behavior of thermodynamic quantities. One of the main problems of the thermodynamics of a critical state is to clarify the character of these anomalies and to study the behavior of thermodynamic quantities in the vicinity of critical points. In [1, 2], this problem was solved in the general case within the thermodynamic method. There, the critical point was considered as a point which conjugates the properties of precritical and supercritical states. The method is based on the constructive definition of a critical state by a system of linear homogeneous equations and on the use of the conditions of the stability of a critical state.

Therefore, it is interesting to study the critical properties of well-known statistical models on the base of the thermodynamic method [1, 2].

Exactly solvable two-dimensional models, most of them being discussed in monograph [3], have significant importance for the theory of the critical state. The Lieb model is the only model that has a solution in the presence of an electrical field and gives a possibility to use, in full, the thermodynamic method of investigations of the critical states in one-component systems. The Lieb model is also interesting because the scaling hypothesis does not hold in it.

The aim of this study is to apply the thermodynamic method to the investigation of critical properties of the Lieb ferroelectric model.

1. Let's use the definition of a critical state according to [1, 2] in the form

$$\left.\begin{aligned} dT &= \left(\frac{\partial T}{\partial S}\right)_x dS + \left(\frac{\partial T}{\partial x}\right)_S dx = 0 \\ dX &= \left(\frac{\partial X}{\partial S}\right)_x dS + \left(\frac{\partial X}{\partial x}\right)_S dx = 0 \end{aligned}\right\} \qquad (1)$$

at $$\left(\frac{dX}{dT}\right)_c = -\frac{dS}{dx} = K_c \ ,$$

where X is a generalized thermodynamic force, x is the generalized coordinate conjugate to the force, K_c is the slope of a phase equilibrium curve at the critical point. For the existence of nontrivial solutions of this homogeneous system, the following condition must be valid on the whole spinodal:

$$\begin{vmatrix} \left(\frac{\partial T}{\partial S}\right)_x & \left(\frac{\partial T}{\partial x}\right)_S \\ \left(\frac{\partial T}{\partial x}\right)_S & \left(\frac{\partial X}{\partial x}\right)_S \end{vmatrix} = 0 \ . \qquad (2)$$

It coincides with the known condition for the existence of a critical state $D = 0$, where $D = \frac{\partial(T,X)}{\partial(S,x)}$ is the stability determinant of the system [4]. By the terminology of [5], let's name the values $\left(\frac{\partial T}{\partial S}\right)_x$, $\left(\frac{\partial T}{\partial x}\right)_S$, $\left(\frac{\partial X}{\partial x}\right)_S$ defined at constant thermodynamic coordinates as adiabatic (AV) and $\left(\frac{\partial T}{\partial S}\right)_X$, $\left(\frac{\partial T}{\partial x}\right)_X$, $\left(\frac{\partial X}{\partial x}\right)_T$ defined at the constant thermodynamic forces as isodynamic (IV). We call $\left(\frac{\partial T}{\partial S}\right)_x$, $\left(\frac{\partial X}{\partial x}\right)_S$, as the adiabatic stability coefficients (ASC) and $\left(\frac{\partial T}{\partial S}\right)_X$, $\left(\frac{\partial X}{\partial x}\right)_T$ as the isodynamic stability coefficients (ISC).

Definition (1) describes the critical state by AV. The critical slope K_c is a solution of the system of linear homogeneous equations. It selects just the critical point on the spinodal and can be expressed in terms of ASC:

$$K_c = \left[\mathrm{sign}\left(\frac{\partial T}{\partial x}\right)_S\right]\sqrt{\frac{\left(\frac{\partial X}{\partial x}\right)_S}{\left(\frac{\partial T}{\partial S}\right)_x}}. \qquad (3)$$

This definition together with the stability conditions of the critical state [1]- [2] result in four alternative types of critical behavior of thermodynamic systems. For each type, the behavior of the whole complex of thermodynamic characteristics of the stability, AV and IV, is established. The behavior type is defined by the behavior of one of the ASC and by the critical slope K_c:

1. $\left(\frac{\partial T}{\partial S}\right)_x \neq 0, \quad \left(\frac{\partial X}{\partial x}\right)_S \neq 0, \quad K_c \neq \{0, \infty\};$
2. $\left(\frac{\partial T}{\partial S}\right)_x \neq 0, \quad \left(\frac{\partial X}{\partial x}\right)_S = 0, \quad K_c = 0;$
3. $\left(\frac{\partial T}{\partial S}\right)_x = 0, \quad \left(\frac{\partial X}{\partial x}\right)_S \neq 0, \quad K_c = \infty;$
4. $\left(\frac{\partial T}{\partial S}\right)_x = 0, \quad \left(\frac{\partial X}{\partial x}\right)_S = 0, \quad K_c = ?$ (4)

The fourth type of critical behavior is the most interesting one. In this type, both ASC tend to zero. Therefore, the slope K_c cannot be evaluated from system (1). The type is the most "fluctuating". For it's realization, there are several possibilities [1, 2]. In particular, for one-component systems, there can be the stable critical points, at which two or even three lines of phase equilibrium converge. Such points have not been found yet experimentally, but we will show further that the critical point of the Lieb model has just the same character.

Thus, we pose the problem to determine the types of the critical behavior that there are inherent in the model and to describe the singularity of the critical point in the Lieb model.

2. After the Ising model, the ice-type models became the most important category of solvable statistical models. Lieb obtained the solution for three main kinds of such models [6, 7].

In the nature, there are a lot of crystals with hydrogen bonds. The most well-known example is ice, in which the atoms of oxygen form a lattice with coordination number four and there is a hydrogen ion between each pair of neighbour oxygen atoms.

The statistical sum of such a system is defined by the expression

$$Z = \sum \exp[-\mathcal{E}/kT] , \qquad (5)$$

where the summation should be carried out over all the configurations of hydrogen ions allowed by the ice rule and $\mathcal{E}$ is the configuration energy.

The bonds between oxygen atoms via hydrogen ions form electric dipoles. By the ice rule, there are only six configurations of hydrogen ions (vertex configurations). Therefore, the ice-type models are sometimes named as six-vertex models.

Each of these six local configurations is characterized by its own energy. Then $\mathcal{E}$ looks as

$$\mathcal{E} = n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots + n_6\varepsilon_6 , \qquad (6)$$

ε_j is the energy of the j-type vertex configuration and n_j is the number of the j-type vertices in the lattice.

As the models of critical phenomena, the ice-type models have some unusual properties. In particular in such models, the ferroelectric ordered state is "frozen" (i.e., there is a complete ordering even at a nonzero temperature).

The symmetry can be broken by the application of vertical and/or horizontal electric fields E and E', respectively.

The generalization is especially simple if $E' = 0$, that is, when only a vertical electric field is applied.

The critical thermal equation of state in the Lieb ferroelectric model [3] derived under these conditions has the form

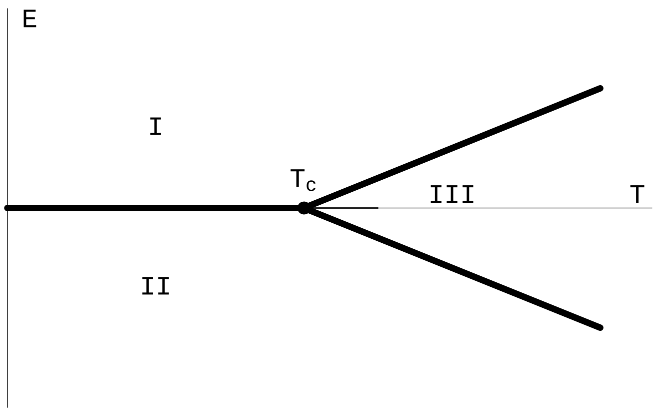
$$P = \begin{cases} \frac{E}{k(T-T_c)} \text{ at } |E| < k(T-T_c) \\ \mathrm{sign}(E) \text{ in other cases.} \end{cases} \qquad (7)$$

The corresponding phase diagram is shown in the figure.

Phases I and II are completely ordered, contain one type of vertices, and differ only in the direction of the polarization vector $\vec{P}$. The supercritical region (the region of self-consistent large-scale fluctuations, phase III in the figure) is an entirely disordered region in the sense that all correlations decrease to zero with increase in the distance proportionally to r in a negative power.

At the critical point, three lines of phase equilibrium converge: I—II, I—III and II—III (I—III and II—III are symmetric).

Consider the thermodynamic properties of the Lieb model. In this case, the electric field strength E will be the generalized thermodynamic force X and the electric polarization P will be the generalized thermodynamic coordinate. $\left(\frac{\partial T}{\partial S}\right)_P$, $\left(\frac{\partial E}{\partial P}\right)_S$, $\left(\frac{\partial T}{\partial P}\right)_S$ are the AV for the Lieb model, and $\left(\frac{\partial T}{\partial S}\right)_E$, $\left(\frac{\partial E}{\partial P}\right)_T$, $\left(\frac{\partial T}{\partial P}\right)_E$ are the IV.



Phase diagram of the Lieb model

The free energy per lattice site in the supercritical region is

$$f = \varepsilon_1 - EP - \frac{1}{2}\,k(T-T_c)(1-P^2)+$$

$$+O\left[\left(\frac{T-T_c}{T_c}\right)^{3/2}\right]. \qquad (8)$$

As $T \to T_c^-$, the free energy equals simply $\varepsilon_1 - EP$, where ε_1 is the vertex configuration energy. In this case, the heat capacity is finite, $\alpha' = 0$, $\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P} \neq \{0, \infty\}$, $\left(\frac{\partial E}{\partial P}\right)_S = 0$. Therefore according to (3), the critical slope of the phase equilibrium line upon the approach to the critical point from the precritical region equals $K_c = 0$. This corresponds to the second type of critical behavior following the thermodynamic classification (4).

From (8), we obtain that the second derivative of the free energy with respect to temperature, the heat capacity, diverges in the supercritical region as $\left(\frac{T-T_c}{T_c}\right)^{-1/2}$, that is, $\alpha = 1/2$ i $\left(\frac{\partial T}{\partial S}\right)_P = C\sqrt{\frac{T-T_c}{T_c}}$.

Let's approach to the critical point from the supercritical region along the lines of first-order phase transitions I—III and II—III. It's known that at least one of the jumps ΔP, ΔS must exist along these lines. That is, on the transition line,

$$\Delta P = P_{\rm I} - P_{\rm III} = 1 - \frac{E}{k(T-T_c)} \neq 0. \qquad (9)$$

At the critical point, we have $\Delta P = 0$.

The entropy jump can be defined from the known behavior of the heat capacity. For the phase I, $\alpha' = 0$, i.e. $C_P = C = \text{const}$. So, $S_{\rm I} = C\ln T + \text{const}$. For phase III, $\alpha = 1/2$, i.e. $S_{\rm III} = C\sqrt{T_c(T-T_c)} + \text{const}$. Then, for the jump, we have

$$\Delta S = S_{\rm I} - S_{\rm III} = C\ln T - C\sqrt{T_c(T-T_c)} + \text{const}. \qquad (10)$$

At the critical point, $\Delta S = \text{const}$. Such a behavior of entropy is connected with the divergence of C_P in the supercritical region.

Analogous results can be obtained for phases II—III as well.

For the line of phase equilibrium I—II, we have $\Delta P = 2$, $\Delta S = 0$. At the critical point, $\Delta P = 0$.

Thus, the found values of jumps correspond to the data of works [1, 2], and the point T_c for the lines of the phase transitions I—II and I—III and for the symmetric line II—III is critical. That is, three lines of equilibrium converge at the point C in the diagram (see the figure). The possibility for such a stable critical point to exist was predicted in work [2].

Let's investigate a behavior of the whole complex, AV and IV. In view of the already found behavior of the heat capacity, by using the thermic equation of state and the relations between adiabatic and isodynamic values,

$$\left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial E}{\partial P}\right)_E = \left(\frac{\partial T}{\partial S}\right)_E \left(\frac{\partial E}{\partial P}\right)_T =$$

$$= -\left(\frac{\partial T}{\partial P}\right)_E \left(\frac{\partial T}{\partial P}\right)_S, \qquad (11)$$

we obtain the following expressions for AV and IV:

$$\left(\frac{\partial T}{\partial S}\right)_P = C\sqrt{\frac{T-T_c}{T_c}},$$

$$\left(\frac{\partial E}{\partial P}\right)_S = \frac{k\sqrt{T_c(T-T_c)^3}}{kP^2 + C\sqrt{T_c(T-T_c)}},$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{kP(T-T_c)}{kP^2 + C\sqrt{T_c(T-T_c)}},$$

$$\left(\frac{\partial T}{\partial S}\right)_E = \frac{T-T_c}{kP^2 + C\sqrt{T_c(T-T_c)}},$$

$$\left(\frac{\partial E}{\partial P}\right)_T = k(T-T_c), \quad \left(\frac{\partial T}{\partial P}\right)_E = -\frac{T-T_c}{P}. \qquad (12)$$

The critical slope equals $K_c^{(1)} = kP$ for the line I—III and $K_c^{(2)} = -kP$ for line II—III.

From (12), we see that, at $T \to T_c^+$, all thermodynamic characteristics of stability tend to zero:

$$\left(\frac{\partial T}{\partial S}\right)_P \to 0, \quad \left(\frac{\partial E}{\partial P}\right)_S \to 0, \quad \left(\frac{\partial T}{\partial P}\right)_S \to 0,$$

$$\left(\frac{\partial T}{\partial S}\right)_E \to 0, \quad \left(\frac{\partial E}{\partial P}\right)_T \to 0, \quad \left(\frac{\partial T}{\partial P}\right)_E \to 0.$$

According to the thermodynamic classification of critical states (4), at $K_c \neq \{0, \infty\}$ and ACS $\to 0$, we have the fourth type of critical behavior and the convergence of two lines of phase equilibrium with the different finite slopes $K_c = \pm kP$ at the critical point. That is, upon the approach to the critical point along the line of phase equilibrium I—II, the second type is fulfilled. While approaching along II—III (I—III), we have the fourth type. Thus, this fact explains the violation of the scaling hypothesis in the model.

Thus, the application of the thermodynamic method to the Lieb model results in the conclusion that the model corresponds to two types of critical behavior, the second and fourth ones. From the point of view of this method, it is interesting to analyze the types of critical behavior which are realized in real ferroelectrics. Below, we present some examples.

Crystal KH_2PO_4 (KDP) [8] has the critical indices $\alpha = 1/2$ and $\gamma = 1$. Then the stability coefficients are $\left(\frac{\partial T}{\partial S}\right)_P = 0$, $\left(\frac{\partial E}{\partial P}\right)_T = 0$. According to classification (4), we conclude that the fourth type of critical behavior is realized in KDP.

Ferroelectric $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (triglycine sulphate) with the order-disorder transition has critical coefficients $\alpha' = \alpha = 0, \gamma = 1$ [10]. That is. $\left(\frac{\partial T}{\partial S}\right)_P \neq 0$, $\left(\frac{\partial E}{\partial P}\right)_T = 0$, which corresponds to the second type of critical behavior. Let's consider another example of the critical phenomena in ferroelectrics named "weak" due to the smallness of both the Curie–Weiss constant and the value of the spontaneous polarization. In particular, they include crystals of lithium heptagermanate $Li_2Ge_7O_{15}$ and crystals of $(CH_3NHCH_2COOH)_3 \cdot CaCl_2$. The critical indices for these crystals are $\alpha = 1/2, \gamma = 1$ [13, 14]. This means that $\left(\frac{\partial T}{\partial S}\right)_P = 0$, $\left(\frac{\partial E}{\partial P}\right)_T = 0$, which corresponds to the fourth type of critical behavior.

Thus, the analysis of the critical behavior of some real ferroelectrics, which is performed within the thermodynamic method on the base of experimental data, results in the conclusion that the second and fourth types of critical behavior are realized in such crystals like in the Lieb model.

So, we have investigated the critical properties of the two-dimensional solvable Lieb ferroelectric model within the thermodynamic method based on the constructive definition of the critical state and conditions of its stability. The results of the study are the following:

— we have analyzed the behavior of the complete complex of characteristics of the stability and obtained the proper expressions;

— we have proved that, in the precritical and supercritical regions, the second and fourth types of critical behavior are realized, respectively;

— violation of the scaling hypothesis in the Lieb model is explained by the existence of different types of critical behavior in the supercritical and precritical regions;

— it is established that, at the critical point of the model, three lines of phase equilibrium converge; the possibility for such a point to exist was predicted by the thermodynamic method [2];

— the application of the thermodynamic method in the analysis of the experimental data on some ferroelectrics have established the realization of the second or fourth type of critical behaviour in them.

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ДОСЛІДЖЕННЯ ТЕРМОДИНАМІЧНИХ ВЛАСТИВОСТЕЙ СЕГНЕТОЕЛЕКТРИЧНОЇ МОДЕЛІ ЛІБА В ОКОЛІ КРИТИЧНОЇ ТОЧКИ

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Р е з ю м е

На основі термодинамічного методу дослідження критичних станів однокомпонентних систем розглянуто критичні властивості точно розв'язуваної двовимірної сегнетоелектричної моделі Ліба. Проаналізовано поведінку повного комплексу характеристик стійкості з наближенням системи до критичної точки і встановлено тип критичної поведінки за термодинамічною класифікацією. При $T \to T_c^-$ реалізується другий тип критичної поведінки, а при $T \to T_c^+$ — четвертий тип. Порушення гіпотези скейлінгу в моделі ($\alpha' \neq \alpha$) пояснено саме реалізацією різних типів критичної поведінки в околі критичної точки. Встановлено існування у моделі критичної точки нового типу, в якій сходяться три лінії фазової рівноваги.