The kinetic rate law for a Φ^4 model in the order/disorder limit

S Padlewski†‡ and S Dattagupta†

† School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India
‡ Theory of Condensed Matter, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

Abstract. A kinetic rate law is established for a Φ^4 model on a lattice when the system is initially placed in a configurational state far away from thermal equilibrium. The discussion is based on a Fokker–Planck equation, which is used for describing the relaxation of the non-conserved order parameter. On applying a mean-field approximation, the N coupled integro-differential equations reduce to one self-consistent equation for the order parameter. The relaxation of the order parameter in a quenching procedure is next compared with a molecular dynamic simulation of the same approximate potential. The agreement is excellent. Finally, in the limit of a very deep on-site potential, the rate equation of the order parameter is shown to reduce to the well known Glauber equation for a two-state Ising system and by following the Kramers treatment, one also deduces the rate of jumps from one well to the other. The latter rate is found to be small, as expected. Also considered in brief is the conserved order parameter relaxation behaviour in the order/disorder limit, which is shown to yield the Kawasaki rate equation.

1. Introduction

During the last decade the Φ^4 model on a lattice has been widely employed for modelling structural phase transitions. The model is able to cover a wide range of phenomena, from the so-called soft-mode behaviour (SiO_2, $NaNO_3$, biphenyl, etc) to the order/disorder type of phase transition ($NaNO_2$, $ClNH_4$). In the soft-mode limit the phase transition can be described in terms of the renormalized phonon theory (Bruce 1980, Bruce and Cowley 1980). In this the system is found to possess a mode of lattice vibration that softens as the temperature decreases towards T_c. At the critical temperature this mode freezes completely, and so a static field of displacement of the atom positions is induced within the structure. In the other extreme the system is described by an order/disorder dynamical behaviour characterized by atoms or clusters fluctuating between two more or less discrete states (Bruce 1980). This paper is devoted to the order/disorder case.

For the following, we consider the Hamiltonian form

$$H = \sum_i \frac{m}{2}\left(\frac{dU_i}{dt}\right)^2 + \Phi(\{U_i\}) \tag{1.1}$$

with

$$\Phi(\{U_i\}) = \sum_i \left(\alpha U_i^2 + \gamma U_i^4 - U_i \sum_{j \neq i} J_{ij} U_j\right). \tag{1.2}$$

The parameters α, γ represent the on-site energy parameters ($\gamma > 0$) and the J_{ij} represent the pairwise intersite interactions. The variable U_i can stand for the rotation of the tetrahedral cluster SiO$_4$ in quartz or the torsion of benzene rings relative to each other in crystalline biphenyl (Benckert 1987). The parameter m is a corresponding generalized inertia. The coupling terms J_{ij} determine the wave vector at which the phase transition occurs. By considering strong competition between the J_{ij}, for example, one recovers the Janssen model used for modelling displacive modulated structure (Janssen 1986). For the present purpose we only consider a ferro-distortive phase transition, which can be obtained by setting all the J_{ij} positive in equation (1.2).

The on-site potential controls the dominant behaviour of the system. In particular we have shown recently (Padlewski *et al* 1991) that $\alpha/J > 0$ leads to a soft-mode type of behaviour whose displacement on lowering T freezes at T_c. In the opposite case, for a double-well on-site potential with $\alpha/J < 0$ we have established that the Φ^4 model describes an order/disorder dynamic system because it becomes like an Ising model with U_i near the bottom of one or the other well.

In this paper we study the relaxation behaviour of the system described by the Hamiltonian (1.1) when it is initially placed in a state far away from thermal equilibrium. Our work has been motivated by the recent revival of interest in mineralogy for systems away from equilibrium (Salje 1988) and may be viewed as being complementary to our earlier study of discrete Ising-like systems (Dattagupta *et al* 1991a, b). Although the relaxational time scale is extremely short, i.e. of the order of a phonon process for $\alpha/J > 0$, it can reach geological proportions in the order/disorder limit $\alpha/J \ll 0$.

In our present approach we mainly discuss the dynamic process of (1.1) relevant for a system characterized by a non-conserved order parameter. We show that in the order/disorder limit $\alpha/J \ll 0$, the rate equation of the order parameter takes the form of the well known Glauber rate equation for a two-state Ising system. We also address this problem with a conserved order parameter (section 5) where we recover the Kawasaki rate equation in the order/disorder limit. Thus the present study provides a clear link between the kinetics of continuum and discrete models and helps in the understanding of the domains of applicability of different analytical and numerical schemes.

The plan of the paper is as follows. In section 2 we derive a rate equation of a non-conserved order parameter. This can be done by considering a Fokker–Planck equation characterizing the relaxation of the distribution function in the high-friction limit appropriate to the Hamiltonian (1.1). The rate equation of the order parameter involves a set of N coupled integro-differential equations, whose solution is transparent if one uses a mean-field approximation (MFA). This reduces the problem to a unique self-consistent equation. The mean-field solution can also be recovered exactly by considering an approximate potential Φ_{MF} where each variable U_i interacts identically with all others with

$$J_{ij} = J/N > 0 \qquad \text{for all } (i, j) \text{ neighbours} \qquad (1.3)$$

and N is the total number of sites. The introduction of the potential Φ_{MF}, in fact, makes perfect physical sense if we note that many minerals possess long-range interactions (Salje 1990). In section 3 we compare the relaxation of the non-conserved order parameter predicted for Φ_{MF} with a molecular dynamics simulation (MDS) of

the Hamiltonian with the coupling terms (1.3). One finds a very good agreement, strengthening our confidence in the MFA. However, very deep on-site potentials are not accessible to MDS and therefore, in section 4, we show analytically how the rate equation of the order parameter reduces to the form of the Glauber rate equation for a discrete two-state Ising system (Dattagupta *et al* 1991a, b). This situation is relevant for $\alpha/J \ll 0$ and $kT \ll$ 'hump size' of the double well. In this limit we deduce the Kramers rate of activation from one well to the other for the entity U_i. In section 5 we consider the conserved order parameter case. We also derive a rate equation for the order parameter. In the order/disorder limit we recover the Kawasaki rate equation for a two-state Ising system. Finally, our principal conclusions are summarized in section 6.

2. Rate equation for the order parameter

In this section we establish the rate equation for the non-conserved order parameter when the system (1.1) is initially placed in a state that is far away from thermal equilibrium. It suffices for our purpose to neglect the momentum variables, in the high-friction limit, as we are only interested in the order parameter kinetics. The corresponding equation for the distribution function $W(\{U_i\}, t)$ with $\{U_i\}$ representing a configuration of all entities U_i, has the well known Fokker–Planck structure (Risken 1989)

$$\frac{\partial W(\{U_i\}, t)}{\partial t} = \frac{1}{\varepsilon} \left[\sum_i \frac{\partial}{\partial U_i} \left(\frac{\partial \Phi(\{U_i\})}{\partial U_i} \right) + kT \sum_i \frac{\partial^2}{\partial U_i^2} \right] W(\{U_i\}, t). \tag{2.1}$$

Equation (2.1) has the built-in detailed-balance condition, which ensures that $W(\{U_i\}, t)$ approaches the equilibrium distribution at a final temperature T asymptotically, from any arbitrary initial state. The equation (2.1) can be used to derive the equations of motion of all the moments and correlations of $U_i(t)$. The simplest of these equations is the one for the first moment, which describes the order parameter kinetics. In order to derive this equation we need to multiply both sides of equation (2.1) by U_j and integrate with respect to all entities $\{U_i\}$, using free boundary conditions. As the distribution function and any of its first derivatives with respect to U_k vanish when each variable U_i reaches infinity, it is easy to deduce that

$$\frac{\mathrm{d}\langle U_j \rangle}{\mathrm{d}t} = -\frac{1}{\varepsilon} \int \prod_{k=1}^N \mathrm{d}U_k \frac{\partial \Phi(\{U_i\})}{\partial U_j} W(\{U_i\}, t) = -\frac{1}{\varepsilon} \left\langle \frac{\partial \Phi(\{U_i\})}{\partial U_j} \right\rangle \tag{2.2}$$

where

$$\frac{\partial \Phi(\{U_i\})}{\partial U_j} = 2\alpha U_j + 4\gamma U_j^3 - 2 \sum_{i \neq j} J_{ij} U_i. \tag{2.3}$$

The above set of N coupled integro-differential equations is quite intricate to handle. However, as we mentioned earlier, we are interested in the kinetics of systems with very-long-range interactions over wide ranges of temperatures. Hence it is appropriate to use the MFA, which leads to a drastic simplification of (2.2). In the MFA we assume

that the variable U_j at site j does not feel the fluctuation of its neighbouring sites but only an average local field. One may additionally use the fact that the time dependence of the average value $\langle U_j(t) \rangle$ is independent of the site index j, thus yielding the equation

$$\frac{\mathrm{d}\langle U \rangle}{\mathrm{d}t} = -\frac{1}{\varepsilon}\left[2\left(\alpha - \sum_l J_{0l}\right)\langle U \rangle + 4\gamma\langle U^3 \rangle\right]. \tag{2.4}$$

Whereas, in general, $\langle U^3 \rangle$ should be determined by going back to the Fokker–Planck equation (2.1), we make a simplifying assumption in order to treat this non-linear term. Recall that the detailed-balance relation constrains the distribution function to approach the Boltzmann distribution asymptotically. We now make the additional assumption that the system obeys a 'local' detailed-balance relation at any time during the relaxation process. In other words we take it that any given variable $U_i(t)$, subjected to the local time-dependent field $H_i(t)$, is always in equilibrium with it, so that the distribution function driving the variable $U_i(t)$ at time t is given by a Boltzmann distribution where all the other variables are fixed at $\{U_{j\neq i}\}(t)$. Note that one routinely uses the same assumption in a Metropolis algorithm while simulating systems away from thermal equilibrium (Binder 1979). Thus we write for the non-linear term in (2.4)

$$\langle U^3 \rangle = \int \mathrm{d}U\, U^3 \exp\left[-\beta\left(\alpha U^2 + \gamma U^4 - 2\langle U \rangle U \sum_l J_{0l}\right)\right]$$

$$\times \left\{\int \mathrm{d}U\, \exp\left[-\beta\left(\alpha U^2 + \gamma U^4 - 2\langle U \rangle U \sum_l J_{0l}\right)\right]\right\}^{-1}. \tag{2.5}$$

Equation (2.4), read in conjunction with (2.5), acquires a self-consistent meaning. How good the assumption embodied in equation (2.5) really is will be tested against a molecular dynamics simulation (see section 3).

It may be remarked that one can retrieve the above result by formulating the problem in a somewhat different way. Instead of using the decoupling approximation leading to (2.4) from (2.2), we can handle in an exact way the mean-field potential Φ_{MF} defined as

$$\Phi_{\mathrm{MF}} = \alpha U^2 + \gamma U^4 - 2JU\langle U \rangle \tag{2.6}$$

where

$$J = \sum_l J_{0l}. \tag{2.7}$$

The mean-field potential (2.6) is an exact representation of the potential (1.2) in the limit of long-range interactions where any site is equally coupled to all the others (see equation (1.3)). With reference to equation (2.6), the Fokker–Planck equation (2.1) takes the simplified form

$$\partial W(U,t)/\partial t = (1/\varepsilon)\,\partial J(U,t)/\partial U \tag{2.8}$$

where

$$J(U,t) = [\partial\Phi_{\mathrm{MF}}(U)/\partial U]W(U,t) + kT\,\partial W(U,t)/\partial U. \qquad (2.9)$$

Evidently, the average $\langle U(t)\rangle$, which appears in (2.6), is self-consistently determined by

$$\langle U(t)\rangle = \int \mathrm{d}U\, U W(U,t). \qquad (2.10)$$

This point is exemplified by figure 1 in which the mean-field potential Φ_{MF} is shown to take the form of an asymmetric double well with a marked shift in the two minima.
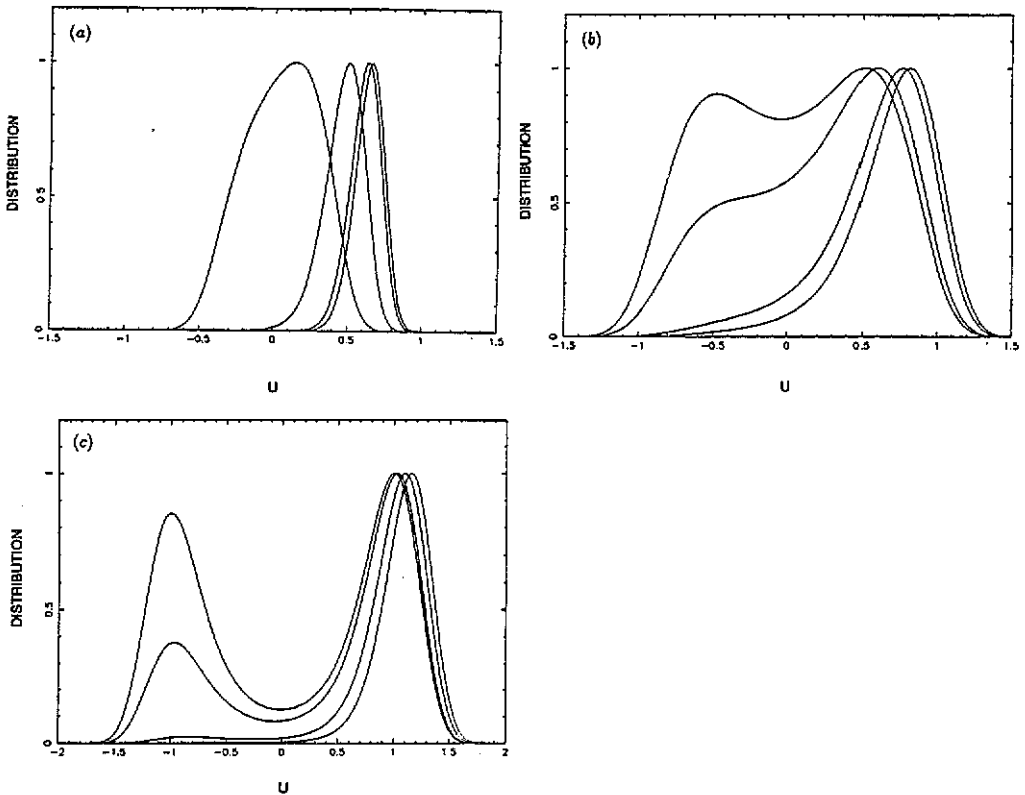

Figure 1. Relaxation of the distribution function in a quenching procedure from $T_{\mathrm{high}} > T_c$ to $T_{\mathrm{low}} < T_c$ taken at different times (intervals of $2.5 \times 10^4\,\delta t$, where the time step of integration is $\delta t = 1.5 \times 10^{-5}$ s). The plots result from the numerical solution of equation (2.8). The initial distribution function is fixed by the Boltzmann distribution at T_{high} and is given by $W(U, t = 0) \approx \exp[-\beta_{\mathrm{high}}\Phi_{\mathrm{MF}}(U)]$ with $\langle U\rangle \ll 1$ (see (2.6)). The maxima of these functions are normalized to unity for the following cases: (a), $\alpha = 0.1$; (b), $\alpha = -0.5$; (c), $\alpha = -2$. In all three cases we used $J = 1$ and $\gamma = 1$ with $T_{\mathrm{high}}/T_c \approx 1.2$, $T_{\mathrm{low}}/T_c \approx 0.3$ and $\epsilon = 1$.

By employing the single-site Fokker–Planck equation (2.8), we can proceed in the same manner as before, that is employ the same 'local' detailed-balance relation, and derive equations (2.4) and (2.5). We wish to emphasize once again that the potential (2.6), introduced here for mathematical simplicity, does indeed provide a valid description of mineral systems in which strain-mediated interactions are known to be very long range (Salje 1990).

3. Comparison with the molecular dynamics simulation

In this section we solve numerically the Fokker–Planck equation (2.8) for different on-site potential shapes and we also compare the results obtained from the rate equation of the order parameter (2.4) with those of molecular dynamics simulations (MDS) of the Hamiltonian dynamics governed by the potential (1.2) under the restriction (1.3), implying that each site is equally coupled to all others with constant strength.

The Fokker–Planck equation (2.8) that we have derived from Φ_{MF} tells us how the relevant distribution function evolves during relaxation processes. We solve this equation numerically following the techniques described in Indira (1982), and in which the system is allowed to evolve from $T > T_c$ towards $T < T_c$. In figure 1(a) we plot the distribution function for $\alpha = 0.1$, i.e. a single well, at different times while the system undergoes relaxation. Note that one finds a single peak shifted towards equilibrium. In figures 1(b) and (c), we present similar sketches for different $\alpha < 0$, corresponding to double-well on-site potentials. Here, the distribution function has a double peak, which evolves in a different manner. Instead of a global shifting of the whole distribution function, the relative size of the two peaks changes during the evolution. The location of the two peaks is, in addition, slightly shifted as can be appreciated by referring to figure 2 in which the mean-field potential Φ_{MF} is shown to take the form of an asymmetric double well with shifted minima. However, for $\alpha/J \ll 0$ the time dependence of $\langle U \rangle$ does not affect the minima of Φ_{MF} as shown in figure 3 and we shall use this fact later in the order/disorder limit of the Φ^4 model.

Next, we present results of an MDS of the potential Φ_{MF} (1.2) in a quenching procedure. In this, we have carried out the simulation on a parallel-processor array (AMT-DAP, Cambridge), which runs on a lattice of $16 \times 16 \times 16$ elements with periodic boundary conditions. In the present study, we only consider the extreme long-range coupling where each site is equally coupled to all other sites with the same coupling constant (1.3). In the framework of the microcanonical ensemble the temperature kT is determined by the kinetic energy via the equipartition theorem (see Dove (1988) for details). The equations of motion of all entities U_i are derived from (1.1) and we integrated them using the Beeman algorithm (Beeman 1976). The system is prepared at a high temperature $(T > T_c)$ and quenched to a low temperature $(T < T_c)$. In this study we only consider the relaxation behaviour of the order parameter

$$\langle U(t) \rangle = \frac{1}{4096} \sum_{i=1}^{4096} U_i(t). \tag{3.1}$$

A few comments are in order regarding the quenching methods, which can be carried out in two distinct ways. In the first, one rescales the average velocity at each time step by the factor

$$f = (k_B T_{\text{low}} / \langle V^2 \rangle)^{1/2}. \tag{3.2}$$

We compare in figure 4 the MDS data for the order parameter relaxation with a numerical solution of equation (2.4), with an appropriate scaling factor ε. Despite the large oscillations seen in the MDS results before the system reaches equilibrium, the agreement between the two plots is very good. Note that one can attribute the oscillations observed to the coupling terms (1.3). In this the dominant mode lies at the zone centre where all the entities U_i oscillate in phase within their on-site
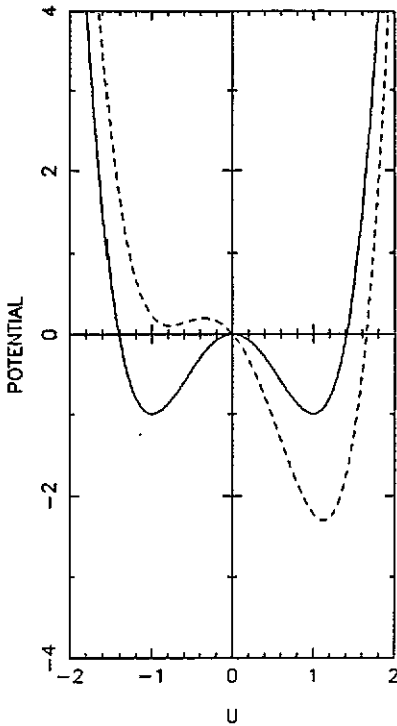
Figure 2. Effective mean-field potential felt by a central site while all the other sites relax. Note that for a shallow double well (here $\alpha = -2$, $J = 1$ and $\gamma = 1$), the location of the two minima is strongly affected by the mean field. The broken curve corresponds to saturation at $T = 0$.
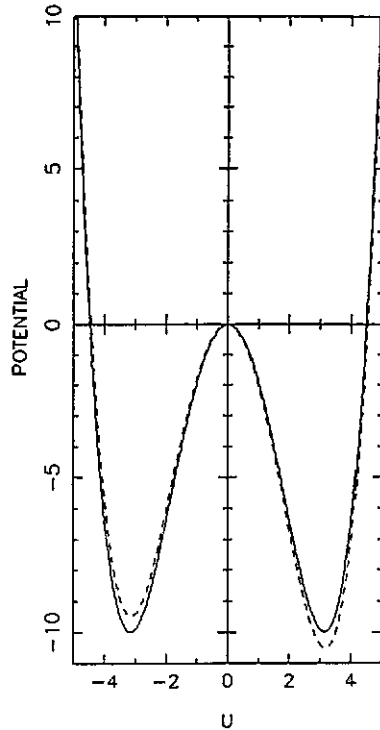
Figure 3. Effective mean-field potential in the limit $\alpha/J \ll 0$ (here $\alpha = -20$, $J = 1$ and $\gamma = 1$). The broken curve corresponds to saturation at $T = 0$. During relaxation the location of the minima is not significantly affected by the mean field unlike the case in figure 2. This situation is relevant to order/disorder systems.

potential. The oscillations are the result of relaxation of the whole cluster which has an important momentum. These oscillations could have been taken into account in (2.4) if we had considered the momentum variables in (2.1). However, we remove this difficulty by adopting a 'soft quenching' method in which we decrease the temperature from T_{high} to T_{low} in steps. This procedure is commonly used for MDS in glassy systems (Watanabe and Tsumuraya 1987). The rate of cooling is chosen in such a way that the system has no time to reach equilibrium at any of the intermediate steps during relaxation. In figure 5 we present such a plot for $\alpha = 0.1$. As the cooling rate is much slower than in the previous technique the large oscillations of the order parameter disappear.

Before closing this section we wish to point out that MDS fail to investigate relaxation processes when the on-site potential has a very deep double well, that is for $\alpha/J \ll 0$ and $kT \ll$ 'hump size'. In this limit the rate of jumps across the barrier becomes extremely slow and cannot be studied on a computer for practical reasons.
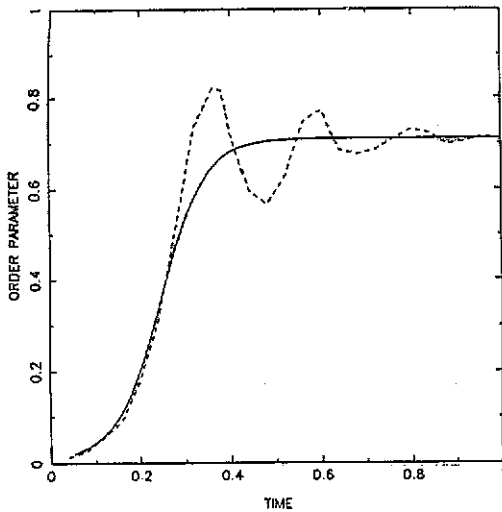
Figure 4. Comparison between MDS and a numerical solution of the rate equation of the order parameter (3.4) (broken curve) for $\alpha = -0.5$, $J = 1$, $\gamma = 1$. The system is initially prepared at $T_{\text{high}}/T_c \simeq 1.2$ for 5000 time steps ($\delta t = 0.02$) and then quenched at $T_{\text{low}}/T_c \simeq 0.3$ by rescaling the velocity on each time step δt by forcibly fixing the temperature at T_{low}. The result presented is obtained by a single run.
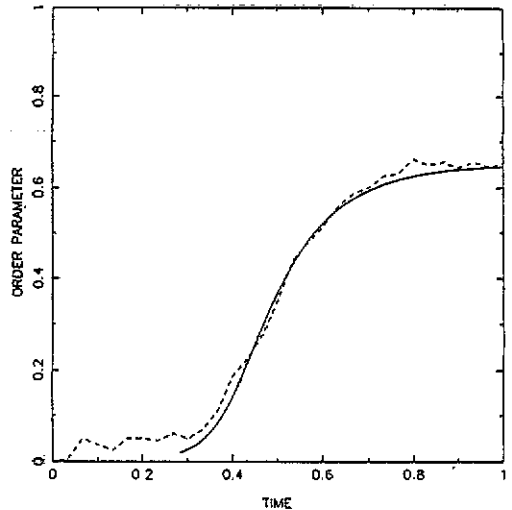
Figure 5. Comparison between MDS and numerical solution (broken curve) for $\alpha = 0.1$, $\gamma = 1$, $J = 1$ with $T_{\text{low}}/T_c \approx 0.3$ and $T_{\text{high}}/T_c \approx 1.2$. The system is initially prepared for 5000 time steps ($\delta t = 0.02$) at T_{high}. The quenching is here performed in stages of 300 intermediate steps of constant temperature (of four time steps). This result is obtained by a single run.

4. The extreme order/disorder case

4.1. The two-state limit

In this section we study the effect of a very deep double-well on-site potential on the relaxation of the order parameter $\langle U \rangle$. This case is realized when α/J reaches some large negative values. In figure 3 we have considered the case $\alpha/J \ll 0$ and we have checked that the mean field did not affect the location of the minima U_m of the potential Φ_{MF}. Even at saturation ($T = 0$), one finds

$$U_m = (|J - \alpha|/2\gamma)^{1/2} \simeq (|\alpha|/2\gamma)^{1/2}. \tag{4.1}$$

Considering again the rate equation of the order parameter (2.4) in conjunction with (2.5), we may very well assume that the range of temperature from $T_{\text{high}} > T_c$ to $T_{\text{low}} < T_c$ is always well below the hump of the double well. One can then replace the nearly Gaussian weight factor $\exp[-\beta(\alpha U^2 + \gamma U^4)]$ in (2.5) by a delta function appropriate to the variable U reaching one of the two minima U_m. The integral is then transformed to a discrete summation and the left-hand side of equation (2.5) leads to a hyperbolic tangent. Using the fact that $|\alpha| \gg J$ (cf (4.1)), the expression (2.4) reduces to the rate equation

$$d\langle U \rangle/dt \propto \langle U \rangle - U_m \tanh(2\beta J U_m \langle U \rangle). \tag{4.2}$$

This equation is identical to the one derived for the Glauber kinetics of a two-state Ising model under the MFA (Dattagupta *et al* 1991a, b). The essential point is that

the Φ^4 model for $|\alpha| \gg J$ and $kT \ll$ 'hump size' (see figure 3) can, to a large degree of accuracy, be viewed as a discrete Ising spin system. However, the above simple consideration that yields (4.2) does not lead to a microscopic expression for the characteristic time of relaxation; one still interprets the 'frictional' term ε in (2.8) as a phenomenological input parameter. For an improved treatment of ε we need to consider the full Kramers problem (Dattagupta 1987) associated with the Fokker–Planck equation (2.8) for the Φ^4 model, as discussed later.

4.2. The Kramers treatment

In the Kramers approach (Kramers 1940) to the relaxation of systems having large barriers, one argues that the evolution of the distribution function is a very slow process. This condition is perfectly fulfilled for the Φ^4 model in the limit of very deep on-site potentials $\alpha/J \ll 0$. In particular, when the temperature kT is small compared with the 'hump size', the entity U is essentially localized near the bottom of one of the two wells: it takes a long while before U succeeds in jumping over the barrier. Accordingly, the distribution function turns out to be a slowly varying function of time and hence, from equation (2.9), the probability current $J(U, t)$ becomes approximately independent of U. The probability distribution is then sharply peaked on the two minima, so we can define an occupational probability $n_\sigma(t)$ (where $\sigma = 1$ or -1 corresponds to the well on the left or right, respectively) as

$$n_\sigma(t) = \int_{\sigma U_m - \delta}^{\sigma U_m + \delta} \mathrm{d}U \, W(U, t) \tag{4.3}$$

where δ measures the spread of the distribution function and U_m is defined in (4.1). By requiring that the probability current coincides with the rate at which $n_\sigma(t)$ evolves, one can show that the rate equation of $n_\sigma(t)$ takes the following form (Dattagupta 1987):

$$\mathrm{d}n_\sigma(t)/\mathrm{d}t = (1/I_{-\sigma}I_0)n_{-\sigma}(t) - (1/I_\sigma I_0)n_\sigma(t) \tag{4.4}$$

where

$$I_\sigma = \int_{\sigma U_m - \delta}^{\sigma U_m + \delta} \mathrm{d}U \, \exp[-\beta\Phi_{\mathrm{MF}}(U)] \tag{4.5}$$

$$I_0 = \int_{-U_m}^{U_m} \mathrm{d}U \, \exp[\beta\Phi_{\mathrm{MF}}(U)]. \tag{4.6}$$

In the limit $|\alpha| \gg J$ the location of the minima of Φ_{MF} does not depend on $\langle U \rangle$, as stated earlier (cf also figure 3). One can then use the Taylor expansion of $\Phi_{\mathrm{MF}}(U)$ around the two minima of the double well as

$$\Phi_{\mathrm{MF}}(U) = \Phi_{\mathrm{MF}}(\sigma U_m) + g(U, \sigma U_m) \tag{4.7}$$

where

$$g(U, \sigma U_m) = 2|\alpha|(U - \sigma U_m)^2 + 4\gamma\sigma U_m(U - \sigma U_m)^3 + \gamma(U - \sigma U_m)^4. \tag{4.8}$$

In the expression (4.8) we have neglected the slight asymmetry resulting from the interaction terms (since $|\alpha| \gg J$). One can also rewrite both integrals (4.5) and (4.6) in the form

$$I_\sigma = \exp[-\beta\Phi_{MF}(\sigma U_m)]f(\alpha, T) \tag{4.9}$$

$$I_0 = \{\exp[-\beta\Phi_{MF}(-U_m)] + \exp[-\beta\Phi_{MF}(U_m)]\}h(\alpha, T) \tag{4.10}$$

where

$$\Phi_{MF}(\sigma U_m) = \text{constant} - 2J\sigma U_m\langle U\rangle. \tag{4.11}$$

The jumping rate can be deduced and, upon employing (4.9)–(4.11), can be shown to be proportional to

$$W_{\sigma \to -\sigma} = 1/I_\sigma I_0 = [1/f(\alpha, T)h(\alpha, T)]\exp[-2\beta J U_m\langle U\rangle]$$
$$\times [\exp(2\beta J U_m\langle U\rangle) + \exp(-2\beta J U_m\langle U\rangle)]^{-1}. \tag{4.12}$$

The characteristic time for which such an event occurs is simply given by the prefactor:

$$\varepsilon = f(\alpha, T)h(\alpha, T) = \int_{U_m-\delta}^{U_m+\delta} dU \, \exp[-\beta g(U, U_m)]$$
$$\times \int_0^{U_m} dU \, \exp[\beta g(U, U_m)]. \tag{4.13}$$

For the given range of parameters, that is $\alpha/J \ll 0$ and $kT \ll$ 'hump size', for which the Kramers treatment is justified, the above quantity is very large and, correspondingly, the jumping rate is very small. Finally, by requiring that

$$\langle U\rangle = [n_+(t) - n_-(t)]U_m \tag{4.14}$$

and combining (4.13) with (4.4), and also using the jumping rate (4.12), one retrieves the Glauber rate equation of a two-state Ising system.

5. The conserved order parameter

Our treatment thus far has been restricted to non-conserved order parameter kinetics. For the sake of completeness, we discuss in this section the relaxation behaviour of the Φ^4 model with a conserved order parameter. In the order/disorder limit we retrieve the 1966 Kawasaki rate equation of a two-state Ising system.

   With a conserved order parameter, a given site U_i does not have the freedom to choose its state irrespective of the other sites. In particular, in an alloy, if one replaces an atom A by B, one has to replace an atom B somewhere else simultaneously by A. Several other instances of conserved order parameter kinetics have been discussed in our earlier work (Dattagupta *et al* 1991a, b). In the latter, however, we based our treatment on a discrete Ising spin system, whereas for the Φ^4 model we have to deal with a continuous variable U_i for which the conservation condition is stated as

$$\sum_i U_i = \text{constant.} \tag{5.1}$$

In particular, the above constraint can be satisfied if one establishes a pairing between sites, such that if U_i increases by $\Delta_{i,li}$, another variable U_{li} must simultaneously decrease by the same quantity (see, for instance, Gunton and Droz 1983). Schematically, one means

$$U_i \longrightarrow U_i + \Delta_{i\,li} \qquad U_{li} \longrightarrow U_{li} - \Delta_{i\,li}. \qquad (5.2)$$

The transformation (5.2) describes the well known Kawasaki process. Such a pairing in alloys has an obvious physical interpretation. Suppose that the probability distribution associated with U_i is peaked around either the left-hand or the right-hand wells corresponding to an A or a B atom, respectively (figure 6). If one considers the pair of sites shown in figure 6 the process described in (5.2) corresponds to the situation depicted in figure 7. As one entity U_i goes continuously from the left-hand to the right-hand side of the double-well potential, that is the atom A transforms itself to B, the first-neighbour entity U_{li} moves in the opposite direction, that is B changes into A. Note that such a description is more realistic for an alloy than that provided by a simple Ising system. In the Ising model a flip-flop process stands for modelling the exchange between two atoms A and B. Hence this model does not take into account the microscopic mechanism that enables the system to realize such an exchange. In particular, no attention is paid to the crossing of the atoms that we have illustrated in figure 7.
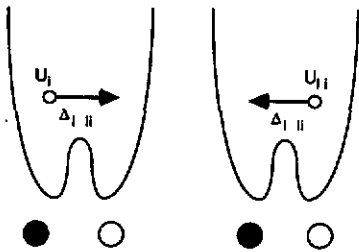

Figure 6. Pair of sites U_i and U_{li} connected to each other in an exchange process. The variable U_i can represent the occupation of an atom A or B at i depending on whether U_i falls into the right or left side of the double-well on-site potential.
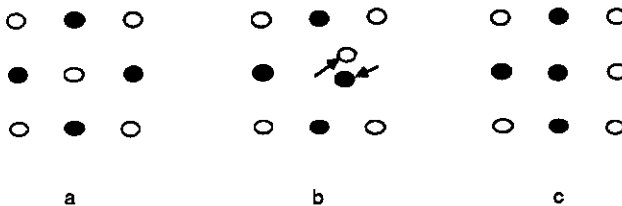

Figure 7. Exchange process between two first neighbours A and B in an alloy. Note that such a process a, b, c involves a continuous sequence, which can be well described within a Φ^4 model while the Ising flip-flop process can only model the initial and final states a and c.

The rate equation of the conserved order parameter can be deduced by employing a treatment described in detail in Langer (1971). One needs to consider the rate equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle U_i \rangle = -\frac{1}{\varepsilon} \sum_k \left(z\delta_{ik} - \sum_{li}\delta_{li\,k} \right) \left\langle \frac{\partial \Phi}{\partial U_k} \right\rangle \qquad (5.3)$$

where z is the number of sites U_{li} that can participate in the exchange process with the central site U_i. This equation is very similar to the phenomenological model developed by Cahn and Hilliard in 1958 (see Langer 1971) where instead of the Φ^4 potential, they consider inside the brackets '$\langle\rangle$' a Ginzburg–Landau free-energy functional with respect to the fluctuation of the order parameter. This model has been widely employed to investigate the relaxation behaviour in relation to the spinodal decomposition with continuous order parameter (Mazenko and Valls 1987, Rogers *et al* 1988). We must, however, emphasize once more that while most studies are devoted to dynamical critical phenomena we are more often than not interested in the kinetics far away from the critical temperature.

In what follows we explicitly consider the rate equation in the order/disorder limit. We assume, as we did in section 2, that the system is in a local detailed-balance condition at any time during the relaxation process. The equation (5.3) takes the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle U_i\rangle = -\frac{1}{\varepsilon}\left[2\alpha\sum_{li}(\langle U_i\rangle - \langle U_{li}\rangle) - 2\left(\sum_j J_{ij}\langle U_j\rangle - \sum_k J_{li\,k}\langle U_k\rangle\right)\right.$$
$$\left. + 4\gamma\sum_{li}\langle U_i^3 - U_{li}^3\rangle\right] \tag{5.4}$$

where

$$\langle U_i^3 - U_{li}^3\rangle = \int\prod_{k=1}^N \mathrm{d}U_k\,(U_i^3 - U_{li}^3)\exp[-\beta\Phi(\{U_i\})]$$
$$\times\left(\int\prod_{k=1}^N \mathrm{d}U_k\,\exp[-\beta\Phi(\{U_i\})]\right)^{-1}. \tag{5.5}$$

In the order/disorder limit $\alpha/J \ll 0$ the exponential is sharply peaked when the variable U_i reaches $\sigma_i U_{\mathrm{m}}$ where $\sigma_i = \pm 1$ (see subsection 4.1). The equation (5.5) is non-zero when the sites i and li have opposite values of σ_i. By isolating the terms that depend on U_i and U_{li} in the exponential (5.5), one finds

$$\langle U_i^3 - U_{li}^3\rangle \approx U_{\mathrm{m}}^3\left\langle(1 - \sigma_i\sigma_{li})(\tanh\beta U_{\mathrm{m}})\left(\sum_j J_{ij}\sigma_i - \sum_k J_{k\,li}\sigma_k\right)\right\rangle. \tag{5.6}$$

This can be inserted in (5.4), giving

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\sigma_i\rangle \propto \sum_{li}(\langle\sigma_i\rangle - \langle\sigma_{li}\rangle) + \sum_{li}\left\langle(1 - \sigma_i\sigma_{li})(\tanh\beta U_{\mathrm{m}})\right.$$
$$\left.\times\left(\sum_j J_{ij}\sigma_i - \sum_k J_{k\,li}\sigma_k\right)\right\rangle. \tag{5.7}$$

The above expression is the rate equation for a conserved two-state Ising system (Binder 1974). The jumping rate ε^{-1} in (5.3) is purely phenomenological but can be calculated with the aid of the Kramers treatment that we employed in section 4.

6. Summary

We have studied the relaxation behaviour of a Φ^4 model on a lattice with conserved and non-conserved order parameter. For the non-conserved order parameter we have deduced, using the Fokker–Planck equation, a rate equation for the order parameter. The solution becomes transparent in the MFA, which is a very good approximation for systems with long-range interactions. The result derived is recovered by considering an approximate potential Φ_{MF} where each variable U_i is supposedly coupled with the same pairwise interaction J/N with all the other N sites. We have then compared the predicted results with the MDS of Φ_{MF} and found very good agreement. Next, we have also investigated the relaxation effects when the on-site potential is characterized by a very deep double well. The rate equation of the order parameter is shown to take the form of the much studied Glauber rate equation for an Ising system. This situation occurs for $\alpha/J \ll 0$ and $kT \ll$ 'hump size'. Finally, in this limiting situation, we have followed a Kramers treatment, and deduced the time scale associated with the relaxation, that is the jumping rate from one well to the other; it is a small quantity, as expected. We have also considered the conserved order parameter relaxation behaviour in the order/disorder limit. As expected, the well known Kawasaki rate equation is recovered. The MDS results lend credence to the MFA for systems with long-range interactions. On the other hand, the MDS have limited applicability, especially for deep on-site potentials and one must find an alternative approach. Using the MFA we have shown analytically how the relaxation kinetics for the continuum Φ^4 model, for deep on-site potentials, become nearly the same as that for the discrete two-state Ising model. While this result was not unexpected, our explicit derivation gives a clear picture of the parameter values α, γ and J for which the crossover from continuum to discrete-like behaviour occurs. This is useful, because in the 'discrete' domain one may resort to other methods of attack of the problem such as Monte Carlo techniques. Thus a combination of analytical, molecular dynamics simulation and Monte Carlo approaches would enable a comprehensive analysis of the kinetics of the Φ^4 model to be performed over a wide range of the parameters that characterize different relaxational aspects of the structural phase transitions.

Acknowledgments

References

Beeman D 1976 *J. Comput. Phys.* **20** 130
Benckert C 1987 *J. Phys. C: Solid State Phys.* **20** 3369
Binder K 1979 *Monte Carlo Methods in Statistical Physics* (Berlin: Springer)
—— 1974 *Z. Phys.* **267** 313
Bruce A D 1980 *Adv. Phys.* **29** 117

Bruce A D and Cowley R A 1980 *Adv. Phys.* **29** 219

Dattagupta S 1987 *Relaxation Phenomena in Condensed Matter* (Orlando, FL: Academic)

Dattagupta S, Heine V, Marais S and Salje E 1991a *J. Phys.: Condens. Matter* **3** 2963

—— 1991b *J. Phys.: Condens. Matter* **3** 2975

Dove M 1988 *NATO Advanced Sciences Institutes Series C* vol 225, ed E Salje (Nato) p 501

Gunton J D and Droz M 1983 *Introduction to the Theory of Metastable and Unstable States (Lecture Notes in Physics 183)* (Berlin: Springer) p 1

Indira R 1982 *Stochastic Processes (Lecture Notes in Physics 184)* ed G S Agarwal and S Dattagupta (Berlin: Springer) p 122

Janssen T 1986 *Modern Problems in Condensed Matter Sciences* vol 14.1, ed R Blinc and A P Levanyuk p 67

Kramers H A 1940 *Physica* **7** 284

Langer J S 1971 *Ann. Phys.* **65** 53

Mazenko G F and Valls O T 1987 *Phys. Rev. Lett.* **59** 680

Padlewski S, Evans A K, Ayling C and Heine V 1991 *J. Phys.: Condens. Matter* submitted

Risken H 1989 *The Fokker–Planck Equation: Methods of Solution and Application* 2nd edn (Berlin: Springer)

Rogers T M, Elder K R and Desai R C 1988 *Phys. Rev.* B **37** 9638

Salje E 1988 *Phys. Chem. Minerals* **15** 336

—— 1990 *Phase Transitions in Ferroelastic and Co-elastic Crystals* (Cambridge: Cambridge University Press)

Watanabe M S and Tsumuraya K 1987 *J. Chem. Phys.* **87** 4891