Thermodynamic stability of ice models in the vicinity of a critical point

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Abstract

The properties of the two-dimensional exactly solvable Lieb and Baxter models in the critical region are considered based on the thermodynamic method of investigation of a one-component system critical state. From the point of view of the thermodynamic stability the behaviour of adiabatic and isodynamic parameters 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.

Key words: scaling law hypotheses; universality hypotheses; stability coefficients; critical state

1 Introduction

The 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 connected with the evaluation of the partition function of real systems are unavailable at present because of the impossibility of accounting exactly for the interactions and, moreover, 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] forming the most valuable possession of statistical mechanics) are of great importance. The second approach is connected mainly with the 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 in various variants 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.

Our aim is the examination of the critical properties of these models based on the thermodynamic method of investigation of the critical state [2]–[4] which is developed on the first principles without any hypotheses.

The method is based on the constructive critical state definition and the critical state stability conditions. The method describes a variety of critical state nature manifestations. The violation of the scaling law and universality hypotheses in the Lieb and Baxter models is explained just by this variety.

The Lieb and Baxter models give a reasonable fit to real ferroelectrics (antiferroelectrics) and ferromagnets (antiferromagnets). So, the application of the thermodynamic method [2]–[4] to them could be interesting for the development of the critical state theory.

2 The thermodynamic method of investigation of the critical state

Let us consider the basic theses of the thermodynamic method and the terminology. The critical state definition, which considers both the properties of homogeneous and heterogeneous system can be written in the form [2]–[4]:

\[
\begin{align*}
    dT &= \left( \frac{\partial T}{\partial S} \right)_x dS + \left( \frac{\partial T}{\partial x} \right)_S dx = 0, \\
    dX &= \left( \frac{\partial X}{\partial S} \right)_x dS + \left( \frac{\partial X}{\partial x} \right)_S dx = 0, \\
    \left( \frac{\partial X}{\partial T} \right)_c &= -\frac{dS}{dx} = K_c.
\end{align*}
\]  

(1)

Here $X$ is the generalized thermodynamic force, $x$ is the conjugated thermodynamic variable (the external parameter of a system), $K_c$ is the critical
slope of a phase equilibrium curve. Eq. (1) has non-trivial solutions, if the condition

\[
\begin{bmatrix}
\frac{\partial T}{\partial S} & \frac{\partial X}{\partial x} \\
\frac{\partial T}{\partial x} & \frac{\partial T}{\partial x}
\end{bmatrix}
\begin{bmatrix}
\frac{\partial T}{\partial x} \\
\frac{\partial T}{\partial x}
\end{bmatrix}
= D = \left(\frac{\partial T}{\partial S}\right)_x \left(\frac{\partial X}{\partial x}\right)_S - \left(\frac{\partial T}{\partial x}\right)_S^2 = 0.
\]

(2)

is fulfilled all over the spinodal. It coincides with the well-known critical state condition $D = 0$, where $D$ is the stability determinant of the system [5, 6]. According to the terminology of Refs. [5, 6] the parameters concerned under the constant thermodynamic variables, $\left(\frac{\partial T}{\partial S}\right)_x, \left(\frac{\partial T}{\partial x}\right)_S, \left(\frac{\partial X}{\partial x}\right)_S$, are the adiabatic parameters (AP’s); the parameters concerned under the constant thermodynamic forces, $\left(\frac{\partial T}{\partial S}\right)_S, \left(\frac{\partial T}{\partial x}\right)_T, \left(\frac{\partial X}{\partial x}\right)_T$, are the isodynamic parameters (IP’s). The parameters $\left(\frac{\partial T}{\partial S}\right)_x$ and $\left(\frac{\partial X}{\partial x}\right)_S$ are called the adiabatic stability coefficients (ASC’s); whereas $\left(\frac{\partial T}{\partial S}\right)_S$ and $\left(\frac{\partial X}{\partial x}\right)_T$ are called the isodynamic stability coefficients (ISC’s). The stability coefficients are related to the fluctuations of the external parameters of the system (the first and the second Gibbs lemmas) which infinitely increase near the critical point.

The definition (1) describes the critical state by means of the AP’s. The solution of the homogeneous linear equations (1) is the critical slope $K_c$ which distinguishes the critical point on the spinodal. It is the fundamental characteristic of the critical state and it can be expressed via the ASC’s:

\[
-dS\frac{dx}{dx} = K_c = \left[\text{sign} \left(\frac{\partial T}{\partial x}\right)_S\right] \left(\frac{\partial T}{\partial x}\right)_S^{-1} \left(\frac{\partial T}{\partial x}\right)_x^{1/2}.
\]

(3)

This definition, being combined with the critical state stability conditions, leads to the existence of four alternative types of the critical behaviour of thermodynamic systems [2–4]. The behaviour type is defined by the value of one ASC and $K_c$.

The behaviour of the whole set of the stability characteristics of the system (the AP’s and IP’s) is determined for each type. The fourth type of the
critical behaviour is the most interesting and the most "fluctuating" one. In this case it is necessary to consider the differential equations of higher orders. Then the solution is realized by several possibilities [2]–[4]. The case of two or even three phase equilibrium curves converging at the critical point is of special interest. Such a point has not yet been found experimentally, but in this paper we demonstrate that the critical point of the ferroelectric Lieb model has just this feature.

3 The ferroelectric 6-vertex Lieb model

There are a lot of crystals with the hydrogen bonds in the nature [1]. The ions in such crystals (with the coordination number four) must obey the ice rule. The bonds between atoms via hydrogen ions form the electric dipoles. So, it is convenient to represent them as the arrows on the bond curves. These arrows are directed to that end of the bond which is occupied by the ion. There are only six such configurations of arrows, therefore the ice models are sometimes called the six-vertex models. The partition function of such a system is defined by the expression

\[ Z = \exp\left[-(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots + n_6\varepsilon_6)/kT\right], \]  

(4)

where the summation should be carried out over all the configurations of the hydrogen ions allowed by the ice rule, \( \varepsilon_i \) 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, considered in this paper, can describe \( KH_2PO_4 \) (KDP), the crystal with hydrogen bonds, which is characterized by the coordination number four and orders ferroelectrically at low temperatures under the appropriate choice of \( \varepsilon_1, \varepsilon_2, \ldots, \varepsilon_6 \). For the square lattice this choice is

\[ \varepsilon_1 = \varepsilon_2 = 0, \ \varepsilon_3 = \varepsilon_4 = \varepsilon_5 = \varepsilon_6 > 0. \]  

(5)

In the ground state all the arrows are directed either up and to the right or down and to the left. Both these states are typical for the ordered ferroelectric.

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

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

(6)
Figure 1: The phase diagram of Lieb model [1]

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

$$P = \begin{cases} 
\frac{E}{k(T - T_c)}, & \text{if } |E| < k(T - T_c) \\
\text{sign}(E), & \text{otherwise}
\end{cases}$$  \quad (7)$$

It corresponds to the phase diagram in Fig. [1].

It is necessary to emphasize that the ice model allows the investigation on the basis of the thermodynamic method. 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 the given model are $\left(\frac{\partial T}{\partial S}\right)_P$, $\left(\frac{\partial T}{\partial P}\right)_S$ and $\left(\frac{\partial E}{\partial P}\right)_S$, and the isodynamic parameters are $\left(\frac{\partial T}{\partial S}\right)_E$, $\left(\frac{\partial T}{\partial P}\right)_E$ and $\left(\frac{\partial E}{\partial P}\right)_T$. As $T \to T_c^+$ the free energy per lattice point coincides with expression (6), 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 the critical exponent is $\alpha' = 0$. Both the phases 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 \([3]\): \( \left( \frac{\partial T}{\partial S} \right)_P = \frac{T}{C_P} \neq \{0, \infty\} \), \( \left( \frac{\partial E}{\partial P} \right)_S = 0 \). Thus, the critical slope of the equilibrium curve of the phases \( I \) and \( II \) equals to zero, \( K_c = 0 \).

As we can see from Eq. (6), in the supercritical region \( (T \rightarrow T_c^+) \) the heat capacity diverges as \( \left( \frac{T - T_c}{T_c} \right)^{1/2} \), i.e. the thermic ASC is \( \left( \frac{\partial T}{\partial S} \right)_P = C \sqrt{\frac{T - T_c}{T_c}} \). Let us approach to the critical point from the supercritical region along the curve of the first-kind phase transition \( I \rightarrow III \) and \( II \rightarrow III \). It is known that at least one of the jumps \( \Delta P, \Delta S \) must exist along these curves. I.e., on the transition curve

\[
\Delta P = P_I - P_{III} = 1 - \frac{E}{k(T - T_c)} \neq 0.
\]

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. \( C_P = \text{const} \). Consequently, the entropy of the phase \( I \) is \( S_I = C_1 \ln T + \text{const} \). For the phase \( III \) we have \( \alpha = 1/2 \), i.e. \( S_{III} = C_2 \sqrt{T_c(T - T_c)} + \text{const} \). Then, for the jump, we have

\[
\Delta S = S_I - S_{III} = C_1 \ln T - C_2 \sqrt{T_c(T - T_c)} + \text{const}.
\]

At the critical point \( \Delta S = \text{const} \neq \{0, \infty\} \). 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 \( II \rightarrow III \) as well.

For the equilibrium line \( I \rightarrow II \) 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 \([2\text{-}4]\), and the point \( T_c \) is critical for the phase equilibrium line \( I \rightarrow II \), for the line \( I \rightarrow III \) and for the line \( II \rightarrow III \). So, the point \( C \) in the phase diagram (Fig. 1) is the point of the convergence of three phase equilibrium lines. The possibility of such a point has been predicted in papers \([2\text{-}4]\).
Let us analyze the behaviour of the whole set of the system stability characteristics (the AP’s and the IP’s). The relations between the adiabatic and isodynamic parameters exist:

\[
\left( \frac{\partial T}{\partial S} \right)_P \left( \frac{\partial E}{\partial P} \right)_T = \left( \frac{\partial T}{\partial S} \right)_E \left( \frac{\partial E}{\partial P} \right)_S = - \left( \frac{\partial T}{\partial P} \right)_S \left( \frac{\partial T}{\partial P} \right)_E.
\]

(10)

Using Eqs. (7) and (10), we can obtain the following expressions for the AP’s and the IP’s:

\[
\left( \frac{\partial T}{\partial S} \right)_P = C \sqrt{\frac{T - T_c}{T_c}}, \quad \left( \frac{\partial E}{\partial P} \right)_S = \frac{k \sqrt{T_c(T - T_c)^3}}{k P^2 + C \sqrt{T_c(T - T_c)}},
\]

\[
\left( \frac{\partial T}{\partial P} \right)_S = \frac{k P(T - T_c)}{k P^2 + C \sqrt{T_c(T - T_c)}}, \quad \left( \frac{\partial T}{\partial S} \right)_E = \frac{k P(T - T_c)}{T - T_c},
\]

\[
\left( \frac{\partial E}{\partial P} \right)_T = \frac{k P(T - T_c)}{T - T_c}, \quad \left( \frac{\partial T}{\partial P} \right)_E = - \frac{k P}{P},
\]

(11)

where \( C = -\frac{4 T_c^2}{3 A} = 6.2831908 \cdot \frac{T_c}{k} \). The critical slope equals \( K_c^{(1)} = k P \) for the line \( I - III \) and \( K_c^{(2)} = -k P \) for the line \( II - III \).

As it follows from Eq. (11), at \( T \to T_c^+ \) all the thermodynamic stability characteristics 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 critical behaviour classification \[3\] at \( K_c \neq \{0, \infty\} \) and ASC’s \( \to 0 \) we have the fourth type of the critical behaviour, and two phase equilibrium lines with different critical slopes \( K_c^{(1,2)} = \pm k P \) converge at the critical point. This behaviour type is the most fluctuating one (the fluctuations of the energy and polarization \( (\Delta H)^2, (\Delta P)^2 \to \infty \)). Approaching to the critical point from the subcritical region (along the phase equilibrium line \( I - II \) with the slope \( K_c = 0 \)) the second type of critical behaviour is realized (the fluctuations of the energy \( (\Delta H)^2 \) is finite and the fluctuations of the polarization \( (\Delta P)^2 \to \infty \)).

As it is known, stability characteristics are inversely proportional to fluctuations of external parameters of the system. At the continuous transitions \[6\] \( D \) and 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 subvritical phases and supercritical one.

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

$$\frac{dD}{dx} + \left(\frac{\partial D}{\partial x} \right)_S = 0,$$

or, equivalently,

$$\left(\frac{\partial D}{\partial S} \right)_x = 0,$$

$$\left(\frac{\partial D}{\partial x} \right)_S = 0.$$

Using results (11) to find the determinant of stability for Lieb model, and investigating where condition (12) is fulfilled, we obtain $E = 0$. This is equation of quasispinodal for ferroelectric Lieb model. The resulting phase diagram is shown in Fig. 2. 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 it is realized the case of continuous passage of the equilibrium curve into the lowered stability curve 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 $T_c^-$ 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.

4 8-vertex Baxter model

The eight-vertex Baxter model is a generalization of the six-vertex Lieb model. The ice models as the models of the 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); the critical behaviour of antiferroelectrics is characterized by the more complicated law instead of a simple power dependence of \((T - T_c)\).

The first of these unusual properties is connected with the ice structure. In the case of an unlimited lattice with the ferroelectric ordering the infinite energy is needed for a deformation. So, the deformation gives an infinitesimal contribution to the partition function \[1\].

The following generalization of the ice-type models was proposed \[10\]–\[12\]:

- there is only one arrow on each square lattice edge;
- the configurations with an even number of arrows getting in (and getting off) each vertex are allowed only;
- eight possible configurations of the arrows to a vertex exist.

The formation of \(j\)-type vertex needs the energy \(\varepsilon_j\) (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 for which all the arrows get either in a vertex
or off a vertex. Now the finite energy is needed for the local deformation of the lattice state (e.g. for reversing of all the arrows which are lying on the square side), in which all the arrows are directed up or to the right. So the ferroelectric state is ordered not completely.

As it was mentioned above, 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 interplay. In this case the model corresponds to ferromagnets.

The Baxter model has the exact solution only in the absence of an external field. The critical exponents of this model equal [1]

\[ \alpha = \alpha' = 2 - \frac{\pi}{\mu}, \]
\[ \beta = \frac{\pi}{16\mu}, \beta_e = \frac{\pi - \mu}{4\mu}, \]
\[ \gamma = \frac{7\pi}{8\mu}, \gamma_e = \frac{\pi + \mu}{2\mu}, \]
\[ \delta = 15, \delta_e = \frac{3\pi + \mu}{\pi - \mu}. \]

Here the index \( e \) denotes the electric exponents. The exponents \( \beta, \gamma \) and \( \delta \) are related to ferromagnet. The exponent \( \alpha \) is the same both for the ferromagnet and for the ferroelectric. \( \mu \) is the interaction parameter, it takes a value from \((0, \pi)\). Thus, as we can see, the critical exponents depend on the interaction parameter continuously. This fact is in the contrary to the universality hypothesis. This result distinguishes the Baxter model among the others two-dimensional exactly solvable models. Taking this into the consideration, one should expect that the type of the critical behaviour according to the thermodynamic classification and the value of the critical slope change depending on the interaction parameter. Let us show this.

### 4.1 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 \( t = \frac{T - T_c}{T_c} \). It is necessary to note that in the absence of the external field the behaviour of the isodynamic parameters coincides with the behaviour of the adiabatic parameters. When \( 0 < \mu \leq \frac{\pi}{2} \) the exponent \( \alpha \) is negative, the exponent \( \gamma \) takes a positive value, i.e.

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

and the second type of critical behaviour is fulfilled. At \( \frac{\pi}{2} < \mu < \frac{15\pi}{16} \) the fourth type of critical behaviour is realized, the exponent \( \alpha \) increases \((0 < \alpha < \frac{14}{15})\) and the exponent \( \gamma \) decreases \((\frac{7}{4} > \gamma > \frac{14}{15})\), where \( \alpha < \gamma \).

![Figure 3: The temperature dependence for reduced thermic coefficient of stability](image)

\[
\left( \frac{\partial T}{\partial S} \right)_M = 0, \quad \left( \frac{\partial H}{\partial M} \right)_S = 0 \Rightarrow \left( \frac{\partial T}{\partial M} \right)_S = 0.
\]
Figure 4: The temperature dependence for reduced magnetic coefficient of stability

All the parameters in this case tend to zero, but \( \left( \frac{\partial H}{\partial M} \right)_S \) and \( \left( \frac{\partial H}{\partial M} \right)_T \) tend to zero faster than other parameters. The value of the critical slope is \( K_c = 0 \). The case \( \mu = \frac{15\pi}{16} \) corresponds also to the fourth type of critical behaviour, but \( \alpha = \gamma = \frac{14}{15} \) and all the parameters tend to zero according to the same law, the critical slope is \( K_c \neq \{0, \infty\} \). At \( \frac{15\pi}{16} < \mu < \pi \) the fourth type of critical behaviour is also fulfilled, \( \frac{14}{15} < \alpha < 1 \) and \( \frac{14}{15} > \gamma > \frac{7}{8} \) and everywhere \( \alpha > \gamma \). All the parameters tend to zero, but \( \left( \frac{\partial T}{\partial S} \right)_M \) and \( \left( \frac{\partial T}{\partial S} \right)_H \) 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 \( \mu \) are presented in Figs. 3, 4.

Thus, the performed analysis has determined that at \( 0 < \mu \leq \frac{\pi}{2} \) the crit-
ical behaviour of the Baxter model corresponds to the second type according to the thermodynamic classification \([2]–[4]\) with \(K_c = 0\), and at \(\frac{\pi}{2} < \mu < \pi\) it corresponds to the fourth type which is fulfilled by three possibilities for the critical slope \((K_c = 0, K_c \neq \{0, \infty\}, K_c = \infty)\) depending on the value of \(\mu\) varying within the mentioned interval.

4.2 The ferroelectric Baxter model

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

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

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

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

5 Conclusion

Thus, in the paper the consideration of the thermodynamic stability of the Lieb and Baxter models by the method of Ref. \([2]–[4]\) has been 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 given models are clarified. So, we determine that the second and the fourth type of critical behaviour is fulfilled 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 the 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]–[4]. 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 fulfillment 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 \( \mu \). It is interesting to emphasize that in each model while one hypothesis is violated the another one is nevertheless holds. In addition, the special case of the eight-vertex Baxter model, in which the universality hypothesis is violated, is the Lieb model (\( \mu = 0 \)), where the universality hypothesis is satisfied, but the scaling law hypothesis is violated, and the Ising model (\( \mu = \frac{\pi}{2} \)), where both hypotheses are fulfilled. Therefore, the abilities of the thermodynamic method of investigation of the one-component system critical state have been illustrated by the example of the above-mentioned models and the global reasons for the violation of the scaling law and universality hypotheses concerned with the variety of the critical state nature manifestation are revealed.

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