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A phenomenological approach to ordering kinetics for partially conserved order parameters

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Abstract. The kinetics of cation ordering in complex crystal structures, such as minerals and ceramics, is discussed with regard to the applicability of time-dependent Ginzburg–Landau theory (TDGL). Deviations from the predictions made by TDGL may arise due to partial conservation of continuous and non-uniform order parameters at low temperatures. Under these conditions the movement of areas with large order parameter gradients ('walls') provides a local alternative to the continuous ordering kinetics described by TDGL. A simple phenomenological description of order parameter kinetics taking these constraints into consideration can be obtained. The underlying assumption is that the geometry of spatial order parameter variation close to equilibrium resembles that of a phase-separated system. The resulting kinetics differs substantially from the predicted TDGL behaviour.

1. Introduction

In recent years the kinetics of cation ordering has been studied experimentally for various mineral structures [1–3], the aim has been to test the applicability of time-dependent Ginzburg–Landau theory (TDGL) to such processes. The experiments were accompanied by theoretical and computational studies of relevant model systems [4–6]. Both approaches confirm that the driving force of the kinetic process can generally be identified with the excess Gibbs free energy of an underlying phase transition.

Theoretical considerations have already focused on the kinetics of systems in which the order parameter is spatially non-uniform and partially conserved [5, 7]. Whereas most studies undertaken so far indicated the possibility of pattern formation as a result of the non-equilibrium state [8, 9], our primary interest here is in how initial non-uniformities will influence the time evolution of the macroscopic order parameter.

An experimental approach for examining such a situation involves the low-temperature quenching of a crystal structure undergoing an order–disorder transition. Starting from T_0 below the phase transition temperature T_c , a subsequent rapid quench to $T \ll T_0 < T_c$ establishes the new equilibrium state at this temperature after some time delay. The macroscopic symmetry remains unaffected, and the order parameter domains of opposite sign have coarsened considerably before the quench, effectively reducing the system size to that of a single domain.

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The relevant order parameter for cation ordering—or, in more general terms, for substitutional ordering—is defined by the linear combination of sublattice concentrations. It is equivalent to the staggered magnetization of an antiferromagnet. This order parameter is non-conserved, whereas the total concentration of cations is conserved for any closed system.

TDGL theory describes the motion of a continuous order parameter as a function of the driving force, determined by a Gibbs free energy G_{kin} :

$$\frac{\partial Q}{\partial t} \propto \frac{\partial G_{\text{kin}}}{\partial Q} \quad (1)$$

which can be identified with the coarse-grained free energy of an underlying phase transition $G_{\text{kin}} = G_{\text{L}}$. This is normally approximated using the standard Ginzburg–Landau form

$$G_{\text{L}} = \int dr \left[\frac{1}{2} g |\nabla Q|^2 + f_{\text{L}}(Q) - hQ \right] \quad (2)$$

$$f_{\text{L}}(Q) \cong \frac{1}{2} A Q^2 + \frac{1}{4} B Q^4 + \dots \quad (3)$$

where the coefficient of the gradient energy, g , is given by

$$g = |A| \xi^2. \quad (4)$$

ξ is the correlation length of the phase transition and $\xi_0(T = 0 \text{ K})$ defines the range of interactions. The coefficient A is temperature dependent, and is negative for $T < T_{\text{c}}$. In the mean-field case, ξ diverges with a critical exponent $\nu = 1/2$ at T_{c} :

$$\xi = \xi_0 \left(\frac{|T - T_{\text{c}}|}{T_{\text{c}}} \right)^{-\nu}. \quad (5)$$

The temperature dependence of the higher-order terms in (3) becomes significant in the case of non-harmonic entropy contributions. We will assume that no field h couples to the order parameter in the following.

The kinetics of phase transitions is usually described in terms of two different models. If the order parameter varies continuously, even on a length scale comparable to the unit-cell dimensions, TDGL theory predicts the ordering kinetics correctly [10]. In contrast, if the order parameter varies discontinuously, the kinetics is described by kinetic Ising models [4, 10]. In the case of a two-state Ising model, the order parameter per lattice site is either -1 or $+1$ (the pseudo-spin model). If the total spin is conserved, the configurations can only change through spin-exchange processes (Kawasaki dynamics). This corresponds to a simple microscopic model of cation ordering. Continuous order parameters now can be obtained via coarse graining, and G_{kin} differs substantially from G_{L} [4].

In real systems, and especially in complex structures, the situation is not always as clear cut as in these two models. Whether the order parameter varies continuously or not depends crucially on ξ . This in turn is bound to change with temperature, and it has been shown that in fact at temperatures not too far below T_{c} , the time evolutions of the order parameter predicted in the two models are almost indistinguishable [4], whereas this is not the case at low temperatures $T \leq 0.8T_{\text{c}}$, where Kawasaki dynamics predicts far slower ordering kinetics than TDGL theory.

2. Fluctuations, order parameter flux and the concept of mixed kinetics

The following discussion will be limited to a strictly deterministic model, as the primary interest lies in low-temperature quenches, i.e. the limit $T = 0$. However, if thermal

fluctuations become important, as is certainly the case at temperatures close to T_c and then especially for ordering states close to equilibrium, a Langevin approach (cf. e.g. [11]) using stochastic forces is more appropriate.

A well known equation describing the time dependence of non-uniformities—of an otherwise conserved order parameter—is the Cahn–Hilliard equation (CHE) [11]. It describes the phase separation processes following spinodal decomposition at least qualitatively correctly:

$$\frac{\partial Q}{\partial t} = \nabla \left[(\tau_2 RT)^{-1} \nabla \frac{\partial G}{\partial Q} \right] \quad (6)$$

where Q is defined by

$$Q(r, t) = Q_0 + Q(r, t) \quad (7)$$

with Q_0 as the conserved quantity, i.e. the concentration.

It is tempting to introduce ‘mixed kinetics’ by setting $Q_0 = Q(t)$, and hence describing the kinetics of a non-uniform order parameter using the CHE on a background of non-conserved ordering. To illustrate this, let us for the moment assume that $Q(r)$ varies only between two extremes.

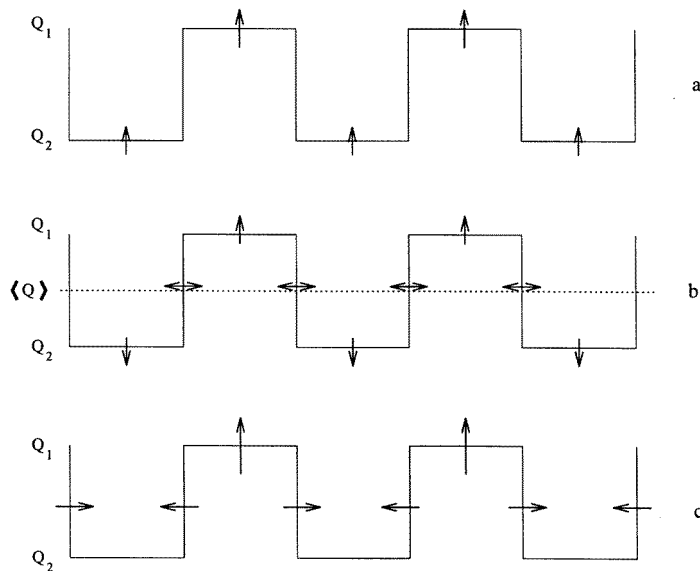


Figure 1. Schematic diagrams of a spatially varying order parameter. (a) The non-conserved case: equilibrium is attained via order parameter increase (upwards arrows). (b) The conserved case: equilibrium is attained via decomposition into two phases. $\langle Q \rangle$ is constant. Wall movement coarsens the resulting pattern. (c) The partially conserved case: ordering at Q_2 slows down, while $\langle Q \rangle$ increases due to the increase of Q_1 and due to wall movement. Eventually, ordered clusters coalesce to form a uniform structure.

Figure 1(a) shows the fluctuating order parameter $Q(r)$ sketched as a pulse-shaped line, oscillating between the two values Q_1 and Q_2 . Order parameter increase, as dictated by the driving force, is tantamount to elevation of the horizontal sections. This behaviour corresponds to purely non-conserved ordering and it will proceed with non-identical rates at

the two levels. The walls[†] separating the two order parameter levels will broaden, but their position will remain unchanged. The time dependence of the fluctuations will be governed by the initial order parameter distribution.

In contrast, in a phase-separation process with fully conserved order parameter $\langle Q \rangle$ the vertical motion points in opposite directions at Q_1 and Q_2 (figure 1(b)). Therefore volume fractions p_α and p_β , constrained by $\langle Q \rangle = p_\alpha Q_\alpha + p_\beta Q_\beta$, develop. The initial pattern will then coarsen in order to minimize the interface between the two phases.

Figure 1(c) shows the superposition of the two schemes: ordering at small local levels of $Q(r)$ is substantially inhibited by order parameter flow towards the wall. The walls therefore progress into these disordered regions. Simultaneously, ordering within the well ordered regions accelerates. Hence, the deciding effect of conservation is the stabilization of fluctuations, as opposed to the suppression of fluctuations in a purely non-conserved picture.

The coarsening process anticipated for the late stages of phase separation follows a power-law behaviour: $L(t) \propto t^n$ (for a review see [12]), where $L(t)$ denotes the characteristic length scale, either given by the scale size of an interpenetrating network of the two phases ($p_\alpha \approx p_\beta$) or given by the average size of isolated grains of a minority phase ($p_\alpha \neq p_\beta$). The exponent n in this growth law is generally determined by the order parameter dynamics: if the order parameter is conserved, $n = \frac{1}{3}$; if it is non-conserved, $n = \frac{1}{2}$.

In order to adjust rate equation (1) to the general picture of a spatially non-uniform order parameter, equation (8) has been introduced [7]:

$$\frac{\partial Q}{\partial t}(r) = -(\tau RT)^{-1} \left(1 - \frac{\xi_c^2}{\xi^2} \frac{\sinh(\xi \nabla)}{\xi \nabla} \right) \frac{\partial G}{\partial Q}(r) \quad (8)$$

where ξ_c is the typical length scale of conservation, e.g. the average distance over which cation exchange processes ('Kawasaki jumps') occur, while τ sets the timescale of the kinetic process. The operator part of this rate equation effectively interpolates between (1), i.e. non-conserved kinetics, and the CHE (6).

Using the relation $\xi_c^2 = \xi^2 \tau_2^{-1} / (\tau_1^{-1} + \tau_2^{-1})$ [7], we can write down (8) in terms of the two time constants τ_1 and τ_2 , for non-conserved and for conserved dynamics respectively:

$$\frac{\partial Q}{\partial t}(r) = -\frac{\tau_1^{-1} + \tau_2^{-1}}{RT} \left(1 - \frac{\tau_2^{-1}}{\tau_1^{-1} + \tau_2^{-1}} \frac{\sinh(\xi \nabla)}{\xi \nabla} \right) \frac{\partial G}{\partial Q}(r). \quad (9)$$

By setting $\xi_c^2/\xi^2 = 1$ while truncating at the lowest-order term in the operator, the CHE is recovered from (8).

In the long-wavelength limit, equation (8) rescales the rate of ordering by a factor of $1 - \xi_c^2$. Any reduction in the ordering rate of the less-ordered regions is fully compensated by accelerated kinetics inside the better-ordered regions. This balance however has to break down as soon as these regions have equilibrated locally[‡]. Therefore we expect deviations of the order parameter kinetics from the strictly non-conserved behaviour during the late stages of ordering.

[†] The notion of a *wall* in this context is not that of a domain boundary, but rather that of an interface between ordered and less-ordered regions.

[‡] This holds in the deterministic picture—if thermal fluctuations are considered, the local threshold extends to $Q(r) = 1$, i.e. the order parameter saturates locally.

3. A simple driving force

Following (2), the simplest Ginzburg–Landau approximation to the coarse-grained free energy of a continuous phase transition is given by

$$G_{\text{LG}} = \int \left\{ \frac{1}{2} \alpha (T - T_c) Q^2 + \frac{1}{4} \mathcal{B} Q^4 + \frac{1}{2} g' \left(\frac{\partial Q}{\partial \mathbf{r}} \right)^2 \right\} dV. \quad (10)$$

Here $T_c = \mathcal{B}/\alpha$, and the equilibrium order parameter has the temperature dependence $Q = (1 - \hat{t})^{1/2}$ with $\hat{t} = T/T_c$. A change to dimensionless quantities is achieved by defining $B = \mathcal{B}/k_B T$, $a = \alpha/k_B$ and $g = g'/k_B T$. Furthermore, we will define Fourier coordinates Q_k , using

$$Q(\mathbf{r}) = \sum_k Q_k e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (11)$$

The temperature dependence is accommodated as $A = a\hat{t} - B$. Assuming that the modes Q_k are decoupled, we can write down the energy density as a function of the wavevector \mathbf{k} :

$$\mathcal{G}_{\text{LG}}(\mathbf{k}) = \frac{1}{2} (A + gk^2) (Q_k)^2 + \frac{1}{4} B (Q_k)^4 \quad (12)$$

obtaining the *driving force*

$$\frac{\partial \mathcal{G}}{\partial Q}(\mathbf{k}) = (A + gk^2) Q_k + B (Q_k)^3. \quad (13)$$

The general rate equation (8) becomes

$$\frac{\partial Q_k}{\partial t} = -\tau^{-1} \left(1 - \frac{\xi_c^2}{\xi^2} \frac{\sin(\xi k)}{\xi k} \right) \frac{\partial \mathcal{G}}{\partial Q}(\mathbf{k}) \quad (14)$$

with the solution

$$Q_k^2(t) = \frac{(Q_k^0)^2 \phi(k) \exp(-2 \Delta t \tau^{-1} \psi(k) \phi(k))}{\phi(k) + B (Q_k^0)^2 \{1 - \exp(-2 \Delta t \tau^{-1} \psi(k) \phi(k))\}} \quad (15)$$

where $\phi(k) = A + gk^2$ and

$$\psi(k) = \left(1 - \frac{\xi_c^2}{\xi^2} \frac{\sin(\xi k)}{\xi k} \right)$$

define the k -dependence of internal energy and time constant respectively. Q_k^0 is the profile of Q_k at $t = t_0$ and $\Delta t = t - t_0$ is the time-step.

4. Ordering and growth combined

As we expect the cluster growth to be governed by simple scaling behaviour, it is convenient to separate the contributions of this growth process from the collective ordering process. Hence we will define two order parameter components Q_μ and Q_ν , each of which contributes to the macroscopic order parameter with a weight given by the degree of order parameter conservation.

The component μ obeys (15) with $k = 0$. The timescale is reduced to $(1 - \xi_c^2/\xi^2)/\tau = (1 - p)/\tau$, due to order parameter conservation.

Q_ν scales with the size of ordered clusters, with the initial randomly distributed spatial variation serving as a nucleation centre. With the only source of order parameter restricted to the μ -component, the growth of Q_ν is limited by the timescale $(1 - p)/\tau_2$. The sum $\tau_1^{-1} + \tau_2^{-1} = \tau^{-1}$ defines the total rate of ordering, as introduced in (9).

The macroscopic average $\langle Q \rangle$ is

$$\langle Q \rangle = (1 - p)Q_\mu(t) + pQ_\nu(t). \quad (16)$$

For any scalar order parameter the growth of ordered regions will proceed according to a power law $L(t) \propto t^m$. The order parameter can therefore be expected to scale with an exponent $m = dn/2$, where d is the dimensionality of the ordered clusters and the factor $1/2$ derives from the conventional case in which the transformed volume is proportional to the square of the order parameter.

The nucleation process is identified with the local equilibration of ordered droplets. Therefore the nucleation rate will quickly subside and we can, in a first approximation, assume that the number of nuclei per unit volume, N_ν , is constant. The resulting growth law is

$$q_\nu(t) = N_\nu \left(\frac{(1-p)t}{\tau_2} \right)^m. \quad (17)$$

Growth eventually has to cease, due to the coalescence of ordered particles. This saturation effect can be taken into account by using (17) as the argument of the Kolmogorov–Johnson–Mehl–Avrami (KJMA) equation (e.g. [13]). Appropriate normalization then yields

$$Q_\nu(t) = Q^0 + (Q_{\text{eq}} - Q^0)[1 - \exp(-q_\nu(t))]. \quad (18)$$

If the ordering process is thermally activated, we expect $\tau^{-1} = \gamma \exp(-\Delta\mathcal{G}/RT)$, where $\Delta\mathcal{G}$ is a Gibbs free energy of activation and γ sets the timescale. If the temperature dependence of τ_2 differs from that of τ_1 , then ξ_c^2/ξ^2 will be temperature dependent. One would generally expect this to be the case, as ξ diverges on approaching T_c , while the temperature dependence of ξ_c is dominated by the activation energy of the underlying diffusion process.

The approximation outlined in this section is useful if $Q(t)$ is known from experiment. Then ξ_c^2/ξ^2 can be determined without explicit consideration of the k -dependence. Further adjustments to the model can be introduced via a non-zero nucleation rate, i.e. by defining N_ν as a function of Q_μ .

4.1. The structure factor and the definition of the coarsening stage

Experimentally, the order parameter kinetics in an order–disorder system is usually followed via scattering experiments. If the critical point is at the zone boundary of the high-symmetry phase, the degree of long-range order is given by the intensity of a superstructure reflection. The measured quantity is the *structure factor*:

$$S(\mathbf{k}, t) = \langle |Q(\mathbf{k}, t)|^2 \rangle = \int \langle Q(\mathbf{r}, t) Q(\mathbf{r}', t) \rangle \exp(i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')) \, d\mathbf{r} \, d\mathbf{r}'. \quad (19)$$

This is the Fourier transformation of the equal-time pair correlation function. Its integrated intensity measures the degree of short-range order (SRO), while the $k = 0$ component gives the uniform part, $S(k = 0, t) = Q^2(t)$, i.e. the intensity of the Bragg reflection (which is of finite width in any realistic experimental setting). For the non-uniform part, the sum rule

$$\int_{\mathbf{k} \neq 0} S(\mathbf{k}, t) \, d\mathbf{k} = \langle [Q(\mathbf{r}) - Q]^2 \rangle \quad (20)$$

holds. Here the integration is cut off at the inverse coarse-graining length.

If the order parameter is conserved, equation (20) can be evaluated as

$$\langle [Q(\mathbf{r}) - Q]^2 \rangle \cong (Q_\beta - Q)(Q - Q_\alpha)$$

during the late stages of phase separation [11].

However, in the case considered here, Q is a function of time, and instead of a phase mixture we expect a uniform order parameter Q_{eq} for $t \rightarrow \infty$. We can argue that fluctuations will be limited to the interval $Q_2 < Q(r) < Q_1 = Q_{\text{eq}}$ during the late stages (figure 1). Splitting the order parameter in analogy to section 4, we now have $Q_\mu = Q_{\text{eq}}$ and $Q_\nu = Q_2(t)$. The fluctuation average is then approximated by

$$\langle [Q(r) - Q]^2 \rangle \cong [Q_{\text{eq}} - Q(t)][Q(t) - Q_2(t)] \quad (21)$$

with

$$Q_2(t) = \frac{Q(t) - (1 - p)Q_{\text{eq}}}{p} \quad (22)$$

for $p > 0$.

After addition of the Bragg reflection intensity, Q^2 , and substitution for the integral in (20) with the average of discrete structure factor components Q_k^2 , one obtains

$$\langle Q_k^2 \rangle_k = Q(t)Q_{\text{eq}} + Q_2(t)(Q(t) - Q_{\text{eq}}). \quad (23)$$

The time derivative of (23) determines the growth rate of the macroscopic order parameter:

$$\left(\frac{\partial Q}{\partial t} \right) = \frac{p}{Q(t) - (1 - p)Q_{\text{eq}}} \left\langle Q_k \frac{\partial Q_k}{\partial t} \right\rangle_k. \quad (24)$$

Equation (24) describes the time dependence of the order parameter during what we will refer to as the *coarsening stage*. The onset of this regime requires Q_2 to be positive, and therefore (24) is the valid rate equation for $Q(t) > (1 - p)Q_{\text{eq}}$. Below this threshold no local order parameter saturation occurs and the conservation process has no effect on the time evolution of the long-range-order parameter other than a time constant rescaling.

In order to solve (24), we have to plug in $Q_k(t)$ as given by (15) (or generally the corresponding solution of (14)). Then one can solve (24) numerically, averaging over a sufficient number of components $Q_k(t)$.

5. Specific results for a second-order phase transition

In order to define a realistic starting point we assume that the pair correlation function close to the critical temperature is well described by the Ornstein–Zernike formalism. The structure factor at $t = 0$ and $\hat{t} = T_0/T_c$ will hence be given by the Lorentzian

$$Q_k^2 = \frac{T_0}{T_c(|A| + gk^2)}. \quad (25)$$

We further assume that the local order parameter variation has no preferred orientation and we will henceforth restrict the model to one dimension in k . The temperature dependence of ξ is given by (5), and we stipulate that $\xi_c = \xi(T = 0)$. The underlying basic length scale, a_c , is, in the simplest case, the cell edge of a primitive cubic lattice, although in most cases of practical interest the symmetry will be lower. For complex structures a_c is large compared to the interatomic distances, and we expect a single unit cell to provide a large number of possible configurations for the ordering process. It is therefore sufficient to identify the coarse-graining length with a_c for our model calculations.

As we postulate ξ_c to be temperature independent, the mixing coefficient is $p = \xi_c^2/\xi^2 = 1 - \hat{t}$. The model parameters are $a = 1$, $T_c = 1$ and $\xi_c = 2a_c$. $Q_k(t)$ is calculated for 100 modes in the range $0 \leq k \leq 1/a_c$.

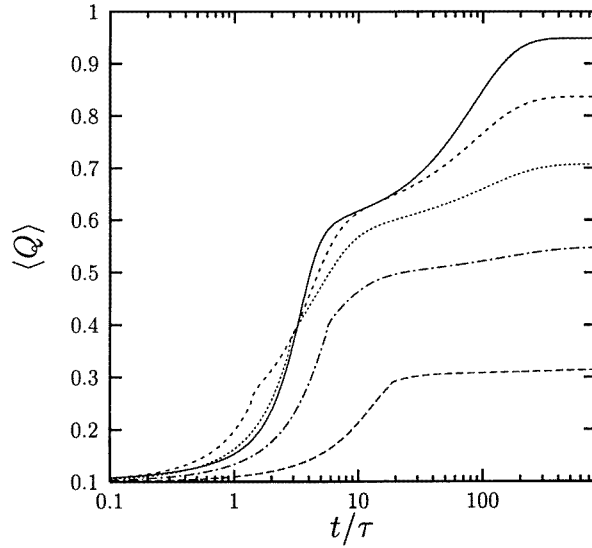


Figure 2. The calculated order parameter kinetics for isothermal annealing at $0.9T_c$, $0.7T_c$, $0.5T_c$, $0.3T_c$ and $0.1T_c$ (in order of ascending equilibrium order parameter) after a quench from $0.99T_c$. The mixing coefficient depends on temperature as $\xi_c^2/\xi^2 = 1 - \hat{t}$.

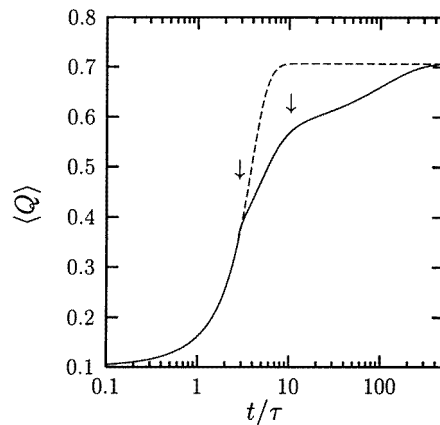


Figure 3. The order parameter kinetics at $\hat{t} = 1/2$, $\xi_c^2/\xi^2 = 1/2$ (solid curve). The dashed curve shows the uncorrected TDGL kinetics resulting from (15). Arrows mark crossover times between different stages of the ordering process, as referred to in the text.

Figure 2 shows the ordering kinetics obtained for the phase transition defined in section 3. Three stages can be identified, as indicated in figure 3 for $\hat{t} = 1/2$, $p = 1/2$. The first stage is identical to TDGL kinetics. Above $Q(t) = Q_{eq}/2$ the coarsening stage sets in, marking the formation of the first nuclei of ordered phase. Their growth, together with the ongoing ordering process, dominates the kinetics during the intermediate stage. By the time Q_{eq} would have been reached for a uniform order parameter, the nucleation process ceases and further ordering is dominated by growth and coalescence of previously formed clusters. At this stage, the only remaining contributions to the numerator in equation (24)

are located at $k \approx \xi_c^{-1}$ and $k = 0$. The particular duration of each stage is determined by the degree of conservation (figure 2). For $\xi_c^2/\xi^2 \simeq 1$ the first stage is irrelevant and, after some time delay, nucleation proceeds rapidly; this is then followed by the growth process.

If the postulated growth law, equation (17), dominates the late stages of the ordering, then a plot of $\ln\{-\ln[1 - (Q_v - Q^0)/(Q_{eq} - Q^0)]\}$ versus the logarithm of time should reveal a linear behaviour. This is confirmed in figure 4, where Q_v is calculated using $Q_v = (\langle Q \rangle - (1-p)Q_\mu)/p$. Though deviations from the expected line become more obvious with larger degrees of conservation, the overall behaviour is consistent with $t^{1/2}$ -growth of the order parameter during the late stages. Assuming growing clusters of dimensionality $d = 3$, this suggests a growth exponent $n = 1/3$, in accordance with the fact that the cluster growth is triggered by order parameter conservation.

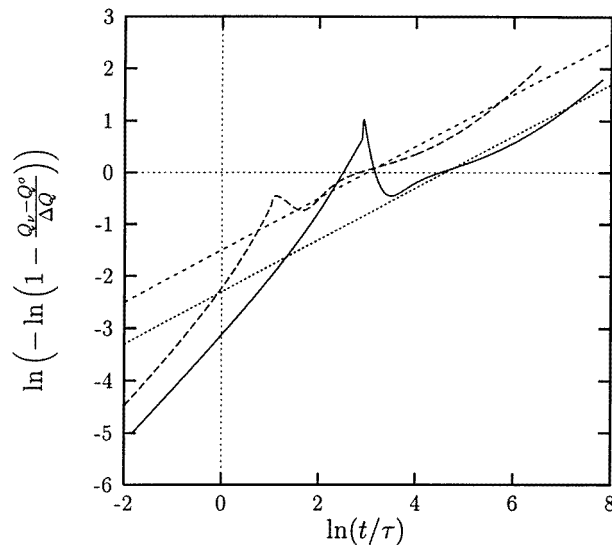


Figure 4. A log-log plot of $Q_v = (\langle Q \rangle - (1-p)Q_\mu)/p$ for $\hat{t} = 9/10$, $\xi_c^2/\xi^2 = 1/10$ (solid curve) and $\hat{t} = 1/2$, $\xi_c^2/\xi^2 = 1/2$ (dashed curve). The lines correspond to a time exponent of $m = 1/2$.

6. Conclusions

We have seen that non-uniformity of the order parameter can dramatically alter the ordering kinetics at low temperatures. We now have to address the actual mechanism giving rise to partial order parameter conservation.

Given a large correlation length, i.e. at high temperatures, ordering can proceed rapidly via correlated cation exchange processes, giving rise to the applicability of the TDGL approach. However, if the temperature falls far below T_c a different mechanism becomes favourable, as soon as parts of the structure have established the equilibrium state or even a fully ordered structure locally. In this case any cation exchange process involving the ordered part of the material is energetically unfavourable. Successful cation exchange processes will thus involve cations in front of the propagating wall. This, on the other hand, impedes ordering there, i.e. it conserves the local order parameter *outside* of the ordered clusters. The order parameter is effectively redistributed from the disordered regions

towards the boundaries of ordered clusters, and the fluctuations which were initially present are stabilized or even amplified. Further increase of the average order parameter is now only possible via growth of the ordered clusters.

The approach that we have outlined in this paper emphasizes the importance of the adjustments made to the time constant of TDGL rate laws. These adjustments are necessary if the correlation length of the underlying order–disorder phase transition approaches the average length scale of the diffusion processes. In that case the kinetic process crosses over from a stage dominated by TDGL kinetics to a stage dominated by growth and coalescence of ordered clusters.

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