THE PHENOMENON OF PHASE SEPARATION AT LOW TEMPERATURES IN SOME LATTICE GAS MODELS

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THE PHENOMENON OF PHASE SEPARATION AT LOW TEMPERATURES IN SOME LATTICE GAS MODELS

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In a number of recent works ($^{1-5}$) a proof has been obtained of the existence of a first-order phase transition in some lattice gas models at sufficiently low temperatures. In other words, it has been established that for $\beta = 1/kT \geqslant \beta_0$ there exists an interval of values of the specific volume v, $v_1(\beta) \leqslant v \leqslant v_2(\beta)$, on which the pressure $p(v, \beta) = \text{const}$ (with $v_1(\beta) \to 1$, and $v_2(\beta) \to \infty$ as $\beta \to \infty$).

In the present work we consider the problem of describing typical configurations of particles in the small canonical ensemble with specific volume v lying inside the phase-transition region. Such a description (as well as other closely related results) has been obtained by us for a number of lattice gas models. We shall present these results as applied to the two-dimensional Ising model.

Recall that in the Ising model the interaction energy of two particles located at distance r ($r \geqslant 1$) is equal to

$$u(r) = \begin{cases} \varepsilon, & r = 1, \\ 0, & r > 1, \end{cases}$$

where ε is a real constant. In what follows we shall assume it negative and, without loss of generality, put $\varepsilon = -1$. Let L be the plane square lattice (with step 1), and let Ω be the part of this lattice enclosed inside a large square (of area $|\Omega|$). Let M be an arbitrary subset of nodes from Ω. The Gibbs distribution for the Ising model generates, on the set of all subsets $M \subseteq \Omega$, the probability distribution

$$p(M) = (\Xi)^{-1} \exp\left\{ \beta\mu N(M) - \beta \sum_{\substack{x \in M,\ y \in M \\ x \neq y}} u(|x-y|) \right\}, \tag{1}$$

where $N(M)$ is the number of elements in M; $\mu, \beta > 0$ are parameters, and the normalizing factor is equal to

$$\Xi = \sum_{M \subseteq \Omega} \exp \left\{ \beta \left(\mu N(M) - \sum_{\substack{x \in M,\ y \in M \\ x \neq y}} u(|x-y|) \right) \right\}.$$

The ensemble of all subsets of Ω, on which the distribution (1) is introduced, will be denoted by $\mathfrak{A}(\Omega, \mu, \beta)$ and called the **grand canonical ensemble**. The subensemble $\mathfrak{A}(\Omega, N, \beta)$, consisting of subsets with a fixed number of elements $N(M) = N$, together with the conditional probability distribution induced by the Gibbs distribution, will be called the **small canonical ensemble**.

The distribution (1) can be represented in the form

$$p(M) = (\Xi)^{-1} \exp\{\beta[(\mu+4)N(M) - \Gamma(M)]\}, \tag{2}$$

where the quantity $\Gamma(M)$ is equal to the number of pairs of neighboring points in Ω of which one and only one point belongs to M. The quantity $\Gamma(M)$ admits the following

geometric description: around each point of the set M we draw a unit square. The collection of squares constructed for all points of M is divided into connected regions; the connected components of the boundaries of these regions, which are closed non-self-intersecting polygonal lines made up of links of the lattice shifted relative to L by the vector $(\frac{1}{2}, \frac{1}{2})$, will be called the **contours** of the configuration M and denoted by $\Gamma_1, \Gamma_2, \dots, \Gamma_k$ (the same letters denote their lengths). Then

$$\Gamma(M) = \Gamma_1 + \Gamma_2 + \cdots + \Gamma_k.$$

Among the contours of the configuration M we can single out the **external contours** $\Gamma_{i_1}, \Gamma_{i_2}, \dots, \Gamma_{i_s}$, i.e., those which are not enclosed by any other contour of the configuration M. We shall call an external contour c-small if its length

$$\Gamma \le c \ln |\Omega|,$$

where c is a fixed sufficiently small constant. Otherwise we shall call the contour **large**. The class of congruent contours (differing by a shift along the lattice) will be denoted by γ.

In the works mentioned above ([1],[2]) it is shown that the phase transition in the Ising model occurs at $\mu = -4$. In this case the distribution (2) takes the form

$$p(M) = (\Xi)^{-1}\exp\{-\beta\Gamma(M)\}. \tag{3}$$

After all these definitions, let us turn to the formulation of the main result. Let β be sufficiently large and let v be such that

$$v_1(\beta) < v < v_2(\beta). \tag{4}$$

Consider a sequence of small canonical ensembles $\mathfrak{A}(\Omega, N, \beta)$, where $N = [\frac{1}{v}|\Omega|]$ and $|\Omega| \to \infty$. Below, for each ensemble $\mathfrak{A}(\Omega, N, \beta)$, a set of particle configurations $S_{v,\Omega} \subset \mathfrak{A}(\Omega, N, \beta)$ will be indicated such that $p_{\mathfrak{A}(\Omega,N,\beta)}(S_{v,\Omega}) \to 1$ as $|\Omega| \to \infty$. The configurations from $S_{v,\Omega}$ will, for brevity, be called **typical configurations** corresponding to the specific volume v. Their description is given by the following theorem.

Theorem. The following configurations from $\mathfrak{A}(\Omega, N, \beta)$ are typical:

1. In the configuration M there exists exactly one large external contour $\Gamma_{\max}$.
2. The area $v(\Gamma_{\max})$ enclosed by it lies within the limits

$$\big|\, |v(\Gamma_{\max})| - \overline{\Omega}\,\big| < c_1(\beta)|\Omega|^{3/4}. \tag{5}$$

Here $\overline{\Omega}$ is determined from the equation

$$\frac{1}{v_1(\beta)}\overline{\Omega} + \frac{1}{v_2(\beta)}(|\Omega| - \overline{\Omega}) = N, \tag{6}$$

$c_1(\beta) \to 0$ as $\beta \to \infty$.

3. The contour $\Gamma_{\max}$ has a shape close to a square, in the following sense:

$$\left|\Gamma_{\max} - 4\sqrt{|v(\Gamma_{\max})|}\right| < c_2(\beta)\sqrt{|\Omega|}, \tag{7}$$

where $c_2(\beta) \to 0$ as $\beta \to \infty$.

4. Let $1 > k_1 > 0$ and $k_2 > 0$ be arbitrary fixed numbers, and let $T_{k_1,k_2}[v'(\Gamma_{\max})]$ denote the collection of connected regions $\widetilde{\Omega} \subseteq v'(\Gamma_{\max}) = \Omega \setminus v(\Gamma_{\max})$, located outside $\Gamma_{\max}$, and such that $|\widetilde{\Omega}| > k_1|\Omega|$, while $\Gamma(\widetilde{\Omega}) < k_2\sqrt{|\Omega|}$. Suppose, further, that for each such region $k(\gamma \mid \widetilde{\Omega}, M)$ denotes the number of c-small contours of the class γ from M that have fallen inside $\widetilde{\Omega}$. Then

$$\sup_{\widetilde{\Omega}\in T_{k_1,k_2}[v'(\Gamma_{\max})]} \left| k(\gamma \mid \widetilde{\Omega}, M) - \pi(\gamma \mid \beta)|\widetilde{\Omega}| \right| < c_3(\gamma \mid \beta, k_1, k_2)|\Omega|^{3/4}. \tag{8}$$

where the number $\pi(\gamma|\beta)$ (the limiting frequency of contours of class γ) depends only on the class γ, and $\pi(\gamma|\beta) \to 0$ as $\beta \to \infty$; $c_3(\gamma|\beta, k_1, k_2) \to 0$ as $\beta \to \infty$. In particular, the total number of contours of class γ lying outside $\Gamma_{\max}$ (by virtue of (5) and (7)) satisfies the estimate

$$\left| k(\gamma|\nu'(\Gamma_{\max}), M) - \pi(\gamma|\beta)(|\Omega| - \overline{\Omega}) \right| < c_5(\gamma|\beta)|\Omega|^{3/4} \tag{9}$$

and $c_5(\gamma|\beta) \to 0$ as $\beta \to \infty$.

5. Let $N_1(\widetilde{\Omega}, M)$ be the number of points of M that have fallen into $\widetilde{\Omega} \in T_{k_1,k_2}[\nu'(\Gamma_{\max})]$. Then

$$\sup_{\widetilde{\Omega}\in T_{k_1,k_2}[\nu'(\Gamma_{\max})]} \left| N_1(\widetilde{\Omega}, M) - \frac{1}{v_2(\beta)}|\widetilde{\Omega}| \right| < c_6(\beta)|\Omega|^{3/4}, \tag{10}$$

where $c_6(\beta) \to 0$ as $\beta \to \infty$.

In particular, $N_1(\nu'(\Gamma_{\max}), M)$, by virtue of (5) and (7),

$$\left| N_1[\nu'(\Gamma_{\max}), M] - v_2^{-1}(\beta)(|\Omega| - \overline{\Omega}) \right| < c_6(\beta)|\Omega|^{3/4}, \tag{11}$$

where $c_6(\beta) \to 0$ as $\beta \to \infty$.

6. All contours located inside $\Gamma_{\max}$ and exterior with respect to it are c-small. The number of such contours of class γ that have fallen into any region $\widetilde{\Omega} \in T_{k_1,k_2}(\nu(\Gamma_{\max}))$ inside $\Gamma_{\max}$ admits an estimate analogous to estimate (8). The total number of such contours $k(\gamma|\nu(\Gamma_{\max}), M)$ inside $\Gamma_{\max}$ is subject to the estimate

$$\left| k(\gamma|\nu(\Gamma_{\max}), M) - \pi(\gamma|\beta)\overline{\Omega} \right| < c_5(\gamma|\beta)|\Omega|^{3/4}, \tag{12}$$

where again $c_5(\gamma|\beta) \to 0$ as $\beta \to \infty$.

7. For the number of particles $N_2(\widetilde{\Omega}, M)$ that have fallen into any region $\widetilde{\Omega} \in T_{k_1,k_2}(\nu(\Gamma_{\max}))$, and also for the total number of particles $N_2(\nu(\Gamma_{\max}), M)$, estimates hold analogous to estimates (10) and (11), only with $v_2(\beta)$ replaced by $v_1(\beta)$.

The intuitive meaning of the theorem just stated is almost evident. If the part of a typical arrangement $M \in \mathfrak{A}(\Omega, N, \beta)$ that has fallen inside $\Gamma_{\max}$ is called the crystalline (or, if desired, liquid) phase, and the remaining part the rarefied (gaseous) phase, then we see that the phases are two connected spatially separated regions, the boundary between which is close to the minimally possible boundary length (let us recall that the solution of the isoperimetric problem on the lattice is a square). Further, the rarefied phase consists of small (of order $\sim \ln|\Omega|$) and sparsely located clusters of particles, while the crystalline phase, filled mainly with particles, has the same small and sparsely located inclusions of vacancies. Finally, both phases are homogeneous in the sense that in any sufficiently large parts of them they are arranged approximately alike—the number of contours of class γ, and also the number of particles per unit area, is with high accuracy close to one and the same value, $\pi(\gamma|\beta)$ and $1/v_2(\beta)$ (or $1/v_1(\beta)$), respectively. Thus, in the case of the Ising model, the formulated theorem serves as a basis for the intuitive notion of the phases of matter, and also of their spatial separation in the region of a phase transition.

Let us point out some consequences of the main theorem.

1. Let $\rho_k(x_1, x_2, \dots, x_k|\Omega, N, \beta)$ be the correlation functions in the ensemble $\mathfrak{A}(\Omega, N, \beta)$, and let

$$\tilde{\rho}_k(x_1, x_2, x_3, \dots, x_k|\Omega, N, \beta) =$$

$$= \frac{1}{T} \sum_{\substack{x_i+t\in\Omega \\ i=1,2,\dots,k}} \rho_k(x_1+t, x_2+t, \dots, x_k+t|\Omega, N, \beta) \tag{13}$$

(T is the number of terms in (13))—the averaged correlation functions.

Then the limit exists $(v_1(\beta) < v < v_2(\beta))$

$$\tilde{\rho}_k(x_1, x_2, \dots, x_k \mid v, \beta) = \lim_{\substack{|\Omega|\to\infty \\ N=[\frac{1}{v}|\Omega|]}} \tilde{\rho}_k(x_1, x_2, \dots, x_k \mid \Omega, N, \beta). \tag{14}$$

2. The well-known Mayer relation is satisfied (see ([8]))

$$\tilde{\rho}_k(x_1, x_2, \dots, x_k \mid v, \beta) = \xi_1 \rho_k(x_1, x_2, \dots, x_k \mid v_1(\beta), \beta) + \xi_2 \rho_k(x_1, x_2, \dots, x_k \mid v_2(\beta), \beta), \tag{15}$$

where ξ_1 and ξ_2 are determined from the relations

$$\xi_1 v_1^{-1}(\beta) + \xi_2 v_2^{-1}(\beta) = v^{-1}, \qquad \xi_1 + \xi_2 = 1. \tag{16}$$

3. There exists a limiting Gibbs distribution $P_{v,\beta}(\cdot)$ (for $v_1(\beta) < v < v_2(\beta)$), which is a mixture of the "extreme" distributions $P_{v_1(\beta),\beta}(\cdot)$ and $P_{v_2(\beta),\beta}(\cdot)$

$$P_{v(\beta)}(\cdot) = \xi_1 P_{v_1(\beta),\beta}(\cdot) + \xi_2 P_{v_2(\beta),\beta}(\cdot), \tag{17}$$

where ξ_1 and ξ_2 are defined by relations (16) (for more detail on the limiting distribution, see the work of one of the authors ([9])).

Let us note that all the results formulated by us for the case of the Ising model are readily transferred to the more general lattice models studied, for example, in ([3,5]). For a detailed proof of the theorem and its corollaries, see ([6,7]).

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Note: Figure translations are in progress. See original paper for figures.

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