A rate equation for atomic ordering in mean field theory: II. General considerations

Sushanta Dattagupta†§, Volker Heine†, Simon Marais† and Ekhard Salje‡

† Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK
‡ Deparment of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK

Abstract. The general question addressed here is: what is the appropiate rate equation when one has mixed kinetics of the order parameter, i.e. of both conserved and non-conserved types? The study is motivated by first considering various examples of atomic ordering processes in which it makes sense to analyse the importance of mixed kinetics. The discussion is based on Glauber and Kawasaki types of stochastic processes in a kinetic Ising model with long range interactions, described very well by the mean field approximation. It is found that in the limiting case in which one is not far from the uniform state (i.e. spatially homogeneous) and thermal equilibrium, the rate equation can be cast into the form assumed sometimes in phenomenological rate theories of mixed kinetics. This identification allows for a critical analysis of various length scales, time scales and mixing coefficients that occur in mixed kinetic processes. In the far-from-equilibrium situation, however, the derived rate equation has a rather complex structure, not amenable to a simple interpretation. Finally, the possibilities of observing mixed kinetics are indicated by way of examples borrowed from atomic ordering phenomena in certain minerals, and a few general conclusions are drawn.

1. Introduction: the conceptual framework

Structural phase transitions in crystalline solids form an important topic in physics, chemistry, metallurgy and mineralogy. While the equilibrium behaviour (the degree of ordering, etc.) has been well studied, the same is not true of the kinetics of ordering or (dis)ordering except for the case of exsolution in alloys. Recently Salje and others [1] have put forward the rate equation (cf (1.1) of the preceding paper, henceforth referred to as I)

$$\frac{\partial Q_k}{\partial t} = -\frac{1}{\tau k_{\mathrm{B}} T}\left[1 - \left(\frac{\xi_{\mathrm{C}}^2}{\xi^2}\right)\exp(\tfrac{1}{2}\xi^2 k^2)\right]\left(\frac{\partial G}{\partial Q(r)}\right)_k \qquad (1.1)$$

where the k refers to the kth Fourier component. Here $Q(r)$ is the spatially varying order parameter, τ is a time which sets the basic time scale of the rate process, G is the free energy defined as a function of $Q(r)$ and the temperature T, and ξ, ξ_{C} are

§ Permanent address: School of Physical Sciences, Jawaharlal Nehru University, New Delhi, 110067, India.

parameters that will be discussed further below. The form (1.1) was introduced intuitively as a mixed equation to represent very general ordering situations in minerals, interpolating as it does with mixing coefficient ξ_C^2/ξ^2 between the two well known extreme cases describing so-called conserved and non-conserved order parameters. For $\xi_C = 0$ and a suitable form of G, the form (1.1) reduces to the Ginzburg–Landau equation for a non-conserved order parameter. On the other hand setting $\xi_C^2/\xi^2 = 1$ and taking the lowest terms of the exponential yields

$$\frac{\partial Q_k}{\partial t} = -\frac{1}{\tau k_B T}(\tfrac{1}{2}k^2\xi^2)\left(\frac{\partial G}{\partial Q(r)}\right)_k \tag{1.2}$$

which is the diffusion-type equation of Cahn and Hilliard for a conserved order parameter. The relation of (1.1) to these two limiting cases is discussed more fully in [1], but the main point here is that (1.1) was proposed to cover a wide variety of complex rate processes, and to interpolate between the extreme cases if necessary.

The purpose of the present paper is to discuss more critically several questions about (1.1), the first being whether it makes physical sense to interpolate between the conserved and non-conserved cases: are these not discrete, mutually exclusive categories? We can consider this question by going back to the microscopic stochastic mechanism underlying the kinetics from which the macroscopic or mesoscopic rate equation (1.1) can be derived. The stochastic process is intended to represent the thermal excitations of the system and hence what actually happens at the atomic level. We start by considering the well known 'discrete ϕ^4' model (figure 1), namely a lattice of atoms or more general entities, each bound to its lattice site, i, by a double-well potential and coupled by interactions J_{ij} to other sites. Of course u_i may represent something more complex than an atomic displacement, e.g. the distortion of a SiO$_4$ tetrahedron in a silicate or the twist of a molecul in biphenyl. Let us suppose the parameters and the temperature T are such that each atom or entity spends an appreciable amount of time in its left or right well before changing to the other, i.e. we have a displacive system in its order/disorder regime. We may expect two types of processes. Firstly, suppose the two atoms in figure 1 are nearest neighbours with a strong coupling J_{ij} between them. When they are in the particular positions shown in figure 1, the spring J_{ij} is strongly compressed, thus exerting a strong force leftwards on atom i and rightwards on atom j. It is then likely that atom i would make a transition from its right well to its left well, with atom j making simultaneously a transition from its left well to its right one. Indeed such a process is commonly observed in a molecular dynamic simulation of the system [2]. Secondly, however, it is possible that there is a strong force to the left on atom i in figure 1 such as to make it change to the left well, but that this force results from the combined effect of the couplings J_{ij} with several neighbours j without the reaction impulse on any one of them being large enough to make it jump to the right. This is particularly likely when there are many other atoms in the material besides those participating in the ordering process. For example u_i may be the displacement of a cation inside a cage consisting of an octahedron of oxygen atoms, in which case the thermal velocity fluctuations of cation i will come more from its cage of oxygen atoms than from interaction with other cations j. Now since the system is in its order/disorder regime, we may approximate by discretizing it as usual by a set of Ising spins, with $s_i = \pm 1$ denoting u_i being in the right or left well respectively. The process of the first type then becomes an interchange of spins s_i and s_j, known as a Kawasaki process [3], whereas a type 'two' jump just flips spins s_i, a Glauber process [4].
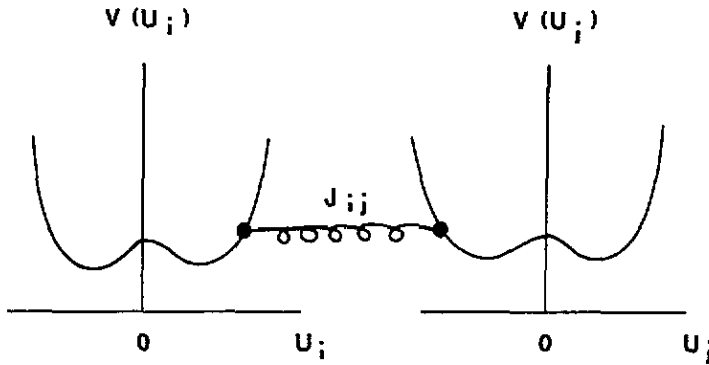
Figure 1. Two atoms or entities at sites i and j with displacements u_i, u_j each feeling an on-site potential $v(u) = -\alpha u^2 + \beta u^4$. The coupling interaction between sites is $-J_{ij} u_i u_j$. The black dots represent the displacements u_i, u_j at some particular instant.

We conclude that mixing Kawasaki and Glauber stochastic processes is physically allowable for the displacive motel of figure 1. The significance of this lies in the fact that the Kawasaki process conserves the total spin of the system, whereas the Glauber process does not. For that reason Kawasaki and Glauber dynamics are usually associated with conserved and non-conserved order parameters respectively. But we see that in our example it is entirely reasonable to mix them, and as we shall show in section 2 this leads to a mixed equation of type (1.1).

Having seen that we can mix Glauber- and Kawasaki-type processes for a displacive system, can we also mix them in the case of atomic A/B ordering? At first sight it seems not, because if we represent A and B atoms on site i by a spin variable $s_i = \pm 1$, then a Kawasaki process interchanges the atoms on sites i and j which is perfectly allowable, but a Glauber process would turn an A atom into a B atom or vice versa which makes physical nonsense. However, we can mix them again if we generalize our model somewhat. Suppose we have a material with two sites per unit cell on which to order the A and B atoms as shown in figure 2(a). Then instead of s_i referring to individual atoms we can take it to refer to the two ordered configurations in figure 2(a). An interchange of the two atoms in one cell is then a Glauber process, whereas a Kawasaki process exchanges the configurations in two cells. Of course a cell may contain two A atoms or two B atoms so that its contents have to be described by a four-state model (though it may be that two like atoms are comparatively rare for energetic reasons so that we recover again approximately an Ising model).

A further case is suggested by figure 2(b) with four atoms per cell: again we can imagine (dis)ordering processes that are Glauber-like intracell, and Kawasaki-like ones that are intercell. Such examples are not far fetched: Na/K feldspar is a simple case by the standards of mineralogy, with Si/Al ordering on (only!) four sites per unit cell [5].

We may summarize the above discussion as follows. We have chosen to represent the behaviour of real minerals with displacive or atomic ordering using a generalized Ising model. In such a context it is sensible to consider atomic intracell (Glauber-like) and intercell (Kawasaki-like) ordering processes occurring simultaneously, which will lead in section 3 to the mixed case of the type described by (1.1). We note that the examples of atomic ordering in figure 2 and others such as silicate minerals
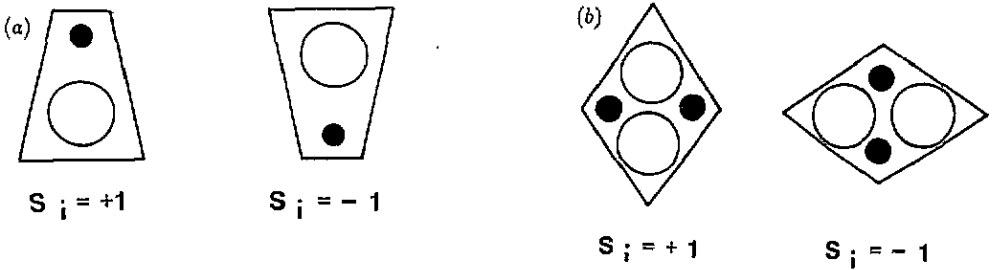
Figure 2. Two different ordering patterns in a unit cell represented by an Ising spin $s_i = \pm 1$. The first type (a) leads to fully anti-ferromagnetic phase transitions, while the second (b) results in a ferromagnetic transition.

involve 'antiferromagnetic' patterns, i.e. an ordering pattern of two types of atom in one superlattice cell, *not* exsolution of the two types of atom. Only in the latter case of exsolution must one use the strictly 'conserved' type of rate equation.

Having answered our first question that a mixed equation (1.1) makes sense, we can enquire what the physical interpretation of the mixing coefficient ξ_C^2/ξ^2 and the length scale ξ in the exponential is [1]. We shall see (section 4 below) how the mixing coefficient may be related to the ratio of basic time scales characterizing Glauber-like and Kawasaki-like stochastic processes, with the ξ of (1.1) being identified with the separation distance ξ_K of the Kawasaki process. However, our model calculation shows that the exponential form in (1.1) is *not* general and can only be justified to first order (i.e. in the regimes of low k). In so far as the operand in (1.1) may be viewed as a driving force derivable from a kinetic potential that may or may not have anything to do with a model Ising system, we may expect our conclusion regarding the length scale ξ and the mixing coefficient to apply at least qualitatively to situations such as are illustrated in figure 1 and 2.

Finally we may query if the correct driving force on the right hand side of (1.1) is derivable from the derivative of the equilibrium form of the Gibbs free energy. This is discussed in detail in the companion paper where we solve the specific cases of a uniform Ising system under Glauber and Kawasaki stochastic processes respectively, in the mean field approximation. The resultant driving force is not equal to $\partial G/\partial Q$ in either case (see I for details) and is therefore also expected to be different in the case of mixed kinetics. Of course there may be other physical situations in which the appropriate driving force is well approximated by $\partial G/\partial Q$.

With the preceding survey of the conceptual background, the outline and purpose of the present paper are as follows. In section 2 we carry out a formal treatment of the order parameter kinetics for an Ising model under mixed Glauber and Kawasaki processes. A perturbation treatment in the regime of small deviations from the uniform equilibrium state, presented in section 3, will justify the conclusions which we have already put forward above. In section 3 we present also the connection in the simplest cases between our model and the Ginzburg-Landau and Cahn-Hilliard phenomenologies. In section 4 we pursue more generally the interpretation of the rate equation (1.1) and the various length scales and time scales that occur in the mixed kinetic process. Finally, we conclude that when the uniform state is far away from equilibrium, equation (1.1) may not have general validity.

2. Formal development of order parameter kinetics

We begin our analysis of the mixed conserved–non-conserved kinetics from the combination of order parameter equations for the Glauber and Kawasaki models, obtained under the decoupling approximation [3,6]

$$\frac{d}{dt}\mathcal{Q}_j(t) = -\frac{1}{\tau_G}\left[\mathcal{Q}_j(t) - \tanh\left(\beta\sum_l J_{jl}\mathcal{Q}_l(t)\right)\right] - \frac{1}{\tau_K}\sum_{l_j}\left[(\mathcal{Q}_j(t) - \mathcal{Q}_{l_j}(t))\right.$$
$$\left. - (1 - \mathcal{Q}_j(t)\mathcal{Q}_{l_j}(t)) - \tanh\left(\beta\sum_i(J_{ij}\mathcal{Q}_i(t) - J_{il_j}\mathcal{Q}_i(t))\right)\right]. \quad (2.1)$$

Our idea is to study the temporal evolution of the spatially non-uniform state when we perturb away from the uniform state, analysed in depth in I [6]. Thus we split

$$\mathcal{Q}_j(t) = \mathcal{Q}(t) + Q_j(t)$$
$$\mathcal{Q}_{l_j}(t) = -\mathcal{Q}(t) + Q_{l_j}(t) \quad (2.2)$$

and treat terms up to $O(m)$. The left hand side of (2.1) can then be separated into two terms as follows:

$$\frac{d}{dt}\mathcal{Q}(t) = -\frac{1}{\tau_G}\left[\mathcal{Q}(t) - \tanh(\beta J(0)\mathcal{Q}(t))\right] - \frac{N_K}{\tau_K}\left[2\mathcal{Q}(t) - (1 + \mathcal{Q}^2(t))\tanh(2\beta J(0)\mathcal{Q}(t))\right]$$
$$(2.3)$$

$$\frac{d}{dt}Q_j(t) = -\frac{1}{\tau_G}\left[Q_j(t) - \left(\beta\sum_l J_{jl}Q_l(t)\right)\text{sech}^2(\beta J(0)\mathcal{Q}(t))\right]$$
$$- \frac{1}{\tau_K}\sum_{l_j}\left[(Q_j(t) - Q_{l_j}(t))[1 - \mathcal{Q}(t)\tanh(2\beta J(0)\mathcal{Q}(t))]\right.$$
$$\left. - [(1 + \mathcal{Q}^2(t))\text{sech}^2(2\beta J(0)\mathcal{Q}(t))]\left(\beta\sum_i(J_{ij}Q_i(t) - J_{il_j}Q_i(t))\right)\right]. \quad (2.4)$$

The dynamics of the uniform part given by (2.3) has already been the subject of I. Here we concentrate on the non-uniform part, viz. (2.4), which is best handled by Fourier transforms. Thus introducing

$$Q_k(t) = \sum_j \exp(i k \cdot r_j)Q_j(t) \quad (2.5)$$

we may write

$$\frac{d}{dt}Q_k(t) = -\frac{1}{\tau_G}\left[1 - \beta J(k)\text{sech}^2\left(\frac{T_C}{T}\mathcal{Q}(t)\right)\right]Q_k(t)$$
$$- \frac{1}{\tau_K}\sum_{l_j}\left\{\left[1 - \mathcal{Q}(t)\tanh\left(\frac{2T_C}{T}\mathcal{Q}(t)\right)\right]\right.$$
$$\times \left(Q_k(t) - \sum_q \exp[i(k \cdot r_j - q \cdot r_{l_j})]Q_q(t)\right) - (1 + \mathcal{Q}^2(t))\beta\text{sech}^2\left(\frac{2T_C}{T}\mathcal{Q}(t)\right)$$
$$\times \left(J(k)Q_k(t) - \sum_q \exp[i(k \cdot r_j - q \cdot r_{l_j})]J(q)Q_q(t)\right)\right\} \quad (2.6)$$

where

$$J(k) = \sum_l J_{jl} \exp[ik \cdot (r_j - r_l)] \tag{2.7}$$

and T_C has been defined in I.

At this stage we introduce an assumption that Kawasaki jumps occur over a fixed length R_K; of course for every R_K jump there would be a corresponding $-R_K$ jump. (In most cases of interest R_K would be expected to be the nearest neighbour lattice vectors.) Thus (2.6) yields

$$\frac{d}{dt}Q_k(t) = -\frac{1}{\tau_G}\left[1 - \beta J(k)\mathrm{sech}^2\left(\frac{T_C}{T}Q(t)\right)\right]Q_k(t)$$
$$- \frac{N_K}{\tau_K}[1 - \cos(k \cdot R_K)]\left\{\left[1 - Q(t)\tanh\left(\frac{2T_C}{T}Q(t)\right)\right]\right.$$
$$\left. - (1 + Q^2(t))\beta J(k)\mathrm{sech}^2\left(\frac{2T_C}{T}Q(t)\right)\right\}Q_k(t). \tag{2.8}$$

In order to analyse (2.8) we would have to first solve for $Q(t)$ from (2.3) and plug the solution into the right hand side of (2.8).

3. Perturbation of the uniform equilibrium state

The general order parameter equation in (2.8) is quite complicated. In order to simplify the analysis we imagine that we start from the situation when the system is in thermal equilibrium. The uniform magnetization $Q(t)$ is then time-independent and is given by its MFT expression (cf (2.6) of I):

$$Q(t) = Q_{eq} = \tanh\left(\frac{T_C}{T}Q_{eq}\right). \tag{3.1}$$

Equation (2.8) then reduces to

$$\frac{d}{dt}Q_k(t) = -\left[\frac{1}{\tau_G} + \frac{N_K}{\tau_K}\left(\frac{1 - Q_{eq}^2}{1 + Q_{eq}^2}\right)[1 - \cos(k \cdot R_K)]\right]\left\{\left[1 - (1 - Q_{eq}^2)\beta J(k)\right]Q_k(t)\right\}. \tag{3.2}$$

In traditional discussions of order parameter kinetics in systems with long range interactions one is interested in the low k expansion of $J(k)$, i.e.

$$J(k) \approx J(0)(1 - \tfrac{1}{2}k^2 R_J^2) \tag{3.3}$$

which follows from (2.7) and the definition

$$R_J = [J(0)]^{-1}\sum_l J_{jl}(r_j - r_l)^2. \tag{3.4}$$

Naturally, R_J has the interpretation of the 'range' of the interaction. In this limit it is meaningful to set (after averaging over random distributions of R_K over a sphere of radius ξ_K)

$$1 - \cos(\mathbf{k} \cdot \mathbf{R}_K) = 1 - \frac{\sin(k\xi_K)}{k\xi_K} \approx \tfrac{1}{6} k^2 \xi_K^2 \tag{3.5}$$

where ξ_K ia a characteristic Kawasaki jump distance. If we further assume that Q_{eq} is small, then the long wavelength limit of (3.2) reads

$$\frac{d}{dt} Q_k(t) = -\left(\frac{1}{\tau_G} + \frac{1}{6} \frac{N_K}{\tau_K} k^2 \xi_K^2 \right) \left[\left(1 - \frac{T_C}{T} \right) + \frac{1}{2} \frac{T_C}{T} R_J^2 k^2 + \frac{T_C}{T} Q_{\mathrm{eq}}^2 \right] Q_k(t). \tag{3.6}$$

Equation (3.6) subsumes the phenomenological order parameter equations [7]; the term involving τ_G is known as the Ginzburg–Landau equation for non-conserved kinetics [8], whereas the term involving τ_K is called the Cahn–Hilliard equation for conserved kinetics [9]. This identification follows from the recognition that the Ginzburg–Landau free energy may be expressed as

$$G\{Q(r)\} = k_{\mathrm{B}}(T - T_C)(Q(r))^2 + A(Q(r))^4 - B(\nabla Q(r))^2 \tag{3.7}$$

Thus

$$\frac{\delta G\{Q(r)\}}{\delta Q(r)} = 2\left[k_{\mathrm{B}}(T - T_C)Q(r) + 2A(Q(r))^3 - B\nabla^2 Q(r) \right]. \tag{3.8}$$

Hence, upon approximating $(Q(r))^3$ as $3Q_{\mathrm{eq}}^2 Q(r)$, we may express (3.6) in the general form (cf (4.5) of I)

$$\frac{dQ_k(t)}{dt} = -\frac{1}{2\tau k_{\mathrm{B}}T} \left(\frac{\delta G}{\delta Q(r)} \right)_k \tag{3.9}$$

where the index k outside the brackets denote the kth Fourier component and the parameters A and B are identified as

$$A = \frac{1}{6} \frac{T_C}{T} \qquad B = \frac{1}{2} \frac{T_C}{T} R_J^2. \tag{3.10}$$

4. Interpretation, length scales, time scales etc

The equation (3.6), derived in the case in which we are looking at small spatial and temporal fluctuations of the order parameter over and above an equilibrium state close to T_C (i.e. Q_{eq} small), allows for a simple interpretation of our results. As remarked earlier, $(-\delta G/\delta Q(r))_k$ may be viewed as the driving force which in the present instance is given by

$$\left(\frac{-\delta G}{\delta Q(r)} \right)_k = 2\left[k_{\mathrm{B}}(T_C - T) - \frac{T_C}{T} Q_{\mathrm{eq}}^2 - \frac{1}{2} \frac{T_C}{T} R_J^2 k^2 \right] Q_k. \tag{4.1}$$

This driving force is derived from a Landau–Ginzburg-type free energy (3.7) which lends a physical meaning to the range parameter R_J (cf (3.4)): R_J measures the length scale over which the spatial modulation of the order parameter occurs as it is proportional to the coefficient of the 'gradient energy'. On the other hand the effective 'relaxation time' for mixed conserved–non-conserved kinetics is

$$\frac{1}{\tau_r} = \frac{1}{\tau_G} + \frac{N_K}{6\tau_K} k^2 \xi_K^2. \tag{4.2}$$

Thus unlike the driving force which is related to an equilibrium property, the origin of τ_r is entirely kinetic. However, τ_r also depends on another length scale, viz. ξ_K, the jump distance over which correlated jumps for conserved kinetics occur.

While all this is fine near the critical point, our main interest is in fact in ordering phenomena far away from the critical point in systems with long range interactions. In that case the order parameter kinetics, at least in one limit such as the one which is obtained when the system is initially in thermal equilibrium is given by (3.2). Interestingly however, we could still write down our rate equation in the form of (3.9), but now the driving force is given by

$$\left(\frac{-\delta G}{\delta Q(r)}\right)_k = 2\big[(1 - Q_{eq}^2)J(k) - k_B T\big]Q_k \tag{4.3}$$

whereas the relaxation time is

$$\frac{1}{\tau_r} = \frac{1}{\tau_G} + \frac{N_K}{\tau_K}\frac{1 - Q_{eq}^2}{1 + Q_{eq}^2}[1 - \cos(k \cdot R_K)]. \tag{4.4}$$

(Note that an equilibrium property, viz. Q_{eq}, has already crept into the expression for τ_r.) Additionally, if we average over the directions of R_K (cf comment preceding (3.5)) equation (4.4) reduces to

$$\frac{1}{\tau_r} = \frac{1}{\tau_G} + \frac{N_K}{\tau_K}\frac{1 - Q_{eq}^2}{1 + Q_{eq}^2}\left(1 - \frac{\sin(k\xi_K)}{k\xi_K}\right). \tag{4.5}$$

The question now is, what is the appropriate kinetic potential corresponding to the driving force in (4.3)? A moment's reflection shows that it is given by the integral equation:

$$G\{Q(r)\} = (Q_{eq}^2 - 1)\int\int J(r - r')Q(r)Q(r')\,dr\,dr' + k_B T Q^2(r). \tag{4.6}$$

In a different context where the order parameter $Q(r)$ characterizes a phonon-mediated displacive phase transition, it is tempting to interpret the first term in (4.6) as the enthalpy and the second term as a 'harmonic' entropy.

Coming back to the question of the relaxation time we could rewrite (4.5), in the regime in which non-conserved kinetics dominate (i.e. τ_G is 'small'), as

$$\frac{1}{\tau_r} = \frac{1}{\tau_G}\left(1 - \frac{N_K \tau_G}{\tau_K}\frac{1 - Q_{eq}^2}{1 + Q_{eq}^2}\frac{\sin(k\xi_K)}{k\xi_K}\right) \tag{4.7}$$

Because in the diffusive limit (cf (4.2) and (3.5)) we could introduce a 'diffusion coefficient' of conserved kinetics as

$$D \equiv \frac{N_K}{6\tau_K}\xi_K^2 \tag{4.8}$$

we could express (4.7) as

$$\frac{1}{\tau_r} = \frac{1}{\tau_G}\left(1 - \frac{6D\tau_G}{\xi_K^2}\frac{1 - Q_{eq}^2}{1 + Q_{eq}^2}\frac{\sin(k\xi_K)}{k\xi_K}\right) \tag{4.9a}$$

We could thus introduce another length scale for non-conserved kinetics as

$$\xi_G^2 \equiv 6D\tau_G\frac{1 - Q_{eq}^2}{1 + Q_{eq}^2} \tag{4.9b}$$

to rewrite (4.9) in a form analogous to (1.1)

$$\frac{1}{\tau_r} = \frac{1}{\tau_G}\left(1 - \frac{\xi_G^2}{\xi_K^2}\frac{\sin(k\xi_K)}{k\xi_K}\right). \tag{4.10}$$

Thus the term within the square parentheses measures the effective reduction in the rate of non-conserved kinetics.

We close this section by remarking that in a more general situation of ordering kinetics, such as the one described by (2.8), it is not possible to write the rate equation in the form of (3.9) and provide separate interpretations for the driving force and the relaxation time. The two concepts are inexorably mixed up when we have a combination of conserved and non-conserved kinetics. In a sense this is not an unexpected result in view of our findings in I; we show there that there is really no unique driving force for describing complicated ordering kinetics.

5. Conclusion

We have discussed in this paper the question of under what constraints and assumptions the kinetic behaviour of a mixed Glauber and Kawasaki Ising system leads to the phenomenological rate law assumed by Salje and collaborators [10–13]. In all cases where competing processes lead to both conserved and non-conserved kinetics, the rate constant (cf (4.4)) is expected to be strongly k-dependent, especially when the Kawasaki jumps are not restricted to nearest neighbour distances. This has consequences for structural modulation and texture. As is evident from (4.5) the effective time constant for the rate process decreases with increasing k implying a coarsening of the texture [1,11]. This texture is different from microstructures arising from the k-dependence of the driving force (i.e. the operand in (1.1)), which is related to the width of twin walls, anti-phase boundaries etc [14].

Experimental evidence for the relevance of microstructures in ordering processes (in contrast to exsolution processes) is relatively rare. For instance, Al/Si (dis)ordering in sanidine [12] and the cation ordering in omphacite [13] do not show any texture and appear to follow the non-conserved version of (1.1) with the driving force given by a Landau–Ginzburg G. On the other hand, a large admixture of non-conserved

and conserved processes is expected to dominate the NaK exsolution kinetics in alkali feldspars—coarse microstructures are observed here in perthite and cryptoperthite [15]. Although the global chemical composition is conserved in this case, the local ordering process may contain some elements of a Glauber-like mechanism.

Finally, crystals with order parameters which describe chemical ordering (e.g. $C\bar{1}$–$I\bar{1}$ transition in plagioclases [16] and mixed fluorites [17]) appear to lead to kinetic processes in which the Kawasaki length is finite, although Glauber-like kinetics is also locally possible. These systems exhibit extreme microstructures and appear well suited for further studies in order to elucidate the respective contributions of the various kinetic processes.

References

[1]   Salje E 1988 *Phys. Chem. Mineral.* **15** 336
[2]   Parlinski K and Grimm H 1988 *Phys. Rev.* B **37** 1925
[3]   Binder K 1974 *Z. Phys.* **267** 313
[4]   Suzuki M and Kubo R 1968 *J. Phys. Soc. Japan* **24** 51
[5]   Salje E 1985 *Phys. Chem. Mineral.* **12** 99
[6]   Binder K 1977 *Phys. Rev.* B **15** 4425
[7]   Metiu H, Kitahara K and Ross J 1987 *Fluctuation Phenomena* ed E W Montroll and J L
        Lebowitz (Amsterdam: North-Holland) p259
[8]   Ginzburg V L and Landau L D 1958 *Zh. Eksp. Teor. Fiz.* **20** 1064
[9]   Cahn J W and Hilliard J E 1958 *J. Chem. Phys.* **28** 258; 1959 *J. Chem. Phys.* **31** 688
        See also
        Cahn J W 1961 *Acta Metall.* **9** 795; 1962 *Acta Metall.* **10** 907
[10] Wruck B, Salje E and Greame-Barber A 1990 *Phys. Chem. Mineral.* at press
[11] Carpenter M A and Salje E 1989 *Mineral Mag.* **53** 483
[12] Salje E and Kroll H 1990 *Phys. Chem. Mineral.* at press
[13] Carpenter M A, Domenighetti and Tazzoli V 1990 *Eur. J. Mineral.* **2** 19
[14] Salje E 1990 *Phase Transitions in Ferroelastic and Co-elastic Crystals*
        (Cambridge: Cambridge University Press)
[15] Smith V 1974 *Feldspar Mineralogy II* (Berlin: Springer)
[16] Salje E 1987 *Phys. Chem. Mineral.* **14** 189
[17] Cowley R A, Shirane G, Yoshizawa H and Uemura Y J 1989 *Z. Phys.* B **75** 303