phys. stat. sol. (b) **140**, 415 (1987)

Subject classification: 64.10 and 65.50

Department of Physics, University of Strathclyde, Glasgow[1])

The Exact Solution of the Real Square-Lattice-Gas System

By

A. Szász[2])

The square-lattice-gas model is calculated exactly by a special process. This model previously had no exact solution because it requires a general solution of the square-lattice-Ising model with external magnetic field, which also to-date does not have an exact solution. In the present calculation an exact solution to the square-lattice-model is obtained in a form that does not require the solution of the external field contained in the Ising model.

Mittels eines speziellen Verfahrens wird das Rechteckgitter-Gasmodell exakt berechnet. Dieses Modell hat bisher keine exakte Lösung, weil es eine allgemeine Lösung des Rechteckgitter-Ising-Modells mit äußerem Magnetfeld erfordert, das bis heute keine exakte Lösung hat. In der angegebenen Berechnung wird eine exakte Lösung des Rechteckgitter-Modells in einer Form erhalten, die nicht die Lösung des Ising-Modells mit äußerem Feld erfordert.

1. Introduction

In this paper some results are presented for the exact solution of a square-lattice-gas system, which was introduced by Yang and Lee [1] and is based on the Ising model.

The present model is based on Onsager's pioneering calculation of a square Ising lattice [2] and uses the matrix formalism introduced by Kaufman [3]. For simplicity we can adopt the Onsager-Kaufman procedure, interpreted by Huang [4] and using Huang's symbols throughout.

The well-known Hamiltonian of the Onsager problem in the isotropic homogeneous case without the external magnetic field, is

$$H = -J \sum_{ij}^{N} S_{ij}[S_{i+1j} + S_{ij+1}] , \tag{1}$$

where J is the interaction energy of nearest-neighbour pairs of spins, S_{ij} gives the state of the particle at site (i, j), and N is the number of spins in the lattice.

The partition function, yielding all physical thermodynamic information, etc., is determined by

$$Z = \exp\left(-\frac{H}{k_B T}\right) = \sum_{\langle ij \rangle} \exp\left[\Phi \sum_{ij}^{N} (S_{i+1j} + S_{ij+1})\, S_{ij}\right] , \tag{2}$$

where k_B is the Boltzmann constant, Φ a parameter characterising $Z(\Phi = J/k_B T)$, and $\langle ij \rangle$ denotes a summation for all the states. In the simplest form $S_{ij} = \begin{cases} +1 \\ -1 \end{cases}$

[1]) Colville Building, 48 North Portland Street, Glasgow G11XN, Great Britain.

[2]) Permanent address: Laboratory of Surface and Interface Physics, Eotvos University, H-1088 Budapest, Muzeum krt. 6—8, Hungary.

and the boundary conditions are Born-von Karman boundary conditions.

$$S_{iN+1} = S_{i1}\,, \qquad S_{N+1j} = S_{ij}\,. \tag{3}$$

2. The Onsager Solution

In the following the Onsager's solution is examined briefly, indicating the steps, relevant to our calculation. A $2^N \times 2^N$ transfer matrix P is defined with matrix elements

$$\langle S_{i1}, \ldots, S_{iN}|\ P\ |S_{i+1,1}, \ldots, S_{i+1N}\rangle \equiv \exp\left[\Phi \sum_j S_{ij}(S_{i+1j} + S_{ij+1})\right]. \tag{4}$$

Thus we have

$$Z = \mathrm{Tr}\,[P^N]\,.$$

It can be shown that the largest eigenvalue of P is sufficient for a solution of the problem in the infinite limit of N, reducing the task to finding the largest eigenvalue of P.

The transfer matrix P may be expressed as the product of tractable matrices, V_1' and V_2'; thus

$$P = V_2(\Phi)\ V_1'(\Phi) \tag{5}$$

and

$$V_1'(\Phi) = \langle S_{i1}, \ldots, S_{iN}|\ V_1'\ |S_{i+1,1,}, \ldots, S_{i+1N}\rangle \equiv \prod_{j=1}^{N} \exp\,(\Phi S_{ij}S_{i+1j})\,,$$

$$V_2(\Phi) = \delta_{S_{ij}S_{i+1j}} \ldots \delta_{S_{iN}S_{i+1N}} \prod_{j=1}^{N} \exp\,(\Phi S_{ij}S_{ij+1})\,.$$

Clearly V_1' is a direct product of N identical matrices,

$$V_1'(\Phi) = a \times a \times \ldots \times a\,, \tag{6}$$

where

$$a = \begin{bmatrix} \mathrm{e}^{\Phi} & \mathrm{e}^{-\Phi} \\ \mathrm{e}^{-\Phi} & \mathrm{e}^{\Phi} \end{bmatrix} = \sqrt{2\sinh 2\Phi}\ \ \mathrm{e}^{\theta^* X} \tag{7}$$

and

$$X = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \tag{8a}$$

$$\tanh\,(\theta^*) \equiv \mathrm{e}^{-2\Phi}\,. \tag{8b}$$

The two matrices $V_1'(\Phi)$ and $V_2(\Phi)$ may be described by X_α, Y_α, and Z_α quaternic matrices, defined by X, Y, and Z Pauli matrices [4]. Then

$$V_1(\theta^*) = \prod_{\alpha=1}^{N} \exp\,(\theta^* X_\alpha)\,, \tag{9a}$$

$$V_2(\Phi) = \prod_{\alpha=1}^{N} \exp\,(\Phi Z_\alpha Z_{\alpha+1}) \tag{9b}$$

with V_2 of diagonal form and where

$$V_1'(\Phi) = V_1(\theta^*)\,[2\sinh 2\Phi]^{N/2} \tag{10}$$

for which we can again use Born-von Karman boundary conditions

$$Z_{N+1} = Z_1\,. \tag{11}$$

Expressions (9a) and (9b) make possible a description of V_1 and V_2 with Γ_μ spinors (following Huang [4]). Thus

$$V_1(\theta^*) = \prod_{\alpha=1}^{N} \exp\left(-i^*\Gamma_{2\alpha}\Gamma_{2\alpha-1}\right), \tag{12}$$

$$V_2(\Phi) = \exp\left(i\Phi U\Gamma_1\Gamma_{2N}\right) \prod_{\alpha=1}^{N-1} \exp\left(-i\Phi\Gamma_{2\alpha+1}\Gamma_{2\alpha}\right). \tag{13}$$

Equation (13) involves the Born-von Karman boundary conditions in the matrix U.

The form of V_1 and V_2 represented in (12) and (13) are useful for extending from 2^N-dimensional space to $2N$ space from the spin representative of rotations to normal rotations.

By diagonalization of matrices, in the $2N$-dimensional space of rotations, Onsager finds the largest eigenvalue of P, which leads to the solution of our problem

$$\ln Z = \frac{1}{2}\ln\left(2\sinh 2\Phi\right) + \frac{1}{2\pi}\int_0^{\pi} \operatorname{arcosh} q(x)\, dx \tag{14}$$

and

$$q(X) = \cosh 2\theta^* \cosh 2\Phi - \sinh 2\theta^* \sinh 2\Phi \cos X;$$
$$\tanh\theta^* \equiv e^{-2\Phi} \quad \text{therefore} \quad \sinh 2\theta^* \sinh 2\Phi = 1. \tag{15}$$

The anisotropic case of the square lattice shows Φ_1 and Φ_2 to be independent of each other, and thus the mathematical transformation (8b) can be used. We then introduce Φ_1 and θ_1 as interaction variables for one direction and Φ_2, θ_2 for the other. In all cases

$$\tanh\theta_i = e^{-2\Phi i} \qquad (i = 1, 2)$$

which can be used independently for the matrices V_i $(i = 1, 2)$.

The Kramer-Wannier equation for dual transformation [5] gives a condition for the variables θ_i and Φ_j $(i \neq j.\ i, j = 1, 2)$,

$$\sinh 2\theta_i \sinh 2\Phi_j = 1$$

represented in (15) by the variables $\theta^*(=\theta_1)$ and $\Phi(=\Phi_2)$.

3. The Lattice-Gas Model Solution

The crucial step of the construction of the lattice-gas model, that the transformation from the magnet-like set of spins $\left(S = \begin{cases} +1 \\ -1 \end{cases}\right)$ to the gas-like spin, $\sigma_i = \begin{cases} 1 \\ 0 \end{cases}$ is given by the transformation

$$\sigma_i = \tfrac{1}{2}(S_i + 1) \tag{16}$$

which gives an external-field-like term in the Hamiltonian [6], corresponding to the chemical potential (μ) for the lattice-gas system.

The square-lattice gas (SQ) with external field has no exact solution, so the lattice gas with the transformation represented in (16) is not solvable. We therefore examine another transformation.

The symmetrical, isotropic Hamiltonian was built with particle states $S_i = \begin{cases} +1 \\ -1 \end{cases}$. Let us introduce the states for particles

$$\alpha_i = \begin{cases} a \\ a' \end{cases} = \begin{cases} \delta + \varepsilon \\ \delta^{-1} + \varepsilon \end{cases}.$$

In this system there are

$$V_1^{\alpha}(\Phi_1) = A \times A \times \ldots \times A\,, \tag{17}$$

where

$$A = \begin{bmatrix} e^{\Phi_1 a^2} & e^{\Phi_1 a a'} \\ e^{\Phi_1 a a'} & e^{\Phi_1 a'^2} \end{bmatrix} = \exp\frac{\Phi_1}{2}(a^2 + a'^2) \begin{bmatrix} e^{(\Phi_1/2)(a^2-a'^2)} & e^{(\Phi_1/2)(2aa'-a^2-a'^2)} \\ e^{(\Phi_1/2)(2aa'-a^2-a'^2)} & e^{(\Phi_1/2)(a'^2-a^2)} \end{bmatrix}$$

and

$$A = \gamma \begin{bmatrix} e^D & e^B \\ e^B & e^{-D} \end{bmatrix}; \qquad \gamma = \exp\left[\frac{\Phi_1}{2}(\delta^2 + \delta^{-2} + 2\varepsilon(\delta + \delta^{-1}) + 2\varepsilon^2)\right],$$

$$D = \frac{\Phi_1}{2}[\delta^2 - \delta^{-2} + 2\varepsilon(\delta - \delta^{-1})]\,,$$

$$B = \frac{\Phi_1}{2}[2 - \delta^2 - \delta^{-2}]\,.$$

Accordingly

$$V_1 = \gamma^{N/2} \begin{bmatrix} e^D & e^B \\ e^B & e^{-D} \end{bmatrix} \times \ldots \times \begin{bmatrix} e^D & e^B \\ e^B & e^{-D} \end{bmatrix}.$$

From the mathematical and physical symmetry of the system described by (1) it is evident that the vectors $\alpha^{(1)} = [a, a']$ and $\alpha^{(2)} = [a', a]$ are equivalent, so the partition function in absence of an external magnetic field is the same at $\alpha^{(1)}$ and $\alpha^{(2)}$, i.e. $Z(\alpha^{(1)}) = Z(\alpha^{(2)})$. Hence we may write[3])

$$Z(\alpha) = \tfrac{1}{2}[Z(\alpha^{(1)}) + Z(\alpha^{(2)})]\,.$$

Thus

$$A^{(\alpha)} = \gamma \begin{bmatrix} \cosh D & \exp B \\ \exp B & \cosh D \end{bmatrix}$$

with the simple transformation

$$A^{(\alpha)}(\theta_1) = \gamma \frac{\cosh D}{\cosh \theta_1} \begin{bmatrix} \cosh\theta_1 & \sinh\theta_1 \\ \sinh\theta_1 & \cosh\theta_1 \end{bmatrix},$$

where

$$\tanh\theta_1 = \frac{\exp\left[\dfrac{\Phi_1}{2}(2 - \delta - \delta^{-2})\right]}{\cosh\left[\dfrac{\Phi_1}{2}(\delta^2 - \delta^{-2} + 2\varepsilon(\delta - \delta^{-1}))\right]}.$$

The matrices $V_1(\theta^*)$ (6) and $V_1^{\alpha}(\theta_1)$ (17) correspond formally; only the mathematical transformations $\theta^* \leftrightarrow \Phi$ and $\theta_1 \leftrightarrow \Phi_1$ are different functions.

The V_2 matrices, on simple calculation, (finding the largest eigenvalue) can be written in the original form

$$V_2 = \prod_{\alpha=1}^{N} \exp(\Phi_2 Z_\alpha Z_{\alpha+1})\,. \tag{18}$$

---

[3]) This symmetry follows from the absence of external magnetic field, $Z(M) = Z(-M)$, where M is the magnetisation (the parameter of order) of the system.

This is essentially the same problem as the square-lattice Ising model (see (5)),

$$V = CV_2(\Phi_2)\ V_1(\theta_1); \qquad C = \gamma \frac{1}{\cosh \theta_1}\ ; \tag{19}$$

so Onsager's solution can be used,

$$\lim_{N\to\infty}\left[\frac{1}{N}\ln Z\right] \lim_{N\to\infty}\left[\frac{1}{N}\ln C\right] + \frac{1}{2\pi}\int_0^{\pi} \operatorname{arcosh} q'(X)\, \mathrm{d}X\,, \tag{20}$$

where

$$q'(X) = \cosh 2\Phi_2 \cosh 2\theta_1 - \sinh 2\Phi_2 \sinh 2\theta_1 \cos X$$

with the condition

$$\tanh \theta_1 = \frac{\exp\left[\frac{\Phi_1}{2}\,(2 - \delta^2 - \delta^{-2})\right]}{\cosh\left[\frac{\Phi_1}{2}\,(\delta^2 - \delta^{-2} + 2\varepsilon(\delta - \delta^{-1}))\right]}. \tag{21}$$

The steps in this calculation are subject to the conditions $a = i$ ($i^2 = -1$) and $\varepsilon = 0$. Here the set of α_i are the same as for S_i, so the Hamiltonian includes a square-Ising-lattice term and yields the well-known Onsager solution. Boundary conditions follow from (21) in the isotropic case of $\Phi_1 = \Phi_2$, and with the Kramer-Wannier dual transformation $\Phi_2 = \theta_1$ corresponding to

$$\tanh \Phi_C = \mathrm{e}^{-2\Phi_C}$$

at the Curie temperature giving

$$\sinh^2 2\Phi_C = 1 \tag{22}$$

as in the Onsager solution. The largest eigenvalue of P to be at

$$\cos X = 1 \quad \text{and} \quad q' = 1 \tag{23}$$

in the lattice-gas model is required in the limit $\delta \to \infty$ and $\varphi_i = 4\Phi_i$ [4]. Normalisation gives

$$k_i = \frac{\varphi_i}{\delta^2} \quad \text{and} \quad \varepsilon = \delta m\,. \tag{24}$$

Thus

$$\tanh \theta_1 = \frac{\exp\left[2k_1(-1 + 2\delta^{-2} - \delta^4)\right]}{\cosh\left[2k_1\left(1 + 2m - \frac{2m}{\delta^2} - \frac{1}{\delta^4}\right)\right]}$$

and, for $\delta \to \infty$ (the lattice-gas limit),

$$\tanh \theta_1 = \frac{\mathrm{e}^{-2k_1}}{\cosh\left[2k_1(1 + 2m)\right]} \tag{25}$$

with $m = 1/2$, this corresponds exactly to the Onsager solution because $\Delta \to 1$ and $\Delta' \to 0$, so that $a = 1/2$ and $a' = -1/2$, where Δ and Δ' are the δ and δ^{-1} terms, respectively, used the normalisation indicated in (24).

4. Discussion

The exact grand canonical partition function, originating the thermodynamic functions for a real lattice-gas model [6], in our model is

$$Z_G = \sum_{\langle ij \rangle} \exp\left[K \sum_{ii} \Delta_i \Delta_j + (2\mu + Kmq) \sum_i \Delta_i + (\tfrac{1}{2} NKm^2 q + 2\mu)\right], \tag{26}$$

where q is the coordination number, $K = k_1 = k_2$, $\Delta_i = \begin{cases} \Delta \\ \Delta' \end{cases}$, and N is the number of sites.

In our model m is a free parameter and it can be chosen as $m = -2\mu/Kq$ so the logarithmic partition function ((20) and (25)) is

$$Z = \lim_{N \to \infty} \left(\frac{1}{N} \ln Z\right) = \lim_{N \to \infty} \left(\frac{1}{2\pi} \int_0^{\pi} \operatorname{arcosh} q'(X)\, \mathrm{d}X\right), \tag{27}$$

where

$$q'(X) = \cosh 2\Phi_2 \cosh 2\theta_1 - \sinh 2\theta_1 \sinh 2\Phi_2 \cos X \tag{28}$$

and

$$\tanh 2\theta_1 = \frac{\mathrm{e}^{-2k_1}}{\cosh\left[2k_1(1 + 2m)\right]}. \tag{29}$$

This solution (as assumed in [7]) has the same critical temperature as the Onsager solution but the details of the partition function are different.

From the analysis of the above results we can calculate the important characteristic of the solution.

The critical chemical potential at $m = 1/2$ is

$$\frac{\mu_c}{kT_c} = -2k_c q$$

as required, [6].

An inflection point is found in the coexistence curve at $K = 0.3979$ at $m \approx \approx -1/2 \pm 0.3843$. We could define this as the triple-point isotherm. The curve above this temperature can be approximated by a parabola corresponding well to the Van-der-Waals-type solution [8].

The model can be applied not only to the particle–vacancy-type binary lattice gas $\left(\Delta = \begin{cases} 1 \\ 0 \end{cases}\right)$ but to gas lattices involving different interactions in which δ does not have an infinite limit.

Acknowledgement

A careful reading of the manuscript by Dr. D. J. Fabian is gratefully acknowledged.

References

[1] C. N. Yang and T. D. Lee, Phys. Rev. 87, 404 (1952).
[2] L. Onsager, Phys. Rev. 65, 117 (1944).
[3] B. Kaufmann, Phys. Rev. 76, 1232 (1949).
[4] K. Huang, Statistical Mechanics, John Wiley & Sons Inc., New York/London 1963.
[5] H. A. Kramers and G. H. Wannier, Phys. Rev. 60, 252 (1941).
[6] R. J. Baxter, Exactly Solved Models in Statistical Mechanics, Academic Press, New York/Toronto 1982.
[7] A. Munster, Statistical Thermodynamics, Vol. 2, Springer-Verlag & Academic Press, Berlin/New York 1969.
[8] M. Kac, G. E. Uhlenbeck, and P. L. Hemmer, J. math. Phys. (New York) 4, 216 (1963); 5, 60 (1964).

(Received August 5, 1986; in revised form January 16, 1987)