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Condensation of Lattice Gases

J. GINIBRE
Laboratoire de Physique Théorique, 91. Orsay — France

A. GROSSMANN and D. RUELLE
Institut des Hautes Etudes Scientifiques, 91. Bures-sur-Yvette — France

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Abstract. Techniques due to R. L. DOBRUSHIN and R. GRIFFITHS are combined to prove the existence of a first order phase transition at low temperature for a class of lattice systems with non nearest-neighbour interaction.

1. Introduction

In recent papers, DOBRUSHIN [2] and GRIFFITHS [5] have proved that a gas with nearest-neighbour attractive interaction on a cubic lattice in ν dimensions ($\nu \geqq 2$) undergoes a first order phase transition. DOBRUSHIN and GRIFFITHS compute explicitly a region where two phases coexist and the pressure is a constant function of density at constant temperature.

While the result and techniques used are not quite new (see [7], [9], [10]), they are important in giving a simple model for proofs of condensation[1]. In this note we shall combine the techniques of DOBRUSHIN and GRIFFITHS (these authors worked independently) to prove the existence of a first order phase transition at low temperature for a class of lattice systems with non nearest-neighbour interaction. Our main result is the theorem of Section 3, which the reader may consult at this point. Section 2 contains preparatory material for the proof of the theorem.

2. Systems with pair interactions on a lattice

We collect in this section some definitions and known results.

We consider a ν-dimensional lattice with vertices $\mathbf{k} = (k^1, \ldots, k^\nu)$ where $k^1, \ldots, k^\nu$ are integers. Particles on the lattice are assumed to interact through a pair potential Φ such that $\Phi(\mathbf{k}) = \Phi(-\mathbf{k})$ and

$$\Phi(0) = +\infty, \sum_{k \neq 0} |\Phi(\mathbf{k})| = D < +\infty . \tag{2.1}$$

[1] One of us (D. R.) has been informed by V. ARNOLD and R. BALESCU that further results in this direction have been obtained by SINAI and BEREZIN; on the other hand DOBRUSHIN has extended his results to certain lattice gases with non nearest neighbour interaction (private communication).

The total potential energy for n particles located at $\mathbf{k}_1, \ldots, \mathbf{k}_n$ is then

$$U(\mathbf{k}_1, \ldots, \mathbf{k}_n) = \sum_{1 \leqq i < j \leqq n} \Phi(\mathbf{k}_j - \mathbf{k}_i) . \tag{2.2}$$

Let $K^1, \ldots, K^\nu$ be integers >0 and define a "box" $\Lambda(\mathbf{K})$ and its "volume" $V(\mathbf{K})$ by

$$\Lambda(\mathbf{K}) = \{\mathbf{k} : 0 \leqq k^i < K^i \text{ for } i = 1, \ldots, \nu\} \tag{2.3}$$

$$V(\mathbf{K}) = \prod_{i=1}^{\nu} K^i .$$

The (configurational) canonical partition function is

$$Q(\mathbf{K}, n) = \frac{1}{n!} \sum_{\mathbf{k}_1 \in \Lambda(\mathbf{K})} \cdots \sum_{\mathbf{k}_n \in \Lambda(K)} e^{-\beta U(\mathbf{k}_1, \ldots, \mathbf{k}_n)} \tag{2.4}$$

and the grand partition function at activity ζ is

$$\Xi(\mathbf{K}, \zeta) = \sum_n \zeta^n Q(\mathbf{K}, n) . \tag{2.5}$$

Let us write $\mathbf{K} \to \infty$ if $K^1 \to +\infty, \cdots, K^\nu \to +\infty$.

Proposition 1. 1. *Let* $K \to \infty$, $V(\mathbf{K})^{-1} n \to \varrho$ *where* $0 < \varrho < 1$; *then the limit*

$$g(\varrho) = \lim V(\mathbf{K})^{-1} \log Q(\mathbf{K}, n) \tag{2.6}$$

exists and is finite and concave in ϱ.

2. *Let* $\mathbf{K} \to \infty$, $\zeta > 0$; *then the limit*

$$P(\zeta) = \lim V(\mathbf{K})^{-1} \log \Xi(\mathbf{K}, \zeta) \tag{2.7}$$

exists, is finite and satisfies

$$P(\zeta) = \max_{\varrho} [\varrho \log \zeta + g(\varrho)] . \tag{2.8}$$

A proof of Proposition 1, with the conditions (2.1) on the potential, does not seem to be published but is an easy exercise (published results on the thermodynamic limit include [8], [4], [3], [1]).
Furthermore if one assumes that $\Phi(\mathbf{k})$ vanishes except for a finite number of values of $\mathbf{k}$, then Proposition 1 follows from [4].

Let us write

$$C = \sum_{\mathbf{k} \neq 0} \Phi(\mathbf{k}) . \tag{2.9}$$

Furthermore if Δ is a subset of $\Lambda(\mathbf{K})$, let $n(\Delta)$ be the number of elements in Δ and define

$$\hat{Q}(\mathbf{K}, n) = \sum_{n(\Delta) = n} \prod_{\mathbf{k}_1 \in \Delta} \prod_{\mathbf{k}_2 \in \Lambda(\mathbf{K}) - \Delta} \exp\left(\frac{1}{2} \beta \Phi(\mathbf{k}_2 - \mathbf{k}_1)\right) \tag{2.10}$$

$$\hat{\Xi}(\mathbf{K}, z) = \sum_n z^n \hat{Q}(\mathbf{K}, n) . \tag{2.11}$$

Proposition 2. 1. *If* $\mathbf{K} \to \infty$, $V(\mathbf{K})^{-1} n \to \varrho$ *where* $0 < \varrho < 1$, *then*

$$\lim V(\mathbf{K})^{-1} \log \hat{Q}(\mathbf{K}, n) = g(\varrho) + \frac{1}{2} \beta C \varrho = \hat{g}(\varrho) . \tag{2.12}$$

2. *If* $\mathbf{K} \to \infty$ *and* $z = \exp\left(-\frac{1}{2}\beta C\right)\zeta > 0$, *then*

$$\lim V(\mathbf{K})^{-1} \log \hat{\Xi}(K, z) = \hat{P}(\zeta) = \hat{p}(z) \tag{2.13}$$

$$\hat{p}(z) = \max_{\varrho}[\varrho \log z + \hat{g}(\varrho)]\,. \tag{2.14}$$

Apart from boundary effects we would have $Q = \hat{Q} \cdot \exp\left(-\frac{1}{2} n \beta C\right)$ and $\Xi = \hat{\Xi}$ (see [6]), but it is easily checked from (2.1) that the boundary effects disappear in the limit, proving Proposition 2.

Proposition 3. *The following identities hold*

$$\hat{g}(\varrho) = \hat{g}(1-\varrho), \quad \hat{p}(z) = \log z + \hat{p}(z^{-1})\,. \tag{2.15}$$

Proposition 4. *If* $\Phi(\mathrm{k}) \leqq 0$ *for* $\mathrm{k} \neq 0$, *then the polynomial* $\hat{\Xi}(\mathbf{K}, z)$ *in* z *has its roots on the circle* $|z| = 1$. *From this follows that* $\hat{p}(z)$ *is real-analytic on the intervals* $[0, 1)$ *and* $(1, +\infty)$ *but may be non-analytic at* $z = 1$. *The system may thus undergo at most one phase transition* (for $z = 1$).

Proposition 3 is obvious, Proposition 4 is a deep theorem by Lee and Yang [6].

According to Propositions 3 and 4 a first-order phase transition would be likely to occur as a horizontal segment in the graph of the function $\hat{g}$. To exhibit such a behaviour we shall make use of the following result.

Proposition 5. *For each* $\mathbf{K}$ *we choose a set* $\mathscr{P}_{\mathbf{K}}$ *of subsets of* $\Lambda(\mathbf{K})$ *and define*

$$Z(\Delta) = \prod_{\mathrm{k}_1 \in \Delta} \prod_{\mathrm{k}_2 \in \Lambda(\mathbf{K}) - \Delta} \exp\left(\frac{1}{2}\beta\,\Phi(\mathrm{k}_2 - \mathrm{k}_1)\right) \tag{2.16}$$

$$Z(\mathbf{K}, n) = \sum_{\Delta \in \mathscr{P}_{\mathbf{K}},\, n(\Delta) = n} Z(\Delta)\,. \tag{2.17}$$

If

$$\lim_{\mathbf{K} \to \infty} V(\mathbf{K})^{-1} \log \sum_{n=0}^{V(K)} Z(\mathbf{K}, n) = \hat{p}(1) \tag{2.18}$$

$$\lim_{\mathbf{K} \to \infty} \inf \left(\sum_{n=0}^{V(\mathbf{K})} Z(\mathbf{K}, n)\right)^{-1} \sum_{n=0}^{V(\mathbf{K})} V(\mathbf{K})^{-1} n\, Z(\mathbf{K}, n) \leqq \varrho_0 < \frac{1}{2} \tag{2.19}$$

then $\hat{g}$ *reduces to a constant on the interval* $[\varrho_0, 1-\varrho_0]$.

Given $\varepsilon > 0$, there exists a sequence $(\mathbf{K}_j)$ such that

$$\mathbf{K}_j \to \infty, \ (\sum_n Z(\mathbf{K}_j, n))^{-1} \sum_n V(\mathbf{K}_j)^{-1} n Z(\mathbf{K}_j, n) \leqq \varrho_0 + \varepsilon/2\,. \tag{2.20}$$

Then,

$$[(\sum_n Z(\mathbf{K}_j, n))^{-1} \sum_{n \geqq (\varrho_0 + \varepsilon) V(\mathbf{K}_j)} Z(\mathbf{K}_j, n)]\,(\varrho_0 + \varepsilon) \leqq \varrho_0 + \varepsilon/2 \tag{2.21}$$

or

$$\left(\sum_n Z(\mathbf{K}_j, n)\right)^{-1} \sum_{n<(\varrho_0+\varepsilon)V(\mathbf{K}_j)} Z(\mathbf{K}_j, n) \geqq \frac{\varepsilon/2}{\varrho_0+\varepsilon} \tag{2.22}$$

hence

$$\lim_{j\to\infty} V(\mathbf{K}_j)^{-1} \log \sum_{n<(\varrho_0+\varepsilon)V(\mathbf{K}_j)} Z(\mathbf{K}_j, n) = \hat{p}(1)\,. \tag{2.23}$$

Let n_j be such that

$$Z(\mathbf{K}_j, n) = \max_{n<(\varrho_0+\varepsilon)V(\mathbf{K}_j)} Z(\mathbf{K}_j, n)\,; \tag{2.24}$$

then

$$\lim_{j\to\infty} V(\mathbf{K}_j)^{-1} \log Z(\mathbf{K}_j, n_j) = \hat{p}(1)\,. \tag{2.25}$$

Possibly taking a subsequence of $(\mathbf{K}_j)$ we may assume that

$$V(\mathbf{K}_j)\, n_j \rightharpoonup \varrho_1 \leqq \varrho_0 + \varepsilon\,. \tag{2.26}$$

Since $Z(\mathbf{K}_j, n_j) \leqq \hat{Q}(\mathbf{K}_j, n_j)$, it follows from (2.25) that

$$\hat{p}(1) \leqq \hat{g}(\varrho_1) \leqq \hat{g}(\varrho_0+\varepsilon) \leqq \hat{g}\left(\frac{1}{2}\right) = \hat{p}(1) \tag{2.27}$$

which proves Proposition 5.

3. Existence of a first order phase transition

Theorem. *Consider a system of particles on the lattice of points* $\mathrm{k} = (k^1, \ldots, k^\nu)$ *with integral coordinates in* ν *dimensions,* $\nu \geqq 2$. *We assume that the particles interact through a pair potential* Φ *such that* $\Phi(\mathrm{k}) = \Phi(-\mathrm{k})$ *and* $\Phi(0) = +\infty$. *Let* $\Phi_1, \ldots, \Phi_\nu$ *be the values of* Φ *for nearest neighbours in the directions of the* ν *coordinate axes and put*

$$D_i = \frac{1}{2} \sum_{\mathrm{k}}{}' |k^i| \cdot |\Phi(\mathrm{k})| \tag{3.1}$$

where $\sum'$ *extends over all* k *except* 0 *and the* 2ν *nearest neighbours of* 0.
If we have

$$\Phi_i + D_i < 0 \tag{3.2}$$

for $i = 1, \ldots, \nu$, *then the system undergoes a first order phase transition at low temperature.*

Let us define

$$\Lambda'(\mathbf{K}) = \{\mathrm{k} \in \Lambda(\mathbf{K}) : 1 \leqq k^i < K^i - 1 \quad \text{for} \quad i = 1, \ldots, \nu\}\,. \tag{3.3}$$

We shall base our proof of the above theorem on Proposition 5, taking for $\mathscr{P}_{\mathbf{K}}$ the set of subsets of $\Lambda'(\mathbf{K})$, i.e. the set of configurations which have no point along the "boundary" of $\Lambda(\mathbf{K})$. Equation (2.18) is then clearly satisfied.

To evaluate the l.h.s. of (2.19) we now follow DOBRUSHIN and GRIFFITHS. Given $\Delta \in \mathscr{P}_{\mathbf{K}}$ we draw around each $\mathrm{k} \in \Delta$ the 2ν faces of the unit cube centered at k and suppress the faces which occur twice: we obtain in this way a *closed polyhedron* $\Gamma(\Delta)$. Each face of $\Gamma(\Delta)$ separates a point $\mathbf{k}_1 \in \Delta$ and a point $\mathbf{k}_2 \notin \Delta$. Along a ν-2-dimensional edge of $\Gamma(\Delta)$ there may be either 2 or 4 faces meeting. In the case of 4 faces, we deform slightly the polyhedron, "chopping off" the edge from the cubes containing a particle. When this is done $\Gamma(\Delta)$ splits into disconnected polyhedra $\gamma_1, \ldots, \gamma_r$, which we shall call *cycles.*

It will be convenient to consider a polyhedron $\Gamma(\Delta)$ as the set formed by the cycles into which it splits: $\Gamma(\Delta) = \{\gamma_1, \ldots, \gamma_r\}$. Given a cycle γ, we denote by $n(\gamma)$ the number of lattice points inside of γ and by $|\gamma|_i$ the number of its faces orthogonal to the i-th coordinate axis. We call origin site of γ the lattice point $\mathbf{k}$ inside of γ which is smallest in lexicographic order.

We shall make use of the following easy lemmas which give in terms of the parameters $|\gamma|_1, \ldots, |\gamma|_\nu$ estimates of the entropy, number of particles, and energy associated with a cycle. It would be easy to obtain better estimates, which would improve the r.h.s. of (3.12) (see [2], [5]) but not our theorem.

Lemma 1. *At least ν faces of the unit cube around the origin site of a cycle γ belong to γ* (one orthogonal to each coordinate axis). Building up γ face by face, with 3 possible orientations for each face, one finds that *there are at most $\prod_{i=1}^{\nu} 3^{|\gamma|_i - 1}$ cycles with $|\gamma|_i$ faces orthogonal to the i-th coordinate axis and given origin site, hence less than $V(\mathbf{K}) \prod_{i=1}^{\nu} 3^{|\gamma|_i - 1}$ cycles with arbitrary origin site.*

Lemma 2. *If $\Gamma(\Delta) = \{\gamma_1, \ldots, \gamma_r\}$, then*

$$n(\Delta) \leqq \sum_{j=1}^{r} n(\gamma_j) \tag{3.4}$$

and for any cycle γ

$$n(\gamma) \leqq \prod_{i=1}^{\nu} \left(\frac{1}{2} |\gamma|_i\right)^{1/(\nu-1)}. \tag{3.5}$$

We leave the proofs of Lemma 1 (see [9]) and Lemma 2 to the reader.

Lemma 3. *Let the cycle γ belong to $\Gamma(\Delta)$ and let Δ' be such that $\Gamma(\Delta') = \Gamma(\Delta) - \{\gamma\}$; then*

$$Z(\Delta)/Z(\Delta') \leqq \exp\left[\frac{1}{2} \beta \sum_{i=1}^{\nu} |\gamma|_i (\Phi_i + D_i)\right]. \tag{3.6}$$

To prove Lemma 3 notice that two lattice points which are both inside or outside of γ yield the same contribution to $Z(\Delta)$ and $Z(\Delta')$ (see (2.16)). Each face of γ separates two lattice points of which one is empty and the other occupied for Δ, but both are empty or occupied for

Δ'; this yields the factor $\exp\left[\frac{1}{2}\beta\sum_{i=1}^{\nu}|\gamma|_i\,\Phi_i\right]$ in (3.6). The number of ways in which $\mathbf{k}=(k^1,\ldots,k^\nu)$ may occur as the difference $\mathbf{k}_1-\mathbf{k}_2$ or $\mathbf{k}_2-\mathbf{k}_1$ with $\mathbf{k}_1$ inside of γ and $\mathbf{k}_2$ outside of γ is at most $\sum_{i=1}^{\nu}|\gamma|_i\,|k^i|$ (draw between $\mathbf{k}_1$ and $\mathbf{k}_2$ a broken line constituted of ν segments parallel to the coordinate axes; it must cross a face of γ and if this face is orthogonal to the i-th coordinate axis, can do so in only $|k^i|$ ways). Therefore, apart from the factor due to nearest neighbours, $Z(\Delta)$ and $Z(\Delta')$ differ by at most a factor

$$\exp\left[\frac{1}{4}\beta\sum_{\mathbf{k}}{}'|\Phi(\mathbf{k})|\sum_{i=1}^{\nu}|\gamma|_i\,|k^i|\right]=\exp\left[\frac{1}{2}\beta\sum_{i=1}^{\nu}|\gamma|_i\,D_i\right], \tag{3.7}$$

which concludes the proof.

We come now to the proof of the theorem. We notice that by (3.4)

$$\begin{aligned}\sum_{\Delta\in\mathscr{P}_{\mathbf{K}}} V(\mathbf{K})^{-1}\,n(\Delta)\,Z(\Delta) &\leqq \sum_{\Delta\in\mathscr{P}_{\mathbf{K}}} Z(\Delta)\sum_{j=1}^{r} V(\mathbf{K})^{-1}\,n(\gamma_j)\\ &=\sum_{\gamma} V(\mathbf{K})^{-1}\,n(\gamma)\,N(\gamma)\,,\end{aligned} \tag{3.8}$$

where

$$N(\gamma)=\sum_{\Gamma(\Delta)\ni\gamma} Z(\Delta)\,. \tag{3.9}$$

By Lemma 3 we have

$$\begin{aligned}\Big(\sum_{\Delta\in\mathscr{P}_{\mathbf{K}}} Z(\Delta)\Big)^{-1} N(\gamma) &\leqq \sum_{\Gamma(\Delta)\ni\gamma} Z(\Delta)\Big/\sum_{\Gamma(\Delta)\ni\gamma} Z(\Delta')\leqq\\ &\leqq \exp\left[\frac{1}{2}\beta\sum_{i=1}^{\nu}|\gamma|_i\,(\Phi_i+D)\right].\end{aligned} \tag{3.10}$$

By (3.8), (3.10) and (3.5)

$$\begin{aligned}&\Big(\sum_{\Delta\in\mathscr{P}_{\mathbf{K}}} Z(\Delta)\Big)^{-1}\sum_{\Delta\in\mathscr{P}_{\mathbf{K}}} V(\mathbf{K})^{-1}\,n(\Delta)\,Z(\Delta)\leqq\\ &\leqq\sum_{\gamma} V(\mathbf{K})^{-1}\prod_{i=1}^{\nu}\Big(\frac{1}{2}|\gamma|_i\Big)^{1/(\nu-1)}\exp\left[\frac{1}{2}\beta\sum_{i=1}^{\nu}|\gamma|_i\,(\Phi_i+D)\right].\end{aligned} \tag{3.11}$$

Replacing the sum over γ by a sum over $|\gamma|_1=2l_1,\ldots,|\gamma|_\nu=2l_\nu$ we obtain thus by Lemma 1

$$\begin{aligned}&\Big(\sum_{\Delta\in\mathscr{P}_{\mathbf{K}}} Z(\Delta)\Big)^{-1}\sum_{\Delta\in\mathscr{P}_{\mathbf{K}}} V(\mathbf{K})^{-1}\,n(\Delta)\,Z(\Delta)\leqq\\ &\leqq\sum_{l_1=1}^{\infty}\cdots\sum_{l_\nu=1}^{\infty}\prod_{i=1}^{\nu}\big(l_i^{1/(\nu-1)}\,3^{2l_i-1}\exp[l_i\beta(\Phi_i+D)]\big)\\ &=\prod_{i=1}^{\nu}\left[\sum_{l=1}^{\infty} l^{1(\nu-1)}\,3^{2l-1}\exp(l\beta(\Phi_i+D))\right].\end{aligned} \tag{3.12}$$

It is immediate that if (3.2) holds then, for sufficiently large β, the r.h.s. of (3.12) is smaller than $\frac{1}{2}$ and the theorem follows from Proposition 5.

Remark. The result we have obtained could of course be easily extended to more general lattices. Furthermore, by well-known arguments, it is possible to translate it into statements about spin systems in a magnetic field or about mixtures. This yields in particular a proof of the spontaneous magnetization of a ferromagnet under fairly realistic assumptions. On the other hand the method could be applied for instance to prove the segregation into two phases of a mixture of two different kinds of dimers on a lattice in the close-packing limit.

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