JOURNAL OF MATERIALS SCIENCE **35** (2000) 1177 – 1180

A Ginzburg-Landau treatment of ternary spinodal decomposition

J. S. KIRKALDY
Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1

Following the suggestion of Goryachev in seeking a formulation of binary spinodal decomposition which better accords with the tenets of irreversible thermodynamics and with the experimental and computational modelling record we have revised de Fontaine's ternary version of Cahn's binary linearized theory. This modification was motivated by the fact that his version with Bragg-Williams thermodynamics does not accommodate the formulation of a differential initial value problem since the two 2 × 2 coefficient matrices cannot be simultaneously brought to the diagonal. In the time-dependent Ginzburg-Landau representation suggested by Goryachev the corresponding matrices are proportionate, abetting commutation and therefore simultaneous diagonalization well into the high amplitude range of decomposition. This suggests the need for revision of ternary small angle scattering theory. © *2000 Kluwer Academic Publishers*

1. Introduction

Early attempts at observing spinodal decomposition focussed on the ternary alloy Cu-Ni-Fe [1, 2, 3] so it was highly appropriate that de Fontaine, an associate of Hilliard and Cahn [4, 5], should in his thesis [6] have explored a ternary generalization of Cahn's theory of binary spinodal decomposition [5]. De Fontaine's contribution was later expanded by Kirkaldy and Purdy [7], Morral and Cahn [8], Kirkaldy *et al.* [9], and most recently by Hoyt [10], who focussed on the completion of the appropriate small angle scattering theory. On the other hand, Kirkaldy *et al.* [9] found that a general formulation of the initial value problem for ternary spinodal decomposition within de Fontaine's formulation does not appear to be possible. A Ginzburg-Landau formulation overcomes this difficulty.

Since 1961, a large amount of binary scattering data was accumulating, leading Binder [11] in a recent review to state that for scattering functions in metals "the hallmarks of the linearized Cahn theory (exponential increase of intensity with time, time-independent intersection point of $S(\vec{k}, t)$, maximum position k_m of $S(\vec{k}, t)$ independent of time) are never found [11]." Furthermore, during this decade, the proposition has arisen in the physics literature that the Cahn theory is defective for irreversible thermodynamic reasons [12], simulations indicating that rather than the generated $t^{1/3}$ coarsening [13], it yields the same $t^{1/2}$ behaviour as for second order, order-disorder processes [14]. Goryachev has therefore suggested that the appropriate concentration (c) equation is the time- dependent Ginzburg-Landau (TDGL) equation [12]

$$\frac{\partial c}{\partial t} = -M\left(\frac{\delta F}{\delta c} - \mu_o\right); \quad F = \int_V f \, dV \tag{1}$$

where $\delta F/\delta c$ is symbolic of the variational derivative, M is a rate constant, and μ_o is a Lagrange Multiplier chosen so as to assure off-symmetry solute conservation. For the same reason, the free energy density f is to be expressed in the usual *even* Ginzburg-Landau form containing a gradient energy term. Kawasaki [15] has made the crucial point that in accessing Equation 1 one is dealing with a chemical reaction not an uphill diffusion process. Clearly, this can be atomistically justified, for metals and alloys quenched sufficiently below the critical point will very rapidly reach a vacancy density which is not appreciably different than that for incipient precipitates so the reaction between the highly mobile vacancies and the unsaturated bonds will in the linear early stages be essentially homogeneous. The only changes from order-disorder will be correlated vacancy motions which sustain unmixing rather than ordered mixing and the possibility of induced coherency strain effects [16]. The present paper is designed to give credence to these binary considerations by demonstrating that the ternary initial value problem *is* capable of formulation only within the Ginzburg-Landau representation.

2. The de Fontaine ternary formulation

For comparison purposes we briefly review Morral and Cahn's phrasing of the de Fontaine formulation [6, 8] starting with the conjectured generalization of the Cahn *linearized* or low amplitude binary equation containing the uphill second order term ($D^{(1)} < 0$) and the downhill fourth order gradient energy term ($D^{(2)} > 0$), viz.,

$$\frac{\partial c_1}{\partial t} = D_{11}^{(1)}\nabla^2 c_1 + D_{12}^{(1)}\nabla^2 c_2 - D_{11}^{(2)}\nabla^4 c_1 - D_{12}^{(2)}\nabla^4 c_2 \tag{2}$$

and

$$\frac{\partial c_2}{\partial t} = D_{21}^{(1)}\nabla^2 c_1 + D_{22}^{(1)}\nabla^2 c_2 - D_{21}^{(2)}\nabla^4 c_1 - D_{22}^{(2)}\nabla^4 c_2 \tag{3}$$

General Fourier solutions are constructed of the form

$$\begin{aligned} c_1 - \bar{c_2} = \sum_{\beta} \big[&\alpha_{11} \exp\!\big(-\beta^2 \tilde{D}_2 t\big) \cos(\vec{\beta}\cdot\vec{r} + \phi_1(\beta)) \\ &+ \alpha_{12} \exp\!\big(-\beta^2 \tilde{D}_2 t\big) \cos(\vec{\beta}\cdot\vec{r} + \phi_2(\beta))\big] \end{aligned} \tag{4}$$

and

$$\begin{aligned} c_2 - \bar{c_2} = \sum_{\beta} \big[&\alpha_{21} \exp\!\big(-\beta^2 \tilde{D}_1 t\big) \cos(\vec{\beta}\cdot\vec{r} + \phi_1(\beta)) \\ &+ \alpha_{22} \exp\!\big(-\beta^2 \tilde{D}_2 t\big) \cos(\vec{\beta}\cdot\vec{r} + \phi_2(\beta))\big] \end{aligned} \tag{5}$$

subject to

$$\tilde{D}_1 \alpha_{11} = D_{11}\alpha_{11} + D_{12}\alpha_{21} \tag{6}$$

$$\tilde{D}_1 \alpha_{21} = D_{21}\alpha_{11} + D_{22}\alpha_{21} \tag{7}$$

and

$$\tilde{D}_2 \alpha_{12} = D_{11}\alpha_{12} + D_{12}\alpha_{22} \tag{8}$$

$$\tilde{D}_2 \alpha_{22} = D_{21}\alpha_{12} + D_{22}\alpha_{22} \tag{9}$$

with

$$D_{\mathrm{ij}} = D_{\mathrm{ij}}^{(1)} + \beta^2 D_{\mathrm{ij}}^{(2)} \tag{10}$$

Elimination of the α's yields two eigenvalues $\tilde{D}_1(\beta)$ and $\tilde{D}_2(\beta)$. It is suggested that the initial value problem can be formulated in terms of

$$c_1^0 - \bar{c_1} = \sum_{\beta} A_1^0 \cos(\vec{\beta}\cdot\vec{r} + \theta_1(\beta)) \tag{11}$$

and

$$c_2^0 - \bar{c_2} = \sum_{\beta} A_2^0 \cos(\vec{\beta}\cdot\vec{r} + \theta_2(\beta)) \tag{12}$$

accessing four relations between the α's, ϕ's and θ's for *every* β, a process which for reasons of excessive complication is never actually accessed. It was apparently this complication which discouraged Hoyt [10] from seeking a rigorous evaluation of the structure functions relevant to the analysis of low angle scattering. While the de Fontaine arithmetic appears to be sound, it is not at all clear that a physically meaningful initial condition normally framed in the binary case via a Fourier *integral* can be framed as the Fourier *series* (11) and (12). As Hillert suggested in his original one-dimensional model [17], one should be able to start with a conservative localized perturbation which has a Fourier integral decomposition giving in the binary case a unique coefficient $A(\beta)$, an approach subsequently verified by Cahn [5]. In attempting to proceed in this way towards an initial value solution of (2) and (3), Kirkaldy *et al.* [9] discovered that this can only be done with sufficient generality if de Fontaine's constant matrices $\{D^{(1)}\}$ and $\{D^{(2)}\}$ can simultaneously be brought to the diagonal. They demonstrated that for this to obtain the matrices must commute, with the sufficient corollaries that either one of the matrices is diagonal or they are proportionate. The explicit evaluation of the two matrices in Onsager *diffusion* kinetics and Bragg-Williams ternary mean field theory given in Ref. 9 indicates that these conditions are met only in extreme and unlikely configurations. Since the ternary physics, if correct, must encompass an initial value problem of the Hillert class, and since the generalization of the Cahn binary formulation through Equations 2 and 3 may according to Goryachev imply incorrect physics of irreversible processes, we choose to seek an alternative. We will now demonstrate that a Ginzburg-Landau structure involving *chemical reaction* has the required symmetry and analytic capability in respect to the initial value problem.

3. A Ginzburg-Landau ternary spinodal structure

The early stage binary Ginzburg-Landau equation which at symmetric stoichiometry omitting the cubic term, valid up to normalized concentration amplitudes of one half the spinodal values, is

$$\frac{\partial c}{\partial t} = 2M\kappa\nabla^2 c - 2M\alpha c; \quad \alpha < 0 \tag{13}$$

where in terms of Bragg-Williams pair energies [18], the gradient energy parameter $\kappa = zN_{\mathrm{A}}a^2[e_{AB} - (e_{AA} + e_{BB})/2]/2$ and the enthalpic volume parameter $\alpha = -ZN_{\mathrm{A}}(1 - T/T_{\mathrm{c}})[e_{A\bar{B}}(e_{AA} + e_{BB})/2]/2$. Here M is a chemical rate constant, z and Z are surface and volume coordination numbers, respectively, a is the lattice parameter and N_{A} is Avogadro's number. The periodic solutions of these exhibit coarsening from time zero, an absence of a fastest growing wavelength and no nucleation barrier emerging from amplitudes beyond the spinodes [12]. This generalizes to

$$\begin{aligned} \frac{\partial c_1}{\partial t} = {} & 2M_{11}\kappa_{11}\nabla^2 c_1 + 2M_{12}\kappa_{12}\nabla^2 c_2 \\ & - 2M_{11}\alpha_{11}c_1 - 2M_{12}\alpha_{12}c_2 \end{aligned} \tag{14}$$

and

$$\begin{aligned} \frac{\partial c_2}{\partial t} = {} & 2M_{21}\kappa_{21}\nabla^2 c_1 + 2M_{22}\kappa_{22}\nabla^2 c_2 \\ & - 2M_{21}\alpha_{21}c_1 - 2M_{22}\alpha_{22}c_2 \end{aligned} \tag{15}$$

where all c's as in Equations 4 and 5 are understood to be normalized to the mean. Note that since the location of the spinodes is irrelevant in this formulation the miscibility gap can always be symmetrized about a temperature-dependent line in the binary case and a surface $\bar{c}(T, \bar{c}_1, \bar{c}_2)$ in the ternary case. Accordingly for the alloys at the averages $\bar{c}_1$ and $\bar{c}_2$ used to normalize c_1 and c_2, Equations 14 and 15 are linear such as to conserve solute following a conserved perturbation. Lagrange Multipliers as anticipated by Goryachev [12] need be entered only for off-symmetry alloys so-defined. From the binary limit (13) and the ternary thermodynamic calculations of Kirkaldy *et al.* [9] using Becker's method for gradient energies [19] on the advice of Hillert [20], we can obtain the near neighbour matrices in Ginzburg-Landau form,

$$\{\kappa\} = zN_{\mathrm{A}}a^2 \cdot \frac{1}{4}\begin{Bmatrix} (2\varepsilon_{AC} - \varepsilon_{AA} - \varepsilon_{CC}) & (\varepsilon_{AC} + \varepsilon_{BC} - \varepsilon_{AB} - \varepsilon_{CC}) \\ (\varepsilon_{AC} + \varepsilon_{BC} - \varepsilon_{AB} - \varepsilon_{CC}) & (2\varepsilon_{BC} - \varepsilon_{BB} - \varepsilon_{CC}) \end{Bmatrix} \tag{16}$$

for an areal chemical reaction, and

$$\{\alpha\} = -ZN_{\mathrm{A}}\left(1 - \frac{T}{T_{\mathrm{c}}}\right) \cdot \frac{1}{4}\begin{Bmatrix} (2\varepsilon_{AC} - \varepsilon_{AA} - \varepsilon_{CC}) & (\varepsilon_{AC} + \varepsilon_{BC} - \varepsilon_{AB} - \varepsilon_{CC}) \\ (\varepsilon_{AC} + \varepsilon_{BC} - \varepsilon_{AB} - \varepsilon_{CC}) & (2\varepsilon_{BC} - \varepsilon_{BB} - \varepsilon_{CC}) \end{Bmatrix} \tag{17}$$

for a volumetric chemical reaction. It is highly appropriate to our general thesis that the two sets of reaction rate coefficients differ only in the geometric and thermal factors. Note that on account of the assumed symmetrization of the alloy relative to the critical point composition that both $\{2M\kappa\}$ and $\{2M\alpha\}$ turn out to be symmetric since $\{M\}$ is always symmetric {Onsager Reciprocity}. The mean field Au (C) Ag(A) Cu (B) phase diagram may be taken as representative [21]. Accordingly, since

$$\{\kappa\} \propto \{\alpha\} \tag{18}$$

on the isotherm we have demonstrated that $\{2M\kappa\}$ and $\{2M\alpha\}$ *can* simultaneously be brought to the diagonal on the isotherm and an initial value problem accommodated.

4. Discussion

The two questions raised earlier in respect to solutions of the de Fontaine formulation of the ternary problem [6–9] must now be readdressed. Firstly, it is important to specify how the solutions define scattering functions which are to be compared with low angle X-ray or neutron scattering experiments extending from the binary results reviewed by Binder [11]. Secondly, there was an intuitive consensus among interested researchers [7–9] that an initial arbitrarily directed sub-critical composition fluctuation represented as a two-pronged arrow on the Gibbs isotherm would in the linearized version of the Cahn-de Fontaine theory spontaneously rotate toward parallelism with a solute-conserving tie-line of the phase diagram thus expressing an early time approach towards the equilibrium state. This proposition cannot be sustained within the TDGL formulation for the isothermal equilibration trend is now clearly vested within the generalization of the cubic term dropped from Equation 13 so as to define linearization. Thus, as research in progress we must first specify how the cubic terms are to be entered into Equations 14 and 15, hopefully via the inclusion of a 2 × 2 $\{\beta\}$ matrix of coefficients explicitly dependent on the $\{\alpha\}$ matrix through the ternary phase diagram. At best, a computational problem of some complexity is necessarily to be addressed.

The linearized problem for the early time scattering functions as a modification of Hoyt's contribution [10] remains of interest. This should start with a generalization to Equations 14 and 15 of Goryachev's reciprocal space solutions of Equation 13 [12]. This problem offers the prospect of a closed form representation.

For solid state systems, the effect of coherency strains becomes important [5]. Equations 14 and 15, pertaining to the ternary case, can be adapted by adding a matrix $\{\alpha'\}$ to $\{\alpha\}$. This follows from Cahn's demonstration that this is an enthalpic correction linear in normalized c.

In summary, Goryachev has demonstrated that a binary spinodal formulation according to Equation 1, and arranged to subsume solute conservation, incorporates the beginning of coarsening at early times and is free of a fastest growing wavenumber, so unlike the linearized Cahn theory agrees in this respect with the observations [11]. Our ternary development is consistent with this binary intelligence while demonstrating that the approach to equilibration and subsequent self-similar coarsening is predicated upon the cubic terms in the driving force for advance of the reaction. The all-important ternary scattering functions [10] which remain to be worked out in both the linear and non-linear representations of this formalism will undoubtedly reflect the same trends.

References

1. M. HILLERT, M. COHEN and B. L. AVERBACH, *Acta Met.* **9** (1961) 536.
2. P. J. TUFTON, PhD Thesis, Cambridge University 1963.
3. R. K. HAM, J. S. KIRKALDY and J. T. PLEWES, *Acta Met.* **15** (1967) 861.
4. J. W. CAHN and J. E. HILLIARD, *J. Chem. Phys.* **28** (1958) 258.
5. J. W. CAHN, *Acta Met.* **9** (1961) 795.
6. D. DE FONTAINE, PhD Thesis, Northwestern University, 1967.
7. J. S. KIRKALDY and G. R. PURDY, *Can. J. Phys.* **47** (1969) 865.
8. J. E. MORRAL and J. W. CAHN, *Acta Met.* **19** (1971) 1037.

9. J. S. KIRKALDY, K. BALASUBRAMANIAN and Y. J. M. BRECHET, in "Fundamentals and Applications of Ternary Diffusion," edited by G. R. Purdy (Pergamon, Toronto, 1990) p. 41.
10. J. J. HOYT, *Acta Met. et Mat*. **38** 227 (1990).
11. K. BINDER, in "Materials Science and Technology," Vol. 5 edited by R. W. Cahn, P. Haasen and E. J. Kramer (VCH Weinheim, Germany, 1991) p. 405.
12. S. B. GORYACHEV, *Phys Rev. Letts*. **27** (1994) 1850.
13. T. M. ROGERS, M. R. ELDER and C. R. DESAI, *Phys. Rev. B* **37** (1988) 9638.
14. J. F. ANNETT and J. R. BANAVAR, *Phys. Rev. Letts*. **68** (1992) 2941.
15. K. KAWASAKI, in "Proceedings of the 1986 Summer School in Statistical Mechanics," edited by C-K. Hu (Institute of Physics, Academica Sinica, Taipei) 1987.
16. J. S. KIRKALDY, *Scripta Mat*. **39** (1998) 611.
17. M. HILLERT, *Acta Met*. **9** (1961) 525.
18. P. MAUGIS, *Phys. Rev. B* **53** (1996) 5276.
19. R. BECKER, *Zeits. für Metallkunde* **29** (1937) 245.
20. M. HILLERT, private communication, 1988.
21. J. S. KIRKALDY and D. J. YOUNG, "Diffusion in the Condensed State" (Institute of Metals, London, 1987) p. 248.

Received 23 February
and accepted 24 August 1999