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Abstract

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ON THE APPLICATION OF THE VARIATIONAL PRINCIPLE TO THE ISING MODEL OF AN ANTIFERROMAGNET

(Presented by Academician N. N. Bogolyubov on 4 XII 1956)

The Ising antiferromagnet is described by the Hamiltonian

$$E = \frac{1}{2}\sum_{ij}^{N} e(i-j)\sigma_i\sigma_j - h\sum_{i=1}^{N}\sigma_i, \tag{1}$$

where i, j are the numbers of the lattice sites; σ_i takes the values ± 1; $e(i-j)$ are quantities characterizing the interaction of the i-th and j-th spins; h is the external magnetic field multiplied by the Bohr magneton. This model, which is very crude for an antiferromagnet, can with greater justification be applied to the description of order-disorder processes in binary alloys ([1]). In this case the free energy of the alloy associated with ordering processes, $F_A = -\Theta \ln Z_A$, can be calculated if the statistical sum of system (1) is known. Indeed, for the function Z_A one can obtain the expression:

$$Z_A = \exp\left\{-\frac{1}{\Theta}\left[\frac{NM}{2}(\mu_1-\mu_2) + \frac{N}{8}\sum_i \left(e^{11}(i-j)+e^{22}(i-j)+2e^{12}(i-j)\right)\right]\right\} Z_{IS}(h, \{e(i-j)\}), \tag{2}$$

where the exchange integrals $e(i-j)$ and the magnetic field h are related to the interaction energies of the alloy atoms $e^{11}(i-j)$, $e^{22}(i-j)$, and $e^{12}(i-j)$ in the following way:

$$e(i-j) = \frac{e^{11}(i-j)+e^{22}(i-j)-2e^{12}(i-j)}{4},$$

$$h = \frac{1}{4}\left[2(\mu_1-\mu_2) - \sum_i \left(e^{11}(i-j)-e^{22}(i-j)\right)\right], \tag{3}$$

and the Ising sum of states is determined by expression (5).

In this model the magnetization M is a prescribed quantity determining the percentage composition of the alloy,

$$N_1 = \frac{N}{2}(1+M), \qquad N_2 = N - N_1 = \frac{N}{2}(1-M),$$

and the external magnetic field is a function of the temperature Θ. The unknown quantity $(\mu_1 - \mu_2)$ is eliminated from expression (2) by means of the equation

$$\frac{1}{N}\frac{\partial \ln Z_{IS}}{\partial H} = M, \tag{4}$$

where

$$Z_{IS} = \sum_{\sigma_1 \ldots \sigma_N} \exp\left\{-\frac{1}{2}\sum_{ij} E(i-j)\sigma_i\sigma_j + H\sum_i \sigma_i\right\}, \tag{5}$$

$$E(i-j) = \frac{e(i-j)}{\Theta}, \qquad H = \frac{h}{\Theta}.$$

The problems of the thermodynamics of an adsorbed monolayer and of a lattice gas [(1)] also reduce to the determination of the sum (5) (in this model it is assumed that each of the cells into which the volume of the gas is divided can contain no more than one particle, while the interaction potential of two atoms is a step function of the distance between them).

As in the preceding note [(2)], let us suppose that the lower bound of the statistical sum (5), $Z_{\text{inf}} \leq Z$, obtained with the aid of N. N. Bogolyubov' s variational principle, is an approximate expression for the statistical sum of our problem. For simplicity we shall assume that the system can be divided into two sublattices—an even and an odd one—so that the nearest neighbors of an atom from one lattice are atoms of the other. We introduce

$$E_0 = -(h-u_1)\sum_{\text{even}} \sigma_i - (h-u_2)\sum_{\text{odd}} \sigma_i; \qquad E_1 = E - E_0. \tag{6}$$

It is convenient to replace the quantities u_1 and u_2 by other variational parameters:

$$y - x = u_1, \qquad y + x = u_2. \tag{7}$$

Then, after simple transformations, one can obtain the following expression for the lower bound of the sum of states (5):

$$Z_{\text{inf}}^{1/N} = 2\left[\text{ch}(Y - X + H)\,\text{ch}(Y + X - H)\right]^{1/2} \exp\left\{-\frac{\Theta}{2\Theta_0}Y^2 + \frac{\Theta}{2\Theta_n}X^2\right\}, \quad (8)$$

where the functions $X = x/\Theta$ and $Y = y/\Theta$ are determined from the equations

$$\text{th}(Y - X + H) = \frac{\Theta}{\Theta_0}Y + \frac{\Theta}{\Theta_n}X,$$

$$\text{th}(Y + X - H) = \frac{\Theta}{\Theta_0}Y - \frac{\Theta}{\Theta_n}X. \quad (9)$$

The quantities Θ_0 and Θ_n are constants depending on the characteristics of the given lattice:

$$\Theta_0 = \frac{2}{N}\sum_{\text{even, odd}} e(i-j) - \frac{2}{N}\sum_{\text{even, even}} e(i-j),$$

$$\Theta_n = \frac{2}{N}\sum_{\text{even, odd}} e(i-j) + \frac{2}{N}\sum_{\text{even, even}} e(i-j) = \frac{1}{N}\sum_{ij} e(i-j). \quad (10)$$

If one assumes that only nearest neighbors interact, i.e. $e(i-j) = e \cdot a_{ij}$, then

$$\Theta_0 = \Theta_n = ce. \quad (11)$$

We shall assume that the system has the property $\Theta_0 > 0$. Let us note that the magnetization, calculated by formula (4), can be written in the form

$$M = \frac{\Theta}{\Theta_n}X. \quad (12)$$

Eliminating X from (9), we obtain relations for the magnetization M that coincide with the equations of the theory of the internal molecular field [3]. The solution of equations (9) in the general case is possible only numerically.

In the case $\Theta \sim 0$, for the sum of states (8) one can obtain the approximate formula

$$Z^{1/N} \simeq 2\left[\text{ch}\,\frac{\Theta_0 + h}{\Theta}\,\text{ch}\,\frac{\Theta_0 - h}{\Theta}\right]^{1/2} \exp\left\{-\frac{\Theta_0}{2\Theta}\right\}, \quad (13)$$

which, under assumption (11), coincides with the expression that follows directly from (5) at low temperatures. In the range of temperatures such that $\Theta < \Theta_0$, but $h/\Theta \ll 1$, equations (9) can be written in the form

$$\operatorname{th} Y = \frac{\Theta}{\Theta_0} Y, \qquad H - X = \frac{\Theta}{\Theta_n} X \operatorname{ch}^2 Y. \tag{14}$$

The temperature Θ_0 at which Y vanishes is the Curie point. In the region close to Θ_0, the expression for the magnetic susceptibility has the form

$$\chi = \frac{\mu^2}{\Theta_n + \Theta \left[1 + 3 \left(\frac{\Theta}{\Theta_0}\right)^2 \frac{\Theta_0 - \Theta}{\Theta_0}\right]}. \tag{15}$$

Using the formula for the mean energy, calculated per particle:

$$\bar{E} = -\frac{\Theta}{\Theta_n} hX - \frac{1}{2}\frac{\Theta^2}{\Theta_0} Y^2 + \frac{1}{2}\frac{\Theta^2}{\Theta_n} X^2, \tag{16}$$

one can obtain the value of the heat capacity, in units of Boltzmann' s constant, to the right of the Curie point as $\Theta \to \Theta_0$,

$$c = \frac{3}{2} - h^3 \left[\frac{1}{\Theta_0(\Theta_0 + \Theta_n)} - \frac{\Theta_0 - \Theta_n}{(\Theta_0 + \Theta_n)^3}\right]. \tag{17}$$

In the paramagnetic region $\Theta > \Theta_0$ we have $Y = 0$, and therefore the analytic form of (8) and of equations (9) coincides, up to the sign of the quantity Θ_n, with the corresponding expressions for the Ising ferromagnet ([2]), (6) and (7). Noting that the condition $h/\Theta \ll 1$ is satisfied for any practically reasonable magnetic fields, one can obtain, from (12), (9), and (16), expressions for the magnetic susceptibility and heat capacity:

$$\chi = \frac{\mu^2}{\Theta + \Theta_n}, \tag{18}$$

$$c = \frac{\Theta h^2}{(\Theta_n + \Theta)^3}. \tag{19}$$

Comparing (19) and (17), we note that the heat capacity undergoes at the point $\Theta = \Theta_0$ a jump equal, in the absence of an external field, to 3/2.

In the problem of a binary alloy, the mean energy is determined by the expression

$$\bar{E} = \frac{1}{8}\sum_i \{e^{11}(i-j) + e^{22}(i-j) + 2e^{12}(i-j)\} - \frac{M\Theta^2}{2}\frac{\partial}{\partial\Theta}\frac{\mu_1 - \mu_2}{\Theta} +$$

$$+\Theta^2 M \frac{dH}{d\Theta} - \frac{\Theta^2}{2\Theta_0} Y^2 + \frac{\Theta^2}{2\Theta_n} X^2. \tag{20}$$

In the paramagnetic region $\Theta > \Theta_0$ it follows that the energy of the alloy does not depend on temperature.

In the antiferromagnetic region, solutions of the type (14), (15), (17) cannot be obtained, since the "magnetic field" h is not a small quantity (as also in problems of an adsorbed monolayer and the lattice gas); therefore equations (9) must be solved numerically. The exception is the case of a 50% alloy, when $M = 0$. Then, as is seen from (12) and (9), $H = X = 0$, and equation (14) is correct. Defining the long-range order by the expression

$$\xi = \frac{e^Y - e^{-Y}}{e^Y + e^{-Y}} = \operatorname{th} Y,$$

we obtain from (20) and (14) the relations determining the energy of the alloy:

$$\overline{E} = E_0 - \frac{\Theta_0}{2}\xi^2, \qquad \operatorname{th}\frac{\Theta_0}{\Theta}\xi = \xi,$$

which coincide with the Bragg–Williams equations, the first of them being, in essence, an assumption of the theory.

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CITED LITERATURE

[1] C. F. Newell, E. W. Montroll, Rev. Mod. Phys., **25**, 353 (1953); P. W. Kasteleijn, Physica, **22**, 397 (1956); R. Peierls, Proc. Cambr. Phil. Soc., **32**, 471 (1936). [2] I. A. Kvasnikov, DAN, **110**, No. 5, 759 (1956). [3] T. H. Van Vleck, J. Chem. Phys., **9**, 369 (1941).

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