CHAPTER 2

BASES OF PHASE TRANSITION THEORY

2.1 Introduction

This chapter gives a very brief review of the transition routes which are relevant to the work described in this thesis. Most attention is given to the examination of continuous behaviour and its kinetic treatments, since tests of the appropriate equations comprise part of the work of the experimental chapters. The essential characteristics of other types of conventional behaviour are discussed, however (and see also general reviews e.g. Wayman 1971; Meyrick and Powell 1973; Jack and Nutting 1974; Christian 1975, 1979; Raghavan and Cohen 1975).

2.2 Continuous transitions

2.2.1 General formulation of kinetic theories

Thermodynamic instability has already been discussed in Chapter 1 (above) as the essential characteristic of systems which exhibit continuous transition behaviour. This criterion is satisfied if

(E1.1)

$$\frac{\partial^2 \Phi}{\partial c^2} \leqslant 0$$

where Φ is a free energy function containing terms for strain and chemical gradient energies.

Kinetic descriptions of continuous reactions require the incorporation of this necessary and sufficient condition into a diffusion equation. This problem was solved originally by Hillert (1961) for a discrete lattice and by Cahn (1961, 1962a) for a

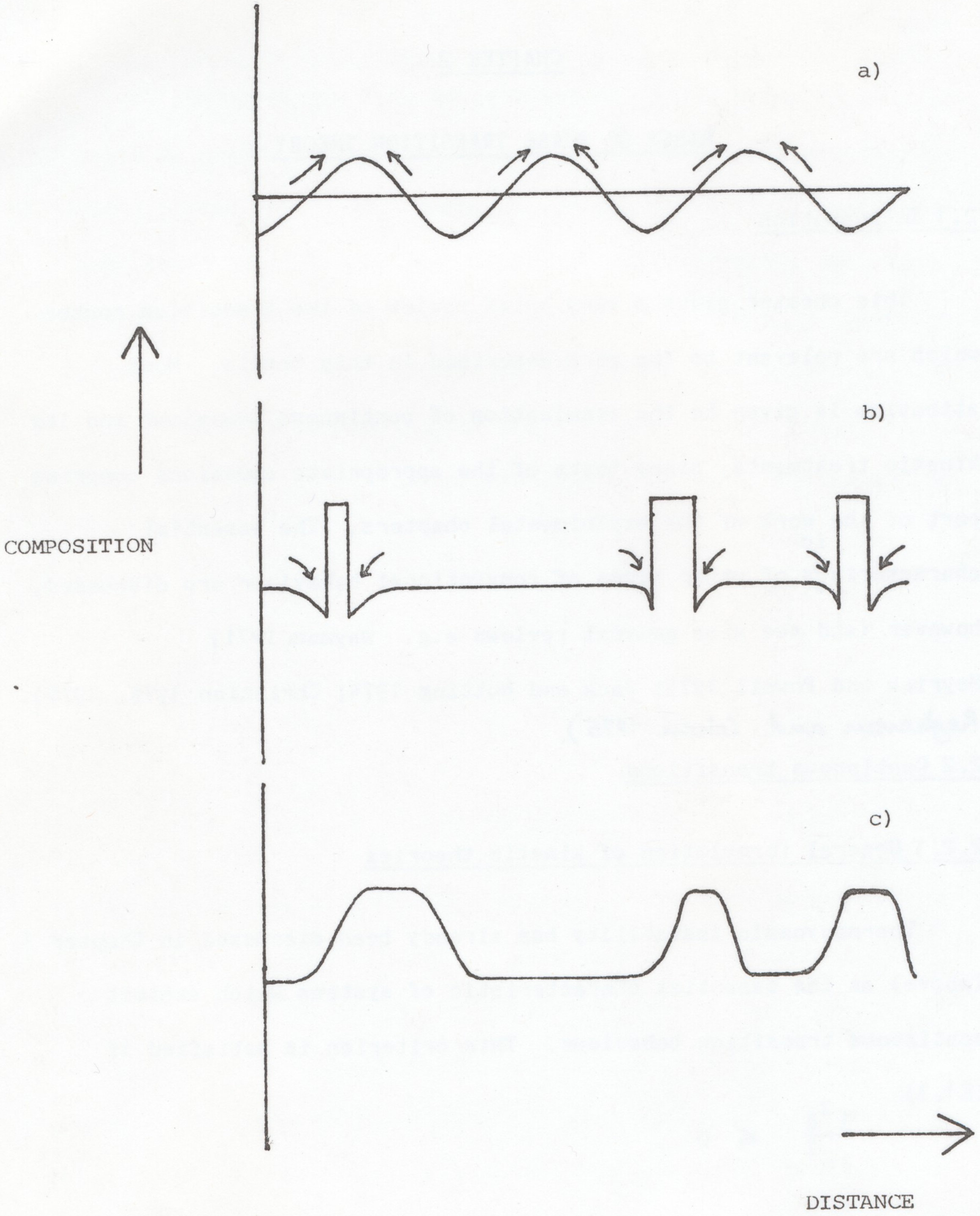

Figure 2.1 Idealized composition profiles for three cases of phase separation:- a) spinodal clustering, b) classical nucleation, c) non-classical nucleation.

continuum. The solution which is considered below is that of Cahn, upon which much research into spinodal processes has been based. Order-disorder transitions, which may only be modelled using lattice theories, are introduced in section 2.2.3 and are discussed as solution of unified theories of continuous transitions in Section 2.2.4.

2.2.2 Spinodal decomposition

2.2.2i The linearized diffusion equation (one-dimensional)

The linearized equation, due originally to Cahn (1961, 1962a), has been reviewed several times (e.g. Cahn 1968, 1971; Hilliard 1970; Cahn and Hilliard 1971; de Fontaine 1975a). For a system containing two atomic species, A and B, the flux of each species is proportional to the gradient in chemical potential with respect to a fixed reference plane. The change in chemical potential itself corresponds to the variation in free energy with composition. Therefore, in the absence of strain or composition gradient effects :

$$-\tilde{J}_A = M f''_A \nabla c_A \qquad \text{....E2.1}$$

By comparison with Fick's second law and conversion to interdiffusional flux, this equation may be rewritten as :

$$-\tilde{J} = \tilde{D} \nabla c_A \qquad \text{....E2.2}$$

in which $\tilde{D}$ takes the sign of the derivative $(\partial^2 f/\partial c^2)$ and is thus negative inside the spinodal. Figure 2.1a illustrates this "uphill" diffusion for a simple clustering sine wave composition profile. This may be compared with diffusion down the concentration gradient in fig.2.1b. Figures 2.1b and c depict model profiles for two cases of nucleation (classical and non-classical respectively) which are considered in section 2.2. below.

A composition gradient term (Cahn and Hilliard 1959a) may be added next to the chemical potential equation :

$$(\mu_A - \mu_B) = f'_A - 2K\nabla^2 c_A \qquad \text{....E2.3}$$

giving the flux equation :

$$-\tilde{J} = M f'' \nabla c - 2 M K \nabla^3 c \qquad \text{....E2.4}$$

The time dependent diffusion equation required is then obtained by taking the divergence of equation E2.4 to yield :

$$\frac{\partial c}{\partial t} = Mf''\nabla^2 c - 2MK\nabla^4 c + \text{non-linear terms} \qquad \text{....E2.5}$$

This equation (E2.5) has a sine-wave solution (Cahn 1961) :

$$c - c_o = \exp(\, R(\tilde{\beta})t\,)\cos\underline{\beta}.\underline{r} \qquad \text{....E2.6}$$

Resubstitution of the solution into the diffusion equation then produces the relationship

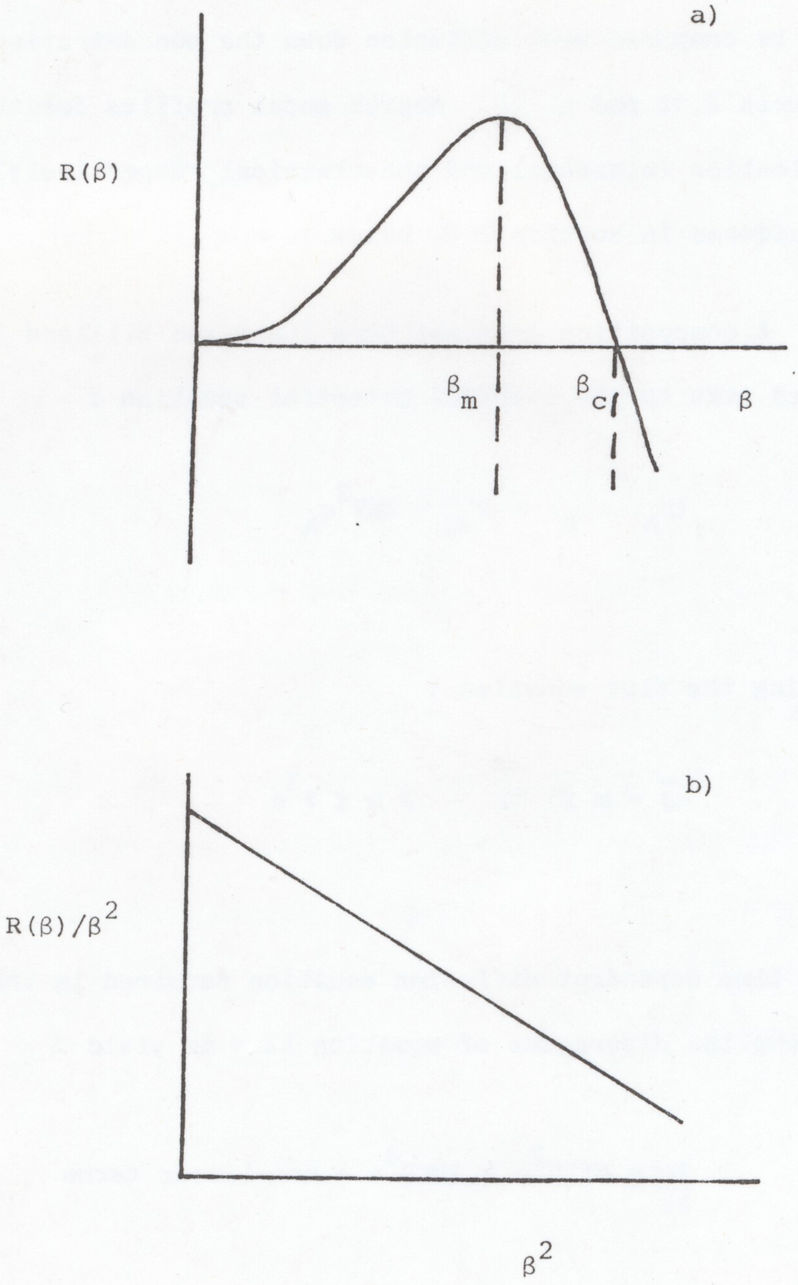

Figure 2.2 Idealized plots for testing the validity of Cahn's linear diffusion equation for spinodal decomposition:- a) $R(\beta)$ vs. β, b) $R(\beta)/\beta^2$ vs. β^2.

$$R(\beta) = -M\beta^2 (f'' + 2K\beta^2) \qquad \text{....E2.7}$$

in which the amplification rate of a selected composition modulation of wave-number β is an experimentally measurable quantity.

The addition of other factors, such as strain energies, to the flux equation (Cahn 1962a), results in the addition of more terms to the amplification factor equation. Thus for coherent isotropic solids (Cahn 1961):

$$R(\beta) = -M\beta^2 (f'' + 2\eta^2 Y + 2K\beta^2) \qquad \text{....E2.8}$$

given that

$$Y = E/ (1 - \nu) \qquad \text{....E2.9}$$

The important predictions of equation, E2.8, are that i) the plot of $R(\beta)$ versus β shows a positive maximum at small β, falling towards a cut-off at β_c as β increases and ii) $R(\beta)/\beta^2$ against β^2 is linear and of negative gradient. These criteria are illustrated in figure 2.2. Experimental tests of this equation, shown in many cases to be a good approximation for spinodal studies (although incorrect in some details), are discussed by Hilliard 1970 and Ditchek and

Schwartz 1979.

2.2.1ii Extensions of the Cahn theory

There are many extensions of the Cahn model (e.g. applications to ternary systems (Morral and Cahn 1971), continuous cooling (Huston, Cahn and Hilliard 1966), elastic anisotropy and coarsening (reviews Hilliard 1970 and Ditchek and Schwartz 1979)). Of particular interest for the present study is the result of Cahn 1966 that cubic materials showing some strain field develop compositional modulations in preferred directions, <100> and <111> for f.c.c. and b.c.c. alloys respectively. This eventually leads, by stress field interactions, to the alignment of coarsening microstructures (Cahn 1969) such as are found in nickel-base alloys (e.g. Tyapkin 1977). Further theoretical development and specific study of coarsening in terms of the behaviour of harmonic solutions of the diffusion equation were provided by extension of the non-linear equation to three dimensions (Cahn 1966 and see also Ditchek and Schwartz 1980).

Recent developments of spinodal theory (see Ditchek and Schwartz 1979) have also considered the construction and solution of non-linear equations. Contributions include the work of Cook 1970 on thermal fluctuations, the theory of Langer and co-workers which encompasses thermal fluctuations and other non-linear terms (Langer 1971, 1973, Langer and Bar-on 1973, Langer, Bar-on and Miller 1975) and studies by Abraham 1976. An alternative analysis by Binder and co-workers (Binder and Stauffer 1976, Mirold and Binder 1977) approaches the spinodal from the metastable region. This method allows the activation barrier to nucleation (see section 2.3 below for the probabilistic equation) to decrease to <kT, but not to zero. The

result correctly models behaviour at the miscibility gap itself. Computer simulations of spinodal decomposition have been made by Lebowitz and Kalos 1976.

2.2.3 Order-disorder transitions

2.2.3i Statistical theories

Prior to the development of continuous reaction theory studies of order-disorder transitions and their kinetics were purely statistical. A complete examination of all these models, based variously upon superlattice site occupation (see below) or bond energy summations (e.g. Clapp and Moss 1968a, 1968b) is beyond the scope of this dissertation. Details may be obtained from reviews (e.g. Krivoglaz and Smirnov 1964; Cohen 1970; Moss 1973).

The Bragg-Williams theory may be taken as a simple example. This theory, in its simplest form, specifies the degree of long range order, S, as a function of "correct" lattice site occupation:

$$S = a + b\alpha_r \qquad \text{....E2.10}$$

However, there exist two immediate draw-backs to this representation. Difficulties are experienced in the modelling of off-stoichiometric alloys and in summation over anti-phase domain boundaries. A more complex weighted summation must be employed in the latter case (Cohen 1970). An example of kinetic treatment of the Bragg-Williams theory has been provided by Dienes 1955.

2.2.3ii Continuous Theories

Four major continuous ordering theories, all of which consider the growth of ordering waves of superlattice dimensions are due to Ling and Starke 1971, Taunt and Ralph 1974 ("modular ordering"), Khachaturyan 1978 and de Fontaine 1979 (also Yamauchi and de Fontaine 1974). Recently Kubo and Wayman 1980 have also considered spinodal decomposition in ordered alloys. The two treatments by Khachaturyan and de Fontaine, which are essentially parallel developments of the same "static concentration wave" theory, have both been reviewed recently by their originators (Khachaturyan 1978, de Fontaine 1979). For the purpose of brevity the present dissertation considers only the de Fontaine formulation.

2.2.4 Unified theories of continuous transformation

2.2.4i The Cook,de Fontaine and Hilliard theory

The first unified theory (Cook, de Fontaine and Hilliard 1969) amalgamated the instability treatments of Hillert 1961 and Cahn 1961, 1962a to produce a discrete lattice diffusion equation with appropriate solutions for both ordering and clustering reactions. In terms of modification of the equations quoted above for the Cahn theory, the new ordering solution is generated by replacing β^2 by

$$B^2 = \left(\frac{2}{d^2}\right)(1 - \cos(\beta d)) \qquad \text{....E2.11}$$

Interestingly, further expansion of cos(βd) shows that the error in

Figure 2.3 (after Cook, de Fontaine and Hilliard 1969).

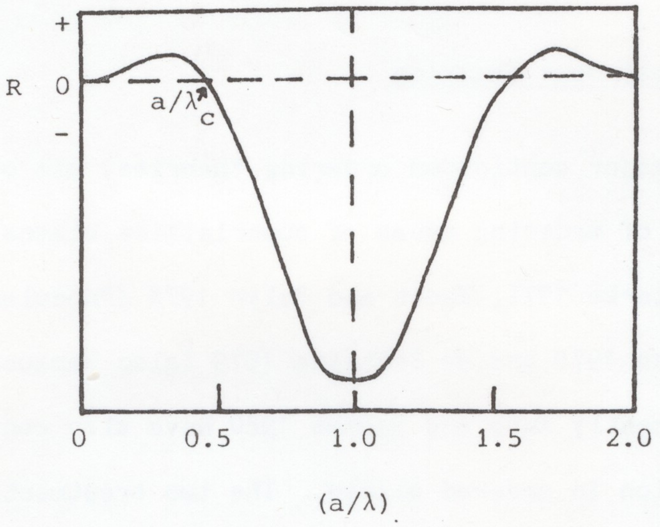

Figure 2.3a Plot of amplification factor R vs. a/λ for a system inside the spinodal.

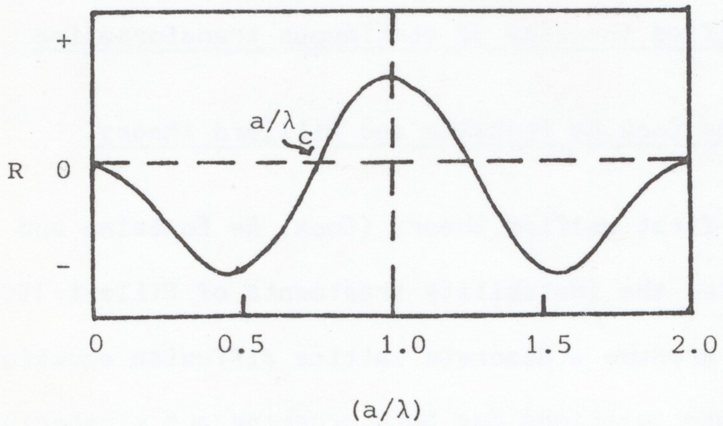

Figure 2.3b Plot of amplification factor R vs. a/λ for an ordering system below the critical temperature.

the continuum theory is of the order of $(\beta^2 d^2/12)$, which is small for most clustering phenomena. Figure 2.3 reproduces the amplification factor versus a/λ plots of Cook, de Fontaine and Hilliard for ordering and clustering systems, demonstrating that many characteristics of the separate reactions are inverses of one another.

2.2.4ii Fourier Representation

A full unified and reformulated theory, encompassing the work of Cahn 1961, 1962a, Hillert 1961, and Cook, de Fontaine and Hilliard 1969, the fluctuation studies of Cook 1970 and the microelasticity considerations of Cook and de Fontaine 1969 was provided by de Fontaine and Cook 1971. Defining a function Ψ(h) as

$$\Psi(h) = F(h) + G(h) \qquad \text{....E2.12}$$

where F and G are the elastic free energy and chemical free energy respectively and h an allowed lattice site. The total free energy may then be written in Fourier notation as

$$F_t = \frac{N}{2} \sum_h \Psi(h) Q(h) \qquad \text{....E2.13}$$

where Q(h) is the Fourier transform of the concentration covariance (harmonic concentration waves). Just as in the Cahn approach, a diffusion equation for the rate of concentration variation is constructed, giving a general amplification factor

$$\alpha(h) = -M\ \beta(h)\Psi(h) \qquad \text{....E2.14}$$

with a solution

$$V(h) = V_o(h)\ \exp(\ \alpha(h)t\ ) \qquad \text{....E2.15}$$

such that the composition waves V(h) again grow exponentially with time.

This theory was then developed to produce a lattice wave description of clustering and ordering in multicomponent systems(de Fontaine 1972, 1973a,b, 1975a-c), using a time-averaged concentration in order to represent the n components. Of particular value to the present study is a detailed description (de Fontaine 1975a) of different modes of ordering in terms of symmetry properties of the reciprocal lattice (see Landau and Lifshitz 1969). Defining spinodal clustering and spinodal ordering respectively as long- and short-wavelength events governed solely by kinetic factors (i.e. equilibrium vectors are not necessarily produced upon initial decomposition), these may be differentiated from continuous ordering, in which

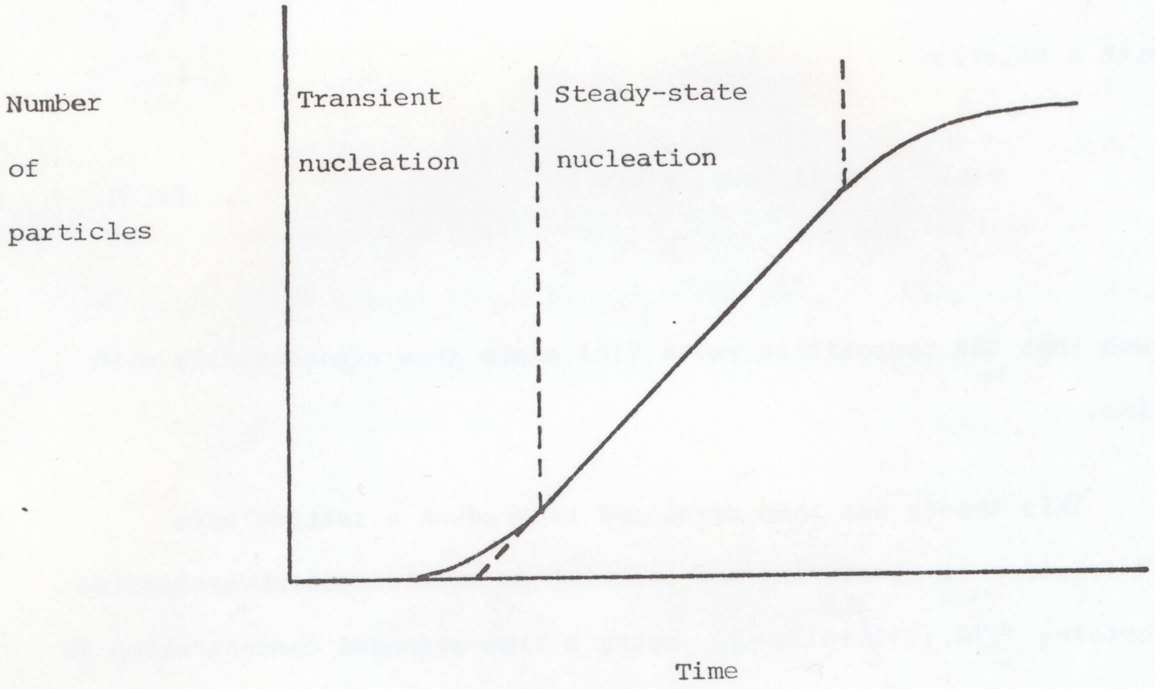

Figure 2.4 Number of particles nucleated per unit volume, N/V, vs. time, t, showing the incubation period, steady state nucleation and termination of the reaction (after Russell 1969a).

equilibrium structures are always generated.

2.3 Homogeneous Nucleation

2.3.1 General kinetic principles

In contrast to phenomenological treatments of continuous decomposition, kinetic analyses of nucleation are probabilistic, calculating expectation values for the rate at which critical nucleus formation is achieved as a sum of the probabilities of growth and decay of all cluster sizes.

2.3.2 Development of the classical theory

Classical theories of nucleation (reviews Russell 1970; Christian 1975) are founded upon expressions of Volmer and Weber 1926 and Becker and Doering 1935. These expressions calculated the statistical distribution function of embryos and the nucleation rate for the steady state. Current theories of solid state nucleation treat the quasi-steady state in two parts, namely the approach to dynamic equilibrium and the steady state itself. For the approach to the steady state Russell 1970 shows that the rate of critical nucleus formation is given by

$$J_k(t) = J_k^s \exp(-\tau/t) \qquad \text{....E2.16}$$

with an incubation time τ. A profile of nucleation rate against time, taken from Russell 1969a, is shown in figure 2.4. Present theories for the steady state regime are based upon the analysis of Turnbull and Fisher 1949. This is essentially an expansion of the Becker-

Doering approach. The net nucleation rate is then given by

$$J_k^{\,s} = Z \beta_k \, c_k^{\,o} \qquad \text{....E2.17}$$

where

$$Z = \left(\frac{-1}{2\pi kT} \left(\frac{\partial^2 \Delta G_n^{\,o}}{\partial n^2} \right) \right)^{1/2} \qquad \text{....E2.17a}$$

The above analyses assume that the nucleus and matrix are completely incoherent and that the nucleus is of uniform and equilibrium composition. These assumptions, and their correction in classical analysis, are discussed in reviews by Russell 1970 and Christian 1975. Also discussed are the effects of surface and elastic anisotropy (see Eshelby 1957 for study of precipitate shape changes). Alternative studies of nucleation using statistical mechanics have been provided by Lothe and Pound 1969. An example of experimental investigation is the work of Servi and Turnbull 1966 on copper-cobalt alloys.

2.3.3 Non-classical nucleation

An alternative approach for studies of diffuse-interface phenomena has been provided by Cahn 1962b. This non-classical method, based upon an earlier study of fluids by Cahn and Hilliard 1959b, closely resembles continuum studies (see section 2.2.2i above) in that a free energy function having the properties of a chemical potential is formulated. Again the function contains terms for gradient energy (i.e. free energy change with composition) and for strain. Thus the critical nucleus which is deduced as a fluctuation of the system describes most coherent nucleation phenomena with equilibrium composition strictly only at the centre of the new phase. Composition profiles for classical and non-classical nucleation models are shown in figures 2.1b and 2.1c respectively.

2.4 Heterogeneous Processes

2.4.1 General heterogeneous nucleation

Heterogeneous reactions (reviews Hornbogen 1965; Nicholson 1970; Russell 1970; Christian 1975; Aaronson, Lee and Russell 1978), "catalysed" by access to stored energy at a host defect, are favoured kinetically with respect to homogeneous nucleation because the activation barrier is lower. Complete dominance of the faster process is only limited by the availability of "catalyst" sites.

Examples of studies of the roles of specific defects (considered individually in the reviews) are the work of Cahn 1956 and Russell 1969a (grain boundaries), Cahn 1957 (dislocations) and Russell 1969b (vacancy effects). Microstructural aspects of the transformations are reviewed by Hornbogen 1969 and Nicholson 1970. Specific examples of general heterogeneous nucleation are grain boundary carbides in steels (e.g. Edmonds and Honeycombe 1978), dislocation decoration in iron-nitrogen systems (Hornbogen 1962) and so-called "athermal nucleation" on pre-existing particles in aluminium-zinc (Lorimer and Nicholson 1969).

2.4.2 Cellular decomposition

Cellular precipitation is a specific case of heterogeneous activity. The general features of the transformation are i)nucleation of particles of one new phase at a grain boundary, the particles matching a habit plane in one grain and presenting an incoherent boundary to the second (see Turnbull and Tu 1970 for details), ii) subsequent growth of two product phases in lamellar fashion by advance of the incoherent boundary.

The various theories describing both nucleation and growth events have been reviewed several times. The following reviews and original references give further details: Turnbull 1955; Cahn 1959; Liu and Aaronson 1968; Hillert 1969, 1972; Tu and Turnbull 1969; Turnbull and Tu 1970; Aaronson and Aaron 1972; Fournelle and Clarke 1972; Hornbogen 1972; Tu 1972; Sundquist 1973; Christian 1975; Meyrick 1976, 1979; Gust 1979; Ecob, Bee and Ralph 1980.

2.5 Growth and coarsening

Particle growth is defined to occur when diffusion fields of neighbouring particles do not overlap (e.g.Christian 1975). Coarsening relates to increase in particle size at constant volume fraction, while a change in volume fraction of second phase coupled with overlap of diffusion fields impies growth-plus-coarsening.

2.5.1 Interface versus diffusion control

Two modes of growth and coarsening may be distinguished. The first employs interface control (IC), where the rate-determining step is the chemical reaction of addition of solute to the new phase and the second occurs under volume diffusion control (VDC) which is limited only by solute accessibilty (see reviews by Christian 1975; Hillert 1975; Aaronson 1979). The exact mechanism of IC i.e. random solute addition or step motion, depends upon the driving force for the reaction (Cahn 1960). A step motion (Hillert 1969; Aaronson, Laird and Kinsman 1970; Aaronson, Lee and Russell 1978; Aaronson 1979;) represents metastable equilibrium.

VDC, occurring only by random and simultaneous solute addition, generally operates where there is a compositional change across a moving boundary, with associated composition gradient and often volume change effects (e.g. nickel-aluminium alloys, Ardell and Nicholson 1966). Specific details of the effects upon growth of precipitate morphology, interface structure and strain are discussed by Christian 1975 and Aaronson 1979.

2.5.2 Kinetics of Coarsening

The most generally accepted rate equations for both VDC and IC are founded upon analyses by Lifshitz and Slyozov 1961 and Wagner 1961 (known collectively as the L-S-W theory, see also Greenwood 1956, 1969; Christian 1975; Kahlweit 1976). Based upon the assumption that uniform attachment and detachment of solute occurs over the entire surface, the L-S-W theory predicts the following rate equations:

$$\text{VDC} \quad r^3 - r_o^3 = k_1 t \qquad \text{....E2.18}$$

$$\text{IC} \quad r^2 - r_o^2 = k_2 t \qquad \text{....E2.19}$$

These equations have been shown to obtain approximately in many experimental situations e.g. Ardell 1969, Ardell, Nicholson and Eshelby 1966.

Alternative kinetic analyses depending upon step growth rather than uniform interface advance are presently appearing in the literature e.g. Shiflet, Aaronson and Courtney 1979.

Summary

This chapter briefly reviews theories of some possible transition behaviours which may be displayed by supersaturated nickel-base alloys. On a general basis, and assuming as a first approximation that transformations are independent, the observable characteristics are:

1)Spinodal: a negative diffusion coefficient.

2)Order-disorder: the appearance of superlattice reflections in diffraction experiments.

3)Homogeneous nucleation: an incubation time for appearance of the second phase. The new phase should be randomly dispersed i.e. independently of defects.

4)General heterogeneous precipitation: decoration of defects.

5)Cellular decomposition: coupled nucleation and growth of two phases in colonies emanating from grain boundaries.

6)General coarsening: increase in mean particle size, with accompanying shape changes and alignment (constant volume fraction).