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1991 J. Phys.: Condens. Matter 3 6571

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## On the origin of kinetic rate equations: Salje–Glauber–Kawasaki

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Received 25 February 1991, in final form 8 May 1991

**Abstract.** The implicit approximations made in the derivation of the kinetic rate laws proposed by Salje, Glauber and Kawasaki are discussed. The Glauber and Kawasaki rate processes are relevant for discrete Ising systems with non-conserved or conserved order parameters, respectively. The Salje rate equation describes continuous rate processes. Molecular dynamics simulations of the  $\varphi^4$ -Hamiltonians are in close agreement with the predictions of the Salje rate law.

### 1. Introduction

The study of kinetic rate laws in non-metallic systems has become one of the main preoccupations of mineralogists, material scientists and physical chemists (Ganguly 1982, Carpenter and Salje 1989, Carpenter *et al* 1990, Besancon 1981, Kroll *et al* 1990, Mueller 1967). Their original motivation was to analyse and predict time dependent processes related to structural phase transitions in order to understand geological features or to produce materials with desired properties. By doing so, a substantial body of quantitative experimental observations has been built up that can now be used to foster our understanding of the fundamental physical processes which determine kinetic rate laws (e.g. Carpenter *et al* 1990, Wruck *et al* 1991, Salje and Kroll 1991, Salje and Wruck 1988). Most of these observations are concerned with cation ordering processes with large coupling between the order parameter (OP) and the lattice strain (see Salje 1990).

If we now compare the experimental evidence with predictions of the standard rate theories we find substantial disagreement. In fact, both the Glauber (Glauber 1963) and the Kawasaki (Kawasaki 1966) models appear to predict rate processes that are too slow. An alternative rate law was proposed by Salje (1988), which seems to agree better with the experimental observations, for a continuously variable order parameter  $Q$  as

$$\partial Q/\partial t = -(C/kT)(1 + (\xi_c/\xi)^2 e^{\nabla^2/\xi^2})(\partial G/\partial Q) \quad (1)$$

where  $G$  is the excess free energy of the phase transition and  $\xi_c$ ,  $\xi$  are lengths related to the conservation behaviour of the order parameter. Here we will be concerned only with

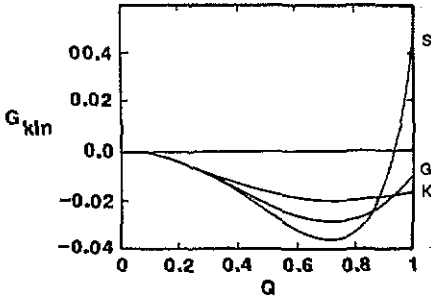


Figure 1. Kinetic Gibbs free energy ( $\dot{Q} \propto \partial G_{\text{kin}}/\partial Q$ ) for  $T = 0.8 T_c$ . The three rate laws shown are S (Salje), G (Glauber) and K (Kawasaki).

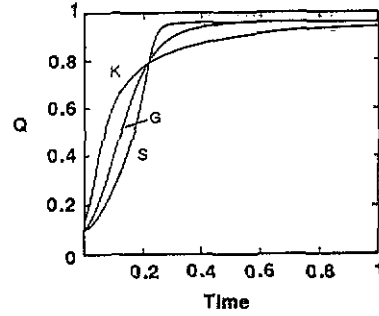


Figure 2. A best fit of the Salje (S), Glauber (G) and Kawasaki (K) systems for a mean field Ising-spin system quenched to  $T = 0.5 T_c$ . For the  $\varphi^4$ -model the results are qualitatively the same. The Kawasaki prediction is always much slower than the other two rate equations.

systems that have uniform, non-conserved order parameters ( $\xi_c = 0$ ) so that the relevant law reduces to

$$\partial Q/\partial t = -(C/kT)/(\partial G/\partial Q). \quad (2)$$

Here  $C$  is some constant that depends on the specifics of the kinetic process. Its formal description is now equivalent to a relaxational rate law of the classic Landau–Khalatnikov type, the main difference is, however, that  $G$  is taken as the driving excess energy of the (nearly) full parameter space of  $Q$ .

Although this rate law has often been applied, the approximations necessary in order to derive it from a master equation have never been clear. In fact, Dattagupta *et al* (1991) have shown that an Ising system with either Glauber (non-conserved) or Kawasaki (conserved) dynamics does not follow the predictions of equation (2). These authors showed that so-called ‘kinetic’ Gibbs energies  $G_{\text{kin}}$  can be formulated in these cases that when inserted in (2) give the correct rate law. These ‘kinetic’ energies differ substantially from the equilibrium excess Gibbs free energy used by Salje (1988). The numerical differences become significant for  $T \ll T_c$ ; an example is shown in figures 1 and 2.

We will show in this paper that the Salje rate law is, indeed, an excellent approximation for the kinetic behaviour of ordering processes in which the value of order parameter at each site can change continuously. An Ising-spin system with OP magnetization, for example, is *not* continuous in this sense, since its value at a specific site can only change from  $+1$  to  $-1$  or vice versa. On the other hand a coupled double-well system as described in section 3 is continuous, since the OP values at each well can change continuously. We will show how such a system can be derived theoretically in section 2 and explain the approximations involved. In section 3 we will carry out a computational simulation that shows that the double-well system indeed describes the observed rate of ordering very well.

## 2. Approximations inherent in the rate law

The general rate equation describes a system that continually attempts ‘jumps’ from its initial state to neighbouring states (in configuration space). Whether a particular jump

attempt is successful or not depends on the Boltzmann probability ratio between the states, e.g. for a jump from A to B the probability,  $\rho$ , that a jump attempt will succeed is given by

$$\rho = \exp(-\beta E_B) / [\exp(-\beta E_A) + \exp(-\beta E_B)] \quad (3)$$

where  $\beta = 1/kT$  and  $E_A, E_B$  are the energy levels of the two states (e.g. Binder 1979). Let the system be in the thermodynamic state characterized by the order parameter  $Q(t)$  at the time  $t$ . Let us also assume that  $E$  depends only on  $Q$ . This step is necessary to reduce our parameter space. Effectively it assumes, for a given  $Q$ , that all other variables of the system are in equilibrium with each other and with the value of  $Q$  so that  $Q$  specifies the thermodynamic state of the system uniquely. This assumption is obviously not correct for systems in which substantial domain structures occur. Model systems would be the traditional nearest neighbour Ising system which is most relevant for magnetic and some metallic cation ordering kinetics. On the other hand, the atomic ordering in minerals and systems dominated by long range interactions (such as strain and Coulomb interactions) the approximation appears to be valid. In fact, minerals such as Omphacite (Carpenter *et al* 1990), orthopyroxene (Ganguly 1982), and sanidine (Kroll and Knitter 1990; Salje and Kroll 1991) do not form any domain structure during the kinetic process, only weak strain modulations occur in Na-feldspar (Wruck *et al* 1991).

Now let the system attempt jumps by  $\pm \delta Q$  so that

$$\rho = \exp(-\beta E(Q \pm \delta Q)) / [\exp(-\beta E(Q)) + \exp(-\beta E(Q \pm \delta Q))]. \quad (4)$$

In a Glauber master equation we assume that during a short time interval,  $\delta t$ , the probability that a specific jump is attempted is proportional to  $N\delta t$ , i.e.  $DN\delta t$  where  $D$  is the proportionality constant. The expected change in  $Q$  is then

$$(\delta Q) = DN\delta t \left\{ A(Q, Q + \delta Q) \frac{\exp(-\beta E(Q + \delta Q))}{\exp(-\beta E(Q)) + \exp(-\beta E(Q + \delta Q))} - A(Q, Q - \delta Q) \frac{\exp(-\beta E(Q - \delta Q))}{\exp(-\beta E(Q)) + \exp(-\beta E(Q - \delta Q))} \right\}. \quad (5)$$

The function  $A$  gives the weights for the number of ways in which the system can attempt the jump, i.e. the total number of ways in which a system can go from a particular state with OP  $Q$  to any state with OP  $Q \pm \delta Q$  divided by  $N$ . In an Ising system with Glauber dynamics,  $A$  corresponds to the number of ways in which one down or up spin can be flipped. The total number of ways of going from all the states with a given value of  $Q$  to  $Q - \delta Q$  has to be the same as the total number of ways of going from  $Q - \delta Q$  to  $Q$  (i.e. the paths can be reversed). It is assumed that the number of ways of going from  $Q$  to  $Q \pm \delta Q$  are the same for all  $Q$  states. The validity of this assumption is discussed elsewhere (Marais *et al* 1991); it appears that although some theoretical limitations might occur for specific model systems, these limitations are not relevant for most practical systems. It follows then that

$$W(Q)A(Q, Q - \delta Q) = W(Q - \delta Q)A(Q - \delta Q, Q) \quad (6)$$

with  $W(Q)$  as the total number of states with the order parameter  $Q$ , i.e.

$$W(Q) = \exp(S(Q)/k) \quad (7)$$

where  $S$  is the entropy related to  $Q$ . For large systems,  $W(Q)$  increases with the number

of relevant particles as  $N!$ , whereas  $A$  remains finite even in the thermodynamic limit.  $A$  is also normalized so that

$$A(Q, Q + \delta Q) + A(Q, Q - \delta Q) = 1. \quad (8)$$

If  $A$  is a smoothly varying function of  $Q$  (i.e.  $A(Q, Q + \delta) \approx A(Q - \delta, Q)$ ), we can use equation (8) to solve equation (6) as

$$A(Q, Q \pm \delta Q) = W(Q \pm \delta Q) / [W(Q \pm \delta Q) + W(Q)] \quad (9)$$

or, in terms of  $S(Q)$ ,

$$A(Q, Q \pm \delta Q) \approx \exp(S(Q \pm \delta Q)/k) / \exp(S(Q \pm \delta Q)/k) + \exp(S(Q)/k). \quad (10)$$

So far the assumptions made are identical for the derivation of all rate laws considered in this paper. The significant differences between them arise from the treatment of the energy and entropy terms as functions of the variation in  $Q$ . For an infinitesimal time  $\delta t$ , the change  $\delta Q$  in  $Q$  will be of the order of  $1/N$  for any realistic model. The energy and entropy functions in equations (5) and (10) can thus be expanded to first order

$$E(Q \pm \delta Q) = E(Q) \pm \delta Q(\partial E/\partial Q) \quad (11)$$

$$S(Q \pm \delta Q) = S(Q) \pm \delta Q(\partial S/\partial Q). \quad (12)$$

Since  $E$  and  $S$  are of order  $N$  while  $(\delta Q)^2$  is proportional to  $1/N^2$ , we have from (5) the rate equation

$$\frac{dQ}{dt} = DN\delta Q \left\{ \frac{\exp[(1/k)(\partial S/\partial Q)\delta Q]}{1 + \exp((1/k)(\partial S/\partial Q)\delta Q)} \frac{\exp(-\beta(\partial E/\partial Q)\delta Q)}{1 + \exp(-\beta(\partial E/\partial Q)\delta Q)} - \frac{\exp(-(1/k)(\partial S/\partial Q)\delta Q)}{1 + \exp(-(1/k)(\partial S/\partial Q)\delta Q)} \frac{\exp(\beta(\partial E/\partial Q)\delta Q)}{1 + \exp(\beta(\partial E/\partial Q)\delta Q)} \right\}. \quad (13)$$

The proportionality function  $D$  may depend implicitly on  $Q$  for thermally activated processes, or  $D$  may modify the jump probability via an explicit  $Q$  dependence. These dependencies are relevant for the integration of the rate equation but do not matter for the course of our arguments: we will allow for an appropriate implicit  $Q$ -dependence of  $D$ . Equation (13) can easily be generalized if there is more than one (or even a continuity of) jump possibility. In that case equation (13) changes to

$$\frac{\partial Q}{\partial t} = \sum_i F(\delta Q_i) B(\delta Q_i) \quad (14)$$

where  $B(\delta Q_i)$  is the same function as that on the right-hand side of (13), while  $F(\delta Q_i)$  is some weight function that depends on the specific dynamics of the system.

The right-hand side of (13) vanishes if and only if

$$T \partial S/\partial Q = \partial E/\partial Q \quad \text{i.e. if } \partial G/\partial Q = 0 \quad (15)$$

so that the kinetic process does, indeed, lead to thermodynamic equilibrium.

The difference between the Salje, Glauber and Kawasaki rate equations follows now from the way in which we treat  $\delta Q$ . In processes like the coupled double-well system, we expect  $\delta Q$  to be a continuously varying parameter (at least  $\delta Q \ll 1/N$ ). In this case,

we can expand the exponential functions in (13) to lowest order and find the Salje rate equation

$$\partial Q/\partial t \propto -\beta \partial G/\partial Q. \tag{16}$$

In the case of an Ising system,  $\delta Q$  cannot be smaller than the unit of one spin change. In Glauber kinetics, this smallest possible step is  $\delta Q = 2/N$ . Solving (13) with this value of  $\delta Q$  in the mean field approximation  $E = -NkT_c Q^2/2$  and using the well known expression for the entropy of an Ising-system  $\partial S/\partial Q = -N(k/2) \ln(1 + Q)/(1 - Q)$  leads to the Glauber (Glauber 1963) rate equation

$$\partial Q/\partial t \propto [-\tanh((T_c/T)Q) - Q]. \tag{17}$$

If the system has Kawasaki kinetics (i.e. only spin ‘swaps’ are allowed) and  $Q$  is defined as the staggered magnetization, then  $\delta Q = 4/N$  since one spin ‘swap’ changes two spins and equation (13) gives

$$\partial Q/\partial t \propto [1/(1 + Q^2)]\{(1 + Q^2) \tanh[(2T_c/T)Q] - 2Q\}. \tag{18}$$

This is just the Kawasaki rate equation (Kawasaki 1966) with an extra  $(1 + Q^2)^{-1}$  factor due to the fact that jumps leaving  $Q$  unchanged are ignored. If we take ‘swaps’ between e.g. two up spins into consideration, the extra factor disappears.

So far we have shown that the difference between the three rate laws follow only from the way the variation  $\delta Q$  is treated as a function of the particle number  $N$ . In a physical situation in which  $Q$  varies continuously (i.e. all  $\delta Q \ll 1/N$  in an infinitesimal time  $\delta t$ ) we would, thus, expect that the Salje rate law, but not the Glauber and Kawasaki rate laws, is applicable. Moreover, we expect this to be applicable also for cation ordering processes in systems with large unit cells perceived as having a multitude of intermediate structural states and not just as a simple cation flip.

### 3. Computational test

Following the arguments of Dattagupta *et al* (1991), the numerical differences between the three rate processes are rather small at temperatures close to the transition point and at  $T \gg T_c$ . Significant differences occur at  $T \ll T_c$  and we will now test the validity of the rate laws in a continuous coupled double-well model under these conditions.

We simulated a  $\varphi^4$ -model with the potential energy

$$V = \sum_i \alpha \varphi_i^2 + \gamma \varphi_i^4 - J \varphi_i \bar{\varphi} \tag{19}$$

where  $\bar{\varphi}$  is the average field  $\Sigma \varphi_i/N$ , which is also identified with the macroscopic order parameter  $Q$ . For the mean field  $\varphi^4$ -system  $dG/\partial Q$  can be calculated using the Bogoliubov inequality. The result is

$$\frac{\partial G}{\partial Q} \propto -\min_h \left[ \int_{-\infty}^{\infty} \exp[-\beta(\alpha y^2 + \gamma y^4 - hy)] dy - \frac{1}{2} \delta Q^2 - LQ \right] \tag{20}$$

where the function on the RHS must be minimized WRT  $h$  to yield  $\partial G/\partial Q$ . The Salje rate law for the system now follows trivially from equation (16). The Glauber and Kawasaki rate equations for mean field systems are given by the equations (17) and (18), respectively.

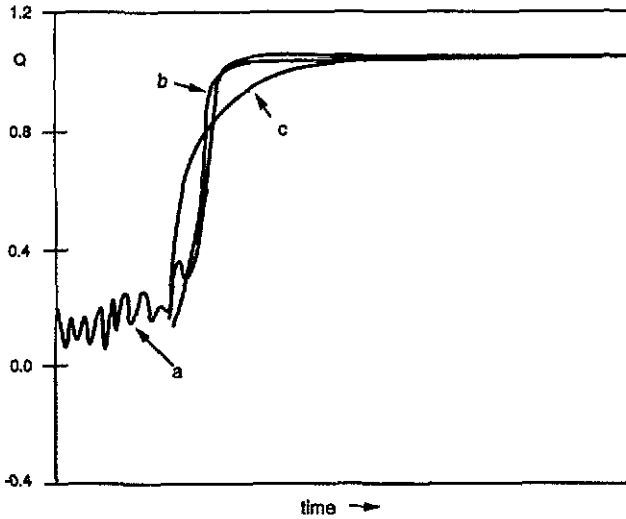


Figure 3. Comparison between the computer simulated rate law (a) and the solutions of the analytical rate equations (Salje (b) and Glauber (c)). The model Hamiltonian is  $H = \sum_i \alpha \varphi_i^2 + \gamma \varphi_i^4 - J \varphi_i \bar{\varphi}$  with  $\alpha = -2$ ,  $\gamma = 1$ ,  $J = 1.5$ ,  $T_{\text{initial}} = 1.33 T_c$ ,  $T_{\text{final}} = 0.2 T_c$ .

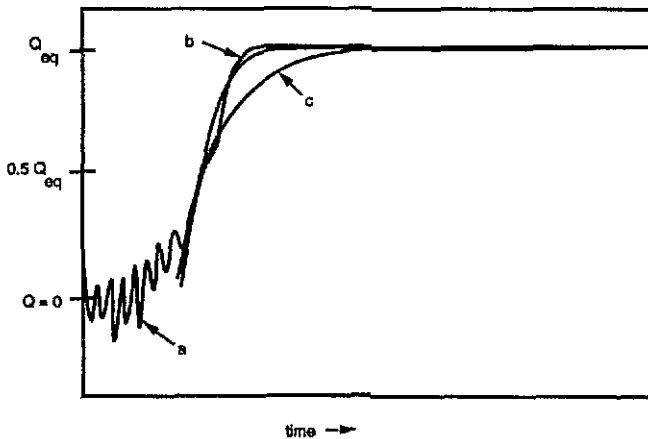


Figure 4. Comparison between the computer simulated rate law (a) and the solutions of the analytical rate equations (Salje (b) and Glauber (c)). The model Hamiltonian is  $H = \sum_i \alpha \varphi_i^2 + \gamma \varphi_i^4 - J \varphi_i \bar{\varphi}$  with  $\alpha = -2$ ,  $g = 1$ ,  $J = 0.8$ . The initial temperature is  $T_{\text{initial}} = 1.47 T_c$ , the final temperature is  $T_{\text{final}} = 0.53 T_c$ ,  $Q_{\text{eq}} = 0.48$ .

It has been shown previously (Dattagupta *et al* 1991) that the latter two solutions are in good numerical agreement with Monte Carlo calculations in Ising-spin systems.

We have also simulated the time evolution of  $Q$  for the  $\varphi^4$ -model using molecular dynamics (MD) techniques (see Marais *et al* 1991 for details) for the same thermodynamic conditions as used for the analytical solutions. The results of the MD solutions are also plotted in figures 3 and 4. Comparing the results of the MD simulations of the  $\varphi^4$ -model with the Salje and Glauber rate laws it can clearly be seen that only the Salje rate law reproduces the numerical MD results. The Glauber and Kawasaki rate laws lead to much slower time evolutions of the order parameter. These Ising model predictions lead, thus, to a wrong prediction of the rate law in a continuous  $\varphi^4$ -model.

This result does not depend on the relative depth of the potential despite the fact that Ising equilibrium behaviour can be approximated in MFT by double potentials with infinitely high barriers. In figure 4 for example the local wells have a central barrier much

higher than  $kT$ . The crucial difference is not the form of the equilibrium potential, but the fact that the variation of  $\delta QN \rightarrow 0$  in the Salje approximation,  $\delta QN = 2$  for Glauber processes and  $\delta QN = 4$  for Kawasaki kinetics. The description of the kinetic time evolution of continuous ordering processes by the latter two models is inadequate, whereas the Salje rate law predicts the correct kinetic equation.

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