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THERMODYNAMIC STABILITY OF 2-DIMENSIONAL MODELS IN THE VICINITY OF A CRITICAL POINT

The properties of two-dimensional exactly solvable Lieb and Baxter models in the critical region are considered on the base of thermodynamical method developed for investigation of critical state of one-component system. From the point of view of the thermodynamic stability the behaviour of the whole set of thermodynamic characteristics of stability for these models is analyzed and the types of their critical behaviour are determined. The reasons for the violation of the scaling law hypothesis and the universality hypothesis for the models are clarified. For ferroelectric Lieb model it is ascertained that in subcritical and supercritical areas two types of critical behavior, different in fluctuation growth of energy and electric polarization are realized. This results in symmetry breaking of subcritical and supercritical indices, in essentially different behaviour of the same thermodynamic parameters on each side of a critical point. Baxter model is characterized by the same two types of critical behaviour, one of which is also presented in three cases, depending on a slope of phase equilibrium curve at the critical point. The type of the behaviour is varying dependently on the interaction parameter of the model.

Keywords: scaling law hypothesis, universality hypothesis, stability coefficients, critical state.

За допомогою термодинамічного методу дослідження критичного стану однокомпонентних систем вивчаються критичні властивості двовимірних точно розв'язуваних моделей Ліба і Бекстера. Проаналізовано поведінку повного комплексу термодинамічних характеристик стійкості цих моделей з точки зору теорії термодинамічної стійкості й визначено типи їх критичної поведінки. З'ясовано причини порушення в цих моделях гіпотез подібності й універсальності. Встановлено, що в сегнетоелектричній моделі Ліба в докритичній та закритичній областях реалізуються два типи критичної поведінки, різні за рівнем розвитку флуктуацій енергії та електричної поляризації, що призводить до порушення симетрії між докритичними і закритичними показниками, до принципово різної поведінки одних й тих самих термодинамічних величин по обидва боки від критичної точки. Модель Бекстера характеризується тими самими двома типами критичної поведінки, один з яких до того ж представлений трьома можливостями – в залежності від нахилу лінії фазової рівноваги в критичній точці. Тип поведінки змінюється залежно від параметра взаємодії моделі.

Ключові слова: гіпотеза подібності, гіпотеза універсальності, коефіцієнти стійкості, критичний стан.

При помощи термодинамического метода исследования критического состояния однокомпонентных систем изучаются критические свойства двумерных точно решаемых моделей Либа и Бэкстера. Проанализировано поведение полного комплекса термодинамических характеристик устойчивости этих моделей с точки зрения теории термодинамической устойчивости и определены типы их критического поведения. Выяснены причины нарушения в этих моделях гипотез подобия и универсальности. Установлено, что в сегнетоэлектрической модели Либа в докритической и закритической области реализуются два типа критического поведения, разные по уровню развития флуктуаций энергии и электрической поляризации, что приводит к нарушению симметрии между докритическими и закритическими показателями, к принципиально разному поведению одних и тех же термодинамических величин по обе стороны от критической точки. Модель Бэкстера характеризуется теми же двумя типами критического поведения, один из которых к тому же представлен тремя возможностями – в зависимости от наклона линии фазового равновесия в критической точки. Тип поведения изменяется в зависимости от параметра взаимодействия модели.

Ключевые слова: гипотеза подобия, гипотеза универсальности, коэффициенты устойчивости, критическое состояние.

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1. Introduction

Description of the behaviour of thermodynamic parameters near the critical points is one of the basic problems of the critical state theory. Direct statistical calculations are unavailable at present because of impossibility of accounting exactly for the interactions and for the fluctuations which are large near the critical point. So, solving the problem by the methods of statistical physics one considers either the simplest models, for which the partition function can be evaluated exactly, or an approximate solution of the problem.

At the first approach the exactly solvable two-dimensional models (the Ising, Lieb, Baxter models and others [1]) are of great importance. The second approach is connected mainly with examination of the asymptotic behaviour of thermodynamic parameters near the critical points, as well as with the development of the scaling law hypothesis, the universality hypothesis and the renormalization group approximation and has appreciably succeeded. Indeed, the large class of real systems and models satisfies the scaling law and the universality hypotheses. The existence of real systems and exactly solvable two-dimensional models, for which these hypotheses are violated, is also remarkable. The six-vertex ferroelectric Lieb model and the eight-vertex Baxter model [1] are such examples.

The Lieb and Baxter models give a reasonable fit to real ferroelectrics (antiferroelectrics) and ferromagnets (antiferromagnets). The aim of this paper is to examine the critical properties of these models on the base of the thermodynamical method of investigation of the critical state [2, 3]. The method is based on the constructive critical state definition and the critical state stability conditions and describes a variety of critical state nature manifestations. On the basis of investigation of the whole set of stability characteristics of a system (adiabatic (the AP's) and isodynamic (the IP's) parameters [4,5]) method establishes four alternative types of critical behaviour for thermodynamic quantities, classified by the value of adiabatic stability coefficients (the ASC's) and the critical slope K_c of the phase equilibrium curve.

2. The ferroelectric 6-vertex Lieb model

There are a lot of crystals with the hydrogen bonds in the nature [6]. The ions in such crystals must obey the ice rule. The bonds between atoms via hydrogen ions form the electric dipoles. The partition function of such a system is defined by the expression

$$Z = \sum \exp\left[-\left(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots + n_6\varepsilon_6\right)/kT\right], \tag{1}$$

where the summation should be carried out over all the configurations of the hydrogen ions allowed by the ice rule, ε_i is the energy of i-type vertex configuration and n_i is the number of i-type vertices in the lattice.

There are three sorts of the ice models which have been solved by E. H. Lieb [7, 8]. One of them can describe KH_2PO_4 (KDP), which is ordered ferroelectrically at low temperatures under the appropriate choice of $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_6$. For the square lattice this choice is

$$\varepsilon_1 = \varepsilon_2 = 0, \quad \varepsilon_3 = \varepsilon_4 = \varepsilon_5 = \varepsilon_6 > 0\,. \tag{2}$$

The ice models as models of critical phenomena have some unusual properties: the ferroelectric state at these models is frozen (i.e. there is complete ordering even at the non-zero temperature). This symmetry can be broken by imposition of external field.

The expression for the free energy per lattice point in the presence of the nonzero external field is given by

$$f = \varepsilon_1 - EP - k(T - T_c)(1 - P^2)/2 + A[(T - T_c)/T_c]^{3/2}, \tag{3}$$

where E is electric field, P is electric polarization [1], and $A = -0.2122064 \cdot kT_c$; k is Boltzmann constant, T_c is critical temperature. The critical equation of state is expressed in the form

$$P = \begin{cases} E/[k(T - T_c)], & \text{if } |E| < k(T - T_c), \\ \text{sign}(E) & \text{otherwise.} \end{cases}, \tag{4}$$

It corresponds to the phase diagram in Fig. 1.

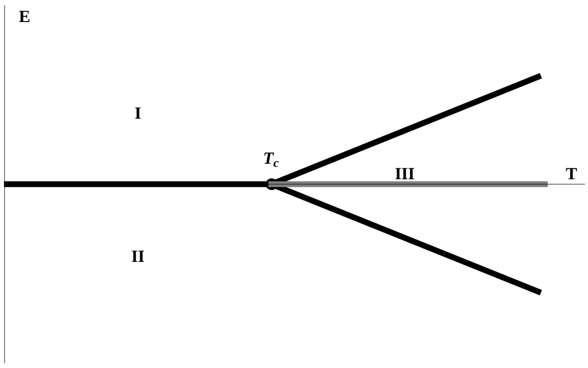

Fig. 1. The phase diagram [1] and quasispinodal (gray line, [10]) of Lieb model

It is necessary to emphasize that the ice model allows the investigation on the basis of the thermodynamic method [2, 3]. In this case the temperature T and the electric intensity E stand for the generalized thermodynamic forces. The conjugated generalized thermodynamic variables are the entropy S and the electric polarization P. Thus, the adiabatic parameters for given model are $(\partial T/\partial S)_P, (\partial T/\partial P)_S$, $(\partial E/\partial P)_S$, and the isodynamic parameters are $(\partial T/\partial S)_E, (\partial T/\partial P)_E$, $(\partial E/\partial P)_T$. As $T \to T_c^+$ the free energy per lattice point coincides with expression (3), and as $T \to T_c^-$ the free energy equals simply to $\varepsilon_1 - EP$. Consequently, the heat capacity is finite in the subcritical region and its critical index is $\alpha' = 0$. Both the phases I and II are quite ordered and then differ from each other only by a direction of the electric polarization vector ($P = \pm 1$). This corresponds to the second critical behaviour type according to the thermodynamic classification of critical behaviour types of one-component systems [2]: $(\partial T/\partial S)_P = T/C_P \neq \{0, \infty\}$, $(\partial E/\partial P)_S = 0$. Thus, the critical slope of the equilibrium curve of the phases I and II (Fig. 1) equals to zero, $K_c = 0$.

As we can see from Eq. (3), in the supercritical region ($T \to T_c^+$) the heat capacity diverges as $[(T - T_c)/T_c]^{-1/2}$, i.e. the thermic ASC is $(\partial T/\partial S)_P = C\sqrt{(T - T_c)/T_c}$. Let us approach to the critical point from the supercritical region along the curve of the first-kind phase transition I-III and II-III (Fig. 1). It is known that at least one of the jumps ΔP, ΔS must exist along these curves. I.e., on the transition curve

$$\Delta P = P_{\text{I}} - P_{\text{III}} = 1 - E/[k(T - T_c)] \neq 0. \tag{5}$$

At the critical point $\Delta P = 0$.

The entropy jump can be determined from the known behaviour of the heat capacity. For the phase I we have $\alpha'=0$, i.e. $C_P = \mathrm{const}$. Consequently, the entropy of the phase I is $S_\mathrm{I} = C_1 \ln T + \mathrm{const}$. For the phase III we have $\alpha = 1/2$, i.e. $S_\mathrm{III} = C_2\sqrt{T_\mathrm{c}(T-T_\mathrm{c})} + \mathrm{const}$. Then, for the jump we have

$$\Delta S = S_\mathrm{I} - S_\mathrm{III} = C_1 \ln T - C_2\sqrt{T_\mathrm{c}(T-T_\mathrm{c})} + \mathrm{const}. \tag{6}$$

At the critical point $\Delta S = \mathrm{const} \neq \{0,\infty\}$. Such a behaviour of the entropy is connected with the divergence of the heat capacity in the supercritical region.

The analogous results can be obtained for phases II-III as well. For the equilibrium line I-II we have $\Delta P = 2$, $\Delta S = 0$. At the critical point $\Delta P = 0$.

Thus, the found values of the jumps correspond to the results of papers [2, 3], and the point T_c is critical for the phase equilibrium line I-II, for the line I-III and for the line II-III. So, point C in the phase diagram (Fig. 1) is the point of convergence of three phase equilibrium lines. The possibility of such a point has been predicted in papers [2, 3].

Let us analyze the behaviour of the whole set of the system stability characteristics. Using Eqs. (3) and (4), we can obtain the following expressions for the AP's and the IP's:

$$\begin{aligned}
&\left(\frac{\partial T}{\partial S}\right)_P = C\sqrt{(T-T_\mathrm{c})/T_\mathrm{c}}, &&\left(\frac{\partial E}{\partial P}\right)_S = \frac{k\sqrt{T_\mathrm{c}(T-T_\mathrm{c})^3}}{kP^2 + C\sqrt{T_\mathrm{c}(T-T_\mathrm{c})}},\\
&\left(\frac{\partial T}{\partial P}\right)_S = \frac{kP(T-T_\mathrm{c})}{kP^2 + C\sqrt{T_\mathrm{c}(T-T_\mathrm{c})}}, &&\left(\frac{\partial T}{\partial S}\right)_E = \frac{T-T_\mathrm{c}}{kP^2 + C\sqrt{T_\mathrm{c}(T-T_\mathrm{c})}},\\
&\left(\frac{\partial E}{\partial P}\right)_T = k(T-T_\mathrm{c}), &&\left(\frac{\partial T}{\partial P}\right)_E = -(T-T_\mathrm{c})/P,
\end{aligned} \tag{7}$$

where $C = -4T_\mathrm{c}^{\,2}/(3A) = 6.2831908\cdot T_\mathrm{c}/k$. The critical slope of phase equilibrium curve equals $K_\mathrm{c}^{(1)} = kP$ for the line I-III and $K_\mathrm{c}^{(2)} = -kP$ for II-III. At $T \to T_\mathrm{c}^{+}$ all the AP's and the IP's tend to zero.

According to the critical behaviour classification [2], at $K_\mathrm{c} \neq \{0,\infty\}$ and ASC's$\to\infty$ we have the fourth type of the critical behaviour, and two phase equilibrium lines with different critical slopes $K_\mathrm{c}^{(1,2)} = \pm kP$ converge at the critical point. This behaviour type is the most fluctuating one (the fluctuations of energy and polarization $\overline{(\Delta H)^2}, \overline{(\Delta P)^2} \to \infty$). Approaching to the critical point from the subcritical region (along the phase equilibrium line I-II with the slope $K_\mathrm{c} = 0$), the second type of critical behaviour is realized (the fluctuations of energy $\overline{(\Delta H)^2}$ is finite and the fluctuations of polarization $\overline{(\Delta P)^2} \to \infty$).

As it is known, stability characteristics are inversely proportional to fluctuations of external parameters of the system. At the continuous transitions [5] determinant of stability D and stability coefficients (the SC's) pass finite minima, that corresponds to the growth of fluctuations. The locus of these minima is curve of supercritical transitions (the lowered stability curve or quasispinodal). The limit case of these continuous transitions, when fluctuations in the system are at the high and D and the SC's pass zero minima, is the critical state. The critical point is also the limit point of some first-kind transition (the limit point of phase equilibrium curve). If the phase equilibrium curve and curve of supercritical transitions pass into each other continuously, i.e. the slopes of these curves are the same, then the tricritical point is observed, where three phases become identical: two subcritical phases and supercritical one.

On the quasispinodal the next condition is fulfilled [9]:

$$dD = \left(\frac{\partial D}{\partial S}\right)_P dS + \left(\frac{\partial D}{\partial P}\right)_S dx = 0\,. \tag{8}$$

Using results (7) to find the determinant of stability for Lieb model and investigating where condition (8) is fulfilled, we obtain $E = 0$ [10]. This is equation of quasispinodal (the gray line in Fig. 1) for ferroelectric Lieb model. So, the maximal growth of fluctuations is observed under zero electric field. The critical slope of the subcritical phase equilibrium curve is $K_c = 0$. It means that for this model the case of continuous passage of the equilibrium curve into the lowered stability curve is realized because of the same critical slopes.

Thus, the violation of the scaling law hypothesis in the Lieb model can be explained by the fact that the model corresponds to two different critical behaviour types: at $T \to T_c^-$ the second type and at $T \to T_c^+$ the fourth type is fulfilled. Besides, the critical point of the Lieb model is the critical point of a special type with the convergence of three phase equilibrium lines. Moreover, the equilibrium curve continuously passes into the lowered stability curve.

3. 8-vertex Baxter model

The eight-vertex Baxter model is a generalization of the six-vertex Lieb model [6, 11-13]. The formation of j-type vertex needs the energy ε_j (where $j = 1, \ldots, 8$). For such a model the partition function is given by (1) where the summation is performed over the eight vertex configurations. Thus, besides the first six vertices coinciding with the Lieb model there are another two new vertices.

The Baxter model is fitted to describe the critical phenomena in ferroelectrics (antiferroelectrics). The eight-vertex model can be considered also as two Ising models with the nearest neighbours interaction (each model is on its sublattice). These sublattices are connected by means of the four-spin interaction. In this case the model corresponds to ferromagnets.

The Baxter model has the exact solution only in the absence of an external field.

The ferromagnetic Baxter model. In the case of ferromagnet the adiabatic stability coefficients get the following asymptotic form:

$$\left(\frac{\partial T}{\partial S}\right)_M \sim t^{2-\frac{\pi}{\mu}}, \quad \left(\frac{\partial H}{\partial M}\right)_S \sim t^{\frac{7\pi}{8\mu}}$$

where $t = |T - T_c|/T_c$; μ is the interaction parameter, it takes a value from $(0, \pi)$. It is necessary to note that in absence of the external field the behaviour of the isodynamic parameters coincides with the behaviour of the adiabatic parameters. When $0 < \mu \le \pi/2$

the heat capacity exponent α is negative, the magnetic susceptibility exponent γ takes a positive value, i.e.

$$\left(\frac{\partial T}{\partial S}\right)_M \neq 0\,, \left(\frac{\partial H}{\partial M}\right)_S = 0 \quad \Rightarrow \left(\frac{\partial T}{\partial M}\right)_S = 0, \quad K_c = 0$$

and the second type of critical behaviour takes place. At $\pi/2 < \mu < 15\pi/16$ the fourth type of critical behaviour is realized, the exponent α increases ($0 < \alpha < 14/15$) and the index γ decreases ($7/4 > \gamma > 14/15$), where $\alpha < \gamma$.

$$\left(\frac{\partial T}{\partial S}\right)_M = 0, \left(\frac{\partial H}{\partial M}\right)_S = 0 \quad \Rightarrow \quad \left(\frac{\partial T}{\partial M}\right)_S = 0\,.$$

All the parameters in this case tend to zero, but $(\partial H/\partial M)_S$ and $(\partial H/\partial M)_T$ tend to zero faster than other parameters. The value of the critical slope is $K_c = 0$. The case $\mu = 15\pi/16$ corresponds also to the fourth type of critical behaviour, but $\alpha = \gamma = 14/15$ and all the parameters tend to zero according to the same law, the critical slope is $K_c \neq \{0, \infty\}$. At $15\pi/16 < \mu < \pi$ the fourth type of critical behaviour is also observed, $14/15 < \alpha < 1$ and $14/15 > \gamma > 7/8$, and everywhere $\alpha > \gamma$. All the parameters tend to zero, but $(\partial T/\partial S)_M$ and $(\partial T/\partial S)_H$ tend to zero faster than other parameters. The value of the critical slope is $K_c = \infty$. The corresponding plots of ASC's for various μ are presented in Figs. 2, 3.

Thus, the performed analysis enables to reveal that at $0 < \mu \leq \pi/2$ the critical behaviour of the Baxter model corresponds to the second type according to the thermodynamic classification [2, 3] with $K_c = 0$, and at $\pi/2 < \mu < \pi$ it corresponds to the fourth type which is realized by three possibilities for the critical slope ($K_c = 0$, $K_c \neq \{0, \infty\}$, $K_c = \infty$) depending on the value of μ, varying within the mentioned interval.

The ferroelectric Baxter model. In the case of the ferroelectric Baxter model the stability coefficients can be written in the form:

$$\left(\frac{\partial T}{\partial S}\right)_P \sim t^{2-\frac{\pi}{\mu}}, \left(\frac{\partial E}{\partial P}\right)_S \sim t^{\frac{\pi+\mu}{2\mu}}.$$

At $0 < \mu \leq \pi/2$, as in the previous case, α is negative and γ is positive. So $(\partial T/\partial S)_P \neq 0$, $(\partial E/\partial P)_S = 0 \quad \Rightarrow (\partial T/\partial P)_S = 0, \quad K_c = 0$ and the second type of critical behaviour is fulfilled. At $\pi/2 < \mu < \pi$ the exponent α takes positive values $0 < \alpha < 1$, but α is less than γ, $3/2 > \gamma > 1$ and the fourth type of critical behaviour with $K_c = 0$ is realized.

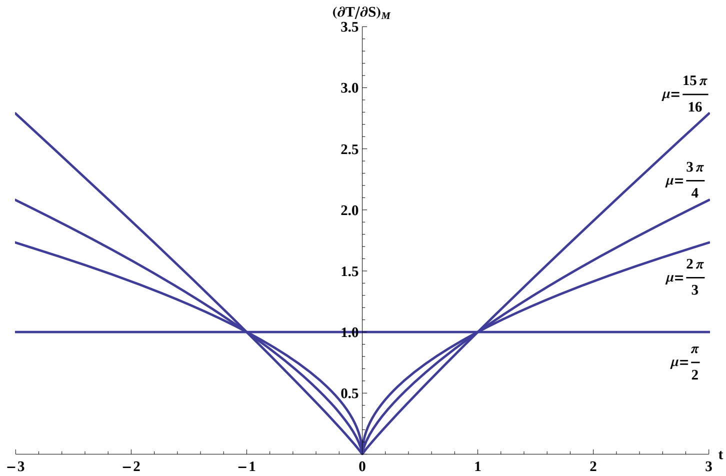

Fig. 2. The temperature dependence for reduced thermic coefficient of stability

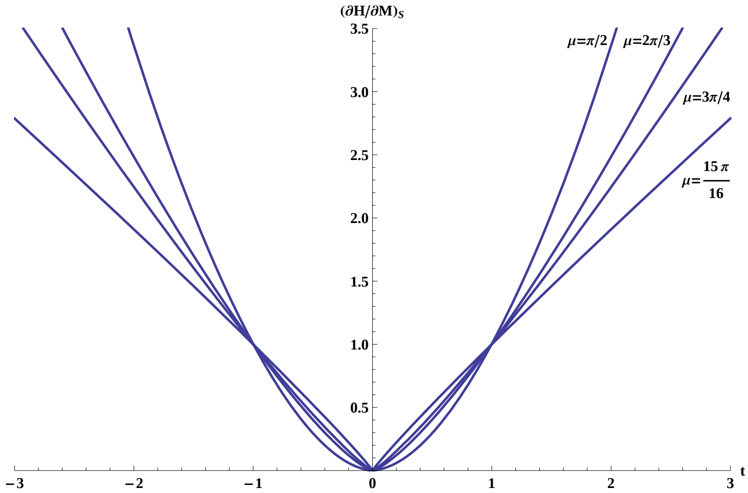

Fig. 3. The temperature dependence for reduced magnetic coefficient of stability

It is necessary to emphasize the fact that for real ferromagnets and ferroelectrics the critical behaviour types are also the second and the fourth ones.

4. Conclusions

Thus, in the paper the consideration of the thermodynamic stability of the Lieb and Baxter models by the method of Refs. [2, 3] is performed. The asymptotic expressions for the whole set of the stability characteristics are determined. The reasons for the violation of the scaling law and universality hypotheses in the models are clarified. So, we determine that the second and the fourth type of critical behaviour take place in the subcritical and in the supercritical region of the Lieb model, correspondingly. The violation of the scaling law hypothesis in the ferroelectric Lieb model can be explained just by difference of the behaviour types. It has been also ascertained that three phase equilibrium lines with different critical slopes converge at the critical point of the model. A possibility of the existence of such a type of the critical point has been predicted in papers [2, 3]. The equation of quasispinodal is obtained and it is shown that the equilibrium curve continuously passes into the lowered stability curve in this model.

In the Baxter model the realization of the second and the fourth type of critical behaviour also occurs, moreover, the fourth type is represented by three possibilities – with three different critical slopes of the phase equilibrium line. The reason for the violation of the universality hypothesis is that each of the mentioned types (the second type, the fourth type with $K_c = 0$, the fourth type with $K_c \neq \{0, \infty\}$ and the fourth type with $K_c = \infty$) is connected either to the certain value or the continuous range of the interaction parameter μ. It is interesting to emphasize that in each model while one hypothesis is violated, another nevertheless holds. In addition, the special case of the eight-vertex Baxter model, where the universality hypothesis is violated, is the Lieb model ($\mu = 0$), in which the universality hypothesis is satisfied, but the scaling law hypothesis is violated, and the Ising model ($\mu = \pi/2$), where both hypotheses are fulfilled.

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