Phase transformations—a physicist's perception

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Abstract. Echoing a recent remark by Prof. Ramaseshan, a perspective review is made of the field of phase transformation, highlighting areas that might appeal to physicists. Prominent in this category are the study of ground state structures, the study of phase diagrams and the study of kinetic phenomena.

Enumeration of ground state structures calls for inputs from group theory as well as reliable potentials, and physicists are therefore well equipped to make significant contributions. The theoretical analysis of phase diagrams (concerning which much experimental information already exists) raises challenging questions in equilibrium statistical mechanics. Since the problems map to Ising models of varying complexity and their generalizations, there are also very interesting connections to magnetism. Lately, computer simulation has added a new dimension, opening up fresh vistas both for theory and experiments. The study of kinetics belongs to the newly emerging area of non-equilibrium statistical mechanics. The focus being on *temporal* phenomena, physicists can play a key role, particularly through the application of various types of relaxation spectroscopy. On the theoretical side too there are challenging problems, especially on account of the dominance of nonlinearities. Indeed if one is bold enough, one could even speculate on possible universalities underlying the complex microstructures invariably seen in late-stage evolution. In short, though the subject of phase transformations has thus far been nursed predominantly by metallurgists, there is enough room for physicists to make an independent entry and to make distinctive contributions.

Keywords. Phase transformations; phase diagrams; spinodal decomposition; ordering kinetics.

1. Introduction

The theme of this paper relates to a remark made by Prof. Ramaseshan at the Baroda Seminar on Thrust Areas in Physics, and it is perhaps relevant to begin by outlining the background.

Around 1980, the Department of Science and Technology (DST) initiated an intensive exercise to identify Thrust Areas in various scientific disciplines. As a part of this, a Seminar was organized in Baroda during November 1981 to which were invited a cross-section of active physicists in the country. Although the ostensible purpose of the Seminar was to aid the DST in identifying areas which it could fund selectively, Dr. Ramanna who presided made the suggestion that since there was a rare gathering of physicists with diverse interests, the occasion should in fact be utilized to draw up something like a National Plan for Physics. A part of this Plan could then be funded by the DST, and the balance by other appropriate agencies. This suggestion was greeted with enthusiasm, and several exciting proposals were unveiled by those present. Intervening in the discussion, Prof. Ramaseshan remarked that while large projects in areas like gamma-ray astronomy or high-energy physics were no doubt to be commended and also needed, some thought should also be given to researchers in small

This paper was originally prepared for the 60th birthday volume of Prof. S Ramaseshan.

universities, most of whom remained outside the orbit of "big science". He went on to emphasize that in drawing up a list of Thrust Areas, consideration must also be given to subjects like phase transformations which not only offered challenge but also did not require massive funding and could therefore be pursued by those with modest resources. I was quite delighted by this suggestion and the specific reference to Phase Transformations since I had just then begun to gravitate towards the subject myself.

Now the subject of phase transformations is well established amongst metallurgists. Physicists, on the other hand, have generally stayed away possibly because it appeared messy to them. However, in the light of many recent developments in physics (*e.g.* advances in the understanding of nonlinear phenomena), some of these so-called messier aspects have acquired an attraction of their own. The main purpose of this article therefore is to draw the attention of physicists to such aspects, and hopefully induce at least some of them to enter this area. The paper is thus essentially a perspective review addressed to physicists, keeping in mind the needs of those who may be totally unfamiliar with the subject. However, in the spirit of Prof. Ramaseshan's remarks, interspersed are several suggestions for further work for those adventurous enough to enter the area.

2. Preliminaries

2.1 Some elementary facts

To most physicists, a phase transition usually calls to mind a change of state like solid to liquid etc. Metallurgists on the other hand, are interested mainly in transformations *within* the solid state. Of the many variations possible even in this category, we restrict attention to order-disorder transformations associated with compositional fluctuations. In the interest of simplicity, we shall further confine ourselves to binary alloys $A_{1-x}B_x$ $0 \leq x \leq 1$ (*e.g.* Al-Zn or Cu-Au).

To fix our ideas, let us consider a Cu-Zn alloy (β -brass) with equiatomic composition *i.e.* $x = 0.5$. Both at high as well as at low temperatures, there is a well-defined lattice (*viz* bcc) associated with this alloy. However, there is a difference in the way the atoms are distributed amongst the lattice sites. Above 468°C , the occupancy of the lattice sites by Cu and Zn atoms is statistical whereas below that temperature, there is a well-defined order in the arrangement (see figure 1). One can intuitively see that entropy considerations must dominate at high temperatures leading to disorder. On the other hand, interatomic forces assert themselves at low temperatures leading to an ordered structure as in figure 1b. The temperature 468°C represents a transition point for the order-disorder process.

In the example just discussed, every atom has an atom of the other species as a nearest neighbour in the ordered state, implying that the potential v_{AB} dominates over v_{AA} and v_{BB} . It could also happen that v_{AB} is not strong enough to achieve this in which case a different type of ordering ensues wherein, the material organizes itself into large crystalline domains rich in either *A* or *B* type atoms. Essentially, "birds of a feather flock together", and the phenomenon is often called *phase separation* or clustering.

Superficially, phase separation and an order-disorder transition (like the one in β -brass) appear different but if we associate a wavelength scale with the two processes as is schematically done for a 1-D example in figure 2, then we can discuss the two in the same framework, as is done for ferro- and antiferromagnetism. Phase separation being

Figure 1. Schematic illustration of order-disorder in β -brass. The structure is bcc in both phases but in the disordered phase, the occupation of the lattice sites by the two species of atoms (shaded and full) is strictly statistical as in (a).

Figure 2. One-dimensional example to illustrate the different wavelength scales for clustering and ordering.

similar to ferromagnetic ordering will be associated with a wavevector $k \sim 0$ while order-disorder transition being similar to antiferromagnetism will be associated with a wavevector $k \sim$ zone boundary.

2.2 Phase diagrams—a primer

A study of phase transformations without some knowledge of phase diagrams is hardly possible. Most physicists are no doubt familiar with phase diagrams for monatomic systems but once one enters the world of multicomponent systems, phase diagrams can become quite complex, indeed even for binaries such as we shall be considering. A brief primer on phase diagrams is therefore useful.

Figure 3. Schematic plot of energy as a function of composition for the three situations discussed in the text.

Broadly speaking, a phase is a state of aggregation. Our interest is in the various phases possible when two atomic species *A* and *B* are mixed together to form a solid at different temperatures and at different compositions. A phase diagram is therefore essentially a map of the various possible states of aggregation in the temperature-composition plane. From thermodynamics we know that the equilibrium state of a system is determined by the minimum of the free energy (FE) with respect to the appropriate thermodynamic variables. Accordingly, we direct attention now to the minimum of the FE at various temperatures and compositions. To start with we note that the free energy is given by

$$F = E - TS$$

where *E* is the internal energy*, *T* the temperature and *S* the entropy. In figure 3, *E* is plotted schematically as a function of composition (Wulff 1971). Here the dashed lines denote the energy before mixing and the solid lines that after the mixing. The 'ideal' situation is that shown in figure 3b where the energy does not change on mixing. More usually, one has either a positive or negative deviation from ideality as in figure 3a or c.

We next consider entropy, for which the situation prior to and after mixing will be as schematically depicted in figure 4. The results of the last two figures may now be

* Strictly speaking, we should have enthalpy $H (= E + pV)$ instead of *E*. However, most material processing is done around atmospheric pressure. From a practical point of view therefore *H* is well approximated by *E*.

Figure 4. (a). entropy of the $A_{1-x}B_x$ system before mixing. (b). sketch of entropy of mixing. The total will then be as in (c).

combined to visualize how F varies with composition at a given T . Of the several possibilities, that corresponding to negative deviation from ideality is of particular interest to us and the free energy curve for this situation is sketched in figure 5. To find the most stable arrangement that results after mixing at the chosen temperature T we must obviously look for the minima in F . Using this criterion, it is clear from the figure that if we prepare a mixture of composition c_B , then this mixture will be unstable. It will seek stability by splitting into a mixture of two solutions of compositions c_B^1 and c_B^2 . Observe that after such a separation, the F value diminishes from F_u to F_s .

The above scenario applies to all mixtures with composition in the range c_B^1 to c_B^2 , and we conclude that for all compositions in this range, a *mixture of two phases* is the most stable state. This is the phase separation briefly mentioned earlier. When T is increased slightly, essentially a similar situation is obtained, with c_B^1 moving slightly away from the A end and c_B^2 moving slightly away from B . As T increases, c_B^1 and c_B^2 approach each other continuously, eventually merging at some temperature T_c . For $T > T_c$, segregation into two phases of different compositions no longer occurs; instead the solid solution itself is stable, and we have a one-phase region. Thus, the locus of c_B^1 and c_B^2 in the temperature-composition plane provides a boundary separating the one-phase and two-phase regions of the solid. Figure 6 shows a portion of the phase diagram of Al-Zn where such a two-phase region exists.

It is of course not necessary that when two atomic species are mixed, one should always get phase separation at low temperatures. Instead one could also obtain ordering, as *e.g.* in Cu-Au systems. We shall have more to say later about these two

Figure 5. Free energy curve corresponding to a particular temperature for negative deviation from ideality. F_u is the value corresponding to the unstable state created immediately after mixing, while F_s is the value corresponding to the stable state. For every composition in the shaded region, the terminal state is a mixture of two phases of compositions c_B^1 and c_B^2 .

Figure 6. Portion of the Al-Zn phase diagram showing the two-phase region.

representative cases of phase separation and ordering.* For the nonce let us note that the solid mixtures we are considering are restricted to the substitutional type *i.e.* if we take a perfect *A* type solid and add *B* type atoms, the latter replace *A* at the lattice sites. For this to be possible, the following criteria must be broadly satisfied:

* Phase separation is *also* a type of ordering! Only the wavelength scale is different.

(i) The atomic radii of the two elements must be within 15% of each other. (ii) The crystal structures of *A* and *B* must be the same. (iii) The valence of *A* and *B* must not differ by more than unity. (iv) The electronegativity must be nearly equal.

While we have sketched the concept of the phase diagram from (elementary) theoretical considerations, we should remember that metallurgists often actually map phase diagrams by doing experiments. Indeed there is a wealth of such data (Hansen 1958), and, as we shall see later, a theoretical analysis of such diagrams is a possible avenue of interest for physicists.

2.3 Areas of interest

Given the fact that metallurgists have already contributed much to the subject, especially on the experimental side, it is natural to wonder whether there is any room for physicists (*e.g.* Chen *et al* (1979) point out that prior to the late sixties, there were at least 36 books and reviews on the subject. Also, there have been several major conferences held on the subject during the last decade). However, a careful appraisal does show that there are certain areas in this vast domain where physicists could bring to bear tools that are their specialities. Prominent among these areas are:

(i) The elucidation of ground state structures, (ii) Calculation of phase diagrams, and (iii) The study of kinetic phenomena.

Of the above, the calculation of phase diagrams belongs to the realm of equilibrium statistical mechanics, and, as we shall see in § 3, raises problems in the traditions of Onsager since one mainly deals with Ising models of various complexity. The study of kinetic phenomena on the other hand, takes one to the newly emerging area of nonequilibrium statistical mechanics. The presence of nonlinearities is an added attraction.

In terms of tools, apart from neutron and x-ray scattering which are already familiar, physicists could also exploit various types of relaxation spectroscopy. No doubt the scattering techniques have already been used to some extent in the past but there is considerable scope for enhancing their applications. Particularly in the case of x-rays, the recent availability of synchrotron radiation opens up many new exciting possibilities. Also, there are many technical innovations like position-sensitive detectors that have hardly been used for such studies. As far as relaxation spectroscopic studies are concerned, the field is literally wide open. Complementing all these is the powerful technique of computer simulation, used already to some extent, but admitting of considerably more exploitation. In short, there is plenty of scope for physicists to make a distinctive contribution of their own to the field, although they may be latecomers.

3. Equilibrium structures

3.1 Ground state structures

Given a disordered structure (say belonging to the fcc lattice), there arises the general question of the type of ordering that will occur at lower temperatures. In a simple situation as in β -brass (see figure 1), one could perhaps have made a good guess of the ordered structure purely from inspection. However, such guesses are not always easy,

requiring, as they do, considerable crystallographic insight. A systematic approach to enumerating the possible ordered structures has been evolved by Soviet scientists, inspired largely by Landau's theory of phase transitions.

Before sketching the work of the Soviet School, we note first that the ground state structure is the atomic arrangement assumed by the solid at absolute zero of temperature. While it is the onus of theory to predict this structure from first principles, a considerable body of information about the structures actually occurring in Nature has already been accumulated through diffraction experiments. Next we remark that ordering is essentially characterized by the appearance of a superlattice. The superlattice structure that emerges depends on (i) the structure of the parent lattice, (ii) the interatomic forces, and (iii) the atomic composition of the system. If, for example, we consider the fcc lattice, then several ordered structures based on it are possible some of which are illustrated in figure 7. The distribution of the various superlattices possible amongst the alloys realizable by combining various elements in the periodic table have been painstakingly compiled by Kozlov *et al* (1974) and the data is worth glancing through.

Returning to the enumeration of possible superlattice structures, the basic idea is the following: Let us first describe the atomic distribution by means of a function $n(\mathbf{r})$ which gives the probability of finding an atom of some definite kind at site $\mathbf{r}$ of the lattice. In a disordered alloy $n(\mathbf{r})$ is a constant c . On the other hand, when the system orders, $n(\mathbf{r})$ assumes m (say) different values $n_1, n_2, \dots, n_m$ at the m sublattices associated with the structure. In brass, *e.g.*, $m = 2$. Of course, $n(\mathbf{r})$ corresponding to a particular sublattice position has the same value in all the unit cells. The problem now is to determine the possible distribution $n(\mathbf{r})$ can have when ordering occurs. Khachaturyan (1974) approaches this by regarding $n(\mathbf{r})$ as being built up of static composition waves as follows:

$$n(\mathbf{r}) = C + \frac{1}{2} \sum_{\mathbf{k}} \{ Q(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) + \text{C.C.} \}. \quad (1)$$

Figure 7. Some of the ordered structures observed in fcc lattices.

Here the summation over $\mathbf{k}$ runs over the first Brillouin zone of the disordered alloy. $Q(\mathbf{k})$ is the (complex) amplitude of the concentration wave of wavevector $\mathbf{k}$. Following Landau, one now writes the sum over $\mathbf{k}$ as sums over various possible stars one can form in the Brillouin zone (see figure 8). With this regrouping,

$$n(\mathbf{r}) = C + \sum_s \eta_s e_s(\mathbf{r}), \quad (2)$$

where

$$e_s(\mathbf{r}) = \frac{1}{2} \sum_i \{ \gamma_s(\mathbf{k}_i(\star s)) \exp i \mathbf{k}_i(\star s) \cdot \mathbf{r} + \text{C.C.} \}. \quad (3)$$

In (3), the summation runs over all the members i of the star s whereas in (2) the sum is over all the possible stars. Together, all the wavevectors in the Brillouin zone are accounted for. Comparing with (1)

$$Q(\mathbf{k}_i) = \eta_s \gamma_s(\mathbf{k}_i). \quad (4)$$

The quantities η_s are the long-range parameters which assume the value 0 in the disordered state, and the value 1 at 0°K. Since composition is conserved, the number of order parameters required to describe the ordered structure will be $(m - 1)$. Later (in § 3.3) we shall see that the order parameters η_s are essentially the analogues of sublattice magnetizations.

Although formally the summation in (2) ranges over all the stars in the Brillouin zone, in practice (—and this is in the spirit of Landau's theory of phase transition) one

Figure 8. Illustration of the concept of star of the wavevector for a square lattice. The dots indicate the reciprocal lattice points, and the dashed line the central Brillouin Zone. The cluster of eight arrows represents a star. Starting from any one of these arrows, one can generate the entire cluster by a systematic application of the point group operations of the lattice.

supposes that a given ordering is associated uniquely with composition waves corresponding to a particular star. For illustration, let us consider ordering in Cu-Au alloys. X-ray experiments have revealed that ordering is linked to the appearance of superlattice $\{100\}$ reflections (which, of course, are forbidden in the disordered state). It is reasonable therefore to suppose that the ordering is governed by the star of the wavevector $[100]$ which comprises of the wavevectors $[100]$, $[010]$ and $[001]$. Thus (2) can be written as

$$n(\mathbf{r}) = C + \eta \{ \gamma_1 \exp(i\mathbf{k}_1 \cdot \mathbf{r}) + \gamma_2 \exp(i\mathbf{k}_2 \cdot \mathbf{r}) + \gamma_3 \exp(i\mathbf{k}_3 \cdot \mathbf{r}) \}. \quad (5)$$

where $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ are the three wavevectors of the star. The lattice vector $\mathbf{r}$ can be expressed in terms of the (cubic) unit cell vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ as

$$\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3 \quad (6)$$

with $(x + y + z) = \text{constant}$. By letting $\mathbf{r}$ vary in (5), it is easily seen that $n(\mathbf{r})$ can take the following values

$$\begin{aligned} n_1 &= C + \eta(\gamma_1 + \gamma_2 + \gamma_3); & n_2 &= C + \eta(\gamma_1 - \gamma_2 - \gamma_3); \\ n_3 &= C + \eta(-\gamma_1 + \gamma_2 - \gamma_3); & n_4 &= C + \eta(-\gamma_1 - \gamma_2 + \gamma_3). \end{aligned} \quad (7)$$

If now we invoke the fact that $(m - 1)$ equals the number of distinct order parameters and remember that in this case there is only one order parameter, namely η , we are led to the fact that $m = 2$ for Cu-Au. Hence n can take only two values at the set of all sites (xyz) of the fcc lattice, leading to the two possibilities

$$(i) \ n_1 = n_4, \ n_2 = n_3; \quad (ii) \ n_2 = n_3 = (n_1 + n_4). \quad (8)$$

The first alternative arises if $\gamma_1 = \gamma_2 = 0$ whence

$$n(xyz) = C + \eta\gamma_3 \exp(2\pi iz) = C \pm \eta\gamma \quad (9)$$

in alternate (001) planes. This is the so-called CuAu I structure. On the other hand, if alternative (ii) is to be realized, then we must have all the γ_i 's equal whence

$$\begin{aligned} n(xyz) &= C + \eta\gamma \{ \exp(2\pi ix) + \exp(2\pi iy) + \exp(2\pi iz) \} \\ &= \begin{cases} C + 3\eta\gamma & \text{at the corners of the unit cell cube} \\ C - 3\eta\gamma & \text{at the face centres.} \end{cases} \end{aligned} \quad (10)$$

This is the Cu_3Au structure.

The above example shows how symmetry considerations may be applied a la Landau's theory to obtain some idea of the superlattice structures possible. Merely enumerating possible superlattice structures alone is not enough. This is somewhat similar to the exercise often done for ferroelectrics, where one uses group theory to enumerate the type of ordered structures that can arise. Symmetry thus picks out the various possibilities; which of these is actually favoured depends of course on the interatomic forces. To illustrate, we once again consider the fcc lattice, and direct attention now to the internal energy. The three potentials to be considered are, $v_{AA}(r)$, $v_{BB}(r)$ and $v_{AB}(r)$. In terms of these pair potentials, the internal energy E may be expressed as

$$\mathcal{E} = \frac{1}{2} \sum_{ij} \sum_{l \neq m} v_{ij}(l - m) \langle \sigma_i(l) \sigma_j'(m) \rangle. \quad (11)$$

Here i, j refer to the species A, B while l and m denote lattice sites. The quantity σ is an occupation operator defined by

$$\begin{aligned}\sigma_A(l) &= 1 && \text{if site } l \text{ is occupied by an A-type atom} \\ &= 0 && \text{if site } l \text{ is not occupied by an A-type atom.}\end{aligned}\quad (12)$$

$\sigma_B(l)$ is defined similarly. The bracket denotes an average (here over the ground state). The lattice energy will evidently be determined by the correlations of the σ 's at the various sites, and the system will choose that atomic configuration for which $\mathcal{E}$ is a minimum.

It is convenient to introduce an operator $\gamma_i(l)$ which describes deviations from mean occupation by

$$\gamma_A(l) = \sigma_A(l) - c_A = \begin{cases} 1 - c_A, \\ -c_A, \end{cases}\quad (13)$$

where c_A is the concentration of A . Since $c_A + c_B = 1$, one has

$$\gamma_B(l) = -\gamma_A(l). \quad (14)$$

Using the γ 's, the part of the internal energy that relates to occupation deviations can be written as

$$E = \frac{1}{2} \sum_{ij} \sum_{l \neq m} v_{ij}(l-m) \langle \gamma_i(l) \gamma_j(m) \rangle. \quad (15)$$

By elementary manipulation, this can be written as

$$E = \frac{1}{2} \sum_{lm} V(l-m) \langle \gamma(l) \gamma(m) \rangle, \quad (16)$$

where we have written γ for γ_A , and V is an effective potential defined by

$$V(\mathbf{r}) = 2v_{AB}(\mathbf{r}) - v_{AA}(\mathbf{r}) - v_{BB}(\mathbf{r}). \quad (17)$$

In terms of Fourier transforms

$$E = \frac{N}{2} \sum_{\mathbf{k}} V(\mathbf{k}) |\Gamma(\mathbf{k})|^2 \quad (18)$$

where $\Gamma(\mathbf{k})$ is the transform of $\gamma(\mathbf{r})$.

The quantity $V(\mathbf{k})$ is periodic in reciprocal space reminiscent of, say, phonon dispersion curves, and will therefore have maxima, minima and saddle points (—the well-known van Hove (1953) singularities). The expectation now is that the state of order is governed primarily by where minima in $V(\mathbf{k})$ occur. One knows that barring unusual circumstances, minima of lattice periodic functions occur at points of high symmetry in the Brillouin zone (van Hove 1953). Thus, ordering is mainly associated with the build up of a compositional wave (also sometimes called concentration wave) with a wavevector corresponding to the special point where $V(\mathbf{k})$ has a minimum. This therefore is also the wavevector at which a superlattice reflection is seen in the diffraction pattern when ordering occurs. As may be expected, around the transition temperature there are critical fluctuations of the composition in this region of $\mathbf{k}$ -space and consequently there is an enhancement of the scattering in the superlattice reflection region just prior to ordering. We shall say more about critical scattering later.

The potential $V(\mathbf{r})$ depends on the details of the electronic structure, and is often not known with sufficient accuracy for present purposes. It is therefore customary to parametrize pair interactions in terms of interactions up to a specified set of neighbours. One now examines minima in $V(\mathbf{k})$ as the ratio (V_2/V_1) is varied (where V_1 and V_2 denote the first and second neighbour interactions). The results can be succinctly paraphrased as in figure 9 due to Clapp and Moss (1968) who followed Villain (1959) who had earlier made such plots for magnetic structures. Incidentally, we see from figure 9 that in a certain range of ratios, ordering occurs for $k = 0$ leading to clustering of like atoms.

Mention should also be made of the work of Richards and Cahn (1971) and various Japanese workers (Katsura and Narita 1973; Kudo and Katsura 1976; Kanamori and Kakehashi 1977) who have studied ground-state structures using a real-space analysis. Recently some rigorous methods for describing low temperature structures of very general lattice systems have also been developed (Progov and Sinai 1975, 1976; Holsztynski and Slawny 1978; Slawny 1979).

Although some territory has no doubt been covered in the work of the various above mentioned authors, there is considerable scope for further work. One might wonder whether ground-state structures are not encompassed in a study of the phase diagram as a whole (§ 3.2). Indeed they are; however an independent knowledge of ground state structures does help phase diagram calculations and in that sense is a worthwhile, stand-alone activity.

Before leaving the subject, a brief reference must be made to off-stoichiometric structures. Suppose, for instance, we consider an alloy where, say, the concentration of A species is slightly less than 0.5. The question now is what happens in the ordered state. One's first guess would be that small deviations from stoichiometry would be absorbed as defects. However, when the deviations are substantial, the situation may not be that

Figure 9. Location of minima of $V(\mathbf{k})$ as a function of the ratio V_2/V_1 for the fcc lattice. (After Clapp and Moss 1968).

simple. Krivoglaz and Smirnov (1965) suggested that at 0°K, an off-stoichiometric alloy decomposes into alloy of stoichiometric composition and a pure metal. It is not clear whether there is any experimental evidence in support of this suggestion. Kozlov *et al* (1974) have advanced the alternate idea that the excess atoms may undergo further ordering at suitable sites, leading to a new complex structure which they refer to as 'super-superstructure'. The experimental situation if assessed from the literature, can be quite bewildering to a physicist! When an alloy is prepared at high temperatures and cooled below the transition, it not only orders but develops a lot of microstructure; one has therefore to be quite careful in drawing the right conclusions.

One case worth mentioning explicitly is CuAu (nominal equiatomic composition). When this alloy is cooled from high temperatures, it transforms below 385°C into what is called the CuAu II structure illustrated in figure 10 (Ogawa 1974). There is an alternation every five cells, and the overall structure can be thought of as composed of antiphase domains of size $5b$. The oscillations are also referred to as long period oscillations (LPO). Such oscillations are reported for many ground state structures, and, in view of the extensive interest amongst physicists on charge density waves etc. are worth a close look (see also § 4.5). Returning to LPO's in Cu-Au alloys, there is evidence that the period $2M$ is not always an integral number (see figure 11) (Ogawa 1974). Noteworthy here is the fact that M varies with composition (which effectively alters the electron/atom ratio). There is also a lattice modulation of density related to the LPO. This, as well as the nonintegral values observed for M are interesting questions (Sato and Toth 1961) but unfortunately we cannot pursue them further here.

Another comment that needs to be made concerns the effective potential $V(r)$ in (17). Now an implicit assumption underlying (15) is that all ions always exactly occupy the lattice sites. In practice this is not so, and ions could deviate, *e.g.* on account of size. One must therefore allow for such 'positional relaxation', and evaluate the energy of the relaxed system. In effect, it amounts to modifying $V(k)$ as

$$V(k) \rightarrow V^{(1)}(k) = V(k) - \text{relaxation energy.} \quad (19)$$

Of course if the potential is parametrised, then the parameters refer actually to the effective potential $V^{(1)}$. For further details concerning the relaxation energy, a recent article by de Fontaine (1979) may be consulted.

Figure 10. Illustration of the long-period oscillation in CuAu II. After every five cells, there is an alternation in the occupancy pattern (after Ogawa 1974).

Figure 11. Variation of M with electron to atom ratio. The solid lines are theoretical curves (due to Sato and Toth 1961) corresponding to two assumptions (after Ogawa 1974).

3.2 Calculation of phase diagrams

The phase diagram problem is a logical extension of the ground state problem in that one now studies when order disappears.

It is convenient to discuss the problem in the language of Ising spins rather than in terms of the occupation operators σ introduced earlier. The Ising spin operator S_l associated to lattice site l is defined in terms of $\sigma_B(l)$ as

$$S_l = 1 - 2\sigma_B(l) = \begin{cases} +1 & \text{if site } l \text{ is occupied by an } A \text{ atom} \\ -1 & \text{if site } l \text{ is occupied by a } B \text{ atom.} \end{cases} \quad (20)$$

Observe that in terms of $\sigma_A(l)$,

$$S_l = 1 + 2\sigma_A(l). \quad (21)$$

Using the Ising spins to describe the Hamiltonian, the statistical mechanics of order-disorder can now be mapped into an appropriate Ising problem, establishing links with the rich traditions that already exist in this area.

Now at absolute zero of temperature, the spin system will be perfectly ordered. As the temperature is raised, some spins will flip (meaning A and B atoms will exchange places). Such flips no doubt cost energy but the entropy term $-TS$ in the expression for free energy provides the required compensation. However, the disorder cannot be increased indefinitely, and at every temperature there is an optimum disorder. If the disorder exceeds the optimum, then F increases due to increase of E whereas if it is less, then it again increases but due to inadequate cancellation from the entropy term. Equilibrium is thus dictated by the minimum of the free energy, and in the calculation

of the phase boundaries, the computation of this minimum is an important step.

Given the range of interaction of the Ising spins, the calculation of E is straightforward (and is discussed further in § 3.3). Far more problematical is the entropy term, and to appreciate the difficulty let us consider a 1-D Ising chain. We assume first that the chain is fully ordered (!) with all spins up (say). The entropy is then zero. At the other extreme where each spin is completely free to flip, there are 2^N configurations possible (N is the number of spins), and the corresponding entropy is $S = k_B \log 2^N = Nk_B \log 2$. The question is how does one calculate the entropy for situations in between where there is intermediate order. If, for example, we *definitely* know two spins alone are down and all the rest up then the number of configurations possible is a simple matter to work out. But unfortunately, we cannot make definitive statements about exactly how many spins are up and how many are down. We can at best have only statistical information about the state of order embodied in the correlation functions

$$\xi_1 = \langle S_l \rangle; \quad \xi_2 = \langle S_l S_m \rangle; \quad \xi_3 = \langle S_l S_m S_n \rangle \dots \quad (22)$$

The set $\{\xi_i\}$ must first be known and using it the entropy and indeed F itself must then be computed. Calculation of S in terms of the ξ 's is precisely where problems enter, for one must in principle know and use all correlation functions up to ξ_N . This evidently is also the place for approximations to make their entry!

Before discussing the approximations, we call attention to Onsager's (1944) famous paper on the 2-D square lattice Ising problem where he calculated the partition function exactly. This is not only a *tour de force* but also a touchstone for evaluating various approximation schemes (as we shall soon see).

The approximation schemes alluded to, reduce in effect to using a suitable subset of the full set $\{\xi_i\}$ of the correlation functions. The subset is so chosen that the group of spins involved form a cluster which is consistent both with the geometry of the lattice and the range of interactions (usually restricted to near neighbours (nn) and next nearest neighbours (nnn)).

Figure 12 gives samples of some clusters used in the study of ordering in fcc Ising lattices. In figure 12a the cluster is a regular tetrahedron made up of nn spins. In figure 12b one has a nn regular tetrahedron and an octahedron consisting of nn and nnn spins. Within a cluster itself one can identify subclusters *e.g.* the triangle (123) in figure 12b, which is in the overlap of the tetrahedron and the octahedron. Likewise, the triangle (126) in figure 12c is a subcluster shared by two irregular tetrahedra.

The entire computational scheme based on cluster approximation is known as the cluster variation method (cvm). As formally developed by Morita (1972), it is based on the exact variational principle of equilibrium statistical mechanics. In any given implementation of the cvm, one first chooses the largest cluster L one is going to work with. One then considers all the subclusters l consistent with L . Corresponding to each subcluster l , one now considers the various possible arrangement of spins/atoms. For instance, the arrangement in the triangle (123) could be (AAA) , (ABA) , (BAB) etc. If J_l denotes a configuration such as above, then we next need to know $x_{J_l}(l)$ the concentration of this configuration in the cluster l . It is in the calculation of the cluster configuration that the correlation functions enter. To illustrate, we again consider the triangular subcluster (123). Let p_1 , p_2 and p_3 denote the lattice sites. The correlation functions we then need are the single spin, two spin and three spin functions ξ_1 , ξ_2 , ξ_3

Figure 12. Some of the clusters used in CVM calculations for fcc lattices (a), tetrahedron used by Kikuchi *et al* 1980 (b) and (c) are larger clusters used by Sanchez and de Fontaine (1978, 1980, 1982).

respectively. In terms of these correlation functions, x_{AAB} , for example will be

$$x_{AAB} = \frac{1}{8} \{ 1 + (+1 + 1 - 1)\xi_1 + [(1 \times 1) + (1 \times -1) + (-1 \times 1)]\xi_2 + (1 \times 1 \times -1)\xi_3 \}. \quad (23)$$

The formal expressions for the cluster probabilities are:

$$\begin{aligned} x_i(p_1) &= \langle \sigma_i(p_1) \rangle = \frac{1}{2} \langle 1 + iS_{p_1} \rangle, \\ x_{ij}(p_1 p_2) &= \langle \sigma_i(p_1) \sigma_j(p_2) \rangle \\ &= \frac{1}{2^2} [1 + i \langle S_{p_1} \rangle + j \langle S_{p_2} \rangle + ij \langle S_{p_1} S_{p_2} \rangle], \\ x_{ijk}(p_1 p_2 p_3) &= \langle \sigma_i(p_1) \sigma_j(p_2) \sigma_k(p_3) \rangle \\ &= \frac{1}{2^3} [1 + i \langle S_{p_1} \rangle + j \langle S_{p_2} \rangle + k \langle S_{p_3} \rangle + ij \langle S_{p_1} S_{p_2} \rangle \\ &\quad + jk \langle S_{p_2} S_{p_3} \rangle \\ &\quad + ki \langle S_{p_3} S_{p_1} \rangle + ijk \langle S_{p_1} S_{p_2} S_{p_3} \rangle] \text{etc.} \end{aligned} \quad (24)$$

Here $i, j, k \dots$ take on values ± 1 for each of the two components in the system. (Result (23) thus readily follows from above).

The entropy can now be expressed as a series in cluster probabilities as

$$S \approx Nk_B \sum_{l=1}^L \gamma_l \sum_{j_l} x_{j_l}(l) \log x_{j_l}(l) \quad (25)$$

where γ_l is an appropriate coefficient (Barker 1953). Once the clusters have been identified and their concentrations or probabilities evaluated, the rest is largely numerical, and will be described shortly.

Historically, one of the early attempts at explaining the order-disorder transformations is due to Bragg and Williams (1934, 1935). Domb (1981) narrates an interesting story concerning these famous papers. Apparently, Bragg gave a seminar in 1933 in Manchester during which he qualitatively described his thoughts on how ordering occurred in binary alloys. Williams, a member of the audience, presented Bragg with a mathematical outline of Bragg's theory at the end of the lecture. (The story of the Rushbrook inequalities is similar! See Stanley 1971). Bragg was impressed but felt that the calculation was so simple, it surely must have been published earlier. However, no such paper had yet appeared and so Bragg and Williams proceeded to publish their ideas!

In the cvm language, the Bragg-Williams theory retains only ξ_1 or point clusters. Next comes the Bethe approximation (1935) which includes pairs *i.e.* also ξ_2 . From these early beginnings, the push has always been towards larger clusters. Modern applications of the cvm have been promoted largely by de Fontaine and coworkers, building upon schemes originally developed by Kikuchi (1951), Barker (1953) and van Baal (1973). Before describing some of these recent results, we refer to figure 13 which gives a feel for the improvements available in going to larger clusters in 2-D square lattice, where Onsager's exact result is available as a bench mark.

Turning now to phase diagrams calculations for real alloys, the main steps in the calculational schemes as implemented at present are as follows (de Fontaine 1982):

- (i) Choose the basic lattice system, the range of interactions and the largest cluster to be used. Form then the ξ 's.
- (ii) Construct the thermodynamic potential Ω (also called the grand potential) defined by

$$\Omega = F - \frac{1}{2}(\mu_A - \mu_B) \sum_i S_i \quad (26)$$

Figure 13. Specific heat variation for the square-Ising lattice. Onsager's result is the exact one. Observe the improvement in going from the Bragg-Williams approximation to the cvm square cluster approximation.

where the μ 's are the chemical potentials of the two atomic species. The chemical potential term is required since we would like to permit concentration C_B to vary (while the total number of atoms is fixed).

(iii) For a fixed $(T, \mu \equiv 1/2(\mu_A - \mu_B))$, minimize Ω with respect to the ξ 's considered *i.e.* the set of ξ 's consistent with the largest cluster L chosen.

(iv) When Ω is minimized, it leads to a set of (nonlinear algebraic) equations for the ξ 's. Solve these equations.

(v) Use the ξ 's obtained in step (iv) to compute the equilibrium potential Ω_{eqbr} .

(vi) Plot Ω_{eqbr} vs T for fixed values of μ for the different phases. The point (T, μ) at which two curves cross is a point of phase coexistence. An example is given in figure 14.

(vii) Vary T and μ and establish the locus of phase coexistence *i.e.* the phase boundaries.

(viii) Every intersection between the Ω curves for two phases, α and β , say, gives two values of the point correlation function ξ_1 . From these, determine the average concentrations c_B^α and c_B^β .

(ix) Assemble the results into phase diagrams in the (T, μ) and (T, c) planes.

Following Iliopoulos (1980), one might also add:

(x) Publish your result,

(xi) Choose another alloy system and GO TO (i)!

The cvm has been extensively applied by Kikuchi, de Fontaine and coworkers, from whose contributions we will now cite a few examples. Firstly in table 1 (de Fontaine 1979) we summarize some results obtained for Ising ferromagnets (which, incidentally, are isomorphous to AB binary solutions; recall earlier remarks about the correspondence between magnetic systems and alloy systems).

Next we consider results for ordering. Kikuchi *et al* (1980) have obtained the phase diagram for the Cu-Au system using mn interactions for the Ising spins, and a tetrahedron cluster. The calculated phase diagram is shown in figure 15b which is to be

Figure 14. Variation of the grand potential with temperature for the A_2B_2 and disordered (α) phases, for zero chemical potential ($c_B = 0.5$). The intersection gives the temperature value at which the two phases coexist. (after de Fontaine 1982).

Table 1. Calculated normalized transition temperature in units of $k_B T/zJ$ where J is the strength of the nearest neighbour interactions and z the number of nearest neighbours (after de Fontaine 1979).

	2D Square lattice	2D Triangular lattice	3D Simple cubic	Remarks
z	4	6	6	
Bragg-Williams (point)	1.0	1.0	1.0	all refer to transition temperatures
cv Bethe (pair)	0.7212	0.8222	0.8222	
cv square or triangle	0.6057	0.62525	0.7683	
cv cube or tetrahedron	—	—	0.7628	
Exact (or best known)	0.567	0.6062	0.7522	

compared with the experimentally determined one (figure 15c) and that calculated by Shockley (1938) using the Bragg-Williams approximation (figure 15a). While those not used to phase diagrams may regard the agreement between cvm and experiment fair, the comparison is actually quite impressive given the approximations involved.

Sanchez and de Fontaine (1978) have gone beyond the tetrahedral approximation to the clusters illustrated in figure 12b and c, and investigated (Sanchez and de Fontaine 1980, 1982) the phase diagram for the $\langle 1\frac{1}{2}0 \rangle$ family of ordered superstructure *i.e.* lattices where ordering is associated with a $\langle 1\frac{1}{2}0 \rangle$ compositional wave. In addition to the usually considered nn interactions, the nnn interactions were also included. Results have been obtained for a range of values of the ratio of second-to-first-neighbour pair interactions in the range 0 to 0.5. The results are relevant for ordering in diverse systems like Ni-Mo, Ni-V etc. Incidentally, a knowledge of the ground state structure is very helpful in testing out a particular ordered state as in figure 14.

These calculations by de Fontaine and coworkers have shown the distinct superiority of the cvm over earlier models in yielding realistic results. For instance, in Cu-Au systems, the Bragg-Williams approximation predicts a first-order transition for Cu_3Au ($L1_2$ ordering) and a second-order transition for CuAuI ($L1_0$ ordering), whereas experimentally the transition is of first order for both the stoichiometric compositions. The Bethe approximation is even worse, and predicts no transition at all. The cvm does much better and predicts correctly a first order transition for both. The main advantage of the cvm is that reasonably accurate results are obtained without too much computational effort (—much of this has no doubt been due to the exercise of ingenuity in arriving at the practical computational scheme). In the results reported thus far, about 30 to 70 nonlinear algebraic equations had to be solved but it was not taxing. However, numerical difficulties were found at low temperatures where some of the cluster probabilities tended exponentially to zero. Where transition temperatures are concerned, the cvm does a respectable job, judging from the 3-D cubic Ising ferromagnet for which independent, reliable results are available from high-temperature expansion methods (table 1). But where exponents are concerned, cvm predicts only classical ones for higher-order transitions. This is not unexpected since the method is built around equilibrium correlation functions and does not include fluctuations. It is perhaps not out of place here to mention that Mahan and Claro (1977) have used the real-space renormalization-group approach to calculate a CuAu-type

Figure 15. Phase diagram for the Cu-Au system (a), results obtained by Shockley (1938). (b), shows the CVM results of Kikuchi *et al* (1980). For comparison, the experimental results are given in (c) (Hansen 1958).

phase diagram. The results are however poor in that the ordering of CuAu ($L1_0$ ordering) is not predicted and the ordering of Cu_3Au ($L1_2$ ordering) is predicted to be of second order.

The stage is now set to consider a totally different approach to the calculation of phase diagrams *viz.*, that of computer simulation.

3.3 Phase diagrams and computer simulation

As in several other branches of physics, computer simulation has proved extremely useful in unveiling various subtle aspects relating to phase transformations. In this subsection, we review the work done in relation to phase diagrams while in a later section, we shall touch upon studies in kinetics.

The basic idea is to start with a representative Hamiltonian that describes configuration interactions, and then use a Monte Carlo technique to deduce the structure appropriate to specific thermodynamic conditions. Since the problem is formulated in the Ising-spin language, there are understandable links with many magnetic problems.

To obtain the desired Hamiltonian, we go back to (11), the expression for internal energy. Adding to it a chemical potential term $(\mu_A - \mu_B) \sum_l \sigma_B(l)$ as earlier, we have

$$\mathcal{H} = \frac{1}{2} \sum_{ij} \sum_{l \neq m} v_{ij}(l-m) \langle \sigma_i(l) \sigma_j(m) \rangle + (\mu_A - \mu_B) \sum_l \sigma_B(l). \quad (27)$$

Introducing Ising spins as in (20), the Hamiltonian in (27) can now be transformed (barring a constant term) as

$$\mathcal{H} = \sum_{l \neq m} J_{lm} S_l S_m - H \sum_l S_l, \quad (28)$$

where

$$J_{lm} = -\{v_{AA}(l-m) + v_{BB}(l-m) - 2v_{AB}(l-m)\}/4, \quad (29)$$

is the exchange integral for Ising spins, and

$$H = \frac{1}{2} \sum_{m(\neq l)} \{v_{AA}(l-m) - v_{BB}(l-m)\} + \frac{1}{2}(\mu_A - \mu_B), \quad (30)$$

is an 'external' field acting on the Ising spins.

As it stands, the spin at site l interacts with spins at all other sites m in the lattice. To make the problem tractable, one restricts, as earlier, the range to the nearest and next nearest neighbours so that $\mathcal{H}$ now is given by

$$\mathcal{H} = -J \sum_{(nn)} S_i S_j + \alpha J \sum_{(nnn)} S_i S_j - H \sum_i S_i. \quad (31)$$

The parameter $(-\alpha)$ is a measure of the relative strength of the nnn interaction.

One now takes a system of $N = 4L^3$ spins on a fcc lattice with periodic boundary conditions. In the actual simulation, N was ~ 15000 . Next one specifies an initial configuration $X_0 = \{S_1, S_2, \dots, S_N\}$, the choice of which will be discussed shortly. Using pseudo random numbers, one then generates a random change of configuration $X_0 \rightarrow X_1$. There are two ways of achieving this, depending on what ensemble one works with. If one is using a canonical ensemble, then the total 'up' spin as well as the total 'down' spin must be individually conserved. Hence $X_0 \rightarrow X_1$ is achieved by choosing at random a nearest neighbour AB pair and exchanging spins. This 'Kawasaki dynamics' (Kawasaki 1972) conserves the concentration c_B of the system. In the case of the grand canonical ensemble, the magnetic field is held constant and $X_0 \rightarrow X_1$ is implemented *via* the flip $S_i \rightarrow -S_i$ of a randomly chosen spin. These spin fluctuations are equivalent to fluctuations of c_B . As is well-known, both ensembles should yield

results equivalent to each other in the thermodynamic limit $N \rightarrow \infty$. Working with finite N as in simulation experiments, it is important to verify that the results do not depend on the ensemble chosen. Having produced a change $X_0 \rightarrow X_1$, one now computes (in both cases) the energy change $\delta U = \mathcal{H}(X_1) - \mathcal{H}(X_0)$ resulting from the configurational change. The transition probability for such a change is

$$W = \exp(-\delta U/k_B T) / \{1 + \exp(-\delta U/k_B T)\}, \quad (32)$$

which is compared to a random number η chosen uniformly from the interval $(0, 1)$. If $W > \eta$, the transition is performed; otherwise the old configuration is counted once more for the averaging, the attempted X_1 is rejected, and another transition is tried. The Monte Carlo steps (mcs) are repeated till an equilibrium distribution is obtained. To achieve convergence within a few thousand mcs, it is necessary to choose the initial state X_0 appropriately.

Two groups, namely that of Lebowitz and of Binder have been active in studying phase diagrams by simulation. Recently they merged their efforts to make a detailed study of a system that is a prototype for Cu-Au alloys (Binder *et al* 1981). Since this is the most comprehensive study to date, we shall present some results from it.

In this work, nearest neighbour interactions alone were considered *i.e.* α was set equal to zero. The initial state was variously chosen as ferromagnetically ordered state, a disordered state or an antiferromagnetic state, as appropriate. Runs using the canonical ensemble were done at various fixed compositions c_B , and for each composition, runs were taken at several temperatures (actually at several values of $k_B T/|J|$). The grand canonical ensemble runs were done for various fields corresponding to a fixed temperature, and the temperature was subsequently varied. The quantities monitored were, (i) the internal energy, (ii) the net magnetization m and (iii) the order parameter $\tilde{m}$. In terms of the sublattice magnetization m_v ($v = 1, 2, 3, 4$) defined by

$$m_v = (1/N) \sum_i \langle S_{i,v} \rangle, \quad (33)$$

over v th sublattice

m is given by

$$m = m_1 + m_2 + m_3 + m_4, \quad (34)$$

while $\tilde{m}$ is given by

$$\begin{aligned} \tilde{m} &= m_1 + m_2 - m_3 - m_4 && (AB \text{ structure}) \\ &= m_1 + m_2 + m_3 - m_4 && (A_3B \text{ structure}). \end{aligned} \quad (35)$$

Figure 16 shows a plot of magnetization as a function of the applied field. When H is zero, there is no magnetization. As H is increased, m also increases, and the increase would have been linear (dashed line) if the system were disordered. Instead, the m value stays below the dashed line indicative of order until a field H'_{C_1} is reached when it jumps. H'_{C_1} is thus a critical field required to derive the system to disorder. Order sets in again at H_{C_2}' and disappears at H_{C_2} . The order parameter variations are also shown in figure 16, from which the field-induced transitions (at a fixed temperature) are clearly evident.

Figure 16 is what is termed 'raw data' by Binder *et al* (1981). For several such data, the phase diagram of the Ising antiferromagnet was constructed as in figure 17. Noting that $\sigma_B(l) = (1 - S_l)/2$, the average concentration C_B of B atoms in the alloy is related to m by $C_B = (1 - m)/2$. Therefore, the diagram of figure 17b which is the phase diagram

Figure 16. Order parameter (top) and magnetization (bottom) for the nearest neighbour Ising antiferromagnet plotted as a function of the field for the temperature $T_{k_B}/|J| = 1.5$. Estimates for the three critical fields H_{C1} , H_{C2}' and H_{C2} are also indicated. (after Binder *et al* 1981).

(b)

(a)

Figure 17. (a) Phase diagram of the nearest neighbour fcc lattice in the temperature-composition plane. Ordered structures are indicated. All transitions are of first order. (b) Phase diagram in the temperature-field plane.

for an Ising antiferromagnet in a magnetic field can be mapped to the temperature-composition plane as in figure 17a to yield a phase diagram appropriate to the alloy AB . The two-phase regions shown here arise from the fact that for certain values of the field, m is multivalued.

Recently, Binder (1981) has extended the above work to include nnn interactions also. The phase diagram is now considerably altered (see figure 18), a noteworthy feature being the occurrence of a multicritical point at $H = 0$. This is an interesting finding in view of a recent theoretical prediction that such a point arises out of a meeting of lines of 3- and 4-state Potts model-like transitions.

Returning to the implications for the alloy problem, the broad finding is that simulation corroborates cvm results as is explicitly brought out in figure 19. At stoichiometric compositions, the two methods come fairly close to each other. This has also been noted from limited simulations done for $\alpha = 0.25$. The feeling therefore is that stoichiometric alloys are rather insensitive to the parameters of the model as well as the accuracy of the approximations used. Study of off-stoichiometric systems (both experimentally and theoretically) may be more worthwhile. In this context, Binder (1980a) has proposed that one could, for example, explore short-range order as a function of composition (see figure 20). Measurements of this type would provide a valuable test of whether a model faithfully represents a real system. Another useful hint to emerge from these studies is that the interaction parameters are probably composition dependent. In other words, the same exchange integral $J(r)$ cannot be used over the entire composition range. The possibility of 'frustration' is yet another interesting finding. To understand this, we refer to figure 21 which shows two neighbouring cells of the A_3B structure. Focussing attention on the spin at the centre of the common plane, it is found that four of its bonds to nn are energetically favourable while the other eight are unfavourable. Therefore at the critical field H'_{C_1} , this spin can be overturned at no cost. One has essentially a 'frustration-type' of situation here since the central spin is under conflicting orders. Binder *et al* (1981) therefore advocate improvements to theoretical methods so as to handle frustration.

As of now, the computer simulation method has some limitations. Being time consuming, it cannot be applied for wide ranging explorations as, for example, the cvm. Also the treatment of the configurational entropy is crude. However, there is no doubt that valuable insight has been gained from whatever has been done so far. And it is also

Figures 18–19. 18. (Left) Phase diagram of the next nearest neighbour Ising antiferromagnet in the T -field and T -composition planes. Observe that the simulated diagram is still far from experiment. (after Binder 1981). 19. (Right) Comparison of the phase diagram for the fcc binary alloy as obtained by simulation and the cvm results (after Binder *et al* 1981).

Figure 20. Schematic plot of the variation of the (Cowley) short-range order parameter as a function of concentration. The temperature is fixed, and below T_c . The sharp variations are related to the crossings of the phase boundaries. See also figure 45 (after Binder 1980a).

Figure 21. Illustration of the concept of a 'spin' under conflicting orders and thereby becoming 'loose' at the critical field. For explanations, see text. According to Binder *et al* (1981) such a 'conflict' leads to a frustration-type of situation as in spin glass (after Binder *et al* 1981).

clear that simulation will always be required both to complement as well as to continually spur experiment and theory.

4. Kinetic phenomena

We turn our attention now to phenomena that occur when one either approaches a phase boundary or crosses it. As is to be expected, there will be manifestations of critical phenomena in the neighbourhood of a transition across the boundary, and such critical effects have indeed been observed even in the twenties. For instance, Johansson and Linde (1928) found that the electrical resistivity of Cu_3Au rose sharply with increasing temperature around 390°C , the transformation temperature. One could therefore envisage extensive studies on critical exponents related to the vast variety of

transformations possible. It is however unlikely that such studies while *very useful* will reveal anything fundamentally *new* concerning the *basic universalities* under lying critical phenomena since the cream has in a sense already been skimmed off. Far more interesting is the study of dynamic phenomena following a quench as it raises questions in nonequilibrium statistical mechanics, currently an active area.

In systems such as we are interested in, quenching (notionally) causes a step function change of temperature. However, although the phonons have readjusted, the atoms are unable to follow suit and occupy their new equilibrium positions with such rapidity. Positional readjustments involve large scale migration of atoms through diffusive processes, necessarily requiring some time. Thus, immediately after a quench, the system is left in a highly non-equilibrium state. It then coasts down (with the atoms readjusting their positions), eventually attaining equilibrium. Studies made during the coastdown can shed valuable light on the behaviour of systems far from equilibrium. The attendant nonlinearities make such investigations even more interesting.

In this Section, we shall review progress in the understanding of such kinetic phenomena and also indicate questions that still await solutions.

4.1 Linear kinetics

The broad question one faces is: What exactly happens after a quench? There is no simple universal answer to such a question for much depends on whether one is considering the early- or the late-stage behaviour, whether it is a clustering or an ordering system, etc. We shall deal with some of these complications as we go along. For the present we will offer a qualitative picture assuming the system responds linearly to the forces set up following the quench (—a bad assumption!).

Let c_B be the average concentration of the B species and $c(r, t)$ the distribution (of the B species) in the quenched alloy. It is convenient to consider $c(k, t)$ the Fourier transform of the composition fluctuation $[c(r, t) - c_B]$. $c(k, t)$ thus represents a compositional wave of wavevector k . If the system behaves linearly, then each Fourier component has an evolution history that is completely delinked from those of the others. The task now reduces to formulating an equation of motion for $c(k, t)$ and solving it. Thanks to the linearity assumption, one has (Cahn 1961, 1968)

$$c(k, t) \sim \exp[\alpha(k)t], \quad (36)$$

where $\alpha(k)$ depends on the forces acting in the quenched system. If α is negative, the fluctuations decay but if α is positive the fluctuations grow, in fact indefinitely, indicative of an instability in the system. The question therefore is: How does $\alpha(k)$ behave as a function of k , and, in particular, is it positive for certain values of k ? The latter would depend of course on the instabilities.

Figure 22 shows some schematic plots of α both above and below the transition temperature for a clustering as well as an ordering system (Cook *et al* 1969). We notice that α becomes positive only below the transition temperature. Only then do certain fluctuations grow to giant proportions, driving the system to a totally new state altogether. For a clustering system α becomes positive near the zone centre, whereas for an ordering system it becomes positive in the neighbourhood of the superlattice position associated with the ordering process.

Now fluctuations cannot really grow in an unbounded manner, and such growth is in fact arrested by nonlinearities. Another way of saying this is that the different Fourier

Figure 22. Schematic plot of α above and below the transition temperature T_c (a). situation for a clustering reaction, where α becomes positive below T_c around $k = 0$. In an ordering reaction on the other hand, α becomes positive in the region of the superlattice reflection. The region where α becomes positive is related to the region where $V(k)$ has a minimum (after Cook *et al* 1969).

components start interacting with each other, checking runaway growth. While the concept of a 'linear' amplification factor $\alpha(k)$ does become blurred to some extent in the presence of non-linearities, it certainly is meaningful in the disordered region at least.

Some interesting experiments on 'disordering kinetics' have been performed to obtain plots of $\alpha(k)$ and they are worth a brief mention (Paulson and Hilliard 1977). In these experiments, a multilayer film several thousand Angstroms thick was prepared by alternately depositing two elements (*e.g.* Cu and Au) in the desired proportions. The as-deposited composition modulation produces satellite peaks in an x-ray diffraction pattern. One now upquenches the specimen, taking it into the one-phase region. The modulation then progressively disappears due to the interdiffusion of the atomic species. By monitoring the time-dependence of the intensity of the satellite peak, $\alpha(k)$ can be obtained. The wavelength of the modulation can be varied by controlling the deposition, and in this way $\alpha(k)$ can be studied as a function of k . A typical plot so obtained is shown in figure 23. We shall return again to the amplification factor for clustering systems in § 4.3.

Linear theories essentially provide first-order answers. They are reasonably adequate

Figure 23. Amplification rates α vs λ observed at 225°C in thin films of Cu-16 at % Au (after Paulson and Hilliard 1977).

in the disordered region where *all* fluctuations decay, and one does not encounter runaway situations. However, such theories are inadequate as one approaches the critical region; and in the ordered region, they totally fail to describe the kinetics.

4.2 Beyond linear theories

For answers beyond linear theories one should look to nonequilibrium statistical mechanics, and presently we shall consider some general aspects. To provide a framework for the discussion, we shall suppose the free energy density f to be given by

$$f(x; a, b) = \frac{1}{2} ax^2 + \frac{1}{4} x^4 + bx. \quad (37)$$

This is the Ginzburg-Landau form, together with a magnetic field term bx . The quantities a and b are the control parameters while x is the order parameter. Our f here is equivalent to the grand potential discussed in § 3.

Our first interest is in the minima of f , and the locus traced by them as a and b are varied. In the language of catastrophe theory (Gilmore 1981), the minima are the critical points of f . The various critical points of f are obtained as follows:

nondegenerate crit. pt.	$(df/dx) = 0$ i.e. $x^3 + ax + b = 0$	
two-fold degenerate		
crit. pt.	$(d^2f/dx^2) = 0$ i.e. $3x^2 + a = 0$	
three-fold degenerate		
crit. pt.	$(d^3f/dx^3) = 0$ i.e. $6x = 0$	(38)

It is easily seen from above that the locus of the doubly degenerate critical points is given by (Gilmore 1981)

$$(a/3)^3 + (b/2)^2 = 0. \quad (39)$$

This 'fold curve' also called the separatrix is sketched in figure 24, and it divides the parameter space into two regions representing functions with one critical point and functions with three critical points. This feature is made explicit with representative

Figure 24. Sketch of the fold curve for f given by (37). Also shown are representative plots of f vs x for the various points in the (a, b) plane indicated by dots (after Gilmore 1981).

plots for f corresponding to various points in the a - b plane. The origin represents the function $f = (x^4/4)$, and corresponds to a three-fold degenerate critical point.

It is helpful also to have some idea of certain surfaces associated with f (Gilmore 1981; Kikuchi and de Fontaine 1976). These are (i) the critical manifold defined by $(df/dx) = 0$, (ii) the critical value surface f_c made up by the values assumed by f when $\nabla f = 0$ and (iii) the critical curvature surface defined by $(d^2 f/dx^2) = 0$. Sketches of these surfaces are given in figure 25, and they aid the analysis of system behaviour following a disturbance to the system. Thus, for instance, the critical curvature surface is useful while discussing the stability of the system.

In nonequilibrium phenomena, the state of the system is governed by f which often changes for one reason or the other. In this changing situation, the system attempts to find a minimum appropriate to the prevailing conditions but when several minima are available, the question naturally arises regarding which minimum the system jumps to. Two extremes are possible as illustrated in figure 26. In figure 26a the system remains in a stable or metastable equilibrium state until that state disappears whereas in figure 26b the system always chooses the global minimum. Between these two limiting conventions, many other possibilities exist. Which of these conventions operate in a given situation depends on the relative values of the barrier height ΔE and the noise level N . If $N/\Delta E \ll 1$, then the delay convention is observed while if $N/\Delta E \gg 1$ the Maxwell convention operates (figure 27).

Another way of looking at a system evolution is *via* the probability distribution function $P(x, t)$. Figure 28a shows a schematic plot of $f(x)$ at some instant of time while figure 28b depicts $P(x, t)$ for that same instant. Notice P peaks away from the minimum, typical of a nonequilibrium situation. As time evolves, $P(x, t)$ will seek to attain a form appropriate to equilibrium. There are two characteristic times T_1 and T_2 associated with

Figure 25. Schematic plots of various critical surfaces associated with the f of (37) (a), surface defined by $\nabla f = 0$. (b), critical value surface f_c which, for a given (a, b) gives the f value corresponding to the condition $\nabla f = 0$. The critical curvature surface $f'' = 0$ is sketched in (c). This is useful for discussing instabilities. At the bottom is projected the fold curve. The relationship of the latter to the various surfaces sketched above it should be clear (after Gilmore 1981).

this approach to equilibrium. Of these, T_1 is the time for relaxation to a local minimum and T_2 from a metastable minimum to a global minimum (see figure 28d). In transiting from a local minimum to a global minimum the system essentially drifts (in x space). Relaxation to a local minimum on the other hand is like a diffusive process.

The regime of the two conventions can also be spelt out in terms of T_1 and T_2 . If $C = \{a, b, \dots\}$ denotes the set of control parameters, then the delay convention operates if (Gilmore 1981)

$$T_1^{-1} \gg (dC/dt) \gg T_2^{-1}, \quad (40a)$$

while the Maxwell convention operates if

$$T_2^{-1} \gg (dC/dt). \quad (40b)$$

Figure 26. Illustration of the two conventions adopted for discussing change of state under nonequilibrium conditions. (a). Delay convention—the system remains in a stable or metastable state until that state disappears, (b). Maxwell convention—the system always chooses the global minimum (after Gilmore 1981).

Figure 27. Illustration of the conditions under which the delay and Maxwell conventions are applicable.

To see the link between these two conventions and the topography of the critical manifold, we present in figure 29 the projections of the critical manifold on the (a, b) as well as the (a, x) plane. When the Maxwell convention is adopted, the critical manifold is a “soldered manifold” because the portions of the manifold $\nabla f = 0$ describing unstable critical points and metastable minima have been removed and replaced by a flat piece which interpolates between the two minima. Later in § 4.3 when we consider phase separation, we will recognize the projections of the two manifolds on the (a, x) plane as the coexistence line and the spinodal respectively. The projections on the (a, b) plane are of special interest in a ferromagnet where one has the practical possibility of varying the magnetic field and inducing a phase transition. It is illuminating to follow the transitions (especially under nonequilibrium conditions), as trajectories on the critical manifold (see Gilmore (1981) for examples and details).

Figure 28. Description of the system evolution in terms of the probability distribution function $P(x, t)$. (a) and (b) depict $f(x)$ and $P(x, t)$ at some instant t , say (after Gilmore 1981).

The quantitative aspects of the approach to equilibrium revolve almost entirely around the probability distribution function $P(x, t)$. A quench, for example, creates a certain $P(x, 0)$. The system not being in equilibrium, P will naturally evolve approaching that appropriate to equilibrium. The questions in this context are: What is the equation that governs the evolution of P , how does one solve this question, and how does one use this knowledge of P to make predictions pertinent to specific experiments?

The evolution of P is governed by the well-known Fokker-Planck equation

$$\frac{\partial P}{\partial t} = -\frac{d}{dx} [K(x) P] + \frac{1}{2} D \frac{d^2 P}{dx^2}, \quad (41)$$

here D is the diffusion coefficient and $K(x)$ a drift force. In many problems, this drift force can be expressed as the gradient of a potential *i.e.*

$$K(x) = -[dV(x)/dx]. \quad (42)$$

In our problems, $K(x)$ will be related to the free energy.

The derivation of the Fokker-Planck equation from the more fundamental Master equation is too involved a question to be discussed here but fortunately good treatments are available in literature (—see, for example, Haken 1978; for a discussion

Figure 29. Projections of the critical manifold ($\nabla f = 0$) on the (a, b) and (a, x) planes.

vis-a-vis problems of materials science, see Venkataraman and Balakrishnan 1977; Venkataraman 1982).

The Fokker-Planck equation is sometimes written as a continuity equation i.e. as

$$\dot{P} + \frac{d}{dx} j = 0, \quad (43)$$

where j the probability current is given by

$$j = \left[K(x) P - \frac{1}{2} D \frac{dP}{dx} \right]. \quad (44)$$

In equilibrium statistical mechanics, one is interested in the stationary solutions of the Fokker-Planck equation; but in our kind of situations, it is the time-dependent solution that is of interest. In general, finding exact solutions is not possible, and one must resort to a suitable approximation scheme. A very readable account of these problems is available in the book of Haken (1978). Figure 30 shows a schematic plot of the evolution of P in a typical problem. Starting off as a δ -function, P drifts (which gives rise to the dotted line trajectory) and it also broadens (due to diffusion).

The probability density function we need for discussing clustering etc is somewhat

Figure 30. The concept of time evolution of $P(x, t)$ is discussed in this figure. For convenience x is assumed to be two dimensional and it is supposed that at $t = 0$, P starts off as a δ -function. With the passage of time, the state of the system *drifts* in x -space as indicated by the dotted trajectory. Simultaneously, due to fluctuations, the distribution function also broadens.

more general, being a functional of the form $P(\{\psi\}, t)$. Here

$$\{\psi\} = (\psi_1, \psi_2, \dots, \psi_n), \quad (45)$$

with ψ_r being the coarse-grained value of the order parameter ψ in the r th cell. *i.e*

$$\psi_r = \frac{1}{n_r} \sum_{l \in \text{cell } r} \psi(l) \quad (46)$$

There are n_r lattice sites l in cell r and there are n cells in all. $\{\psi\}$ comprehensively describes the state of the system.

Like $P(x, t)$ which we considered earlier, $P(\{\psi\}, t)$ is also conserved. In the continuum limit (where sums over coarse-grained cells are replaced by integrals), the continuity equation is given by

$$\frac{\partial}{\partial t} P(\{\psi\}, t) = - \int d\mathbf{r} \frac{\delta J_r}{\delta \psi(\mathbf{r})}, \quad (47)$$

where J_r is the probability current, and δ signifies a functional differentiation.

The expression for J_r depends on whether the order parameter is conserved or not. The latter quantity is said to be conserved if the change $\psi_r \rightarrow \psi_r + \varepsilon$ in the cell r is accompanied by a compensating change $\psi_s \rightarrow \psi_s - \varepsilon$ in a neighbouring cell s . In clustering reactions, the order parameter is composition which obviously is conserved. On the other hand, in ordering reactions the order parameter is *not* conserved (—recall the examples of ferro- and antiferro magnets). Bearing these two possibilities in mind, the expression for J_r can be written as (Billotet and Binder 1979)

$$J_r(\{\psi\}, t) = -C \left[\frac{\delta F\{\psi\}}{\delta \psi(\mathbf{r})} P(\{\psi\}, t) + k_B T \frac{\delta P(\{\psi\}, t)}{\delta \psi(\mathbf{r})} \right], \quad (48)$$

where $F\{\psi\}$ is the (coarse-grained) free energy functional. If the order parameter is conserved, then $C = -M\nabla_r^2$ where M is the mobility*, whereas if the order parameter is not conserved then C is simply a rate factor fixing the time scale.

Equations (47) and (48) are too formal and complex for practical use, and watered down versions are necessary. A common practice is to use the above equations to construct equations of motion for various moments of P . A few illustrative examples follow.

Consider the clustering problem, and let $c(\mathbf{r})$ denote the local concentration of B atoms. This is the order parameter, and being conserved

$$J_r(\{c(\mathbf{r})\}, t) = -M\nabla^2 \left[\frac{\delta F\{c(\mathbf{r})\}}{\delta c(\mathbf{r})} P + k_B T \frac{\delta P(\{c(\mathbf{r})\}, t)}{\delta c(\mathbf{r})} \right]. \quad (49)$$

Multiplying both sides of (47) by $c(\mathbf{r})$ and integrating we get

$$\int \delta\{c(\mathbf{r})\} c(\mathbf{r}) \frac{\partial}{\partial t} P(\{c(\mathbf{r})\}, t) = - \int \delta\{c(\mathbf{r})\} \int d\mathbf{r}' \times \frac{\delta J}{\delta c(\mathbf{r}')} c(\mathbf{r}). \quad (50)$$

After simplifications, this gives the *average* equation

$$\frac{\partial}{\partial t} \langle c(\mathbf{r}) \rangle = -M\nabla^2 \left\langle \frac{\delta F}{\delta c(\mathbf{r})} \right\rangle. \quad (51)$$

(M is assumed to be a constant *i.e.* independent of $c(\mathbf{r})$). At this stage one makes the convenient assumption that P is *always* sharply peaked around $\langle c(\mathbf{r}) \rangle$ *i.e.*

$$P(\{c(\mathbf{r})\}, t) = \pi \delta(c(\mathbf{r}) - \langle c(\mathbf{r}) \rangle) \quad (52)$$

This then leads to

$$\frac{\partial}{\partial t} \langle c(\mathbf{r}) \rangle = -M\nabla^2 \frac{\delta F\{\langle c(\mathbf{r}) \rangle\}}{\delta c(\mathbf{r})}. \quad (53)$$

Being an average equation, the bracket $\langle \rangle$ can be dropped. The assumption (52) is crucial, for it implies that there are no fluctuations. In terms of figure 30 what it implies is a drift of a δ -function with no broadening. In § 4.3 we shall discuss an application of (53).

Our next example relates to ordering where, we must remember, the order parameter is *not* conserved. Binder (1973) has used the same steps as above for this problem. He starts with (47) which, after manipulations, takes the form

$$\frac{\partial P(\{\psi\}, t)}{\partial t} = -C \int d\mathbf{r} \frac{\delta}{\delta \psi(\mathbf{r})} [K(\psi(\mathbf{r}))P] + C \int d\mathbf{r} \frac{\delta^2 P}{\delta \psi(\mathbf{r})^2}, \quad (54)$$

where the drift force $K(\psi(\mathbf{r}))$ is given by

$$K(\psi(\mathbf{r})) = -\frac{\delta F\{\psi\}}{\delta \psi(\mathbf{r})}. \quad (55)$$

Equation (54) is the Fokker-Planck equation generalized to deal with a situation where P is a functional rather than a function; compare with equation (41). For F , Binder assumes the Ginzburg-Landau form. He then calculates the first moment as in (50),

* The mobility is related to the diffusion coefficient by the Einstein relation $D = Mk_B T$.

making an assumption similar to (52). The resulting equation for $(\partial\psi(\mathbf{r})/\partial t)$ is the time-dependent Ginzburg-Landau equation as applied to the alloy problem. Once again, because of the approximation (52), fluctuations are not included in the treatment.

For comparison with experiment, one needs correlation functions involving the order parameter like

$$\langle \psi(\mathbf{r}, t) \psi(\mathbf{r}', t) \rangle = \int \delta\{\psi\} \psi(\mathbf{r}, t) \psi(\mathbf{r}', t) P(\{\psi\}, t). \quad (56)$$

Multiplying both sides of (47) by $\psi(\mathbf{r}, t) \psi(\mathbf{r}', t)$ and integrating, one obtains an equation of motion for the correlation function. This was essentially the starting point for Langer's theory (Langer 1969; Langer and Turski 1973; Langer *et al* 1975) of spinodal decomposition. Billotet and Binder (1979) also used a similar approach in their theory of ordering reactions. Suitable approximations were then introduced by the above authors to make the solution of the equation of motion tractable, for subsequent comparison with experiment. As we shall note in the following subsections such theories while including in some measure the nonlinearities (which the time-dependent Ginzburg-Landau equation does) and fluctuations (which the Ginzburg-Landau equation does not) do not yet give perfect agreement, signalling the need for improved approximations.

In brief, the usual starting point for problems involving nonequilibrium systems is the ('generalized') Fokker-Planck equation. From here, one must make one's way through suitable approximations to an equation which can form the basis for comparison with experiments. The latter aspects will be dealt with shortly.

For historical completeness we must mention that, Dienes (1955) and Vineyard (1956) wrote down by analogy with chemical reactions, a *rate* equation for the (long-range) order parameter $S \equiv \langle \psi \rangle$. Dienes (1955) calculated $\dot{S}$ numerically for both first order and second order transitions, and the trends obtained by him are sketched in figure 31. If $\dot{S}$ is positive for a certain value of S , then a fluctuation in the system corresponding to that particular S value will be unstable. Figure 31 will now show that in a second-order phase transition, the system is unstable to infinitesimal fluctuations whereas in a first-order transition, a large fluctuation (in S) is necessary. Qualitatively, this is often identified with a nucleation and growth mechanism (Yamauchi and Fontaine 1974).

The Dienes-Vineyard approach to ordering kinetics has now been superseded by the more formal treatment based on the Fokker-Planck equation.

4.3 Spinodal decomposition

It was at one time believed that phase separation occurred only through a nucleation and growth process *i.e.* small pockets of *A*-rich and *B*-rich regions first formed scattered throughout the specimen which subsequently grew and coalesced, transforming the entire specimen to the ordered state. Experiments however revealed that under certain conditions of quenching, the approach to ordering was quite different being akin to "continuous" ordering that one usually associates with a second-order phase transition. This mode of decomposition is referred to as spinodal decomposition.

One picture being worth a thousand words (!) it is perhaps desirable at this stage to refer to figure 32 (Oki *et al* 1974) which, incidentally, gives some idea of the diversity of microstructure one can observe in such experiments.

Figure 31. Schematic plots of $\hat{S}$ vs S based on the calculations reported by Dienes (1955). The top half of the figure shows sketches of the free energy as a function of the long-range order parameter S for a first- as well as a second-order phase transition. Sketched below are the variations of $\hat{S}$ at different temperatures.

The fact that ordering occurred (under certain conditions) simultaneously over large distances indicated that a large scale migration of atoms was involved; and yet when a diffusion model was tried, it failed. The first nontrivial insight into the processes actually occurring came from the work of Cahn (1961, 1962, 1968). To obtain his model, we go back to (53) and put

$$F\{c(\mathbf{r})\} = \int d\mathbf{r} \left(\frac{1}{2} K |\nabla c|^2 + f(c) \right), \quad (57)$$

with

$$f(c) = f_0 + \frac{A}{2} (c - c_B^{\text{crit}})^2 + \frac{B}{4} (c - c_B^{\text{crit}})^4, \quad (58)$$

thus obtaining

$$\frac{\partial c(\mathbf{r}, t)}{\partial t} = M \nabla^2 [-K \nabla^2 c + (\partial f / \partial c)_T]. \quad (59)$$

Writing $c(\mathbf{r}, t) = c_B + \delta c(\mathbf{r}, t)$ and linearizing,

$$\frac{\partial \delta c}{\partial t} = M \nabla^2 [-K \nabla^2 + (\partial^2 f / \partial c^2)_{T, c_B}] \delta c. \quad (60)$$

Solving by Fourier transform,

$$\begin{aligned} c(k, t) &= F \cdot T \text{ of } \delta c(\mathbf{r}, t), \\ &= c(k, 0) \exp[\alpha(k)t], \end{aligned}$$

where

$$\begin{aligned} \alpha(k) &= -M k^2 (K k^2 + f''), \\ &= -M K k^2 (k^2 - k_c^2), f'' \equiv (\partial^2 f / \partial c^2)_{c_B T}, k_c^2 = K^{-1} |f''| \text{ for } f'' < 0. \end{aligned} \quad (61)$$

Figure 32. Domain structures of Fe-24.7 at % Al alloy quenched from 630°C and annealed at 570°C. Shown here are the dark field micrographs with 200 reflection. (a). quenched. (b). annealed for 10 min (c). (d). (e). (f). annealed for 100, 1000, 3000 and 10000 min respectively (after Oki *et al* 1974).

This is the gift of Cahn's theory.

At this stage, it is worth emphasizing the contributions made by Cahn. Firstly he noted that instead of writing the diffusion current as

$$j(r) = -M \nabla(\partial f / \partial c) \quad (62)$$

as one usually does, one must allow for the possibility of the chemical potential varying from point to point in the medium and rewrite the current as

$$j(r) = -M \nabla \frac{\delta F \{c(r)\}}{\delta c(r)} \quad (63)$$

with F as in (57) and (58). (It is interesting that Cahn was not aware of the Ginzburg-Landau theory at that time!).

Another question addressed by Cahn is that of coherency strain (figure 33). Sketched in figure 33 are two different scenarios for the coformation of the two phases α and β

Figure 33. Illustration of the concept of the coherency strain. (a). A cluster that is coherent with the matrix. The lattice spacing changes gradually from the grain to the surrounding region through a distortion zone. The strain associated with this distortion is the coherency strain, and makes a contribution to the energy. In the sketch in (b) there is atomic mismatch at the boundary, and no coherency strain. The cluster in this case is said to be incoherent.

(say) after the quench*. In figure 33b there is complete atomic mismatch at the boundaries separating the α and β regions. With such a discontinuity, the clusters are said to be *incoherent*. By contrast, in figure 33a there is a gradual accommodation of the lattice parameter change through a distortion zone; the corresponding clusters are called *coherent*. While incoherency is the terminal state, the phases initially formed are coherent whence the free energy has a contribution associated with coherency strain. Assuming the medium to be elastically isotropic, an energy density $\eta^2 Y (c - c_B^{\text{crit}})^2$ must then be added to $f(c)$. Here $\eta = (d \ln a / da)$, a being the lattice constant, and Y is given in terms of the Young's modulus E and Poisson's ratio ν as $Y = E / (1 - \nu)$. Consequent to this addition, $\alpha(k)$ gets modified as

$$\alpha(k) = -Mk^2(Kk^2 + f'' + 2\eta^2 Y). \quad (64)$$

It is now seen from (61) and (64) that the sign of α depends on a balance of various factors. If coherency strain is absent and if f'' is negative, then α (in (61)) can assume a positive value in the range $0 \leq k \leq k_c$ as illustrated in figure 34. Thus compositional fluctuations with wavevectors in this region will grow, the component corresponding to k_m dominating. All other fluctuations will decay. Simple diffusion theory on the other hand predicts $\alpha(k) = -Mk^2 f''$ whence *all* fluctuations will grow, the short wavelength ones preferentially.

Referring now to figure 35 we see that f'' is negative only for a certain range of compositions. One could therefore plot within the two-phase region, the locus of points where $f'' = 0$. This is the spinodal and, as may be seen from figure 35 it divides the two-phase region into two zones (—see also figure 29).† If a quench is made into the region within the spinodal, an *instability* occurs causing the system to evolve to equilibrium through the growth of long wavelength compositional waves. Ordering thus sets in on a macroscopic scale, and increases gradually in amplitude (—hence the reference to

* It must be mentioned that spinodal decomposition is also possible in certain binary fluid mixtures. However, there, one does not have coherency strain. For a comprehensive review of both alloys and liquid mixtures, see Gunton (1982).

† The Chamber's dictionary defines spinode as a cusp, the root being the Latin word *spina* meaning thorn. From figure 29 we see the relationship of the cusp to the critical manifold, although one is more used to the projection on the (a, x) plane rather than the projection on the (a, b) plane. See also Kikuchi and de Fontaine (1976).

Figure 34. Plots of α vs k as given by linear theories.

Figure 35. At the top is sketched the usual double well form of the free-energy vs composition. (See also figure 5 and (58)). The second derivative f'' is sketched in the middle. Instability is connected with f'' being negative. If coherency strain is included then $(f'' + 2\eta^2\gamma)$ must be negative. At the bottom are shown the coexistence curve 1 and the spinodals 2 and 3.

“continuous” ordering). Outside the spinodal but within the coexistence line, there is *metastability* instead of instability. If a quench is made into the metastable region, the system evolves through the nucleation of order in several localized regions. These pockets grow in size and eventually link up so that order percolates everywhere. It appears that after equilibrium is finally reached, it is immaterial what route exactly was taken towards its attainment *i.e.* whether it was quenched into the metastable or the unstable region. However, immediately after nonequilibrium conditions are established, the scenario does depend on whether one is in the region of metastability or of instability. It is in this context one wishes to know where f'' vanishes, and this is precisely where a plot as in figure 25c is useful.

If coherency strain is included, then

$$k_c^2 = K^{-1} |f'' + 2\eta^2 Y|, \quad (65)$$

and for instability one must have $(f'' + 2\eta^2 Y)$ negative rather than f'' . As a result, the spinodal is depressed with respect to the (incoherent) coexistence curve (see figure 35c). In liquids, such a depression is absent for obvious reasons. In passing, it should also be pointed out that the phase diagrams deduced from theory as in § 3.2 refer to the *coherent* phase diagrams whereas those determined by experiment (Hansen 1958) refer to *incoherent* phase diagrams.

While Cahn's theory gave some clue as to the origin of spinodal decomposition, quantitatively it was inadequate as it assumed linearity. Now one of the stringent tests for a theory is to compare the structure factor $S(k, t)$ predicted by it in the small k region with that observed experimentally. In Cahn's theory

$$S(k, t) \equiv \langle c(k, t)c(-k, t) \rangle = S(k, 0) \exp [2\alpha(k)t]. \quad (66)$$

Based on figure 34, one would expect $S(k, t)$ to peak at k_m for all t whereas experiment showed that $k_m \rightarrow 0$ as $t \rightarrow \infty$. Another failing of Cahn's theory is that it predicts the decay of $S(k, t)$ to zero for $k > k_c$ whereas it must actually approach that appropriate to the fluctuations at temperature T (to which the sample has been quenched). Cook (1970) traced this deficiency to the absence of fluctuations in Cahn's theory (recall remarks circa equation (53)) and therefore modified Cahn's diffusion equation into a Langevin equation, *i.e.* he wrote

$$\frac{\partial c}{\partial t} = -\nabla j + \zeta j = -M \nabla (\delta F / \delta c), \quad (67a)$$

with

$$\langle \zeta(r, t) \zeta(r', t') \rangle = 2M \delta(r - r') \delta(t - t'). \quad (67b)$$

Cook's model produced only marginal improvements to that of Cahn's since it too relied on linearity. The real breakthrough came with the work of Langer and coworkers (Langer 1969, 1980; Langer and Turski 1973; Langer *et al* 1975) who not only included fluctuations (as Cook did), but also the nonlinearities (though only approximately).

To understand Langer's work we start with the formal equation of motion for $S(\mathbf{k}, t)$ which is obtained as described in § 4.2 circa equation (56). Ignoring elastic effects, the equation for $S(\mathbf{k}, t)$ is:

$$\begin{aligned} \frac{\partial S(k, t)}{\partial t} = & -2Mk^2 [(Kk^2 + f'')S(k, t) + \frac{1}{2} (\partial^3 f / \partial c^3)_{c_B} S_3(k, t) \\ & + \frac{1}{6} (\partial^4 f / \partial c^4)_{c_B} S_4(k, t) + \dots] + 2Mk_B T k^2. \end{aligned} \quad (68)$$

Here

$$S_n(\mathbf{r}_1 - \mathbf{r}_2, t) = \langle \delta c^{n-1}(\mathbf{r}_1, t) \delta c(\mathbf{r}_2, t) \rangle \quad (69)$$

and $S_n(k, t)$ is the Fourier transform of $S_n(\mathbf{r}, t)$. From (68) we see that Cahn had only the first term of the series and that Cook added the noise term.

A major difficulty with (68) is that it involves the higher-order correlation function $S_n(k, t)$ to know which we need additional equations of motion! One thus ends up with a hierarchy of coupled equations, a familiar malaise of many-body theory. Langer and coworkers argued that no matter what n is, S_n always involves only two spatial positions $\mathbf{r}_1$ and $\mathbf{r}_2$. It should therefore be possible to compute S_n for any n (albeit approximately), given a knowledge of the two-point distribution function $P_2[c(\mathbf{r}_1), c(\mathbf{r}_2)]$. The latter was approximated by

$$P_2[c(\mathbf{r}_1), c(\mathbf{r}_2)] = P_1[c(\mathbf{r}_1)] P_1[c(\mathbf{r}_2)] \times \left\{ 1 + \frac{\langle \delta c(\mathbf{r}_1) \delta c(\mathbf{r}_2) \rangle \delta c(\mathbf{r}_1) \delta c(\mathbf{r}_2)}{\langle (\delta c)^2 \rangle \langle (\delta c)^2 \rangle} \right\}. \quad (70)$$

If there were no correlations between the concentrations at $\mathbf{r}_1$ and $\mathbf{r}_2$, then P_2 would just be a simple product of the one-point probabilities. In Langer's scheme, the correction is proportional to $\langle \delta c(\mathbf{r}_1) \delta c(\mathbf{r}_2) \rangle$. The equation of motion now simplifies to

$$\frac{dS(k, t)}{dt} = -2Mk^2 [Kk^2 + A(t)] + 2Mk_B T k^2, \quad (71)$$

where $A(t)$ itself depends on $S(k, t)$ and must therefore be calculated by a self-consistent scheme. For comparison, Cahn's theory gives

$$\frac{dS(k, t)}{dt} = -2Mk^2 [Kk^2 + f''], \quad (72)$$

while Cook's theory gives

$$\frac{dS(k, t)}{dt} = -2Mk^2 [Kk^2 + f''] + 2Mk_B T k^2. \quad (73)$$

The major success of the Langer theory is the prediction that k_m shifts towards the origin as time increases, in accord with experiment. Another important finding is that the structure factor satisfies dynamic scaling i.e

$$S_T(k, t; c_B) = \varepsilon^{-\gamma} \tilde{S}[k \varepsilon^{-\nu}, t \varepsilon^{\gamma}, (c - c_B^{\text{crit}})] \quad (74)$$

where $\varepsilon = (1 - T/T_c)$, and β, ν, γ have their usual meanings (Stanley 1971). Equation (74) is significant because it shows that dynamic scaling can apply to relaxation *far from equilibrium*.

The theory of Langer also is not without blemishes. One shortcoming is that it exhibits metastable states of infinite life-time. A related defect is the inability to describe properly the late stages of the separation. According to Binder (1977) these failings can be cured by explicitly building in features related to nucleation and growth. The late stage behaviour will be briefly touched upon again in a subsequent section.

To counter the impression one might get that it is all theory (!), we now present some representative but important experimental results. Figure 36 shows small-angle

Figure 36. Differential scattering cross-section ($d\Sigma/d\Omega$) vs scattering vector β (k in our notation) for Au-60 at % Pt alloy quenched from 1270°C and aged at 550°C. In making the measurements, an "arresting technique" as illustrated in figure 44 was used (after Singhal *et al* 1978).

neutron scattering results for a Au-60 at % Pt alloy obtained by Singhal *et al* (1978). The sample was quenched from 1270 (± 5)°C into iced brine and subsequently aged at 550°C. After aging for a certain time, the sample was quenched into water to prepare for measurements (which were done at room temperature). The sample was then successively subjected to additional aging treatment, followed in each case by a measurement to monitor the state of ordering. The data clearly indicates the shift of k_m towards zero with increasing time.

The next result we discuss is that of Schwahn and Schmatz (1978) for Al-40 at % Zn alloy. This was a clever experiment designed to check the fact that due to coherency strain, T_c the critical temperature associated with the spinodal is depressed below the (incoherent) phase boundary (see figure 35). Starting from the one-phase region, the sample was quenched to a temperature T just above T_c . Holding the sample at T , small-angle neutron scattering measurements were carried out. In contrast to what one observes in a usual second-order phase transition while approaching T_c from above, it was noticed that $S(k)$ changed with time. The reason is that though $T > T_c$, the sample was actually below the equilibrium (*i.e.* incoherent) phase boundary. Thus, with passage of time, ordering occurred slowly *via* nucleation and growth and $S(k)$ probably went over to a form appropriate to that process. Under the circumstances, the spectrum measured just after quench is the one representative of critical scattering *i.e.* the excess scattering arising out of the proximity of T to T_c (coherent). A rapid increase of scattered intensity (so isolated) was indeed observed as $T \rightarrow T_c^+$, and it was firmly established that T_c (coherent) was 28°C below the incoherent critical point of 351.5°C (see figure 37). Further, $S(k)$ immediately after quench had the well-known Ornstein-Zernike (1914) form usually found while approaching a second-order phase transition. Only, in this case the Ornstein-Zernike form was transient, giving way to a fluctuation spectrum appropriate to other processes.

Spinodal decomposition has no doubt been explored by a variety of tools but of these, small-angle neutron scattering is perhaps the most useful for checking out

aspects we are interested in presently. The spectrometers currently available at the various high-flux reactors are quite powerful, being placed in cold-neutron beams and equipped with 2-D detectors and online computers. The possibility of rapid, real-time measurements (as in the Schwahn and Schmatz experiment) is a very attractive feature. At the new DHRUVA reactor at Trombay, a cold neutron source is being planned, and a small-angle measurement facility is also being contemplated. Such a spectrometer would give a great impetus to the above type of experiments in the country. While neutron scattering has an edge at the moment, x-rays have a strong possibility of staging a comeback, especially with the advent of synchrotron-radiation sources.

Computer simulation is another important technique employed to test theoretical predictions. Lebowitz *et al* (1982) for example, have used the Monte Carlo method to study quenching under various conditions (see figure 38). In each case $S(k, t)$ was determined, with time measured in units of α^{-1} where α^{-1} is the average time interval

Figure 37. Differential scattering cross-section *vs* wavevector observed at various temperatures in the neighbourhood of the (coherent) critical temperature ($\sim 324^\circ\text{C}$). The sharp rise at small k is characteristic of critical behaviour. No critical scattering was found at 351°C the incoherent critical temperature. The k -dependence near 324°C follows the Ornstein-Zernike form (after Schwan and Schmatz 1978).

Figure 38. Phase diagram of the Ising model used by Lebowitz *et al* (1982) in their computer simulation studies. The broken lines are spinodals. The dots correspond to the various quenches made. In each case, the system is started from an infinite temperature (after Lebowitz *et al* 1982).

between two attempts at exchanging a specific site. A time range up to $10^4 \alpha^{-1}$ was scanned, and, as expected, phase separation occurred with varying speeds depending on the nature of the quench. The relaxation was fastest for quench 5 and slowest for quench 1. A problem arises in making comparisons with experimental data since time in the latter is measured in real physical units *i.e.* seconds. However a link is possible since the unit of time in the simulations appropriate to a temperature T can be taken as $a^2/6D(T)$ where a is the lattice constant and D is the diffusion coefficient of A atoms in a crystal of B atoms. Using such a scaling, Lebowitz *et al* (1982) made comparisons with data obtained by Singhal *et al* (1978). The comparison is reproduced in figure 39 and the notable feature is that one could make the data from the actual and computer experiment lie on the same curve by only rescaling the vertical axis. Further comments on the scaling behaviour will be made when we consider long-term behaviour.

4.4 Late stages of phase separation kinetics

Subsequent to quenching, the system will after sometime, segregate locally into regions of A -rich and B -rich phases (referred to as grains or droplets or domains). With further passage of time, two things happen. Firstly, within individual grains itself, the atoms continue to approach an organization characteristic of the equilibrium configuration. In addition, the droplets themselves grow, coarsen or ripen, whichever way one wants to describe it. A proper theory for $S(k, t)$ must reflect both these aspects (see figure 40, Binder 1980b), but such a theory does not exist. Present theories have only one length scale whereas what figure 40 shows is the need for two.

Quantitatively, the above ideas may be expressed as

$$S(k, t) \approx S_{\text{DW}}(k, t) + S_{\text{ID}}(k, t) \quad (75)$$

where DW refers to domain wall and ID to intradomain. As $t \rightarrow \infty$, $S_{\text{DW}} \rightarrow \text{const} \times \delta(k)$ while $S_{\text{ID}} \rightarrow S_{\text{ID}}(k, eq)$. Immediately after quench, DW's are not important and $S \sim S_{\text{ID}}$. However, during late stages, it is S_{DW} that is more interesting as it gives an insight into the coarsening processes.

One interesting discovery concerning late-stage behaviour is the existence of scaling. Since there is a characteristic length ($\sim$ domain size), associated with the process, it has

Figure 39. Comparison of the computer simulation results (empty symbols) with experimental data (Singhal *et al* 1978) for Au-60 at %Pt alloy quenched to $T \sim 0.6 T_c$. The broken line is for $t = 0$ (the initial sample was already decomposed to some extent) (after Lebowitz *et al* 1982).

Figure 40. Sketch of $S(k, t)$ vs k at long time. The two arrows show the two wavevectors corresponding to the two length scales (intra domain correlations and domain size). (After Binder 1980b).

been conjectured (Binder 1977; Lebowitz *et al* 1982) that

$$S_{\text{DW}}(k, t) \sim b(t) \mathcal{F}(k/K(t)) \quad (76)$$

where $K(t)$ is the characteristic wavevector associated with the characteristic length, and $b(t)$ is a normalizing function. Lebowitz *et al* (1982) have analyzed the data of Singhal *et al* (1978) for Au-Pt alloy and found good confirmation of this hypothesis (see figure 39).

The question of coarsening has been considered even earlier in the context of nucleation theories. Lifshitz and Slyozov (1961) and independently Wagner (1961) have discussed the growth of droplets of B -rich phase immersed in an A -rich matrix. This theory was really derived for small supersaturation such as one obtains in the late stages of a nucleation and growth process (*e.g.* in clouds). It is however often assumed that the LSW theory can also be applied to the late stage coarsening of a spinodally decomposing system. The basic idea is that larger droplets grow at the expense of smaller droplets *via* the diffusion of B atoms between different droplets. An important conclusion of the theory is that the average droplet size $\bar{R}(t)$ (which is the characteristic length of the system) satisfies a $t^{1/3}$ power law. Lebowitz *et al* (1982) found that $K^{-1}(t)$ derived from simulation studies appeared to show such a behaviour. Attention must here be drawn to the fact that existing studies on grain growth neglect the possible influence of coherency strain, a factor that is pertinent in alloys, though not in liquids (Binder 1977).

There is one aspect of late stage behaviour we now wish to comment on that does not appear to have received attention thus far. It was noticed many years ago by de Fontaine (1967) during a simulation of spinodal decomposition (in one dimension) that whereas a compositional wave of well-defined wavelength develops immediately after instability is established, pretty soon a period doubling occurs. At that time, the possibility of period doubling as a route to chaos was not known (Feigenbaum 1978, 1979, 1980). The question of whether the formation of irregular domains is due to chaos appears worth a fresh examination. It is pertinent here to point out that de Fontaine (1975a) has mapped the problem of concentration evolution into a Hamiltonian problem and examined system evolution in terms of trajectories in a $(c, dc/dx)$ phase space. More recently, Aubry (1981, 1983) has in the study of certain defect structures, carried out a similar trajectory analysis and, what is more interesting, discovered the

possibility of chaos under certain conditions. One wonders whether it would not be worthwhile to go back to the de Fontaine problem and reexamine it from this new perspective. In support of such a suggestion, we call attention to figure 41 which shows a computer simulated spinodal structure and that for a real binary glass (Hopper 1982): The simulated structure was obtained by superposing twenty 3-D waves of a *single* wavelength but of random orientation and phases. Notwithstanding this, there appears to be a regularity of sorts in the simulated pattern as compared to the real micrograph. Perhaps features related to stochasticity arising out of period doubling do play a role.

4.5 Ordering reactions

The extensive theoretical work on spinodal decomposition reviewed in § 4.3 has been extended to some extent (Binder 1973; Billotet and Binder 1979) to ordering reactions, although there has not been matching experimental work on the kinetic aspects. However, some attention has been paid to critical phenomena one expects near phase boundaries.

We have already called attention to the early work of Johansson and Linde (1928). A more recent example is provided by the work of Hashimoto *et al* (1976) who studied ordering in Cu_3Au . Starting from the one-phase region, the sample was quenched to and held at various temperatures T below the (first-order) transition temperature T_i of 391°C . At each temperature, the electrical resistivity was monitored as a function of time, and the relaxation time τ for approach to equilibrium was deduced. A plot of τ vs T showed a sharp increase as $T \rightarrow T_i^-$. Other probes have also been used to study critical phenomena *e.g.* Zener relaxation (Radelaar and Ritzen 1969) and isothermal release of energy (d'Heurle and Gordon 1961).

X-rays have always been popular (see, for example the review by Cohen 1970), a recent example being the study of Hashimoto *et al* (1978). Cu_3Au the work horse, was the material investigated. The specimen was first annealed at a temperature $T > T_i$ and later quenched to a temperature below T_i and annealed at the latter temperature for various spells. After each spell, the sample was quenched into water and the x-ray intensity in the superlattice region (110) was scanned. Initially, only a broad and diffuse

Figure 41. On the right is an electron microscope picture of a real binary glass, showing the phase-separated structure. On the left is the simulated structure obtained using a *single* wavelength (after Hopper 1982).

peak was observed but on increasing annealing time the peak narrowed and intensified, signalling the onset of order. From a plot of linewidth as a function of annealing duration, the relaxation time τ could be extracted. A slowing down of relaxation was markedly evident as $T \rightarrow T_i^-$. Another investigation meriting particular mention is that of Chen and Cohen (1977). The unique feature was that by employing single crystals, Chen and Cohen were able to study τ as a function of k . Figure 42 shows their results for $\text{Cu}_{81.5}\text{Au}_{18.5}$ obtained after a temperature change 355° and 330°C . As expected, τ peaks near the superlattice position.

Earlier (in § 4.3) we noted that under certain conditions, phase separation takes on the character of a continuous transition. Is such a scenario possible in *ordering* systems? Indeed it is, as has been emphasized by de Fontaine (1981). The basic concept is easily understood with a reference to figure 43. In figure 43a is shown a family of free energy curves appropriate to a system undergoing a first-order phase transition. If the temperature is gradually lowered from above, order will set in at $T = T_i$ (figure 43b) via a nucleation and growth process. On the other hand, a sudden quench to a temperature below T_i can produce the situation depicted in figure 43c. The system responds to the instability through the generation of an ordering wave of wavevector corresponding to the minimum of $V(k)$. The wave swells in amplitude gradually, spreading order everywhere. Therefore, vis-a-vis nonequilibrium situations, one can think of an instability temperature $T_{\text{instab}} (< T_i)$ below which *continuous ordering* occurs.

While the concept seems possible, there is as yet no direct evidence for the existence of the instability temperature, although in an experiment due to Bardhan *et al* (1977) on Cu_3Au there is a strong suggestion. The analogue of the Schwahn-Schmatz experiment (§ 4.3) would be desirable. Incidentally, the dashed line in figure 15b is the variation of T_{instab} with composition, as deduced from cvm.

In some situations, continuous ordering is possible with an interesting twist. Following the creation of an instability, the system responds with a compositional wave whose wave vector does *not* coincide with that corresponding to the superlattice reflection.

Figure 42. Wavevector-dependent relaxation time $\tau(k)$. Shown here are data obtained along $\langle h00 \rangle$ and $\langle hh0 \rangle$ lines. The continuous line is a guide to the eye (after Chen and Cohen 1977).

Figure 43. System response to different temperature treatments (a). free energy curves for a first order transition, with transition temperature T_t . When slowly cooled from above, the system experiences metastability on reaching T_t , and orders by a nucleation and growth process. If suddenly cooled to a temperature well below T_t , as schematically illustrated in (c), it experiences an instability.

However, the system somehow seems to realize this during its evolution, and comes up with a suitable mid-course correction (rooted in nonlinearities?) so that the correct ordered structure results on attainment of equilibrium. Apparently, the point of maximum instability in reciprocal space need not always coincide with the wavevector corresponding to the ordering wave. de Fontaine (1975b) has suggested that Ni-Mo is a good candidate system for exhibiting such a schizophrenic behaviour! Here the instability is associated with a $\langle 1 \frac{1}{2} 0 \rangle$ wave whereas the ordering is based on a $\langle 100 \rangle$ wave. There is some evidence from x-ray diffraction (Chakravarti *et al* 1974) and electron microscopy (Das *et al* 1973) in support of the idea but a convincing test would be through a suitably designed real-time experiment.

On the theoretical side, Cook *et al* (1969) extended the Cahn-type analysis (which was essentially applied to a continuum) to discrete lattice systems and demonstrated that under suitable conditions, ordering with the formation of a superlattice was possible. In fact, the curves of figure 22 are the products of such a *linear* theory. In an effort to incorporate nonlinearities, Billotet and Binder (1979) have followed the footsteps of Langer with, however, due allowance for the fact that the order parameter is *not* conserved. (Recall remarks made in § 4.2 regarding conserved and nonconserved order parameters). Earlier, Binder (1973) had tried a time-dependent Ginzburg-Landau type approach, with as much success as may be expected of a mean field theory.

Billotet and Binder (1979) report many numerical calculations but unfortunately, barring some simulation results, they do not have much experimental data to compare

with. In fact Binder and Stauffer (1976) attempted to stimulate experimenters by explicitly calling attention to various aspects of the behaviour of electrical resistivity of binary alloys at phase transitions but the response of the experimental community does not seem to be adequate.

A few remarks now about late stage behaviour in ordering systems. It has been noted (Binder 1980b) that as in clustering reactions, one has to recognize the existence of two length scales (see figure 40), one of which is related to intradomain ordering and the other to domain size. Since one is dealing with an ordering reaction, the intradomain part can be conveniently explored near superlattice positions in a diffraction experiment. The domain-wall effects on the other hand, are best picked up in a small-angle scattering experiment.

There is another aspect of domain walls that has occasionally been mentioned in the literature (*e.g.* Gunton 1982) but does not appear to have been examined in depth. Now the formation of different domains is usually thought of in terms of nucleation of ordering in different regions and the subsequent growth of the latter, leading to the formation of interfaces. In the symmetry-breaking language on the other hand, each ordered region corresponds to a manifestation of one of the possible ground states. The macroscopic physical system is thus trapped in different ground states in different physical regions. The resulting configuration/defect (*i.e.* dw) is therefore a topological entity. The topological aspects of dw's have barely been investigated and are probably worth a closer scrutiny.

Finally, a brief hark back to long-period oscillations (see § 3.1) (Aubry 1981, 1983). One wonders whether some of the considerations in Aubry's analysis of incommensurate structures do not have relevance to LPO seen in some ordered systems. This also appears worth looking into.

We close this section by calling attention to an authoritative review by Freidel (1974) on the electronic aspects of order-disorder transformations (which we have skipped!). Physicists wishing to study order-disorder transformations, should not miss this paper!

5. What can experimenters do?

The title of this section is not intended to suggest that experimenters have been slack but merely that there is a dearth of certain types of information *e.g.* relaxation data.

Now each probe has its own characteristic sensitivity, and it is necessary to integrate for a certain time τ_M during the experiment to obtain a signal above the background. When exploring nonequilibrium phenomena this poses a problem if the relaxation time τ_R is less than τ_M . One then has to use an "arresting" technique as illustrated in figure 44, wherein the system is periodically "frozen" in its coast down and then monitored. For example, the data of figure 36 was obtained in this fashion. However, if the signal is strong, one may be able to follow temporal changes directly in realtime. Improvements are therefore necessary for many techniques, if realtime measurements are to become feasible. In some cases like electrical resistivity, the required sensitivities are already there but nevertheless, the capabilities do not appear to have been fully exploited. Where neutron and x-ray scattering are concerned, increase in the primary source strength is an important factor. The availability of synchrotron radiation sources is therefore a welcome development in respect of x-ray scattering. Hardly any results pertaining to phase transformations have been reported using synchrotron sources, and there is much room for innovation and ingenuity.

Figure 44. (a) Time variations of some property when a system is quenched as in (c). If the decay is rapid as in case (1), then the system must be periodically arrested in its coast down as illustrated in (b). This gives convenient measurement slots whose width τ_M can be chosen suitably to optimize (signal/noise) ratio. However, if the measurement time is small, then one can follow the decay in realtime i.e. the time-temperature profile will be as in (c). In the examples shown, this could be applied to case (2).

While discussing realtime measurements, it must be remembered that depending on the temperature, composition etc., the relaxation times can vary over several orders of magnitude. Attention is drawn in this context to the various quenches attempted by Lebowitz *et al* (1982) in their simulation experiments (see figure 38) and the wide spread in relaxation times observed by them. Thus, many techniques can in fact be used on an as-available basis without waiting for improvements, provided one chooses the conditions of experiment properly. In passing, it is worth noting that computer simulation is an expensive way of obtaining relaxation times. It is therefore very desirable to back it up with more extensive studies using a convenient probe (like resistivity).

The types of probes one could think of are many. Some, like resistivity, have already been mentioned. Others include internal friction, ultrasonic attenuation etc. Binder and Stauffer (1976) have discussed in detail how resistivity measurements can be linked to order parameter dynamics. They have also called attention to the need for conventional studies of scaling behaviour as one crosses the phase boundaries. For instance, it would

be very interesting to follow the variation of resistivity with concentration at various temperatures as sketched in figure 45. The sharp rise and fall in the indicated regions are closely related to critical dynamics of the order parameter.

In contrast to “macroscopic” probes like resistivity, the Mössbauer effect provides a probe that is nucleus sensitive. Oki *et al* (1977) have, for example, exploited this method to examine aspects of transformations in Fe-Al alloys. There is clearly more scope for work of this kind. Indeed, one could also consider NMR. With high-power pulsed NMR systems now commercially available, relaxation studies of the type considered here are no longer a mere theoretical possibility. The neutron is yet another nucleus-sensitive probe. In addition, it can also undergo magnetic scattering. Both these factors can be skilfully exploited, particularly where magnetic alloys are concerned. As of now, there appear to be very few examples of ordering kinetics studied using neutrons. One investigation I am aware of is the experiment of Collins and Teh (1973) on Ni_3Mn . These authors upquenched in the ordered state, and for each step change ΔT of temperature, they measured the time required for the order parameter to stabilize to its new value. The kinetics of the order parameter were monitored *via* Bragg intensity of an appropriate reflection. Of course, a sophisticated technique like neutron scattering is not always required. Nowick and Weisenberg (1958) for example, simply followed the time variation of the Young’s modulus in their upquench experiments on ordered Cu_3Au . In general, there is a paucity of information about system dynamics following a quench. One needs both upquench and downquench experiments, within a given phase (Binder 1977) as well as across a boundary.

While it is natural to think of relaxation time studies in the time domain, we should not forget traditional spectroscopy which also can give information about relaxation time, though of smaller magnitude. An experiment one could think of would be the analogue of the soft-mode studies made in connection with structural phase transitions (—for a review of this area, see Venkataraman 1979). There one has a lattice dynamical

Figure 45. Schematic plot of resistivity vs composition at various temperatures. The dots show the regions where there is a sharp rise or fall. (after Binder and Stauffer 1976).

mode whose frequency diminishes as $T \rightarrow T_c^+$. In ordering reactions, we have a compositional wave but of zero frequency. The scattering of radiation from this wave gives rise to intensity in the superlattice region. If an energy scan is made of the scattered intensity (—and this is possible with neutrons), then one will observe a certain frequency spread around $\omega = 0$, the spread being related to the relaxation time of the concerned compositional fluctuation. As $T \rightarrow T_c^+$, the line width must decrease, indicative of critical slowing down of the compositional fluctuations. A systematic, quasi-elastic scattering investigation of the ‘softening’ of compositional fluctuations does not appear to have been made so far.

Our preoccupation with long-range order should not blind us to short-range order which too is an important quantity! As the name itself indicates, the focus is on ordering on a localized scale. The key quantity is the (Ising) spin correlation $\langle S_i S_m \rangle$. By suitable definitions (de Fontaine 1979), this spin correlation function can be related to the pair correlation function $g(\mathbf{R} = \mathbf{m} - \mathbf{l})$ well-known in theory of liquids, and to experimentally measured quantities like the Warren-Cowley parameters. Clearly, short-range order would be of particular interest in the early stages after a quench, and in the disordered phase close to T_c . With synchrotron sources now available, it may be possible to follow the evolution of short-range order in realtime, at least in select cases. The results can then be linked to models for spin dynamics. Other possible studies concerning short-range order have been mentioned in § 3.3.

At a recent Discussion Meeting on the Physical Basis of Mechanical Behaviour organized under the auspices of the Academy (where, incidentally, Prof. Ramaseshan delivered the keynote address), Dr G Srinivasan raised the interesting question of heat liberated following a quench. In the discussion that followed, Prof. C K Majumdar drew attention to the pioneering work of Bragg and Williams (1935) wherein the approach to order had been discussed in terms of a fictitious temperature. Today, with our knowledge of magnetic resonance etc., we would identify this as the Ising spin temperature and the approach to equilibrium as a spin-lattice relaxation problem. This digression in the Discussion Meeting served to focus attention on the paucity of thermal measurements. Subsequently, I have come across one paper (d’Heurle and Gordon 1961) wherein calorimetry experiments on Au_3Cu during ordering are reported. By and large, studies on the energetics of ordering appear to be rare.

While comparing relaxation times obtained *via* different techniques, we should note that the coupling of the various probes to the order parameter is not the same. Moreover, some like resistivity, integrate the fluctuations of the order parameter over the wavevectors. Two such “integral” probes may not weight the different k ’s in the same manner. In this sense, x-rays and neutrons enjoy the advantage that one can select a specific wavevector for study. All the same, other probes have their own utility in that they are usually faster and also less expensive!

Thus far, we have confined attention to *equal-time* correlation functions of the form $\langle \psi(r, t) \psi(r', t) \rangle$. This function continually changes with time till equilibrium is attained at $t = \infty$. Probes like x-rays sample equal-time correlation function because they essentially produce an “instantaneous snapshot” of the system. We now extend consideration to *unequal* time correlation functions *i.e.*, functions of the form $\langle \psi(r, t) \psi(r', t') \rangle$. The relevance of such functions to experiment will be discussed shortly.

Billotet and Binder (1980) were the first to consider such functions in the context of phase transformations. The kinetics of such functions were modelled closely after Langer’s and their own earlier work on equal-time correlation function. They start with

the conditional probability $P^{\text{cond}}(\{\psi^1\}, t_1; \{\psi^2\}, t_2)$ which is the probability that the system is in the state $\{\psi^2\}$ at time t_2 , given that it was in state $\{\psi^1\}$ at t_1 . The continuity equation for P^{cond} is:

$$\frac{\partial}{\partial t_2} P^{\text{cond}}(\{\psi^1\}, t_1; \{\psi^2\}, t_2) = - \int d\mathbf{r} \frac{\delta J_r^{\text{cond}}(\{\psi^1\}, t_1; \{\psi^2\}, t_2)}{\delta \psi_r^{(2)}}, \quad (77)$$

the expression for J_r^{cond} being an obvious extension of (48). The sequence of steps thereafter is essentially the same as before, and, as earlier, a decoupling approximation is made for $P(\psi_{r_1}^{(1)}, t_1; \psi_{r_2}^{(2)}, t_2)$ which is the probability that we have a state $\psi_{r_1}^{(1)}$ at $\mathbf{r}_1$ at time t_1 and a state $\psi_{r_2}^{(2)}$ at $\mathbf{r}_2$ at time t_2 . In this way, they finally arrive at the following expression for $S(\mathbf{k}, t_2, t_1)$:

$$S(\mathbf{k}, t_2, t_1) = S(\mathbf{k}, t_1) \exp \left[-C \int_{t_1}^{t_2} dt \{Kk^2 + A(t)\} \right], \quad t_2 > t_1. \quad (78)$$

with $C = Mk^2$ if the order parameter is conserved.

The need for unequal-time correlation functions arises from the fact that some techniques probe the system not instantaneously, but over a certain period of time. For example, in an ultrasonic attenuation experiment, a time $\sim (1/\text{frequency})$ is involved. Similarly, in a neutron inelastic scattering experiment, fluctuations on a time scale $t \sim (\hbar/\Delta E)$ are explored where ΔE is the energy transfer (Brockhouse 1958). Now in a system in thermodynamic equilibrium, one can exploit the fact that the system is stationary and express a correlation function of the form

$$\langle \psi(t) \psi(t') \rangle \text{ as } \langle \psi(0) \psi(t' - t) \rangle.$$

Stationarity however does not obtain in our kind of situations. At best, one can divide the whole time range into suitable slots, and hope for stationarity within each slot (Stratanovich 1963).

Figure 46 offers a schematic comparison of the measurement of equal-time and unequal-time correlation functions. The total time span from $t = 0$ (instant of quench) to $t = \infty$ (when terminal equilibrium is attained) is imagined to be divided into convenient (not necessarily equal!) intervals such that there is local stationarity in each time slot in the Stratanovich sense. An experiment like x-ray diffraction if done in real time, would give the "average" structure for each time slot. Fluctuations *within* each slot will not be explored. For that, it is necessary to either use a "frequency sensitive" probe or directly a correlation technique. Owing to the overall nonstationary nature of the process, the correlation function $C(k, \tau; n)$ will depend on the index n of the time slot.

As just indicated, one method of exploring fluctuations is to employ a frequency-dependent probe like slow neutron inelastic scattering. Billotet and Binder (1980) have used their model for fluctuations to compute $S(k, \omega; n)$. Their spectra show pronounced deviations from the usually expected Lorentzian line shapes; also there are oscillations. However, they obtain negative cross-sections which, as they themselves note, is unphysical. Billotet and Binder attribute this to the inadequacy of their approximations. If earlier experience in the theory of liquids is any guide (de Gennes 1959), then I suspect that the trouble probably lies in the fact that the decoupling approximation for P has failed to respect the relevant sum rules.

While as of now theory is in a somewhat poor shape, there is nothing to prevent experimenters from studying fluctuations under nonequilibrium conditions using the various probes at their disposal. In particular, slow neutron scattering, ultrasonic

Figure 46. Shown in the middle are signals and their compartmentalization into slots indexed by n . In each slot, there is assumed to be stationarity. A conventional x-ray experiment measures equal-time correlation function for each slot, and the results finally appear as on the right. By performing an intensity correlation experiment in each slot, one can obtain information related to $\langle \psi(k, t) \psi(k, t + \tau) \rangle_n$ for each slot. Sketches of $C(k, \tau; n)$ are given on the left. For each n , one will have different $C(\tau)$ plots for the different k 's.

attenuation, internal friction are some of the tools which could be tried. Vigorous experimentation could in fact act as a spur to theory!

An alternative method of exploring unequal-time correlation functions is to resort to the newly emerging technique of fluctuation spectroscopy (Magde 1977; Venkataraman 1982). Here one observes a suitable quantity Q (which couples to the order parameter) over a time span corresponding to one of our slots, and records all its fluctuations. One then processes the data to obtain $\langle Q(t)Q(t') \rangle_n$. One example of fluctuations observed by neutron scattering is given in figure 47 (Pederson and Riste 1980). Of course in this particular example the system was in a stationary state but that is not necessarily a requirement. In fact, Kim *et al* (1978) have carried out a similar experiment but using light, and have actually studied phase separation kinetics in a fluid binary mixture. Intensity fluctuation spectroscopy (Berne and Pecora 1976) is being regularly used for exploring biophysical problems but its use in condensed matter physics is still rare. Where alloys are concerned light scattering is not possible but one could resort to a study of resistivity fluctuations (*e.g.* Venkataraman and Balakrishnan 1979). No such experiment relating to kinetics of phase separation in solids has been reported so far. However, Kim *et al* (1980) have used precisely this technique to study fluctuations in a binary fluid mixture near its critical point. If sufficient intensity is available, even x-ray and neutron experiments to explore fluctuations in the time domain can be attempted. In brief, the entire subject of fluctuations during decay to equilibrium is largely unexplored both theoretically and experimentally.

INTENSITY

Figure 47. Fluctuations of the scattered neutron intensity from a liquid crystal with a temperature gradient across. The system is in a stationary but nonequilibrium state. Observe that as the temperature gradient is varied, the fluctuation amplitude becomes large at a certain stage. This is associated with the onset of turbulence in the material (after Pedersen and Riste 1980).

6. Lamellar eutectic growth

In addition to the solid-to-solid transformations so far considered, certain liquid-to-solid transformations are also interesting, besides being important technologically. To understand such transformations, we refer to figure 48 which shows a binary phase diagram of the type we are currently interested in. For example, Ag-Cu and Pb-Sn systems exhibit such diagrams. Consider an alloy of composition C_0 and at a temperature such that its state is represented by the point a in the figure. On cooling and crossing the liquidus curve, one enters the region marked $(\alpha + L)$ which is a two-phase region where a liquid and a solid both coexist, the solid with composition C and the liquid with composition C_L . The relative proportions of the solid and the liquid vary continuously as one moves down the line abc until at the temperature T_E called the eutectic temperature, the liquid (of composition C_e) freezes. Of course one could come down along df ; then one would have a pure liquid phase until T_E at which point freezing occurs. This phase transformation *i.e.*, the freezing of the eutectic liquid is often called a eutectic reaction.

The solid state microstructure of the material having the composition C_e will be an intimate mixture of two phases α and β which are often present in the form of thin (around a few microns) platelets or rods. The lamellar microstructure of a typical

Figure 48. Illustration of the eutectic reaction.

eutectic is shown in figure 49 (Lyman 1972). The pattern is quite striking, undoubtedly reminding physicists of the patterns associated with hydrodynamic instabilities, for example. Indeed Langer has recently noted such similarities and has pointed out that as in the well-known Benard patterns associated with convective instability, the relevant steady state equations are incapable of predicting the unique behaviour observed experimentally. Specifically, the steady state theory of lamellar eutectic permits a wide range of lamellar spacings at any growth velocity whereas experiments seem to indicate a unique spacing. Accordingly, Datye and Langer (1981) have performed (as in hydrodynamics) a stability analysis for a model thinfilm eutectic. A major conclusion to emerge is that for off-eutectic compositions, there occurs a short wavelength instability. Figure 50 taken from the work of these authors shows a sketch of the oscillatory mode at its point of marginal instability. There is apparently some evidence from experiment for the existence of such a mode. As Langer notes, there is scope for much more work in this area both experimental and theoretical (especially in relation to kinetics). It certainly would be interesting to attempt experiments which are the analogue of those discussed in figure 47.

7. Summary

In this article, a broad overview of phase transformations has been attempted, essentially from a physicist's angle. While there are many aspects that might appeal to physicists, three areas have been highlighted since overlap with physics is manifestly evident. They are: The study of ground structures, the study of phase diagrams and the study of kinetics. In each area there are no doubt specifics and important details such as metallurgists are usually interested in, but there are also general features amenable to a basic analysis which physicists are likely to be attracted to.

In the area of ground state structures, the emphasis thus far appears to have been mainly on structures derived from bcc and fcc lattices. There is an obvious need to

Figure 49–50. 49. Picture of a 63 Sn-37 Pb eutectic (softsolder). The lead-rich solution appears dark in a matrix of tin lamellae (light) (after Lyman 1972). 50. Oscillatory mode at its point of marginal instability (after Datye and Langer 1981).

extend this to other systems like hcp etc. We call attention also to formal papers (Progov and Sinai 1975, 1976; Slawny 1979) on the subject lest such activity be dismissed as pedestrian! Inputting potential derived from first principles has thus far been largely avoided but given the vast progress made in pseudopotentials in recent years and the prospects for bigger and faster computers, one could envisage a new thrust. No doubt there is the additional complication of relaxation energy (see equation (19)) but one now knows how to handle this, at least in principle.

Study of phase diagrams *via* simulation has made impressive progress but there is still a vast territory ahead. The viability of the cvm has been well established although there is room for improvement both in terms of going to larger clusters (which, incidentally, will call for fresh computational ingenuity) as well as allowing the exchange integral to vary with composition. The possibility of frustration is a stimulating discovery and so far, theory has not addressed itself to this question. Given the vigorous study made of this concept in spin glass, one could envisage exciting new vistas in the study of ordered systems also. The mappings that phase diagram investigations have achieved vis-a-vis models popular in the study of magnetism should act as an extra stimulant to physicists. Indeed one could probably now hunt around for suitable systems which are proving grounds for various kinds of Potts model etc.

As regards kinetics, there is a pressing need for real-time measurements. This therefore is an area where physicists can make important contributions, given their vast experience with the study of relaxations. Of course the experiments may not be always easy, and ingenuity may be required in many cases! Correlation techniques have a bright future if one is bold enough to apply them (although theoretical support for interpretation is at present not available). Neutron scattering and x-ray scattering (especially using synchrotron radiation sources) are the preferred tools but others like

Mössbauer spectroscopy, ultrasonic attenuation and even resistivity can provide useful complements, being less expensive and also less time-consuming. Thus, while neutron scattering could be reserved for select measurements, back-up wide ranging scans can come from the other probes mentioned. Where theory is concerned, the area of kinetics is a veritable jackpot in as much as one is faced with fascinating questions about phase changes far from equilibrium.

To keep the discussion relatively simple we have confined ourselves to substitutional systems (usually, metals with metals give such systems). If we extend consideration to systems where the *B* atoms enter interstitially in *A* (e.g. O in Ti), then it opens up a new world altogether. And then there are ternaries. No doubt they complicate matters, but who knows what surprises they have in store? In addition, there are the mixed oxides and mixed glasses which too, under certain circumstances, show phase separation. The interesting point about these systems is that they are amenable to study by light scattering (Schroder 1977), a technique we have barely mentioned. In respect of light scattering, the new wave of interest on colloidal crystals (Pieranski 1983) is also noteworthy. It is quite conceivable that various kinetic studies of colloidal crystals can be performed using laser light the way one usually investigates alloys using x-rays.

We have stayed away from defects, for example vacancies. One knows vacancies affect diffusion and therefore the role of vacancies may require examination. Perhaps for the present, these questions are best left to the metallurgists!

We have also not dwelt much on microstructure. Metallurgists relish them! Certainly the patterns are fascinating but one tends to dismiss any underlying universality on the grounds that microstructure is probably controlled by local factors like dislocation density etc. This may be true to some extent but at the same time it is difficult to believe that Nature has no basic rules governing domain formation etc. Now that some links between defects and symmetry have been established (Mermin 1979), it is worth searching for possible universalities governing microstructure formation and evolution. Such deep insight can come only from physics but it requires a really bold venture!

8. Concluding remarks

The story goes that towards the end of the twenties when the Golden Age of quantum mechanics was drawing to a close, Dirac remarked that, 'the rest is all chemistry'. Such an extreme view of physics has continued to prevail, and as late as 1970, van Hove (who has himself made notable contributions to condensed matter physics) observed during an after-dinner address at the Batelle Colloquium on Critical Phenomena that, "We should constantly recall and reassert that the elucidation of the fundamental laws remain the most essential task of physics". Referring to critical phenomena and topics of a similar kind he said, "It seems to me that physics now looks more like chemistry in the sense that in percentage, a much larger portion of the total research activity deals with complex systems, structure and processes, as against a smaller fraction concerned with the fundamental laws of motion and interaction. This Colloquium is a good example. Surely we all believe that the fundamental laws of classical mechanics, of the electromagnetic interaction and of statistical mechanics dominate the multivarious transitions and critical phenomena you discuss this week, and I presume that none of you expects his work on such problems to lead to the modification of these laws. You

know the basic equations better than the phenomena. You are after the missing link between them *i.e.* the intermediate concepts “. . . which should allow a quantitative understanding and prediction of the phenomena . . .”. Domb (1981) from whose essay on Critical Phenomena these quotes have been extracted, strongly disputes such a narrow interpretation of the goals of physics and points out that the goal is not restricted to the discovery of fundamental laws alone but encompasses the understanding of natural phenomena in general. Asserting that the giants of the past followed such an approach Domb observes, “Clerk Maxwell tried to construct a mechanical model to illustrate Faraday’s laws of induction. He drew heavily on the theory of vortices in a perfect fluid and classical elasticity and was thereby led to introduce his famous displacement current. It was only later that he removed the ‘scaffolding’ to reveal the beautifully symmetric pattern of Maxwell’s equations”.

It is ironic that just around the time van Hove expressed his misgivings, Wilson did his celebrated work on critical phenomena which later earned for him the highest accolade of Science—the Nobel Prize. More significant, this paved the way for important feedback from statistical mechanics to particle physics (— *e.g.* there have been Monte Carlo simulations in connection with lattice gauge theories (Callaway and Rahman 1982), not dissimilar to the simulations discussed in §3.3).

In a different context, Anderson (1972) too has taken exception to the excessive importance attached to the study of fundamental laws. He observes, “The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the Universe. In fact, the more the elementary particle physicists tell us about the nature of the fundamental laws, the less relevance they seem to have to the very real problems of the rest of science, . . .”. Illustrating his point with examples from many-body physics, he questions whether a cooperative phenomenon like symmetry breaking (which lies at the heart of a phase transition) can be predicted starting purely from a knowledge of the basic interaction between the constituent elementary objects. As he succinctly puts it, more is different! Incidentally, symmetry breaking is another area where there has been a profitable feedback from condensed matter physics to particle physics.

The purpose of the above remarks and quotes is not merely to reinforce the point that condensed matter physics can as much be a frontier area, as, say, particle physics but also to remind condensed matter physicists that they in turn should avoid a snooty attitude towards materials science. As we have tried to argue in this article, there are many fascinating questions in materials science also, buried in the ‘complexities’ that traditional physicists shun. For those who dare to delve into these complexities and isolate the basic questions, the rewards could be great.

Beauty, it is said, is in the eyes of the beholder. Where physics is concerned, something similar appears to be true. The physics, turned out, often depends more on the investigator than on the phenomenon (at least the usual perception one has of it). We merely have to remind ourselves of the magical touch that Einstein gave to the observations of the botanist Robert Brown on the dancing pollen grain. What if he had dismissed it as ‘not physics’?

In this country, Prof. Ramaseshan was perhaps the first person to establish a bridge between physics and materials science in a big way. Reared in the traditions of the Raman School, where the emphasis always was on natural phenomena in their totality, he was not averse to taking on the problems of materials when the challenge came. On the other hand, he invariably put to use his rich experience in physics and demonstrated

that by doing so, one could introduce novel approaches to familiar problems. Not surprisingly, he made the plea at Baroda for a larger perspective while defining Thrust Areas. It has been a pleasant task for me to amplify and illustrate that theme through this article. I only hope it does full justice to his remarks.

Acknowledgements

My interest in this area was aroused by the lectures I heard a few years ago at Varenna given by Prof. de Fontaine. I am grateful to him for subsequently sending me several of his reprints and preprints which helped me dig deeper into the subject. I would also like to express my thanks to Dr D Sahoo for several discussions, to Radha Ranganathan for assistance with the preparation of the manuscript, to P Subba Rao for efficient and skilful typing and to P Harikumar and R Kannan for taking care of the graphics. Finally, I would like to acknowledge my indebtedness to the many authors whose work I have freely drawn upon in preparing this review.

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