Derivation of a rate law for nonuniform systems and continuous order parameters

LETTER TO THE EDITOR

Derivation of a rate law for non-uniform systems and continuous order parameters

S Marais† and E Salje‡

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

Abstract. A kinetic rate law for a partially conserved order parameter is derived in mean field theory of a continuous order parameter Q: $(\partial Q/\partial t)(r) = -[(\tau_1 + \tau_2)/kT]\{1 - [\tau_2/(\tau_1 + \tau_2)]\sinh(\xi\nabla)/\xi\nabla\}\,\partial G/\partial Q$. The 'driving force' $\partial G/\partial Q$ is related to the excess Gibbs free energy G, τ_1 and τ_2 are time constants and ξ is the characteristic length scale of the conservation law. For Fourier components of Q with wavevectors short compared with $1/\xi$ this rate law agrees with the rate law proposed by Salje in 1988.

Non-equilibrium states in crystals are often the result of rapid changes in thermodynamic conditions related to a structural phase transition. One might envisage as a typical example a phase transition involving cation ordering. If a sample is quenched through the transition point, the new equilibrium state will only be established after some time delay. It is the aim of kinetic rate equations to predict the time evolution of the order parameter between the initial low-equilibrium state and the final equilibrium state. Such rate equations always represent some approximation of the experimentally observed behaviour. Some of the approximations made for the derivation of rate equations (e.g. the mean field approximation for ferroelastic and co-elastic crystals) are in excellent agreement both with computer simulations and experimental observations. Other approximations are less obviously correct (or, indeed, wrong). Dattagupta *et al* (1991a, b) have critically examined the rate equations first proposed by Glauber (1963) and Kawasaki (1966) for Ising spin systems and Salje (1988) for continuous order parameters (also by Binder (1979) for Monte Carlo calculations in the spin case). Dattagupta *et al* (1991a, b) have found that all rate laws could be cast (in MFA) into similar algebraic equations as used by Salje in the case of uniform order parameters Q; namely

$$dQ/dt = (1/\tau)\,\partial G_{kin}/\partial Q. \tag{1}$$

The analytical forms of the kinetic Gibbs free energy G_{kin} are quite different for the three models although the predicted rate equations are not substantially different for

temperatures not too low compared with T_c (e.g. $T \geqslant 0.5\,T_c$). It was found that for a mean field approximation of the Ising model the kinetic Gibbs energies are

$$G_{\text{kin}}^{\text{Glauber}} = -kT\left\{\frac{T}{T_c}\ln\left[\cosh\left(\frac{T_c}{T}Q\right)\right] - \tfrac{1}{2}Q^2\right\} \tag{2}$$

$$G_{\text{kin}}^{\text{Kawasaki}} = -kT\left\{\frac{T}{4T_c}\ln\left[\cosh\left(\frac{2T_c}{T}Q\right)\right] - \tfrac{1}{2}Q^2\right.$$
$$\left. + \frac{T}{4T_c}\sum_1^x \frac{2^{2k}(2^{2k}-1)B_{2k}}{(2k+2)(2k)!}\left(\frac{2T_cQ}{T}\right)^{2k+2}\right\} \tag{3}$$

$$G_{\text{kin}}^{\text{Salje}} = G_{\text{equilibrium}} = \tfrac{1}{2}kT[(1+Q)\ln(1+Q) + (1-Q)\ln(1-Q)] - \tfrac{1}{2}k_B T_c Q^2. \tag{4}$$

In cases where $T \simeq 0.5\,T_c$ subsequent computer simulation for an Ising model using Monte Carlo techniques shows that the Salje rate law equation leads to an overestimation of the speed of ordering whereas the Glauber rate law is in good agreement with the numerical results. This situation is reversed for continuous cation ordering processes. Marais *et al* (1991) have shown analytically and also by using molecular dynamics modelling techniques that the Salje rate law leads to a correct description of the time evolution of the order parameter whereas the Glauber rate equation fails.

So far we have focussed our investigations on uniform and non-conserved order parameters, i.e. we have ignored the possibility of achieving the equilibrium state via correlated local structural changes in which the total order parameter is conserved. This situation is typically encountered in chemical exsolution or correlated ordering processes. In terms of Ising models, such conserved order parameters are described in the Kawasaki rate law in which the decision for an individual spin to flip is determined by a compensating flip somewhere else in the crystal (i.e. the volume-averaged spin $\langle s \rangle$ is unchanged).

Let us now analyse the following conjecture. We have seen that the Salje rate law is a better approximation for the time dependence of a continuous order parameter than the Glauber equation in the case of a non-conserved order parameter. It seems reasonable to assume that a similar situation exists for conserved order parameters: a continuous, conserved order parameter may evolve according to the Salje rate law and *not* following Kawasaki kinetics (which would still hold for discontinuous spin systems). In fact, we can expand this conjecture to include the case of partly conserved order parameters as formulated by Salje (1988) and Dattagupta *et al* (1991a, b).

We shall show in this paper that this rate law is, indeed, a reasonable approximation and we shall clarify the assumptions made for its derivation.

We first consider the order parameter flow in non-uniform systems.

Let us consider a mesoscopic part of a crystal in which the order parameter changes continuously. We also assume that the conservation is achieved by interaction between different areas but not inside the area and that the speed of change of the order parameter is proportional to the gain in Gibbs free energy (Marais *et al* 1991, Marais and Salje 1991)

$$\mathrm{d}Q(r)/\mathrm{d}t_{\text{local}} = -(\tau_1^{-1}/kT)(\partial G/\partial Q)(r) \tag{5}$$

where $G(Q(r))$ may have the simple Landau–Ginzburg form

$$G(Q(r)) = \tfrac{1}{2}a(T - T_c)Q^2 + \tfrac{1}{4}bQ^4 + \tfrac{1}{2}g|\nabla Q|^2 \tag{6}$$

leading to

$$\mathrm{d}Q/\partial t = -(\tau_1^{-1}/kT)[a(T - T_c)Q + bQ^3 + g\nabla^2 Q]. \tag{7}$$

We now turn our attention to the case of fully conserved OPs. The flow between different

spatial regions with different local order parameters $Q(r)$ and $Q(r')$ will then be, in lowest order, proportional to the difference between the driving forces $\partial G/\partial Q$ at r and r'. With this approximation the change in Q at the point r due to an exchange in the order parameter with another point r' becomes

$$\frac{\partial Q}{\partial t_{r \to r'}}(r) = \frac{\tau_2^{-1}}{kT} \left(\frac{\partial G}{\partial Q}(r') - \frac{\partial G}{\partial Q}(r) \right) \tag{8}$$

where τ_2 is some flow constant. The total change in Q at the point r resulting from exchanges follows from integration over r':

$$\frac{\partial Q}{\partial t}(r) = \frac{\tau_2^{-1}}{kT} \int d^3r' \left(\frac{\partial G}{\partial Q}(r') - \frac{\partial G}{\partial Q}(r) \right). \tag{9}$$

We now develop $(\partial G/\partial Q)(r')$ into a Taylor series around r. Convergency is assumed because the correlation between local kinetic events will decrease rapidly with increasing distance between the regions:

$$\frac{\partial G}{\partial Q}(r') = \frac{\partial G}{\partial Q}(r) + \sum_{n=1}^{\infty} \frac{(\Delta r \nabla)^n}{n!} \frac{\partial G}{\partial Q}(r) \tag{10}$$

where $\Delta r = r' - r$. If we now assume that the system is isotropic, and the integration over angles in equation (9) is performed, all terms in the Taylor expansion except those of the form $(\Delta x \, \partial/\partial x)^{2k}(\Delta y \, \partial/\partial y)^{2l}(\Delta z \, \partial/\partial z)^{2m}$, where k, l and m are integers, drops out. Now make the following assumption: any exchange process always occurs over a fixed distance $\Delta r = \xi$—although this is obviously false in many cases, one can think of ξ as a typical exchange process. With this assumption, equation (10) together with the angular integration of equation (9) becomes

$$\frac{\partial Q}{\partial t}(r)_{\text{conserved}} = \frac{\tau_2^{-1}}{kT} \left(\frac{1}{3!} \xi^2 \nabla^2 + \frac{1}{5!} \xi^4 \nabla^4 + \dots \right) \frac{\partial G}{\partial Q}(r). \tag{11}$$

This can be rewritten as

$$\frac{\partial Q}{\partial t}(r)_{\text{conserved}} = \frac{\tau_2^{-1}}{kT} \left(\frac{\sinh(\xi \nabla)}{\xi \nabla} - 1 \right) \frac{\partial G}{\partial Q}(r). \tag{12}$$

Combining this result with equation (5) finally gives the generalized rate equation

$$\frac{\partial Q}{\partial t}(r) = \frac{-(\tau_1^{-1} + \tau_2^{-1})}{kT} \left(1 - \frac{\tau_2^{-1}}{\tau_1^{-1} + \tau_2^{-1}} \frac{\sinh(\xi \nabla)}{\xi \nabla} \right) \frac{\partial G}{\partial Q}(r). \tag{13}$$

In most experimental situations the values of Q are measured via scattering functions. Let Q_k be the kth Fourier component of Q. The operator part of the rate law can then be written as $\xi^2 k^2$, which is for small values of the argument close to an exponential function $\exp(\frac{1}{6}\xi^2 k^2)$. This function was used by Salje (1988) and Metiu *et al* (1976) for the description of the k-dependence of rate laws with conserved order parameters. Although the first-order terms agree between these two rate laws, the second-order terms are smaller in $\sinh(\xi k)/\xi k$ than in the exponential k-dependence. The time constants $\tau_2^{-1}/(\tau_1^{-1} + \tau_2^{-1})$ can be related to diffusion coefficients that define the length scale ξ_c as $\xi_c^2 = \xi^2 \tau_2^{-1}/(\tau_1^{-1} + \tau_2^{-1})$ (Salje 1988, Dattagupta *et al* 1991a, b). We can also compare our rate law with that of Dattagupta *et al* (1991a, b) who discussed the physical ideas behind the mixing of conserved and non-conserved order parameters in a spin

system. In their model, the kinetics of Ising spins in a mixed Glauber–Kawasaki rate law follows

$$\tau^{-1}(k) = \tau_1^{-1}\left[1 - \frac{\tau_1}{\tau_2}N\left(\frac{1 - Q_{eq}^2}{1 + Q_{eq}^2}\right)\frac{\sin k\xi}{k\xi}\right]. \tag{14}$$

The k-dependence is identical to that discussed in this letter (see also Langer 1971). In contrast to the model discussed in this letter, $\tau^{-1}(k)$ in the Ising model depends explicitly on the equilibrium value of the order parameter, which is significant for cooling experiments at low temperatures and large values of Q_{eq}.

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