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Dynamical behavior of a one-dimensional Ising model submitted to continuous heating and cooling processes

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The evolution of a one-dimensional Ising model with Glauber dynamics and an extrinsic energy barrier, submitted to continuous cooling and heating processes, is studied. The model is shown to exhibit many of the properties observed in real glasses. Under slow cooling, the dependence of the residual energy on the cooling law and rate is analyzed. The width of the glass transition is proportional to the inverse of the logarithm of the cooling rate. Heating processes can be studied in terms of a special solution of the master equation. Using the properties of this normal solution, the origin of the hysteresis effects when the system is cooled and reheated is discussed. The heat capacity under continuous heating presents a maximum, whose position and height can be used to characterize the thermal cycle described by the system.

I. INTRODUCTION

The study of the dynamical behavior of glasses has attracted a lot of activity in the last years. In particular, several microscopic models showing similarity with real glasses have been proposed. Some of them have been reviewed by Fredrickson[1] and also by Scherer.[2]

The most studied features have been the shape of the linear response function and the temperature dependence of the linear relaxation time, on the one hand, and the behavior of the system under continuous cooling, on the other. For the response function, a stretched exponential of Kohlrausch-Williams-Watts (KWW) decay has been derived in many different ways. Besides, the models often display behaviors analogous to a glass transition, with a far from equilibrium state being frozen in, if the system is continuously cooled up to low enough temperatures. This is associated with a fast increase of the internal relaxation times as the temperature is lowered. In some models, a divergent relaxation time comes up when the temperature goes to zero, because the system requires an activation energy to relax. In others, the increase of the relaxation time is due to the introduction of some kind of cooperativity upon formulating the kinetics of the system.

Nevertheless, the phenomenology of glassy relaxation is very rich,[3,4] showing a series of features that must be understood, if we want to progress in our knowledge of the mechanisms responsible for the complex dynamical behavior of glasses. One of the objectives here is to take an step in this direction by studying, in addition to cooling processes, heating processes and also the combination of both of them in a simple model.

The model we will consider is a one-dimensional Ising model under Glauber dynamics with an extrinsic energy barrier. The linear response function in energy to a homogeneous temperature perturbation has been studied previously,[5] and shows a transition from being dominated by an exponential decay at high temperatures to an approximate KWW behavior at low temperatures. Moreover, Schilling[6] has carried out an analysis of the cooling rate dependence of the residual energy.

For systems described by master equations, and such that the only effect of the temperature variation of the heat bath is to introduce time-dependent transition rates, we have proved, under quite general conditions, the existence of a special kind of solutions, which we have called "normal solutions."[7] They depend on the law of variation of the temperature and have the property that all the solutions of the master equation, for a given time-dependent temperature program, tend to approach the corresponding normal solution.

Here we will show the relevance of the normal solution to explain the behavior of the system when it is submitted to a continuous heating process. It is precisely the tendency of the system to approach the normal curve which implies, for instance, that the energy of the system presents the hysteresis effects which are so characteristic of glassy behavior. Also, the structure of the normal solution determines the influence that the cooling and reheating rates have on the height of the peak exhibited by the heat capacity during a thermal cycle.

In this paper, an effort will be made to remark on the generality of the results at a qualitative level, in the sense that a similar behavior is expected for a great variety of systems. Physical arguments, easily adaptable to other systems, will be presented to explain what is observed in our numerical calculations. From this point of view, it is our opinion that almost any sensible model will show at low temperatures many of the dynamical properties that are usually considered as key characteristics of glassy behavior. In other words, very different microscopic mechanisms are able to explain, at least, the basic features of the phenomenology of glassy relaxation. Thus, the question should be whether glassy relaxation means something else other than the nonequilibrium behavior observed in any system when it falls out of ther-

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modynamic equilibrium, as a consequence of being submitted to a given process. If the answer is negative, the remaining crucial point should be to identify the microscopic processes leading in each material to a fast increase of the relaxation time as the temperature is lowered.

The organization of this paper is as follows. In Sec. II the model is formulated and an expression for the evolution of the average energy is derived for the general case of time-dependent temperature. Continuous cooling is analyzed in Sec. III, where expressions for the residual energy are obtained. It turns out that the functional form of the residual energy depends on both the cooling rate and the cooling law, similarly to what happens in a two-level system.[8] Section IV is devoted to a more detailed investigation of the freezing of the system. In particular, we determine the cooling rate dependence of the width of the transition.

In Sec. V we consider heating processes following a previous cooling of the system. The normal curve associated with a given heating law is defined and its relationship to the actual evolution of the energy and the equilibrium curve is discussed. In terms of them, it can be easily understood why the system presents hysteresis effects when cooled and reheated. The apparent heat capacity is the subject of Sec. VI, where the origin of the characteristic peak in the heating curve shows up clearly. The paper ends with a brief summary and some comments.

II. THE MODEL

We consider a one-dimensional nearest neighbor Ising model in absence of external field. The Hamiltonian of the system is

$$H = -J \sum_j \sigma_j \sigma_{j+1} , \tag{2.1}$$

with $J > 0$, and $\sigma_j = \pm 1$. The kinetics of the model is given by single-spin-flip Glauber dynamics;[9] i.e., the probability $p(\sigma, t)$ satisfies the master equation

$$\frac{d}{dt} p(\sigma, t) = \sum_j \left[W_j(F_j\sigma) p(F_j\sigma, t) - W_j(\sigma) p(\sigma, t) \right] , \tag{2.2}$$

where $\sigma = \{\sigma_1, \ldots, \sigma_j, \ldots\}$ and $F_j\sigma = \{\sigma_1, \ldots, -\sigma_j, \ldots\}$. The transition rates are given by

$$W_j(\sigma) = \frac{\alpha(T)}{2} \left[1 - \frac{\gamma(T)}{2} \sigma_j (\sigma_{j-1} + \sigma_{j+1}) \right] , \tag{2.3}$$

with

$$\gamma(T) = \tanh \frac{2J}{k_B T} . \tag{2.4}$$

The above definition implies that the transition rates verify the detailed balance condition for arbitrary $\alpha(T)$ and, therefore, the equilibrium canonical distribution is a steady solution of Eq. (2.2). We will take

$$\alpha(T) = \alpha_0 \exp\left(-\frac{\Delta}{k_B T} \right) . \tag{2.5}$$

The physical meaning of $\alpha(T)$ is clear. It introduces an activation energy Δ that is to be surmounted by every spin in order to flip, and that is independent of the state of the system. The constant α_0 will be used to set the time scale and will be taken equal to unity in the following.

We can think of the spin variables as defining cells in the configuration space of a given system. To each cell corresponds a configurational energy given by Eq. (2.1). The evolution of the system is such that only transitions between cells differing in the value of just one of the spins are allowed, and every pair of connected cells is separated by an energy barrier Δ. This is, in fact, the image found by Kob and Schilling[6,10] in their analysis of a chain of particles with anharmonic and competing interactions. Another possibility is that the Ising model is actually representing a magnetic system, and Δ is the energy needed to turn the spin 180°, arising from the anisotropy energy that inhibits the spin from pointing out in any direction other than the considered one.[11]

In our study, we will restrict ourselves to homogeneous situations, and the quantity we will focus on is the average energy per particle $e(t)$, given in adimensional units by

$$e(t) = -\langle \sigma_j \sigma_{j+1} \rangle (t) , \tag{2.6}$$

where the angular brackets denote average with the distribution function $p(\sigma, t)$.

Let us introduce the set of correlation functions

$$C_n(t) = \langle \sigma_j \sigma_{j+n} \rangle (t) . \tag{2.7}$$

From the master equation, it is found that they satisfy the hierarchy of equations[9]

$$\frac{d}{dt} C_n = -2\alpha C_n + \alpha\gamma \left(C_{n-1} + C_{n+1} \right) \tag{2.8}$$

for $n \geq 1$, and $C_0 = 1$. The equilibrium values at temperature T are

$$C_n^{(0)}(T) = \xi^n(T) , \tag{2.9}$$

with

$$\xi(T) = \tanh \frac{J}{k_B T} . \tag{2.10}$$

We notice that Eq. (2.8) is valid even when the quantities α and γ depend on time, for instance through the temperature. This is precisely the case we want to study. We are interested in the time evolution of e when the temperature of the heat bath is changing in time following a given program. Therefore, we need to calculate $C_1(t)$ by solving the set of difference equations given by Eq. (2.8), with time-dependent coefficients $\alpha = \alpha(T(t))$ and $\gamma = \gamma(T(t))$. Although this has already been done,[12] we present in the Appendix an alternative method that leads to a form of the solution which is more convenient for our purposes. The general solution reads

$$C_n(t) = C_n^{(0)}(T) + \int_0^\pi dq\, a(q)\phi_n(q) \exp\left[-\int_0^t dt'\lambda(q,T')\right] - \int_0^\pi dq \int_0^t dt' \frac{dT'}{dt'}\chi(q,T')\phi_n(q)\exp\left[-\int_{t'}^t dt''\lambda(q,T'')\right] , \tag{2.11}$$

where we have used the notation $T = T(t)$, $T' = T(t')$, and so on. In the above expression it is

$$\lambda(q,T) = 2\alpha(T)\left[1-\gamma(T)\cos q\right] , \tag{2.12}$$

$$\phi_n(q) = \left(\frac{2}{\pi}\right)^{1/2} \sin nq , \tag{2.13}$$

and the coefficients $\chi(q,T)$ and $a(q)$ are defined by the formulas (T_0 is the temperature at $t = 0$)

$$\frac{dC_n^{(0)}(T)}{dT} = \int_0^\pi dq\, \chi(q,T)\phi_n(q) \tag{2.14}$$

and

$$C_n(0) = C_n(t=0) = C_n^{(0)}(T_0) + \int_0^\pi dq\, a(q)\phi_n(q) , \tag{2.15}$$

i.e.,

$$\chi(q,T) = \sum_{n=0}^{\infty} \frac{dC_n^{(0)}(T)}{dT}\phi_n(q) \tag{2.16}$$

and

$$a(q) = \sum_{n=0}^{\infty} \left[C_n(0) - C_n^{(0)}(T_0)\right] \phi_n(q) . \tag{2.17}$$

A simple calculation using Eqs. (2.9) and (2.13) gives

$$\chi(q,T) = \frac{1}{\sqrt{2\pi}} \frac{\sin q}{(1-\gamma\cos q)^2} \frac{d\gamma}{dT} . \tag{2.18}$$

To get an expression for the energy per particle we particularize Eq. (2.11) for $n = 1$ and obtain

$$e(t) = e^{(0)}(T) - \int_0^\pi dq\, a(q)\phi_1(q)\exp\left[-\int_0^t dt'\lambda(q,T')\right] + \int_0^\pi dq \int_0^t dt'\frac{dT'}{dt'}\chi(q,T')\phi_1(q)\exp\left[-\int_{t'}^t dt''\lambda(q,T'')\right] . \tag{2.19}$$

As a first application of this equation, let us consider the relaxation of the system at constant temperature after an infinitesimal instantaneous quench. We assume that the system is in equilibrium at temperature $T - \Delta T$ for $t \leq 0$. At $t = 0$, the temperature of the bath is suddenly changed to T, and kept constant from that instant. To first order in ΔT we have

$$C_n(0) = C_n^{(0)}(T-\Delta T) = C_n^{(0)}(T) - \frac{dC_n^{(0)}(T)}{dT}\Delta T , \tag{2.20}$$

and, using Eq. (2.17),

$$a(q) = -\chi(q,T)\Delta T . \tag{2.21}$$

Taking into account that in the present situation T is constant for $t > 0$, Eq. (2.19) reduces to

$$e(t) = e^{(0)}(T) + \Delta T \int_0^\pi dq\, \chi(q,T)\phi_1(q) e^{-t\lambda(q,T)} , \tag{2.22}$$

and the linear response function is

$$\varphi(t) \equiv \frac{e(t) - e^{(0)}(T)}{e(0) - e^{(0)}(T)} = \int_0^\pi dq\, g(q,T)e^{-t\lambda(q,T)} , \tag{2.23}$$

where we have introduced the distribution of relaxation rates at temperature T,

$$g(q,T) = \frac{\chi(q,T)\phi_1(q)}{\int_0^\pi dq\, \chi(q,T)\phi_1(q)} > 0 . \tag{2.24}$$

Using Eq. (2.16) and the orthogonality of the functions $\phi_n(q)$, one obtains

$$\int_0^\pi dq\, \chi(q,T)\phi_1(q) = \frac{dC_1^{(0)}(T)}{dT} = -\frac{de^{(0)}(T)}{dT} = -c(T) , \tag{2.25}$$

with $c(T)$ being the specific heat per particle,

$$c(T) = \frac{J}{k_B T^2} \frac{1}{\cosh^2\left(\frac{J}{k_B T}\right)} . \tag{2.26}$$

Introduction of Eqs. (2.18), (2.25), and (2.26) into Eq. (2.23) yields

$$\varphi(t) = \frac{\psi(t)}{\psi(0)} , \tag{2.27}$$

where

$$\psi(t) = \int_0^\pi dq \, \frac{\sin^2 q}{(1-\gamma\cos q)^2} e^{-2\alpha(1-\gamma\cos q)t} . \tag{2.28}$$

The time dependence of $\varphi(t)$ has been extensively studied elsewhere,[5] and will not be discussed here. Let us only report for further reference that the average linear relaxation time $\tau(T)$, defined as

$$\tau(T) = \int_0^\infty dt \varphi(t) = \int_0^\pi dq \, g(q,T) \left[\lambda(q,T)\right]^{-1} , \tag{2.29}$$

is given by

$$\tau(T) = \frac{1}{4\alpha} \frac{\gamma^2}{(1-\gamma^2)\left[1-(1-\gamma^2)^{1/2}\right]} . \tag{2.30}$$

Next, suppose a process in which the temperature is changed in an arbitrary way, possibly including cooling and heating intervals, but starting from an equilibrium state. Thus, it follows from Eq. (2.17) that $a(q) = 0$ for all q, and Eq. (2.19) becomes

$$e(t) = e^{(0)}(T) - \int_0^t dt' \frac{dT'}{dt'} c(T') M(T,T') , \tag{2.31}$$

with a positive definite memory function

$$M(T,T') = \int_0^\pi dq \, g(q,T') e^{-\int_{t'}^{t} dt'' \lambda(q,T'')} . \tag{2.32}$$

Equation (2.31), together with Eq. (2.32), can be regarded as a generalization of Narayanaswami's equation for structural relaxation in glasses.[13,4] It cannot be cast in the form proposed by Narayanaswami, because the rates do not scale in a way allowing the introduction of an adimensional time scale valid for all of them; i.e., the system is not thermorheologically simple.

III. CONTINUOUS COOLING

Now we are going to study the continuous cooling of the system to $T = 0$ K, starting from equilibrium at high temperatures. It is convenient to describe the variation of the temperature of the heat bath in terms of the variable

$$\zeta = \exp\left(-\frac{4J}{k_B T}\right) . \tag{3.1}$$

Then, we write

$$\frac{d\zeta}{dt} = -\rho_c h(\zeta) , \tag{3.2}$$

where $\rho_c > 0$ is the cooling rate and $h(\zeta)$ is an adimensional positive function of ζ defining the cooling law. Of course, any cooling process given as a law of variation of the temperature can be expressed in the above form. More concretely, Eq. (3.2) is equivalent to

$$\frac{dT}{dt} = -r_c f(T) , \tag{3.3}$$

with

$$r_c = \frac{4J}{k_B}\rho_c \tag{3.4}$$

and

$$f(T) = \frac{h(\zeta)}{\zeta(\ln\zeta)^2} . \tag{3.5}$$

Our goal in this section is to obtain the dependence of the residual energy on the cooling process in the limit of slow cooling. The residual energy is defined as the excess of energy with respect to its equilibrium value in the limit $T \to 0$ K. The detailed calculations depend on the concrete cooling law being considered and, although straightforward, they are laborious and will not be given here. Instead, we present a physical argument that corresponds to the picture that emerges from the calculations and leads to the correct result, except for constant factors. The idea is that the relevant time scale is given by the average linear relaxation time $\tau(T)$. Thus, we define an adimensional time by

$$ds = -\tau^{-1}(T) dt . \tag{3.6}$$

The origin of s is taken such that $s = 0$ for $T = 0$ K ($\zeta = 0$), i.e.,

$$s = \int_t^{t_0} dt' \tau^{-1}(T') , \tag{3.7}$$

where t_0 is the time for which T (and ζ) vanishes. Therefore, s measures the number of effective relaxation times remaining before the system reaches $T = 0$ K. As long as $s \gg 1$, the system is still able to follow the energy equilibrium curve, but when s becomes of the order of unity, the energy will not have time to relax and it freezes.

The introduction of s also allows quite a precise definition of slow cooling. A cooling process starting at temperature T is said to be slow if the system has time to reach the equilibrium curve before becoming frozen, independently of its initial state. According to the above discussion this requires that $s(t=0) \gg 1$.

In terms of ζ we can rewrite Eq. (2.30) as

$$\tau(\zeta) = \frac{1}{16} \frac{\left(1+\zeta^{1/2}\right)^2 (1+\zeta)}{\zeta^{(\delta+1)/\delta}} , \tag{3.8}$$

where

$$\delta = \frac{4J}{\Delta} . \tag{3.9}$$

Taking into account that $\zeta \leq 1$, it is clear that the dominant temperature dependence of τ comes from the denominator of Eq. (3.8), especially at low temperatures. Therefore, we take

$$s = \frac{16}{\rho_c} \int_0^{\zeta} d\zeta' \zeta'^{\frac{\delta+1}{\delta}} \frac{1}{h(\zeta')} \, . \tag{3.10}$$

Suppose a cooling law of the form $h(\zeta) = \zeta^k$. The time t_0 required to reach $T = 0$ K starting from T depends on the value of k. For $k > 1$, $t_0 = \infty$, while for $k < 1$, $t_0 = \zeta^{1-k} [\rho_c(1-k)]^{-1}$. In the case $k = 1$, ζ decays exponentially in time. For these laws, it is

$$s = \frac{16}{\rho_c} \int_0^{\zeta} d\zeta' \zeta'^{\frac{\delta+1}{\delta} - k} \, . \tag{3.11}$$

If $k > \frac{2\delta+1}{\delta}$, s diverges for all values of ζ. That means that the residual energy tends to zero on the equilibrium curve for small values of ζ. In other words, there is no residual energy. On the other hand, if $k < \frac{2\delta+1}{\delta}$ we get

$$s = \frac{16m}{\rho_c} \zeta^{1/m} \, , \tag{3.12}$$

where

$$m = \frac{\delta}{(2-k)\delta + 1} \, , \tag{3.13}$$

and s goes to zero as the temperature decreases. The slow cooling condition is

$$\frac{\rho_c}{16m} \ll 1 \, . \tag{3.14}$$

In order to estimate the value ζ_f for which the energy becomes frozen, we put $s = 1$ in Eq. (3.12) and obtain

$$\zeta_f = \zeta(s=1) = \left(\frac{\rho_c}{16m} \right)^m \, . \tag{3.15}$$

The residual energy e_r will be roughly the equilibrium energy corresponding to ζ_f minus the equilibrium value at $T = 0$ K, i.e.,

$$e_r \sim \frac{2\zeta_f^{1/2}}{1 + \zeta_f^{1/2}} \, , \tag{3.16}$$

which for m not too small reduces to

$$e_r \sim 2 \left(\frac{\rho_c}{16m} \right)^{m/2} \, . \tag{3.17}$$

A cooling process linear in the temperature corresponds to $h(\zeta) = \zeta (\ln \zeta)^2$, and the residual energy in the slow cooling limit can be studied in a similar way. It is found that

$$s = \frac{16\, \zeta^{1/n}}{\rho_c (\ln \zeta)^2} \int_0^1 dx \frac{x^{1/\delta}}{\left(1 + \frac{\ln x}{\ln \zeta} \right)^2} \, , \tag{3.18}$$

where

$$n = \frac{\delta}{\delta + 1} \, . \tag{3.19}$$

If we suppose that the temperature is low in the freezing region, in the sense that $|\ln \zeta| \gg 1$, the integral in Eq. (3.18) can be approximated by n, and

$$s = \frac{16n}{\rho_c} \frac{\zeta^{1/n}}{(\ln \zeta)^2} \, . \tag{3.20}$$

Therefore,

$$\zeta_f = \left[\frac{n}{16} \rho_c (\ln \rho_c)^2 \right]^n \, , \tag{3.21}$$

and, using Eq. (3.16), one finds a dependence of the residual energy on the cooling rate of the form

$$e_r \sim \rho_c^{n/2} (\ln \rho_c)^n \, . \tag{3.22}$$

The slow cooling condition for linear cooling reads

$$\frac{n}{16} \rho_c (\ln \rho_c)^2 \ll 1 \, . \tag{3.23}$$

The above results show the important role played by the cooling law in determining, first, if there is a residual energy and, second, the cooling rate dependence of the residual energy in those cases where it is different from zero. In this context, we want to remark that the simple picture that the system freezes when the rate of cooling equals some average transition rate does not lead to the correct qualitative behavior, because it does not take into account the specific law that is being used to cool the system.[8] A similar, but not equivalent, argument to the one used here has been discussed by Cornell *et al.*[14]

As said above, for a given cooling law, one can easily carry out the asymptotic analysis of Eq. (2.31) in the limit of slow cooling. For instance, for $h(\zeta) = \zeta$ it is found that

$$e_r \sim \frac{2^{\frac{2+\delta}{1+\delta}}}{\pi} \frac{A(\delta)}{\delta^{n/2}} \Gamma\left(1 + \frac{n}{2} \right) \rho_c^{n/2} \, , \tag{3.24}$$

where n is given by Eq. (3.19), Γ is the gamma function, and

$$A(\delta) = \int_0^{\infty} du \frac{u^{1/2}}{(1+u)^2 \left(u + \frac{1}{1+\delta} \right)^{n/2}} \, . \tag{3.25}$$

An analogous expression to Eq. (3.24) has been previously derived by Schilling.[6] He obtained the same dependence on the cooling rate, but we believe that the prefactor in his expression is not correct.

Comparison of Eqs. (3.24) and (3.17) for $k = 1$ shows that both expressions give the same power law behavior. Even more, the naive argument leading to Eqs. (3.16) and (3.17) reproduces quite accurately the numerical values of e_r. As an example, we have plotted in Fig. 1 the residual energy as a function of the cooling rate for $\delta = 1$, using Eqs. (3.16) and (3.24). The exact result, obtained by numerical integration of Eq. (2.31), is also shown. The

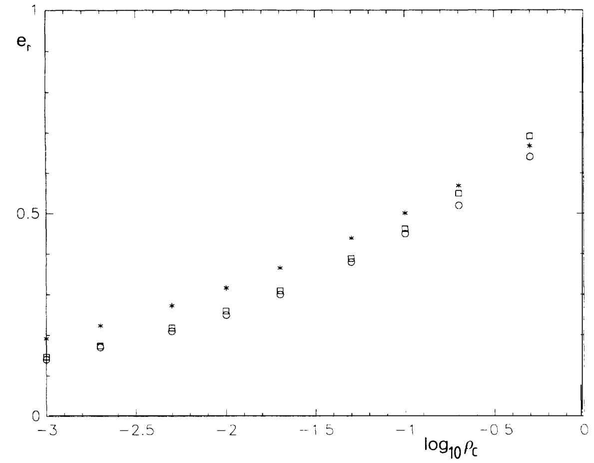

FIG. 1. Residual energy as a function of the cooling rate, for the cooling law $h(\zeta) = \zeta$, and $\delta = 1$. The circles are the numerical evaluation of the exact expression, Eq. (2.31), the squares correspond to Eq. (3.24), and the asterisks to the qualitative approximation given by Eq. (3.16).

agreement is surprising, if one takes into account the simplicity of the analysis leading to Eq. (3.16).

IV. THE LABORATORY GLASS TRANSITION

The reasoning in the previous section can be refined in order to get more detailed information about the way in which the system departs from equilibrium, and eventually becomes frozen, when it is being continuously cooled. Given the similarity that this kinetic freezing out process presents with the glass transition, we will refer to it as a laboratory glass transition.

The cooling process is described again by Eq. (3.2) and, therefore, the evolution of the energy will be given by Eq. (2.31), which we write in compact notation as

$$e(t) = e^{(0)}(\zeta) + \int_0^{\pi} dq\, e(q,t) \; ; \tag{4.1}$$

i.e., we decompose the deviation of the energy from equilibrium into the components associated to each of the modes. The explicit expression of $e(q,t)$ can be easily obtained by comparison of Eqs. (2.31) and (4.1), but it will not be needed here. Let us only notice that simple inspection of Eq. (2.31) shows that $e(q,t) > 0$, for all q. This implies that the system will separate from equilibrium in such a way that its energy at every temperature will be greater than the equilibrium value corresponding to that temperature.

The relaxation rate of mode q at temperature T is $\lambda(q,T)$, which is given by Eq. (2.12). Therefore, we can associate to each mode an adimensional time scale

$$s(q) = \int_t^{t_0} dt' \lambda(q,T') \; , \tag{4.2}$$

where t_0 has the same meaning as in Eq. (3.7). Our description of the freezing will be based on the idea that, at a given temperature T, those modes for which

$$s(q) < 1 \tag{4.3}$$

will have already deviated from equilibrium and will be approximately frozen. Since $\lambda(q,T)$ is an increasing function of q, during cooling we can associate to each temperature a characteristic value q_D, defined by the equation $s(q_D) = 1$. Modes with $q < q_D$ are frozen, while those with $q > q_D$ are still relaxing. Following the terminology introduced in the theory of amorphous semiconductors,[15] we will call q_D the demarcation mode. The notion of a demarcation energy was used by Dyre[16] to study the distribution of frozen in energies in a model for the glass transition.

The departure of the system from equilibrium will begin at that temperature T_1, or ζ_1, for which the demarcation mode coincides with the slowest relaxation mode, $q = 0$, i.e., $s(0) = 1$ or

$$\frac{4}{\rho_c}\int_0^{\zeta_1} d\zeta \frac{1}{h(\zeta)} \frac{\zeta^{(1+\delta)/\delta}}{1+\zeta} = 1 \; . \tag{4.4}$$

In an analogous way, the system will be fully frozen for $q_D = \pi$, i.e., at a temperature T_2, or ζ_2, given by

$$\frac{4}{\rho_c}\int_0^{\zeta_2} d\zeta \frac{1}{h(\zeta)} \frac{\zeta^{1/\delta}}{1+\zeta} = 1 \; . \tag{4.5}$$

To proceed further, let us consider a cooling law $h(\zeta) = \zeta^k$, as in Sec. III. Assuming that both ζ_1 and ζ_2 are small (slow cooling) we get

$$\zeta_1 = \left(\frac{\rho_c}{4m}\right)^m \tag{4.6}$$

for $k < \frac{2\delta+1}{\delta}$, and

$$\zeta_2 = \left(\frac{\rho_c}{4}\frac{1-m}{m}\right)^{\frac{m}{1-m}} \tag{4.7}$$

for $k < \frac{\delta+1}{\delta}$. Outside the indicated ranges of k, ζ_1 or ζ_2 verifying Eqs. (4.4) or (4.5), respectively, do not exist.

What happens for $(\delta+1)/\delta < k < (2\delta+1)/\delta$? We have seen that for this range of k the system separates from equilibrium and exhibits a nonvanishing residual energy. Nevertheless, the above results indicate that some of the modes still remain practically at equilibrium when reaching $T = 0$ K.

Figure 2 represents the evolution of the energy for $\delta = 1$, a cooling rate $\rho_c = 10^{-2}$, and the cooling law

$$h(\zeta) = \frac{\zeta}{1+\zeta} \; , \tag{4.8}$$

which has been chosen to get a greater efficiency in the numerical calculations. The cooling points have been obtained by numerical integration of the exact solution, Eq. (2.31). At low temperatures, $\zeta \ll 1$, the cooling law in Eq. (4.8) is equivalent to $h(\zeta) = \zeta$, and we can use the results derived above, with $k = 1$ ($m = \frac{\delta}{\delta+1}$). In fact, Eqs. (4.6) and (4.7) follow exactly from Eqs. (4.4) and

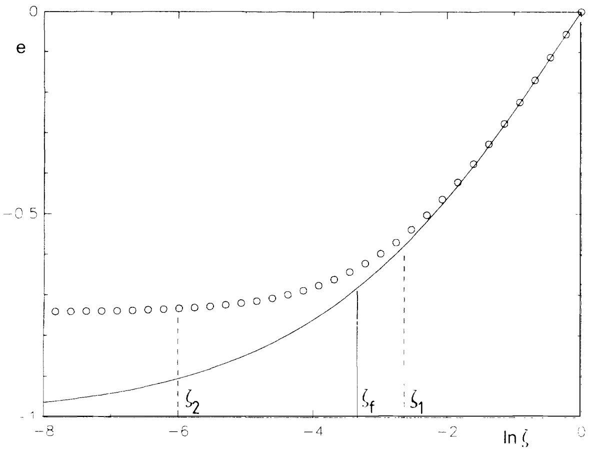

FIG. 2. Evolution of the energy in a cooling process, described by the cooling law given in Eq. (4.8), and $\rho_c = 10^{-2}$. The height of the extrinsic energy barrier corresponds to $\delta = 1$. The solid line is the equilibrium energy. The temperatures ζ_1, ζ_2, and ζ_f defined in the text are also indicated in the figure.

(4.5), without the slow cooling condition, for this particular law. The temperatures ζ_1 and ζ_2 obtained from Eqs. (4.6) and (4.7), respectively, and ζ_f, given by Eq. (3.15), are indicated in the figure. It is seen that the positions of the three values (ζ_1, ζ_2, and ζ_f) agree with the interpretation we have assigned to them. The freezing roughly begins around ζ_1 and ends around ζ_2. Besides, ζ_f gives a good estimation of the temperature at which the equilibrium energy equals the energy at $T = 0$ K. This is the so-called fictive temperature T_f in the glassy relaxation literature.[4] From Eqs. (3.15) and (3.21) it follows, for all the cooling laws we have studied, that

$$T_f \propto -\frac{4J}{k_B}\frac{1}{\ln \rho_c} . \tag{4.9}$$

The same behavior has been observed in real glasses.[4] Nevertheless, here it appears as a consequence of the Arrhenius form of the average relaxation time at low temperatures, while in real glasses the relaxation time often behaves like Vogel-Tamman-Fulcher laws.

A measure of the width of the laboratory glass transition is

$$\Delta T = T_1 - T_2 , \tag{4.10}$$

i.e., the temperature interval between the beginning and the end of the freezing process. Using Eqs. (4.6) and (4.7), we get for the cooling law given in Eq. (4.8),

$$\Delta T = -\frac{4J}{k_B}\left[\frac{1+\delta}{\delta \ln \frac{\rho_c(\delta+1)}{4\delta}} - \frac{1}{\delta \ln \frac{\rho_c}{4\delta}}\right] \simeq -\frac{4J}{k_B}\frac{1}{\ln \rho_c} . \tag{4.11}$$

The same dependence on $\ln \rho_c$ is easily derived for the other cooling laws we have been considering. Therefore, it is quite a general property of our model that the width of the transition depends inverse logarithmically on the cooling rate. The same kind of dependence has been experimentally found in real glasses.[4] It must be noticed that this behavior is implied directly from the fact that the quantities ζ_1 and ζ_2 behave like Boltzmann factors at low temperatures. In this sense, its origin is quite different from the similar dependence obtained for the fictive temperature.

From Eq. (4.11) it follows that

$$\lim_{\rho_c \to 0} \Delta T = 0 . \tag{4.12}$$

Nevertheless, this does not imply the existence in our model of an ideal glass transition at a finite temperature, at which all modes will be instantaneously frozen, because

$$\lim_{\rho_c \to 0} T_1 = \lim_{\rho_c \to 0} T_2 = \lim_{\rho_c \to 0} T_f = 0 , \tag{4.13}$$

and the transition temperature goes to zero as the cooling rate tends to vanish.

In conclusion, under continuous cooling the model exhibits many of the characteristic features of the glass transition, as is observed in real systems.

V. CONTINUOUS HEATING PROCESSES

Although heating processes starting from arbitrary initial conditions could be easily analyzed, we will restrict ourselves to continuous heating processes following a continuous cooling up to very low temperatures, formally $T = 0$ K. Besides, we will assume that the law of variation of the temperature in the heating process has the form

$$\frac{d\zeta}{dt} = \rho_h h(\zeta) , \tag{5.1}$$

where the heating law $h(\zeta)$ is the same as the law used in the previous cooling of the system. On the other hand, the heating rate ρ_h may differ from the cooling rate ρ_c. The evolution we will describe in this way corresponds to the often carried out experiments in which a glass former is cooled and reheated linearly, but with different rates. Equation (5.1) is equivalent to

$$\frac{dT}{dt} = r_h f(T) , \tag{5.2}$$

where

$$r_h = \frac{4J}{k_B}\rho_h \tag{5.3}$$

and $f(T)$ is the function defined in Eq. (3.5).

Since the heating process does not start from an equilibrium state, we ought to keep all the terms in Eq. (2.19), and we need the function $a(q)$, which is determined from the initial condition by means of Eq. (2.17). Nevertheless, we will not use this equation, but instead we will get

$a(q)$ in a more direct way, yielding the right expression. The initial value of the energy for the heating process is the energy at $T = 0$ K after a continuous cooling process, which started at equilibrium at a high temperature, formally $T = \infty$. This energy is given by Eq. (2.31) with $T = 0$ K and $T(t = 0) \to \infty$, i.e.,

$$e = e^{(0)}(0) - \int_0^\infty dT \int_0^\pi dq\, \chi(q,T)\phi_1(q) \times \exp\left[-\frac{1}{r_c}\int_0^T dT' \frac{\lambda(q,T')}{f(T')}\right] , \tag{5.4}$$

where we have used the definitions in Eqs. (3.4) and (3.5). If we now take into account that $e = -C_1$, comparison of Eq. (5.4) with Eq. (2.15) for $n = 1$ immediately leads to

$$a(q) = \int_0^\infty dT \chi(q,T) \exp\left[-\frac{1}{r_c}\int_0^T dT' \frac{\lambda(q,T')}{f(T')}\right] . \tag{5.5}$$

Now we can readily write an expression for the evolution of the energy in the heating process. Substitution of Eqs. (5.2) and (5.5) into Eq. (2.19) yields

$$e(T) = e_N(T) + e_p(T) , \tag{5.6}$$

with

$$e_N(T) = e^{(0)}(T) - \int_0^T dT' c(T') \int_0^\pi dq\, g(q,T') \exp\left[-\frac{1}{r_h}\int_{T'}^T dT'' \frac{\lambda(q,T'')}{f(T'')}\right] \tag{5.7}$$

and

$$e_p(T) = \int_0^\infty dT' c(T') \int_0^\pi dq\, g(q,T') \exp\left[-\frac{1}{r_c}\int_0^{T'} dT'' \frac{\lambda(q,T'')}{f(T'')}\right] \exp\left[-\frac{1}{r_h}\int_0^T dT' \frac{\lambda(q,T')}{f(T')}\right] . \tag{5.8}$$

The contribution $e_p(T)$ contains all the information about the initial conditions for the heating process or, equivalently, about the previous cooling process. On the other hand, $e_N(T)$ only depends on the specific heating law and rate being used. From the expression of $e_p(T)$ it follows that

$$e_p(T) > 0 , \tag{5.9}$$

for all T and, in particular, $e_p(0) = e_r$, the residual energy of the cooling process. For the component $e_N(T)$ it is seen that

$$e_N(T) < e^{(0)}(T) , \tag{5.10}$$

for $T \neq 0$ K, and

$$e_N(0) = e^{(0)}(0) . \tag{5.11}$$

Besides, for heating processes requiring an infinite time to reach $T = \infty$, one has

$$\frac{1}{r_h}\int_{T'}^\infty dT'' \frac{\lambda(q,T'')}{f(T'')} = \int_{t'}^\infty dt'' \lambda(q,t'') \to \infty \tag{5.12}$$

and, therefore,

$$\lim_{T\to\infty} e_N(T) = \lim_{T\to\infty} e^{(0)}(T) . \tag{5.13}$$

In addition, a simple calculation shows that

$$\lim_{T\to\infty} \frac{e_p(T)}{|e_N(T) - e^{(0)}(T)|} = 0 , \tag{5.14}$$

which implies

$$e(T) \sim e_N(T) < e^{(0)}(T) , \tag{5.15}$$

at high enough temperatures.

Thus, three different regimes can be distinguished in the time evolution of the energy under continuous heating. In the initial regime, $e(T)$ depends strongly on the initial conditions and all the contributions in Eq. (5.6) are relevant. The influence of the initial conditions gradually decreases and the system approaches a regime where the energy is completely determined by the heating process. This regime is described by the term $e_N(T)$, which is smaller than the equilibrium energy $e^{(0)}(T)$. We will refer to $e_N(T)$ as the normal energy for the given heating process. Finally, if the heating is not too fast, $e_N(T)$ tends asymptotically to the equilibrium curve $e^{(0)}(T)$. The existence of a normal energy curve follows from the fact that there is a normal solution for the master equation. This is not a peculiarity of the model we are dealing with, but it has been proved for a quite general kind of systems described by master equations with time-dependent transition rates.[7]

By putting together the cooling and heating processes, we arrive to the following description of the evolution of the energy. In the cooling process, the energy of the system becomes larger than the equilibrium one, and it gets eventually frozen. When the system is reheated, the energy tends to approach the normal curve. This requires the crossing of the equilibrium curve, because it lies above the normal one. In conclusion, the energy describes a cycle of hysteresis, similarly to what happens in real glasses. In Fig. 3 two cycles, corresponding to different heating rates and the same rate of cooling, are

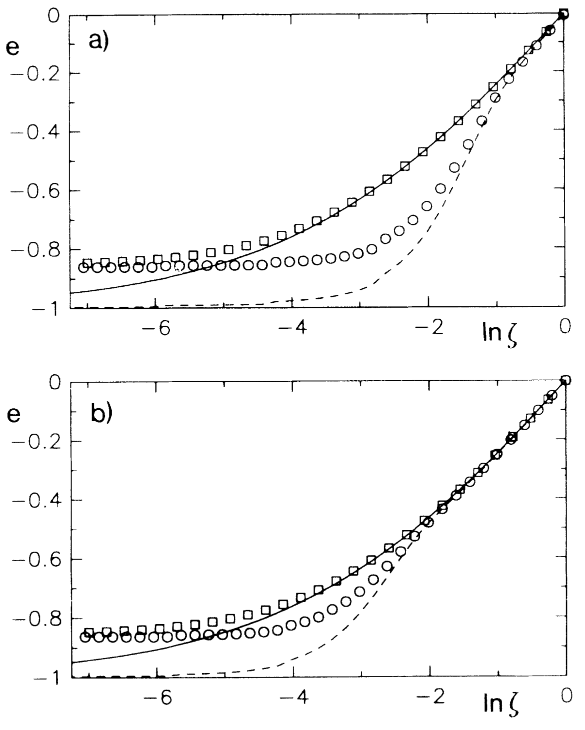

FIG. 3. Two cycles of hysteresis shown by the energy, when the system is cooled and reheated. In all the processes, the law of variation of the temperature is that of Eq. (4.8), and $\delta = 1$. In case (a), $\rho_c = 10^{-3}$ and $\rho_h = 10^{-1}$. In case (b), $\rho_c = 10^{-3}$ and $\rho_h = 10^{-2}$. The solid line is the equilibrium curve, and the dashed line is the normal solution corresponding to the heating process in each case.

presented. They will be discussed in more detail later on.

In the high temperature region, defined by the condition

$$r_h \frac{f(T)}{T} \left[\lambda(q,T)\right]^{-1} \ll 1 , \tag{5.16}$$

for all q, a Laplace analysis of Eq. (5.7) leads to

$$e_N(T) \simeq e^{(0)}(T) - r_h f(T) c(T) \tau(T) , \tag{5.17}$$

where $\tau(T)$ is the linear relaxation time defined in Eq. (2.29). In fact, the structure of Eq. (5.17) is not a particular property of the model considered here, but it is a very general result that can be directly derived from the master equation by means of Hilbert's method.[17] Using the explicit expressions of c, Eq. (2.26), and τ, Eq. (2.30), we can rewrite Eq. (5.17) as

$$e_N(\zeta) = -\frac{1-\zeta^{1/2}}{1+\zeta^{1/2}} - \frac{1}{16}\rho_h \frac{\zeta^{-1/2}(1+\zeta)}{\zeta^{(\delta+1)/\delta}} h(\zeta) . \tag{5.18}$$

Let us consider a heating law for which the temperature $T = \infty$ is reached in a finite time. Then, the equality in Eq. (5.12) does not apply and neither does Eq. (5.13). As an example, consider the law given by Eq. (4.8). Application of Eq. (5.18) yields

$$e_N(\zeta) = -\frac{1-\zeta^{1/2}}{1+\zeta^{1/2}} - \frac{1}{16}\rho_h \frac{\zeta^{1/2}}{\zeta^{(\delta+1)/\delta}} , \tag{5.19}$$

and, in the limit $T \to \infty$ $(\zeta \to 1)$,

$$e_N - e^{(0)} \to -\frac{\rho_h}{16} . \tag{5.20}$$

Thus, although the normal and the equilibrium curve do not coincide for $T \to \infty$, their difference turns out to be proportional to the heating rate. Therefore, for small enough heating rates, all the above discussion on the presence of hysteresis effects will remain valid, although the condition in Eq. (5.13) is not verified. In fact, for $\rho_h = 0.1$, which is not very small, the difference between the normal and the equilibrium energies in the limit $T \to \infty$ $(e^{(0)} = 0)$ is smaller than 0.01, for the concrete heating law we are considering.

Equation (5.18) has another interesting consequence. Since the energy of the system in the heating process approaches the normal curve, it follows that the hysteresis effect, measured by the amount that the energy surpasses the equilibrium value, will be an increasing function of the heating rate. This qualitative behavior has also been observed in real glasses.

To illustrate the results obtained in this section we present in Fig. 3 two hysteresis cycles obtained by numerical integration of Eq. (2.31). The system was in both cases cooled and reheated with the law given by Eq. (4.8). In the first case, the cooling rate was $\rho_c = 10^{-3}$ and the heating rate $\rho_h = 10^{-1}$, while in the second one, $\rho_c = 10^{-3}$ and $\rho_h = 10^{-2}$. The equilibrium energy and the normal curves corresponding to each of the heating processes are also shown in the figure. It is clearly seen that the curves describing heating tend to the normal curves, and not towards the equilibrium one. As discussed above, this is the origin of the hysteresis shown by the energy. Besides, the hysteresis effect is stronger for $\rho_h = 10^{-1}$ than for $\rho_h = 10^{-2}$, as predicted by Eq. (5.18).

VI. APPARENT SPECIFIC HEAT

An interesting property, often used to characterize cooling and heating processes, is the apparent specific heat $c_a(T)$, defined as

$$c_a(T) = \frac{de(T)}{dT} , \tag{6.1}$$

where the derivative is computed along the actual evolution of the system in the cooling or heating process. Therefore, $c_a(T)$ depends not only on the temperature but, in general, also on the process being considered. This must be kept in mind although it has not been made explicit in our notation. Only when the system remains always in equilibrium does $c_a(T)$ coincide with the true specific heat $c(T) = de^{(0)}/dT$. In the following, we will study cooling and heating processes separately.

A. Cooling processes

For continuous cooling processes we can obtain $c_a(T)$ by differentiation of Eq. (2.31). The result is

$$c_a(T) = \frac{1}{r_c f(T)} \int_T^\infty dT' c(T') \int_0^\pi dq\, g(q,T')\lambda(q,T) \times \exp\left[-\frac{1}{r_c} \int_T^{T'} dT'' \frac{\lambda(q,T'')}{f(T'')} \right] , \qquad (6.2)$$

which shows that $c_a(T)$ is positive definite. This is also in agreement with experiments in real glasses, where negative specific heat only shows up in heating processes and at low temperatures. Another experimental feature in real glasses is that

$$c(T) \geq c_a(T) , \qquad (6.3)$$

for all T; i.e., the separation between the actual energy of the system and the equilibrium value increases monotonously during the cooling process. We have investigated the validity of Eq. (6.3) in our model by numerically solving Eq. (6.2), and the conclusion we have reached is that it depends on the cooling law. An example where Eq. (6.3) is verified is given in Fig. 4, which corresponds to the cooling law in Eq. (4.8). We have not been able to derive an exact general criterion determining the cooling laws for which Eq. (6.3) applies. Therefore, we will restrict ourselves to present here some partial arguments, although we want to point out that they have turned out to be correct in all the cases we have checked numerically.

At high temperatures, where $e(T)$ and $e^{(0)}(T)$ are close, we can approximate $e(T)$ by using Laplace's method, obtaining [compare with Eq. (5.17)]

$$e(T) \simeq e^{(0)}(T) + r_c f(T) c(T) \tau(T) \qquad (6.4)$$

or

$$e(\zeta) \simeq e^{(0)}(\zeta) + \frac{1}{16}\rho_c \frac{\zeta^{-1/2}(1+\zeta)}{\zeta^{(\delta+1)/\delta}} h(\zeta) . \qquad (6.5)$$

For cooling laws of the form $h(\zeta) = \zeta^k$ this expression reduces to

$$e(\zeta) - e^{(0)}(\zeta) \simeq \frac{1}{16}\rho_c \frac{1+\zeta}{\zeta^{\frac{1}{\delta}+\frac{3}{2}-k}} . \qquad (6.6)$$

For $k < \frac{\delta+1}{\delta}$, the right hand side of Eq. (6.6) is a decreasing function of the temperature and, therefore, Eq. (6.3) is verified at high temperatures. If we now go to the low temperature region, we know that the energy of the system becomes frozen and

$$e(\zeta) - e^{(0)}(\zeta) \to e_r \sim 2\left(\frac{\rho_c}{16m}\right)^{\frac{m}{2}} , \qquad (6.7)$$

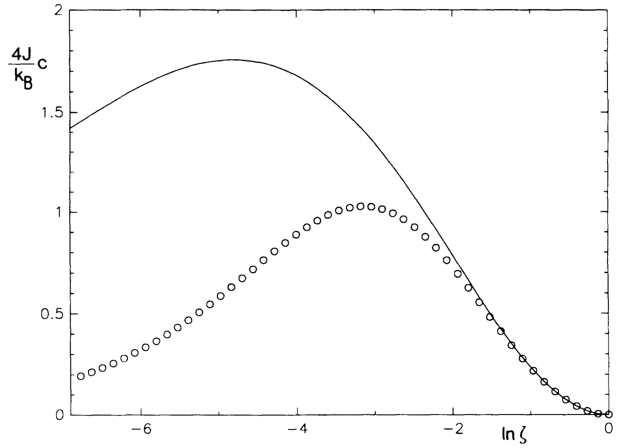

FIG. 4. Apparent specific heat, measured in a cooling process, with a law given by Eq. (4.8), $\rho_c = 10^{-2}$, and $\delta = 1$. The solid line is the true specific heat.

where we have used Eq. (3.17). For slow cooling, $\rho_c \ll 1$, and the values of k indicated above, $\frac{m}{2} < 1$, the separation of energies at low temperatures is greater than in the high temperature region, where we have proved that it increases as the temperature decreases. It seems then plausible to expect that for cooling laws of the form $h(\zeta) = \zeta^k$ with $k < \frac{\delta+1}{\delta}$ the relation given by Eq. (6.3) is verified. This range of values of k is precisely that for which all the modes of the system become frozen during the cooling process, as we saw in Sec. IV.

If $k > \frac{\delta+1}{\delta}$, the right hand side of Eq. (6.6) is not a monotonous decreasing function of ζ, and there is no reason to expect Eq. (6.3) to hold. In fact, it is not true for some cases we have studied numerically. For a cooling law linear in the temperature, it is trivial to check that the two given criteria, corresponding to high and low temperatures, are verified and the numerical results show that Eq. (6.3) also holds in this case.

It is interesting to remark that, in our model, cooling processes leading to a nonvanishing residual energy, but in which Eq. (6.3) is not verified, are possible. These processes are characterized by slow cooling laws, in particular slower than the linear one.

B. Heating processes

We consider again a heating process from $T = 0$ K following a cooling process with the same law but, in general, with different rate. The apparent specific heat c'_a is obtained by taking temperature derivative in Eq. (5.6):

$$c'_a(T) = c'_N(T) + c'_p(T) , \qquad (6.8)$$

where

$$c_N'(T) = \frac{de_N(T)}{dT} = \frac{1}{r_h f(T)} \int_0^T dT' c(T') \int_0^\pi dq\, g(q,T')\lambda(q,T) \exp\left[-\frac{1}{r_h}\int_{T'}^T dT'' \frac{\lambda(q,T'')}{f(T'')}\right] \tag{6.9}$$

and

$$c_p'(T) = \frac{de_p(T)}{dT} = -\frac{1}{r_h f(T)} \int_0^\infty dT' c(T') \int_0^\pi dq\, g(q,T')\lambda(q,T) \times \exp\left[-\frac{1}{r_c}\int_0^{T'} dT'' \frac{\lambda(q,T'')}{f(T'')}\right] \exp\left[-\frac{1}{r_h}\int_0^T dT' \frac{\lambda(q,T')}{f(T')}\right] . \tag{6.10}$$

Simple inspection of the above equations leads to a series of relations. First, we have

$$c_N'(T) > 0 , \tag{6.11}$$

for $T > 0$,

$$c_N'(0) = 0 , \tag{6.12}$$

and

$$c_p'(T) < 0 , \tag{6.13}$$

for all T. From here,

$$c_a'(T) \leq c_N'(T) , \tag{6.14}$$

being, in particular,

$$c_a'(0) < 0 ; \tag{6.15}$$

i.e., the apparent specific heat at $T = 0$ K is negative.

Besides, from Eq. (6.10) it follows that

$$\lim_{r_c \to 0} c_p'(T) = \lim_{r_c \to 0} [c_a'(T) - c_N'(T)] = 0 \tag{6.16}$$

and

$$\frac{d}{dr_c} |c_p'(T)| = \frac{d}{dr_c} |c_a'(T) - c_N'(T)| > 0 . \tag{6.17}$$

In Fig. 5 we present the evolution of the relative apparent specific heat, $c_a' - c$, as a function of the temperature, again for the heating law of Eq. (4.8) and a heating rate $\rho_h = 10^{-2}$. The two curves correspond to different values of the cooling rate of the previous process, namely, $\rho_c = 5 \times 10^{-4}$ and $\rho_c = 5 \times 10^{-1}$, respectively. The cooling law was in both cases the same as in the heating process. The relative apparent specific heat along the normal curve, $c_N' - c$, is also plotted. Once again, the obtained behavior is similar to what happens in real glasses. The specific heat presents a maximum whose height increases as the cooling rate of the previous process decreases. The existence of this maximum appears in our model as a purely dynamical phenomenon, and it is directly associated to the hysteresis effects. To see this clearer, let us denote by T_0 the temperature for which

$$e(T_0) = e^{(0)}(T_0), \;\; c_a'(T_0) < c(T_0) . \tag{6.18}$$

The existence of such a temperature is guaranteed by the relative positions of the cooling curve, the equilibrium curve, and the normal curve, and was discussed in the previous sections. Taking into account that $e(T \to \infty) = e^{(0)}(T \to \infty)$, we have

$$\int_{T_0}^\infty dT' \, [c_a'(T') - c(T')] = 0 . \tag{6.19}$$

Since Eq. (6.18) implies that the integrand is negative at T_0, it follows that there must be a temperature region where $c_a'(T) > c(T)$. On the other hand, $c_a'(T) \sim c(T)$ for $T \to \infty$, and the conclusion is that continuity of $c_a'(T) - c(T)$ requires that it presents a maximum at a temperature greater than T_0.

The difference $c_a'(T) - c(T)$ is bounded by $c_N'(T) - c(T)$ for all T and, consequently, the maximum of the relative apparent specific heat will be bounded by its value along the normal curve. For $r_c \to 0$, the curves $e(T)$ and $e_N(T)$ tend to coincide, and the maximum of the relative spe-

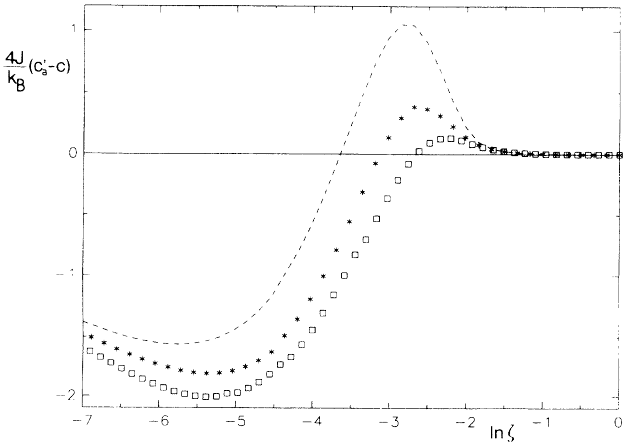

FIG. 5. Relative apparent specific heat, measured in a heating process following a cooling of the system up to $T = 0$ K. In all the processes, the law of variation of the temperature is given by Eq. (4.8), $\rho_h = 10^{-2}$, and $\delta = 1$. The squares correspond to a previous cooling rate $\rho_c = 5 \times 10^{-1}$, and the asterisks to $\rho_c = 5 \times 10^{-4}$. The dashed line is the apparent specific heat measured along the normal curve.

cific heat takes the highest possible value. Besides, the temperature at which it appears will be determined by the maximum of $c'_N(T)-c(T)$, which does not depend on r_c. In this context, we see that the experimentally used definition of the glass transition temperature as that for which the specific heat under continuous heating presents a maximum in the limit of slow cooling when preparing the glass is a sensible one. In our model, it corresponds to heating the system along the normal curve. We remark that, in many practical situations, the true specific heat can be considered as a constant in the glass transition region.[4]

Let us come back to Eq. (6.10). For a fixed value of r_h, the term $c'_p(T)$ will be more important the greater the value of r_c is. Using Eqs. (6.9) and (6.10), one concludes that the width of the initial heating region presenting a negative apparent specific heat will increase with the value of r_c. Conversely, for fixed r_c, the relevance of the negative specific heat region increases as r_h decreases.

The apparent specific heat measured when heating the system in the same way after two different cooling processes is shown in Fig. 6. In all the processes the law was the one in Eq. (4.8). The cooling rate ρ_c was 5×10^{-1} and 5×10^{-4} in each of the cases, while $\rho_h = 10^{-2}$ in both of them. It is seen that, in accordance with the above discussion, the largest value of r_c produces the most pronounced negative region and the shortest maximum.

The position and height of the maximum on the curve of the relative specific heat are two important quantities to characterize heating processes. An exact calculation, using Eqs. (6.8)–(6.10), appears as a formidable task and the expressions should not be useful due to their complexity. We present a physical argument, valid in some asymptotic limit, that provides information about the influence of the heating law and the heating rate. Consider the specific heat along the normal curve. For $T = 0$ K we know that $c'_N = 0$, Eq. (6.12). Physically, it seems clear that there is an initial temperature region where the system is practically frozen, and the normal apparent specific heat is very small. If, in the analogy with Eq. (3.7), we define

$$s' = \frac{1}{\rho_h}\int_0^{\zeta} d\zeta' \frac{1}{h(\zeta')\tau(\zeta')} , \tag{6.20}$$

this region can be characterized by

$$s' \ll 1 . \tag{6.21}$$

In the same way, the high temperature region is defined by $s' \gg 1$, and it is in this region where the normal specific heat will be given by the temperature derivative of Eq. (5.18). Let us consider a heating law $h(\zeta) = \zeta^k$. Thus, for $s' \gg 1$,

$$e_N(\zeta) = -\frac{1-\zeta^{1/2}}{1+\zeta^{1/2}} - \frac{1}{16}\rho_h \frac{1+\zeta}{\zeta^{\frac{3}{2}+\frac{1}{\delta}-k}} . \tag{6.22}$$

If we restrict ourselves to laws with $k < \frac{\delta+1}{\delta}$, it follows from this expression that $c'_N(\zeta)-c(\zeta) > 0$ in this region, while $c'_N(\zeta)-c(\zeta) \sim -c(\zeta) < 0$ at low temperatures. Besides, differentiation of Eq. (6.22) shows that, for $s' \gg 1$, $c'_N(\zeta)-c(\zeta)$ is a decreasing function of the temperature. We conclude that $c'_N(\zeta) - c(\zeta)$ presents its maximum in the intermediate region, i.e., for $s' = O(1)$ or, equivalently, for $\bar{\zeta}$ such that

$$\frac{1}{\rho_h}\int_0^{\bar{\zeta}} d\zeta' \frac{1}{h(\zeta')\tau(\zeta')} = O(1) . \tag{6.23}$$

Using now Eq. (3.8), and the definition of m, Eq. (3.13), one gets to lowest order in ρ_h

$$\bar{\zeta} \sim \left(\frac{\rho_h}{16m}\right)^m , \tag{6.24}$$

which gives an expression for the position of the maximum. To get an estimation for the value of the specific heat there, we use Eq. (6.22) with the result

$$c'_N(\bar{\zeta}) - c(\bar{\zeta}) \sim \rho_h^{\frac{1}{2}\frac{\delta}{(2-k)\delta+1}} (\ln\rho_h)^2 . \tag{6.25}$$

Of course, the maximum of the specific heat actually observed in a cycle will also depend on the cooling rate, but we have seen that the normal part of the specific heat provides an upper bound for it.

It is interesting to notice that the values of k for which our analysis has been limited are precisely those corresponding to cooling laws freezing all the modes of the system, as discussed in Sec. IV. Furthermore, if we use Eq. (6.25) to get an approximation for the height of the maximum of the relative specific heat on the normal curve, we obtain a nonmonotonous function of the heating rate. In fact, from Eq. (6.25) it follows that $c'_N(\bar{\zeta}) - c(\bar{\zeta})$ is bounded by its value at

$$\bar{\rho}_h = \exp\left[-4\frac{(2-k)\delta+1}{\delta}\right] . \tag{6.26}$$

In Fig. 7 the relative specific heat along the normal curve is plotted, again for the heating law of Eq. (4.8) and $\delta =$

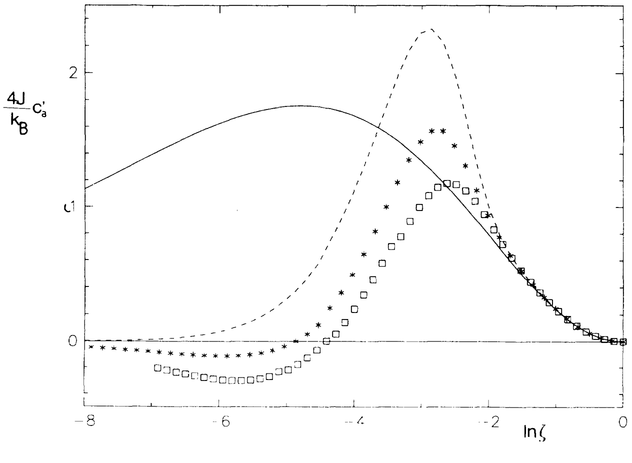

FIG. 6. The same as in Fig. 5, but now the actual values of the specific heat (without subtracting the equilibrium value) are shown. The solid line is the true specific heat.

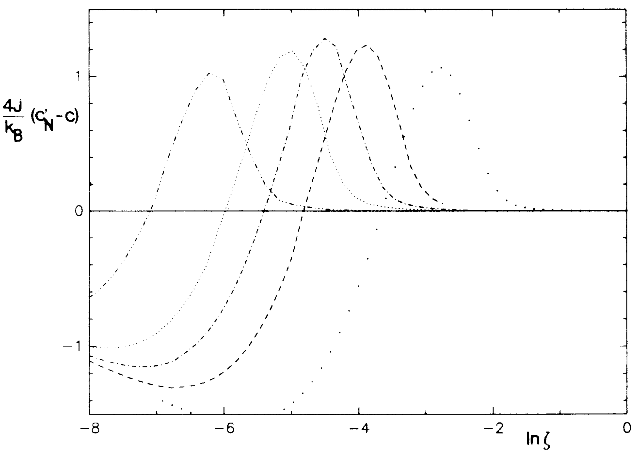

FIG. 7. Relative apparent specific heat along the normal curve, for the heating law given by Eq. (4.8), and $\delta = 1$. The heating rates are, from left to right, $\rho_h = 10^{-5}$, 10^{-4}, 3×10^{-4}, 10^{-3}, and 10^{-2}.

1, for five different values of the heating rate. The height of the maximum is bounded by its value for $\rho_h = 3\times10^{-4}$, which is exactly what we get by particularizing Eq. (6.26) for $k = 1$ and $\delta = 1$. We insist that the law in Eq. (4.8) is equivalent to $h(\zeta) = \zeta$ at low temperatures [$\zeta \ll 1$ if $\rho_h/(16m) \ll 1$].

A linear law, $h(\zeta) = \zeta(\ln\zeta)^2$, can be studied in a similar way, obtaining

$$\bar{\zeta} \sim \left[\frac{\delta}{16(1+\delta)}\rho_h(\ln\rho_h)^2\right]^{\frac{\delta}{1+\delta}} \tag{6.27}$$

and

$$c'_N(\bar{\zeta}) - c(\bar{\zeta}) \sim \rho_h^{\frac{\delta}{2(1+\delta)}}(\ln\rho_h)^{\frac{3\delta+2}{1+\delta}} \tag{6.28}$$

Comparison of Eqs. (6.25) and (6.28) shows that, for a given value of δ, the maximum of the relative specific heat is larger for the linear law than for $h(\zeta) = \zeta$. Besides, if Eq. (6.28) is a good approximation, the maximum is bounded by its value at

$$\bar{\rho_h} = \exp\left[-2\frac{3\delta+2}{\delta}\right] . \tag{6.29}$$

It has been recently reported[18] that the height of the maximum of the specific heat in some metallic glasses, like $Pd_{40}Ni_{40}P_{19}Si_1$, measured in thermal cycles through the glass transition with $r_h = r_c$, increases as the rate decreases. This result, found valid over three decades of the rate, cannot be directly compared with ours, which refers to the normal curve. Nevertheless, both are compatible, since our model presents a range of values of ρ_h, concretely $\rho_h > \bar{\rho_h}$, for which the height of the maximum on the normal curve is a monotonously decreasing function of the heating rate.

VII. CONCLUSIONS

We have studied in detail the evolution of the one-dimensional Ising model under Glauber dynamics with an extrinsic energy barrier, submitted to continuous cooling and heating processes. For slow cooling up to very low temperatures, we have derived the expression of the residual energy for several cooling programs. Its functional dependence on the cooling rate is influenced by the cooling law. The simple argument that the system freezes when the rate of cooling equals the average transition rate, or the lowest relaxation rate associated with the modes, does not lead in general to the correct behavior. Instead, the freezing takes place when the average number of transitions that the system would experience until reaching $T = 0$ K is of the order of unity. This criterion has also been applied to each of the individual modes of the system, and allowed to study the width of the transition from the equilibrium curve to the frozen state. For usual cooling laws, the width decreases as the inverse of the logarithm of the cooling rate.

For continuous heating processes, we have shown the crucial role played by a special solution of the master equation, the normal solution, which is completely determined by the law of variation of the temperature. It is the normal solution that essentially fixes the behavior of the system during heating. In the limit of high temperatures, and for not too fast heating processes, the normal curve approaches the equilibrium one. The hysteresis effects when the system is cooled and reheated, and also the overshoot of the apparent heat capacity above the equilibrium value in the reheating process, follow from the fact that the equilibrium energy at every temperature is larger than the energy of the normal solution at the same temperature. Another interesting result is the presence of a low temperature region where the system shows a negative apparent heat capacity in the heating process.

The properties of the normal solution permit one to analyze the influence of the cooling and heating rates on the maximum of the heat capacity, and to compare the effects of different cooling and heating laws. In fact, for a given experiment, the normal solution contains the information that is independent from the initial conditions.

All the behaviors we have found in our model are strikingly analogous to the phenomenology of real glasses. Given the generality of the arguments we have used, the same is expected to happen for a wide class of models, mainly for those described by means of master equations. This clearly opens the possibility of being able to derive general laws starting from first principles. In particular, the introduction of the normal solution for heating processes represents a step forward in this direction.

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Partial support from the Dirección General de Investigación Científica y Técnica (Spain) through Grant No. PB92-0683 is gratefully acknowledged.

APPENDIX

Here we sketch the derivation of Eq. (2.11). Consider the eigenvalue problem (we use matrix notation)

$$L\phi = -\lambda\phi \,, \tag{A1}$$

where

$$L_{nn'} = -2\alpha\delta_{nn'} + \alpha\gamma\left(\delta_{n-1,n'} + \delta_{n+1,n'}\right) \tag{A2}$$

for $n \geq 1$, $n' \geq 0$, and

$$L_{0n'} = 0 \,. \tag{A3}$$

If we restrict ourselves to eigenfunctions having all the components bounded, the standard procedure leads to the continuous set of eigenvalues

$$\lambda(q,T) = 2\alpha(T)\left[1 - \gamma(T)\cos q\right] \,, \tag{A4}$$

with $0 \leq q \leq \pi$. The eigenfunction corresponding to $\lambda(q,T)$ is

$$\phi_n(q) = \left(\frac{2}{\pi}\right)^{1/2} \sin nq \,, \tag{A5}$$

which does not depend on the temperature. For $n \neq 0$ and $n' \neq 0$, we have

$$\int_0^\pi dq\, \phi_n(q)\phi_{n'}(q) = \delta_{nn'} \,, \tag{A6}$$

while

$$\phi_0(q) = 0 \,. \tag{A7}$$

Equations (A6) and (A7) prove the completeness of the functions $\phi_n(q)$ for all matrices u having $u_0 = 0$. Let us take

$$u = C(t) - C^{(0)}(T) \,. \tag{A8}$$

We can write

$$C_n(t) = C_n^{(0)}(T) + \int_0^\pi dq\, a(q,t)\phi_n(q) \,, \tag{A9}$$

with

$$a(q,t) = \sum_n \left[C_n(t) - C_n^{(0)}(T)\right]\phi_n(q) \,. \tag{A10}$$

The time derivative of Eq. (A9) gives

$$\dot{C}_n(t) = \dot{C}_n^{(0)}(T) + \int_0^\pi dq\, \dot{a}(q,t)\phi_n(q) \,, \tag{A11}$$

and substitution of Eqs. (A9) and (A11) into Eq. (2.8) yields (for $n \geq 1$)

$$\dot{C}_n^{(0)}(T) + \int_0^\pi dq\, \dot{a}(q,t)\phi_n(q) = -\int_0^\pi dq\, a(q,t)\lambda(q,T)\phi_n(q) \,. \tag{A12}$$

Since $\dot{C}_0^{(0)} = 0$, we can formally expand

$$\dot{C}_n^{(0)}(T) = \frac{dC_n^{(0)}(T)}{dT}\frac{dT}{dt} = \int_0^\pi dq\, \chi(q,T)\phi_n(q)\frac{dT}{dt} \,, \tag{A13}$$

where $\chi(q,T)$ is given by Eq. (2.16). Introduction of Eq. (A13) into (A12), and use of the relation

$$\sum_n \phi_n(q)\phi_n(q') = \delta(q-q') \tag{A14}$$

leads to

$$\dot{a}(q,t) + \lambda(q,T)a(q,t) = -\chi(q,T)\frac{dT}{dt} \,. \tag{A15}$$

The solution of this equation is

$$a(q,t) = a(q,0)\exp\left[-\int_0^t dt'\lambda(q,T')\right] - \int_0^t dt'\frac{dT'}{dt'}\chi(q,T')\exp\left[-\int_{t'}^t dt''\lambda(q,T'')\right] \,, \tag{A16}$$

which substituted into Eq. (A9) leads to the desired result, Eq. (2.11).

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