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Correlation function approach to multicomponent systems: Quaternary alloys

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The order-disorder transition in multicomponent systems–in particular quaternary alloys–is investigated using classical fluctuation theory and correlation functions derived by exact high-temperature series expansion techniques. This method, based on the ideas of the Tahir-Kheli, generalizes the successful procedure used in binary systems by investigating singularities in the magnitude of the correlation matrix for multicomponent systems as the system approaches criticality. Contact is then made with the method of static concentration waves in the ordered regime and, in the regular solution limit, with the comprehensive work of Hardy and Meijering. The method presented here clearly shows the relation between the diffuse scattering intensities and the system thermodynamics. In addition it is straightforward to systematically improve the approximation used, as well as to modify the physics of the system.

I. INTRODUCTION

Relative to multicomponent solid solutions the physics of binary systems has been fairly well investigated.[1] Yet even so there is still a vast amount of work to be done in understanding the properties of real binary systems, both from a theoretical and experimental perspective. Theoretically one of the simplest treatments of cooperative phenomena in binary systems, of arbitrary concentrations with central pairwise interactions, is to use the spin-$\frac{1}{2}$ Ising model in an external field. But even this simple model has no exact solution in three dimensions, and one must resort to approximation techniques.[2] If one attempts to go beyond the Ising model and include the often more realistic effects of a compressible lattice, microdomain structure, or noncentral forces, for instance, then the mathematical complexity becomes increasingly greater. For this reason if we can gain insight into existing theoretical models and techniques and see how, and why, they can be extended to other physical systems, we have hopefully contributed to our understanding of these systems.

The study of the properties of multicomponent alloy systems (particularly ternary and quaternary ones) has been prompted lately by the vast number of new materials with both exotic and technologically useful behavior. As examples one might mention the development of multicomponent alloys which have interesting semiconducting, magnetic, and superconducting properties.[3] We can also look upon a binary or ternary system with vacancies as being a ternary or quaternary system, respectively, in which the vacancies act as the additional component. Of course multicomponent systems exhibit a rich spectrum of critical properties, i.e., multicritical points.[4] It would therefore seem appropriate to attempt to sort out from these systems those properties which depend on the structure, by investigating their order-disorder behavior.

The theoretical study of multicomponent ordering and disordering phenomena has been undertaken by a number of researchers. We might mention in particular the work of Meijering[5] and Hardy and Meijering[6] who exhaustively looked at clustering in three- and four-component regular solutions, respectively, using thermodynamic arguments. Murakami *et al.*[7] used a Bragg-Williams model in order to look at β-phase ternary alloys, and they obtained a result having the same form as that of Meijering in the regular solution limit. De Fontaine,[8] using a free-energy expansion in Fourier space (much in the same spirit as the static concentration wave method[9]), and Tahir-Kheli,[10] using Green's function techniques, have also obtained general results for the ternary system which reduce to Meijering's results in the regular solution limit. General theories of multicomponent alloys have also been given by Badalyan and Khachaturyan[11] and Ryzhkov[12]; again using free-energy expansion techniques.

A different approach to the statistical mechanics of multicomponent alloys using Green's function techniques was undertaken by Tahir-Kheli and Taggart.[13,14] In this method exact formal correlation relations were expanded in the inverse temperature. Following successful techniques used in the study of the binary alloy,[15,16] estimates of the ordering temperature for ternary and quaternary alloys were given. However, these results exhibited anomalous behavior in the interaction potentials and did not agree with the previously calculated estimates of the ordering temperature which were done in the ordered regime (e.g., Ref. 7). Tahir-Kheli[17] has recently developed a technique for resolving these problems associated with calculating the transition temperature in the disordered regime and has applied it to the particular case of the ternary alloy.

In Sec. II we review the methodology of obtaining the transition temperature for the binary alloy in the mean-field approximation. This will hopefully lay the physical foundation for extending the technique to multicomponent systems. In Sec. III we formulate the problem of a quarternary alloy, and then present the correlation functions required to investigate the transition region. We then present in Sec. IV, using the language of classical fluctuation theory, the procedure suggested by Tahir-Kheli and thereby give justification for his assumptions. We then look at the critical condition for multicomponent systems and in Sec. V actually derive, by way of example, the equation for the transition temperature for a quarternary alloy. We find that, in the regular solution limit, we regain the results of Hardy and Meijering. In Sec. VI we discuss the implications of the method and the results, and indicate possible extensions of the technique.

II. BINARY SYSTEM

Before we explicitly consider multicomponent systems, and quaternary alloys in particular, let us review some salient features in the treatment of binary alloys. Here as in multicomponent systems the relevant experimental parameter is the kinematical x-ray (or neutron) scattering intensity.[1,18] In the disordered regime, in which we are primarily interested, this would be the diffuse scattering intensity, which in the absence of size effects is given by (in appropriately normalized units)

$$I^{AB}(\vec{k}) = \sum_{\vec{g}-\vec{p}} \alpha^{AB}(gp) e^{-i\vec{k}\cdot(\vec{g}-\vec{p})}, \tag{2.1}$$

where $\alpha^{AB}(gp)$ is the Warren-Cowley short-range-order (SRO) parameter (defined below).

From a theoretical viewpoint the binary alloy of arbitrary concentration with pairwise interactions on a rigid lattice is isomorphic to the spin-$\frac{1}{2}$ Ising model in an external field.[15] As such we can use the magnetic language of the Ising model to describe the binary alloy. We could also choose from a number of other two-state representations.[19] For our purposes here the occupation operator representation is particularly convenient, and we thus define operators σ_g^ν such that

$$\sigma_g^\nu = \begin{cases} +1, & \text{if a } \nu \text{ atom is on site } g \\ 0, & \text{otherwise.} \end{cases} \tag{2.2}$$

In terms of spin-$\frac{1}{2}$ Ising variables ($S_g^z = \pm\frac{1}{2}$; $\hbar = 1$) we can write

$$\sigma_g^A = \tfrac{1}{2} + S_g^z, \quad \sigma_g^B = \tfrac{1}{2} - S_g^z. \tag{2.3}$$

The Warren-Cowley SRO parameter $\alpha^{AB}(gp)$ used in (2.1) can now be defined in terms of the spin or occupation operators, and ($g \neq p$)

$$\begin{aligned} m_A m_B \alpha^{AB}(gp) &= m_A m_B - \langle \sigma_g^A \sigma_p^B \rangle \\ &= \langle S_g^z S_p^z \rangle - \langle S_g^z \rangle^2 . \end{aligned} \tag{2.4}$$

In the above the relative concentration of ν atoms is given by $m_\nu = \langle \sigma_g^\nu \rangle$ and $\langle \;\rangle$ represents the thermal average. As usual we assume that all sites are occupied, i.e., $\sigma_g^A + \sigma_g^B = 1$; $m_A + m_B = 1$. From (2.4) we see that the SRO parameter equals zero in the completely random case ($\langle \sigma_g^A \sigma_p^B \rangle = \langle \sigma_g^A \rangle \langle \sigma_p^B \rangle$), and is positive or negative depending on whether the system tends to cluster or order, respectively. Since we do not allow multiple occupancy of sites we also have the sum rule from (2.4),

$$\alpha^{AB}(gg) = 1 . \tag{2.5}$$

By introducing the Fourier transforms for an arbitrary translationally invariant function $A(gp)$, i.e.,

$$A(\vec{k}) = \sum_{\vec{g}-\vec{p}} A(gp) e^{-i\vec{k}\cdot(\vec{g}-\vec{p})}, \tag{2.6a}$$

$$A(gp) = \frac{1}{N} \sum_{\vec{k}} A(\vec{k}) e^{i\vec{k}\cdot(\vec{g}-\vec{p})}, \tag{2.6b}$$

we see that (2.1) gives for the scattering intensity,

$$I^{AB}(\vec{k}) = \alpha^{AB}(\vec{k}) . \tag{2.7}$$

Likewise we see from (2.4) that the scattering intensity is proportional to either the spin-spin correlation function or the site-site correlation function in Fourier space.

If the binary alloy is initially in a disordered state, $T \gg T_c$, where T_c is the transition temperature for ordering or clustering, and we lower the temperature of the system, we find that $I^{AB}(\vec{k})$ diverges as $T \to T_c$ and $\vec{k} \to \vec{k}_c$. The wave vector $\vec{k}_c$ describes the state of spatial ordering at which the maximum T_c occurs. Now according to classical fluctuation theory[20] the Fourier-transformed SRO parameter, or scattering intensity, is related to the (Gibbs) free energy of the system by

$$m_A m_B \, \alpha^{AB}(\vec{k}) = k_B T \left(\frac{\partial^2 G(\vec{k})}{\partial m_A^2} \right)^{-1} . \tag{2.8}$$

Thus as $T \to T_c$ and $\vec{k} \to \vec{k}_c$ the divergence of $\alpha^{AB}(\vec{k})$, or $I^{AB}(\vec{k})$, is equivalent to

$$\left.\frac{\partial^2 G(\vec{k})}{\partial m_A^2}\right|_{\substack{T\to T_c\\ \vec{k}\to\vec{k}_c}} = 0 \ . \tag{2.9}$$

As has recently been pointed out[21] we see that we can obtain information about the system thermodynamics by studying the scattering intensity (and vice versa). Condition (2.9) is, of course, nothing more than the equation for the spinodal curve in a binary system.[22] In magnetic jargon this curve would be the stability curve.[23]

If we had expanded the free energy in a Taylor expansion in Fourier space, and then looked at the conditions for a phase transition (the Landau theory[24]) we would have arrived at (2.9). This is basically the approach of DeFontaine[8] and the spirit of the method of static concentration waves of Krivoglaz[25] and Khachaturyan.[19] Thus the emphasis would be on finding singularities in (2.9) and hence the critical properties of the system, but from the ordered regime. In the correlation-function approach the emphasis is on the scattering intensity itself, i.e., the left-hand side of (2.8), not the right-hand side.

For the sake of illustration consider a binary regular solution. The free energy is defined in this case as

$$G(0) = m_A(1-m_A)W^{AB}(0) + k_B T\,[m_A \ln m_A + (1-m_A)\ln(1-m_A)] , \tag{2.10}$$

where $W^{AB}(0)$ is a measure of the nearest-neighbor ordering energy. According to (2.8) the scattering intensity is given by

$$\alpha^{AB}(0) = \left(1 - \frac{2m_A m_B W^{AB}(0)}{k_B T}\right)^{-1} \ . \tag{2.11}$$

The critical condition on the scattering intensity is that

$$\alpha^{AB}(0) \to \infty \quad \text{as } T \to T_c \tag{2.12a}$$

or

$$k_B T_c = 2m_A m_B W^{AB}(0) \ . \tag{2.12b}$$

This is the usual regular solution result for phase separation.

An approach to disordered binary alloys emphasizing the correlation function was undertaken by Clapp and Moss[26] (see Ref. 26 for references to earlier work). In their method the correlation function $\alpha^{AB}(\vec{k})$ was calculated directly using the method of moments to the leading order in β ($\beta^{-1} = k_B T$). This gave $\alpha^{AB}(\vec{k})$ in a form similar to (2.11) and thus the critical properties of the system could readily be determined. Tahir-Kheli[15] using high-temperature expansion techniques based on an exact correlation-function identity was able to calculate $\alpha^{AB}(\vec{k})$ to $O(\beta^3)$, and hence obtain better estimates for the critical properties of the system. However, Tahir-Kheli's technique requires that an appropriate series inversions be performed in order that the scattering intensity can be put in the Clapp-Moss form, i.e.,

$$\alpha^{AB}(\vec{k}) = \Delta / [1 - \beta W^{AB}(\vec{k})\delta(\beta)] \ , \tag{2.13}$$

where Δ is determined such that the sum rule (2.5) is obeyed and $\delta(\beta)$ is a function of the interactions, concentrations, and temperature. In Tahir-Kheli's calculation the denominator of (2.13) would lead to a cubic equation for the critical temperature, where the Clapp-Moss result is a linear equation in temperature.

The Clapp-Moss work is accurate to $O(\beta)$, and as such is essentially a mean-field theory. Thus we should be somewhat hesitant about using their results near the transition point, and would anticipate that Tahir-Kheli's cubic results would be more accurate closer to T_c. In real systems it seems that in many cases the linear approximation is adequate near T_c,[27] while in others it is not.[16,28] This seems to depend on what physical property one is trying to calculate, and probably says more about the inadequacy of the Ising model in describing real systems. The method of Tahir-Kheli, however, lends itself very nicely to extensions to higher orders in β,[29] and also to modifying the system Hamiltonian to include other, more realistic, effects, i.e., many-body interactions.[30]

Thus we have seen that there are two equivalent, and complementary, ways of looking at the critical behavior of the binary system based upon (2.8). First, in the spirit of static concentration waves and the Landau theory of phase transitions, we could expand the free energy in a Taylor expansion in Fourier space, and then use (2.9) to determine the critical properties of the systems. Or, we could obtain the correlation function directly and look at its critical properties via (2.13).

It is this second method which we wish to emphasize here, using the techniques proposed by Tahir-Kheli. Using this method it is straightforward, though tedious, to go to higher orders in β in the $\alpha^{AB}(\vec{k})$ expansion. The method can give general results which are of arbitrary concentration, have arbitrary interaction strength and range, and can easily be modified to include many-body interactions (which may arise from size-effect considerations[31] for instance). As opposed to Bragg-Williams type calculations, and like the static concentration wave method, no restrictions are placed on the existence of certain types of lattices, except for general translational invariance. Once we have calculated $\alpha^{AB}(\vec{k})$ to whatever order in β is necessary, then a series inversion is performed to bring the scattering intensity into the Clapp-Moss form, (2.13).

It is this philosophy which we want to use in looking at the transition region of multicomponent systems; particularly quaternary alloys. However, in order to study the critical properties we see from the above analysis that we must first obtain the relevant correlation functions. This we will do in the next section for the quaternary alloy.

III. QUATERNARY CORRELATION FUNCTIONS

The relevant two-site correlation functions for the disordered quaternary alloy have been calculated previously[14] to the leading order in β, i.e., the mean-field result. The interested reader is referred to this paper for details. For the sake of completeness, however, we will present the salient features here.

The system which we wish to consider is a four-component alloy on a rigid lattice of N sites such that each site is occupied by an A, B, C, or D type atom ($N_A+N_B+N_C+N_D=N$). The configurational energy is assumed to be represented by pairwise interactions, i.e.,

$$H=H^{AA}+H^{BB}+H^{CC}+H^{DD}+H^{AB}+H^{AC}+H^{AD}$$

$$+H^{BC}+H^{BD}+H^{CD}, \tag{3.1a}$$

where

$$H^{\nu\nu}=\frac{1}{2}\sum_{g,p} V^{\nu\nu}(gp)\sigma_g^\nu\sigma_p^\nu , \tag{3.1b}$$

$$H^{\nu\rho}=\frac{1}{2}\sum_{g,p} V^{\nu\rho}(gp)(\sigma_g^\nu\sigma_p^\rho+\sigma_p^\nu\sigma_g^\rho), \tag{3.1c}$$

and

$$V^{\nu\rho}(gp)=V^{\rho\nu}(gp)=V^{\rho\nu}(pg)=V^{\nu\rho}(pg) , \tag{3.1d}$$

$$V^{\nu\nu}(gg)=V^{\nu\rho}(gg)=0.$$

As in (2.2) we have defined appropriate occupation operations σ_g^ν in (3.1). We could also use Ising spins [in this case a four-state spin-$\frac{3}{2}$ spin space spanned by the operators S_g^z, $(S_g^z)^2$, $(S_g^z)^3$] which can be written in terms of the occupation operators as,

$$S_g^z=-\tfrac{3}{2}\sigma_g^A-\tfrac{1}{2}\sigma_g^B+\tfrac{1}{2}\sigma_g^C+\tfrac{3}{2}\sigma_g^D, \tag{3.2a}$$

$$(S_g^z)^2=\tfrac{9}{4}\sigma_g^A+\tfrac{1}{4}\sigma_g^B+\tfrac{1}{4}\sigma_g^C+\tfrac{9}{4}\sigma_g^D , \tag{3.2b}$$

$$(S_g^z)^3=-\tfrac{27}{8}\sigma_g^A-\tfrac{1}{8}\sigma_g^B+\tfrac{1}{8}\sigma_g^C+\tfrac{27}{8}\sigma_g^D . \tag{3.2c}$$

The various ordering energies are given by

$$W^{\nu\rho}(gp)=V^{\nu\rho}(gp)-\tfrac{1}{2}[V^{\nu\nu}(gp)+V^{\rho\rho}(gp)] \tag{3.3}$$

and the concentrations are

$$m_\nu=N_\nu/N=\langle\sigma_g^\nu\rangle , \tag{3.4}$$

$$\sum_\gamma m_\gamma=\sum_\gamma\sigma_g^\nu=1 . \tag{3.5}$$

The exact formal relationships for the correlation functions can be generated using Green's function techniques. The actual derivation is somewhat lengthy for the quaternary system and we refer the reader to Ref. 14. The resultant correlation identities can be expanded to arbitrary order in β. The two-site correlation functions necessary for our purpose here [to $O(\beta)$] are

$$\langle\sigma_g^A\sigma_p^A\rangle = m_A^2+\delta_{gp}m_A(1-m_A)-\beta m_A^2\Gamma^{AA}(gp) , \tag{3.6a}$$

$$\Gamma^{AA}(gp)=W^{AB}(gp)2m_B(m_A-1)+W^{AC}(gp)2m_C(m_A-1)$$

$$+W^{AD}(gp)2m_D(m_A-1)+W^{BC}(gp)2m_Bm_C$$

$$+W^{BD}(gp)2m_Bm_D+W^{CD}(gp)2m_Cm_D , \tag{3.6b}$$

and

$$\langle\sigma_g^A\sigma_p^B\rangle=m_Am_B-\delta_{gp}m_Am_B-\beta m_Am_B\Gamma^{AB}(gp) \tag{3.7a}$$

$$\Gamma^{AB}(gp)=W^{AB}(gp)(2m_Am_B+m_C+m_D)+W^{AC}(gp)m_C(2m_A-1)+W^{AD}(gp)m_D(2m_A-1)+W^{BC}(gp)m_C(2m_B-1)$$

$$+W^{BD}(gp)m_D(2m_B-1)+W^{CD}(gp)2m_Cm_D. \tag{3.7b}$$

Since these correlation functions have been calculated in the grand canonical ensemble, we can obtain the remaining correlation functions by interchange of the labels A, B, C, D.

Now the SRO parameters are related to the site-site correlation functions by the generalization of (2.4), i.e.,

$$m_\nu m_\rho \alpha^{\nu\rho}(gp) = m_\nu m_\rho - \langle\sigma_g^\nu \sigma_p^\rho\rangle \,, \tag{3.8a}$$

and,

$$m_\nu(1-m_\nu)\alpha^{\nu\nu}(gp) = \langle\sigma_g^\nu \sigma_p^\nu\rangle - m_\nu^2 \,. \tag{3.8b}$$

Thus we can readily obtain the various SRO parameters, correct to $O(\beta)$, from the results of (3.6) and (3.7).

In order to illustrate the methods discussed in Sec. II, let us use $\alpha^{AB}(gp)$ to determine the critical temperature associated with AB ordering, or clustering. Fourier transform $\alpha^{AB}(gp)$ defined above to get

$$\alpha^{AB}(\vec{k}) = 1 + \beta\Gamma^{AB}(\vec{k}) + O(\beta^2) \,. \tag{3.9}$$

In the spirit of the Clapp-Moss approximation we write (3.9) as

$$\alpha^{AB}(\vec{k}) = \Delta(AB)/[1-\beta\Gamma^{AB}(\vec{k})] \tag{3.10}$$

and $\Delta(AB)$ is determined, as in (2.5), such that the sum rule,

$$\alpha^{AB}(gg) = \frac{1}{N}\sum_{\vec{k}} \alpha^{AB}(\vec{k}) = 1, \tag{3.11}$$

is satisfied. To the first order in β, the mean-field result, this series inversion is exact.

As in the binary system the singularities in (3.10) should give us the critical behavior. In this case we get

$$1 - \beta_c \Gamma^{AB}(\vec{k}_c) = 0 \,, \tag{3.12a}$$

or

$$\begin{aligned}(k_B T_c)^{AB} &= \Gamma^{AB}(\vec{k}_c)\\ &= W^{AB}(\vec{k}_c)(2m_A m_B + m_C + m_D)\\ &\quad + W^{AC}(\vec{k}_c) m_C (2m_A - 1) + W^{AD}(\vec{k}_c) m_D (2m_A - 1)\\ &\quad + W^{BC}(\vec{k}_c) m_C (2m_B - 1) + W^{BD}(\vec{k}_c) m_D (2m_B - 1)\\ &\quad + W^{CD}(\vec{k}_c) 2 m_C m_D .\end{aligned} \tag{3.12b}$$

The spirit in which we write this expression for the transition temperature is that once we have calculated all of the transition temperatures $(k_B T_c)^{\nu\rho}$, we then sweep through the wave vectors $\vec{k}_c$ in order to determine the maximum $(k_B T_c)^{\nu\rho}$, which should be the transition temperature for that particular set of interactions and concentrations. We should note by the way, that as m_c, $m_D \to 0$, and $\vec{k}_c \to (0,0,0)$, we get the transition temperature for clustering in a binary regular solution, i.e., (2.12).

However, we should realize that in multicomponent solutions the number of independent SRO parameters is greater than the one $[\alpha^{AB}(\vec{k}_c)]$ needed in the binary system, and that these parameters are interconnected in a nontrivial way.[33] As such we have to be much more careful in estimating the transition temperature for these systems. This is particularly apparent when we note that (3.12b), even though reducing to the correct binary result, has anomalous behavior when either m_A or m_B approaches $\frac{1}{2}$. We see that in these cases the transition temperature no longer depends on some of the interactions. We thus have to look more closely at the interplay between the various scattering intensities, and determine what is wrong, and right, with (3.12b). It was this type of anomalous behavior in the ternary system which prompted Tahir-Kheli[17] to propose a new method of determining the transition temperature.

IV. MULTICOMPONENT DISORDERED ALLOYS

So far we have seen in Sec. II that for the binary alloy the correlation function approach gives us the same result as that of a free-energy expansion, and that using a self-consistent series expansion for the correlation function one can readily go beyond the mean-field, or $O(\beta)$, result. However, the simple estimate of β_c^{-1}, given for instance by (3.12b), for the quaternary alloy has anomalous concentration behavior, and one must be suspect of the interpretation of the results generated. Prompted by similar problems with the ternary alloy Tahir-Kheli[17] has recently proposed a different method for obtaining the transition temperature of multicomponent systems.

As mentioned in Sec. I, for the ternary alloy there are a number of Bragg-Williams type calculations giving the ordering temperature for these systems. Tahir-Kheli,[13] using comparable methods to those outlined here for the binary and quaternary systems, obtained an estimate for the critical temperature for the ternary alloy which also had anomalous behavior at certain concentrations, similar to that exhibited by (3.12b). In order to see if this anomalous behavior was unique to the first-order expansion in β, Taggart and Tahir-Kheli[32] extended the correlation-function expansion to $O(\beta^3)$. Analysis of the transition region using this higher-order series showed that indeed the anomalous behavior was removed. However, it still didn't explain the problem with the linear approximation, and one still had to be somewhat suspect of the transition temperature so derived.

To overcome these problems with the ternary and other multicomponent alloys Tahir-Kheli proposed that instead of looking at singularities in the individual scattering intensities (SRO parameters), one should instead look for singularities in the magnitude of the scattering matrix. If one does this for the ternary alloy, the results for the transition temperature agree with those calculated previously (i.e., Ref. 7). Likewise, as we shall see, the results for the quaternary system also turn out to be consistent with those previously calculated. This is very appealing since now we find that treatments of multicomponent systems in both the ordered and disordered regimes agree in the transition region.

Basically what Tahir-Kheli proposed is that we should consider the scattering matrix, $\underline{C}(\vec{k})$ (the underline indicates a matrix), whose elements are the correlation functions. In the spin variables this means that we look at the behavior of the matrix formed from the elements,

$$\{C(\vec{k})\}_{lm}=\{\langle(S_g^z)^l(S_p^z)^m\rangle-\langle(S_g^z)^l\rangle\langle(S_p^z)^m\rangle\}_{(\vec{k})}\,, \tag{4.1}$$

where the subscript $(\vec{k})$ indicates the Fourier-transformed correlation function. For the binary alloy $(S=\frac{1}{2})$ the scattering matrix reduces to the one element $\{\langle S_g^z S_p^z\rangle-\langle S_g^z\rangle^2\}_{(\vec{k})}$ or $(\alpha^{AB}(\vec{k})$, or $\langle\sigma_g^A\sigma_p^B\rangle_{(\vec{k})})$ and we retrieve the results of Sec. II, since the singularity in any of these correlation functions should give the same critical behavior.

However, when we go to multicomponent systems we must retain the matrix representation. Thus for the ternary system, for instance, we must look at

$$\underline{C}(\vec{k})=\begin{pmatrix}\{\langle S_g^z S_p^z\rangle-\langle S_g^z\rangle^2\}_{(\vec{k})} & \{\langle S_g^z(S_p^z)^2\rangle-\langle S_g^z\rangle\langle(S_p^z)^2\rangle\}_{(\vec{k})}\\ \{\langle(S_g^z)^2S_p^z\rangle-\langle(S_g^z)^2\rangle\langle S_p^z\rangle\}_{(\vec{k})} & \{\langle(S_g^z)^2(S_p^z)^2\rangle-\langle(S_g^z)^2\rangle^2\}_{(\vec{k})}\end{pmatrix}\,, \tag{4.2}$$

with comparable expressions for the matrices made up of $\alpha^{\nu\rho}(\vec{k})$ and $\langle\sigma_g^\nu\sigma_p^\rho\rangle_{(\vec{k})}$. We note for this case that due to the symmetry of the correlation matrix we have at most three independent correlation functions, or scattering intensities. Since we can calculate the elements of $\underline{C}(\vec{k})$ to various orders in β, say $O(\beta)$, we can write

$$\underline{C}(\vec{k})=\underline{C}_0(\vec{k})+\beta\underline{C}_1(\vec{k})+O(\beta^2), \tag{4.3}$$

or

$$\underline{C}(\vec{k})=\underline{C}_0(\vec{k})[\underline{1}+\beta\underline{\Gamma}_1(\vec{k})], \tag{4.4}$$

where $\underline{1}$ is the unit matrix and

$$\underline{\Gamma}_1(\vec{k})=\underline{C}_0(\vec{k})^{-1}\underline{C}_1(\vec{k})\,. \tag{4.5}$$

Now in the spirit of the Clapp-Moss approximation, we can invert (4.4), i.e.,

$$\underline{C}(\vec{k})\simeq\underline{\Delta}[\underline{1}-\beta\underline{\Gamma}_1(\vec{k})]^{-1}\,, \tag{4.6}$$

where $\underline{\Delta}$ is determined such that the sum rule,

$$\frac{1}{N}\sum_{\vec{k}}\underline{C}(\vec{k})=\underline{C}_0(\vec{k}) \tag{4.7}$$

is obeyed. $\underline{C}_0(\vec{k})$ is the infinite temperature (random) value of $\underline{C}(\vec{k})$, and (4.7) insures that the total scattering intensity is conserved. The critical condition applies when the magnitude of the scattering intensity diverges, or

$$|\underline{C}(\vec{k})|_{\substack{T\to T_c\\ \vec{k}\to\vec{k}_c}}\to\infty\,, \tag{4.8}$$

which from (4.6) is equivalent to

$$|\underline{\Delta}|\,/\,|\underline{1}-\beta\underline{\Gamma}_1(\vec{k})|\to\infty. \tag{4.9}$$

Since $|\underline{\Delta}|$ is assumed finite at all temperatures we get for the critical condition, in analogy to (3.12a).

$$|\underline{1} - \beta_c \underline{\Gamma}_1(\vec{k}_c)| = 0 \,. \tag{4.10}$$

This is the essence of Tahir-Kheli's recent work and an obvious extension of the inversion procedure discussed in Sec. III. Using this formalism Tahir-Kheli was able to obtain the results of Murakami *et al.*,[17] De Fontaine,[8] and others for the ternary alloy using an expansion to $O(\beta)$, but working with correlation functions and in the disordered regime.

Now recall (2.8), i.e., the relationship between the scattering intensity and the free energy derived from classical fluctuation theory. If we generalize this expression for multicomponent systems we immediately see the justification for working with the correlation matrix. This generalization is

$$m_\nu m_\rho \alpha^{\nu\rho}(\vec{k}) = k_B T \left(\frac{\partial^2 G(\vec{k})}{\partial m_\nu \partial m_\rho} \right)^{-1} \,, \tag{4.11}$$

where for an n-component system $\alpha^{\nu\rho}(\vec{k})$ and $\partial^2 G(\vec{k})/\partial m_\nu \partial m_\rho$ are elements of an $(n-1)$-rank matrix. Since we are interested in the magnitude of the scattering matrix, i.e., the scattering intensity, we can rewrite (4.11) as

$$|m_\nu m_\rho \alpha^{\nu\rho}(\vec{k})| = k_B T \left(\left| \frac{\partial^2 G(\vec{k})}{\partial m_\nu \partial m_\rho} \right| \right)^{-1} \,. \tag{4.12}$$

In other words the divergence in the scattering intensity,

$$|m_\nu m_\rho \alpha^{\nu\rho}(\vec{k})| \underset{\vec{k} \to \vec{k}_c}{\underset{T \to T_c}{}} \to \infty \,, \tag{4.13}$$

as proposed by Tahir-Kheli, is equivalent to the vanishing of the determinant of the free-energy second derivatives, i.e.,

$$\left| \frac{\partial^2 G(\vec{k})}{\partial m_\nu \partial m_\rho} \right|_{\substack{T \to T_c \\ \vec{k} \to \vec{k}_c}} \to 0 \,. \tag{4.14}$$

In the classical Gibbs sense, (4.14) is the equation for a spinodal surface for an n-component system. Both ternary and quaternary regular solutions have been studied in detail[5,6] using (4.14), and the results from these studies of the transition region agree with Tahir-Kheli's ternary result and the quaternary result calculated here.

We will now use (4.13) to obtain the transition temperature for a quaternary system using Tahir-Kheli's method. This will serve as an illustration of the technique, as well as to giving the transition temperature for a quaternary solution. In Sec. VI we will discuss the method in more detail.

V. QUATERNARY CRITICAL CONDITION

Using the correlation functions given by (3.6) and (3.7) we can construct the scattering matrix from the individual scattering intensities. We thus obtain

$$\underline{C}(\vec{k}) = \begin{pmatrix} m_A(1-m_A)\alpha^{AA}(\vec{k}) & -m_A m_B \alpha^{AB}(\vec{k}) & -m_A m_C \alpha^{AC}(\vec{k}) \\ -m_A m_B \alpha^{AB}(\vec{k}) & m_B(1-m_B)\alpha^{BB}(\vec{k}) & -m_B m_C \alpha^{BC}(\vec{k}) \\ -m_A m_C \alpha^{AC}(\vec{k}) & -m_B m_C \alpha^{BC}(\vec{k}) & m_C(1-m_C)\alpha^{CC}(\vec{k}) \end{pmatrix} , \tag{5.1}$$

where for the quaternary system we see from (4.1) that there are only six independent two-site spin-correlation functions. Thus we only need six independent SRO parameters, or site correlation functions. Any six will do, i.e., we can interchange A, B, C, D in the above correlation matrix and not effect the result, (5.4), for T_C.

Comparing (5.1) and (4.3) we see that in this case

$$\underline{C}_0 = \begin{pmatrix} m_A(1-m_A) & -m_A m_B & -m_A m_C \\ -m_A m_B & m_B(1-m_B) & -m_B m_C \\ -m_A m_C & -m_B m_C & m_C(1-m_C) \end{pmatrix} , \tag{5.2}$$

and

$$\underline{C}_1(\vec{k}) = \begin{pmatrix} -m_A^2\Gamma^{AA}(\vec{k}) & -m_Am_B\Gamma^{AB}(\vec{k}) & -m_Am_C\Gamma^{AC}(\vec{k}) \\ -m_Am_B\Gamma^{AB}(\vec{k}) & -m_B^2\Gamma^{BB}(\vec{k}) & -m_Bm_C\Gamma^{BC}(\vec{k}) \\ -m_Am_C\Gamma^{AC}(\vec{k}) & -m_Bm_C\Gamma^{BC}(\vec{k}) & -m_C^2\Gamma^{CC}(\vec{k}) \end{pmatrix} . \tag{5.3}$$

We can now construct $\underline{\Gamma}_1(\vec{k}) = \underline{C}_0(\vec{k})^{-1}\underline{C}_1(\vec{k})$ and thus evaluate (4.10), which we note is a cubic equation. After some straightforward, but very tedious algebra, we arrive at the equation for the transition temperature,

$$\beta_c^{-3} - 2\beta_c^{-2}\,\Xi_2(\vec{k}_c) - \beta_C^{-1}\,\Xi_1(\vec{k}_c) - \Xi_0(\vec{k}_c) = 0 . \tag{5.4}$$

Here we have used the notation

$$\Xi_2(\vec{k}) = m_Am_BW^{AB}(\vec{k}) + m_Am_CW^{AC}(\vec{k}) + m_Am_DW^{AD}(\vec{k}) + m_Bm_CW^{BC}(\vec{k}) + m_Bm_DW^{BD}(\vec{k}) + m_Cm_DW^{CD}(\vec{k}) , \tag{5.5a}$$

$$\begin{aligned} \Xi_1(\vec{k}) = {} & m_Am_Bm_C\{[W^{AB}(\vec{k}) + W^{AC}(\vec{k}) + W^{BC}(\vec{k})]^2 - 4W^{AB}(\vec{k})W^{BC}(\vec{k}) - 4W^{AB}(\vec{k})W^{AC}(\vec{k}) - 4W^{AC}(\vec{k})W^{BC}(\vec{k})\} \\ & + m_Am_Bm_D\{[W^{AB}(\vec{k}) + W^{AD}(\vec{k}) + W^{BD}(\vec{k})]^2 - 4W^{AB}(\vec{k})W^{AD}(\vec{k}) - 4W^{AB}(\vec{k})W^{BD}(\vec{k}) - 4W^{AD}(\vec{k})W^{BD}(\vec{k})\} \\ & + m_Am_Cm_D\{[W^{AC}(\vec{k}) + W^{AD}(\vec{k}) + W^{CD}(\vec{k})]^2 - 4W^{AC}(\vec{k})W^{AD}(\vec{k}) - 4^{AC}(\vec{k})W^{CD}(\vec{k}) - 4W^{AD}(\vec{k})W^{CD}(\vec{k})\} \\ & + m_Bm_Cm_D\{[W^{BC}(\vec{k}) + W^{BD}(\vec{k}) + W^{CD}(\vec{k})]^2 - 4W^{BC}(\vec{k})W^{BD}(\vec{k}) - 4W^{BC}(\vec{k})W^{CD}(\vec{k}) - 4W^{BD}(\vec{k})W^{CD}(\vec{k})\} , \end{aligned} \tag{5.5b}$$

and

$$\begin{aligned} \Xi_0(\vec{k}) = 2m_Am_Bm_Cm_D\{ & W^{AB}(\vec{k})W^{CD}(\vec{k})[-W^{AB}(\vec{k}) + W^{AC}(\vec{k}) + W^{AD}(\vec{k}) + W^{BC}(\vec{k}) + W^{BD}(\vec{k}) - W^{CD}(\vec{k})] \\ & + W^{AC}(\vec{k})W^{BD}(\vec{k})[W^{AB}(\vec{k}) - W^{AC}(\vec{k}) + W^{AD}(\vec{k}) + W^{BC}(\vec{k}) - W^{BD}(\vec{k}) + W^{CD}(\vec{k}) \\ & + W^{AD}(\vec{k})W^{BC}(\vec{k})[W^{AB}(\vec{k}) + W^{AC}(\vec{k}) - W^{AD}(\vec{k}) - W^{BC}(\vec{k}) + W^{BD}(\vec{k}) + W^{CD}(\vec{k})] \\ & - W^{AB}(\vec{k})W^{AC}(\vec{k})W^{BC}(\vec{k}) - W^{AB}(\vec{k})W^{AD}(\vec{k})W^{BD}(\vec{k}) - W^{BC}(\vec{k})W^{BD}(\vec{k})W^{CD}(\vec{k}) \\ & - W^{AC}(\vec{k})W^{AD}(\vec{k})W^{CD}(\vec{k})\} . \end{aligned} \tag{5.5c}$$

In the limit that $\vec{k}_c \to 0$, we retrieve the results of Hardy and Meijering,[6] who have exhaustively studied the behavior of clustering in this type of system in the regular solution limit. We should note that (5.4) is valid for arbitrary wave vector $\vec{k}_c$, and should apply to other spatial structures. Since Hardy and Meijering have done such a thorough analysis of (5.4) for clustering in the regular solution limit, we refer the reader to their paper in order to understand the basic behavior of phase transitions governed by (5.4). We will discuss some of the transition behavior derived from (5.4) as it pertains to the general method of the correlation-function approach to multicomponent systems. This will be done in Sec. VI. It should perhaps be emphasized again that (5.4) was derived via (4.13), i.e., the singularity in the magnitude of the scattering matrix, whereas Hardy and Meijering used (4.14).

VI. DISCUSSION

The major results derived here are as follows: (i) The transition temperature for multicomponent systems can be calculated in the disordered regime, by using correlation functions and the correlation matrix inversion technique of Tahir-Kheli, giving results consistent with calculations in the ordered regime using other techniques; (ii) Tahir-Kheli's correlation matrix inversion technique is seen to be equivalent to using classical fluctuation theory, i.e., (4.12), and is thereby justified. Contact is thus made between the correlation-function approach to disordered multicomponent alloys and the free-energy expansion methods in the ordered regime; (iii) we have derived the generalization of Hardy and Meijering's result for the transition temperature of quaternary systems.

It is obvious from (4.1) that for an n-component system we have $\frac{1}{2}n(n-1)$ independent correlation functions, and hence $\frac{1}{2}n(n-1)$ independent SRO parameters, or scattering intensities.[33] Likewise we see that an n-component alloy leads to evaluating an $(n-1)$-dimensional determinant formed by these correlation functions. If we work in the mean-field approximation, i.e., correlation functions expanded to order β, then we will obtain an $(n-1)$th order equation in β for our critical condition (4.10). Thus, in the mean-field approximation, a five-component alloy leads to a quartic equation for T_c. If we calculate the correlation functions to higher orders in β, we obtain higher equations in β, and, in principle, more accurate information closer to T_c.[34]

In reference to the use of the fluctuation relation (4.11), we now see, as was pointed out for binary systems,[21] that by measuring $\alpha^{\nu p}(\vec{k})$ we can obtain thermodynamic information via $G(\vec{k})$. In addition we also see, via the fluctuation relation, that the linear series inversion of (3.10) does have physical justification under the proper circumstances, in spite of anomalous behavior as a function of concentration. In fact this anomalous concentration behavior gives us a clue to the justification.

The argument goes somewhat as follows in the mean-field approximation. For the quaternary system the free energy can be written as a function of the three variables m_A, m_B, and m_C, since $m_D = 1 - m_A - m_B - m_C$. The thermodynamic space is then four-dimensional with coordinates $(G(\vec{k}), m_A, m_B, m_C)$. The critical condition (5.4) defines the spinodal surface in this space. This is a cubic equation in T_c and is applicable for arbitrary concentrations. We call this quaternary ordering since it is governed by a cubic equation in the mean-field approximation.

Now if the concentration of the system is such that $m_A \neq m_B \neq m_C = m_D$ then the free energy is a function of two variables, say m_A and m_B, since $m_C = \frac{1}{2}(1 - m_A - m_B)$. We call this a pseudoternary alloy since we get a quadratic equation in T_c. Likewise we can generate a pseudobinary alloy by expressing the free energy as a function of one variable, in which case we get a linear equation in T_c. This last case can occur in three possible ways: (a) $m_A = m_B = m_C = m_D$; (b) $m_A = m_B \neq m_C = m_D$; (c) $m_A = m_B = m_C \neq m_D$.

In recalling the linear expression for T_c obtained in (3.12b), i.e.,

$$\begin{aligned}(k_B T_c)^{AB} = {} & W^{AB}(\vec{k}_c)(2m_A m_B + m_C + m_D) \\ & + W^{AC}(\vec{k}_c) m_C (2m_A - 1) + W^{AD}(\vec{k}_c) m_D (2m_A - 1) \\ & + W^{BC}(\vec{k}_c) m (2m_B - 1) + W^{BD}(\vec{k}_c) m_D (2m_B - 1) \\ & + W^{CD}(\vec{k}_c) 2 m_C m_D \ ,\end{aligned}$$

with the other critical temperatures given by permutation of A, B, C, and D, we see from the above that this does describe a pseudobinary four-component system if conditions (a)–(c) hold. Condition (a) and (b) require that $m_\nu \neq \frac{1}{2}$, whereas in (c) we could have $m_D = \frac{1}{2}$, say, and $m_A = m_B = m_C = \frac{1}{6}$. Thus the linear expression for T_c should be valid under the proper circumstances. These solutions, of course, are contained in the more general equation (5.4).

For the ternary alloy[13,17] in the mean-field approximation we would have a quadratic equation for ternary ordering since the free energy requires two concentrations, say m_A and m_B, where $m_C = 1 - m_A - m_B$. There are two possibilities for linear equations in T_c, i.e., pseudobinary ordering. These occur when (a) $m_A = m_B = m_C$, and (b) $m_A = m_B \neq m_C$. Condition (a) precludes the concentration $m_\nu = \frac{1}{2}$, while in (b) m_C could equal $\frac{1}{2}$ with $m_A = m_B = \frac{1}{4}$. Thus in this case also the linear approximation is valid so long as we are cognizant of the restrictions (a) and (b).

Finally we should mention that the correlation-function approach to multicomponent systems in the disordered regime is amenable to modification and extension. The correlation functions themselves can be calculated to higher order in β so that improved estimates of T_c can be obtained. Within the present expansions we can include further neighbor effects. The inclusion of many-body interactions is facilitated by the formalism[30] and one can easily see how these interactions influence the system. The study of the growth of SRO and the propagation of SRO is based on knowledge of the time and spatial dependence of correlation functions. Thus the present formalism is particularly suited for studies in these areas.

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