Freezing of Nonequilibrium Domain Structures in a Kinetic Ising Model

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We study the freezing of a disordered spin structure upon continuous cooling to absolute zero for a kinetic Ising spin chain with alternating weak and strong bonds. The kinetic equation for the spin pair correlation function is solved analytically in a continuum approximation. The exponent for the asymptotic dependence of the frozen kink density on a characteristic cooling time is found to be z^{-1}, where z is the equilibrium dynamic critical exponent, for a universality class including power-law and exponential cooling, and $\frac{1}{2}$ for a logarithmic cooling program which exhibits threshold behavior.

Many cases occur in condensed matter physics where a disordered non-equilibrium structure is frozen in during continuous cooling to low temperatures. Examples range from the freezing of random domain structures in certain crystalline and magnetic materials to the glass transition of undercooled liquids (see ref. 1 for a recent review). In these various freezing phenomena the frozen structure typically depends on the conditions of cooling, and this is of practical importance in material preparation. To characterize the structure frozen in at low temperature and to clarify its dependence on the conditions of cooling, a kinetic theory of the structural evolution during the cooling process is called for. In this paper we present such a theory for the freezing of a random domain structure in an Ising spin chain with Glauber kinetics.

Phenomenological descriptions of freezing based on the concept of a "fictive temperature"[2,3] can, for glass transitions, very successfully model

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the nonlinear relaxation of particular physical properties, which reflects the evolution of the internal structure.[4,5] However, nonequilibrium structures are not usually adequately characterized by a single fictive temperature, and fictive temperatures depend on which physical quantity they derive from. Therefore, theoretical models are required in which internal structure is described in more detail and many modes participate in the freezing process. So far, freezing and nonlinear relaxation in such models have only been studied by numerical simulation,[8–10] with the exception of an approximate treatment of disordered Ising spin chains,[11] and the solution of a phenomenologically generalized master equation.[12,18] The spin model put forward in this paper has the advantage of being amenable to analytical calculation.

We consider a one-dimensional kinetic Ising model with Glauber single-spin-flip dynamics[13] and alternating weak (B) and strong (A) exchange couplings between pairs of nearest-neighbor spins. The non-uniformity of the exchange couplings $(A > B)$ is essential for the freezing of nonequilibrium spin configurations at low temperatures. As discovered recently,[14,15] it also gives rise to a nonuniversal dynamic critical exponent $z = 1 + A/B > 2$ for the dynamics of equilibrium fluctuations near zero temperature. This exponent will also play a role in the freezing phenomena discussed here. The structure of the spin chain is characterized by the distribution of "kinks," which are pairs of antiparallel nearest-neighbor spins. The kinks are the boundaries of ordered domains of parallel spins. The energy of a kink is $2A$ on a strong, and $2B$ on a weak bond. At sufficiently low temperature nearly all kinks will occur on weak bonds. For a kink to hop from a weak bond to a neighboring one an activation energy $2(A - B)$ is required for passing the strong bond in between. Upon cooling, the thermally activated diffusion of kinks slows down more and more until, at zero temperature, all remaining kinks, which have escaped pair annihilation at finite temperatures, are frozen. In this work, a kinetic theory of nonequilibrium relaxation and freezing of the spin structure of this model is presented. In particular, we calculate the frozen kink density at zero temperature for three very different types of cooling. Whereas for power-law and exponential cooling a finite kink density is always frozen in, we find a threshold behavior for inversely logarithmic cooling. At the same time, generic features occur, including universal relationships between controlling variables and between frozen-in kink density and cooling rate. In the commonest universality class the kink density/cooling rate relationship for slow cooling involves the critical exponent z. In addition, some memory of the initial equilibrium state is retained in general.

We give special attention to those features of our model which are characteristic of a multivariable description as opposed to a phenome-

nological fictive-temperature theory. These features arise because in the model, as in collective systems in general, the participation of many modes leads to a spectrum of rates than just one Arrhenius rate related to a single energy barrier.

We describe the temporal evolution of the spin structure during cooling by the time-dependent spin pair correlation function $g_{ij}(t) = \langle \sigma_i \sigma_j \rangle_t$. This function determines the average kink and energy density, susceptibility, etc. In the one-dimensional kinetic Ising model used here the equation of motion for the pair correlation function, which derives from the master equation, is not coupled to any correlation functions of higher order. Since each of the two spins in $\langle \sigma_i \sigma_j \rangle$ can be on either sublattice of the alternating chain, four types of correlation function occur. Elimination provides an equation involving just one type. The equation can be simplified, without losing any of the essential physical content, by discarding higher-order time derivatives and using a continuum approximation. These reductions are valid if the cooling process is slow and starts from equilibrium at an initial temperature T_0 low enough to make kinks relatively improbable on strong bonds and to give a long initial correlation length ξ_0 (which is the initial kink separation). The continuum version of the equation of motion which then applies for the translationally invariant spin correlation function $g(x_i - x_j, t) = \langle \sigma_i \sigma_j \rangle_t$ reads

$$(\partial_t + \omega_+ - \omega_- \partial_x^2)\, g(x, t) = 0 \qquad (1)$$

In (1) the length of $x = x_i - x_j$ is measured in units of the nearest neighbor distance and the time is in units of the inverse spin flip attempt frequency; the relaxation rate ω_+ and hopping rate (or diffusion "constant") ω_- are given by the low-temperature expressions $\omega_\pm = \exp[-2\beta(A \pm B)]$ where $\beta = 1/(k_B T)$. Equation (1), on which our calculations of relaxation and freezing are based, is a hybrid between a relaxation equation and a diffusion equation. A discrete version of (1), obtained by introducing ad hoc an Arrhenius temperature dependence of the spin flip rate to the Glauber equation for a uniform Ising chain, has been solved previously to arrive at a detailed discussion for a fast quench.[12] Recently, for the uniform chain some results have also been derived for slow quenches.[18] We emphasize that it is the slow quench (at low temperature) which we treat, for which (1) provides the correct description of the microscopic alternating bond model.

For equilibrium the correlation function is obtained as

$$g_{eq}(x) = \exp(-|x|/\xi), \qquad \xi = (\omega_-/\omega_+)^{1/2} \qquad (2)$$

It is useful to introduce a ratio $\nu = (A + B)/(A - B) > 1$, in terms of which $\omega_+ = \omega_-^\nu$. For continuous cooling from the initial equilibrium tem-

perature T_0 to temperature zero the rates $\omega_\pm$ are functions of time which depend on the particular cooling program (see below). Given these functions, Eq. (1) has to be solved for $x \geqslant 0$ subject to the boundary condition $g(0, t) = 1$ and the initial condition $g(x, 0) = \exp(-x/\xi_0)$, where $\xi_0 \equiv \exp(2\beta_0 B)$ is the correlation length at T_0. Although Eq. (1) is linear, its eigenmodes are coupled by virtue of the boundary conditions.

Equation (1) can be converted to the usual diffusion equation with a constant diffusion coefficient of unity by introducing a new variable $u(t)$ and integrating factor $\exp[I(t)]$, where

$$u = \int_0^t \omega_-(s)\, ds, \qquad I = \int_0^t \omega_+(s)\, ds \equiv J(u) \tag{3}$$

$u(t)$ is an average number of hops of a kink until time t and $I(t)$ is a "reduced time" measured in units of the time-dependent relaxation time $1/\omega_+$. As shown below, the existence of a nonzero kink density at zero temperature depends on whether $u(\infty)$ is finite or infinite. The solution of Eq. (1) is now obtained as

$$g(x, t) = e^{-J(u)}(\Psi(x, u) + \Phi(x, u)) \tag{4}$$

where Ψ, Φ solve the usual diffusion equation with u as time variable and with boundary and initial conditions given by:

(i) $\Psi(x, 0) = g(x, 0)$, $x \geqslant 0$, and $\Psi(0, u) = 0$, $u \geqslant 0$.

(ii) $\Phi(x, 0) = 0$, $x \geqslant 0$, and $\Phi(0, u) = e^{J(u)}$, $u \geqslant 0$.

The function $\Psi(x, u)$ contains a memory of the initial situation, while Φ depends solely on the cooling process. Using standard methods of solution for the diffusion equation,[16] one finds [with $y \equiv x/(2\sqrt{u})$],

$$\Psi(x, u) = \frac{2}{\pi} \int_0^\infty dq\, \frac{q\sin(qx)}{q^2 + \xi_0^{-2}}\, e^{-q^2 u}$$

$$\Phi(x, u) = \frac{2}{\sqrt{\pi}} \int_y^\infty ds\, e^{J(u - (x/2s)^2) - s^2} \tag{5}$$

The solution (4), (5) for the pair correlation function depends on the particular cooling program through the functions $u(t)$ and $J(u)$ defined in (3). We consider three typical cases, in which the inverse temperature increases with time linearly (I), exponentially (II), and logarithmically (III). In each case zero temperature is reached only asymptotically for $t \to \infty$, in agreement with the principle of the unattainability of absolute

zero. In all three cases the same generic form of $J(u)$ is obtained, which reads

$$J(u) = [1 - (1 - cu)^\mu]/(c\mu\xi_0^2) \qquad (6)$$

However, the results for $c = 1/u(\infty)$ and μ differ in case III from those in cases I and II, leading to markedly different freezing-in behavior. With $b = (2 \ln \xi_0)/(v - 1)$, the values of the parameters together with the functions $u(t)$ are given by:

(I) $c = (be^b)/\tau$, $\mu = v$, with

$$u(t) = [1 - \exp(-bt/\tau)]/c \qquad \text{for} \quad \beta(t) = \beta_0(1 + t/\tau)$$

(II)   The same expressions for c and μ as in case I, with

$$u = \{1 - \exp[b - b \exp(t/\tau)]\}/c \qquad \text{for} \quad \beta(t) = \beta_0 \exp(t/\tau)$$

where $b \gg 1$ is assumed.

(III) $c = (d - 1) \tau^{d-1}$, $\mu = (vd - 1)/(d - 1)$, with

$$u(t) = [1 - (1 + t/\tau)^{1-d}]/c \qquad \text{for} \quad \beta(t) = \beta_0 \ln(t + \tau)/\ln \tau$$

with $d = b/\ln \tau$.

While in the linear (I) and exponential (II) cases $u(\infty) = c^{-1}$ diverges only for $\tau \to \infty$, in case III, the logarithmic cooling program, τ has a finite critical value of e^b. Moreover $u(\infty) = c^{-1}$ and $J(u(\infty)) = (c\mu\xi_0^2)^{-1}$ diverge simultaneously in cases I and II, whereas in case III there is a range of τ values $e^b \leqslant \tau < e^{vb}$ where $u(\infty)$ is infinite, but $J(u(\infty))$ is still finite. As a result of these differences, the conditions for the freezing of a disordered domain structure at zero temperature are different for the linear or exponential case on one hand and the logarithmic case on the other. The cooling processes thus divide into two classes, within each of which universal freezing behavior occurs, because of (6).

The most important parameter describing a frozen disordered spin structure is the average concentration $K(\infty)$ of kinks. Therefore, we are particularly interested in the dependence of this quantity on the time τ characterizing the speed of cooling for the various cooling programs. The average kink density $K(t)$ is determined by the spin correlation function as

$$K(t) = 1 - g(x = 1, t) \qquad (7)$$

where we dropped a factor $1/2$ for convenience. The asymptotic behavior of $K(\infty)$ for slow cooling, when $u(\infty) \to \infty$, $c \to 0^+$, can be evaluated

explicitly. Using Eqs. (4)–(6), we obtain two contributions to $K(\infty)$. The contribution of Ψ, which is negative, is proportional to $c^{3/2}$ and negligible for small c. The leading contribution comes from Φ and is given by

$$K(\infty) \sim c^{\sigma}$$

with an exponent σ equal to z^{-1} in cases I and II, where $z = 2\nu/(\nu - 1)$ is the dynamic critical exponent,[13,14] and $\sigma = 1/2$ in case III. In the latter case $K(\infty) \propto (\tau_c - \tau)^{1/2}$ for τ just less than the critical value $\tau_c = e^b$, while $K(\infty)$ is zero for $\tau > \tau_c$. As follows from expressions (4), (5), and (7), $K(\infty)$ vanishes if $u(\infty)$ is infinite and $J(u(\infty))$ is finite, which is the case for the logarithmic cooling program when $\tau_c < \tau < \tau_c^{\nu}$. Figure 1 gives the result of a numerical evaluation of the asymptotic kink density as a function of the rate variable c for cases I and II, using (4)–(7) for the specific values $\xi_0 = 100$, $\nu = 2$. It shows that the asymptotic law (8) correctly describes the decay of the initial kink density for slow cooling when c falls below ξ_0^{-2}. For faster cooling (actually for $c > 1/\xi_0$), $K(\infty)$ approaches the initial value $1/\xi_0$, corresponding to the initial equilibrium state, and provided by the "memory" contribution Ψ. The exponent z^{-1}, which governs the slow cooling result for the linear and exponential cases, can be derived from the following simple physical argument. The average relaxation rate of the average kink concentration near equilibrium is given by $\omega_+ = \omega_-/\xi^2 \propto \exp[-2\beta(A + B)]$. Equating this relaxation rate to a characteristic rate of
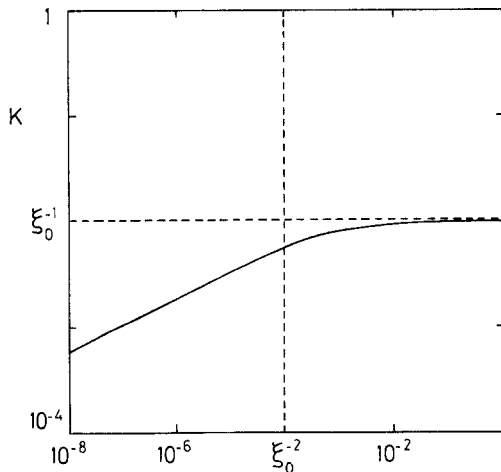

Fig. 1. A log–log plot of frozen ($t = \infty$) kink density K versus cooling rate c for linear and exponential cooling processes (I, II of the text). The system has $\nu = 2$ and initial correlation length $\xi_0 = 100$. For $c \ll \xi_0^{-2}$, $K \sim c^{(\nu-1)/2\nu}$; and for $c \gg \xi_0^{-1}$, $K \sim \xi_0^{-1}$.

the cooling process, which is inversely proportional to the time τ, we obtain the dependence of the freezing temperature $T_f = (k_B \beta_f)^{-1}$ on τ. The frozen kink density then follows as $K(\infty) = \exp(-2\beta_f B) \propto \tau^{-z}$. A related anomalous diffusion/crossover argument has been given for the dynamic critical exponent z in the different context of equilibrium fluctuations near absolute zero.[14] Our argument is different from that used by Huse and Fisher,[17] according to which the exponent would be given by the ratio $2B/(A-B)$ between the energy $4B$ of a pair of kinks on weak bonds and the activation energy $2(A-B)$ for kink hopping and kink pair annihilation. In our case the correlation length ξ also enters as the characteristic length of diffusion because of the truly collective character of the model. Recent work[18] on the Reiss model[12] has also yielded a power-law behavior like (8): here the exponent is related to phenomenological barrier parameters, and can provide an account of the recent computations for Schilling's chain model.[10,19,20] We note, however, that real glass-forming liquids show a logarithmic rather than a power-law dependence of the intensity of frozen structural fluctuations on the cooling rate.[1,3]

The argument leading in the previous paragraph to the exponent z^{-1} is convincing if the freezing of the kink density occurs within a relatively narrow temperature interval. Figure 2 gives in terms of the time-varying temperature $T(t)$ the evolution of the kink density during cooling programs I and II. These linear and exponential cases give the same result because elimination of t between $u(t)$ and $\beta(t)$ leads to the same function $u = \{1 - \exp[b(\beta_0 - \beta)/\beta_0]\}/c$. This is an explicit manifestation of the universality referred to earlier. Figure 2 shows that in cases I and II freezing over a narrow temperature interval indeed occurs if the cooling is sufficiently slow. Lowering the cooling rate both shifts the region of freezing to lower temperatures and makes the transition sharper. For the logarithmic cooling program III the physical crossover argument fails because in this case $K(\infty)$ vanishes for $\tau \to e^b$ rather than for the "critical" limit $\tau \to \infty$, and a simple diffusion exponent $1/\sigma = 2$ applies. The richness of the behavior of the system is related to the existence of a broad spectrum of relaxation times, which corresponds to the distribution of wavelengths of the diffusion modes. The superposition of these occurring depends on universal characteristics of the cooling program in general, and the difference between the dependence of asymptotic kink density on cooling rates in cases I and II and in case III clearly reveals the existence of two different classes of distributions of relaxation times participating in the freezing process.

The participation of many modes is apparent also from the form of the spin correlation function $g(x, \infty)$ characterizing the frozen spin structure. For small x the relation $g(x, \infty) \sim \exp[-K(\infty)x]$ follows from Eq. (7), whereas for very large x the decay of $g(x, \infty)$ is still determined by
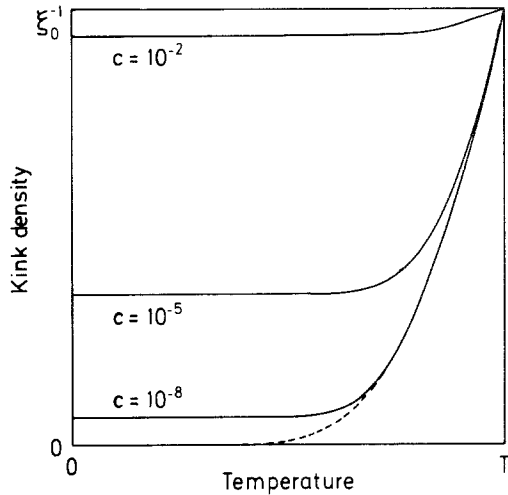
Fig. 2. Kink density as a function of temperature for cooling processes I and II at three different cooling rates c. The dashed line shows the equilibrium kink density at any temperature. In all cases $v = 2$ and $\xi_0 = 100$.

the initial correlation length ξ_0, though with an enhanced coefficient: $g(x; \infty) \sim a \exp(-x/\xi_0)$, where $a = \exp[(\mu - 1)/(\mu c \xi_0^2)] > 1$. Thus, the correlation function deviates strongly from the simple exponential decay of the equilibrium form (2), so a characterization in terms of a fictive temperature is at best approximate. The multimode dynamics of our model also leads to a nonexponential relaxation of the kink density after a temperature jump to a nonzero final temperature. These results will be described in more detail in a separate publication.

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