

Research Article

Evaluation of the Component Chemical Potentials in Analytical Models for Ordered Alloy Phases

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Received 17 November 2010; Accepted 27 January 2011

Academic Editor: Brian J. Edwards

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The component chemical potentials in models of solution phases with a fixed number of sites can be evaluated easily when the Helmholtz energy is known as an analytical function of composition. In the case of ordered phases, however, the situation is less straightforward, because the Helmholtz energy is a functional involving internal order parameters. Because of this, the chemical potentials are usually obtained numerically from the calculated integral Helmholtz energy. In this paper, we show how the component chemical potentials can be obtained analytically in ordered phases via the use of virtual cluster chemical potentials. Some examples are given which illustrate the simplicity of the method.

1. Introduction

Chemical potentials for the components in alloy phases are often required: they are useful, for example, in phase diagram calculations. In the case of a binary substitutional alloy model, (A,B) , which uses a fixed number of sites, N_S , containing N_A and N_B atoms of element A and B , respectively, functions like $(\partial F/\partial N_A)_{N_S}$ are not chemical potentials. They are equal to the difference between the component chemical potentials, for example, $(\partial F/\partial N_B)_{N_S} = \mu_B - \mu_A$. This difference is usually referred to as the diffusion potential [1].

This problem with definition does not mean that the individual component chemical potentials are unobtainable in solution phases with a fixed number of sites. They can be obtained from the partial derivative of the calculated Helmholtz energy, F , for example, $\mu_A = (\partial F/\partial N_A)_{V,T,N_B}$ in circumstances where F can be expressed as a function of N_A and N_B . In a completely disordered solution the Helmholtz energy and the component chemical potentials are well defined

$$\begin{aligned}\Delta_{\text{mix}}F_m &= RT \sum_i x_i \ln x_i, \\ \Delta_{\text{mix}}\mu_i &= RT \ln x_i.\end{aligned}\quad (1)$$

Analytical expressions for the chemical potentials can also be derived for models of single lattice phases which take into account deviations from random mixing. Results for the pair quasichemical (Q-C) approximation [2, 3] and for a four-point cluster in the same approximation [4, 5] have been reported.

It is the evaluation of the component chemical potentials in ordered (or antiferromagnet) phases which poses a problem, because there is no longer an explicit relation between F and N_A , N_B . Instead, F is a functional involving internal order parameters. It is because of this that the usual way of obtaining the component chemical potentials has been to numerically differentiate the calculated integral Helmholtz energy.

In this paper, we show how component chemical potentials can be easily obtained in any cluster approximation in either ordered or the single lattice state via the use of virtual chemical potentials (VCPs). VCPs are defined in Section 2. Previously, only point VCPs appear to have been used, but cluster VCPs are also definable and, as we show, are equally useful. The use of cluster VCPs in calculating the equilibrium distribution of clusters and species in partially ordered phases is discussed in Section 3. In Section 4, we show how the component chemical potentials are simply

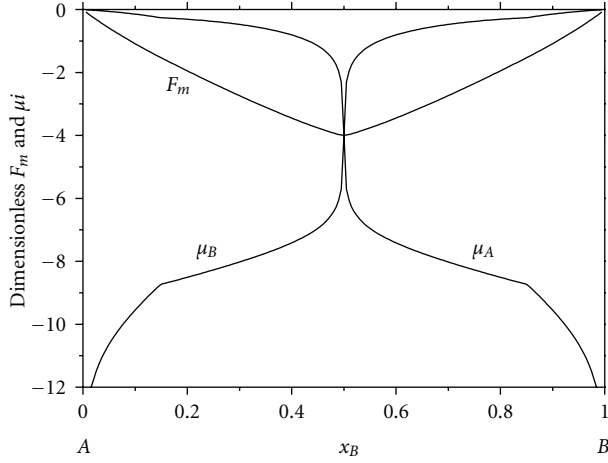


FIGURE 1: The integral molar Helmholtz energy, F_m and the component chemical potentials obtained from VCPs for $z = 8$, n.n. $W_{AB} = -1.0$ in the Q-C n.n. pair approximation.

related to the VCPs, and in Section 5, we present the results for some example model calculations.

2. Virtual Chemical Potentials

In their original treatment for calculating the equilibrium distribution of lattice defects in solids, Wagner and Schottky used the law of mass action [6], but later, Schottky gave a more formal treatment of this approach in terms of point VCPs [7]. These point VCPs were used extensively by Kröger [8] in discussing defect equilibria in ionic and semiconductor compounds.

Schottky distinguished between two types of constituent of a solution phase, building units and structural elements. The building units can be regarded as the normal components, while the structural elements are the majority and defect species occurring on the sublattice sites. When a structural element is created, the number of complementary structural elements cannot be kept constant due to the requirement of a definite site ratio; it is, therefore, not possible to assign a true chemical potential to a structural element, nor can they be accessed experimentally. It is possible, however, to define a point VCP for a species A on a sublattice i as

$$\mu_{A_i} = \left(\frac{\partial F}{\partial N_A^{(i)}} \right)_{V,T,N_1^{(j)}}, \quad (2)$$

where F is the Helmholtz energy, $N_A^{(i)}$ the number of species or constituents of type A on sublattice i , and $N_1^{(j)}$ to all other point species on all sublattices. We have used the notation μ_{A_i} here rather than $\mu_A^{(i)}$ since the latter is often used to denote the chemical potential of a component A in a phase i .

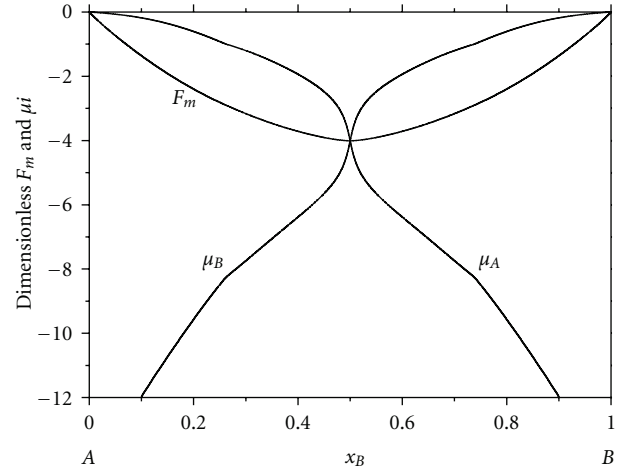


FIGURE 2: The integral molar Helmholtz energy, F_m and the component chemical potentials obtained from VCPs for $z' = 8$; $z'' = 6$; dimensionless n.n. $W_{AB} = -1.0$; n.n.n. $W_{AB} = -0.5$ in the CVM tetrahedron approximation.

The concept of VCPs is readily extended to consider larger clusters than the point. For example, the following can be defined for pair and four-point clusters:

$$\begin{aligned} \mu_{A_1B_2} &= \left(\frac{\partial F}{\partial N_{AB}^{(12)}} \right)_{V,T,N_2^{(12)}}, \\ \mu_{P_1Q_2R_3S_4} &= \left(\frac{\partial F}{\partial N_{PQRS}^{(1234)}} \right)_{V,T,N_4^{(1234)}}, \end{aligned} \quad (3)$$

where $N_2^{(12)}$ and $N_4^{(1234)}$ refer to all other pairs and four-point clusters, respectively.

3. Equilibrium Distribution of Species in Ordered Phases

Schottky showed that the value of point VCPs lies in their computational convenience in a modeling context. This can be illustrated by considering a model for an ordered phase comprising two elements, A and B , distributed between two sublattices, 1 and 2. If the sublattices are assumed to be of equal size, then this ordered phase can be represented as $(A, B) : (A, B)$.

We will consider this phase in the nearest neighbor pair Q-C approximation. If we consider a closed system, Lagrangian multipliers can be assigned to the mass balances

$$\begin{aligned} \lambda_A \quad zN_A &= 2N_{AA}^{(12)} + N_{AB}^{(12)} + N_{BA}^{(12)}, \\ \lambda_B \quad zN_B &= 2N_{BB}^{(12)} + N_{BA}^{(12)} + N_{AB}^{(12)}. \end{aligned} \quad (4)$$

Minimization of the Lagrangian

$$\begin{aligned} L &= A + \lambda_A \left(zN_A - 2 \left(N_{AA}^{(12)} + N_{AB}^{(12)} + N_{BA}^{(12)} \right) \right) \\ &\quad + \lambda_B \left(zN_B - 2 \left(N_{BB}^{(12)} + N_{BA}^{(12)} + N_{AB}^{(12)} \right) \right), \end{aligned} \quad (5)$$

followed by the elimination of the Lagrangian multipliers gives the following equilibrium relations between the pair VCPs

$$\begin{aligned}\mu_{A_1A_2} + \mu_{B_1B_2} &= \mu_{A_1B_2} + \mu_{B_1A_2}, \\ \mu_{A_1B_2} &= \mu_{B_1A_2}.\end{aligned}\quad (6)$$

The solution of these equations, subject to normalization and mass balance constraints, leads to the equilibrium values for the pair probabilities.

In the Q-C approximation the relation between the VCPs and the pair probabilities can be obtained from

$$\Delta_{\text{mix}} U_m = \frac{z}{2} \sum_{i \neq j} p_{ij}^{(12)} W_{ij}^{(12)}, \quad (7)$$

$$\Delta_{\text{mix}} S_m = \frac{z}{2} S_2 - (z-1) S_1, \quad (8)$$

where $W_{ij} = \varepsilon_{ij} - 0.5(\varepsilon_{ii} + \varepsilon_{jj})$ is the pair exchange energy (the $\varepsilon_{ij}^{(12)}$ are the bond energies), z is the coordination number, and $p_{ij}^{(12)}$ is the mean pair probability.

The dimensionless pair and point entropies in (8), S_2 , and S_1 are given by

$$S_2 = - \sum_{ij} p_{ij}^{(12)} \ln p_{ij}^{(12)}, \quad (9)$$

$$S_1 = - \sum_A \sum_i \frac{1}{2} p_A^{(i)} \ln p_A^{(i)},$$

where $p_A^{(i)}$ is the mean probability or sublattice mole fraction of the species A on sublattice i .

The pair VCPs may then be obtained from the Helmholtz energy minimization (dimensionless) $F_m = U_m - S_m$. For example,

$$\mu_{B_1B_2} = \varepsilon_{BB}^{(12)} + \ln p_{BB}^{(12)} - \left(\frac{z-1}{z} \right) (\ln p_B^{(1)} p_B^{(2)}). \quad (10)$$

Substitution of such expressions for the VCPs into (6) then leads to the solution for the equilibrium pair distribution.

It should be noted that this use of VCPs is not the only, nor necessarily the most convenient, method to calculate equilibrium cluster distributions. Many using the CVM, for example, use the natural iteration method [9] to calculate these distributions.

4. Component Chemical Potentials

A principal advantage of VCPs lies in their relation to the component chemical potentials. We will first consider the same example as was used in the previous section and then present analogous relations for other examples.

Consider a system which is open to the component B . We lose the mass balance constraint for B and must now consider a Lagrangian based on the grand potential, $\Omega = A - \mu_B N_B$:

$$\begin{aligned}L &= A - \lambda_A \left(zN_A - \left(2N_{AA}^{(12)} + N_{AB}^{(12)} + N_{BA}^{(12)} \right) \right) \\ &\quad - \mu_B \left(N_B^{(1)} + N_B^{(2)} \right) \\ &= A - \lambda_A \left(zN_A - \left(2N_{AA}^{(12)} + N_{AB}^{(12)} + N_{BA}^{(12)} \right) \right) \\ &\quad - \mu_B \left(\frac{1}{z} \left(2N_{BB}^{(12)} + N_{AB}^{(12)} + N_{BA}^{(12)} \right) \right),\end{aligned}\quad (11)$$

from which we can obtain,

$$\frac{\partial L}{\partial N_{BB}^{(12)}} = \mu_{B_1B_2} - \frac{2}{z} \mu_B = 0, \quad (12)$$

so that in this case, the component chemical potential is related to just the one pair VCP

$$\mu_B = \frac{z}{2} \mu_{B_1B_2}. \quad (13)$$

Similar simple expressions are readily obtained for other cluster models. The following lists some examples (n.n. refers to nearest neighbor interactions and n.n.n. to next nearest neighbor interactions).

Four-sublattices, Bragg-Williams (B-W) approxn.

$$\Delta_{\text{mix}} \mu_B = \mu_1(B), \quad (14)$$

bcc, n.n., Q-C approxn.

$$\Delta_{\text{mix}} \mu_B = 4\mu_2(B) - 7\mu_1(B), \quad (15)$$

bcc, n.n. & n.n.n., Q-C approxn.

$$\Delta_{\text{mix}} \mu_B = 4\mu_2'(B) + 3\mu_2''(B) - 13\mu_1(B), \quad (16)$$

fcc CVM-T approxn.

$$\Delta_{\text{mix}} \mu_B = 2\mu_4(B) + 6\mu_2(B) - 5\mu_1(B), \quad (17)$$

bcc CVM-T approxn.

$$\Delta_{\text{mix}} \mu_B = 6\mu_4(B) - 12\mu_3(B) + 4\mu_2'(B) + 3\mu_2''(B) - \mu_1(B), \quad (18)$$

where

$$\begin{aligned}\mu_4(B) &= \sum_{ijkl} \frac{1}{n} \ln p_{BBBB}^{(ijkl)}, \\ \mu_3(B) &= \sum_{ijk} \frac{1}{n} \ln p_{BBB}^{(ijk)}, \\ \mu_2(B) &= \sum_{ij} \frac{1}{n} \ln p_{BB}^{(ij)}, \\ \mu_1(B) &= \sum_i \frac{1}{n} \ln p_B^{(i)}.\end{aligned}\quad (19)$$

Here, n is the number of different types of cluster or subcluster; for example, $n = 4$ and $n = 2$, respectively, for the number of types of n.n. and n.n.n. clusters in the bcc n.n. and n.n.n. Q-C approximation.

It should be noted that there is no relation similar to those given for chemical potentials which permit the analytical calculation of partial molar energies or entropies.

5. Example Calculations

In the examples shown in Figures 1 and 2 for a solution phase A-B, the molar integral Helmholtz mixing energy, $\Delta_{\text{mix}}F_m$, has been calculated from the integral mixing energy and integral mixing entropy. For example, in the Q-C n.n. two-sublattice approximation, the following equations have been used:

$$\Delta_{\text{mix}}U_m = \frac{z}{2} \sum_{i \neq j} p_{ij} W_{ij},$$

$$\Delta_{\text{mix}}S_m = - \sum_{ij} p_{ij} \ln p_{ij} + (z-1) \sum_i \frac{1}{2} y_A^{(i)} \ln y_A^{(i)}. \quad (20)$$

The chemical potentials shown in the figures have been obtained from (14) and (18). Explicitly, the chemical potentials of A shown in Figure 2 have been obtained from

$$\begin{aligned} \mu_A = & 6 \ln p_{AAAA}^{(1234)} \\ & - \frac{12}{4} \left(\ln p_{AAA}^{(123)} + \ln p_{AAA}^{(124)} + \ln p_{AAA}^{(134)} + \ln p_{AAA}^{(234)} \right) \\ & + \frac{4}{4} \left(\ln p_{AA}^{(13)} + \ln p_{AA}^{(14)} + \ln p_{AA}^{(23)} + \ln p_{AA}^{(24)} \right) \\ & + \frac{3}{2} \left(\ln p_{AA}^{(12)} + \ln p_{AA}^{(34)} \right) \\ & - \frac{1}{4} \left(\ln p_A^{(1)} + \ln p_A^{(2)} + \ln p_A^{(3)} + \ln p_A^{(4)} \right). \end{aligned} \quad (21)$$

Here, the n.n.n. have been taken to involve the sublattices 1-2 and 3-4.

The chemical potentials calculated from the VCPs agree well with those obtained numerically from the independently calculated integral quantity from CVM. Slight difference is due to the n.n. approximation in the VCP calculation, which can obviously be overcome by a straightforward employment of the n.n.n. approximation in the present method.

Besides the simplicity in definition, the use of VCPs also reduces the number of independent variables in the calculation of chemical potentials. In the CVM calculations for n -component alloy, there are necessarily 2^n independent variables, whereas it is significantly decreased to $2n$ through the definition of VCPs.

6. Conclusion

Component chemical potentials are easily obtained in analytical forms by virtue of cluster VCPs in ordered alloy phases, instead of the usual numerical calculations from the

integral Helmholtz energy. The example calculation based on pair quasichemical approximation is compared with the CVM calculation with a four-point cluster in the same approximation, illustrating the simplicity of the method.

Furthermore, the use of VCPs benefits direct comparisons with simulation results, in which systems are always restricted to a fixed number of total sites.

Acknowledgments

The support of the Ministry of Science and Technology of China under Grant no. 2006CB605104 and the Natural Science Foundation of China under Grant no. 50631030 is gratefully acknowledged. W. A. Oates wishes to acknowledge support for a short visit to the Institute of Metal Research, CAS, Shenyang, China.

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