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UNIVERSALITY IN THE KINETICS OF FIRST-ORDER PHASE TRANSITIONS

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Summary : The problem of the existence of universality classes in the kinetics of first order phase transitions is considered in view of the latest theoretical and experimental results.

1. Introduction

The kinetics of first order phase transitions studies the dynamical evolution induced by a sudden change of external thermodynamic parameters in a system which exhibits a first order phase transition. Let us illustrate the problem on a simple example, the binary alloy A - B. The phase diagram of this system is drawn on Fig. 1. The states above the coexistence curve are homogeneous. Below the coexistence curve, the spinodale line divides the states into metastable and unstable ones.

One considers the following process. An alloy of a given concentration c prepared in a homogeneous state (i.e. at temperature T_1) is suddently quenched at a temperature T_2, below the coexistence curve in a far from equilibrium state. This system will evolve to reach eventually a new equilibrium state in which it is formed of two phases, one rich in A (concentration c_A), the other rich in B (concentration c_B). What is the dynamical evolution between the initial and final equilibrium states is the question one would like to answer.

Transmission electron microscope experiments show that two different situations occur. A metastable system phase separates via the birth and growth of droplets and one speaks of nucleation process. An unstable system phase separates via the formation of a finely dispersed precipitate which gradually coarsens. One speaks of spinodal decomposition. In both cases, it is suitable to distinguish two distinct regimes : the early and late time regimes. The main

features of the dynamical evolution for all cases is summarized in Table 1.

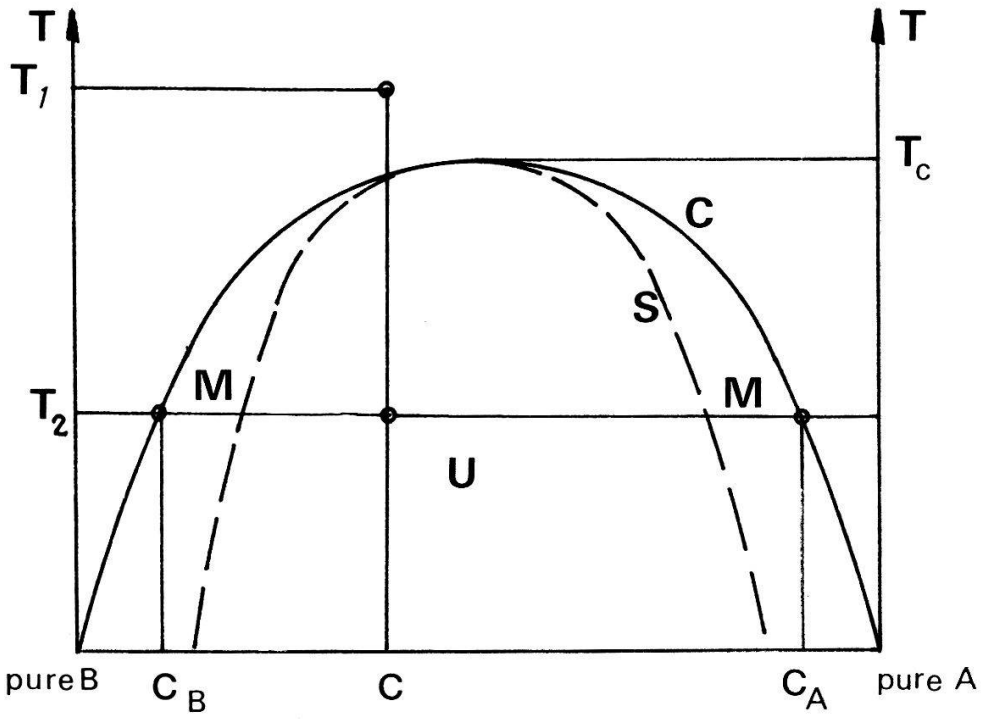

Figure 1 : Phase diagram temperature-concentration for a binary alloy. C is the coexistence curve, S the spinodale line. M and U are respectively the metastable and unstable states.

Note that the homogeneous nucleation and the spinodal decomposition are just two asymptotic limits of a same phenomenon. Indeed, the spinodale line is a mean-field concept and thus one should observe a smooth crossover between the two limit cases when one varies continuously the concentration of the alloy. Note also that the hamiltonian describing the static properties of the binary alloy can be mapped onto the one of an Ising system. Working at fixed concentration means in Ising terms working at fixed magnetization.

A very important quantity accessible to experiment is the nonequilibrium structure factor $S(q,t)$. Experimentally one finds that after a transient time t_o following the quench, $S(q,t)$ scales according to [1,2] :

$$S(q,t) \simeq L^d(t) F[x(t)] \qquad (1)$$

where $x(t) = qL(t)$ and d is the dimensionality of the system. Thus the

Table 1

HOMOGENEOUS NUCLEATION (dynamical evolution of a metastable state)	SPINODALE DECOMPOSITION (dynamical evolution of an unstable state)
EARLY TIME	
- Localized droplets with finite size, needed to initiate the phase separation. - Instability towards large localized fluctuations. - Finite activation energy. - Critical droplet radius R_c. Droplets with $R < R_c$ shrink and with $R > R_c$ grow.	- Spontaneous formation of a finely dispersed precipitate (inter connected pattern). - Instability towards small and long wave-length fluctuations. - No activation energy.
LATE TIME	
- Growth of the droplets of the minority phase. - Well defined droplet interface.	- Growth of the interconnected pattern. - Formation of well defined interfaces

problem is characterized by one lenght $L(t)$. Eq. (1) expresses the self-similarity observed in the coarsening of the pattern. Moreover, $L(t)$ behaves for large times as

$$L(t) \approx A + Bt^n[1 + t^{-m} + \ldots] \quad . \tag{2}$$

The exponent n is called the growth exponent and characterizes the long time behaviour of $L(t)$.

In view of what we know from the theory of critical phenomena, it is a natural question to ask if there exist or not some universality classes for these

far from equilibrium phenomena. If universality holds what are the parameters which define an universality class. The theoretical problem one has to face is to compute from first principles the structure factor. This is a difficult problem. The main approaches will be briefly reviewed in the next section.

2. Theoretical Approaches

Three types of approaches have been used for this problem [1] :

2a. The semi-microscopic approach

The microscopic degrees of freedom (i.e. the local concentrations c_i or the local spins s_i) interact with the heat bath. The evolution is given in terms of a master equation for the probability $P\{c,t\}$ that the configuration $c = \{c_i\}$ is realized at time t, namely

$$d_t P\{c,t\} = -\sum_{c'} \omega(c,c') P(c,t) + \sum_{c'} \omega(c',c) P(c,t) \quad . \tag{3}$$

Most of the physics is contained in the transition rate $\omega(c,c')$. This rate can be chosen in such a way that the order parameter (i.e. the concentration or the magnetization) is conserved or not conserved. This leads respectively to the well known Kawasaki [3] or Glauber [4] dynamics. The structure factor is given by

$$\tilde{S}_{ij}(t) = \mathrm{Tr}_c \{ (c_i - \langle c_i \rangle)(c_j - \langle c_j \rangle) P(c,t) \} \quad . \tag{4}$$

The equation of motion for $\tilde{S}_{ij}(t)$ follows from (3). It turns out that, except for a special choice of ω in the one dimensional case with non conserved order parameter [4], the equation of motion for $\tilde{S}_{ij}(t)$ is not closed. Higher order correlations are involved and one has to face an infinite hierarchy of equations. Accordingly, there is no analytical solution to this problem.

Different approximations have been proposed. In two dimensions, an ad hoc real space renormalization group method leads to reasonable results for the Ising model [5] but its applicability to other models is questionable [6]. The

most widely used technique to compute the structure factor in this semi-microscopic framework is the Monte Carlo method [7]. However, this technique is not free of difficulties. Different values of the growth exponent can be obtained by using different spin updating in the Monte Carlo simulation [8,9].

2b. Phenomenological cluster dynamics

In this less microscopic approach, one considers the time evolution of $n(\ell,t)$, the average number of clusters of size ℓ. This is a generalization of the celebrated Becker-Döring theory of nucleation [10]. We shall not discuss this phenomenological approach in details here (see for example [11]).

2c. Semi-macroscopic approach : field theory for coarse-grained variables

Instead of looking to the problem on a microscopic scale, one considers coarse-grained variables $c(\vec{x},t)$. The $c(\vec{x},t)$ are obtained by averaging the microscopic variables c_i over domains of size D of the order of the correlation length ξ of the system. The description is thus semi-macroscopic. The coarse-grained free energy functional $F\{c(\vec{x})\}$, describing the equilibrium properties of the system, could in principle be computed from the microscopic hamiltonian [2], but one seldom is able to perform explicitly this procedure. One rather assumes a phenomenological Ginzburg-Landau form for $F\{c(\vec{x})\}$ such as to reflect the physical properties of the microscopic model, i.e. the presence of a phase transition at T_c. Accordingly,

$$F\{c(\vec{x})\} = \int d^d\vec{x}\left[\frac{K}{2}(\vec{\nabla}c)^2 + f(c)\right] \tag{5}$$

where $f(c)$ is an one well potential for $T > T_c$ and a two well potential for $T < T_c$.

Through the coarse-graining process, the dynamics of the field $c(\vec{x},t)$ is now given by a non linear Langevin equation [2]. Here again, the various conservation laws should be taken into account. Two particularly simple models, corresponding respectively to a non conserved or conserved order parameter, and called "model A" and "model B" in the literature [12], are characterized by the following Langevin equations :

$$\partial_t c(\vec{x},t) = -M_\alpha \frac{\delta F}{\delta c(\vec{x},t)} + \xi(\vec{x},t) \tag{6}$$

where $\langle \xi(\vec{x},t) \rangle = 0$,

$$\langle \xi(\vec{x},t)\,\xi(\vec{x}',t') \rangle = -2k_B T M_\alpha \delta(\vec{x}-\vec{x}')\,\delta(t-t') \tag{7}$$

and $$M_\alpha = \begin{cases} M' & \text{for model A} \\ M\nabla^2_{\vec{x}} & \text{for model B} \end{cases} . \tag{8}$$

The binary alloy is thus described by model B. In this case, the equation of motion for the structure factor is [2] :

$$d_t S(q,t) = -2Mq^2[Kq^2 + f_o^{(2)}]S(q,t) + 2k_B T M q^2 + \sum_{n\geq 3} \frac{1}{(n-1)!} f_o^{(n)} S_n(q,t) \tag{9}$$

where $S_n(q,t)$ is the Fourier transform of $\langle \delta c^{(n-1)}(\vec{x},t)\,\delta c(\vec{0},t) \rangle$ with $\delta c(\vec{x},t) = c(\vec{x},t) - \langle c(\vec{x},t) \rangle$ and $f_o^{(n)} = (\partial^n f/\partial c^n)_{eq}$.

Again, the equation of motion for $S(q,t)$ is not closed. Higher order correlation functions appear. A general solution is not possible and one has recourse to approximations. Two regimes should be distinguished : the early time and late time regime.

Note that a description of the dynamics in terms of non linear Langevin equations has been widely used in the framework of the critical dynamics when approaching T_c from above. It turns out that in this case, the universality classes are characterized by [12] :

- the dimensionality of the system d
- the number of components of the order parameter n
- the symmetry of the model
- the conservation laws
- the "hydrodynamic modes".

This could give some clues about the universality classes for the first order

phase transitions.

3. Early and Late Stage Approximations

Let us return to the simple case of the binary alloy, or the Ising model, and discuss some important approximations.

3a. Early stage approximations

The simplest approximation consists in neglecting the non linear terms in the equation of motion (9) for $S(q,t)$, keeping [13] or not [14] the noise term. The main feature is that the structure factor initially grows exponentially with time for all q smaller than a critical value q_c. Such an exponential growth is only correct for very early times. The only reasonably successful early time theory of spinodal decomposition which treats the non linear dynamical effects is due to Langer, Bar-on and Miller [15]. Their theory is a particular truncation of the exact equation of motion (9) which is plausible but not systematic. The higher order correlation-functions S_n are approximatively expressed in terms of S and of the moments of the one point distribution functional $P_1\{c,t\}$. With the ansatz that P_1 is the sum of two Gaussians, the calculation of $S(q,t)$ is carried out numerically. It turns out that this approach quite satisfactorily explains the main qualitative features of the early time development. However, focusing on long wave-length instabilities, this theory is not able to describe nucleation and growth.

3b. Late stage approximations

For late stages, the interfaces between phases are well defined and gently curved. Accordingly, it is natural to look for a description in terms of dynamics of interfaces. At great deal of effort has been recently devoted to the dynamics of interfaces for a system whose order parameter is non conserved (model A). These works are based on the so-called kinetic drumhead model. A deterministic version of this model was first derived by Allen and Cahn [16]. They showed that the normal component of the interface velocity is simply given by :

$$v = KM'\Gamma \tag{10}$$

where Γ is the mean local curvature of the interface, which is acting as a driving force. The average domain size is $L(t) \sim t^{1/2}$ and thus the growth exponent is :

$$n = 1/2 \tag{11}$$

in good agreement with experimental results for 2 and 3 dimensions.

A non deterministic version of this problem has been worked out by Kawasaki and Otha [17]. Several developments of these works have been performed. Otha, Jasnow and Kawasaki [18] obtained an approximate solution of the Allen-Cahn equation in d-dimensions. They derived an explicit form for the structure factor in 2 and 3 dimensions which is in reasonable agreement with Monte Carlo studies of the kinetic antiferromagnetic Ising model. The scaling function F depends explicitly on the dimension d. The role of the thermal fluctuations on the interface dynamics has been considered by Grant and Gunton [19]. There is competition between the flattening of the interface due to the driving force associated with the curvature and the roughening of the interface due to thermal fluctuations. This leads to a slowing down of the growth process. However, this slowing down does not show up in the growth exponent but only in the amplitudes. Note also that all the above works do not treat properly the non linear aspect of the problem.

In the case of a conserved order parameter (model B), one has one of the few reasonably well established theoretical result. The late stage growth of droplets in the case of a small initial supersaturation has been solved by Lifshitz and Slyozov [20]. The growth exponent in this case is :

$$n = 1/3 \ . \tag{12}$$

This value is in good agreement with some experiments in 2 and 3 dimensions.

The above results show how the conservation laws and the dimensionality enter into the determination of the growth exponent. However, only the case of an one component order parameter was considered until now. Many questions remain unanswered such as : what is the role played by the number of components of the order parameter (i.e. the degeneracy of the ground state), the

depth of the quench, the presence of disorder in the system ?

4. Recent Developments

We briefly review what is the present situation concerning the above questions.

4a. Degeneracy of the ground state and depth of the quench

An old phenomenological argument due to Lifshitz [21] and rederived more recently by Safran [22] claims that if the degeneracy p of the ground state is too large, there is a slowing down of the growth mechanism due to the pinning of the vertices formed by the intersections of interfaces. More quantitatively, it is predicted that if $p > d + 1$, then $L(t) \sim \ell nt$. This prediction has been tested by Monte Carlo simulations in two dimensions. For q-state Potts model on a triangular lattice no pinning has been observed and the growth exponent vary smoothly from $n = 1/2$ for $q = 2$ to $n \simeq 0.42$ for $q > 26$ [23]. For the same system on a square lattice, the results are similar to the triangular case for a quench at a temperature $T > 0.5T_c$. For $T < 0.5T_c$ pinning is observed [24]. The situation is somehow similar for the N-state clock model [25]. However, it is yet not clear if there is pinning or not at low temperature.

Recent studies on classical xy model with anisotropy (for which $p = 4$) lead to the introduction of the concepts of "soft wall" or "hard wall" between phases [26]. This would lead to two different universality classes related to the rigidity of the interfaces. The situation is thus still very unclear.

4b. Quenched disorder in the system

Recent Monte Carlo simulations for 2 dimensional Potts models with quenched disorder [27] have shown that the characteristic lenght $L(t)$ was growing for intermediate times similarly to the pure case. However, for large time, the interfaces get pinned by the quenched impurities and the growth mechanisms stops.

In conclusion, we see that many questions about the universality classes in kinetics of first order transition are unanswered. The reason is that we do

not have yet a good and complete theory to explain the (real or numerical) experimental results. Only asymptotic predictions (early or late stage) are known. All theories assume that for late stage the growth is finally dominated by one mechanism. However, a worse situation could happen. Recently, Fukurawa speculatively suggested a possible chaotic competition between various growth mechanisms [28]. It results corrections to the growth exponent similarly as intermitency does in turbulent flow.

Even in the simplest case in which one mechanism finally dominates, it would be crucial to know when one has reached this asymptotic regime. Thus, it would be of great interest to know how one crosses over from the early stage to the late stage.

At lot of work remains to be done but progress is slow due to both the non linear and non equilibrium character of the problem.

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