

A Simple Model for the Dynamics Towards Metastable States

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Received March 18, 1986

Circumstances under which a quenched system will “freeze” in a metastable state are studied in simple systems with long-range order. The model used is the time-dependent pair approximation, based on the most probable path (MPP) method. The time dependence of the solution is shown by means of flow diagrams. The fixed points and other features of the differential equations in time are independent of the choice of the rate constants. It is explained qualitatively how the system behaves under varying descending temperatures: the role of the initial conditions, the dependence on the quenching rate, and the response to precooling.

KEY WORDS: Supercooling; quenching; metastable equilibrium; order parameter; frozen-in states; system far from equilibrium.

1. INTRODUCTION

In order to study the question of when and how a system will freeze in a metastable state under the influence of rapid cooling, we study a simple system with long-range order. Rather than rely on a single order parameter and a fluctuating term, we introduce a dynamic equation for long- and short-range order. This enables the system to move “perpendicular” (i.e., in the sense of the unstable coordinate direction of a saddle point) to the long-range order parameter and leads to the possibility of an escape from a seemingly trapped state. The fixed points of the resulting equations represent the stable, metastable, and unstable points. The flow diagram at

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fixed temperature and field indicates how a system should be quenched in order to become trapped into a metastable state.

First we describe the simplest possible model that leads to a frozen-in state. Then we generalize to (a) a system far from equilibrium, and (b) the influence of more than one order parameter.

We show that the dynamics of such a system cannot be described by the free energy as a function of the long-range order parameter and that the unstable state is actually a saddle point in a two-dimensional phase space with the long-range order and the short-range order as coordinates.

2. GENERAL CONSIDERATIONS FOR SYSTEMS WITH ONE ORDER PARAMETER

To obtain a simple picture of frozen-in systems we consider the following model. The state of any cooperative system can be characterized by a long-range order parameter n . This parameter depends on the temperature and is nonzero below the ordering temperature. At $T=0$ the order achieves its maximum value, that is, $n=1$. We assume that if the system is not in equilibrium, it will return to equilibrium by means of a thermodynamic driving force proportional to the deviation. The equation of motion will be of the form

$$\frac{dn}{dt} = k(n - \bar{n}) \quad (1)$$

where \bar{n} is the equilibrium value. The rate constant k is usually taken proportional to the second derivative of the free energy with respect to n evaluated at $n = \bar{n}$:

$$k = M \left(\frac{\delta^2 F}{\delta n^2} \right)_{\bar{n}}. \quad (2)$$

This rate constant is in general a function of the temperature. Equations (1) and (2) have found widespread applications.⁽¹⁻³⁾

In most applications, cooling takes place at a constant rate. In general, the system is in a nonequilibrium state because its temperature is time dependent, $T(t)$, and the system is not always able to adapt itself to the new situation. Consequently, we have $k(T(t)) = k(t)$ as well as $\bar{n}(T(t)) = \bar{n}(t)$, that is, both the rate of return to equilibrium and the equilibrium value of the order parameter change with time.

For a given cooling rate R ,

$$T = T_0(1 - Rt) \quad (3)$$

one can estimate at what moment the system freezes in. Here T_0 is the temperature at $t=0$. Let us assume that cooling is done by lowering the tem-

perature stepwise ΔT at every Δt seconds. In each step the system has an order parameter n' , which lies below the equilibrium value n at the same temperature. The system will now relax toward equilibrium in a "vertical" way, and it will take approximately k^{-1} seconds to reach this equilibrium. The next temperature decrease takes place after R^{-1} seconds; hence, if $k^{-1} < R^{-1}$ the system will be able to follow the equilibrium values of $\bar{n}(t)$, but as soon as $k > R$, the system will lag further behind. An example of such behavior is given in the work of Sato and Kikuchi⁽⁴⁾ (see Fig. 1). In this example we see how the order parameter reaches a constant value. The value of n is almost equal to the value of n at the temperature where the system "froze," that is, the temperature at which $k \approx R$.

In this qualitative picture we have assumed that $n(t)$ is a smooth function; however, this need not be. Also, we have assumed that the rate constant k is decreasing with decreasing temperature and this is not necessarily the case either: near the critical temperature the rate constant may decrease with increasing temperature, the so-called critical slowdown. Furthermore, and this is of primary interest to us, the situation may be altered by the fact that the system has more than one order parameter. To

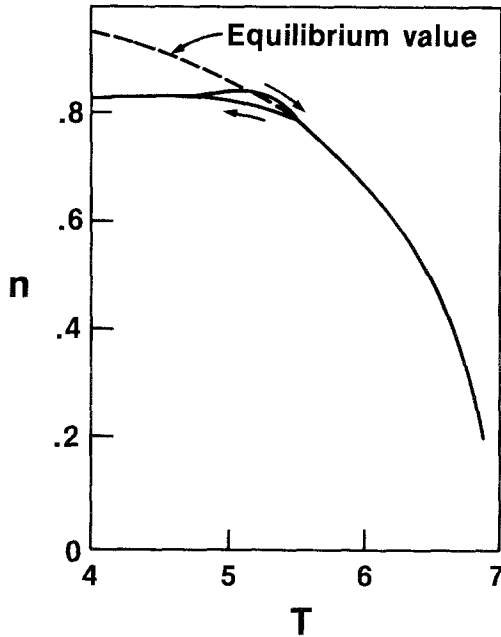


Fig. 1. Calculated temperature dependence of the long-range order parameter for a system cooled (and heated) at a constant temperature rate (from Ref. 4). n is the long-range order parameter.

give a more precise description of the simple, one-parameter process, we write

$$dn/dt = -k(t)[n - \bar{n}(t)] \quad (4)$$

This is solved by

$$n(t) = \exp[-K(t)] \left\{ \int_0^t dt' k(t') \bar{n}(t') \exp[K(t')] + n_0 \right\} \quad (5)$$

where

$$K(t) = \int_0^t k(t') dt'$$

The function $K(t)$ can be considered as a dimensionless time scale which transforms Eq. (4) into

$$dn/dK = n - \bar{n}(K) \quad (6)$$

provided the function $K(t)$ can be inverted. This dimensionless time comes to a standstill when the relaxation rate is much smaller than the cooling rate.⁽⁵⁾

To estimate the value of the frozen-in order parameter at very low temperatures, we make the following simplifying assumptions: (1) Let $n(t)$ be independent of the temperature; consequently, it does not depend on the time either. (2) We assume a hypothetical temperature dependence of k to be $k = AT$, so that the rate is zero at $T = 0$; A is a constant. The solution of (4) with the cooling given by (3) is

$$n(t) = n_{\text{eq}} + (n_0 - n_{\text{eq}}) \exp[-AT_0(1 - \frac{1}{2}Rt)t] \quad (7)$$

where n_0 is the value of n at $t = 0$ and n_{eq} is the equilibrium value of n .

The frozen-in value at $T = 0$ is given by

$$n_f = n_{\text{eq}} + (n_0 - n_{\text{eq}}) \exp(-AT_0/2R) \quad (8)$$

This differs from the equilibrium value simply because at a certain moment ($t = 1/R$) the "time is up." Since the system has reached $k = 0$ at that moment, it cannot relax any further. The result for n_f depends on R , as is observed in experiments (see Grest and Cohen⁽⁶⁾). In this simple model we need to take $n_0 \neq n_{\text{eq}}$; otherwise nothing happens. If the system is subsequently heated, it will resume its motion toward n_{eq} ; Fig. 2 illustrates that the path is not reversible.

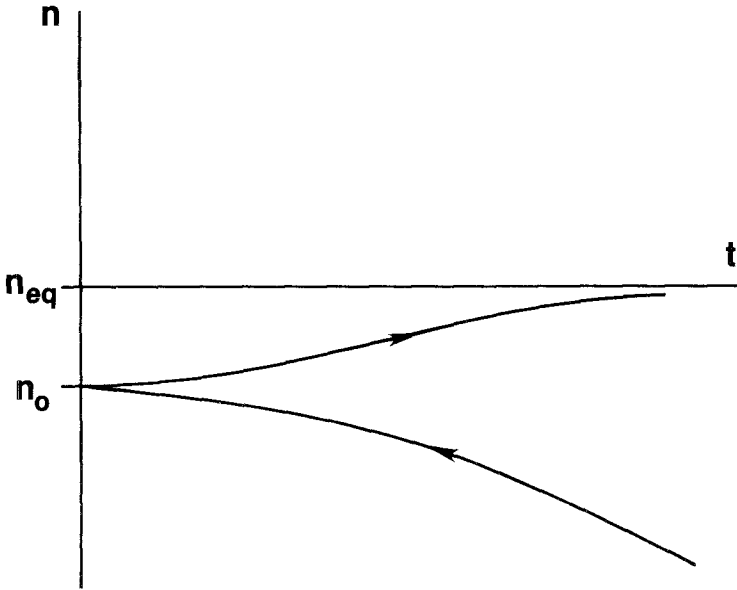


Fig. 2. Illustration of cooling and heating of a system where \bar{n} is independent of the temperature.

This picture is oversimplified: the value of n_{eq} is not constant, but is given by $\bar{n}(t)$, and the deviation from equilibrium ($n_0 \neq n_{\text{eq}}$) comes about because the value of n at a previous temperature is not the same as the value of \bar{n} at a later moment. The change of the reference value provides the driving force in the differential equation.

The above equations describe the return to equilibrium of systems governed by one order parameter and are close to equilibrium. We would like to generalize this description to systems that are governed: (a) by two or more order parameters and (b) are far from equilibrium. Using Eqs. (1) and (2), but without the restriction that $n \approx \bar{n}$, so that k is a function of n , one obtains the generalized form of the rate equation. Solving this equation is impossible, but a fairly general description can be given for the case in which the free energy is written as a power series in n . In order to be able to describe the behaviour of such a system in the presence of a secondary minimum, we take the series up to the fourth order in n . Assuming that the Taylor series representing the derivative of the free energy is factorized, one obtains an equation of motion of the form

$$dn/dt = M \delta F / \delta n = k_1(n - n_1)(n - n_2)(n - n_3) \quad (9)$$

with $n_1 < n_2 < n_3$. This corresponds to a maximum at n_2 between two minima at n_1 and n_3 , provided $k_1 > 0$. The solution of this equation is given in Appendix A, for $n_1 < n_2 < n_3$ and for the case that $n_1 < n_2 = n_3$; the latter represents the disappearance of the secondary minimum.

The conclusion is that the system will relax either toward n_1 or toward n_3 , provided $k_1 \neq 0$. Once the system is on the "wrong side of the fence" it will move toward the metastable equilibrium. We want to show that this is no longer the case when a short-range order is introduced.

3. THE EQUATIONS OF MOTION FOR THE PAIR APPROXIMATION

3.1. Describing the Model

In this section, the order-disorder phenomena with the incorporation of a short-range order parameter is described in the notation used by Kikuchi.⁽⁷⁾ The equilibrium solution corresponds to the pair approximation, also called the Bethe or quasichemical approximation.

The motivation for this model is the following. It is generally assumed that crystallization is triggered by a local fluctuation. Consequently, the main goal is to establish whether a deviation of the short-range order in the metastable state could start a motion toward equilibrium. The short-range or pair order is the simplest form of correlation that can be introduced to accomplish this. The option of more complicated clusters is not introduced in the calculation, mainly to keep things as simple as possible. A drawback of the model is not the lack of higher correlations, but the fact that the short-range order parameter is actually not a local parameter, as its name seems to suggest. The short-range order is an average of the local order over the whole crystal. It is possible to introduce a truly local short-range order, but that is beyond the scope of the present paper.

Let us consider a spin system and assume that only the relative orientation of the neighboring spins contributes to the energy. A nearest neighbor pair is called a "bond," interchangeable. The spin pairs $(+, -)$ or $(-, +)$ are antiparallel spins and contribute an energy $+J$, and the spin pairs $(+, +)$ or $(-, -)$ are parallel spins and contribute an energy $-J$. We assume J to be positive.

We choose for internal variables those that express the fraction of each kind of nearest neighbor pairs. The meaning of the pair variables y_i is as follows.⁽⁷⁾ If the number of pairs in a system is N_p , the number of $(+, +)$ bonds in the system is $y_1 N_p$, the number of $(+, -)$ bonds $y_2 N_p$, and the number of $(-, -)$ bonds $y_3 N_p$. In the second case there is a degeneracy

$g = 2$, which indicates the number of different configurations having the same probability. The y_i are normalized by the equation

$$\sum_{i=1}^3 g_i y_i = 1; \quad g_1 = g_3 = 1; \quad g_2 = 2 \quad (10)$$

The fractions of (+) spins and (-) spins given by x_1 and x_2 are called the point variables. The x_i are normalized by the equation

$$x_1 = y_1 + y_2; \quad x_2 = y_2 + y_3; \quad x_1 + x_2 = 1 \quad (11)$$

The long-range order parameter S and the short-range order parameter Q are defined by

$$S = x_1 - x_2 = y_1 - y_3 \quad (12)$$

$$Q = y_1 - 2y_2 + y_3 = 1 - 4y_2 \quad (13)$$

Using (10), (12), and (13), one can determine the bond variables as a function of the order parameters,

$$\begin{aligned} y_1 &= \frac{1}{4}(2S + Q + 1) \\ y_2 &= \frac{1}{4}(1 - Q) \\ y_3 &= \frac{1}{4}(1 + Q - 2S) \end{aligned} \quad (14)$$

Similarly, from Eqs. (11) and (12) the point variables can be written as

$$x_1 = \frac{1}{2}(1 + S), \quad x_2 = \frac{1}{2}(1 - S) \quad (15)$$

To determine the free energy in terms of the pair variables y_i we need the internal energy E . The internal energy E can be written

$$E = \sum_{i=1}^3 g_i \varepsilon_i y_i \quad (16)$$

with $\varepsilon_1 = -(J + 2H)$, $\varepsilon_2 = J$, and $\varepsilon_3 = -(J - 2H)$, where H is the magnetic field. The number of ways independent pairs can be arranged on the lattice is

$$W_p = \frac{[\frac{1}{2}\gamma N]!}{[\frac{1}{2}\gamma y_1 N]! ([\frac{1}{2}\gamma y_2 N]!)^2 [\frac{1}{2}\gamma y_3 N]!}$$

since there are $N_p = \frac{1}{2}\gamma N$ pairs. γ is the coordination number of the lattice,

i.e., the number of nearest neighbors. The number of ways the sites can be arranged is

$$W_x = \frac{N!}{(x_1 N)! (x_2 N)!}$$

This leads to an entropy

$$\begin{aligned} \frac{\bar{\mathcal{F}}}{k} = \ln W = & -\frac{1}{2}\gamma N \sum_{i=1}^3 g_i y_i \ln y_i - N \sum_{i=1}^2 x_i \ln x_i \\ & + \gamma N \sum_{i=1}^2 x_i \ln x_i \end{aligned} \quad (17)$$

where the last term is introduced to compensate for the fact that the pair contribution contains γN site contributions.⁽⁸⁾

Using (16), and (17) with $F = E - T\bar{\mathcal{F}}$, one finds the free energy as

$$\begin{aligned} \Phi \equiv \frac{\beta F}{N} = & \frac{\gamma}{2} \beta \sum_{i=1}^3 g_i \varepsilon_i y_i + \frac{\gamma}{2} \sum_{i=1}^3 g_i y_i \ln y_i \\ & - (\gamma - 1) \sum_{i=1}^2 x_i \ln x_i + \beta \lambda \left(1 - \sum_{i=1}^3 g_i y_i \right) \end{aligned} \quad (18)$$

where λ is introduced to obtain the normalization condition.

3.2. Solution for the System at Equilibrium

In Eq. (18) the free energy is given in terms of the internal variables. Minimization of (18) with respect to y_i gives

$$\partial \Phi / \partial y_i = 0, \quad i = 1, 2, 3 \quad (19)$$

which leads to three self-consistent equations:

$$\begin{aligned} \frac{\partial \Phi}{\partial y_1} = & \frac{\gamma}{2} \beta \varepsilon_1 + \frac{\gamma}{2} \ln y_1 - (\gamma - 1) \ln x_1 + \beta \lambda \\ \frac{\partial \Phi}{\partial y_2} = & \gamma \beta \varepsilon_2 + \gamma \ln y_2 - (\gamma - 1)(\ln x_1 + \ln x_2) + 2\beta \lambda \\ \frac{\partial \Phi}{\partial y_3} = & \frac{\gamma}{2} \beta \varepsilon_3 + \frac{\gamma}{2} \ln y_3 - (\gamma - 1) \ln x_2 + \beta \lambda \end{aligned} \quad (20)$$

This gives

$$\begin{aligned} y_1 e^{-2\beta\lambda/\gamma} &= e^{-\beta e_1} x_1^{2\bar{\gamma}} \equiv e_1 \\ y_2 e^{-2\beta\lambda/\gamma} &= e^{-\beta e_2} (x_1 x_2)^{\bar{\gamma}} \equiv e_2 \\ y_3 e^{-2\beta\lambda/\gamma} &= e^{-\beta e_3} (x_2)^{2\bar{\gamma}} \equiv e_3 \end{aligned} \tag{21}$$

where $\bar{\gamma} = (\gamma - 1)/\gamma$. We can find λ from the partition sum:

$$e^{-2\beta\lambda/\gamma} = e_1 + 2e_2 + e_3 \equiv Z \tag{22}$$

From (21), y_1 , y_2 , and y_3 can be computed using either the natural iteration method of Kikuchi⁽⁹⁾ or the Newton–Raphson method. One of the advantages of the natural iteration method is that the free energy always decreases as the iteration proceeds, with the consequence that iteration always converges to a stable solution. However, if one is interested in metastable and unstable solutions, the Newton–Raphson method is needed, since the natural iteration method is only capable of “homing-in” on stable solutions. After determining the y_i the order parameters S and Q are calculated using Eq. (12) and (13). For later use we express Eqs. (21) and (22) in the form $S = \bar{S}(S)$ and $Q = \bar{Q}(S)$, where the functions \bar{S} and \bar{Q} are given by

$$\bar{S} = \frac{\sinh(2\beta H + h)}{\exp(-2\beta J) + \cosh(2\beta H + h)} \tag{23a}$$

$$\bar{Q} = 1 - \frac{2}{1 + \exp(2\beta J) \cosh(2\beta H + h)} \tag{23b}$$

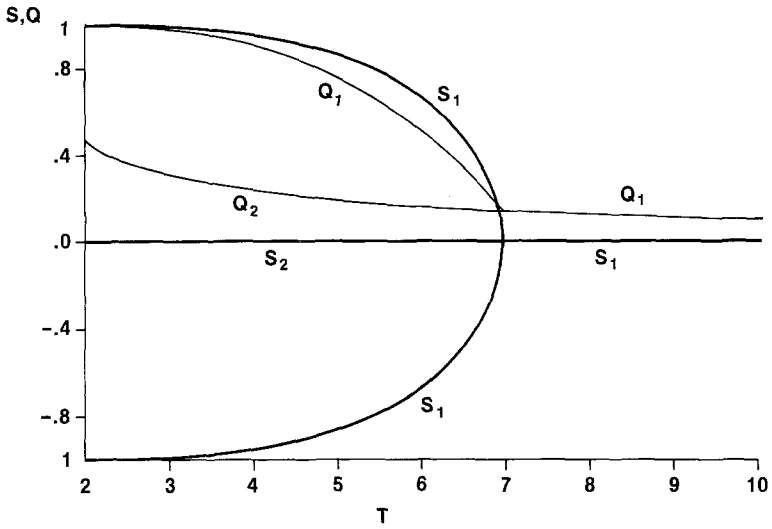
with $h = \bar{\gamma} \ln[(1 + S)/(1 - S)]$.

Since the argument Q does not appear in the equations, only the first condition, $S = \bar{S}$, is a self-consistency equation; the second expression, $Q = \bar{Q}$, merely determines the value of Q that follows. The first equation has either one or three roots and consequently the second leads to the same number of options for Q . Figure 3a shows S and Q versus T for $H = 0$ and $\gamma = 8$ (a bcc lattice). We show S and Q versus T for $H = 0.005, 0.01,$ and 0.1 in Fig. 3b. In all cases the stable, metastable, and unstable solutions are plotted. The distinction between these three types of states can be most easily seen by constructing a contour map of the free energy (see Ref. 10).

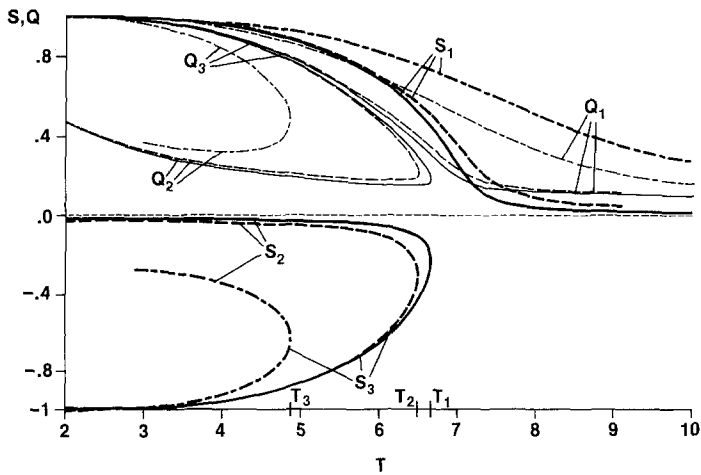
3.3. System Far from Equilibrium

In order to construct a possible set of dynamic equations, we use the most probable path (MPP) method of Kikuchi.⁽¹¹⁾ In this method the rate change of the internal variables is given by

$$dy_{ij}/dt = \sum_{i \neq j} (Y_{ij} - Y_{ji}) \tag{24}$$



(a)



(b)

Fig. 3. (a) Long-range order parameter S (heavy lines) and short-range order parameter Q (thin lines) for the stable (subscript 1), the unstable (subscript 2), and the metastable (subscript 3) states for $H=0$ ($J=1$). (b) The same for three different nonzero fields: (—) $H=0.005$, (---) $H=0.01$, and (-·-) $H=0.1$.

where Y_{ij} is the path probability rate for the system to go from state i to j . The coefficients Y_{ij} are the product of the three factors: k_{ij} , the rate constant; a temperature-dependent factor which guarantees that the equilibrium state is the time-independent state; and a third factor, which is the probability that the system is in the state i , e.g., y_i . Detailed balancing requires that

$$Y_{ij} = Y_{ji} \quad (\text{all } i, j) \tag{25}$$

Following the method of Kikuchi, we can either make the assumption that the temperature-dependent factor is given by the exponential of $\beta/2$ times the energy increase in the transition (called recipe I in Ref. 11) or β times the total energy of activation (recipe II). Our formulas are based on the second choice. Some of the numerical work was done with both options, however. The resulting expression is

$$Y_{ij} = k_{ij} e_j y_i \tag{26}$$

where e_j is given by the identities of Eq. (21). It seems arbitrary to include or not to include (as is done here) the partition function as a denominator, but this only changes the time scale and consequently has no influence on the shape of the flow lines. There also may be an intrinsic temperature dependence in the rate constants. This will be of importance in cooling experiments where T is time dependent, but this was not introduced in our description.

The possible transitions are depicted in Fig. 4. We make the following assumptions for the rate constant:

$$k_{12} = k_{21} = k_1; \quad k_{23} = k_{32} = k_2; \quad k_{13} = k_{31} = 0 \quad (k_1 \neq k_2) \tag{27}$$

This choice is based on the idea that insertion of a particle is different when a neighbor is present than when a neighbor is not present (see Ref. 5). Also, we assumed that double processes, the simultaneous insertion or removal of two particles, do not take place.^(12,13)

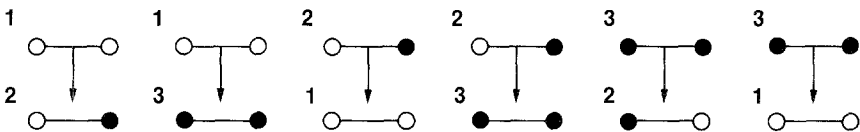


Fig. 4. The six possible transitions in the pair approximation.

The resulting rate equations for the pair variables are

$$\begin{aligned} dy_1/dt &= k_1(e_1 y_2 - e_2 y_1) \\ 2 dy_2/dt &= k_1 e_2 y_1 + k_2 e_2 y_3 - k_1 e_1 y_2 - k_2 e_3 y_2 \\ dy_3/dt &= k_2(e_3 y_2 - e_2 y_3) \end{aligned} \quad (28)$$

With Eqs. (12) and (13) the rate equations can be written in the form

$$\begin{aligned} dS/dt &= -a_{11}(S - \bar{S}) - a_{12}(Q - \bar{Q}) \\ dQ/dt &= -a_{21}(S - \bar{S}) - a_{22}(Q - \bar{Q}) \end{aligned} \quad (29)$$

where the a 's are in general still functions of S and Q . The form (29) is advantageous when one is considering the behavior near a fixed point.

To obtain the rate equation in the form (29) we subtract the equilibrium values given by (23) from each pair of terms. For instance,

$$e_1 y_2 - e_2 y_1 = e_1(y_2 - \bar{y}_2) - e_2(y_1 - \bar{y}_1) \quad (30)$$

If one applies the same procedure to all other terms in (28), the rate equations are given by

$$\begin{aligned} dS/dt &= -\frac{1}{2}e_2(k_1 + k_2)(S - \bar{S}) \\ &\quad - \frac{1}{4}[k_1 e_1 + (k_1 - k_2)e_2 - k_2 e_3](Q - \bar{Q}) \end{aligned} \quad (31)$$

$$\begin{aligned} dQ/dt &= -e_2(k_1 - k_2)(S - \bar{S}) \\ &\quad - \frac{1}{2}[k_1 e_1 + (k_1 + k_2)e_2 + k_2 e_3](Q - \bar{Q}) \end{aligned} \quad (32)$$

We will display the results in the form of a flow diagram,⁽¹⁴⁾ which consists of a graphical solution of these rate equations in the two-dimensional phase space of S and Q . One starts with initial values very close to the boundary, then, as time progresses (by given small steps) the values of S and Q are computed, and the point representing them moves in the plane. A set of solution curves is created by considering all different initial values.

The form (29) is somewhat misleading. In order to determine the character of the fixed points, we need to evaluate the determinant associated with the coefficients of the first-order deviations. Since \bar{S} is a function of S , the determinant is given by

$$D = D_0 \left(1 - \frac{d\bar{S}}{dS} \right); \quad D_0 = (a_{11}a_{22} - a_{12}a_{21}) = \frac{k_1 k_2}{8} (1 - \bar{Q}) \quad (33)$$

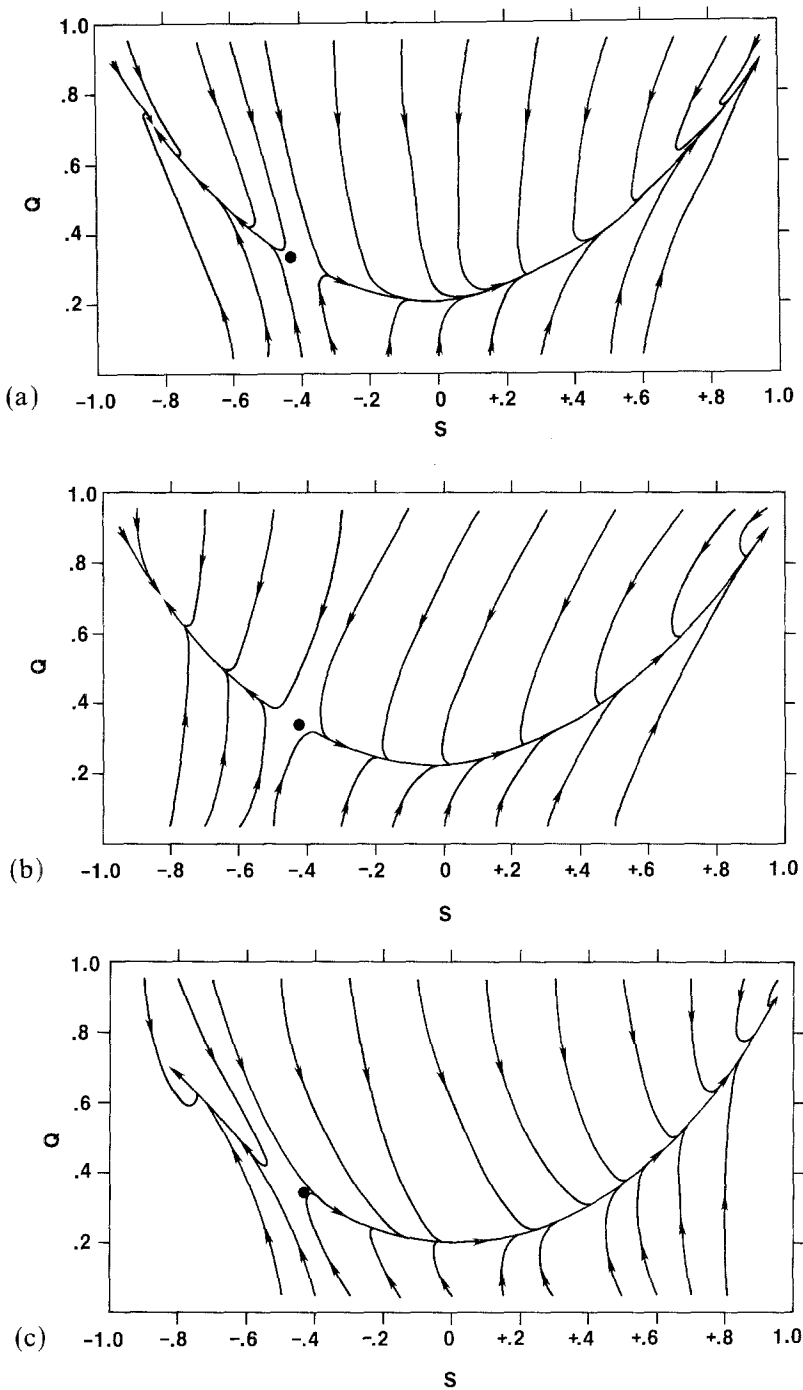


Fig. 5. Flow diagram of the system at $T=4.5$ and $H=0.1$ in units J . The black dot indicates the saddle point. (a) With $k_1 = k_2 = 1$; (b) with $k_1 = 10.0$ and $k_2 = 1.0$; (c) with $k_1 = 100.0$ and $k_2 = 1.0$.

It is the second factor in the first equation that determines the sign, which establishes, using the terminology of Ref. 14, whether the fixed point is a node or a saddle point.

Equations (31) and (32) were solved for different values of k_1 and k_2 with $T=4.5$ and $H=0.1$ (Fig. 5). The coordinates of the fixed points can be found from the dash-dotted lines in Fig. 3b.

4. DISCUSSION OF THE SOLUTION

In order to obtain the appropriate reference points that occur in the solution of the dynamic equations we discuss first the equilibrium, or actually the time-independent, solutions as a function of the temperature for zero field (Fig. 3a) and for three values of the magnetic field (Fig. 3b). For given nonzero field, there are three solutions for the long-range order parameter below a certain temperature. For lack of a better name, we will call this the quasicritical temperature T'_c (in Fig. 3b, $T'_c = T_1$ for $H=0.005$, T_2 for $H=0.01$, and T_3 for $H=0.1$). From the figure we see that two of three solutions for $S(T < T'_c)$ join at T'_c . The stable solution S_1 is always positive for $H > 0$. The unstable solution S_2 is negative and rather small in absolute value at lower temperatures. This solution is of course zero if the field is absent. The metastable solution S_3 is negative; its absolute value is less than S_1 at the same temperature. Each branch has its corresponding Q values: Q_1 is similar to the zero-field solution, but this branch has no discontinuity in the derivative; Q_2 , the unstable solution, lies in the neighborhood of the Q_2 for $H=0$; and Q_3 , the metastable solution, has about the same value as Q_1 , but terminates at T'_c . The curves of S_2 and S_3 meet at T'_c with a vertical tangent, the same holds for Q_2 and Q_3 . The values of T'_c in Fig. 4b are labeled T_1 (corresponding to the $H=0.005$ curves; solid line); T_2 (corresponding to the $H=0.01$ curves; dashed); and T_3 (the $H=0.1$ curves; dash-dotted). The value of Q_2 goes to one for T going to zero.

To describe the solutions of the dynamic equations we choose a given temperature and field and plot the flow diagram in S - Q space (see Fig. 5). The lines in the flow diagram will depend on the choice of the method (recipe I versus recipe II) as well as on the values chosen for the rate constant k . In similar work⁽¹²⁾ we found that the choice of I versus II did not change the character of the diagram very much. We use here recipe II.

In this flow diagram there are three fixed points: one in the upper right corner, the stable solution; one in the upper left corner, the metastable solution; and one in the lower-middle part of the figure, the so-called unstable solution. This last point would be somewhat above the origin if the field were zero. The upper left fixed point lies lower than the upper

right fixed point since the field was chosen positive. The coordinates of the fixed points in this diagram are: $S_1 = 0.95$, $Q_1 = 0.90$; $S_2 = -0.43$, $Q_2 = 0.34$; and $S_3 = -0.82$, $Q_3 = 0.70$. The position of these points is independent of the choice of the values of the rate constants since they do not enter the self-consistency equations (23). Also, the character of the fixed points is independent of the rate constants, since the sign of the determinant remains the same when the k 's are modified. The unstable fixed point is avoided by the flow lines. Inserting the coordinates in Eq. (33) gives $D < 0$; hence this is indeed a saddle point. If we imagine a circle around it, all points on a 180° sector on the left lead to the metastable fixed point and all points on a 180° sector on the right lead to the stable fixed point. The orientation of the separation depends on the value of k , the ratio of the rate constants.

It is also clear from the figure that there is a confluence of the flow lines and by comparing different values of the ratio k one can see that this line of confluence is independent of k . Comparing Eqs. (31) and (32), we obtain

$$\frac{dS}{dQ} = \frac{f_1 + kf_2}{g_1 + kg_2} \quad (34)$$

where f_1 and g_1 are the terms that do not contain k ($=k_1/k_2$) and f_2 and g_2 are the remaining parts. The function is independent of k on the line

$$f_1/g_1 = f_2/g_2 \quad (35)$$

This "invariant" depends on the temperature and on the field. All three fixed points lie on this invariant line. At higher temperature there is only one fixed point on the invariant line, since the unstable point and the metastable point eventually merge and disappear.

In Fig. 5c one sees that, contrary to the one-parameter model, the initial value of $S < S_2$ will not necessarily relax toward S_3 since the behavior will depend on the initial value for Q . The diagram shows that for Q above the confluent line, the system will relax toward the stable state.

For the sake of completeness we mention earlier and different treatments of this problem, by Meijer and Edwards,⁽¹³⁾ using a four-state master equation (in this paper all six rate constants are equal), Geschwend *et al.*⁽¹⁴⁾ on vacancies in alloys, and van Baal,⁽¹⁵⁾ who describes the same problem by a slightly different method.

Finally, we suggest the following scenario for a time-dependent temperature: If quenching is done rapidly, that is, at a rate larger than the largest of the two rate constants, the system still finds itself in the positive quadrant of the two-dimensional phase space. At the final temperature it

may lie on one of the flow lines that descend to the left (see Fig. 5b) and reach the metastable state, and hence becomes frozen-in in the non-equilibrium state. This is actually a well-known case in rapid solidification (e.g., Refs. 18 and 19). If subsequently the temperature is somewhat raised, the metastable fixed point and the unstable fixed point will approach each other (and eventually annihilate each other) and the system may find itself at the new temperature on one of the other flow lines, so that it will move to the stable fixed point.

APPENDIX A

Assuming that the derivative of the free energy is factorized, one obtains an equation of motion of the form

$$\frac{dn}{dt} = M \frac{\delta F}{\delta n} = k(n - n_1)(n - n_2)(n - n_3) \quad (\text{A1})$$

with $n_1 < n_2 < n_3$ this corresponds to a maximum at n_2 between two minima at n_1 and n_3 , provided $k > 0$. The solution

$$\left(\frac{n - n_1}{n_0 - n_1}\right)^{\tau_1} \left(\frac{n - n_3}{n_0 - n_3}\right)^{-\tau_3} \left/\left(\frac{n - n_2}{n_0 - n_2}\right)^{\tau_2}\right. = \exp[k(t - t_0)] \quad (\text{A2})$$

where n_0 is the value of n at $t = 0$. The values of τ are given by

$$\tau_1 = \frac{n_2 - n_3}{\Delta} < 0; \quad \tau_2 = \frac{n_3 - n_1}{\Delta} > 0; \quad \tau_3 = \frac{n_1 - n_2}{\Delta} < 0$$

and

$$\Delta = n_2^2 n_3 - n_3^2 n_2 + n_3^2 n_1 - n_1^2 n_3 + n_1^2 n_2 - n_2^2 n_1$$

The dependence of $n(t)$ is given in Fig. 6. For all $n < n_2$ the system will end up at n_1 and for all $n > n_2$ the system will end up at n_3 . In both cases it will remain at that point. The result is obvious and there is no "overshoot," as is well known for a relaxation equation. The point $n = n_2$ is singular.

If the secondary minimum becomes an inflection point, i.e., if $n_2 = n_3$, the solution changes in character, since the decomposition in fractions changes. The result is

$$\tau^2 \ln \frac{n - n_3}{n_0 - n_1} - \tau^2 \ln \frac{n - n_2}{n_0 - n_2} + \tau \frac{n_0 - n}{(n - n_2)(n_0 - n_2)} = k(t - t_0) \quad (\text{A3})$$

where $\tau = 1/(n_2 - n_1) > 0$. The result leads to the conclusion that the inflec-

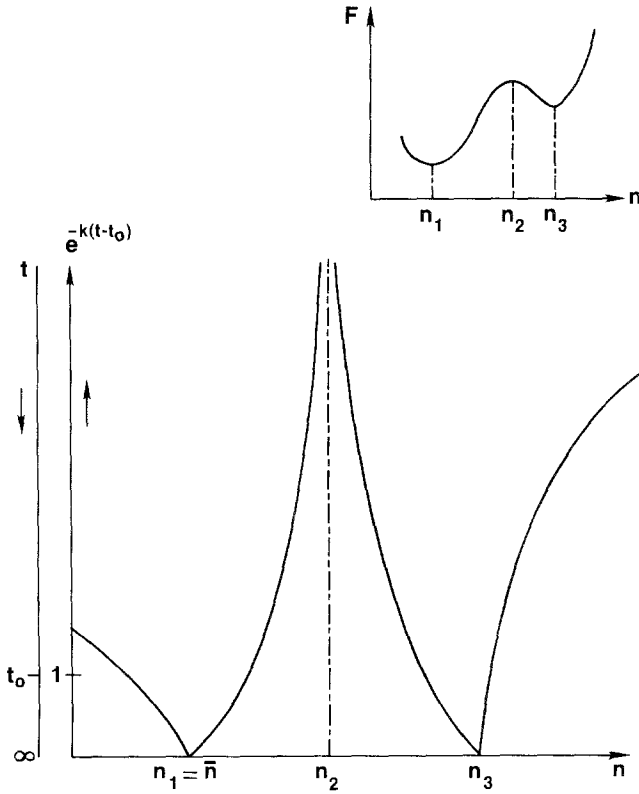


Fig. 6. Time dependence of the long-range order parameter for the rate equations given by (A2). Insert: the free energy as a function of the order parameter n .

tion point is metastable in an unusual way. For $n_1 < n_2 = n_3$ we have the following property of this instability. If $n = n_2 + \Delta n$, the system will relax to n_3 , but for $n = n_2 - \Delta n$, the system will relax to n_1 .

ACKNOWLEDGMENTS

This work was supported by ONR N0014-78-C0518 and by NATO grant 1928. We express our thanks to the computer center of the Catholic University of America; one of us (M. K.) thanks the Turkish government.

REFERENCES

1. E. K. Biggs, *Proc. Phys. Soc. Lond. B* **66**:688 (1953).
2. R. Evans and M. M. Telo da Gama, *Mol. Phys.* **38**:687 (1979).

3. Y. M. Wong and P. H. E. Meijer, *Physica* **110A**:188 (1981).
4. H. Sato and R. Kikuchi, *Acta Metal.* **24**:797 (1976).
5. E. W. Montrol and H. Reiss, *Proc. Natl. Acad. Sci. USA* **78**:2659 (1981).
6. G. S. Grest and M. H. Cohen, *Phys. Re.* **21**:4113 (1980); M. H. Cohen and G. S. Crest, *Phys. Rev.* **24**:4091 (1981).
7. R. Kikuchi, *Phys. Rev.* **81**:988 (1951).
8. T. Morita, *J. Phys. Soc. Jpn.* **12**:1060 (1957).
9. R. Kikuchi, *J. Chem. Phys.* **60**:1071 (1974).
10. M. Keskin, *Doğa Bilim Dergisi, A1* **9/3**:210 (1985).
11. R. Kikuchi, *Progr. Theor. Phys. (Suppl.)* **35**:1 (1966).
12. M. Keskin and P. H. E. Meijer, *Physica A* **122**:1 (1983).
13. M. Keskin, *Physica* **135A**:226 (1986).
14. M. Minorski, *Nonlinear Oscillations* (van Nostrand, New York, 1962); H. Poincaré, *J. Math. (Paris)* **1881**(3):7 (1881); *Oeuvres*, Vol. 1 (Gauthier-Villars, Paris, 1928).
15. P. H. E. Meijer and J. C. Edwards, *Ann. Phys. (N.Y.)* **54**:240 (1969).
16. K. Geschwend, H. Sato, and R. Kikuchi, *J. Chem. Phys.* **69**:5006 (1978).
17. C. van Baal, *Physica (Utr.)* **111A**:591 (1982).
18. P. Duwez, in *Rapid Solidification Technology*, R. L. Ashbrood, ed. (American Society of Metals, Cleveland, Ohio, 1983).
19. F. E. Luborsky, in *Amorphous Metallic Alloys*, F. E. Luborsky, ed. (Butterworth, London, 1983).