PHYSICAL REVIEW B VOLUME 20, NUMBER 2 15 JULY 1979

# Correlation-function approach to multicomponent systems: Ternary alloys at intermediate temperatures

G. Bruce Taggart*
*Department of Physics, University of Illinois at Urbana-Champaign,*
*Urbana, Illinois 61801*
(Received 20 February 1979)

In this last of three papers dealing with the correlation-function approach (CFA) to multicomponent alloys we look at the first-order approximation beyond the mean-field approximation (MFA) for ternary alloys. We first discuss the properties of binary phase diagrams (using clustering systems by way of example) in order to understand what information can be obtained from the CFA. We then briefly discuss previous theoretical attempts to go beyond the MFA for binary alloys using CFA-like formalism. Having examined binary alloys we then formulate the problem for ternary alloys, and present the results for the correlation functions for this system. The resulting equation for the transition temperature is a quartic in $T_c$, where $T_c$ is a stability temperature at which the alloy decomposes into separate phases, or assumes an ordered ground state. We look explicitly at the case of a symmetric ternary alloy, $m_A = m_B = \frac{1}{2}(1 - m_C)$ with positive interactions of equal magnitude. We find that the resulting phase diagram can be appreciably changed from the MFA. We then discuss implications of the technique.

## I. INTRODUCTION

In the first in this series of papers[1] we introduced and discussed the correlation-function approach (CFA) to multicomponent systems. In particular we applied the technique to calculating the transition temperature for a quaternary alloy within the mean-field approximation (MFA). The basic ideas of the CFA (to be described in more detail below) are attributable to Tahir-Kheli[2] and have their roots in classical fluctuation theory. In the following paper[3] in the series the CFA was applied to calculating, again within the MFA, the transition temperature for a ternary alloy in which static irreducible three-body potentials are present.

It is our intent here to use the CFA to investigate the behavior of the simplest nontrivial multicomponent system—the ternary alloy—based on first-order corrections beyond the MFA. This should give us some indication of how the system moves away from mean-field behavior, and in addition should also say something about the validity of the CFA when one goes beyond the MFA.

In order to lay the basis for our discussion of ternary alloys, in Sec. II we briefly review the properties of binary phase diagrams, using in particular clustering systems for an example. In Sec. III we discuss the CFA for binary alloys, but with emphasis on approximations which have tried to improve on the MFA. We then review some previous work in ternary and multicomponent alloys in Sec. IV. In Sec. V we formulate the problem for ternary alloys with pairwise interactions and present the results for the correlation functions. The CFA is briefly discussed in Sec. VI and our formal results for the transition temperature are given. Finally in Sec. VII we present results for a symmetric alloy, $m_A = m_B = \frac{1}{2}(1 - m_C)$, in both the MFA and the approximation of this paper. We then discuss the technique.

## II. BINARY PHASE DIAGRAMS

The phase diagrams of interest here are the traditional ones of metallurgy,[4] i.e., composition versus temperature diagrams. The theoretical determination of these phase diagrams has long been an active area in the statistical mechanics of solid solutions.[5] The interest in phase diagrams is prompted, of course, by their great technical utility, as well as by the theoretical challenge of reproducing real diagrams from model systems.

The last few years have seen an upsurge in studying and understanding ordering and clustering solid solutions,[6–8] and consequently the phase diagrams for these systems. This increased activity has been prompted in part by the pioneering work of Hillert, Cahn, and Hillard on spinodal decomposition in binary systems,[6,8,9] and by the great strides made in the past decade in understanding phase transitions and critical phenomena.[10] Naturally there has been overlap between these areas,[11,12] as well as in other systems far from equilibrium.[13] Regardless, the basic problem is to calculate phase diagrams from equilibrium statistical mechanics and use these, if possible, to determine information about ordering, or clustering, kinetics.

A schematic phase diagram, based on a regular solution model, for a binary alloy with a miscibility gap (we use the clustering, or phase separating, system as an example from here on) is shown in Fig. 1(a). Here we can distinguish three regions: (I) stable, (II) metastable, and (III) unstable. These three regions are separated by the miscibility gap,

$$\frac{\partial g}{\partial m_A}=0\,, \qquad (2.1)$$

where $g$ is the free energy per particle and $m_A$ is the concentration of $A$ atoms, and the spinodal,

$$\frac{\partial^2 g}{\partial m_A^2}=0\,. \qquad (2.2)$$

The highest point at which the two curves touch, i.e., Eqs. (2.1) and (2.2) are simultaneously satisfied, defines the critical point.

If the disordered alloy is quenched from the stable region ($T \gg T_c$) into the metastable region, then phase separation takes place by a nucleation and growth process. On the other hand if the quench is into the unstable region then clustering can take place via spinodal decomposition. These ideas are highly simplified and one must be cautious when treating real systems. This is because most real systems do not have symmetric phase diagrams based on the regular solution model [as in Fig. 1(a)], and we must always be careful about extending equilibrium concepts to problems which are intrinsically dynamic.

However for solid solutions we can improve on the regular solution model by including strain-energy effects, as was first pointed out by Cahn.[14] Basically an alloy can phase separate in two different ways[6]: (i) the two regions having different lattice constants can form an incoherent interface between the phases, across which there are lattice discontinuities, or (ii) the lattice constants of the two phases coherently meld together. In this latter case there will be elastic energy in the system, and this will consequently have an effect on the phase diagram.

For isotropic solids the net effect of this elastic energy is to modify the equation of the spinodal by [6]

$$\frac{\partial^2 g}{\partial m_A^2} \rightarrow \frac{\partial^2 g}{\partial m_A^2}+\frac{2\eta^2 E}{1-\nu}\,, \qquad (2.3)$$

where $E$ is Young's modulus, $\nu$ is Poisson's ratio, and for lattice constant $a$,

$$\eta=\frac{1}{a}\,\frac{da}{dm_A}\,. \qquad (2.4)$$

This produces a suppression of the spinodal and the coherent miscibility gap, so that the phase diagram looks somewhat as in Fig. 1(b). We consequently have a incoherent miscibility gap, a coherent miscibility gap, and a coherent spinodal.

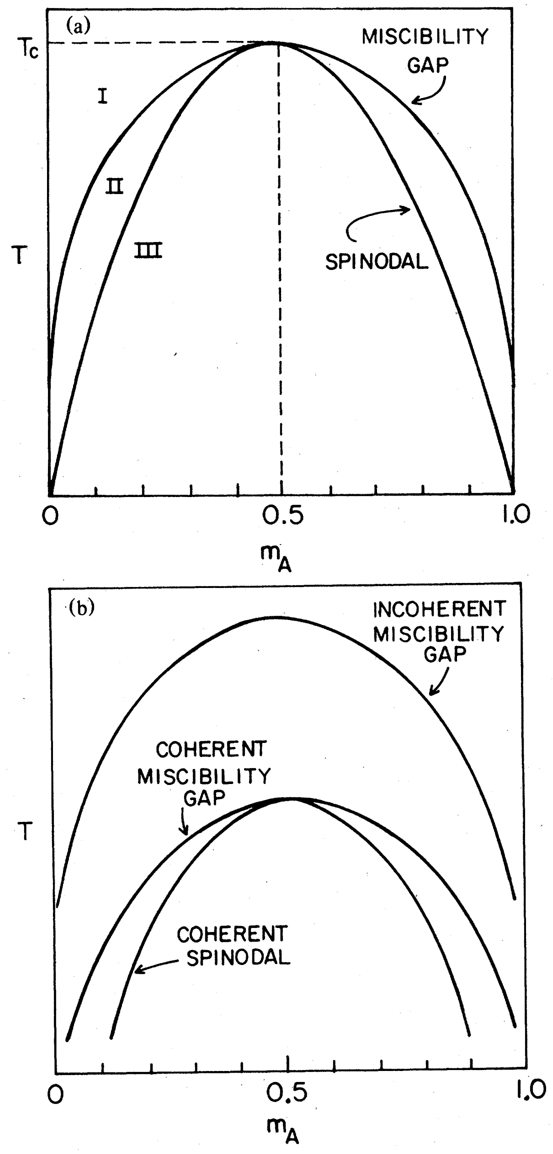

FIG. 1. (a) Schematic phase diagram for a clustering binary alloy showing the spinodal and the miscibility gap. Regions I, II, and III are, respectively, the regions of stability, metastability, and instability. The critical point is defined as the point where the two curves touch. (b) Schematic phase diagram showing the effect of elastic energy in suppressing the miscibility gap.

Thus if one is to study the thermodynamics of even the binary alloy a knowledge of which phase boundary is being measured is crucial.[15–17] This depends of course on the sample, the sample preparation and the type of experiment being done.

Of primary importance is the spinodal curve since it separates the phase diagram into stable and unstable regions. Once the alloy is quenched into the unstable region, how the system decomposes or orders is dependent, among other parameters, on the relative location of the spinodal.[18] In addition as one approaches the phase boundary from either side various pretransition phenomena are expected due to composition fluctuations.[19,20] Again, accurate knowledge of the phase boundary is important for understanding these phenomena.

In Sec. III we will look at various approximations to calculating the transition temperature for binary alloys based on a correlation function approach. We will see that this approach basically leads to knowledge of the incoherent, or chemical spinodal. We note, however, that the coherent spinodal for an isotropic solid solution can readily be obtained from the incoherent spinodal by using the prescription of Eq. (2.3).

## III. CFA FOR BINARY ALLOYS

The CFA[1] is based on determining singularities in the diffuse scattering intensity as the system approaches criticality. Basically, as the temperature of a binary alloy is lowered from the disordered regime ($T >> T_c$) the diffuse scattering intensity $I(\vec{k})$ diverges at some critical wave vector $\vec{k}_c$, and temperature, $T_c$. $I(\vec{k})$ is directly proportional to the Fourier-transform of the Warren-Cowley short-range-order (SRO) parameter[21,22] and subsequently can be related to the interactions between the component species.

For clustering systems the critical wave vector is the long-wavelength one $\vec{k}_c = (0,0,0)$, i.e., the ferromagnetic ground state, while for ordering systems $\vec{k}_c$ is finite, and an antiferromagnetic ground state obtains. For binary systems the SRO parameter is given by

$$m_A m_B \alpha^{AB}(gp) = m_A m_B - \langle \sigma_g^A \sigma_p^B \rangle \ , \tag{3.1}$$

where $\langle \cdots \rangle$ represents the usual thermal average and $\sigma_g^\nu$ are the site-occupation operators,

$$\sigma_g^\nu = \begin{cases} +1, & \text{for a } \nu \text{ atom at site } g \\ 0, & \text{otherwise} \ . \end{cases} \tag{3.2}$$

The Fourier-transform of $\alpha^{AB}(gp)$, which is proportional to the diffuse scattering intensity, is given by

$$\alpha^{AB}(\vec{k}) = \sum_{\vec{g}-\vec{p}} \alpha^{AB}(gp) e^{-i\vec{k}\cdot(\vec{g}-\vec{p})} \ , \tag{3.3a}$$

$$\alpha^{AB}(gp) = \frac{1}{N} \sum_{\vec{k}} \alpha^{AB}(\vec{k}) e^{i\vec{k}\cdot(\vec{g}-\vec{p})} \ . \tag{3.3b}$$

From Eq. (3.1) we see that we also have the sum rule

$$\alpha^{AB}(gg) = \frac{1}{N} \sum_{\vec{k}} \alpha^{AB}(\vec{k}) = 1 \ . \tag{3.4}$$

A number of authors have calculated $\alpha^{AB}(\vec{k})$ within various approximations for binary alloys, which are isomorphous with the usual spin-$\frac{1}{2}$ Ising model.[5,23] We should mention in particular the work of Krivoglaz[24] and Clapp and Moss,[25] who arrived at similar forms for $\alpha^{AB}(\vec{k})$, i.e.,

$$\alpha^{AB}(\vec{k}) = \frac{\Delta}{1 - \beta m_A m_B V(\vec{k})} \ , \tag{3.5}$$

where $\beta = (k_B T)^{-1}$, $k_B$ = Boltzmann's constant, $V(\vec{k})$ is the average ordering energy,

$$V(\vec{k}) = 2V^{AB}(\vec{k}) - V^{AA}(\vec{k}) - V^{BB}(\vec{k}) \ ,$$

and $\Delta$ is determined such that the sum rule, Eq. (3.4), is obeyed.

We see that by measuring $\alpha^{AB}(\vec{k})$ we can obtain information about $V(\vec{k})$,[26] and that as $T \rightarrow T_c$ and $\vec{k} \rightarrow \vec{k}_c$, we get a singularity in $\alpha^{AB}(\vec{k})$ when

$$1 - \beta_c m_A m_B V(\vec{k}_c) = 0 \ . \tag{3.6}$$

Thus a theoretical calculation of $\alpha^{AB}(\vec{k})$ can give us the transition temperature as a function of concentration and interaction.

Modification and improvements of the approximant of Eq. (3.5) have been proposed by Philhours and Hall[27] and Hoffman[28] based on the spherical model, by Tahir-Kheli[29,30] based on a high-temperature expansion, and by Shirley and Wilkins[31] based on an expansion in $z^{-1}$, where $z$ is the number of nearest neighbors. The utility of the various forms seems to differ with the system under study.[32,33] However here we wish to emphasize the high-temperature methods of Tahir-Kheli. Basically Eq. (3.5) can be looked upon as the first term in a high-temperature expansion in $\beta$. Expansions up to $\beta^5$ have been obtained[30] and have, in many cases, been shown to be an improvement[32] on the approximant of Eq. (3.5). In the limit of the equicomposition alloy, i.e., the zero-field Ising limit, the transition temperature approaches that obtained from series expansions.[23]

Now the Fourier-transform of the SRO parameters $\alpha^{AB}(\vec{k})$ also obeys the thermodynamic sum rule[26] for $\vec{k} = \vec{k}_c$,

$$m_A m_B \alpha^{AB}(\vec{k}) = k_B T \left( \frac{\partial^2 g(\vec{k})}{\partial m_A^2} \right)^{-1} \ . \tag{3.7}$$

Thus we see that singularities in $\alpha^{AB}(\vec{k})$, via Eq. (3.5), are giving us information about the spinodal curve of the system, i.e., Eq. (2.2). Consequently we see that the transition temperature we have been talking about is that of the spinodal, i.e., a stability temperature, and it is defined by taking the limit on Eq. (3.5) for $\vec{k} \rightarrow \vec{k}_c$ and $T \rightarrow T_c$. The curve so defined separates the phase diagram into regions of stability (or metastability) and instability.[6,8,34]

The thermodynamic sum rule, Eq. (3.7), is derived from classical fluctuation theory, and has been applied to alloys in a number of ways by various authors.[6–8,18,19,35] The essence of the CFA is to emphasize the left-hand side of Eq. (3.7) and to calculate the correlation function $\alpha^{AB}(\vec{k})$ directly in order to obtain information about the spinodal. The inverse problem of calculating the free energy, and then the spinodal, is the usual method of studying solid solutions. Within the MFA, calculations done by both techniques give the same results for the spinodal, and as such should be considered complementary. However, one of our purposes here is to evaluate the CFA for approximations beyond the MFA. We will do this after we briefly discuss ternary alloys and other multicomponent alloys in Sec. IV.

## IV. MULTICOMPONENT ALLOYS

We wish to briefly review some of the previous work on multicomponent alloys, with particular emphasis on ternaries, in order to see where the results of this paper fit in. To begin with, we recognize that experimental[36] and theoretical[37–44] work on ternary alloys has been scant in comparison to that on binary alloys. Furthermore, studies of quaternary alloys,[1,45,46] and multicomponents,[47,48] are even scarcer.

Generally the theoretical studies on ternaries can be classified as those which are done in the ordered regime ($T < T_c$) and those done in the disordered regime ($T > T_c$). Those done in the disordered regime by Tahir-Kheli and Taggart[38,39] are in the spirit of the CFA. The vast majority of work has been in the ordered regime and has used either a Bragg-Williams–type MFA,[41,44] or a free-energy expansion in reciprocal space.[47,48] The classic work in clustering ternary systems based on the regular solution model is that of Meijering.[37]

Since the CFA yields information about the spinodal—in this case a spinodal surface for a ternary system—we are particularly concerned with the question of stability versus instability. Meijering's work[37] essentially classified the stability behavior of the ternary system based on whether the average interactions were attractive or repulsive. Again, this analysis was based on the regular solution model. Morral[43] later presented a very elegant geometric interpretation of stability in ternary systems and looked particularly at the regular solution model. Finally de Fontaine,[47] using free-energy-expansion techniques in reciprocal space, has analyzed the stability of multicomponent systems. For the case of the regular solution, his results are equivalent to Meijering's. For a review of the stability problem the interested reader is referred to de Fontaine's two fine reviews.[6,8]

Work done so far in going beyond the MFA, which is basically equivalent to the regular solution model, has used Kikuchi's cluster-variation method.[49,50] This has been shown to be marked improvement on the traditional MFA, or Bragg-Williams approximation. It is with this background that we look at the first-order approximation beyond the MFA for the CFA to ternary alloys. We begin this by formulating the problem in Sec. V.

## V. FORMULATION AND CORRELATION FUNCTIONS

The formulation of the static three-component system has been presented before,[38,39] so we will just present the salient features here. We will assume that static pair interactions[3] exist between atoms on a rigid lattice of $N$ sites. The configurational energy of the system can be written

$$H = \frac{1}{2} \sum_{\nu,\rho} \sum_{g,p} V^{\nu\rho}(gp)\, \sigma_g^\nu \sigma_p^\rho \ , \tag{5.1}$$

where the sum over $g$ and $p$ is over all lattice sites, and the sum on $\nu$ and $\rho$ is over atomic labels ($\nu, \rho = A,B,C$). The site-occupation operators have been defined in Eq. (3.2) and the pair interactions have the usual symmetry under site and species labels, i.e.,

$$V^{\nu\rho}(gp) = V^{\nu\rho}(pg) = V^{\rho\nu}(pg) = V^{\rho\nu}(gp) \ , \tag{5.2a}$$

$$V^{\nu\rho}(gg) = V^{\nu\nu}(gg) = 0 \ . \tag{5.2b}$$

The configurational Hamiltonian defined by Eq. (5.1) is a three-component static one and as such is isomorphous to a spin-1 Ising Hamiltonian. This is evidenced by transforming to spin variables ($S = 1; \hbar = 1$),

$$\sigma_g^A = \frac{1}{2}[(S_g^z)^2 + S_g^z] \ , \tag{5.3a}$$

$$\sigma_g^B = 1 - (S_g^z)^2 \ , \tag{5.3b}$$

$$\sigma_g^C = \frac{1}{2}[(S_g^z)^2 - S_g^z] \tag{5.3c}$$

and recasting Eq. (5.1) in the form,

$$\begin{aligned}\mathcal{H} = -\mu_1 \sum_g S_g^z - \mu_2 \sum_g (S_g^z)^2 - \sum_{g,p} I_1(gp) S_g^z S_p^z \\ - \sum_{g,p} I_2(gp) S_g^z (S_\rho^z)^2 \ - \sum_{g,p} I_3(g\rho)(S_g^z)^2 (S_p^z)^2 \ .\end{aligned} \tag{5.4}$$

Here the interaction parameters $I_j(gp)$ are linear combinations of the interactions $V^{\nu\rho}(gp)$[38] and the chemical potentials $\mu_j$ are determined such that the number of particles is conserved, i.e., the concentration of species $\nu$ is given by

$$m_\nu = \frac{N_\nu}{N} = \langle \sigma_g^\nu \rangle \; . \tag{5.5}$$

In addition we assume that all lattice sites are occupied, i.e.,

$$N = \sum_\nu N_\nu \; , \tag{5.6}$$

$$\sum_\nu \sigma_g^\nu = 1 \; . \tag{5.7}$$

It is a straightforward procedure[38,39] to derive exact correlation function equalities for the system governed by Eq. (5.1) or Eq. (5.4). These correlation-function identities can then be formally expanded for arbitrary chemical potentials (concentration) to arbitrary order in $\beta$. Consequently one can calculate, in principle, any correlation-function (pair, triplet, etc.) to arbitrary order in $\beta$. The procedure, for the general case, rapidly becomes tedious and cumbersome. However the site-site correlation function $\langle \sigma_g^A \sigma_p^C \rangle$ has been calculated for the general case to $O(\beta^3)$.[39] However it is our intent here to look at just the first-order correction to the linear expansion in $\beta$, i.e., the MFA, by investigating the pair correlation function to $O(\beta^2)$.

Looking at this correction to the MFA is motivated by (a) the fact that the terms to $O(\beta^2)$ are much more tractable than those to $O(\beta^3)$, (b) the fact that in our procedure we also need the correlation function $\langle \sigma_g^A \sigma_p^A \rangle$, which has not been calculated to $O(\beta^3)$, and (c) the fact that the first-order correction will often suffice to judge the adequacy of the MFA. We should be cautious though of the cyclic nature of $\alpha^{\nu\rho}(\vec{k})$.

The pair correlation functions calculated from this procedure[39] can be written

$$\begin{aligned}\langle \sigma_g^A \sigma_p^C \rangle &= (1-\delta_{gp}) m_A m_C - \beta m_A m_C \Lambda_1^{AC}(gp) \\ &\quad + \beta^2 \Lambda_2^{AC}(gp) + O(\beta^3) \; ,\end{aligned} \tag{5.8a}$$

and

$$\begin{aligned}\langle \sigma_g^A \sigma_p^A \rangle &= m_A^2 + \delta_{gp} m_A (1-m_A) - \beta m_A^2 \Lambda_1^{AA}(gp) \\ &\quad + \beta^2 \Lambda_2^{AA}(gp) + O(\beta^3) \; .\end{aligned} \tag{5.8b}$$

Since we have used grand-canonical averaging, the other correlation functions can be determined by cyclic permutation of $A$, $B$, and $C$.

In Eq. (5.8) we have used the notation

$$\Lambda_1^{AC}(gp) = U^{AC}(gp)(2m_A m_C + m_B) + U^{AB}(gp) m_B (2m_A - 1) + U^{BC}(gp) m_B (2m_C - 1) \; , \tag{5.9a}$$

$$\Lambda_1^{AA}(gp) = U^{AC}(gp) 2m_C (m_A - 1) + U^{AB}(gp) 2m_B (m_A - 1) + U^{BC}(gp) 2 m_B m_C \; , \tag{5.9b}$$

and

$$U^{\nu\rho}(gp) = V^{\nu\rho}(gp) - \tfrac{1}{2}[V^{\nu\nu}(gp) + V^{\rho\rho}(gp)] \; . \tag{5.10}$$

In addition we have,

$$\begin{aligned}\Lambda_2^{AC}(gp) = \frac{m_A m_C (1-m_C)}{(1-m_A)} & \\ \times \big( [m_A(1-2m_A) U(gp) - 2m_A m_C U^{BC}(gp)] & \Lambda_1^{AA}(gp) - 2m_A m_C U^{BC}(gp) \Lambda_1^{AC}(gp) - \tfrac{1}{2}(m_C - m_B) \\ \times \{(1-m_A)(1-2m_A) U(gp)^2 & - m_C(1-2m_C)[2U^{BC}(gp)]^2 - 4m_C(1-2m_A) U(gp) U^{BC}(gp)\}\big) \\ - \frac{m_A^2 m_C}{(1-m_C)} \big( [m_C(1-2m_A) 2U^{AB}(gp) & - m_C^2 U(gp)] \Lambda_1^{AC}(gp) - m_C^2 U(gp) \Lambda_1^{CC}(gp) \\ + \tfrac{1}{2}(m_B - m_A) \{ (1-m_A) & (1-2m_A)[2U^{AB}(gp)]^2 - m_C(1-2m_C) U(gp)^2 \\ & - 4m_C(1-2m_A) U(gp) U^{AB}(gp)\}\big) \\ + m_A m_C \sum_f \{ m_A \Lambda_1^{AA}(gf) & [2m_A U^{AB}(fp) - (1-m_C) U(fp)] + m_C \Lambda_1^{CC}(gf) \\ \times [m_A U(fp) & - (1-m_C) 2U^{BC}(fp)] \}\end{aligned} \tag{5.11a}$$

and

$$\begin{aligned}\Lambda_2^{AA}(gp) = {} & \frac{m_A^2(1-m_A)}{(1-m_C)} \\ & \times \left([m_C(1-2m_A)2U^{AB}(gp) - m_C^2 U(gp)]\Lambda_1^{AC}(gp) - m_C^2 U(gp)\Lambda_1^{CC}(gp) + \tfrac{1}{2}(m_B - m_A)\right. \\ & \left.\times \{(1-m_A)(1-2m_A)[2U^{AB}(gp)]^2 - m_C(1-2m_C)U(gp)^2 - 4m_C(1-2m_A)U(gp)U^{AB}(gp)\}\right) \\ & - \frac{m_A^2 m_C}{(1-m_A)}\left([m_A(1-2m_A)U(gp) - 2m_A m_C U^{BC}(gp)]\Lambda_1^{AA}(gp) - 2m_A m_C U^{BC}(gp)\Lambda^{AC}(gp)\right. \\ & \quad - \tfrac{1}{2}(m_C - m_B)\{(1-m_A)(1-2m_A)U(gp)^2 - m_C(1-2m_C)[2U^{BC}(gp)]^2 \\ & \quad \left. - 4m_C(1-2m_A)U(gp)U^{BC}(gp)\}\right) \\ & + m_A^2\{m_A\Lambda_1^{AA}(gf)[m_C U(fp) - 2(1-m_A)U^{AB}(fp)] + m_C\Lambda_1^{AC}(gf)[2m_C U^{BC}(fp) - (1-m_A)U(fp)]\}\,,\end{aligned} \tag{5.11b}$$

---

where

$$U(gp) = U^{AB}(gp) + U^{BC}(gp) - U^{AC}(gp)\,. \tag{5.12}$$

We now want to use these pair correlation functions to calculate the spinodal surface for a ternary alloy. We should again emphasize that these correlation functions are valid for arbitrary concentration, and arbitrary range and strength of interaction.

## VI. CFA AND THE SPINODAL SURFACE

The pair correlation functions of Eqs. (5.8) can be used to calculate SRO parameters via generalizations of Eq. (3.1), i.e.,

$$m_\nu m_\rho \alpha^{\nu\rho}(gp) = m_\nu m_\rho - \langle \sigma_g^\nu \sigma_p^\rho \rangle\,, \tag{6.1a}$$

$$m_\nu(1-m_\nu)\alpha^{\nu\nu}(gp) = \langle \sigma_g^\nu \sigma_p^\nu \rangle - m_\nu^2\,. \tag{6.1b}$$

We can also generalize the thermodynamic sum rule, Eq. (3.7), for multicomponent systems and write for $\vec{k} = \vec{k}_c$

$$m_\nu m_\rho \alpha^{\nu\rho}(\vec{k}) = k_B T \left(\frac{\partial^2 g(\vec{k})}{\partial m_\nu \partial m_\rho}\right)^{-1}. \tag{6.2}$$

The various values of $\alpha^{\nu\rho}(\vec{k})$ for an $n$-component system form the elements of an $(n-1)$-order matrix for the scattering intensity. This is particularly transparent if one considers all the independent pair correlation functions in a spin-space spanned by $S_g^z$ and $(S_g^z)^2$.

The CFA is thus to look for singularities in the scattering matrix, and consequently obtain information about the spinodal surface. Thus the system instability occurs when the magnitude of the scattering matrix

$$|m_\nu m_\rho \alpha^{\nu\rho}(\vec{k})| \to \infty \tag{6.3a}$$

for

$$\vec{k} \to \vec{k}_c\,,\ T \to T_c\,,$$

which from Eq. (6.2) is equivalent to

$$\left|\frac{\partial^2 g(\vec{k})}{\partial m_\nu \partial m_\rho}\right| \to 0 \tag{6.3b}$$

for

$$\vec{k} \to \vec{k}_c\,,\ T \to T_c\,.$$

For the ternary alloy under consideration here this implies that we look at the correlation matrix,

$$\underline{C}(k) = \begin{vmatrix} m_A(1-m_A)\alpha^{AB}(\vec{k}) & -m_A m_C \alpha^{AC}(\vec{k}) \\ -m_A m_C \alpha^{CA}(\vec{k}) & m_C(1-m_C)\alpha^{CC}(\vec{k}) \end{vmatrix}\,. \tag{6.4}$$

If we substitute for the elements of $\underline{C}(\vec{k})$ using our results from Eqs. (5.8), we can formally write

$$\underline{C}(k)=\underline{C}_0+\beta\underline{C}_1(\vec{k})+\beta^2\underline{C}_2(\vec{k})+O(\beta^3)\ , \tag{6.5}$$

or

$$\underline{C}(\vec{k})=\underline{C}_0[\underline{1}+\beta\underline{\Gamma}_1(\vec{k})+\beta^2\underline{\Gamma}_2(\vec{k})]\ . \tag{6.6}$$

We can now invert the series expansion in order to bring the scattering matrix into the form of Eq. (3.5), i.e.,

$$\underline{C}(\vec{k})=\underline{\Delta}[\underline{1}-\beta\underline{\gamma}_1(\vec{k})-\beta^2\underline{\gamma}_2(\vec{k})]^{-1}\ , \tag{6.7}$$

where $\underline{\Delta}$ is determined so that the total scattering intensity is conserved, i.e.,

$$\frac{1}{N}\sum_{\vec{k}}\underline{C}(\vec{k})=\underline{C}_0\ . \tag{6.8}$$

The elements of $\underline{C}(\vec{k})$ are related to the correlation functions (for cubic lattices) via

$$\underline{\gamma}_1(\vec{k})=\underline{\Gamma}_1(\vec{k})\ , \tag{6.9a}$$

$$\underline{\gamma}_2(\vec{k})=\underline{\Gamma}_2(\vec{k})-\underline{\Gamma}_1(\vec{k})^2\ . \tag{6.9b}$$

As the system approaches criticality the magnitude of the scattering intensity diverges, i.e.,

$$|\underline{C}(\vec{k})|\rightarrow\infty \tag{6.10}$$

for

$$\vec{k}\rightarrow\vec{k}_c\ ,T\rightarrow T_c\ ,$$

and thus from Eq. (6.7),

$$|\underline{1}-\beta\underline{\gamma}_1(\vec{k})-\beta^2\underline{\gamma}_2(\vec{k})|=0 \tag{6.11}$$

for

$$\vec{k}\rightarrow\vec{k}_c\ ,T\rightarrow T_c\ .$$

If we neglect the $\beta^2$ term in Eq. (6.11) we retrieve the mean-field results of Tahir-Kheli,[2] who used this technique. Likewise we obtain the same results as Murakami *et al.*[41] who used a Bragg-Williams technique, and Tahir-Kheli[44] who used Green's function techniques in the random-phase approximation. We note that Eq. (6.11) yields a quartic equation in $\beta_c$ in this approximation. Generally, for an $n$-component system in which the correlation function has been expanded to $\beta^m$, we obtain an $m(n-1)$-order polynomial in $\beta_c$. In Sec. VII we consider a specific example.

## VII. RESULTS AND DISCUSSION

For the approximation of this paper Eq. (6.11) yields a quartic equation in $\beta_c$ whose solutions define a surface in composition space. The general solution is a function of arbitrary concentration and of arbitrary range and strength of pair potentials. Conventionally the resultant phase diagrams are drawn on a Gibbs triangle. The surface in composition space is a spinodal surface for the ternary alloy and separates the space into regions of stability and instability. Since we are dealing with a high temperature, or disordered, formalism, we interpret the solutions of Eq. (6.11) such that the largest, positive solution is the point at which the instability sets in. Any comments about real solutions below this first instability should be made with extreme caution.

For the sake of clarification we are going to examine the binary section of a ternary system which is known to undergo spinodal decomposition, and which has been discussed previously in the MFA, using a different technique.[47] The system we wish to consider is a clustering ternary which has equal nearest-neighbor interactions and symmetric concentration in two components, i.e.,

$$\begin{gathered}\vec{k}_c=(0,0,0)\ ,\\ U^{AB}(\vec{k}_c)=U^{AC}(\vec{k}_c)=U^{BC}(\vec{k}_c)=zU\ ,\\ m_A=m_C=x\ ,\quad m_B=1-2x\ .\end{gathered} \tag{7.1}$$

This particular case has been discussed by de Fontaine[47] using free-energy expansions in reciprocal space. He has also shown that the coherent spinodal must always be below the incoherent, or chemical, spinodal for multicomponent alloys. One can thus look at the chemical spinodal, as calculated here, as an upper bound. Likewise de Fontaine has constructed a formalism to take into account the effects of elastic energy on the incoherent spinodal for multicomponent systems. This is in the same spirit as Eq. (2.3) for binary alloys.

If we neglect the terms in Eq. (6.11) which go as $\beta^2$ and make the substitutions (7.1), we obtain the MFA (or regular solution) result,

$$\tau^2-2x(2-3x)\tau+3x^2(1-2x)=0\ , \tag{7.2a}$$

with solutions

$$\begin{gathered}\tau_1=x\ ,\\ \tau_2=3x(1-2x)\ ,\end{gathered} \tag{7.2b}$$

where $\tau^{-1}=\beta zU$. We have plotted these results in Fig. 2. We note that the two curves intersect at the point $\tau=\frac{1}{3}$, $x=\frac{1}{3}$. De Fontaine has observed that the coherent spinodal also goes through this point and consequently, as opposed to binary alloys, multicomponent systems could phase separate without strain even if a large size effect exists between the component species, if the separation occurs at the intersection of incoherent spinodals.

By including the terms in Eq. (6.11) proportional to

$\beta^2$ we obtain a quartic equation in $\tau$ which can be written

$$\tau^4 - a_3(x)\tau^3 + a_2(x)\tau^2 - a_1(x)\tau + a_0(x) = 0 \,, \tag{7.3}$$

where

$$a_3(x) = 2x(2-3x) \,, \tag{7.4a}$$

$$a_2(x) = x^2(2-3x)^2 - 3x^2(1-3x)^2 - (1/z)2x(1-2x)(18x^2 - \tfrac{21}{2}x + 2) \,, \tag{7.4b}$$

$$\begin{aligned} a_1(x) &= 6x^3(1-3x)^2(1-x) - 2x^3(1-3x)^2(2-3x) \\ &\quad + (1/z)[x^2(1-2x)(1-12x)(1-3x)^2 - 2x^2(1-2x)(2-3x)(18x^2 - \tfrac{21}{2}x + 2)] \,, \end{aligned} \tag{7.4c}$$

and

$$\begin{aligned} a_0(x) &= x^4(1-3x)^4 - 9x^4(1-3x)^2(1-x)^2 \\ &\quad + (1/z)[2x^3(1-3x)^2(1-2x)(18x^2 - \tfrac{21}{2}x + 2) - 3x^3(1-3x)^2(1-x)(1-2x)(1-12x)] \\ &\quad + (1/z)^2[x^2(1-2x)^2(18x^2 - \tfrac{21}{2}x + 2)^2 - \tfrac{1}{4}x^2(1-2x)^2(1-12x)^2(1-3x)^2] \,. \end{aligned} \tag{7.4d}$$

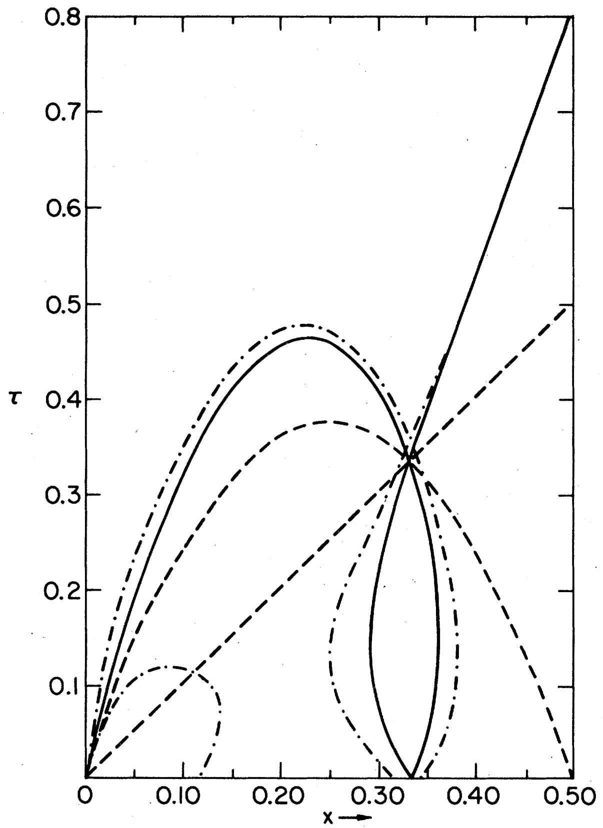

FIG. 2. Binary section of a ternary phase diagram for a clustering system with equal nearest-neighbor interactions and $m_A = m_C = \frac{1}{2}(1 - m_B) = x$. The mean-field results are given by the dashed line. The approximation of this paper is given by the solid line for $z = \infty$ and the dot-dash line for $z = 6$.

We note that Eq. (7.3) includes both $1/z$ and $(1/z)^2$ corrections. In the limit that $x = \frac{1}{2}$, the $1/z$ terms drop out, and we retrieve the results for an $AC$ binary alloy, with the binary intersection point going from the MFA value of $\tau_{AC} = 0.5$ to $\tau_{AC} \simeq 0.81$. We have plotted the positive, real solutions of Eq. (7.3) in Fig. 2 for the cases $z = 6$ and $z = \infty$. We note that in both cases the uppermost spinodal surface maintains its general shape and similarity to the MFA results. However the lower curve is altered appreciably. This behavior is consistent with a high-temperature approach only commenting on the uppermost stability surface.

We also note that the maximum $\tau$ for finite $x$ is shifted to lower $x$ from the mean-field value of $x = 0.25$. The intersection point of the spinodals is also shifted from the mean-field value for small $z$, but as $z$ becomes infinite, i.e., the model becomes more mean-field-like, the intersection returns to the MFA results. Again we should caution that generally the high-temperature expansion for $\alpha^{\nu\rho}(\vec{k})$ is cyclic in nature, and $\beta^3$ corrections to the linear approximation should also be considered before attempting any definitive statements.

In conclusion we have hopefully demonstrated the usefulness of the CFA to multicomponent alloys. We believe that it can nicely complement calculations done in the ordered regime. Admittedly, the high-temperature expansions can be somewhat awkward and tedious. However, the effort can be reduced appreciably by considering special cases, i.e., nearest neighbors only. Also we have seen how first-order corrections to the MFA affect the structure of the spinodal surface for a ternary alloy.

## ACKNOWLEDGMENTS

I would like to thank the Department of Physics, University of Illinois at Urbana-Champaign for their hospitality and support. I would particularly like to thank Professor Michael Wortis for informative conversations and the Research Board for a grant of computer time. The hospitality of the Statistical Physics Group of NBS is also gratefully acknowledged. In addition I would like to thank Professor de Fontaine for sending me a preliminary version of his review article.

---

[*] Permanent address: Dept. of Phys., Va. Commonwealth Univ., Richmond, Va. 23284.

[1] G. B. Taggart, Phys. Rev. B 19, 3230 (1979).

[2] R. A. Tahir-Kheli, Phys. Rev. B (to be published).

[3] G. B. Taggart, Phys. Rev. B 19, 2895 (1979).

[4] R. A. Swalin, *Thermodynamics of Solids*, 2nd ed. (Wiley, New York, 1972).

[5] F. C. Nix and W. Shockley, Rev. Mod. Phys. 10, 1 (1938); T. Muto and Y. Takagi, Solid State Phys. 1, 193 (1955); L. Guttman, Solid State Phys. 3, 145 (1956); H. Sato, in *Physical Chemistry: An Advanced Treatise*, edited by W. Jost (Academic, New York, 1970), Vol. X, p. 579.

[6] D. de Fontaine, in *Treatise on Solid State Chemistry*, edited by N. B. Hannay (Plenum, New York, 1975), Vol. V, p. 129.

[7] A. G. Khachaturyan, Prog. Mater. Sci. 22, 1 (1978).

[8] D. de Fontaine, Solid State Phys. (to be published).

[9] J. W. Cahn, Trans. AIME 242, 166 (1968); J. E. Hilliard, in *Phase Transformations*, edited by H. I. Aaronson (American Society of Metals, Cleveland, 1970), p. 497.

[10] *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1973–1976), all volumes.

[11] J. S. Langer, Acta Metall. 21, 1649 (1973); J. S. Langer, M. Bar-on, and H. D. Miller, Phys. Rev. A 11, 1417 (1975).

[12] K. Binder, C. Billotet, and P. Mirold, Z. Phys. B 30, 183 (1978).

[13] *Fluctuations, Instabilities and Phase Transitions*, edited by T. Riste (Plenum, New York, 1975).

[14] J. W. Cahn, Acta Metall. 10, 179, 907 (1962).

[15] R. Acuña and A. Bonfiglioli, Acta Metall. 22, 399 (1974).

[16] S. M. Allen and J. W. Cahn, Acta Metall. 23, 1017 (1975); 24, 425 (1976).

[17] D. Schwahn and W. Schmatz, Acta Metall. 26, 1571 (1978).

[18] D. de Fontaine and H. E. Cook, in *Critical Phenomena in Alloys, Magnets and Superconductors*, edited by R. E. Mills, E. Ascher, and R. I. Jaffee (McGraw-Hill, New York, 1971), p. 257.

[19] H. E. Cook, M. Suezawa, T. Kajitani, and L. Rivaud, J. Phys. (Paris) 38, C7-430 (1977); H. E. Cook, Mater. Sci. Eng. 25, 127 (1976).

[20] P. Bardhan and J. B. Cohen, Acta Crystallogra. Sect. A 32, 597 (1976); H. Chen, J. B. Cohen, and R. Ghosh, J. Phys. Chem. Solids 38, 855 (1977).

[21] J. M. Cowley, Adv. High Temp. Chem. 3, 35 (1971).

[22] V. I. Iveronova and A. A. Katsnelson, in *Order-Disorder Transformations in Alloys*, edited by H. Warlimont (Springer, New York, 1974), p. 306.

[23] M. E. Fisher and R. J. Burford, Phys. Rev. 156, 583 (1967).

[24] M. A. Krivoglaz, *Theory of X-Ray and Thermal Neutron Scattering by Real Crystals* (Plenum, New York, 1969).

[25] P. C. Clapp and S. C. Moss, Phys. Rev. 142, 418 (1966); 171, 754 (1968); S. C. Moss and P. C. Clapp, *ibid.* 171, 764 (1968).

[26] N. H. March, S. W. Wilkins, and J. E. Tibbals, Crys. Lattice Defects 6, 253 (1976).

[27] J. Philhours and G. L. Hall, Phys. Rev. 170, 496 (1968); 177, 976 (1969).

[28] D. W. Hoffman, Metall. Trans. 3, 3231 (1972).

[29] R. A. Tahir-Kheli, Phys. Rev. 188, 1142 (1969).

[30] D.-H. Wu and R. A. Tahir-Kheli, J. Phys. Soc. Jpn. 31, 641 (1971); G. B. Taggart and R. A. Tahir-Kheli, Physica (Utrecht) 68, 93 (1973).

[31] C. G. Shirley and S. W. Wilkins, Phys. Rev. B 6, 1252 (1972); B 16, 3484 (1977).

[32] J. Vrijen, C. van Dijk, and S. Radelaar, in *Proceedings of the Conference on Neutron Scattering, Gatlinburg (1976)*, edited by R. M. Moon (NTIS, Springfield, 1976), p. 92; J. Vrijen, E. W. van Royen, D. W. Hoffman, and S. Radelaar, J. Phys. (Paris) 38, C7-187 (1977); J. Vrijen and S. Radelaar, Phys. Rev. B 17, 409 (1978).

[33] E. Metcalfe and J. A. Leake, Acta Metall. 23, 1135 (1974).

[34] N. W. Ashcroft, in *Liquid Metals 1976*, edited by R. Evans and D. A. Greenwood (Institute of Physics, Bristol, 1977), p. 39.

[35] A. B. Bhatia, in *Liquid Metals 1976*, edited by R. Evans and D. A. Greenwood (Institute of Physics, Bristol, 1977), p. 21; A. B. Bhatia and D. E. Thornton, Phys. Rev. B 2, 3004 (1970); 4, 2325 (1971).

[36] L. Muldawer, J. Appl. Phys. 37, 2062 (1966); M. E. Brookes and R. W. Smith, Scripta Metall. 3, 667 (1969); Y. Murakami, N. Nakamishi, and S. Kachi, Acta Metall. 19, 93 (1971); R. C. Bowe and L. Muldawer, J. Appl. Phys. 43, 4495 (1972).

[37] J. L. Meijering, Philips Res. Rep. 5, 333 (1950); 6, 183 (1951).

[38] R. A. Tahir-Kheli, Phys. Rev. 169, 517 (1968).

[39] G. B. Taggart and R. A. Tahir-Kheli, Phys. Rev. B 3, 1059 (1971).

[40] J. S. Kirkaldy and G. R. Purdy, Can. J. Phys. 47, 865 (1969).

[41] Y. Murakami, S. Kachi, N. Nakanishi, and H. Takehara, Acta Metall. 19, 97 (1971).

[42] J. E. Morral and J. W. Cahn, Acta Metall. 19, 1037 (1971).

[43] J. E. Morral, Acta Metall. 20, 1061, 1069 (1972).

[44] R. A. Tahir-Kheli, Phys. Status Solidi B 79, 93 (1977).

[45] H. K. Hardy and J. L. Meijering, Philips Res. Rep. 10, 358 (1955).

[46] R. A. Tahir-Kheli and G. B. Taggart, Prog. Theor. Phys. 42, 1265 (1969).

[47] D. de Fontaine, J. Phys. Chem. Solids 33, 297 (1972); 34, 1285 (1973).

[48] D. A. Badalyan and A. G. Khachaturyan, Sov. Phys. Solid State 14, 2270 (1973); V. I. Ryzhkov, Fiz. Met. Metalloved. 41, 7 (1976).

[49] N. S. Golosov and A. M. Tolstik, J. Phys. Chem. Solids, 35, 1575, 1581 (1974).

[50] R. Kikuchi, Acta Metall. 25, 195 (1977); R. Kikuchi, D. de Fontaine, M. Murakami, and T. Nakamura, Acta Metall. 25, 207 (1977).