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# A beyond-mean-field approximation for classical solid solutions

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**Abstract.** Two sub-series of Mayer's virial series are summed to infinite order. The resulting equations are a natural generalization of the Bethe–Peierls–Guggenheim approximation. They are solved for three simple yet non-trivial cases to illustrate the physics involved. It seems that both vacancies and the strong correlations of neighbouring particles have been taken into account simultaneously.

## 1. Introduction

In a previous article (Wu 1975a) a mean-field approximation (MF) for concentrated solid solutions was obtained by summing a sub-series of Mayer's virial series (Salpeter 1958) to infinite order. The resulting equation has an appearance which suggests itself as a proper generalization of Lennard-Jones' cell model (Barker 1963). Like the cell model our MF neglects particle correlation between different lattice sites. In the present paper we go one step further by summing the next sub-series. We obtain a complicated algebraic integral equation. If multipole expansion (Wu 1975b) is executed and the monopole alone is retained the equation reduces to the well known Bethe–Peierls–Guggenheim approximation (Wu 1976).

## 2. The self-potential of a pair of lattice sites

The same solid solution and the same notation as in Wu (1975a) are used in the present paper. The self-potential of a single site was obtained previously (Wu 1975b). Let us apply the same method to sum the next sub-series. Let a pair of sites be denoted by  $\Omega_1$  and  $\Omega_2$  respectively. The grand partition function  $Z^*$  of the reference system (Wu 1975b) is truncated because the pair can at most accommodate two atoms only. Therefore

$$Z^* = 1 + \sum_{i=1}^n \left( \int d\mathbf{1} z_i(\mathbf{1}) + \int d\mathbf{2} z_i(\mathbf{2}) \right) + \sum_{i=1}^n \sum_{j=1}^n \int d\mathbf{1} \int d\mathbf{2} z_i(\mathbf{1}) z_j(\mathbf{2}) e_{ij}(\mathbf{1}, \mathbf{2}). \quad (1)$$

The following abbreviations have been used:

$\mathbf{1}$ : a vector within  $\Omega_1$

$$z_i(\mathbf{1}) = \frac{1}{v_i} \exp[-\beta(V_i^*(\mathbf{1}) - u_i)]$$

and similar definitions for  $\mathbf{2}$  and  $z_i(\mathbf{2})$ ,  $e_{ij}(\mathbf{1}, \mathbf{2})$  is related to Mayer's  $f$  function by

$$e_{ij}(\mathbf{1}, \mathbf{2}) = f_{ij}(\mathbf{1}, \mathbf{2}) + 1 = \exp(-\beta V_{ij}(\mathbf{1}, \mathbf{2})). \quad (2)$$

Differentiating  $\ln Z^*$  with respect to  $\ln z_i(\mathbf{1})$  and  $\ln z_i(\mathbf{2})$  one obtains the density functions  $\rho_i(\mathbf{1})$  and  $\rho_i(\mathbf{2})$  as

$$\rho_i(\mathbf{1}) = \frac{1}{Z^*} z_i(\mathbf{1}) \left( 1 + \sum_j \int d\mathbf{2} z_j(\mathbf{2}) e_{ij}(\mathbf{1}, \mathbf{2}) \right) \quad (3)$$

and other

where 'and other' stands for the other equation which can be obtained by permuting 1 and 2 in the above equation. Let  $\rho_{ij}(\mathbf{1}, \mathbf{2})$  be defined by

$$\rho_{ij}(\mathbf{1}, \mathbf{2}) = \frac{1}{Z^*} z_i(\mathbf{1}) z_j(\mathbf{2}) e_{ij}(\mathbf{1}, \mathbf{2}); \quad (4)$$

then (3) is easily converted into

$$\frac{1}{Z^*} z_i(\mathbf{1}) = \rho_i(\mathbf{1}) - \sum_j \int d\mathbf{2} \rho_{ij}(\mathbf{1}, \mathbf{2}) \quad (5)$$

and other.

Combining (1), (4) and (5) one obtains

$$\frac{1}{Z^*} = 1 - \theta_1 - \theta_2 + \theta_{12} \quad (6)$$

where  $\theta_1$  and  $\theta_2$  are given by

$$\theta_1 = \sum_i \int d\mathbf{1} \rho_i(\mathbf{1}) \quad (7)$$

and other.

$\theta_{12}$  is given by

$$\theta_{12} = \sum_i \sum_j \int d\mathbf{1} \int d\mathbf{2} \rho_{ij}(\mathbf{1}, \mathbf{2}). \quad (8)$$

Substituting (6) and (5) into (3) one obtains

$$\begin{aligned} \rho_i(\mathbf{1}) = & z_i(\mathbf{1})(1 - \theta_1) \left( 1 + \sum_j \int d\mathbf{2} f_{ij}(\mathbf{1}, \mathbf{2}) \rho_j(\mathbf{2}) \right) \\ & - \frac{1}{1 - \theta_1} \sum_m \sum_j \int d\mathbf{1}' \int d\mathbf{2} f_{ij}(\mathbf{1}, \mathbf{2}) h_{mj}(\mathbf{1}', \mathbf{2}) \end{aligned} \quad (9)$$

where  $h_{mj}(\mathbf{1}', \mathbf{2})$  is defined by

$$h_{mj}(\mathbf{1}', \mathbf{2}) = \rho_{mj}(\mathbf{1}', \mathbf{2}) - \rho_m(\mathbf{1}') \rho_j(\mathbf{2}). \quad (10)$$

Comparing (9) with (3.6) of Wu (1975b) one obtains the self-potential at  $\mathbf{1}$  of  $i$ th species as

$$-\frac{1}{\beta} \ln(1 - \theta_1) - \frac{1}{\beta} \ln \left( 1 + \sum_j \int d\mathbf{2} f_{ij}(\mathbf{1}, \mathbf{2}) \rho_j(\mathbf{2}) - \frac{1}{1 - \theta_1} \sum_m \sum_j \int d\mathbf{1}' \int d\mathbf{2} f_{ij}(\mathbf{1}, \mathbf{2}) h_{mj}(\mathbf{1}', \mathbf{2}) \right). \quad (11)$$

It is easily recognized that the first term is the self-potential of the single lattice site obtained previously. It is the sum of virial series of the internal field (Wu 1975b, equation (3.2)) restricting all dummy variables to within  $\Omega_1$ . On the other hand total expression (11) is the sum of virial series restricting all dummy variables to within  $\Omega_1$  and  $\Omega_2$ . Hence the second term of (11), which is the difference between the two sums just mentioned, can be considered as the net contribution to the internal field from the pair  $\Omega_1$  and  $\Omega_2$ . It is the sum of the virial series restricting all dummy variables to lie within either  $\Omega_1$  or  $\Omega_2$  plus the condition that at least one of the dummy variables is within  $\Omega_2$ . This term is zero unless  $\Omega_1$  and  $\Omega_2$  are within interaction range because of the factor  $f_{ij}(\mathbf{1}, \mathbf{2})$ . Summing all the contributions from neighbouring sites of  $\Omega_1$  one obtains an approximation to the internal field (Wu 1976):

$$-\beta V_i^{\text{int}}(\mathbf{1}) = \ln(1 - \theta_1) + \sum' \ln \left( 1 + \sum_j \int d\mathbf{2} f_{ij}(\mathbf{1}, \mathbf{2}) \rho_j(\mathbf{2}) - \frac{1}{1 - \theta_1} \sum_m \sum_j \int d\mathbf{1}' \int d\mathbf{2} f_{ij}(\mathbf{1}, \mathbf{2}) h_{mj}(\mathbf{1}', \mathbf{2}) \right) \quad (12)$$

where  $\Sigma'$  means summing over neighbouring sites. To express  $h_{mj}(\mathbf{1}, \mathbf{2})$  in terms of  $\rho_i(\mathbf{1})$ ,  $\rho_j(\mathbf{2})$  and  $f_{ij}(\mathbf{1}, \mathbf{2})$  one divides (4) by  $Z^*$  and then substitutes (6) and (5) into it to eliminate  $Z^*$ ,  $z_i(\mathbf{1})$  and  $z_j(\mathbf{2})$ . Afterwards (10) is used to obtain the following equation:

$$h_{ij}(\mathbf{1}, \mathbf{2}) + \frac{\rho_i(\mathbf{1})}{1 - \theta_1} \sum_m \int d\mathbf{1}' h_{mj}(\mathbf{1}', \mathbf{2}) + \frac{\rho_j(\mathbf{2})}{1 - \theta_2} \sum_k \int d\mathbf{2}' h_{ik}(\mathbf{1}, \mathbf{2}') + D \rho_i(\mathbf{1}) \rho_j(\mathbf{2}) + D h_{ij}(\mathbf{1}, \mathbf{2}) - \frac{1}{(1 - \theta_1)(1 - \theta_2)} \sum_k \sum_m \int d\mathbf{1}' \int d\mathbf{2}' h_{mj}(\mathbf{1}', \mathbf{2}) h_{ik}(\mathbf{1}, \mathbf{2}') = \left( \rho_i(\mathbf{1}) - \frac{1}{1 - \theta_2} \sum_k \int d\mathbf{2}' h_{ik}(\mathbf{1}, \mathbf{2}') \right) \left( \rho_j(\mathbf{2}) - \frac{1}{1 - \theta_1} \sum_m \int d\mathbf{1}' h_{mj}(\mathbf{1}', \mathbf{2}) \right) f_{ij}(\mathbf{1}, \mathbf{2}) \quad (13)$$

where  $D$  is defined by

$$D = \frac{1}{(1 - \theta_1)(1 - \theta_2)} \sum_m \sum_k \int d\mathbf{1}' \int d\mathbf{2}' h_{mk}(\mathbf{1}', \mathbf{2}'). \quad (14)$$

For each pair of  $i, j$  there is an equation of (13). For a system of  $n$ -species there are  $n \times n$  of them. They are simultaneous non-linear integral equations for  $h_{ij}(\mathbf{1}, \mathbf{2})$ . If they are solved and substituted in (12) then an approximation to the internal field is obtained. Hence summing the next sub-series is equivalent to solving (13).

### 3. Physical implications via simple examples

Equation (13) is quite complicated. In this section its physical implications are explored by considering three cases where it can be solved easily.

#### 3.1. Bethe–Peierls–Guggenheim approximation

If only monopoles are considered then  $\rho_i(\mathbf{1})$  and  $\rho_j(\mathbf{2})$  become  $\delta$  functions centred at equilibrium positions.  $h_{ij}(\mathbf{1}, \mathbf{2})$  can be written as product of  $\delta$  functions. After proper integrations to eliminate  $\delta$  functions equation (13) becomes an algebraic equation for the strengths of  $\delta$  functions. If only one species is considered then the equation becomes

$$h = (\theta_1 - \theta_1\theta_2 - h)(\theta_2 - \theta_1\theta_2 - h)f \quad (15)$$

where  $h$  denotes  $D(1 - \theta_1)(1 - \theta_2)$ . This is a quadratic equation and is easy to solve. It was mentioned previously (Wu 1975a) that the lattice gas model can be derived from virial series by taking monopole approximation. It was further shown (Rushbrooke and Scoins 1955, Wu 1976) that for the lattice gas model equation (12), which is obtained by summing two sub-series, is equivalent to the Bethe–Peierls–Guggenheim approximation. Thus equations (12) and (13) together constitute a natural generalization of the Bethe–Peierls–Guggenheim approximation. Since this approximation takes short-range order into account so do equations (12) and (13).

#### 3.2. The fluctuation of internal field

If the distance between  $\Omega_1$  and  $\Omega_2$  is larger than the hard-core diameters then one can solve  $h_{ij}(\mathbf{1}, \mathbf{2})$  in powers of Mayer's  $f$  function. To do this let us adopt the following abbreviations:

$$\begin{aligned} \langle O_{ij} \rangle_1 &= \sum_i \int d\mathbf{1} O_{ij}(\mathbf{1}, \mathbf{2}) \\ \langle O_{ij} \rangle_2 &= \sum_j \int d\mathbf{2} O_{ij}(\mathbf{1}, \mathbf{2}) \\ \langle\langle O_{ij} \rangle\rangle &= \langle\langle O_{ij} \rangle_1 \rangle_2 \end{aligned}$$

where  $O_{ij}(\mathbf{1}, \mathbf{2})$  is a function of  $i, j, \mathbf{1}$  and  $\mathbf{2}$ . In (13) if  $f_{ij}(\mathbf{1}, \mathbf{2})$  is a small parameter then  $h_{ij}(\mathbf{1}, \mathbf{2})$  and hence  $D$  are of first order. If orders higher than first in (13) are dropped one obtains

$$h_{ij}(\mathbf{1}, \mathbf{2}) + \frac{\rho_i(\mathbf{1})}{1 - \theta_1} \langle h_{mj} \rangle_1 + \frac{\rho_j(\mathbf{2})}{1 - \theta_2} \langle h_{ik} \rangle_2 + \frac{\rho_i(\mathbf{1})\rho_j(\mathbf{2})}{(1 - \theta_1)(1 - \theta_2)} \langle\langle h_{mk} \rangle\rangle = \rho_i(\mathbf{1})\rho_j(\mathbf{2})f_{ij}(\mathbf{1}, \mathbf{2}). \quad (16)$$

Applying  $\langle\langle \dots \rangle\rangle$  to equation (16) one obtains

$$\langle\langle h_{ij} \rangle\rangle = (1 - \theta_1)(1 - \theta_2) \langle\langle \rho_i(\mathbf{1})\rho_j(\mathbf{2})f_{ij} \rangle\rangle;$$

applying  $\langle \dots \rangle_1$  to (16) and using the above result one gets

$$\frac{1}{1 - \theta_1} \langle h_{ij} \rangle_1 = \langle \rho_i(\mathbf{1})\rho_j(\mathbf{2})f_{ij} \rangle_1 - \rho_j(\mathbf{2}) \langle\langle \rho_i(\mathbf{1})\rho_j(\mathbf{2})f_{ij} \rangle\rangle. \quad (17)$$

To express the internal field in powers of  $\beta V_{ij}(\mathbf{1}, \mathbf{2})$  one substitutes (17) into (12), expands the second logarithm of (12) in powers of  $f_{ij}(\mathbf{1}, \mathbf{2})$  and then expands  $f_{ij}(\mathbf{1}, \mathbf{2})$  in powers of  $-\beta V_{ij}(\mathbf{1}, \mathbf{2})$ . To second order one obtains:

$$\begin{aligned}
 -\beta V_i^{\text{int}}(\mathbf{1}) = & \ln(1 - \theta_1) - \beta \sum' \langle V_{ij}(\mathbf{1}, \mathbf{2}) \rho_j(\mathbf{2}) \rangle_2 \\
 & + \frac{1}{2} \beta^2 \sum' (\langle V_{ij}^2(\mathbf{1}, \mathbf{2}) \rho_j(\mathbf{2}) \rangle_2 - \langle V_{ij}(\mathbf{1}, \mathbf{2}) \rho_j(\mathbf{2}) \rangle_2^2) \\
 & + \beta^2 \sum' (\langle \langle \langle V_{ij}(\mathbf{1}, \mathbf{2}) V_{mk}(\mathbf{1}', \mathbf{2}') \rho_j(\mathbf{2}) \rho_m(\mathbf{1}') \rho_k(\mathbf{2}') \rangle_{1'} \rangle_{2'} \rangle_2 \\
 & - \langle \langle V_{ik}(\mathbf{1}, \mathbf{2}) V_{mk}(\mathbf{1}', \mathbf{2}') \rho_m(\mathbf{1}') \rho_k(\mathbf{2}') \rangle_{1'} \rangle_{2'}). \tag{18}
 \end{aligned}$$

The second term is the mean field obtained previously (Wu 1975a). The third and fourth terms are the fluctuation fields. They vanish if there is a particle of  $j$ th species within  $\Omega_2$  and it does not move. In the monopole approximation (18) reproduces the high-temperature series, for the lattice gas model, up to second order (Wu 1972). This is the first time that the fluctuation field has been derived since the inception of the Lennard-Jones cell model (Barker 1963).

### 3.3. *The system of hard rods*

Equations (12) and (13) together are equivalent to summing two sub-series of virial series. It was shown that this is equivalent to making the Bethe–Peierls–Guggenheim approximation (Rushbrooke and Scoins 1955, Wu 1976) which is exact for a Bethe lattice. Thus equations (12) and (13) are exact for a Bethe lattice if interstitial atoms are not considered. Now, a one-dimensional system with nearest-neighbour interactions is a Bethe lattice of coordination number two. Hence (12) and (13) should yield exact results for such systems. In the appendix we demonstrate this for the system of hard rods. This example indicates that equations (12) and (13) are capable of handling the hard-core interaction which the mean-field (perturbational) approach of § 3.2 is not.

## 4. Discussion

From the three examples of § 3 one can now understand why equation (13) has such a complicated appearance.

It is because both vacancies and correlations between neighbouring particles are considered simultaneously. As vacancies are taken into account already in the mean-field approximation (Wu 1975a) the vacancy pair's contribution should be contained within (18). To conclude let us mention that the bulk of theories on quantum crystals (Werthamer 1969) is concerned with correlation between neighbouring particles. Most of these theories are based on variational principles of ambiguous accuracies. Our approach to classical correlation could be relevant to the problem. In particular the vacancies, which are very difficult to deal with by other methods, are contained naturally in our equations.

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### Appendix. Exact solution for a system of hard rods

Let the real number axis be divided into intervals of equal length 'a' which is the length of a rod. Then each interval can at most accommodate one rod. Hence the intervals can be regarded as the  $\Omega(R)$  of Wu (1975a). There are no interstitial particles because the  $\Omega$  fill the whole real line. Let  $\Omega_1$  be the interval  $[0, a]$  and  $\Omega_2$  the interval  $[a, 2a]$ . Let  $x$  be a point in  $\Omega_1$  and  $y$  in  $\Omega_2$ . Both of them will be measured from the centres of their respective intervals. Then the following facts are obvious:

$$\begin{aligned}\rho(x) &= \rho(y) = \rho = \theta/a \\ \rho(x, y) &= \rho(-y, -x)\end{aligned}\tag{A.1}$$

where  $\theta$  is the total number of particles within an interval. Dividing (4) by  $Z^*$  and using (5) and (6) one obtains

$$\left(1 - 2\theta + \int dx' \int dy' \rho(x', y')\right) \rho(x, y) = \left(\rho - \int dy' \rho(x, y')\right) \left(\rho - \int dx' \rho(x', y)\right) e(x, y).\tag{A.2}$$

Denoting the expression within the first brackets on the right-hand side of (A.2) by  $F(x)$  and using (A.1) one obtains

$$\left(1 - \theta - \int_{-a/2}^{a/2} dx' F(x')\right) \rho(x, y) = F(x) F(-y) e(x, y).\tag{A.3}$$

Integrating the  $y$  variable one obtains

$$\left(1 - \theta - \int_{-a/2}^{a/2} dx' F(x')\right) (\rho - F(x)) = F(x) \int_{-a/2}^{-x} F(x') dx'.\tag{A.4}$$

Setting  $x = -a/2$  in (A.4) one can solve for the integral of  $F(x')$  over  $[-a/2, a/2]$ . Substituting this back into (A.4) one obtains

$$(1 - \theta) \frac{F(-a/2)}{\rho} (\rho - F(x)) = F(x) \int_{-a/2}^{-x} F(x') dx'.\tag{A.5}$$

Combining (12) with (1) of Wu (1975a) one obtains

$$\rho = e^{\beta\mu} (1 - \theta) \left( \frac{F(-a/2)}{\rho} + \frac{1}{1 - \theta} \int_{-a/2}^{-x} dx' F(x') \right) \left( \frac{F(-a/2)}{\rho} + \frac{1}{1 - \theta} \int_{-a/2}^x dx' F(x') \right).\tag{A.6}$$

Substituting (A.5) into (A.6) one has

$$\rho = e^{\beta\mu} (1 - \theta) \frac{F(-a/2)}{F(x)} \left( \frac{F(-a/2)}{\rho} + \frac{1}{1 - \theta} \int_{-a/2}^x dx' F(x') \right).\tag{A.7}$$

Setting  $x = -a/2$  in (A.7) one obtains

$$\rho = e^{\beta\mu} (1 - \theta) \frac{F(-a/2)}{\rho}.\tag{A.8}$$

Substituting this back into (A.7) one obtains

$$F(x) = F\left(-\frac{a}{2}\right) + \frac{\rho}{1 - \theta} \int_{-a/2}^x dx' F(x').\tag{A.9}$$

Hence

$$F(x) = F\left(-\frac{a}{2}\right) \exp\left[\frac{\rho}{1-\theta}\left(x + \frac{a}{2}\right)\right]. \quad (\text{A.10})$$

From (A.4) one obtains that

$$F(a/2) = \rho.$$

This, with (A.10) and (A.8), gives one

$$\rho = e^{\beta\mu} (1-\theta) e^{-\theta/(1-\theta)}. \quad (\text{A.11})$$

Using (A.11) to integrate the thermodynamical identity

$$\left(\frac{\partial p}{\partial \mu}\right)_T = \rho \quad (\text{A.12})$$

one recovers the well known equation of state:

$$\beta p = \frac{\rho}{1-a\rho}. \quad (\text{A.13})$$

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