

THE CRITICAL TEMPERATURE AND DISCONTINUITY OF SPECIFIC HEAT OF A SUPERLATTICE

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ABSTRACT

General formulas for the critical temperature and the discontinuity of the specific heat of a superlattice are obtained by the generalized quasi-chemical method. The results may be applied to any approximation.

1. Introduction

In a recent paper¹ the author has developed a generalized quasi-chemical method which gives an explicit expression for the free energy of a superlattice in any approximation. It is possible to derive from this free energy expression all the thermodynamic properties of the crystal. Two of these, the critical temperature and the discontinuity of the specific heat, are of especial interest and will be calculated in this paper. Only binary alloys with atomic concentration 1:1 come under our consideration. The results obtained hold for the face-centred cubic lattice (e. g. of CuAu) as well as for the simple or body-centred cubic lattices.

1. "A Generalization of the Quasi-Chemical Method in the Statistical Theory of Superlattices", to be published. This paper will be referred to as I.

2. Expansion of the Free Energy

To start with we expand² the free energy of the crystal into a power series in $s (=1-2w)$:

$$-\frac{F}{kT} = F_0 + F_2 s^2 + F_4 s^4 + \dots, \quad (1)$$

The odd powers of s are missing because F is an even function of s , as already proved in I, § 4, (iii).

It is necessary in order to calculate the coefficients F_0, F_2, F_4, \dots first to expand the selective variables μ_1, μ_2, \dots . Now by I, (39), $\log \mu_i$ is an odd function of s , hence assume

$$\log \mu_i = J_i s + K_i s^3 \quad (2)$$

As already proved (I, § 4), the selective variables of sites symmetrically situated in the group are equal, so we shall give them the same symbol. This will not affect the results, but the calculation will be very much simplified. Let the first μ , namely, μ_1 , be the parameter of m_1 (m for multiplicity) symmetrically situated sites, and μ_2 that of m_2 sites etc.. The equations determining these μ 's become (I, (32))

$$\frac{\partial \Phi}{\partial \xi} = N_1, \quad (3)$$

$$\mu_i \frac{\partial \Phi}{\partial \mu_i} = m_i N_1 w. \quad (4)$$

Write $\frac{\Phi}{\xi} = Y = Y(x, \mu_1, \mu_2, \dots), \quad (5)$

and divide (4) by (3), we get

$$\frac{\partial \log Y}{\partial \log \mu_i} = m_i w = \frac{1}{2} m_i - \frac{1}{2} m_i s. \quad (6)$$

Now by (2), $\mu_i = 1$ when $s = 0$. Hence introducing the notations

2. The notations used in this paper are the same as in I.

$$(11) \quad y = (Y) \mu_i = 0, \quad 0 = 1, 1, 1, \dots, 1 \quad (17)$$

$$(12) \quad y_i = \left(\frac{\partial Y}{\partial \log \mu_i} \right) \mu_1 = \mu_2 = \dots = 1, \quad 1 = 1, 1, 1, \dots, 1 \quad \text{and}$$

$$y_{ij} = \left(\frac{\partial^2 Y}{\partial \log \mu_i \partial \log \mu_j} \right) \mu_1 = \mu_2 = \dots = 1, \quad 1 = 1, 1, 1, \dots, 1$$

$$L = (\log Y) \mu_i = 1, \quad 1 = 1, 1, 1, \dots, 1$$

$$(13) \quad L_i = \left(\frac{\partial \log Y}{\partial \log \mu_i} \right) \mu_1 = \mu_2 = \dots = 1, \quad 1 = 1, 1, 1, \dots, 1$$

$$(14) \quad L_{ij} = \left(\frac{\partial^2 \log Y}{\partial \log \mu_i \partial \log \mu_j} \right) \mu_1 = \mu_2 = \dots = 1, \quad 1 = 1, 1, 1, \dots, 1$$

$$\text{etc.} \quad (7)$$

we may expand the left-hand-side of (6) as follows

$$\frac{\partial \log Y}{\partial \log \mu_i} = L_i + \sum_j L_{ij} \log \mu_j + \frac{1}{2} \sum_{j,l} L_{ijl} \log \mu_j \log \mu_l + \dots$$

Substitute (2) into this last equation and arrange the terms into a power series (of s). The result is

$$\begin{aligned} \frac{\partial \log Y}{\partial \log \mu_i} = & L_i + \sum_j L_{ij} J_j s + \frac{1}{2} \sum_{j,l} L_{ijl} J_j J_l s^2 + \dots \\ & + \left(\sum_j L_{ij} K_j + \frac{1}{6} \sum_{j,l,n} L_{ijln} J_j J_l J_n \right) s^3 + \dots \end{aligned} \quad (8)$$

By (6) this is equal to $\frac{1}{2} m_i - \frac{1}{2} m_i s$. Hence

$$L_i = \frac{1}{2} m_i, \quad \log 9$$

$$(9) \quad \sum_j L_{ij} J_j = -\frac{1}{2} m_i, \quad (10)$$

$$\sum_{j,l} L_{ijl} J_j J_l = 0 \quad (11)$$

$$\text{and } \sum_i L_{ij} K_j + \frac{1}{6} \sum_{j,l,n} L_{ijln} J_j J_l J_n = 0. \quad (12)$$

The coefficients J_i can now be obtained in the following way. Let λ_j denote the cofactor of L_{ij} in the determinant $|L_{ij}|$ divided by the determinant, such that

$$\sum_i \lambda_{ii} L_{ij} = \delta_{ij} \quad (13)$$

Then the solution of (10) is

$$J_i = -\frac{1}{2} \sum_l \lambda_{li} m_l \quad (14)$$

The coefficients K_i can also be calculated in the same way from (12); but since only combinations of the form $\sum_j L_{ij} K_j$ occur in what follows, we shall leave (12) as it is.

The free energy is, by I, (36),

$$F(w, T) = -\frac{2}{\gamma} N_1 kT \left[\log Y + \left(a + b - \frac{2\gamma}{2} \right) \times \left\{ (1-w) \log (1-w) + w \log w \right\} - \sum m_i w \log \mu_i \right] \quad (15)$$

When $\log Y$ and $\log \mu_i$ are expanded into power series in s , and (15) compared with (1), we find

$$\begin{aligned} F_0 &= \frac{2}{\gamma} N_1 [\log Y - D \log 2], \\ F_2 &= \frac{2}{\gamma} N_1 \left[\frac{1}{2} \sum_{i,j} L_{ij} J_i J_j + \frac{1}{2} D + \sum_i \frac{1}{2} m_i J_i \right], \\ \text{and } F_4 &= \frac{2}{\gamma} N_1 \left[\sum_{i,j} L_{ij} J_i J_j + \frac{1}{24} \sum_{i,j,l,n} J_i J_j J_l J_n L_{ijln} \right. \\ &\quad \left. + \frac{D^2}{12} + \frac{1}{2} \sum_i m_i K_i \right], \end{aligned} \quad (16)$$

where

$$D = a + b - \frac{2\gamma}{z} \quad (17)$$

By (10) and (12) F_2 and F_4 may be reduced to

$$F_2 = \frac{z}{\gamma} N_1 \left[\frac{1}{2} D + \frac{1}{4} m_i J_i \right] \quad (18)$$

$$F_4 = \frac{z}{\gamma} N_1 \left[\frac{1}{12} D + \frac{1}{24} \sum_{i,j,l,n} L_{ijkl} J_i J_j J_l J_n \right] \quad (19)$$

Thus we know the first four derivatives of the free energy with respect to s .

3. The Critical Temperature and the Discontinuity of the

Specific Heat

Since the free energy (1) is an even function of s , it has always an extremum at $s=0$, i.e. at the point of vanishing long-distance order. Whether this point represents the equilibrium state of order of the crystal depends on whether it gives the absolute minimum of the free energy. Experiments show that for temperatures T greater than a certain critical temperature T_c , the long-distance order of the superlattice actually disappear. Moreover, the value of s is vanishingly small for temperatures immediately below T_c (only the AB type of superlattice is here discussed). In other words, the order-disorder transformation is not accompanied by a discontinuous change in s . All these can be explained in our theory if the free energy (15) has its absolute minimum at $s=0$ for $T > T_c$ and $s=\epsilon$ for $T < T_c$, where ϵ is a small quantity vanishing together with $T_c - T$. This is completely born out by Bethe's first and second approximations, and it seems that the same is true for all approximations. If this is the case, the critical temperature is the temperature at which $\frac{d^2 F}{ds^2} = 0$ when $s = 0$; i.e. the temperature at which

$$\sum_i m_i J_i = -2D \quad (21)$$

To calculate the specific heat of the crystal we notice that the relation between x and s is given by the equation

$$(17) \quad \frac{\partial F}{\partial (s^2)} = F_2 + 2F_4 s^2 + \dots = 0. \quad (22)$$

With this in mind the specific heat can easily be calculated from (1)

$$(18) \quad C_v = - \frac{d}{dT} \left[T^2 \frac{d}{dT} \left(\frac{F}{T} \right) \right] = k T^2 \left(\frac{d^2 F_0}{dT^2} + \frac{d^2 F_2}{dT^2} s^2 + \dots \right) \\ (19) \quad + 2kT \left(\frac{dF_0}{dT} + \frac{dF_2}{dT} s^2 + \dots \right) + kT^2 \left(\frac{dF_2}{dT} + 2 \frac{dF_4}{dT} s^2 + \dots \right) \frac{d(s^2)}{dT}.$$

The only quantity on the right that has a discontinuity at $T=T_c$ is the factor $\frac{d(s^2)}{dT}$ of the last term. It vanishes for all $T > T_c$ and its value for $T < T_c$ is, by (22),

$$(21) \quad \frac{d(s^2)}{dT} = - \frac{\frac{dF_2}{dT} + \frac{dF_4}{dT} 2s^2 + \dots}{2F_4 + 6F_6 s^2 + \dots}.$$

Remembering that s is continuous at $T=T_c$ we find the discontinuity of the specific heat at the critical temperature to be

$$(22) \quad \Delta C_v = - \frac{kT^2}{2F_4} \frac{dF_2}{dT} \frac{dF_2}{dT} = - \frac{k(\log x)^2}{2F_4} \left(\frac{dF_2}{d \log x} \right)^2. \quad (23)$$

The labor of computing this quantity lies almost entirely in the calculation of F_4 by (19). To facilitate the calculation it is desirable to change equ. (19) into one containing $y_{i/l/n}$ but not $L_{i/l/n}$. This is only a matter of algebraic computation and will not be given here in detail. It suffices to give only the final result when $T=T_c$:

$$(24) \quad 0 = \frac{1}{2} F_4 = - \frac{2N_1}{24\sqrt{y}} \left[D^4 + 6D^3 + 3D^2 - 2D - \frac{y_{i/l/n} J_i J_j J_l J_n}{y} \right].$$

In deriving this use has been made of (10), (11) and (21).

To calculate the critical temperature and the discontinuity of the specific heat the procedures are therefore as follows

- (i) To calculate the coefficients J_i from (14).
- (ii) To calculate the critical value x_c of x from (21).
- (iii) To compute ΔC_v from (23), with F_4 calculated from (24).

4. Application

The method discussed above yields the values of x_c and ΔC_v immediately when applied to Bethe's first approximation. We shall now apply it to two other approximations, the "square" approximation and the "cube" approximation.

In the square approximation the group considered is four sites forming a square in a plane lattice. The value of x_c has been found in I to be

$$(62) \quad x_c = (\sqrt{5} - 2)^{1/2} = .4858$$

for this approximation. The discontinuity of the specific heat, which was not given in I, can be calculated from (23) as follows.

$$Y = 1 + 4x^2\mu_1 + (4x^2 + 2x^4)\mu_1^2 + 4x^2\mu_1^3 + \mu_1^4.$$

(Hence

$$y = 2 + 12x^2 + 2x^4,$$

$$y_{11} = 16 + 56x^2 + 8x^4,$$

$$y_{1111} = 256 + 392x^2 + 32x^4.$$

The value of J_1 is therefore by (14),

$$(72) \quad J_1 = -\frac{x^4 + 6x^2 + 1}{2x^2 + 2}.$$

Now $D=2$, $m_1=4$. Hence at $T=T_c$, $J_1=-1$. Thus

$$\frac{x_c^4 + 6x_c^2 + 1}{2x_c^2 + 2} = 1$$

which leads to the value of x_c given above.

The value of ΔC_v is given by (23) as :

$$\Delta C_v = (2N_1k) 4 (\log x_c)^2 x_c^2 \frac{(x_c^2 + 2)^2}{1 + x_c^2} = 1.99 R;$$

where

$$R = 2N_1k.$$

This is slightly higher than the value obtained in Bethe's first approximation.

The other approximation we want to consider is the "cube" approximation

for a simple cubic lattice. For this type of lattice only Bethe's first and second approximations have so far been worked out. The new approximation consists in taking as our group of interest eight sites forming the corners of a "unit cube" in the crystal. The function Y is

$$Y = 1 + 8x^3\mu_1 + (12x^4 + 16x^5)\mu_1^2 + (24x^5 + 24x^7 + 8x^9)\mu_1^3 + (6x^4 + 32x^6 + 30x^8 + 2x^{12})\mu_1^4 + (24x^5 + 24x^7 + 8x^9)\mu_1^5 + (12x^4 + 16x^5)\mu_1^6 + 8x^8\mu_1^7 + \mu_1^8. \quad (25)$$

The values of m_1 (the multiplicity) and D are respectively

$$m_1 = 8, \quad D = 4.$$

J_1 is found from (14),

$$J_1 = -\frac{4y}{y_{11} - 16y}. \quad (26)$$

At $x = x_c$, $J_1 = -1$, hence $y_{11} = 20y$. This leads to the equation determining x_c :

$$x_c^{12} + 6x_c^9 + 15x_c^8 + 18x_c^7 + 16x_c^6 + 18x_c^5 + 3x_c^4 - 10x_c^3 - 3 = 0 \quad (27)$$

The solution is

$$x_c = .6615.$$

From this we easily find the value of ΔC_v to be

$$\Delta C_v = 1.83 R,$$

which is about the arithmetical mean of the same quantity in Bethe's first and second approximations (1.78 R and 1.94 R respectively).

This is slightly higher than the value obtained in Bethe's first approximation. The other approximation we want to consider is the "cube" approximation