A rate equation for atomic ordering in mean field theory: I. Uniform case

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Abstract. A critical discussion is given of the kinetics of (dis)ordering in a simple system of Ising spins with respectively Glauber and Kawasaki types of stochastic processes. The question addressed is whether the rate is governed by the same free energy excess (in equilibrium) as assumed in frequently used rate equations. We focus for simplicity on uniform systems with long range interactions whose equilibria are well described by mean field theory. Such situations are realized in systems with effective spin interactions mediated by strain. We find that the rate equation can be expressed in terms of a Glauber or Kawasaki potential. Their analytical forms are found to be quite different from each other and also different from the equilibrium mean field energy. However, the predicted rate equations are not substantially different for most temperatures of interest.

1. Introduction

The present paper and its companion (which we will refer to as II) examine critically the rate equation often used to describe the kinetics of atomic ordering and disordering in structural phase transitions. For the present the reader may envisage, say, Al/Si ordering in a silicate mineral such as feldspar as an example of what we have in mind. Paper II discusses in more detail the range of applications.

The theory of the equilibrium thermodynamics of such a system is well established. However, there remain unanswered fundamental questions about the kinetics of (dis)ordering. Broadly speaking, the question to be addressed in the present paper is: what precisely is the driving force pushing the system towards equilibrium? The rate equation is customarily written in the form [1]

$$\partial Q/\partial t = [\dots]f(Q) \tag{1.1}$$

where Q is the order parameter measuring the degree of order and the square bracket contains an operator to be discussed further in II. The last term $f(Q)$ is the driving force which is usually taken to be

$$f(Q) = -\partial G/\partial Q \tag{1.2}$$

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where $G(Q)$ is the free energy of the system. This looks plausible because thermodynamic equilibrium is defined by

$$\partial G/\partial Q = 0 \tag{1.3}$$

which when substituted into (1.1) and (1.2) correctly gives $\partial Q/\partial t = 0$. But is (1.2) valid far from equilibrium? We are interested in applying the rate equation to quenching from above the ordering temperature T_C to well below T_C (i.e. ordering), and to shock heating from below to above T_C (i.e. disordering). We shall refer to them together as (dis)ordering; they cover a wide range of Q and T.

Incidentally we can dispose of one red herring sometimes raised in connection with (1.2), namely that G normally pertains to equilibrium whereas in (1.2) we require G as a function of Q and T when they are out of equilibrium with one another. The point is that one can define consistently the free energy for a constrained system in which the quantities Q and T are held to some specific values, in the case of Q by some appropiate (real or fictitious) force. This concept is used routinely in Landau's treatment of continuous phase transitions and is discussed for example in a wide variety of papers [2–5].

We proceed by considering two simple specific systems (to be referred to as G and K respectively) for which we can solve the kinetics analytically to a high degree of approximation in an Ising-type model. By writing the rate equations in the form (1.1) we can identify $f_G(Q)$ and $f_K(Q)$ for the two cases and see whether they are equal to (1.2). The answer turns out to be 'No'. To make a more detailed comparison, it is convenient to define what we shall call 'kinetic potentials' $G_G(Q,T)$, $G_K(Q,T)$ from

$$f_G = -\partial G^G/\partial Q \qquad f_K = -\partial G^K/\partial Q. \tag{1.4}$$

As expected G_G, G_K and G lead to the same equilibrium value of Q, but they can be quite different far from equilibrium. Nevertheless, at sufficiently high temperatures ($T \geqslant 0.8T_C$) the dynamical rate laws are not substantially different. We shall discuss the broader conclusions and applications of these results further in paper II.

We must now specify our systems G and K. Both concern A/B ordering on a simple cubic lattice represented as usual by Ising spins $s_i = \pm 1$ at lattice sites i (see figure 1). Couplings $J_{ij}s_is_j$ act between the spins and are such that the ordering is 'antiferromagnetic' in each of the x, y, z directions, i.e. the order parameter is

$$Q = \langle(-1)^{l+m+n}s_{lmn}\rangle \tag{1.5}$$

where l, m, n are the coordinates of the lattice site i. The J_{ij} are supposed long ranged, a condition that is realized in practice if the J_{ij} are indirect interactions mediated by coupling the spins to local strains in an elastic lattice structure. A particular choice of local strain coupling guarantees the particular 'antiferromagnetic' (see section 5) ordering above. As a consequence of the long range interactions, each spin more or less 'feels' all the others so that the system remains uniform during (dis)ordering i.e. its state at any time t is specified by just two macroscopic variables Q and T. We emphasize that the ordering does not [6] proceed by the inhomogeneous ' nucleation and growth' process observed with nearest neighbour interactions [7]. Another consequence of the long range coupling is that correlations between spins are small and mean field theory (MFT) is a very good approximation as will be demonstrated in
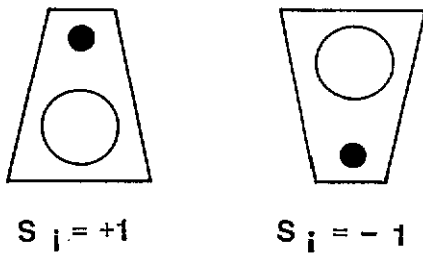
$$S_i = +1 \qquad S_i = -1$$

Figure 1. A physical example of AB ordering that can be modelled as an Ising-spin coupled to a lattice. This type of coupling with T_{2g} symmetry leads to a fully antiferromagnetic phase transition.

section 5. We believe a further consequence of the long range coupling is that the behaviour of the system does not depend sensitively on the cubic symmetry and simple structure used here: indeed no specific assumptions about the structure are involved in the analysis.

Our systems G and K differ from one another in the assumed microscopic stochastic process representing the thermal excitation of the spins and hence originating the (dis)ordering process. In K we assume 'Kawasaki dynamics' [8], i.e. interchanging spins on sites i and j separated by a lattice vector l with probability $1/\tau_K$. There is no difficulty envisaging this as an activated jump process interchanging atoms at i and j, and the jump l may or not be nearest neighbour. In system G we assume 'Glauber' dynamics in which the spin s_i is flipped in sign with probability $1/\tau_G$ [9]. This is not a physically realisable process if we take $s_i = \pm 1$ to represent distinct atoms A and B, but it is realisable if $s_i = \pm 1$ represent alternative ordering arrangements of two or more atoms in one unit cell at lattice point i (figure 1). In real systems with complex ordering patterns one would have a mixture of Kawasaki-like and Glauber-type mechanisms. All these points about physical realisability are discussed more fully in paper II.

The plan of the paper is as follows. In section 2 we introduce the model and briefly outline its equilibrium properties. In section 3 we write down the probabilistic 'master equation' governing the Glauber and Kawasaki dynamics specialising to the case of a uniform system for the reasons discussed above. With the help of MFT, a very good approximation for our chosen system of indirect strain coupling as already mentioned, we derive the rate equation explicitly in terms of Q and T in section 4 and in section 5 we give numerical evidence of how good MFT is from a comparison with a computer simulation. In section 6 we construct the kinetic potentials for systems G and K as defined by (1.4) and compare them with the free energy in MFT.

The conclusion is that the type of stochastic process (Glauber or Kawasaki) does not only affect the nature of the operator in the rate equation (1.1), it also determines the correct form for the driving force which is the operand in (1.1). This conclusion appears to be new. The use of the free energy in (1.1), (1.2) is quite a good approximation for many ranges of Q and T, but not all.

2. The model and its equilibria

Our aim is to describe atomic ordering processes in a lattice, each site of which is endowed with a pseudo-spin s that can take two discrete values 1 and -1. The state $s = 1$ ($s = -1$) is viewed to represent the presence (absence) of an atom in the 'lattice-gas' sense, or presence of an A atom (B atom) in the 'AB-alloy' sense. In

either case the simplest possible interaction Hamiltonian can be written in terms of an Ising model [10]:

$$\mathcal{H} = \sum_{ij} -\tfrac{1}{2} - J_{ij} s_i s_j - \sum_i H s_i \tag{2.1}$$

Here the sum runs over all pairs i and j of lattice sites, J_{ij} is an 'exchange' energy related to atomic interactions and H is a 'field' that accounts for chemical potentials. As mentioned in section 1 our main interest is in systems in which the J_{ij} are very long ranged as can be realized in the presence of strain couplings (see section 5 below). In that case the equilibrium statistical mechanical properties of the system are well described by a Gibbs free energy (per site) calculated in MFT in the Bragg–Williams limit [11]:

$$G^{\mathrm{BW}}(Q,T) = -(\tfrac{1}{2}J(0)Q^2 + HQ) + \tfrac{1}{2}k_{\mathrm{B}}T[(1+Q)\ln(1+Q) + (1-Q)\ln(1-Q) - 2\ln 2]. \tag{2.2}$$

In the above expression

$$J(0) \equiv \sum_j J_{ij} \qquad Q \equiv \langle s_i \rangle \tag{2.3}$$

and k_{B} is the Boltzmann constant. The first term (inside the brackets) is the enthalpy while the second term (divided by $-T$) is the entropy. It may be mentioned that in the context of magnetism an identical free energy (2.2) is obtained in the Weiss molecular field theory [12]. It may also be pointed out that in writing (2.2) we have assumed *uniformity*, i.e. the value of the order parameter, defined as the expectation value of s_i (indicated by angular brackets), is independent of the site index i. As much of our discussion will be centred on antiferromagnetic-type atomic (dis)ordering systems, Q will be interpreted as the sublattice magnetization in the simplest two-sublattice picture [12].

From now on we shall drop the field H without sacrificing any essential physics. It is evident then that the equilibrium value of Q is obtained from (2.2) by setting

$$\left(\frac{\partial G}{\partial Q} \right)_{\mathrm{eq}} = 0 \tag{2.4}$$

leading to

$$Q_{\mathrm{eq}} = \frac{k_{\mathrm{B}}T}{2J(0)} \ln \left(\frac{1 + Q_{\mathrm{eq}}}{1 - Q_{\mathrm{eq}}} \right) \tag{2.5}$$

which may be re-expressed as

$$Q_{\mathrm{eq}} = \tanh \left(\frac{J(0)Q_{\mathrm{eq}}}{k_{\mathrm{B}}T} \right). \tag{2.6}$$

It is useful also to define a 'critical temperature' T_{C} which has its MFT value:

$$T_{\mathrm{C}} \equiv \frac{J(0)}{k_{\mathrm{B}}}. \tag{2.7}$$

For our purposes T_{C} will be used simply as a parameter defined through microscopic interactions J_{ij} (cf (2.3)). In addition, all theories (Bragg–Williams, Weiss, etc) which lead to an order parameter equation in equilbrium of the sort (2.6) will be referred to (somewhat loosely) as the MFT.

3. Master equation for kinetics

The Ising model as given in (2.1) does not have dynamics of its own. In order to describe non-equilibrium phenomena one has to therefore imagine the presence of a heat bath with which the Ising spins are presumed to be loosely coupled. The role of the heat bath is to induce thermal fluctuations into the Ising system in such a way that from any initial non-equilibrium state the system must reach (at time $t = \infty$) an equilibrium governed by the Hamiltonian (2.1) and the temperature T of the heat bath. This picture can be realized by postulating a master equation for the probability $P(\{s\})$ (the set $\{s\}$ defines a certain spin configuration $(s_1, s_2, \ldots, s_N)$) appropriate for a stochastic process that is stationary and Markovian [13]:

$$\frac{\mathrm{d}}{\mathrm{d}t} P(\{s\}, t) = W(\{s\})\, P(\{s\}, t). \tag{3.1}$$

The essential physical input goes into the question of how one models the 'rate matrix' or 'relaxation matrix' W.

　　Two such models of W have been extensively used in the literature under the names of Glauber [9] and Kawasaki [8]. In the Glauber model it is imagined that the contact with the heat bath causes fluctuations that are a collection of single spin-flip processes. At a microscopic level such a process can be visualized to be described by an interaction Hamiltonian (between the Ising system and the heat bath) given by

$$\mathcal{H}_\mathrm{I} = \sum_i g_i\, (b_i^+ s_i^- + b_i^- s_i^+) \tag{3.2}$$

where s_i^-, s_i^+ are the usual spin projection operators, b_i^+, b_i^- are operators describing heat bath excitations (e.g. phonons) and g_i is a coupling constant. We do not go into the question of how one can derive the Glauber master equation by treating $\mathcal{H}_\mathrm{I}$ in a suitable perturbation theory of the density matrix of the entire system (i.e. the spins plus the bath) [14]; suffice it to note that the Glauber model describes *non-conserved* kinetics in that the spin-flip processes render the total magnetization ($\sum_i \langle s_i \rangle$) time-dependent. On the other hand, in the Kawasaki model the elementary fluctuation process is viewed to be a spin exchange between a pair of sites. Thus the corresponding interaction Hamiltonian may be chosen as

$$\mathcal{H}_\mathrm{I} = \sum_{ij} g_{ij}(c_{ij}^+ s_i^- s_j^+ + c_{ij}^- s_i^+ s_j^-) \tag{3.3}$$

where the c_{ij} are again certain bath operators and the g_{ij} are coupling parameters. In contrast to the Glauber model, since every 'spin flip' is now accompanied by a simultaneous 'spin flop' at another site, the Kawasaki model describes *conserved* kinetics.

　　Our interest here is not to analyse the complete probability distribution $P(\{s\})$ but to focus attention onto the rate equation for the order parameter which is obtained by considering simply the first moment of $P(\{s\})$. The exact equations available in the literature from the works of Suzuki and Kubo [15] and Binder [16] are:

(i) Glauber

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle s_j(t)\rangle = -\frac{1}{\tau_G}\left(\langle s_j(t)\rangle - \left\langle \tanh\ \beta \sum_l J_{jl}s_l(t)\right\rangle\right) \tag{3.4}$$

(ii) Kawasaki

$$\frac{d}{dt}\langle s_j(t)\rangle = -\frac{1}{\tau_K}\sum_{l_j}\left[(\langle s_j(t)\rangle - \langle s_{l_j}(t)\rangle) - \left\langle(1 - s_j s_{l_j})\tanh\ \beta\left(\sum_i(J_{ij}s_i - J_{il_j}s_i)\right)\right\rangle\right].$$
$$(3.5)$$

In (3.4) τ_G sets the basic time scale of the Glauber process which is usually assumed to be independent of temperature and spin configurations. Similarly, in (3.5), τ_K is the basic Kawasaki time, while l_j refers to the site which participates as the partner of the jth site in the spin exchange process.

4. Rate equations in the decoupling approximation

The exact rate equations in (3.4) and (3.5) are quite intractable; for instance, expanding the tanh function in (3.4) one easily sees how the equation of motion of $\langle s_j(t)\rangle$ is coupled to $\langle s_l(t)s_{l'}(t)s_{l''}(t)\rangle$ etc. The simplest decoupling approximation is to assume that there is no correlation between different sites, i.e. the average of the product of spin operators can be replaced by the product of their averages. As we are dealing with long range interactions we believe it is not unreasonable to make such a random-phase-like decoupling. We thus obtain

(i) Glauber

$$\frac{d}{dt}Q_j(t) = -\frac{1}{\tau_G}\left(Q_j(t) - \tanh\ \beta\sum_l J_{jl}Q_l(t))\right)$$
$$(4.1)$$

(ii) Kawasaki

$$\frac{d}{dt}Q_j(t) = -\frac{1}{\tau_K}\sum_{l_j}\left[(Q_j(t) - Q_{l_j}(t))\right.$$
$$\left. - (1 - Q_j(t)Q_{l_j}(t))\tanh\ \beta\left(\sum_i(J_{ij}Q_i(t) - J_{il_j}Q_i(t))\right)\right].$$
$$(4.2)$$

While (4.1) and (4.2) form a setting for our general discussions of order parameter kinetics in the Glauber and Kawasaki models (see II) we restrict our attention here to the uniform case. That is, we replace Q_j by Q and Q_{l_j} by $-Q$, recalling that each Kawasaki jump involves a pair of sites belonging to two distinct sublattices. Hence

(i) Glauber

$$\frac{d}{dt}Q(t) = -\frac{1}{\tau_G}\left[Q(t) - \tanh\left(\frac{T_C}{T}Q(t)\right)\right]$$
$$(4.3)$$

(ii) Kawasaki

$$\frac{d}{dt}Q(t) = -\frac{N_K}{\tau_K}\left[2Q(t) - (1 + Q^2(t))\tanh\left(\frac{2T_C}{T}Q(t)\right)\right]$$
$$(4.4)$$

where T_C has been defined in (2.7). In (4.4) N_K is the number of sites that can be reached by a Kawasaki jump from any given site.

It is evident that the equilibrium MFT solution given in (2.6) satisfies both (4.3) and (4.4). That is to say, the particular decoupling we have effected on the Glauber and Kawasaki models is consistent with MFT in equilibrium. In contrast the dynamics described by the right hand sides of (4.3) and (4.4) are quite different! This point may be reinforced by considering in conjunction with (4.3) and (4.4), the oft-quoted phenomenological rate equation in which the kinetics is assumed to be driven by the mean field free energy of (2.2):

$$\frac{\mathrm{d}}{\mathrm{d}t}Q(t) = -\frac{1}{\tau k_{\mathrm{B}}T}\frac{\partial G^{BW}(Q)}{\partial Q} \tag{4.5}$$

where τ is a phenomenological time constant. Equation (4.5) yields together with (2.2):

(iii) Phenomenological

$$\frac{\mathrm{d}}{\mathrm{d}t}Q(t) = \frac{1}{\tau}\left[\frac{T_C}{T}Q(t) - \frac{1}{2}\ln\left(\frac{1+Q(t)}{1-Q(t)}\right)\right]. \tag{4.6}$$

Therefore, equations (4.3), (4.4) and (4.6) describe three distinct dynamic models of order parameter kinetics even though all of them have a unique equilibrium governed by (2.6).

5. Numerical test of the decoupling approximation

As we have mentioned before, our model with long range interactions can be realized in systems with strain couplings [6]. As a particular example let us consider a harmonic cubic lattice of atoms with an Ising spin in each unit cell which couples linearly to the atoms. Schematically the Hamiltonian for the system can be written as

$$\mathcal{H} = \boldsymbol{u}^{\mathrm{T}}\mathbf{A}\boldsymbol{u} + \boldsymbol{\sigma}^{\mathrm{T}}\mathbf{B}\boldsymbol{u} \tag{5.1}$$

where $\boldsymbol{u}$ is a $3N$-dimensional vector depicting the atom displacements and $\boldsymbol{\sigma}$ represents the N spins. $\mathbf{A}$ is the dynamical matrix for the system and $\mathbf{B}$ gives the spin–strain coupling. It can be shown [17] that the Hamiltonian can be decoupled i.e. it can be written as two independent terms:

$$\mathcal{H} = \overline{\boldsymbol{u}}^{\mathrm{T}}\mathbf{A}\overline{\boldsymbol{u}} + \boldsymbol{\sigma}\mathbf{J}\boldsymbol{\sigma}. \tag{5.2}$$

Note that the spins are now completely separated from the displacements. They can thus be studied independently of the strain. The renormalized coupling between the spins is given by $\mathbf{J}$. This spin–spin coupling is long ranged and it depends upon the specific type of spin–strain coupling. It can be ferromagnetic or antiferromagnetic. The long-rangedness of the coupling means that MFT gives a very good description of the system in (5.1). This makes it ideal for studying rate processes.

We study the spin dynamics of this system by standard Monte Carlo techniques [7], both in the Glauber and Kawasaki models for a system with $16 \times 16 \times 16$ spins. For our model Hamiltonian system with antiferromagnetic couplings, the numerical results allow us to test the validity of the decoupling approximation leading to (4.3) and (4.4). The comparison is shown in figure 2. It is evident that the results predicted by (4.3) and (4.4) are close to the exact numerical ones.
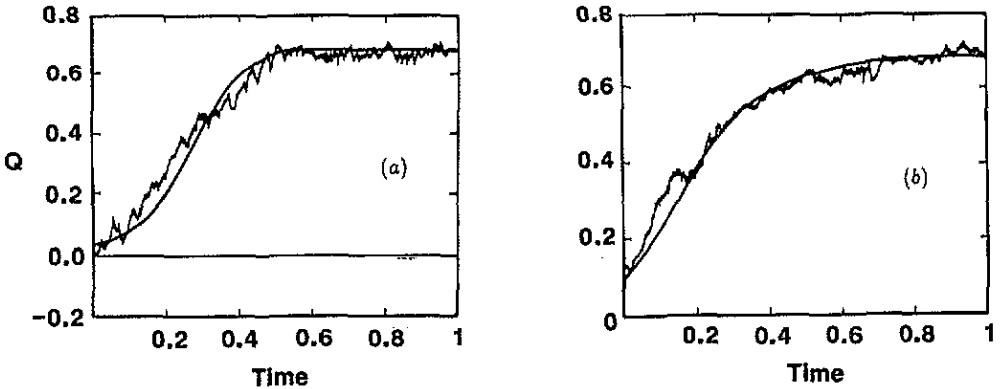
Figure 2. Comparison of the (a) Glauber and (b) Kawasaki rate laws with the observed behaviour in our strain coupling model (with spin strain coupling as in figure 1) with Glauber and Kawasaki dynamics respectively. The system is quenched from $T \gg T_C$ to 0.8 T_C.

6. Comparison between different dynamic models and conclusions

The results of section 5 reconfirm our faith in the decoupling approximation discussed in section 4. The stage is now set to make a comparative analysis of the dynamics described by (4.3), (4.4) and (4.6). In carrying out this task it helps to recast (4.3) and (4.4) in the form of (4.5). The point is that in phenomenological rate theories of the sort described by (4.5), $\partial G / \partial Q$ is viewed as a 'driving force' and the crucial *ansatz* is that the *kinetic* potential has the same form as the potential governing the equilibrium. Thus in MFT, the kinetic potential is taken as

$$G_{\text{kin}}^{\text{BW}}(Q,T) = \tfrac{1}{2}k_{\text{B}}T[(1+Q)\ln(1+Q) + (1-Q)\ln(1-Q)] - \tfrac{1}{2}k_{\text{B}}T_{\text{C}}Q^2. \tag{6.1}$$

It is by no means obvious that (6.1) is the right model for kinetics and in fact the whole question hinges on the nature of dynamics itself, i.e. whether it is of conserved or non-conserved type. Furthermore, our numerical analysis in section 5 suggests that within a stipulated form of dynamics, equation (4.3) or (4.4) may be a better description of the state of affairs than equation (4.6). Hence the question is, what are the relevant kinetic potentials for Glauber and Kawasaki kinetics? This question can be addressed in a meaningful way if we rescale all the time constants such that at least for small Q (i.e. the linearized domain), all three models of (4.3), (4.4) and (4.6) have the same dynamics. This identification easily leads to

$$\tau_G = \tau_K / 2N_K = \tau. \tag{6.2}$$

We then find

(i) Glauber

$$G_{\text{kin}}^G(Q,T) = -k_{\text{B}}T\left\{ \frac{T}{T_{\text{C}}} \ln\left[\cosh\left(\frac{T_{\text{C}}}{T}Q\right)\right] - \tfrac{1}{2}Q^2 \right\} \tag{6.3}$$

(ii) Kawasaki

$$G_{\text{kin}}^K(Q,T) = -k_{\text{B}}T\left\{ \frac{T}{4T_{\text{C}}} \ln\left[\cosh\left(\frac{2T_{\text{C}}}{T}Q\right)\right] - \frac{1}{2}Q^2 \right.$$
$$\left. + \frac{T}{4T_{\text{C}}} \sum_{k=1}^{\infty} \frac{2^{2k}(2^{2k}-1)B_{2k}}{(2k+2)(2k)!}\left(\frac{2T_{\text{C}}Q}{T}\right)^{2k+2} \right\} \tag{6.4}$$

The B_{2k} are the Bernoulli numbers. Comparative plots of $G_{\text{kin}}(Q,T) - G_{\text{kin}}(Q = 0,T)$ for the three cases are shown in figure 3.
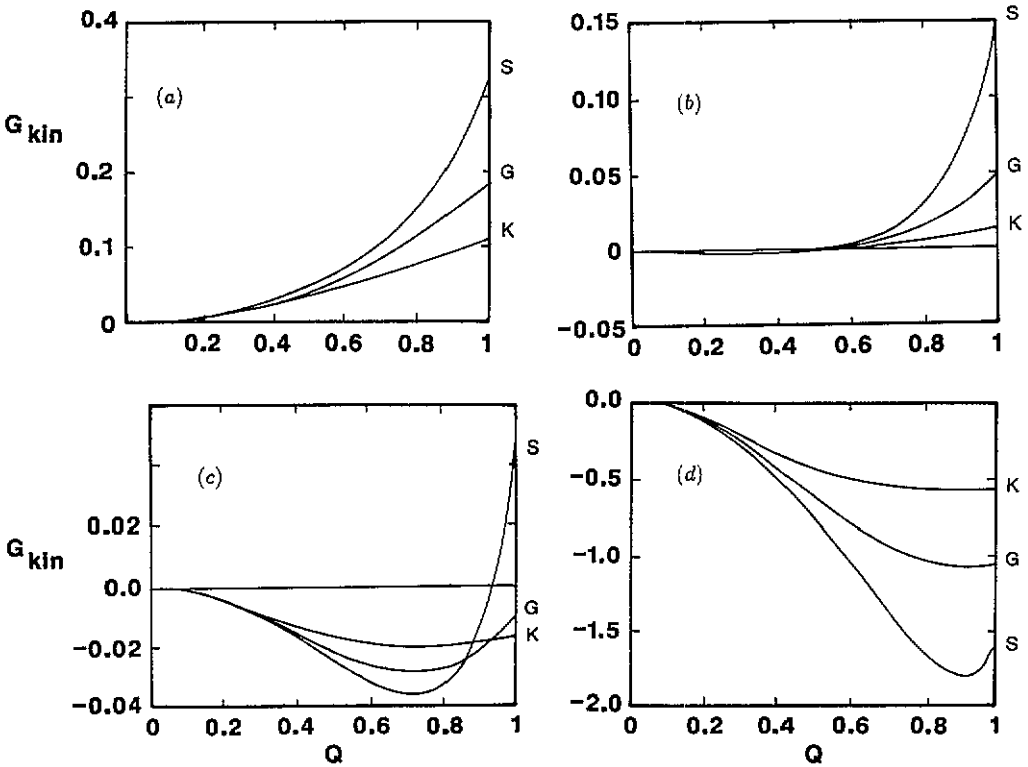

Figure 3. G_{kin} for the three different models for (a) $T = 1.5T_C$, (b) $T = 0.95T_C$, (c) $T = 0.8T_C$ and (d) $T = 0.5T_C$. In figures 3–5, G denotes the Glauber case, K the Kawasaki case and S the phenomenological case.
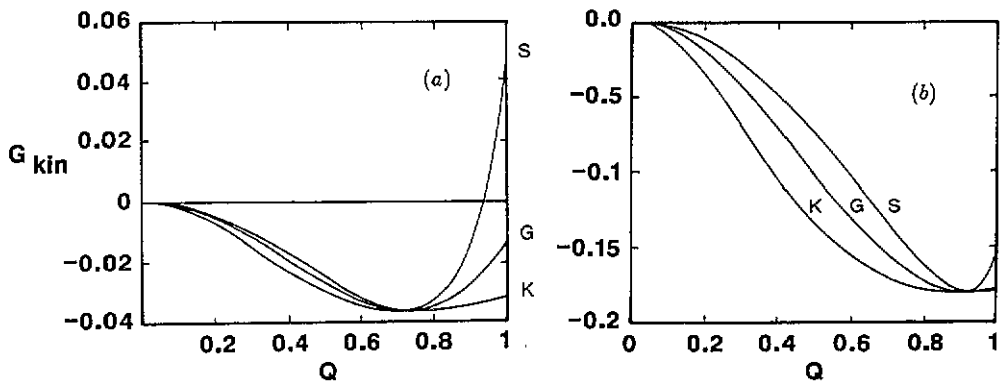

Figure 4. G_{kin} for the three models rescaled so that they have the same minimum point with (a) $T = 0.8T_C$ and (b) $T = 0.5T_C$.

In figure 4 we show the same potentials numerically rescaled so that the total energy gained in a kinetic experiment (starting from Q equal to zero) is identical
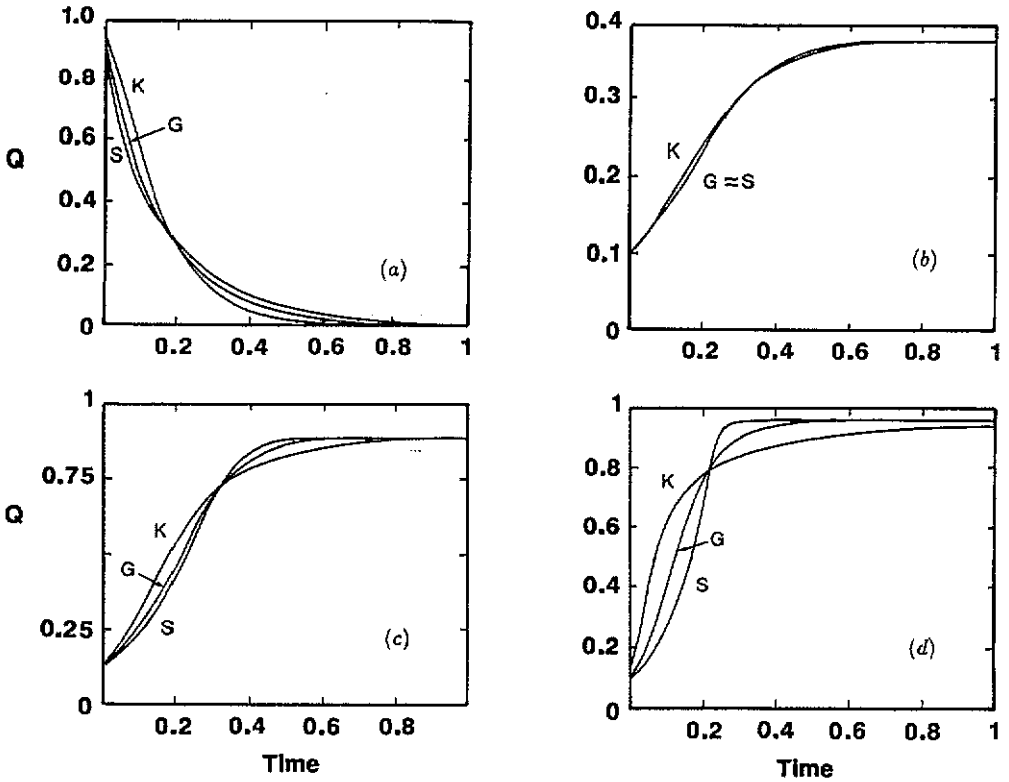
Figure 5. A comparison of the three rate law predictions for a system shock heated to (a) 1.5 T_C and quenched to (b) 0.95 T_C, (c) 0.8 T_C and (d) 0.5 T_C.

for all three cases. This represents an experimental situation encountered in many thermodynamic measurements.

In figure 5 we show the rate laws for four different selected temperatures for all three cases. We see from the comparison between these curves that there is numerical agreement to within 5% with $T \geqslant 0.85 T_C$. Only in the case $T = 0.5 T_C$ do we see significant differences, with the Kawasaki model giving the slowest and the phenomenological model the fastest kinetic processes. This is to be expected because of the conserved nature of the dynamics in the Kawasaki case. In order to see the differences between these three models experimentally, one thus has to quench to temperatures far below T_C.

Acknowledgments

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