Role of Three-Body Potentials in Disordered Alloys. III
—Quasi-Binary Alloys—

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A formulation of the statistical mechanics for the quasi-binary alloy of the form \(A \_{\alpha}B_{1-\alpha}C\) is presented which includes static two- and three-body potentials. The \(C\) atoms are treated exactly, and the \(A\) and \(B\) atoms are replaced by an effective \(AB\) atom which randomly occupies lattice sites in proportion to the relative concentrations of \(A\) and \(B\). This approximation introduces effective, concentration-dependent, two- and three-body potentials into the formulation of the previous two papers of this series. The more complicated three-level system is thus reduced to a quasi-two-level one, and hence the analysis, expounded in one of these earlier works, of the influence of three-body potentials in the binary alloy becomes applicable to that of a ternary alloy.

In a recent series of papers\(^1\) (hereafter Refs. 1 and II, respectively) the influence of static three-body potentials on the order-disorder properties of the binary and ternary alloys was investigated. In particular, it was shown how the three-body potential affects the two- and three-particle correlation functions, as well as the behavior of the critical temperature. That is to say, it was shown that by including higher-order terms in a high-temperature expansion (causing the expansion to be valid in a smaller neighborhood about \(T_c\), the ordering temperature), the effective interaction potential could no longer be represented by a simple composition-dependent two-body potential, and that the three-body potentials made their own peculiar contributions to the correlation functions, and hence the ordering temperatures. It is the purpose of this short paper to show how the influence of three-body potentials can be incorporated into a recently proposed theory\(^3\) of disordered quasi-binary alloys,\(^4\) which reduces the three-level system to a quasi-two-level one, and hence provide a bridge between the first two papers in this series. The merits of this approach, as mentioned in Ref. 3), are that the more extensive results of the two-level calculation can now be applied to the three-level one, and that, within this approximation, certain peculiarities\(^5\) of the three-level system are removed, even in the linear approximation.

As in II, we consider a ternary alloy of \(N\) atoms distributed on \(N\) sites on a rigid, isotropic lattice such that \(N^A\) are \(A\) atoms, \(N^B\) are \(B\) atoms, and \(N^C=N-N^A-N^B\) are \(C\) atoms. The configurational Hamiltonian is given as a sum of
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static two- and three-body potentials, i.e.,

\[ H = \frac{1}{2!} \sum_{i,j} V^{\nu\nu}(ij) \sigma_i^\nu \sigma_j^\nu + \frac{1}{3!} \sum_{i,j,l} W^{\nu\nu\nu}(ijl) \sigma_i^\nu \sigma_j^\nu \sigma_l^\nu, \]

where \( V^{\nu\nu}(ij) \) and \( W^{\nu\nu\nu}(ijl) \) are irreducible static two- and three-body interactions, respectively. The sums are over all atom types \((\mu, \nu, \rho = A, B, C)\), and over all lattice sites due to the properties of the occupation operators,

\[ \sigma_i^\nu = 1, \text{ if site } i \text{ is occupied by a } \mu \text{ atom,} \]
\[ = 0, \text{ otherwise.} \]

For the quasi-binary alloy \( A_xB_{1-x}C \), we consider, as in Ref. 3), that the \( C \) atoms are treated exactly, and that the \( A \) and \( B \) atoms are replaced by an effective \( AB \) atom (pseudo-atom) which randomly occupies lattice sites in proportion to the relative concentration of \( A \) and \( B \). This essentially consists of defining an averaged occupation operator, \( \sigma_i^\nu \), such that,

\[ \sigma_i^A = x \sigma_i, \]
\[ \sigma_i^B = (1-x) \sigma_i, \]
\[ \sigma_i = \sigma_i^A + \sigma_i^B, \]

where

\[ \sigma_i = 1, \text{ if site } i \text{ is occupied by an } A \text{ or } B \text{ atom,} \]
\[ = 0, \text{ otherwise.} \]

The substitution of (2) and (3) into (1) results in a quasi-binary Hamiltonian consisting of concentration-dependent two- and three-body interactions, and the occupation operators \( \sigma_i^\nu \) and \( \sigma_i^\varepsilon \), which in turn can be reformulated in terms of spin \((h=1)\) operators, as in I, by defining,

\[ \sigma_i^\varepsilon = -\frac{1}{2} + S_i, \]
\[ \sigma_i^\varepsilon = -\frac{1}{2} - S_i, \]

where \( S_i \) is the \( z \)-component of a spin one-half vector at site \( i \).

The system Hamiltonian (1) can finally be written,

\[ \mathcal{H} = -\mu \sum_i S_i^z - \frac{1}{2} \sum_{i,j} I_{ij} S_i^\varepsilon S_j^\varepsilon - \frac{1}{3} \sum_{i,j,l} I_{ijl} S_i^\varepsilon S_j^\varepsilon S_l^\varepsilon, \]

where \( \mu \) is a chemical potential determined such that

\[ \langle N^\sigma \rangle = N^\sigma \]

and

\[ \langle [\ldots] \rangle = \frac{\text{Tr} \, e^{-\beta \mathcal{H}} [\ldots]}{\text{Tr} \, e^{-\beta \mathcal{H}}}. \]
As opposed to I, however, the two- and three-body interactions are now defined as

\[ I_s(ij) = 2x V^{AG}(ij) + 2(1-x) V^{BG}(ij) - V^{OG}(ij) - 2x(1-x) V^{AB}(ij) - (1-x)^2 V^{BB}(ij) \]

\[ -x^2 V^{AA}(ij) - \frac{1}{2} \sum \{ x^2 W^{AAA}(ijl) + (1-x)^2 W^{BBB}(ijl) + W^{OOG}(ijl) \} \]

\[ + x^2(1-x) \left[ W^{AAB}(ijl) + W^{BAA}(ijl) + W^{ABA}(ijl) \right] + x(1-x) \left[ W^{OBO}(ijl) - W^{GOA}(ijl) - W^{OOG}(ijl) \right] \]

\[ + W^{BBB}(ijl) + W^{BBA}(ijl) \] \[ + x^2 \left[ W^{AAC}(ijl) - W^{AAC}(ijl) \right] \]

\[ + (1-x)^2 \left[ W^{ABB}(ijl) - W^{BBA}(ijl) - W^{BBB}(ijl) \right] + x(1-x) \]

\[ \times \left[ W^{ABC}(ijl) + W^{ABC}(ijl) - W^{ABC}(ijl) - W^{ABC}(ijl) \right] \]

(9)

and

\[ I_s(ijl) = \left\{ x^2 \left[ W^{AAC}(ijl) + W^{AAC}(ijl) + W^{AAC}(ijl) \right] + (1-x) \left[ W^{BBB}(ijl) + W^{BBB}(ijl) \right] \]

\[ + W^{BBB}(ijl) + W^{BBB}(ijl) \] \[ - (1-x) \left[ W^{OOG}(ijl) + W^{OOG}(ijl) + W^{OOG}(ijl) \right] \]

\[ - x \left[ W^{OOG}(ijl) + W^{OOG}(ijl) + W^{OOG}(ijl) \right] - x(1-x) \left[ W^{BBA}(ijl) + W^{BBA}(ijl) \right] \]

\[ + W^{BBB}(ijl) + W^{BBA}(ijl) \] \[ - x^2(1-x) \left[ W^{AAC}(ijl) + W^{AAC}(ijl) \right] \]

\[ + W^{ABB}(ijl) - W^{BBA}(ijl) \] \[ + W^{BBA}(ijl) \]

\[ \times \left[ W^{ABC}(ijl) + W^{ABC}(ijl) - W^{ABC}(ijl) + W^{ABC}(ijl) \right] + \] \[ W^{ABC}(ijl) \]

(10)

i.e., the interactions of I have been replaced by effective concentration-dependent interactions. These new interactions between the AB atoms, or pseudo-atoms, and the C atoms describe our new quasi-binary alloy. Having reformulated the quasi-binary alloy, the pertinent physical parameters can then be calculated, and by way of (3), related back to the original three-level system. Thus the high-temperature expansion for the two- and three-particle correlation functions, calculated in I, can now be applied to the ternary system of II. One must be careful, as in Ref. 3), to redefine

\[ \rho = (m^A + m^B) m^C, \]

(11)

\[ m = \langle S_f \rangle = \frac{1}{2} (m^A + m^B - m^C), \]

(12)

where

\[ m^e = \langle N^e \rangle / N \]

(13)

is the relative concentration of \( \mu \) atoms and, of course, \( I_s(ij) \) and \( I_s(ijl) \) are now given by (9) and (10). In applications to actual ternary systems one must weigh the value of the higher order high-temperature expansion of I, within this approximation, with the mathematical complexity of a high-temperature expansion to
the corresponding order within the framework of II.

In particular, in the notation of I, the two-particle spin-spin correlation function, which can be related back to the occupation operator correlation function via (3) and (5), is given, exact to the third order in $T_c/T$, as

$$\langle S_i^+ S_j^- \rangle = m^2 + \delta_{ij} \Phi_4(\beta) + \beta \Phi_1(ij) + \beta^2 \Phi_2(ij) + \beta^4 \Phi_2(ij) + O(\beta^6),$$

(14)

where the $\Phi_n(ij)$ are given explicitly in Appendix 1 of I. The interactions $I_s(ij)$ and $I_s(ijl)$, as well as the parameters $\rho$ and $m$, are now given by (9)~(12), respectively. Similarly, the three-particle correlation function is given, to the second order, as

$$\langle S_i^+ S_j^+ S_k^- \rangle = m^3 + \gamma \Phi_1(ijl) + \beta^2 \Phi_2(ijl) + O(\beta^4),$$

(15)

where the values of $\gamma(ijl)$ are given in Appendix 2 of I. The corresponding expansion of II is given only out to the linear result in $T_c/T$. Of course, in the present work, if $x$ equals 0(1), one retains the exact results of I for a BC (AC) binary alloy. In addition, if the three-body potentials are zero, then the results of Ref. 3) are obtained.

References