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Thermodynamic picture of the glassy state gained from exactly solvable models

Th. M. Nieuwenhuizen
Department of Physics and Astronomy, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

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A picture for thermodynamics of the glassy state was introduced recently by us [Phys. Rev. Lett. **79**, 1317 (1997); **80**, 5580 (1998)]. It starts by assuming that one extra parameter, the effective temperature, is needed to describe the glassy state. This approach connects responses of macroscopic observables to a field change with their temporal fluctuations, and with the fluctuation-dissipation relation, in a generalized, nonequilibrium way. Similar universal relations do not hold between energy fluctuations and the specific heat. In the present paper, the underlying arguments are discussed in greater length. The main part of the paper involves details of the exact dynamical solution of two simple models introduced recently: uncoupled harmonic oscillators subject to parallel Monte Carlo dynamics, and independent spherical spins in a random field with such dynamics. At low temperature, the relaxation time of both models diverges as an Arrhenius law, which causes glassy behavior in typical situations. In the glassy regime, we are able to verify the above-mentioned relations for the thermodynamics of the glassy state. In the course of the analysis, it is argued that stretched exponential behavior is not a fundamental property of the glassy state, though it may be useful for fitting in a limited parameter regime.

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I. INTRODUCTION

Thermodynamics is an old but very powerful subject. It applies to a wide variety of systems ranging from ideal gases to crystals and black holes. Important contributions to its development were made by Carnot, Clausius, Kelvin, and Boltzmann. Equilibrium thermodynamics, better called ''thermostatics,'' is a well understood subject, and applied every day in many fields of science. The work of Gibbs showed its tremendous generality via its relation to statistical physics (i.e., partition sums). We shall explain, however, that precisely this success has been a barrier in the way of the systems of our interest, namely glasses.

Nonequilibrium thermodynamics for systems close to equilibrium was worked out in the first half of this century. Typical applications are systems with heat flows, electrical currents, and chemical reactions. The basic assumption is the presence of local thermodynamical equilibrium, and the basic task is to calculate the entropy production. Important contributions to this field were made by de Donder, Prigogine, de Groot, and Mazur.

Nonequilibrium thermodynamics for systems far from equilibrium has long been a field of confusion. A typical application is window glass. Such a system is far from equilibrium: a cubic micron of glass is neither a crystal nor an ordinary undercooled liquid. It is an undercooled liquid that, in the glass-formation process, has fallen out of its own metastable equilibrium. The glassy state is inherently a nonequilibrium state: a substance that is a glass in daily life (time scale of years) would behave as a liquid on geological time scales. If each 500 years a picture would be taken of a window glass, then the movie composed of these pictures would look very much like a movie of a soap film.

Until our recent works on this field, the general consensus reached after more than half a century of research was that *thermodynamics does not work for glasses, because there is no equilibrium*. Even before going into any detail, it is clear that this conclusion itself is confusing, because *thermodynamics should also apply outside equilibrium*. Inspired by the success of Gibbsian theory, the whole nonequilibrium part of thermodynamics had been forgotten. The correct formulation should of course have been that *equilibrium thermodynamics does not work for glasses, because there is no equilibrium*, surely a less surprising and nonembarrassing statement. (This history shows once more how regretful it is that equilibrium thermodynamics did not become known under its most proper name, ''thermostatics.'')

The negative conclusion about the applicability of thermodynamics was mainly based on the failure to understand the Ehrenfest relations and the Prigogine-Defay ratio. It should be kept in mind that, so far, the approaches leaned very much on equilibrium ideas. Well known examples are the 1958 Gibbs-DiMarzio [1] and the 1965 Adam-Gibbs [2] papers, while a 1981 paper by DiMarzio has the title ''equilibrium theory of glasses'' and a subsection ''an equilibrium theory of glasses is absolutely necessary'' [3]. In our opinion such approaches are not applicable, due to the inherent nonequilibrium character of the glassy state. In the course of the present work, we shall encounter many instances where such approaches indeed fail to describe the physics. Notice, however, that this immediately rules out by far the most discussed model glass, namely the Gibbs-DiMarzio theory [1], as a viable model for a realistic glass. For instance, it would predict the original Ehrenfest relations to be always satisfied, in contrast with experiments to be discussed.

In our view the current lack of a thermodynamic description is quite unsatisfactory, since so many decades in time are involved, ranging from the microscopic subpicosecond regime to, for silicate-rich glasses, almost the age of the solar system, thus covering more than 25 decades. Naively we expect that each decade has its own dynamics, basically independent of the other ones. We shall find support for this point in the models that we shall investigate below.

Near the glass transition, a glass-forming liquid exhibits smeared discontinuities in quantities such as the heat capacity, the expansivity, and the compressibility. This looks similar to continuous phase transitions of the classical type, i.e., with specific-heat exponent $\alpha=0$, even though the analogy is not perfect, because the smaller specific-heat value occurs below the glass transition. It was then investigated whether the jumps satisfy the two Ehrenfest relations (the analogs for second-order transitions of the Clausius-Clapeyron relation of a first-order transition). As reviewed recently [4], it was found that the first Ehrenfest relation, involving the jump in the compressibility, is always violated, while the second one, involving the jump in the specific heat, is usually satisfied, but not always. It has become fashionable to combine these two relations by introducing the so-called Prigogine-Defay ratio Π. For equilibrium transitions this quantity should be equal to unity, and it was generally expected that it cannot take values below unity. In glasses, typical values are said to lie in the range $2<\Pi<5$, even though a very careful experiment on polystyrene led to $\Pi\approx 1$ [5].

Our recent studies have radically changed the viewpoint. We have realized that the first Ehrenfest relation is automatically satisfied, the only subtlety being its proper interpretation. We have also put forward that the Maxwell relation and the second Ehrenfest relation are modified in the glassy state, due to lack of equilibrium [6].

We have investigated the possibility that, within a yet unknown class of systems, the glassy state is described by one extra state variable. This is basically the age of the system, or the cooling rate under which the glass has been formed. We realized that in thermodynamics the *effective temperature* T_e is a more useful extra parameter [7,10].

This approach has led to a picture for thermodynamic relations between values of macroscopic observables [7,6] Later it was extended to their fluctuations [10]. The picture also incorporates the so-called fluctuation-dissipation relation (FDR), put forward in works by Sompolinsky [11], Horner [12–13] and Cugliandolo and Kurchan [14]; for a review, see [15]. This relation has become a central point in research on off-equilibrium systems. Our more general approach shows that the effective temperature that occurs in thermodynamics and the one that occurs in the fluctuation-dissipation relation are almost identical.

In the course of our work we gained insights from analytical results combined with educated guessing on the *p*-spin interaction spin glass. Some initial studies had the purpose to find the physical meaning of the nonequilibrium replica free energy in spin-glass models [16]. It has turned out that replica theory provides the two-temperature off-equilibrium free energy that we shall discuss in a much more general context [7]. The basic drawback of the *p*-spin model is that dynamics is not solved in the activated regime. For a model of directed polymers in a correlated random potential the situation is a little better, but so far it also lacks a complete solution in the activated regime [17]. Another model is the backgammon model, for which the dynamics at zero field has been partly solved [18,19]. One could couple the system to a particle bath, and the chemical potential would play the role of an external field. So far this case remains to be worked out.

More promising is a model of independent harmonic oscillators with parallel Monte Carlo dynamics, introduced recently by Bonilla, Padilla, and Ritort [20]. For this model the Hamiltonian and thus the statics is trivial. Nevertheless, the exactly solvable dynamics exhibits interesting glassy aspects. Since it has a too simple behavior in a field, we have recently studied a related simple non-mean-field model with trivial statics and interesting dynamics, namely the parallel Monte Carlo dynamics of independent spherical spins in a quenched random field [10]. We expect that both models lie in the same class as the lattice-gas models with kinetic constraints of Kurchan, Peliti, and Sellitto [21,22]. The latter model, however, cannot be solved analytically.

In this work we shall give details underlying the picture proposed in Ref. [10]. In Sec. II, we shall recall this picture. In Sec. III, we shall derive dynamical equations for averages, correlations, and responses in a model of uncoupled harmonic oscillators subject to Monte Carlo dynamics, introduced in Ref. [20]. In Sec. IV, we analyze these equations in the nonequilibrium low-temperature regime. In Sec. V, we analyze the closely related model of uncoupled spherical spins, introduced in [10]. We close with a discussion and summary.

II. THERMODYNAMIC PICTURE FOR A SYSTEM DESCRIBED BY AN EFFECTIVE TEMPERATURE

A state that slowly relaxes to equilibrium is characterized by *t*, the elapsed time, sometimes called ‘‘age’’ or ‘‘waiting time.’’ For glassy systems this is of special relevance. For experiments on spin glasses it is known that nontrivial cooling or heating trajectories can be described by an effective age [23]. Yet we do not wish to discuss spin glasses in this work. They have an infinity of long time scales, or infinite-order replica symmetry breaking. Their phase transition is continuous, and involves power laws.

We shall restrict our treatment to systems with one diverging time scale, having, in the mean-field limit, one step of replica symmetry breaking. They are systems with first-order-type phase transitions, with discontinuous order parameter, though usually there is no latent heat. However, the same approach applies to true first-order glassy transitions that do have a latent heat. This occurs, for instance, in the transition from low-density amorphous ice to high-density amorphous ice [24,25]. Theoretically such behavior occurs in spin glasses in a transverse field, see, e.g., [26–29].

We shall consider glassy transitions for liquids as well as for random magnets. The results map onto each other by interchanging volume *V*, pressure *p*, compressibility $\kappa=-\partial\ln V/\partial p$, and expansivity $\alpha=\partial\ln V/\partial T$, by magnetization *M*, field *H*, susceptibility $\chi=(1/N)\partial M/\partial H$, and ‘‘magnetizability’’ $\alpha=(-1/N)\partial M/\partial T$, respectively.

The picture to be investigated in this work starts by describing a nonequilibrium state characterized by three parameters, namely T,H and the *effective temperature* $T_e(t)$. As we shall see below, $T_e(t)$ enters naturally in the dynamical solution of the problem. For a set of smoothly related cooling experiments $T_i(t)$ at different fields H_i, one may express the effective temperature as a continuous function: $T_{e,i}(t)\to T_e(T,H)$. This sets a surface in (T,T_e,H) space, which becomes multivalued if one first cools and then heats. For covering the whole space one needs to do very many experiments, e.g., at different fields and at different cooling rates. The results should agree with findings from heating experiments and aging experiments. Thermodynamics amounts to giving differential relations between observables at nearby points in this space.

For thermodynamics of glassy systems in the absence of currents, all previous results can be summarized by expressing the change in heat as [6,7]

$$đQ = T\,dS_{\mathrm{ep}} + T_e\,d\mathcal{I}, \tag{2.1}$$

where S_{ep} is the entropy of the fast or equilibrium processes (β processes) and $\mathcal{I}$ the configurational entropy of the slow or ''configurational'' processes (α processes). This object is also known as information entropy or complexity. Both S_{ep} and $\mathcal{I}$ are state functions in the sense that they depend on T, T_e, and on H or p. In particular, they are defined for any T_e, and, within the present framework of one effective parameter, they do not depend on the path along which this value was reached.

Notice that our separation in Eq. (2.1) goes according to time scales. In the common use of the word, the configurational entropy S_c is the entropy of the glass minus the entropy of the vibrational modes of the crystal [1]. For polymers, in particular, it still includes short-distance rearrangements, which is a relatively fast mode. For the Gibbs-DiMarzio model it was confirmed numerically that S_c indeed does not vanish at any temperature, thus violating the Adam-Gibbs relation $\tau \sim \exp(\mathrm{const}/S_c)$ between time scale and configurational entropy [8]. Our $\mathcal{I}$, on the other hand, only contains the slow components; the fast ones are supposed to be in equilibrium, and are counted in S_{ep}. The properly formulated Adam-Gibbs relation should only refer to slow quantities, so it should read $\tau \sim \exp(\mathrm{const}/\mathcal{I})$. Its applicability remains an open issue. In a certain model glass with nontrivial fast and slow modes that has a Kauzmann transition it is actually satisfied [9].

In the presence of currents Eq. (2.1) would become $đQ \leqslant T\,dS_{\mathrm{ep}} + T_e\,d\mathcal{I}$. This decomposition is based on a system consisting of two parts, with a slow exchange of heat between them, thus having two time scales. A well known case is a cup of coffee at temperature T_e in a room at temperature T. In that case $\mathcal{I}$ is the entropy of the cup and the coffee, S_{ep} the entropy of the air and matter in the room, and Q the heat of the combined system. To mention one case, cooling of the coffee in an isolated room will be described by $đQ = 0$ and $T_e\,d\mathcal{I} = -T\,dS_{\mathrm{ep}} < 0$.

It is both surprising and satisfactory that a glass can be described by the same general law. If also an effective pressure or field would be needed, then $đQ$ is expected to keep the same form, but $đW$ would change from its standard value $-p\,dV$ for liquids, or $-M\,dH$ for magnets. In the latter case it would become $-M_1\,dH - M_2\,dH_e$, where H_e is the effective field, and M_1 and M_2 add up to M. Such a complication could be needed in a larger class of systems. It would make the picture technically a bit more difficult, and is the subject of current research.

A. First and second law

For a glass-forming liquid the first law $dU = đQ + đW$ becomes

$$dU = T\,dS_{\mathrm{ep}} + T_e\,d\mathcal{I} - p\,dV. \tag{2.2}$$

One can define the generalized free enthalpy

$$G = U - TS_{\mathrm{ep}} - T_e\mathcal{I} + pV \tag{2.3}$$

that satisfies

$$dG = -S_{\mathrm{ep}}\,dT - \mathcal{I}\,dT_e + V\,dp. \tag{2.4}$$

The total entropy is

$$S = S_{\mathrm{ep}} + \mathcal{I}. \tag{2.5}$$

(We should stress that the total entropy is not equal to $S_{\mathrm{ep}} + T_e\mathcal{I}/T$; there are many reasons why this unsymmetric form is incorrect. Let us mention that if the probability distribution decomposes into fast and slow processes as $P(\mathrm{fast},\mathrm{slow}) = P(\mathrm{fast}|\,\mathrm{slow})P(\mathrm{slow})$, then the standard expression $S = -\mathrm{tr}\,P\ln P$ leads to Eq. (2.5) with

$$S_{\mathrm{ep}} = \mathrm{tr}_{\mathrm{slow}}\,P\,(\mathrm{slow})[-\mathrm{tr}_{\mathrm{fast}}\,P(\mathrm{fast}|\,\mathrm{slow})\ln P(\mathrm{fast}|\,\mathrm{slow})],$$

just the entropy of the fast processes, averaged over the slow ones, and $\mathcal{I} = -\mathrm{tr}_{\mathrm{slow}}\,P(\mathrm{slow})\ln P(\mathrm{slow})$, just the entropy of the slow processes.)

The second law requires $đQ \leqslant T\,dS$, so

$$(T_e - T)\,d\mathcal{I} \leqslant 0. \tag{2.6}$$

Since $T_e = T_e(T,p)$, and both entropies are functions of T, T_e, and p, the expression (2.1) yields a specific heat

$$\begin{aligned} C_p &= \left.\frac{\partial(U+pV)}{\partial T}\right|_p \\ &= T\left(\left.\frac{\partial S_{\mathrm{ep}}}{\partial T}\right|_{T_e,p} + \left.\frac{\partial S_{\mathrm{ep}}}{\partial T_e}\right|_{T,p}\left.\frac{\partial T_e}{\partial T}\right|_p\right) \\ &\quad + T_e\left(\left.\frac{\partial \mathcal{I}}{\partial T}\right|_{T_e,p} + \left.\frac{\partial \mathcal{I}}{\partial T_e}\right|_{T,p}\left.\frac{\partial T_e}{\partial T}\right|_p\right). \end{aligned} \tag{2.7}$$

In the glass-transition region it holds that $T_e \approx T$. Since the derivatives of S_{ep} and $\mathcal{I}$ are smooth functions, all factors, except $\partial_T T_e$, are basically constant. This leads to

$$C_p = C_1 + C_2\left.\frac{\partial T_e}{\partial T}\right|_p. \tag{2.8}$$

Precisely this form has been assumed half a century ago by Tool [30] as a starting point for the study of caloric behavior in the glass-formation region, and has often been used for the explanation of experiments [31,32]. It is thus a direct consequence of Eq. (2.1). Let us mention that Tool uses the term ''fictive temperature'' for T_e.

For magnetic systems the first law brings

$$dU = T\,dS_{\mathrm{ep}} + T_e\,d\mathcal{I} - M\,dH. \tag{2.9}$$

One can define the free energy

$$F = U - TS_{\mathrm{ep}} - T_e\mathcal{I} \tag{2.10}$$

that satisfies

$$dF = -S_{\mathrm{ep}}\,dT - \mathcal{I}\,dT_e - M\,dH. \tag{2.11}$$

B. Modified Maxwell relation

For a smooth sequence of cooling procedures of a glassy liquid, Eq. (2.2) implies a modified Maxwell relation between macroscopic observables such as $U(t,p) \to U(T,p) = U(T,T_e(T,p),p)$ and V. This solely occurs since T_e is a nontrivial function of T,p for the smooth set of experiments under consideration.

The consistency relation $\partial^2 G/\partial T\,\partial p = \partial^2 G/\partial p\,\partial T$ yields

$$-\frac{\partial S_{\mathrm{ep}}}{\partial p}\bigg|_T - \frac{\partial \mathcal{I}}{\partial p}\bigg|_T \frac{\partial T_e}{\partial T}\bigg|_p = \frac{\partial V}{\partial T}\bigg|_p - \frac{\partial \mathcal{I}}{\partial T}\bigg|_p \frac{\partial T_e}{\partial p}\bigg|_T. \tag{2.12}$$

Notice that difference relations such as Eq. (2.9), and the Legendre transformation that leads to Eq. (2.11), do not invoke the functional dependence $T_e(T,p)$, since they hold for any functional dependence, and even in the absence of it. However, it does become relevant when dividing these equations by dT or dp, as was done to derive Eq. (2.12).

Equation (2.2) implies

$$T\frac{\partial S_{\mathrm{ep}}}{\partial p}\bigg|_T = \frac{\partial U}{\partial p}\bigg|_T - T_e\frac{\partial \mathcal{I}}{\partial p}\bigg|_T + p\frac{\partial V}{\partial p}\bigg|_T. \tag{2.13}$$

Eliminating $\partial S_{\mathrm{ep}}/\partial p$ leads to

$$\frac{\partial U}{\partial p}\bigg|_T + p\frac{\partial V}{\partial p}\bigg|_T + T\frac{\partial V}{\partial T}\bigg|_p = T\frac{\partial \mathcal{I}}{\partial T}\bigg|_p \frac{\partial T_e}{\partial p}\bigg|_T - T\frac{\partial \mathcal{I}}{\partial p}\bigg|_T \frac{\partial T_e}{\partial T}\bigg|_p + T_e\frac{\partial \mathcal{I}}{\partial p}\bigg|_T. \tag{2.14}$$

This is the modified Maxwell relation between observables U and V. In equilibrium $T_e = T$, so the right-hand side vanishes, and the standard form is recovered.

Similarly, one finds for a glassy magnet

$$\frac{\partial U}{\partial H}\bigg|_T + M - T\frac{\partial M}{\partial T}\bigg|_H = T_e\frac{\partial \mathcal{I}}{\partial H}\bigg|_T + T\left(\frac{\partial T_e}{\partial H}\bigg|_T \frac{\partial \mathcal{I}}{\partial T}\bigg|_H - \frac{\partial T_e}{\partial T}\bigg|_H \frac{\partial \mathcal{I}}{\partial H}\bigg|_T\right). \tag{2.15}$$

C. Modified Clausius-Clapeyron relation

Let us consider a first-order transition between two glassy phases A and B. An example could be the transition from low-density-amorphous ice to high-density-amorphous ice [24]. For the standard Clausius-Clapeyron relation one uses that the free enthalpy G is continuous along the first-order phase-transition line $p_g(T)$. Since $T_e \neq T$, it is actually not obvious that G should still be continuous there. The so far always confirmed fact that in mean-field models replica theory brings the relevant physical free energy leads us to expect that the generalized free enthalpy (2.3) is indeed continuous.

Let us consider a first-order transition between phases A and B, which have their own T_e, S_{ep}, and $\mathcal{I}$. Let us denote the discontinuities in observables O of the two states as

$$\Delta O(T,p_g(T)) \equiv O_A - O_B. \tag{2.16}$$

Taking $O = G$ and differentiating $\Delta G = 0$, one gets

$$\left[\Delta V - \Delta\left(\frac{\partial T_e}{\partial p}\bigg|_T\right)\right]\frac{dp_g}{dT} = \Delta S_{\mathrm{ep}} + \Delta\left(\frac{\partial T_e}{\partial T}\bigg|_p \mathcal{I}\right). \tag{2.17}$$

S_{ep} can be eliminated by means of Eq. (2.3). Using again that $\Delta G = 0$, this yields

$$\Delta V\frac{dp_g}{dT} = \frac{\Delta U + p_g\Delta V}{T} + \Delta\left(\frac{dT_e}{dT}\mathcal{I} - \frac{T_e}{T}\mathcal{I}\right), \tag{2.18}$$

where $d/dT = \partial/\partial T + (dp_c/dT)\partial/\partial p$ is the "total" derivative, i.e., the derivative along the transition line. This is the modified Clausius-Clapeyron relation. It would be very interesting to test this relation for ice. For that substance Mishima and Stanley [25] have presented a thermodynamic construction of the free enthalpy or Gibbs potential G. It is, however, based on equilibrium ideas and does not involve the effective temperature in the amorphous phases. In particular, it assumes the validity of the original Clausius-Clapeyron relation. We feel that the results are not the physically relevant ones, and that the analysis should be redone within our nonequilibrium thermodynamic framework.

When phase A is an equilibrium undercooled liquid, and phase B is a glass, it holds that $T_e = T$ in phase A, and its $\mathcal{I}$ terms will cancel from Eq. (2.18), so this relation reduces to

$$\Delta V\frac{dp_g}{dT} = \frac{\Delta U + p\Delta V}{T} + \left(\frac{T_e}{T} - \frac{dT_e}{dT}\right)\mathcal{I}, \tag{2.19}$$

where T_e and $\mathcal{I}$ are properties of the glassy phase B. Notice that Eq. (7) of Ref. [6] contains a misprint in the prefactor of $\mathcal{I}$.

For standard glass-forming liquids, there are no discontinuities in U and V. It then holds that along the glass-transition line $T_e(T,p_g(T)) = T$, implying $dT_e/dT = 1$, which indeed removes the $\mathcal{I}$ terms from the last two relations.

D. Ehrenfest relations and Prigogine-Defay ratio

In the glass-transition region a glass-forming liquid exhibits smeared jumps in the specific heat C_p, the expansivity α, and the compressibility κ. If one forgets about the smearing, one may consider them as true discontinuities, yielding an analogy with continuous phase transitions of the classical type.

Following Ehrenfest, one may take the derivative of $\Delta V(T,p_g(T)) = 0$. Using the definitions of α and κ, given above, the result for a glass-forming liquid may be written as

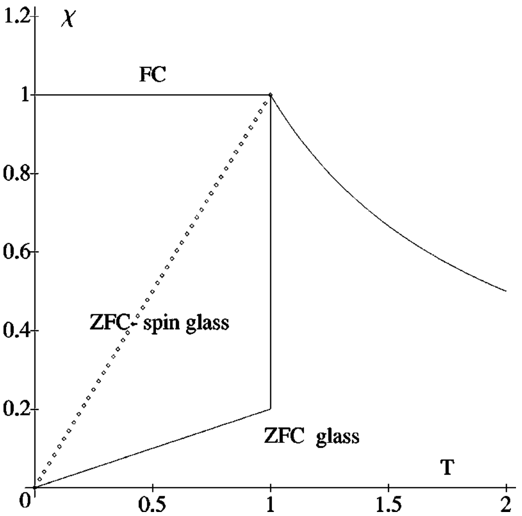

FIG. 1. Schematic plot of the field-cooled (FC) and zero-field-cooled (ZFC) susceptibility in realistic spin glasses and in glassy magnets, as a function of temperature, in arbitrary units. In realistic spin glasses the infinite time or field-cooled susceptibility is larger than the short time or zero-field-cooled susceptibility. In magnetic analogs of realistic glasses, the short time susceptibility even has a smeared discontinuity at the glass transition. In glass-forming liquids the same happens for the compressibility.

$$\Delta\alpha=\Delta\kappa\frac{dp_g}{dT} \tag{2.20}$$

while for a glassy magnet

$$\Delta\alpha=\Delta\chi\frac{dH_g}{dT}. \tag{2.21}$$

The conclusion drawn from half a century of research on glass-forming liquids is that this relation is never satisfied [31,33,34,4]. This has greatly hindered progress on a thermodynamical approach. However, from a theoretical viewpoint it is hard to imagine that something could go wrong when just taking a derivative. We have pointed out that this relation is indeed satisfied automatically [6], but it is important to say what is meant by κ in the glassy state.

Let us make an analogy with spin glasses. In mean-field theory they have infinite-order replica symmetry breaking. From the early measurements of Canella and Mydosh [35] on AuFe it is known that the susceptibility depends logarithmically on the frequency, and therefore on the time scale. The short-time value, called zero-field-cooled (ZFC) susceptibility, is a lower bound, while the long-time value, called field-cooled (FC) susceptibility, is an upper bound. Let us use the term ''glassy magnets'' for spin glasses with one step of replica symmetry breaking. They are relevant for comparison with glass-forming liquids. For them the situation is worse, as the ZFC value is discontinuous immediately below T_g. (At $H=0$ one has $\chi_{\rm ZFC}=\beta(1-q_{\rm EA})$, while $\chi_{\rm FC}=\beta[1-(1-x_1)q_{\rm EA}]$ matches $\chi_{\rm PM}=\beta$ at $x_1=1$.) This occurs since giving the system more time to react on the field will lead to a much larger response, and it explains why already directly below the glass transition different measurements yield different values for κ. These notions are displayed in Fig. 1.

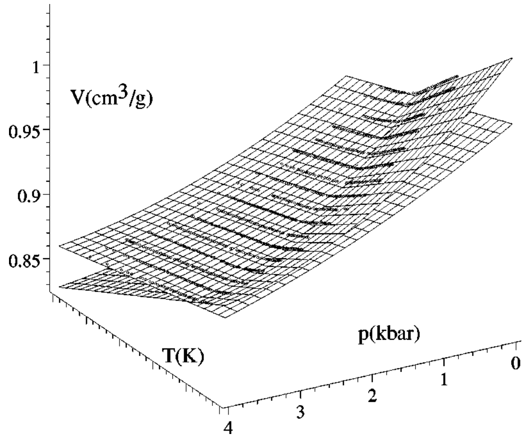

FIG. 2. Data of the glass transition for cooling atactic polystyrene at rate 18 K/h, scanned from the paper of Rehage and Oels (1976): specific volume V (cm^3/g) versus temperature T (K) at various pressures p (kbar). As confirmed by a polynomial fit, the data in the liquid essentially lie on a smooth surface, and so do the data in the glass. The first Ehrenfest relation describes no more than the intersection of these surfaces, and is therefore automatically satisfied. The values for the compressibility derived in this manner will generally differ from results obtained via other procedures.

Previous claims about the violation of the first Ehrenfest relation can be traced back to the equilibrium thermodynamical idea that there is one ideal κ, to be inserted in Eq. (2.20). Indeed, investigators usually considered cooling curves $V(T,p_i)$ at a set of pressures p_i to determine $\Delta\alpha$ and dp_g/dT. (An alternative route, often followed in polymer physics, and leading to a very similar problem, is to change p at many constant values of T; then κ depends strongly on the rate of change of p.) However, $\Delta\kappa$ was always determined in another way, often from measurements of the speed of sound, or by making more complicated pressure steps [5]. In equilibrium such alternative determinations would yield the same outcome. In glasses this is not the case: the speed of sound is a short-time process, and additional pressure steps modify the glassy state. Therefore, alternative procedures are not allowed, and only the cooling curves $V(T,p_i)$ should be used. They constitute a liquid surface $V_{\rm liquid}(T,p)$ and a glass surface $V_{\rm glass}(T,p)$ in (T,p,V) space. These surfaces intersect, and the first Ehrenfest relation is no more than a mathematical identity about the intersection line of these surfaces. It is therefore automatically satisfied [6]. The most careful data we came across were collected by Rehage and Oels for atactic polystyrene [5]. In Fig. 2 we present those data in a 3D plot, underlining our point of view.

After submitting the original version of this paper, we realized that McKenna has stressed that in experiments on glasses the isothermal compressibility differs from the isochoral compressibility [36]. He also concludes that alternative experiments are not allowed, and that the first Ehrenfest relation indeed is merely a tautology.

The second Ehrenfest relation derives from differentiating $\Delta U(T,p_g(T))=0$. The obtained relation will also be satisfied automatically. However, one then eliminates $\partial U/\partial p$ by means of the Maxwell relation. In equilibrium this would yield

$$\frac{\Delta C_p}{T_g V}=\Delta\alpha\frac{dp_g}{dT}. \tag{2.22}$$

We have already discussed that outside equilibrium it is modified, see Eq. (2.14). We thus obtain instead

$$\begin{aligned}\frac{\Delta C_p}{T_g V}&=\Delta\alpha\frac{dp_g}{dT}+\frac{1}{V}\left(1-\left.\frac{\partial T_e}{\partial T}\right|_p\right)\frac{d\mathcal{I}}{dT}\\&=\Delta\alpha\frac{dp_g}{dT}+\frac{1}{V}\left(1-\left.\frac{\partial T_e}{\partial T}\right|_p\right)\left(\left.\frac{\partial\mathcal{I}}{\partial T}\right|_p+\frac{dp_g}{dT}\left.\frac{\partial\mathcal{I}}{\partial p}\right|_T\right),\end{aligned} \tag{2.23}$$

where $d\mathcal{I}/dT$ is the ''total'' derivative of the configurational entropy along the glass-transition line. The last term is new and vanishes only at equilibrium. For magnets one gets

$$\frac{\Delta C}{NT}=\Delta\alpha\frac{dH_g}{dT}+\frac{1}{N}\left(1-\left.\frac{\partial T_e}{\partial T}\right|_H\right)\left(\left.\frac{\partial\mathcal{I}}{\partial T}\right|_H+\frac{dH_g}{dT}\left.\frac{\partial\mathcal{I}}{\partial H}\right|_T\right). \tag{2.24}$$

Along the glassy transition line, the equality $T_e(T,H_g(T))=T$ implies

$$\frac{dT_e}{dT}=\left.\frac{\partial T_e}{\partial T}\right|_H+\left.\frac{\partial T_e}{\partial H}\right|_T\frac{dH_g}{dT}=1. \tag{2.25}$$

Combining the two original Ehrenfest relations, one may eliminate the slope of the transition line. This leads us to consider the so-called Prigogine-Defay ratio,

$$\Pi=\frac{\Delta C_p\Delta\kappa}{TV(\Delta\alpha)^2}. \tag{2.26}$$

For equilibrium transitions it should be equal to unity. Assuming that at the glass transition a number of unspecified parameters undergo a phase transition, Davies and Jones showed that $\Pi\geqslant 1$ [31], while DiMarzio showed that in that case the correct value is $\Pi=1$ [37]. In glasses typical experimental values are reported in the range $2<\Pi<5$. It was therefore generally expected that $\Pi\geqslant 1$ is a strict inequality.

We have pointed out, however, that as the first Ehrenfest relation is satisfied but the second is not, it holds that

$$\Pi=\frac{\Delta C_p}{TV\Delta\alpha(dp_g/dT)}=1+\frac{1}{V\Delta\alpha}\left(1-\left.\frac{\partial T_e}{\partial T}\right|_p\right)\frac{d\mathcal{I}}{dp}. \tag{2.27}$$

Depending on the set of experiments to be chosen, dp_g/dT can be small or large, and Π can also be below unity. Rehage and Oels found $\Pi=1.09\approx 1$ at $p=1$ kbar, using a short-time value for κ [5]. Reanalyzing their data we find from Eq. (2.27), where the physically relevant κ has been inserted, a value $\Pi=0.77$, which is, surprisingly enough, below unity [6].

The definition (2.26) of Π looks like a combination of equilibrium quantities. This is misleading, however, since κ_{glass} depends sensitively on how the experiment is done. We conclude that the commonly accepted inequality $\Pi\geqslant 1$ is based on equilibrium assumptions. Our theoretical arguments and the Rehage-Oels data show that such ideas are incorrect. In particular this rules out the Gibbs-DiMarzio model as a principally correct model for the glassy state. It is an equilibrium model, and as such it will, e.g., lead to $\Pi=1$, in contradiction to experiments.

E. Fluctuation formula

The basic result of statistical physics is that it relates fluctuations in macroscopic variables to response of their averages to changes in external field or temperature. We have wondered whether such relations generalize to the glassy state. We have found arguments in favor of such a possibility both from the fluctuation-dissipation relation and by exactly solving the dynamics of model systems [10]. Susceptibilities appear to have a nontrivial decomposition, which looks very general. Here we give arguments leading to it.

Later we shall consider models where two fields H_a $(a=1,2)$ are present, and two magnetizations M_a $(a=1,2)$. In cooling experiments at fixed field $H=(H_1,H_2)$, it holds that $M_a=M_a(T(t),T_e(t,H),H)$. For thermodynamics one eliminates time to express $T_e(t,H)\to T_e(T,H)$, implying $M_a=M_a(T,T_e(T,H),H)$. One may then expect three terms:

$$\chi_{ab}\equiv\frac{1}{N}\left.\frac{\partial M_a}{\partial H_b}\right|_T=\chi_{ab}^{\mathrm{fluct}}(t)+\chi_{ab}^{\mathrm{loss}}(t)+\chi_{ab}^{\mathrm{conf}}(t). \tag{2.28}$$

The first two are defined by

$$\chi_{ab}^{\mathrm{fluct}}(t)+\chi_{ab}^{\mathrm{loss}}(t)=\frac{1}{N}\left.\frac{\partial M_a}{\partial H_b}\right|_{T,T_e}. \tag{2.29}$$

To calculate them separately, we switch from a cooling experiment to an aging experiment at the considered T, T_e, and H, by keeping, in Gedanken, T fixed from then on. The system will continue to age, expressed by $T_e=T_e(t;T,H)$. We may then use the equality

$$\left.\frac{\partial M_a}{\partial H_b}\right|_{T,t}=\left.\frac{\partial M_a}{\partial H_b}\right|_{T,T_e}+\left.\frac{\partial M_a}{\partial T_e}\right|_{T,H}\left.\frac{\partial T_e}{\partial H_b}\right|_{T,t}. \tag{2.30}$$

We have conjectured [10] that the left-hand side may be written as the sum of fluctuation terms for fast and slow processes,

$$\begin{aligned}\chi_{ab}^{\mathrm{fluct}}(t)&=\frac{1}{N}\left.\frac{\partial M_a}{\partial H_b}\right|_{T,t}\\&=\frac{\langle\delta M_a(t)\,\delta M_b(t)\rangle_{\mathrm{fast}}}{NT(t)}+\frac{\langle\delta M_a(t)\,\delta M_b(t)\rangle_{\mathrm{slow}}}{NT_e(t)}.\end{aligned} \tag{2.31}$$

The first term is just the standard equilibrium expression for the fast equilibrium processes. Notice that slow processes enter with their own temperature, the effective temperature. This decomposition is confirmed by use of the fluctuation-dissipation relation in the form to be discussed below. Combination of Eqs. (2.29), (2.30), and (2.31) yields

$$\chi_{ab}^{\mathrm{loss}}(t)=-\frac{1}{N}\,\frac{\partial M_a}{\partial T_e}\bigg|_{T,H}\,\frac{\partial T_e}{\partial H_b}\bigg|_{T,t}. \tag{2.32}$$

The fluctuation terms are instantaneous, and thus the same for aging and cooling. The loss term is a correction, related to an aging experiment. It measures the decrease of fluctuations below the glass transition, which will be small in the models to be discussed later on.

In the models to be considered below, dynamics in the glassy phase is essentially independent of the actual T, leaving almost no difference between cooling and aging. This is due to the simplicity of the model.

Since $T_e\neq T$, there occurs in Eq. (2.28) also a new configurational term

$$\chi_{ab}^{\mathrm{conf}}=\frac{1}{N}\,\frac{\partial M_a}{\partial T_e}\bigg|_{T,H}\,\frac{\partial T_e}{\partial H_b}\bigg|_{T}. \tag{2.33}$$

It originates from the difference in the system's structure for cooling experiments at nearby fields. For glass-forming liquids such a term occurs in the compressibility. Its existence was anticipated in some earlier works. Goldstein [33] points out that V_{glass} depends stronger on the pressure of formation p_{form} than on the one remaining after partial release of pressure, p_{final}. Jäckle [34] then assumes that for infinitely slow cooling p_{form} is the only additional system parameter, and argues that $\Delta\kappa_T\rightarrow\Delta\kappa=\Delta\kappa_T+\partial\ln V/\partial p_{\mathrm{form}}=\Delta\alpha\, dT_g/dp$ and that this implies $\Pi=\Delta\kappa_T/\Delta\kappa>1$. He thus also considers one extra system variable, and also argues the existence of a configurational term. We do not wish to restrict to adiabatically slow cooling, and we do not agree with his conclusion on Π. Notice that our approach allows, in principle, to find the configurational term (2.33) for typical cooling procedures from construction of $V(T,T_e,p)$ in full (T,T_e,p) space.

From the analysis to be given below, we find no reason why such universal quasiequilibrium relations could also hold between the specific heat and the energy fluctuations. In the models of the present paper the energy fluctuations are smaller by one order of magnitude, and model-dependent. The absence of such a general relation allowed us to apply the very same two-temperature approach to black holes, without obtaining a contradiction with their negative specific heat [38].

F. Fluctuation-dissipation relation

Nowadays quite a lot of attention is paid to the fluctuation-dissipation relation in the aging regime of glassy systems. It was first put forward in works by Sompolinsky [11], Horner [12,13], and then by Cugliandolo and Kurchan [14]. This relation has become a central point in research on off-equilibrium systems; for a review, see [15].

Our formulation is that in the aging regime there holds the following relation between the cross correlation $C_{ab}(t,t')=\langle O_a(t)O_b(t')\rangle-\langle O_a(t)\rangle\langle O_b(t')\rangle$ of macroscopic observables $O_a(t)$ and $O_b(t')$, and the response $G_{ab}(t,t')=\delta\langle O_a(t)\rangle/\delta H_b(t')$ of $O_a(t)$ to a short, small field change applied at an earlier time t':

$$\frac{\partial C_{ab}(t,t')}{\partial t'}=\tilde{T}_e(t')G_{ab}(t,t') \tag{2.34}$$

with $\tilde{T}_e(t)$ being the effective temperature for the FDR, while in the equilibrium or short-time regime, T replaces $\tilde{T}_e$. This relation has been confirmed numerically, e.g., for a soft sphere glass [42]. It is remarkable that the $\tilde{T}_e$ is a function of one of the times only. However, one should keep in mind that C and G typically have a t'/t scaling, while $\tilde{T}_e$ typically is a smooth function of $\ln t$, a variable that basically equals $\ln t'$.

One expects that $\tilde{T}_e(t)$ is close to the ''thermodynamic'' effective temperature $T_e(t)$. Let us show how this comes about.

The two fluctuation terms in Eq. (2.31) are consistent with Eq. (2.34). To prove this, let us neglect switching effects (see Sec. III D) and use the definition

$$\frac{1}{N}\,\frac{\partial M_a}{\partial H_b}\bigg|_{T,t}=\int_0^t G_{ab}(t,t')\,dt'. \tag{2.35}$$

We split the integral up in the regions $(t-\tau_\beta,t)$ and $(0,t-\tau_\beta)$, where τ_β is the time after which the fast or β processes have died out. Their contribution has the equilibrium form, while in the second interval we may insert Eq. (2.34), which yields

$$\frac{1}{N}\,\frac{\partial M_a}{\partial H_b}\bigg|_{T,t}=\frac{\langle\delta M_a(t)\,\delta M_b(t)\rangle_{\mathrm{fast}}}{NT(t)}+\int_0^{t-\tau_\beta}dt'\,\frac{1}{\tilde{T}_e(t')}\,\frac{\partial C_{ab}(t,t')}{\partial t'}. \tag{2.36}$$

We perform a partial integration, and can neglect the value at the lower boundary $t=0$. In the remaining term we insert a factor $1=\partial_{t'}C_{ab}(t,t')/\partial_{t'}C_{ab}(t,t')$. We can then do another partial integral, and we could, in principle, repeat this process. All terms at $t-\tau_\beta$ share a common factor, namely the plateau value of $C_{ab}(t,t')$,

$$C_{ab}^{\mathrm{plateau}}(t)\equiv C_{ab}(t,t-\tau_\beta)=\frac{\langle\delta M_a(t)\,\delta M_b(t-\tau_\beta)\rangle_{\mathrm{slow}}}{N}, \tag{2.37}$$

which also enters the relation

$$\frac{1}{N}\langle\delta M_a(t)\,\delta M_b(t)\rangle_{\mathrm{fast}}=C_{ab}(t,t)-C_{ab}^{\mathrm{plateau}}(t). \tag{2.38}$$

As a result, we derive from Eq. (2.34) our ansatz (2.31) with a factor

$$\frac{1}{T_e(t)}=\frac{1}{\tilde{T}_e(t)}+\frac{\partial_t\tilde{T}_e(t)}{\tilde{T}_e^2(t)}\,\frac{C_{ab}(t,t')}{\partial_{t'}C_{ab}(t,t')}\bigg|_{t'=t-\tau_\beta}+\cdots. \tag{2.39}$$

This may be inverted, to yield

$$\tilde{T}_e(t)=T_e(t)+\dot{T}_e(t)\left(\left.\frac{\partial \ln C_{ab}(t,t')}{\partial t'}\right|_{t'=t-\tau_\beta}\right)^{-1}+\cdots. \tag{2.40}$$

It is clear that the effective temperatures T_e and $\tilde{T}_e$ are not identical. However, in the models to be analyzed later on, we shall find that the difference is small.

Notice that the ratio $\partial_{t'}C(t,t')/G(t,t')=\tilde{T}_e(t')$ is allowed to depend on time t'. The situation with constant T_e $(=T/x$, with x the break point of the Parisi function) is well known from mean-field spin glasses, but we shall not find such a constant T_e in the models to be studied. In [15] it is reviewed that in mean-field spin glasses the fluctuation-dissipation parameter $X(t,t')\equiv TG(t,t')/\partial_{t'}C(t,t')$ simplifies to $X(t,t')\equiv\hat{X}(C(t,t'),t')=\hat{X}(0,t')\rightarrow\text{const}$. As our $T_e(t')$ will depend logarithmically on time, the t' dependence of our $\hat{X}(0,t')=T/T_e(t')$ cannot be neglected. We can therefore conclude that such a time independence is an artifact of the mean-field approximation. This supports our earlier conclusion that only at exponential time scales $\sim\exp(N)$ the dynamics of the mean-field spin glass is related to that of realistic systems [7]. In the numerical evaluation of the ''fluctuation-dissipation ratio'' T/T_e one should therefore keep in mind the realistic possibility of a slow time dependence of T_e.

G. Time-scale arguments

Consider a simple system that has only one type of process (α process), which falls out of equilibrium at some low T. When it ages a time t at $T=0$ it will have achieved a state with effective temperature T_e, which can be estimated by equating time with the equilibrium time scale. Let us define $\overline{T}_e$ by

$$t=\tau_{\mathrm{eq}}(\overline{T}_e). \tag{2.41}$$

We shall check in the models to be studied below that, to leading order in $\ln t$, it holds that $\overline{T}_e=T_e$. (The first nonleading-order turns out to be nonuniversal, since it already depends on numerical prefactors of τ_{eq}.) This equality also is found in cooling trajectories, when the system is well inside the glassy regime. It says that the system basically has forgotten its history, and ages on its own, without caring about the actual temperature. We feel that this is caused by the fact that dynamics in each new time decade is basically independent of the previous decade.

In less trivial systems, for instance those having a Vogel-Tammann-Fulcher law, the time scale may have parameters that depend on the actual temperature, implying $\tau_{\mathrm{eq}}=\tau(T,T_e)$. We then expect that, to leading order, T_e follows by equating this expression with time t.

In many systems one finds a t'/t scaling in the aging regime of two-time quantities. There is a handwaving argument to explain that

$$C(t,t')\approx C\left(\frac{t-t'}{\tau_{\mathrm{eq}}(T_e(t'))}\right)\approx C\left(\frac{t-t'}{t'}\right)=C\left(\frac{t}{t'}\right) \tag{2.42}$$

showing indeed the familiar t/t' scaling. In the models to be studied below we shall find logarithmic scaling corrections. They become strong at low T, and change the $\sqrt{t'/t}$ decay at $T>0$ to a t'/t decay at $T=0$. So this argument might apply only to a subset of systems that fall within the scope of our approach.

H. Results for simple systems that become glassy near $T=0$

In the remainder of this paper we shall consider two simple systems having only one type of process (α process), which fall out of equilibrium at some low T. Then the effective temperature $T_e(t)$ is expected to show up in the following deviations from the equilibrium situation: (i) matching the internal energy: $U(t,H)=U_{\mathrm{eq}}(T_e(t),H)$; (ii) matching the magnetization: $M(t,H)=M_{\mathrm{eq}}(T_e(t),H)$; (iii) from the configurational entropy via $dU=T_e d\mathcal{I}-MdH$; (iv) matching time with the equilibrium time scale: $t\sim\tau_{\mathrm{eq}}(T_e(t))$; (v) via the fluctuation formula: $\chi^{\mathrm{fluct}}=\beta_e(t)\langle\delta M^2(t)\rangle$; (vi) from the fluctuation-dissipation relation: $\partial C(t,t')/\partial t'=\tilde{T}_e(t')G(t,t')$. Even though these relations are not all independent, it is pretty clear that the whole glassy dynamics is strongly governed by one parameter: the effective temperature.

III. MONTE CARLO DYNAMICS OF UNCOUPLED HARMONIC OSCILLATORS

Bonilla, Padilla, and Ritort have recently considered an exactly solvable model with slow dynamics [20]. It showed interesting, glassy behavior at low temperatures. In this section we present many details and further results for this model. This will also be a pedagogical step for the analysis of the spin model of Sec. V.

After including an external field, the Hamiltonian reads

$$\mathcal{H}=\frac{1}{2}K\sum_i x_i^2-H\sum_i x_i\equiv\frac{1}{2}KM_2-HM_1, \tag{3.1}$$

where

$$M_k=Nm_k=\sum_i x_i^k \quad (k=1,2). \tag{3.2}$$

We introduce the shifted energy

$$E=N\varepsilon=\mathcal{H}+N\frac{H^2}{2K}. \tag{3.3}$$

In a Monte Carlo step with parallel updates one replaces $x_i\rightarrow x_i'=x_i+r_i/\sqrt{N}$, defining $M_k'=\Sigma(x_i+r_i/\sqrt{N})^k$. The thermal noise variables r_i are independent Gaussian random variables with average zero and variance Δ^2. For a parallel update of all x_i, this leads to the noise-averaged transition probability from a state with (M_1,M_2) to states with $(M_1',M_2')=(M_1+y_1,M_2+y_2)$,

$$P(y_1,y_2|M_1,M_2)=\left(\prod_i \int_{-\infty}^{\infty}\frac{dr_i}{\sqrt{2\pi\Delta^2}}e^{-r_i^2/2\Delta^2}\right)\times\delta(M_1'-M_1-y_1)\,\delta(M_2'-M_2-y_2)$$
$$=\frac{1}{4\pi\Delta^2\sqrt{m_2-m_1^2}}\times\exp\left[-\frac{y_1^2}{2\Delta^2}-\frac{(y_2-\Delta^2-2y_1m_1)^2}{8\Delta^2(m_2-m_1^2)}\right]$$
$$\equiv p(y_1,y_2|m_1,m_2), \tag{3.4}$$

where we took the convention that probabilities involving extensive parameters are written with capitals, while those that involve intensive parameters are written in lower case. To derive this result, the δ functions have been written in a plane-wave representation, and the limit $N\to\infty$ has been taken. Setting $y_1=y$, we introduce the variable x by

$$x=\frac{K}{2}y_2-Hy_1,\quad y_2=\frac{2}{K}(x+Hy). \tag{3.5}$$

A Monte Carlo move implies a change $E'=E+x$. The transition probability may be decomposed as

$$P(y,y_2|M_1,M_2)dy\,dy_2=P(x,y|E,M_1)dx\,dy$$
$$=p(x|\varepsilon)\,p(y|x,\varepsilon,m_1)dx\,dy \tag{3.6}$$

with conditional probabilities

$$p(x|\varepsilon)=\frac{1}{\sqrt{2\pi\Delta_x}}\exp\left(-\frac{(x-x_0)^2}{2\Delta_x}\right), \tag{3.7}$$

$$p(y|x,\varepsilon,m_1)=\frac{1}{\sqrt{2\pi\Delta_y}}\exp\left(-\frac{(y-y_0)^2}{2\Delta_y}\right), \tag{3.8}$$

having parameters

$$x_0=\frac{\Delta^2K}{2},\quad \Delta_x=\Delta^2(K^2m_2-2HKm_1+H^2)=2K\Delta^2\varepsilon, \tag{3.9}$$

$$y_0=\frac{-(K\Delta^2-2x)(Km_1-H)}{2(K^2m_2-2HKm_1+H^2)}=\frac{K\Delta^2-2x}{4\varepsilon}\mu_1,$$

$$\Delta_y=\frac{\Delta^2K^2(m_2-m_1^2)}{K^2m_2-2HKm_1+H^2}=\Delta^2\left(1-\frac{K\mu_1^2}{2\varepsilon}\right), \tag{3.10}$$

where we defined the deviations from equilibrium,

$$\varepsilon=\frac{1}{2}K(m_2-m_1^2+\mu_1^2),\quad \mu_1=\frac{H}{K}-m_1. \tag{3.11}$$

We shall frequently encounter the energy scale

$$A=\frac{\Delta^2K}{8}. \tag{3.12}$$

In one Monte Carlo step the probability of E evolves as [20]

$$P\left(E',t+\frac{1}{N}\right)$$
$$=\int dE\,P(E,t)\int dx\,p\left(x\middle|\frac{E}{N}\right)\times\{W(\beta x)\,\delta(E'-E-x)+[1-W(\beta x)]\,\delta(E'-E)\}$$
$$=P(E',t)+\int dE\,P(E,t)\int dx\times p\left(x\middle|\frac{E}{N}\right)W(\beta x)[\delta(E'-E-x)-\delta(E'-E)], \tag{3.13}$$

where $W(\beta x)=1$ for $x<0$ and $W(\beta x)=e^{-\beta x}$ for $x>0$ is the Metropolis acceptance rate. The second term describes the rejected moves. Notice that the energy aspects are independent of the field H, for the physical reason that H merely causes a shift of the equilibrium position, but not in $E=(K/2)\Sigma_i(x_i-H/K)^2$. This is due to the simplicity of the model.

If one also keeps track of the magnetization, one has

$$P\left(E',M',t+\frac{1}{N}\right)=P(E',M',t)+\int dE\,dM\,P(E,M,t)\times\int dx\,dy\,P(x,y|E,M)W(\beta x)\times[\delta(E'-E-x)\,\delta(M'-M-y)-\delta(E'-E)\,\delta(M'-M)], \tag{3.14}$$

which, of course, is consistent with $P(E,t)=\int dM\,P(E,M,t)$.

A. Evolution of average observables

We can now calculate the evolution of physical observables. One derives from Eq. (3.13) that

$$\left\langle E\left(t+\frac{1}{N}\right)\right\rangle=\int dE'\,dM'\,E'P\left(E',M',t+\frac{1}{N}\right)$$
$$=\langle E(t)\rangle+\int dE\,dx\,W(\beta x)P(E,t)\,x\,p\left(x\middle|\frac{E}{N}\right), \tag{3.15}$$

where $\langle E(t)\rangle$ arises from the term without $W(\beta x)$. In the thermodynamic limit (i.e., for large N), $P(E,t)$ will be sharply peaked around $\langle E(t)\rangle$, so one obtains a closed equation for the scaled average $\varepsilon(t)=\langle E(t)\rangle/N$ [20],

$$\frac{d\varepsilon(t)}{dt}=\int dx\,W(\beta x)\,x\,p(x|\varepsilon(t)). \tag{3.16}$$

This simplifying property is due to the lack of interaction between the oscillators.

In the same way we proceed for the evolution of the magnetization,

$$\left\langle M\left(t+\frac{1}{N}\right)\right\rangle =\langle M(t)\rangle+\int dE\, dM\, dx\, dy\, W(\beta x)P(E,M,t)y \times p\left(x\middle|\frac{E}{N}\right)p\left(y\middle|x,\frac{E}{N},\frac{M}{N}\right). \tag{3.17}$$

Here, and everywhere in the sequel, the y integrals are Gaussian, and can be carried out analytically. This makes the problem with a field hardly more complicated than without. We obtain

$$\frac{dm(t)}{dt}=\int dx\, W(\beta x)\, y_0\, p(x|\varepsilon(t))=-\left(m(t)-\frac{H}{K}\right)f(t), \tag{3.18}$$

where

$$f(t)=-\int_{-\infty}^{\infty}dx\, W(\beta x)\frac{\partial y_0}{\partial m}p(x|\varepsilon(t)) =\int_{-\infty}^{\infty}dx\, W(\beta x)\frac{4A-x}{2\varepsilon(t)}p(x|\varepsilon(t)). \tag{3.19}$$

B. Fluctuations

The evolution of bilinear forms is a bit more involved. Let us consider the energy fluctuations. One has

$$\left\langle E^2\left(t+\frac{1}{N}\right)\right\rangle=\langle E^2(t)\rangle+\int dE\, dx\, W(\beta x)P(E,t) \times(2xE+x^2)p\left(x\middle|\frac{E}{N}\right). \tag{3.20}$$

Using Eq. (3.15) this may be written as

$$\left\langle E^2\left(t+\frac{1}{N}\right)\right\rangle-\langle E^2(t)\rangle-2\langle E(t)\rangle \times\left[\left\langle E\left(t+\frac{1}{N}\right)\right\rangle-\langle E(t)\rangle\right] =\int dE\, dx W(\beta x)P(E,t)p\left(x\middle|\frac{E}{N}\right)(2x\,\delta E+x^2), \tag{3.21}$$

where $\delta E=E-\langle E(t)\rangle$. Expanding $p(x|E/N)$ around $E=\langle E(t)\rangle$ one obtains for large N,

$$\frac{d}{dt}\frac{\langle\delta E^2\rangle}{N}=\int dx\, W(\beta x)\left(\frac{\langle\delta E^2\rangle}{N}2x\frac{\partial}{\partial\varepsilon}+x^2\right)p(x|\varepsilon). \tag{3.22}$$

In the same way one derives for the evolution equation for fluctuations in M,

$$\frac{d}{dt}\frac{\langle\delta M^2\rangle}{N}=\int dx\, dy\, W(\beta x)\left(\frac{\langle\delta M^2\rangle}{N}2y\frac{\partial}{\partial m} +\frac{\langle\delta E\,\delta M\rangle}{N}2y\frac{\partial}{\partial\varepsilon}+y^2\right)p(x|\varepsilon)p(y|x,\varepsilon,m). \tag{3.23}$$

The y integral is Gaussian, and can be carried out. The result reads

$$\frac{d}{dt}\frac{\langle\delta M^2\rangle}{N}=\int dx\, W(\beta x)\left(\frac{\langle\delta M^2\rangle}{N}\frac{\partial}{\partial m}2y_0 +\frac{\langle\delta E\,\delta M\rangle}{N}\frac{\partial}{\partial\varepsilon}2y_0+y_0^2+\Delta_y\right)p(x|\varepsilon), \tag{3.24}$$

while for the cross correlations

$$\begin{aligned}\frac{d}{dt}\frac{\langle\delta E\,\delta M\rangle}{N}&=\int dx\, dy W(\beta x)\left[\frac{\langle\delta M^2\rangle}{N}x\frac{\partial}{\partial m} +\frac{\langle\delta E\,\delta M\rangle}{N}\left(x\frac{\partial}{\partial\varepsilon}+y\frac{\partial}{\partial m}\right) +\frac{\langle\delta E^2\rangle}{N}y\frac{\partial}{\partial\varepsilon}+xy\right]p(x|\varepsilon)p(y|x,\varepsilon,m)\\ &=\int dx\, W(\beta x)\left[\frac{\langle\delta E\,\delta M\rangle}{N}\left(x\frac{\partial}{\partial\varepsilon}+\frac{\partial}{\partial m}y_0\right) +\frac{\langle\delta E^2\rangle}{N}\frac{\partial}{\partial\varepsilon}y_0+xy_0\right]p(x|\varepsilon).\end{aligned} \tag{3.25}$$

Recalling that $M=M_1$ and the definition (3.2) of M_2, and adopting the definition of correlators to be given in Eq. (3.32), we may also cast these results in the form

$$\frac{d}{dt}C_{ab}(t,t)=\int dx\, W(\beta x)\left\{\overline{y}_a\overline{y}_b+\Delta_y\left(-\frac{H_1}{H_2}\right)^{a+b-2} +\sum_{c=1}^{2}\frac{\partial}{\partial m_c}[\overline{y}_aC_{cb}(t,t)+\overline{y}_bC_{ca}(t,t)]\right\} \times p(x|m_1,m_2), \tag{3.26}$$

where $a,b=1,2$, $H_1=H$, $H_2=-K/2$, and, in the present model, $p(x|m_1,m_2)=p(x|\varepsilon)$, with ε defined in Eq. (3.11). Furthermore,

$$\overline{y}_1=y_0,\quad \overline{y}_2=-\frac{x+H_1y_0}{H_2}. \tag{3.27}$$

Since $\delta E=(K/2)\delta M_2-H\delta M_1=-\Sigma_cH_c\delta M_c$, previous results are recovered from these relations.

C. Correlation and response functions

One can also consider the evolution of two-time quantities. The correlation and response functions for magnetization and energy are defined as

$$C_{mm}(t,t')=\frac{1}{N}\langle\,\delta M(t)\,\delta M(t')\rangle,$$

$$G_{mm}(t,t')=\frac{1}{N}\,\frac{\delta\langle M(t)\rangle}{\delta H(t')},\tag{3.28}$$

$$C_{\varepsilon m}(t,t')=\frac{1}{N}\langle\,\delta E(t)\,\delta M(t')\rangle,\quad G_{\varepsilon m}(t,t')=\frac{1}{N}\,\frac{\delta\langle E(t)\rangle}{\delta H(t')},\tag{3.29}$$

$$C_{m\varepsilon}(t,t')=\frac{1}{N}\langle\,\delta M(t)\,\delta E(t')\rangle,$$

$$G_{m\varepsilon}(t,t')=\frac{T(t')}{N}\,\frac{\delta\langle M(t)\rangle}{\delta T(t')},\tag{3.30}$$

$$C_{\varepsilon\varepsilon}(t,t')=\frac{1}{N}\langle\,\delta E(t)\,\delta E(t')\rangle,$$

$$G_{\varepsilon\varepsilon}(t,t')=\frac{T(t')}{N}\,\frac{\delta\langle E(t)\rangle}{\delta T(t')}.\tag{3.31}$$

In Eq. (3.2) we have introduced the macroscopic observables $M_1=M$ and M_2. The related correlators and responses are

$$C_{ab}(t,t')=\frac{1}{N}\langle\,\delta M_a(t)\,\delta M_b(t')\rangle,$$

$$G_{ab}(t,t')=\frac{1}{N}\,\frac{\delta\langle M_a(t)\rangle}{\delta H_b(t')}\quad(a,b=1,2).\tag{3.32}$$

They code the same information, but will be more useful at some stages. C_{mm} is just another notation for C_{11}, while $C_{\varepsilon m}=(K/2)C_{21}-HC_{11}$ and $C_{\varepsilon\varepsilon}=(K^2/4)C_{22}-(HK/2)(C_{12}+C_{21})+H^2C_{11}$. Similar relations hold for the G's: $G_{\varepsilon m}=(K/2)G_{21}-HG_{11}$, $G_{m\varepsilon}=-(K/2)G_{12}-HG_{11}$, and $G_{\varepsilon\varepsilon}=(4/K^2)G_{22}+(HK/2)G_{12}-(HK/2)G_{12}+H^2G_{11}$, where we used that $G_{12}(t,t')=-G_{21}(t,t')$.

To derive the evolution of the correlations, one considers

$$\begin{aligned}\left\langle M\left(t+\frac{1}{N}\right)M(t')\right\rangle&\equiv\int dE'\,dM'\,dE_1\,dM_1\,P\left(E',M',t+\frac{1}{N};E_1,M_1,t'\right)M'M_1\\&=\langle M(t)M(t')\rangle+\int dE\,dM\,dE_1\,dM_1\,dx\,dy\;W(\beta x)P(E,M,t;E_1,M_1,t')P(x,y|E,M)yM_1.\end{aligned}\tag{3.33}$$

Subtracting $\langle M[t+(1/N)]-M(t)\rangle\langle M(t')\rangle$ and expanding $P(x,y|E,M)$, this yields the evolution equation for C_{mm}. The y integral can again be performed. In similar ways one proceeds for the other correlation functions. One finally has

$$\begin{aligned}\frac{\partial}{\partial t}C_{mm}(t,t')=\int dx\;W(\beta x)\bigg(&C_{mm}(t,t')\,\frac{\partial}{\partial m}\\&+C_{\varepsilon m}(t,t')\,\frac{\partial}{\partial\varepsilon}\bigg)y_0p(x|\varepsilon),\end{aligned}\tag{3.34}$$

$$\frac{\partial}{\partial t}C_{\varepsilon m}(t,t')=\int dx\;W(\beta x)xC_{\varepsilon m}(t,t')\,\frac{\partial}{\partial\varepsilon}p(x|\varepsilon),\tag{3.35}$$

$$\begin{aligned}\frac{\partial}{\partial t}C_{m\varepsilon}(t,t')=\int dx\;W(\beta x)\bigg(&C_{m\varepsilon}(t,t')\,\frac{\partial}{\partial m}\\&+C_{\varepsilon\varepsilon}(t,t')\,\frac{\partial}{\partial\varepsilon}\bigg)y_0p(x|\varepsilon),\end{aligned}\tag{3.36}$$

$$\frac{\partial}{\partial t}C_{\varepsilon\varepsilon}(t,t')=\int dx\;W(\beta x)x\frac{\partial}{\partial\varepsilon}p(x|\varepsilon)C_{\varepsilon\varepsilon}(t,t').\tag{3.37}$$

Their equal-time values follow from the above fluctuation formulas.

The equivalent formulation is

$$\begin{aligned}\frac{\partial}{\partial t}C_{ab}(t,t')=\sum_c\;&C_{cb}(t,t')\,\frac{\partial}{\partial m_c}\\&\times\int dx\;W(\beta x)\overline{y}_a p(x|m_1,m_2).\end{aligned}\tag{3.38}$$

D. Response functions

The energy-energy response function $G_{\varepsilon\varepsilon}(t,t')$, defined in Eq. (3.31), takes the form

$$G_{\varepsilon\,\varepsilon}(t,t')=\frac{-\beta}{N}\int dE\,dE_1\,dx_1\,E$$
$$\times\left[P\left(E,t\middle|E_1+x_1,t'+\frac{1}{N}\right)\right.$$
$$\left.-P\left(E,t\middle|E_1,t'+\frac{1}{N}\right)\right]\frac{\partial W(\beta x_1)}{dt\,\partial\beta}$$
$$\times p\left(x_1\middle|\frac{E_1}{N}\right)P(E_1,t'). \qquad (3.39)$$

For our parallel Monte Carlo updates it holds that $dt=1/N$. Both terms satisfy the same evolution equation, implying

$$\frac{\partial}{\partial t}G_{\varepsilon\,\varepsilon}(t,t')=-g(t)G_{\varepsilon\,\varepsilon}(t,t') \qquad (3.40)$$

with

$$g(t)=-\int dx\,W(\beta x)x\frac{\partial}{\partial\varepsilon}p(x|\varepsilon). \qquad (3.41)$$

Since in the oscillator model the energy evolves independently of H, it is obvious that $G_{\varepsilon\,m}=0$ at all times. The relation $G_{\varepsilon\,m}=-\Sigma_c H_c G_{c1}$ then implies $G_{21}(t,t')=-(H_1/H_2)G_{11}(t,t')$. In the spherical spin model, to be introduced later, this argument does not hold.

From the evolution (3.18) of $m(t)$ one gets immediately that G_{mm} and $G_{m\varepsilon}$ satisfy

$$\frac{\partial}{\partial t}G_{mm}(t,t')=-f(t)G_{mm}(t,t'),$$
$$\frac{\partial}{\partial t}G_{m\varepsilon}(t,t')=-f(t)G_{m\varepsilon}(t,t'). \qquad (3.42)$$

The equivalent formulation is

$$\frac{\partial}{\partial t}G_{ab}(t,t')=\sum_c G_{cb}(t,t')\frac{\partial}{\partial m_c}$$
$$\times\int dx\,W(\beta x)\overline{y_a}p(x|m_1,m_2). \qquad (3.43)$$

The derivation of equal-time responses is a bit tedious. Let us take $a=b=1$ and change the field from H to $H+\Delta H(k)$ at the time steps $t+k/N$ $(k=1,\ldots,n)$. It holds that

$$\left\langle M_1\left(t+\frac{k+1}{N}\right)\right\rangle-\left\langle M_1\left(t+\frac{k}{N}\right)\right\rangle$$
$$=\int dy_1\,dy_2\,dM_1\,dM_2\,W(\beta\delta E_k)y_1p(y_1,y_2|M_1,M_2)$$
$$\times p\left(M_1,M_2,t+\frac{k}{N}\right), \qquad (3.44)$$

where

$$\delta E_k=\frac{K}{2}y_2-[H+\Delta H(k)](M_1+y_1)$$
$$+[H+\Delta H(k-1)]M_1 \quad (k=1,\ldots,n). \qquad (3.45)$$

Generalizing to all four cases, we have a response,

$$G_{ab}(t^+,t)\equiv\lim_{N\to\infty}\frac{1}{\Delta t}\frac{\partial\langle m_a(t+\Delta t)\rangle}{\partial\Delta H_b}$$
$$\equiv\lim_{N\to\infty}\frac{\left\langle m_a\left(t+\dfrac{n+1}{N}\right)\right\rangle-\mathrm{idem}[\Delta H(k)=0]}{dt\sum_k\Delta H(k)}$$
$$=G_{ab}^{\mathrm{main}}(t^+,t)+G_{ab}^{\mathrm{switch}}(t^+,t) \qquad (3.46)$$

where we used that $dt=1/N$ and $\Delta t=n/N$. The main term arises from the y_a terms in Eq. (3.45),

$$G_{ab}^{\mathrm{main}}(t^+,t)=-\beta\int dy_1\,dy_2\,W'(\beta x)y_ay_bp(y_1,y_2|m_1,m_2)$$
$$=-\beta\int dx\,W'(\beta x)\left[\overline{y_a}\,\overline{y_b}+\left(-\frac{H_1}{H_2}\right)^{a+b-2}\Delta_y\right]$$
$$\times p(x|m_1,m_2) \quad (a,b=1,2), \qquad (3.47)$$

where $W'(\beta x)=-\exp(-\beta x)$ for $x>0$ and zero for $x<0$. The contribution for switching on and off comes from the $M_a[\Delta H_a(k)-\Delta H_a(k-1)]$ terms,

$$G_{ab}^{\mathrm{switch}}(t^+,t)=\beta\frac{d}{dt}\left\{m_b(t)\int dy_1\,dy_2\,W'(\beta x)\right.$$
$$\left.\times y_ap(y_1,y_2|m_1(t),m_2(t))\right\}. \qquad (3.48)$$

It does not depend on the precise switching procedure, but neither does it not vanish for adiabatic procedures. In our models this term will have contributions proportional to $\dot m_{1,2}\sim 1/t$, so in the large-t domain it is much smaller than the terms of our interest. We shall neglect it from now on. We should point out, however, that the responses $G_{m\varepsilon}$ and $G_{\varepsilon\,\varepsilon}$ do not involve such switching terms. This is related to the nature of the Monte-Carlo dynamics.

For the responses with respect to an instantaneous temperature pulse, one has

$$G_{m\varepsilon}(t^+,t)=-\beta\int dx\,W'(\beta x)xy_0p(x|\varepsilon), \qquad (3.49)$$

$$G_{\varepsilon\,\varepsilon}(t^+,t)=-\beta\int dx\,W'(\beta x)x^2p(x|\varepsilon). \qquad (3.50)$$

The relation with G_{ab} is exactly as for the C's, see below Eq. (3.32), as these two quantities do not suffer from switching effects.

IV. GLASSY DYNAMICS OF THE OSCILLATOR MODEL

We are considering a system with one mode. In view of the equilibrium relation $\varepsilon_{\mathrm{eq}}=T/2$ we may introduce the effective temperature T_e by

$$T_e(t)\equiv 2\varepsilon(t). \tag{4.1}$$

The dynamics of the oscillator model simplifies in the region $T\ll A=K\Delta^2/8$. Technically this occurs since for $\varepsilon\ll A$ or $T_e\ll A$ we can approximate in the expression

$$p(x|\varepsilon)=\frac{1}{4\sqrt{\pi A T_e}}\exp\left(-\beta_e A+\frac{\beta_e x}{2}\right)\exp\left(-\frac{(\beta_e x)^2}{16\beta_e A}\right) \tag{4.2}$$

the last Gaussian factor by $1-x^2/16AT_e$, leaving only exponential integrals. We shall investigate the dynamics in this region, and look for relations satisfied by observables.

A. Equilibrium regime

In equilibrium one has $\varepsilon=T/2$, $m=H/K$. Then there holds the detailed balance

$$W(\beta x)p(x|\varepsilon)=W(-\beta x)p(-x|\varepsilon) \tag{4.3}$$

assuring that $\dot{\varepsilon}=0$ in Eq. (3.16). For Eq. (3.22) this implies

$$\langle\delta E^2\rangle=\frac{1}{2}NT^2 \tag{4.4}$$

in accordance with the equilibrium relation $dU/dT=\beta^2\langle\delta\mathcal{H}^2\rangle$. The relation (3.24) amounts to

$$\langle\delta M^2\rangle=\frac{NT}{K}. \tag{4.5}$$

This is also expected, since only the diagonal $i=j$ terms in $\langle\delta M^2\rangle=\Sigma_{ij}\langle\delta x_i\,\delta x_j\rangle$ contribute at equilibrium, showing that $K\langle\delta M^2\rangle/2$ will indeed reduce to $NT/2$, the equilibrium value of E. Finally, Eq. (3.25) shows that the cross correlation $\langle\delta E\,\delta M\rangle$ vanishes.

The evolution equation (3.16) for the energy can be expressed in the notation of Ref. [20],

$$\frac{d\varepsilon(t)}{dt}=-\left(2\varepsilon(t)-\frac{T}{2}\right)f(t)+2A\,\mathrm{erfc}(\alpha(t)), \tag{4.6}$$

where $A=K\Delta^2/8$, $\alpha(t)=\sqrt{A/2\varepsilon(t)}$, $f(t)$ was defined in Eq. (3.19), and

$$\mathrm{erfc}(\alpha)=\frac{2}{\sqrt{\pi}}\int_\alpha^\infty dx\,e^{-x^2} \tag{4.7}$$

$$\approx\frac{e^{-\alpha^2}}{\alpha\sqrt{\pi}}\left(1-\frac{1}{2\alpha^2}+\frac{3}{4\alpha^4}\right)\quad(\alpha\gg 1). \tag{4.8}$$

We can look at relaxation close to equilibrium, where $\alpha_{\mathrm{eq}}=\sqrt{\beta A}$. We set $\varepsilon=T/2+\delta\varepsilon$. Equation (3.16) becomes to linear order

$$\frac{d\delta\varepsilon}{dt}=-\delta\epsilon\left(8\beta A(2\beta A+1)\mathrm{erfc}(\sqrt{\beta A})-16\beta A\sqrt{\frac{\beta A}{\pi}}e^{-\beta A}\right)\equiv-\frac{\delta\epsilon}{\tau_{\mathrm{eq}}^{(\varepsilon)}}. \tag{4.9}$$

When $T\ll A$, the equilibrium time scale becomes, due to the expansion (4.7),

$$\tau_{\mathrm{eq}}^{(\varepsilon)}\approx\sqrt{\frac{\pi\beta A}{64}}e^{\beta A}. \tag{4.10}$$

The latter also follows from Eq. (3.16) by performing the x integral, after neglecting the $\exp(-x^2/2\Delta_x)$ factor of $p(x|\varepsilon)$.

From Eq. (3.18) it is clear that the magnetization relaxes to its equilibrium value $m_{\mathrm{eq}}=H/K$ at time scale

$$\tau_{\mathrm{eq}}^{(m)}=\frac{1}{f(\infty)}=\frac{2T}{A}\tau_{\mathrm{eq}}^{(\varepsilon)}. \tag{4.11}$$

The important fact for us is that both time scales have an Arrhenius behavior $\sim\exp(A/T)$ at low T. This implies that the oscillators, subject to parallel Monte Carlo dynamics, can easily fall out of equilibrium at low enough T, and thus exhibit interesting glassy behavior.

B. Cooling procedures and the glassy transition

Equation (3.16) simplifies in the regime $T_e\ll A$. Indeed, as $x^2\sim T_e^2\ll\Delta_x=8AT_e$, we can neglect the Gaussian factor $\exp(-x^2/2\Delta_x)$ of $p(x|\varepsilon)$ in Eq. (4.2). We thus obtain

$$\dot{T}_e=-\frac{2T_e^2}{\sqrt{\pi A T_e}}\left(1-\frac{T^2}{(2T_e-T)^2}\right)e^{-\beta_e A}. \tag{4.12}$$

The condition $T_e>T/2$ is typically satisfied, since $T_e>T$ in cooling and aging experiments, and $T_e\to T$ in heating the glass.

Using Eq. (4.10), we can write this for T_e close to T in the universal form

$$\dot{T}_e=\frac{T-T_e}{\tau_{\mathrm{eq}}(T_e)}. \tag{4.13}$$

We can now introduce the inverse function $\tau_{\mathrm{eq}}^{-1}(t)$; in our case (4.10) it reads to leading order $\tau_{\mathrm{eq}}^{-1}(t)=A/\ln t$. Let us then consider a nonlinear cooling process of the form [10]

$$T(t)=(1-R)T_g+R\,\tau_{\mathrm{eq}}^{-1}(t)\approx(1-R)T_g+R\frac{A}{\ln t}. \tag{4.14}$$

It involves two parameters: the glassy transition temperature T_g and the dimensionless cooling speed R. A nonlinear cooling experiment of this form could be performed in any system with a quickly diverging equilibrium time scale.

We first show that a glassy transition occurs around time scale $t_g=\exp\beta_g A$, where one has $T(t)\approx T_g$. The time scale during which the system basically remains at temperature T is

$$\tau_{\text{cooling}}=\frac{T(t)}{|\dot{T}(t)|}\sim t. \tag{4.15}$$

Its ratio to the equilibrium time scale is

$$\frac{\tau_{\text{cooling}}(T(t))}{\tau_{\text{eq}}(T(t))}\sim\left(\frac{t_g}{t}\right)^{R-1}. \tag{4.16}$$

We can discriminate three cases. (a) When $R>1$, then for $t \ll t_g$ there is equilibrium at the instantaneous temperature $T(t)$. For $t>t_g$ the instantanous equilibration time τ_{eq} is larger than the cooling time scale τ_{cooling}, and the system becomes glassy. (b) For $0<R<1$, this process describes cooling in a glassy state so slowly that equilibrium is reached around time t_g. (c) Finally, for $R<0$ it describes heating in the glassy state, and equilibrium is reached around time t_g.

Equation (4.14) implies that

$$\dot{T}=\frac{R}{\tau_{\text{eq}}'[T_g-(T_g-T)/R]}. \tag{4.17}$$

This allows us to combine Eqs. (4.13) and (4.17) into the time-independent form

$$\left.\frac{\partial T_e}{\partial T}\right|_H=\frac{T-T_e}{R}\,\frac{\tau_{\text{eq}}'[T_g-(T_g-T)/R]}{\tau_{\text{eq}}(T_e)}. \tag{4.18}$$

For $T-T_g \gg T_g^2/A$ one has the equilibrium value $T_e=T$, with exponentially small corrections. Well below the glass transition $T-T_g \ll -T_g^2/A$ one has $T_e=T_g-(T_g-T)/R$. Due to Eq. (4.10) this implies that $\tau_{\text{eq}}(T_e)\sim \exp\beta_e A\sim t$, so $T_e \approx A/\ln t$. As we shall see in the next section, this is the same behavior as occurs for aging at $T=0$. We may conclude that the system then basically has forgotten its cooling history, and just ages as at any low enough temperature. Similar behavior was found by Godrèche and Luck in the backgammon model [19].

We may go to dimensionless variables by setting

$$T=T_g+\frac{T_g^2}{A}x, \quad T_e=T_g+\frac{T_g^2}{A}y, \tag{4.19}$$

and obtain

$$\frac{dy}{dx}=\frac{y-x}{R}e^{y-x/R}. \tag{4.20}$$

This equation is probably universal. Indeed, it is a small excercise to check that the very same equation follows from Eq. (4.18) when τ_{eq} has a Vogel-Tammann-Fulcher-type law $\tau_{\text{eq}}\sim\exp[A^{\gamma}(T-T_0)^{-\gamma}]$, and a glass transition occurs in a narrow range around some T_g with $T_g-T_0 \ll A$.

Equation (4.20) can be solved analytically for large negative and large positive x. Let us introduce

$$w=\left(\frac{1}{R}-1\right)x. \tag{4.21}$$

For large negative w one sets

$$y=x-\ln z(v), \quad v=e^{w}=e^{-(R-1)x/R}, \tag{4.22}$$

to obtain

$$(R-1)v^2z'(v)+\ln z(v)+Rvz(v)=0. \tag{4.23}$$

By series expansion one finds

$$\begin{aligned} z=1-Rv&+\frac{R}{2}(5R-2)v^2-\frac{R}{3}(29R^2-27R+6)v^3\\ &+\frac{R}{24}(1181R^3-1812R^2+900R-144)v^4\\ &-\frac{R}{5}(1529R^4-3345R^3+2690R^2-940R+120)v^5\\ &+\cdots. \end{aligned} \tag{4.24}$$

This implies for the specific-heat factor an exponential approach to equilibrium,

$$\begin{aligned} \left.\frac{\partial T_e}{\partial T}\right|_H&=\frac{dy}{dx}\\ &=-\frac{\ln z(v)}{Rvz(v)}=1+(R-1)\\ &\quad\times\left(-v+2(2R-1)v^2-\frac{3}{2}(5R-2)(3R-2)v^3\right.\\ &\quad\left.+\frac{4}{3}(4R-3)(29R^2-27R+6)v^4\right)+\cdots. \end{aligned} \tag{4.25}$$

When $R>1$ or $R<0$, this applies for large positive x. If $0<R<1$, it applies for large negative x.

For large positive w one sets

$$s=\frac{1}{w}=-\frac{R}{(R-1)x} \tag{4.26}$$

and

$$y=-\frac{1}{(R-1)s}+\ln s-\ln u(s) \tag{4.27}$$

yielding

$$u(s)=1+s\ln s-s\ln u(s)-(R-1)su(s)+(R-1)s^2u'(s). \tag{4.28}$$

By iteration one finds an expansion in powers of s and $\Lambda = \ln s$,

$$\begin{aligned} u(s)=1&+(\Lambda-R+1)s+(2R-2-\Lambda)s^2\\ &+\left(-8R+\frac{11}{2}+3\Lambda+\frac{1}{2}\Lambda^2-2\Lambda R+\frac{5}{2}R^2\right)s^3\\ &+\left(-\frac{57}{2}R^2+\frac{16}{3}R^3+45R+18\Lambda R+2\Lambda^2R-5\Lambda R^2\right.\\ &\left.-\frac{1}{3}\Lambda^3-\frac{7}{2}\Lambda^2-14\Lambda-\frac{131}{6}\right)s^4, \end{aligned} \tag{4.29}$$

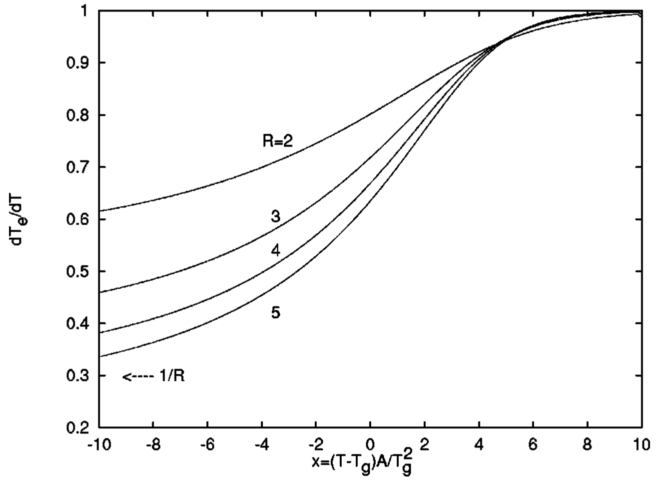

FIG. 3. Specific-heat factor $\partial T_e/\partial T$ as a function of reduced temperature in nonlinear cooling experiments with different speed parameter R. The asymptotic values are 1 to the right and $1/R$ to the left.

This implies for the specific-heat factor an algebraic approach to the value $1/R$, with logarithms in the subleading terms

$$\begin{aligned}\left.\frac{\partial T_e}{\partial T}\right|_H &= \frac{1+s\Lambda - s\ln u(s)}{Ru(s)}\\ &= \frac{1}{R}+\frac{R-1}{R}\bigg(s+(R-\Lambda-2)s^2+(R^2-2R\Lambda-7R\\ &\quad +\Lambda^2+7+5\Lambda)s^3+(2R^3-35R^2-6R^2\Lambda+46R\Lambda\\ &\quad +92R+6\Lambda^2R-52\Lambda-17\Lambda^2-61-2\Lambda^3)\frac{s^4}{2}\bigg)\\ &\quad +\cdots . \end{aligned} \tag{4.30}$$

When $R>1$ or $R<0$ this applies for large negative x. If $0<R<1$ it applies for large positive x. It is trivial to see that both Eqs. (4.25) and (4.30) go the correct value $\partial T_e/\partial T=1$ in the equilibrium limit $R\to 1$. In that limit the system will remain in equilibrium, because the cooling procedure is very slow.

In Figs. 3–6 we present the universal line shapes for the specific-heat factor $dT_e/dT=2c$ for several values of R. They exhibit the features known from experiments.

The analysis of this section thus shows that cooling in systems with an Arrhenius law leads to glassy behavior quite similar to that expected for realistic glasses.

C. Aging in the glassy regime

Suppose we quench the system at time $t=0$ from an equilibrium state at temperature $T_{\mathrm{quench}} \ll A$ to a lower temperature T. As opposed to the preceding section, we now assume that after the quench the system is far from equilibrium (viz. $T_{\mathrm{quench}}-T \gg T_{\mathrm{quench}}^2/A$). Then Eq. (4.13) may be written as

$$\frac{d(e^{\beta_e A})}{(1-r^2)\sqrt{\beta_e A}}=\frac{2}{\sqrt{\pi}}dt, \tag{4.31}$$

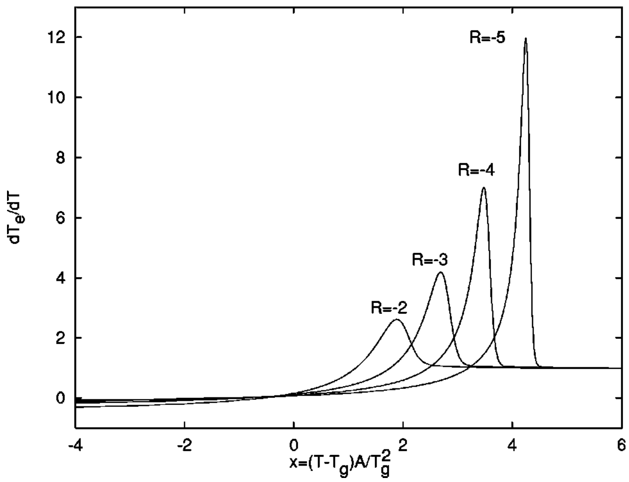

FIG. 4. Specific-heat factor $\partial T_e/\partial T$ as a function of reduced temperature in nonlinear heating experiments with different speed parameter R.

where we use the short hand

$$r=\frac{T}{2T_e-T}. \tag{4.32}$$

Its integral is

$$\frac{e^{\beta_e A}}{(1-r^2)\sqrt{\beta_e A}}=\frac{2}{\sqrt{\pi}}(t+t_0), \tag{4.33}$$

where t_0 follows by inserting at $t=0$ the value $T_e=T_{\mathrm{quench}}$. This result may be written as

$$\beta_e A-\frac{1}{2}\ln \beta_e A=\ln\frac{t+t_0}{\tau_0}, \qquad \tau_0=\frac{\sqrt{\pi}}{2(1-r^2)}. \tag{4.34}$$

For large t one has to leading order $T_e=A/\ln t$, while the initial condition gives a small correction of order $t_0/t \sim \exp(-\beta_e A)$; it may thus be neglected for $t>10t_0$. This says

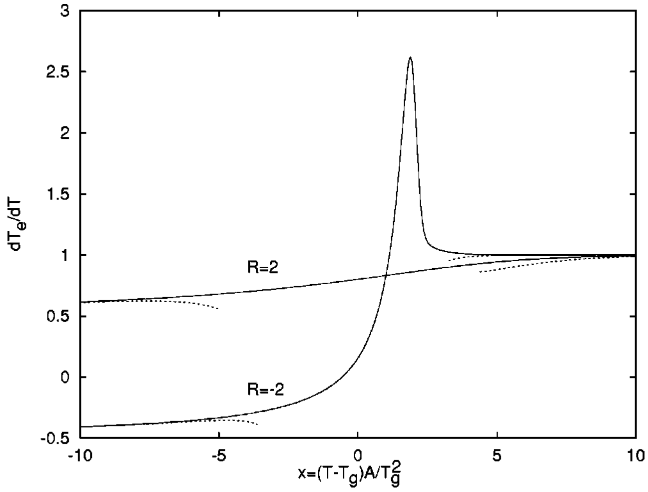

FIG. 5. Specific-heat factor $\partial T_e/\partial T$ as a function of reduced temperature in a nonlinear cooling experiment with $R=2$ and in a nonlinear heating experiment with $R=-2$. Dashed lines are asymptotes from Eqs. (4.25) and (4.30).

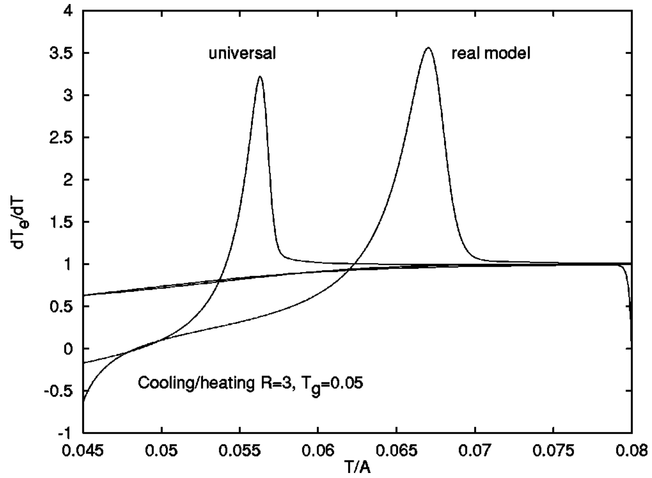

FIG. 6. Specific-heat factor $\partial T_e/\partial T$ as a function of reduced temperature in a nonlinear cooling experiment with $R=3$, and for a nonlinear heating experiment with $R=-3$. The ‘‘universal’’ curve is from previous theory. In the ‘‘real model’’ the original differentio-integral equations have been used, and R has changed from $R=3$ to $R=-3$ after reaching $T=0.045A$.

the initial condition is washed out, and is the basis for our interpretation that each decade is practically independent of the previous one. Likewise, the effect of a finite T is very small, and to leading order one could set $T=0$. This says that in the glassy regime the energy essentially evolves as if the system had been quenched to $T=0$. Only near the return to equilibrium does the T-dependent factor in Eq. (4.34) bring a vanishing argument in the logarithm, from which nontrivial behavior results, as discussed in Sec. IV B.

To leading order one may invert Eq. (4.34) to obtain

$$T_e(t)\approx\frac{A}{\ln\dfrac{t}{\tau_0}+\dfrac{1}{2}\ln\ln\dfrac{t}{\tau_0}}. \tag{4.35}$$

In practice this need not be a good approximation since $1/\ln t$ is usually not very small. For our purposes (leading-order expansion in powers of T_e) this is equivalent to $A/(\ln t+\frac{1}{2}\ln\ln t)$, and actually even to $A/\ln t$. It is a simple excercise to check that one has

$$\tau_{\rm eq}^{(\varepsilon)}(T_e)\approx\left(1-\frac{T^2}{(2T_e-T)^2}\right)\frac{2t}{\sqrt{\pi}}\sim t \tag{4.36}$$

proving our general assertion that in the aging regime the effective temperature also follows by equating the equilibrium time scale to t.

In the aging regime Eq. (3.19) becomes

$$\begin{aligned} f&=2\sqrt{\frac{\beta_eA}{2}}e^{-\beta_eA}(1+r)\left(1-\frac{T_er^2}{2A}\right)\\ &=\frac{1}{(1-r)t}=\frac{2T_e-T}{2(T_e-T)t}. \end{aligned} \tag{4.37}$$

Let us define its integral as

$$h(t)=\text{const}\times\,\exp\int_0^t dt'\,f(t'). \tag{4.38}$$

Using $d\ln h/d\varepsilon=f/\dot{\varepsilon}$, we obtain

$$h(t)=\left(1-\frac{T\beta_e}{2}\right)\frac{(\beta_eA)^{3/2}e^{\beta_eA/2}}{(1-T\beta_e)^{\beta A/2+5/4}}. \tag{4.39}$$

For $T>0$ this behaves as $\sqrt{t}$, with logarithmic corrections. At $T=0$ the resulting asymptotic scaling $h(t)\sim t(\ln t)^2$ differs from the result $h\sim t\sqrt{\ln t}$ reported by [20]. However, their Fig. 2 already show a deviation between the data and their asymptotic formula, which becomes increasingly worse in the asymptotic limit. We were informed by Hennes that the present expressions (4.39) and (4.34) give for $t'\geqslant100$ an almost perfect agreement with the numerical solution of the integro-differential equations [39].

For later use, we mention the results

$$g=2e^{-\beta_eA}\sqrt{\frac{\beta_eA}{\pi}}\left(1-r^2+\frac{T_e}{2A}r^2(1+r)(1+3r)\right) \tag{4.40}$$

and

$$\tilde{h}(t)=\text{const}\times\,\exp\int_0^t dt'\,g(t')=(\beta_eA)^{3/2}\frac{(1-T\beta_e/2)^2}{1-T\beta_e}e^{\beta_eA}. \tag{4.41}$$

Due to Eq. (3.18), the magnetization relaxes as

$$m(t)=\frac{H}{K}+\left(m(t_0)-\frac{H}{K}\right)\frac{h(t_0)}{h(t)}. \tag{4.42}$$

In the regime of large times and small $T_e\sim1/\ln t$, the deviation $m(t)$ from H/K is exponentially small in T_e. As compared to the power law that occurs in the energy (recall that $\varepsilon=T_e/2$), this can be neglected. This says that the magnetization quickly goes to its quasistationary value.

D. Correlations

Bonilla *et al.* considered the on-site correlation function $\langle x_i(t)x_i(t')\rangle$ [20]. At nonzero field it would become $\langle\delta x_i(t)\delta x_i(t')\rangle$, with $\delta x_i=x_i-\langle x_i\rangle(t)$. However, the correlation function related to thermodynamics is the global correlator $C_{mm}(t,t')=\Sigma_{i,j}\langle\delta x_i(t)\delta x_j(t')\rangle$, defined in Eq. (3.28). Its equal-time value is found from Eq. (3.24). We shall now study its two-time structure.

Let us introduce

$$\begin{aligned} \langle x\rangle&=\frac{\displaystyle\int dx\,W(\beta x)xp(x|\varepsilon)}{\displaystyle\int dx\,W(\beta x)p(x|\varepsilon)}\\ &\approx-4T_e\frac{T_e-T}{2T_e-T}\\ &=-2T_e(1-r), \end{aligned} \tag{4.43}$$

where the explicit result holds for T_e and T much smaller than A. After dividing by Eq. (3.16), we may write Eq. (3.24) as

$$2\langle x\rangle \frac{\dot{C}_{mm}(t,t)}{\dot{T}_e(t)} = \frac{C_{mm}(t,t)}{T_e(t)}(2\langle x\rangle - K\Delta^2) + \Delta^2, \quad (4.44)$$

where we used that $\langle \delta E\,\delta M\rangle$ is exponentially small in T_e. The dominant behavior follows by neglecting the $\langle x\rangle \sim T_e$ terms. However, they can be fully taken into account, as the solution to this equation reads

$$C_{mm}(t,t) = \frac{T_e(t)}{K}. \quad (4.45)$$

Corrections are exponentially small in T_e. This result even holds when T, occurring in $\langle x\rangle$, depends on time. It also allows a simple check: The result $K\langle \delta M^2\rangle/2 \approx E = NT_e/2$ is in accordance with the expectation of Bonilla *et al.* [20] that off-diagonal terms $\langle \delta x_i\ \delta x_j\rangle$ with $i \neq j$ are subleading.

Solving Eq. (3.34) for $t' \neq t$, we can neglect the $C_{\varepsilon m}$ term, since it is exponentially small in T_e. This yields

$$C_{mm}(t,t') = \frac{T_e(t')}{K}\,\frac{h(t')}{h(t)}, \quad (4.46)$$

where $h(t)$ was defined in Eq. (4.39).

1. Stretched exponential fitting and arguments against doing that

In the study of glasses, where often at best two orders of magnitude of C can be determined, it is commonly assumed that there occurs a stretched exponential decay,

$$C_{mm}(t,t') = a(t')\exp(-(t/\tau)^{\gamma}). \quad (4.47)$$

It is often stated that such stretched exponential decay is one of the basic properties of the glassy state.

In our case we would need that

$$h(t) = \exp(-d + (t/\tau)^{\gamma}) \quad (4.48)$$

for some set of parameters d, τ, γ, or, equivalently, that $\ln[d + \ln h(t)]$ is linear in $\ln t$ with slope γ. In view of the exact expression, this is certainly not an exact description. Let us, however, look at the plot for $d=0$ in Fig. 7.

It is seen that $\ln\ln h(t) = \gamma \ln t - \gamma \ln \tau$ can be a reasonable approximation in a not-too-wide large-time window $t_{\min} < t < t_{\max}$. In agreement with the usual findings, the effective exponent γ will decrease with T, and be bounded by the finite $T=0$ value. Notice, however, that it will also depend on the time window where the fit is made.

In the stretched exponential fitting procedure there is one more adjustable parameter, namely the overall prefactor $\exp(-d)$. In Fig. 8 we take $T=0.0025A$ and give plots of $\ln(d + \ln h)$ versus $\ln t$ for various d. In intervals where this curve is flat, h is well described by a stretched exponential (4.48).

This information can be used to obtain $C(t,t') \sim h(t')/h(t)$. To exaggerate what happens, we take a very simple linear fit to the data of Fig. 8: we consider the interval $10 \leq \ln t \leq 20$ and make, for a given value of d, a linear interpolation through the data points at $\ln t = 10$ and $\ln t = 20$. Taking $t' = \exp(10)$ we plot in Fig. 9 the fits to $\ln[h(t')/h(t)]$ for the cases $d=10$, $d=100$, and compare with the exact result $h(t')/h(t)$ from Eq. (4.39). By our construction, the results agree at $\ln t = 10$ and 20. It is seen that in all cases the fits are reasonable with regard to the scale presented in the figure, and that increasing d improves the overall fit.

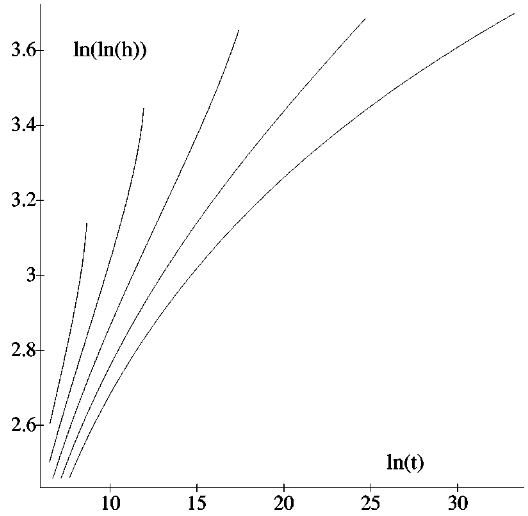

FIG. 7. The decay of the correlation function can be described by a stretched exponential in a time window where the data for $\ln\ln h$ are linear in $\ln t$. The stretching exponent then equals the slope in this figure, and will depend on T and on the chosen time window. From left to right, $T/A = 0.1$, 0.075, 0.05, 0.025, 0. The bending of the lines on the left (having a relatively large T) indicates that equilibrium is approached at the considered time scale.

The free fitting parameter d is not present in reality. It occurs if one overlooks that $h(t)/h(t')$ should be fitted as function of *two* parameters, namely both t and t'. Indeed, at one given t' one is free to choose d; however, emposing the asymmetry $t \rightarrow t'$ would bring $d \rightarrow (t'/\tau)^{\gamma}$. This reduced

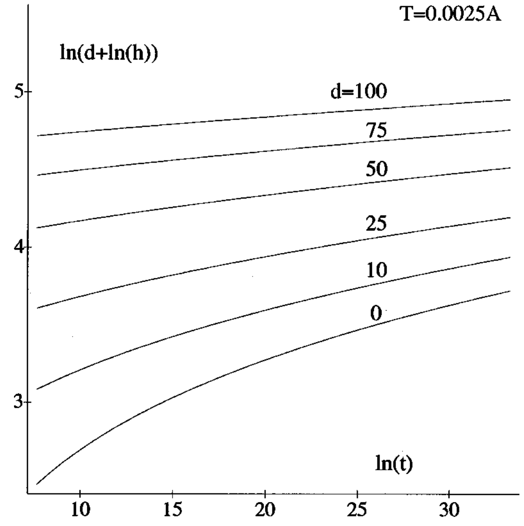

FIG. 8. Log-log plots of the function $d + \ln h(t)$ at $T=0.0025A$ for various d. h is well described by a stretched exponential $h(t) \sim \exp[-d + (t/\tau)^{\gamma}]$ in an interval where one of the plotted lines is straight. Then the slope yields γ and the offset $-\gamma \ln \tau$.

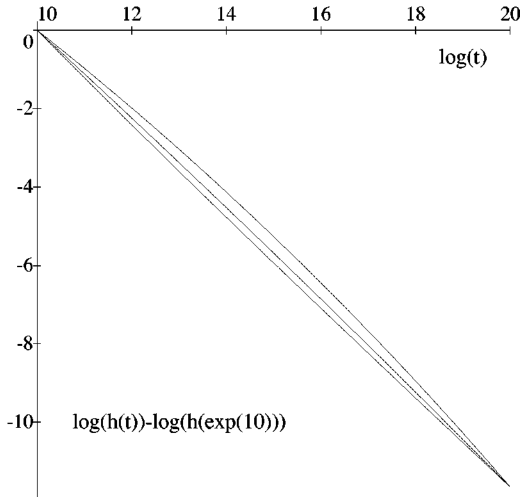

FIG. 9. Log-log plot of stretched exponential fits to the ratio $h(t')/h(t)$ at fixed $t'=\exp(10)$ and $T=0.0025A$. Upper line: by taking a linear interpolation between the points $\ln t=10$ and $\ln t=20$ for the case $d=10$ of the preceding figure. Middle line: the same for $d=100$. Lower line: exact result.

freedom would decrease the overall accuracy of the fit. In practice this is typically not done, partly because of the lack of data curves $C(t,t')$ at enough t' values. Nevertheless, whenever fitting of stretched exponentials is attempted, we stress to make a two-parameter fit of $C(t,t')$.

In our opinion the present fitting procedures merely say that stretched exponential fits can too often be made, without yielding too much insight. The standard statement that stretched exponential decay is one of the basic properties of the glassy state should, in our view, be taken with caution. What really happens is a slow decay, of which too few orders of magnitude are known to draw firm conclusions on their analytical form. It seems needless to say that in experiments the tails of the correlations have large relative errors, which, in our opinion, make the problem quite insensitive to stretched exponential or many other fitting procedures.

We feel that the situation even becomes worse if such fitting is applied for showing the presence of critical behavior near a supposed critical temperature in the glass, as is sometimes done.

E. Fluctuation-dissipation relations

We now consider aging dynamics at fixed $T\ll A$. Neglecting all y_0 contributions, we find from Eq. (3.46) the equal-time value $G_{mm}(t,t)=f(t)/K$. This result is exact for $H=0$ [20]. Its two-time form follows from Eq. (3.42),

$$G_{mm}(t,t')=\frac{f(t')}{K}\,\frac{h(t')}{h(t)}. \tag{4.49}$$

We can now consider the fluctuation-dissipation relation. We define the effective temperature $\tilde{T}_e$ by

$$\frac{\partial_{t'}C_{mm}(t,t')}{G_{mm}(t,t')}=\tilde{T}_e(t'). \tag{4.50}$$

By direct evaluation of the left-hand side, we find from Eq. (4.46), using Eqs. (4.12) and (4.37),

$$\tilde{T}_e(t)=T_e(t)+\frac{\dot{T}_e(t)}{f(t)}=T_e-\frac{T_e^2}{A}\,\frac{2(T_e-T)}{2T_e-T}+\mathcal{O}\left(\frac{T_e^3}{A^2}\right). \tag{4.51}$$

Due to Eq. (3.34) this agrees with the general result (2.40), which assures consistency with single-time expressions. As the second term is smaller by a factor T_e/A with respect to T_e, we thus see that to leading order the same effective temperature occurs as in the energy and the time scale. (The same happens when the local correlator is considered [20].) Notice, however, that the leading correction is nonuniversal, as it depends on the model parameter A. When equilibrium is approached, $T_e\to T$, and the correct limit $\tilde{T}_e=T$ is reproduced.

Let us now look at the energy fluctuations. To leading order we may neglect $d\langle\delta E^2\rangle/dt$ in Eq. (3.22). This brings

$$\frac{1}{N}\langle\delta E^2\rangle=C_{\varepsilon\varepsilon}(t,t)=\frac{-T_e^2\langle x^2\rangle}{4A\langle x\rangle}\approx\frac{T_e^3(t)}{A}\,\frac{1+r^3}{1-r^2}. \tag{4.52}$$

This result shows various points. First, even at $r=T=0$ it is one order of magnitude smaller than what one would anticipate from the equilibrium expression $C_{\varepsilon\varepsilon}=T^2/2$. Only in the glass-transition region $T_e-T\sim(1-r)T\sim T^2/A$ is the equilibrium scaling $C_{\varepsilon\varepsilon}\sim T^2$ recovered. We conclude that there is a complicated, nonuniversal T dependence in the whole aging regime $T<T_e$. The possibility of a model-independent generalization outside equilibrium of the relation $dU/dT=\beta^2\langle\delta E^2\rangle$ will be discussed in the Discussion.

For different times we find from Eqs. (3.37) and (4.41) that

$$C_{\varepsilon\varepsilon}(t,t')=\frac{T_e^3(t')}{A}\,\frac{1+r^3(t')}{1-r^2(t')}\,\frac{\tilde{h}(t')}{\tilde{h}(t)}. \tag{4.53}$$

Likewise, the Green's function follows from Eqs. (3.50) and (3.40) as

$$G_{\varepsilon\varepsilon}(t,t')=\frac{\tilde{h}(t')}{\tilde{h}(t)}\left(\frac{2T_e^2r^2(1+r)e^{-\beta_eA}}{\sqrt{\pi AT_e}}\right)(t'). \tag{4.54}$$

To leading order this yields the fluctuation-dissipation relation

$$\frac{\partial_{t'}C_{\varepsilon\varepsilon}(t,t')}{G_{\varepsilon\varepsilon}(t,t')}=T_e^{(\varepsilon\varepsilon)}(t'), \tag{4.55}$$

where the t dependence again has dropped out. The quantity

$$T_e^{(\varepsilon\varepsilon)}(t)=\frac{T_e(t)[1+r^3(t)]}{r^2(t)[1+r(t)]}=\frac{T_e(4T_e^2-6T_eT+3T^2)}{T^2} \tag{4.56}$$

is also an effective temperature that also has the correct limit when $T_e\to T$. Unlike T_e itself, it has no obvious model-independent interpretation. We feel that this is due to the fact that it relates to subleading quantities.

For the fluctuations (4.45) in M the nonuniversal terms are exponentially small in T_e. This shows that for the fluctuations in $M=M_1$ a quasiuniversal behavior takes place. As $C_{\varepsilon m}$ is negligible, the M_1M_2 cross fluctuations are also simple,

$$C_{12}(t,t')=\frac{2HT_e(t')h(t')}{K^2h(t)}, \tag{4.57}$$

plus exponentially small corrections in T_e, or power law in $1/t$. The M_2 correlations and responses have the form

$$C_{22}(t,t')=\frac{4H^2}{K^2}C_{11}(t,t')+\frac{4}{K^2}C_{\varepsilon\varepsilon}(t,t'),$$

$$G_{22}(t,t')=\frac{4H^2}{K^2}G_{11}(t,t')+\frac{4}{K^2}G_{\varepsilon\varepsilon}(t,t'). \tag{4.58}$$

In both expressions the first term is two orders of magnitude in T_e larger. On top of that, the second term decays faster ($\sim t'/t$ versus $\sqrt{t'/t}$) whenever T is nonzero. It thus holds that in all four cases [10]

$$\frac{\partial_{t'}C_{ab}(t,t')}{G_{ab}(t,t')}=\widetilde{T}_e(t') \quad (a,b=1,2). \tag{4.59}$$

This simple result suggests that in general the fields could also stand for a chemical potential, a pressure, or a quenched randomly directed forcing strength.

F. Nonequilibrium thermodynamics

We now wish to view previous results in the thermodynamic framework of Sec. II.

Since there is only one type of process, which is by definition slow, the entropy of the equilibrium processes S_{ep} vanishes. For such cases the configurational entropy can be derived simply. It is defined by the degeneracy of states with energy U, and given by the microcanonical partition sum

$$e^{\mathcal{I}}=\int Dx\,\delta[\mathcal{H}(x)-U]=\int_{-i\infty}^{i\infty}\frac{d\widetilde{\beta}}{2\pi i}e^{\widetilde{\beta}U}\int Dx\,e^{-\widetilde{\beta}\mathcal{H}(x)}, \tag{4.60}$$

where $Dx=\Pi_i\,dx_i$ is the integration measure. By the saddle-point method one obtains

$$\mathcal{I}=\max_{\widetilde{T}}\widetilde{\beta}[U-F_{\mathrm{eq}}(\widetilde{T})]=S_{\mathrm{eq}}(T_e), \tag{4.61}$$

where we used that for $U=U_{\mathrm{eq}}(T_e)$ the minimum is assumed at $\widetilde{T}=T_e$. This result holds generally in simple systems with only one time scale that diverges near $T=0$. Here we have

$$\mathcal{I}=S_{\mathrm{eq}}(T_e)=\frac{N}{2}\left(\ln\frac{T_e}{K}+1\right). \tag{4.62}$$

Since $dU=N\,dT_e/2-(NH/K)dH$, it is now clear that the formulation (2.9) of the first law is satisfied in the present nonequilibrium state. As $S_{\mathrm{ep}}=0$, the free energy reads

$$F=U-T_e\mathcal{I} \tag{4.63}$$

and it satisfies the relations (2.11).

As $m_1=H/K$ is temperature-independent, the modified Maxwell relation reduces to the standard one: in Eq. (2.15) the terms proportional to T vanish, and the other terms follow already from Eq. (2.9) with $S_{\mathrm{ep}}=0$. Neither is it interesting to investigate the first Ehrenfest relation (2.21): It holds trivially, as one has $\alpha=0$, $\chi=1/K$, implying $\Delta\alpha=\Delta\chi=0$. Notice, however, that the present results already require that the second Ehrenfest relation (2.22) is modified outside equilibrium [6]. Indeed, from Sec. IV B we have $\Delta C=N(R-1)/(2R)\neq 0$, while $\Delta\alpha=0$. Equation (2.24) is nevertheless satisfied, since $\partial T_e/\partial T=1/R$ and $d\mathcal{I}/dT=\partial\mathcal{I}/\partial T=N/(2T_g)$.

The fluctuation formula (2.31) is also satisfied. To show this explicitly, let us take $a=b=1$. Since there are no fast processes, the first term vanishes. The same holds for the third term, since $m=H/K$ leads to $\partial m/\partial T_e=0$. Due to Eq. (4.45) the second term equals $(NT_e/K)/(NT_e)=1/K$, which is the desired result. We can also check it by integrating up the instantaneous field pulses, as was done more generally in the argument starting with Eq. (2.35). The same conclusions hold for the other three cases. We have already mentioned that the fluctuation-dissipation relation (2.34) is satisfied with $\widetilde{T}_e$ given in Eq. (4.51), and that the apparent specific heat $C_H=N(\partial T_e/\partial T)/2$ has no simple connection with the energy fluctuations (4.52).

In all situations considered we have seen that $T_e\sim A/\ln t$ is to leading order in agreement with the time-scale relation $\tau_{\mathrm{eq}}(T_e)\sim t$. We have also seen that the correlation function has the scaling $h(t')/h(t)$, with, at finite T, $h(t)\sim\sqrt{t}$ times a function of $\ln t$. In the $T\rightarrow 0$ limit they become so strong that they replace the $h(t)\sim\sqrt{t}$ scaling by $h=t\times\mathrm{function}(\ln t)$.

In conclusion, the proposed picture applies to the harmonic oscillator model, even though a few aspects are quite trivial. In the next section we shall consider a model of spherical spins, which has a richer behavior when changing field, and in regard to the Ehrenfest relations.

V. MONTE CARLO DYNAMICS OF FREE SPHERICAL SPINS IN A RANDOM FIELD

The previous model had the drawback that the effect of a field was rather trivial. It was therefore of no great interest to check the first Ehrenfest relation: it is satisfied in a trivial way, having $\Delta\alpha=\Delta\chi=0$.

We have therefore considered a closely related model, containing free spherical spins in the presence of a random external field, which does not share these drawbacks [10]. Also in this very simple model Monte Carlo dynamics can be solved exactly and leads to glassy behavior. In fact, the dynamics just maps to leading order onto that of the oscillator model of the preceding section.

The Hamiltonian contains two parts, a ‘‘self-interaction’’ term involving fields Γ_i and a coupling to an external field H,

$$\mathcal{H}=-\sum_{i=1}^{N}\Gamma_i S_i-H\sum_{i=1}^{N}S_i\,. \tag{5.1}$$

The model is solvable for any set of quenched random fields Γ_i that have average zero and variance Γ^2. To simplify the discussion, we make the additional (but technically unneeded) assumption that $\Gamma_i=\pm\Gamma$, implying that at each spin position there is a quenched random unit vector Γ_i/Γ, along which the spins wish to point for large pinning field Γ. This limitation allows the exact gauge transformation $S_i\to\Gamma_i S_i/\Gamma$, which interchanges the role of H and Γ. Without the additional assumption, this interchange would also exist; this is due to the spherical nature of the spins.

In terms of the ‘‘staggered’’ magnetization $M_s\equiv(1/\Gamma)\Sigma_i\Gamma_i S_i$ one simply has $\mathcal{H}=-\Gamma M_s-HM$. When defining $H_1=H$, $H_2=\Gamma$, $M_1=M$, $M_2=M_s$, we may also write this as

$$\mathcal{H}=-\sum_{c=1}^{2}H_c M_c\,. \tag{5.2}$$

The spins are spherical, which means that they can take all real values compatible with

$$\sum_i S_i^2=N. \tag{5.3}$$

In equilibrium the system has a free energy,

$$\frac{F_{\rm eq}}{N}=\frac{T}{2}\ln\beta\mu-\frac{K^2}{2\mu}-\frac{\mu}{2}, \tag{5.4}$$

where

$$K=\sqrt{\Gamma^2+H^2} \tag{5.5}$$

and with chemical potential μ fixed by optimization, implying

$$\mu=\sqrt{K^2+\frac{1}{4}T^2}+\frac{1}{2}T. \tag{5.6}$$

This yields for the internal energy, the magnetization, and for the entropy

$$\frac{1}{N}U_{\rm eq}=-\frac{K^2}{\mu}=-\sqrt{K^2+\frac{1}{4}T^2}+\frac{1}{2}T\approx-K+\frac{1}{2}T-\frac{T^2}{8K}, \tag{5.7}$$

$$\frac{1}{N}M_{\rm eq}=\frac{H}{\mu}\approx\frac{H}{K}-\frac{HT}{2K^2}+\frac{HT^2}{8K^3}, \tag{5.8}$$

$$\frac{1}{N}S_{\rm eq}=\frac{1}{2}\ln\frac{T}{\mu}+\frac{1}{2}\approx\frac{1}{2}\ln\frac{T}{K}+\frac{1}{2}. \tag{5.9}$$

The approximations hold for low T.

A. Monte Carlo dynamics

As for the oscillators, one makes parallel Monte Carlo moves $S_i\to S_i'=S_i+r_i/\sqrt{N}$, with the r_i independently drawn from a Gaussian with average zero and variance Δ^2. Next one makes a global rescaling of the length of the spins, to reinforce the spherical constraint. This leads to the final update per time step,

$$S_i'=S_i+\frac{r_i}{\sqrt{N}}-S_i\sum_j\left(\frac{r_jS_j}{N\sqrt{N}}+\frac{r_j^2}{2N^2}\right)+\cdots\,. \tag{5.10}$$

This conserves the constraint (5.3). It implies for the change in the energy and in the total magnetization $M=\Sigma_i S_i$,

$$\mathcal{H}'-\mathcal{H}=\sum_i\left\{-\frac{(\Gamma_i+H)r_i}{\sqrt{N}}-\mathcal{H}\frac{r_iS_i}{N\sqrt{N}}-\mathcal{H}\frac{r_i^2}{2N^2}\right\},$$

$$M'-M=\sum_i\left\{\frac{r_i}{\sqrt{N}}-M\frac{r_iS_i}{N\sqrt{N}}-M\frac{r_i^2}{2N^2}\right\}. \tag{5.11}$$

Introducing the new variables

$$\varepsilon=K+\frac{\mathcal{H}}{N},\qquad m=\frac{M}{N},$$

$$\mu_1=m_{\rm eq}(\varepsilon)-m=-m+\frac{H}{K}-\frac{H}{K^2}\varepsilon\,, \tag{5.12}$$

which are small near equilibrium, this leads to moves $\mathcal{H}'=\mathcal{H}+x$, $M'=M+y$ with Gaussian transition probabilities of the type (3.6) and (3.7), having parameters

$$x_0=\frac{1}{2}\Delta^2(K-\varepsilon),\qquad \Delta_x=\Delta^2\varepsilon\,(2K-\varepsilon), \tag{5.13}$$

$$y_0=-\frac{H}{K^2}x+\mu_1\frac{\Delta^2K^2-2Kx+2x\varepsilon}{2\varepsilon\,(2K-\varepsilon)},$$

$$\Delta_y=\Delta^2\left(\frac{\Gamma^2}{K^2}-\frac{K^2\mu_1^2}{\varepsilon\,(2K-\varepsilon)}\right), \tag{5.14}$$

where

$$K=\sqrt{\Gamma^2+H^2}. \tag{5.15}$$

In particular at small ε the model of spherical spins in a random external field leads to a problem very similar to that of the uncoupled, identical oscillators in a steady field. The previous general formulas for variances, correlation, and response functions remain valid here.

B. Glassy transition and the Ehrenfest relations

The evolution for ε again satisfies Eq. (3.16), with the new expressions for x_0 and Δ_x. We can again introduce T_e by equating $U=-K+\varepsilon=U_{Eq}(T_e)$, so that

$$T_e=\frac{(2K-\varepsilon)\varepsilon}{K-\varepsilon}\approx2\varepsilon\left(1+\frac{\varepsilon}{2K}\right),$$

$$\varepsilon=K+\frac{T_e}{2}-\sqrt{K^2+\frac{T_e^2}{4}}\approx\frac{T_e}{2}-\frac{T_e^2}{8K}. \tag{5.16}$$

We also define

$$A = \frac{\Delta^2 K}{8}, \quad B = \frac{\Delta^2}{8}(K-\varepsilon). \tag{5.17}$$

$p(x|\varepsilon)$ takes the form (4.2) with $A \to B$. For $T_e \ll B$ one can again approximate it by an exponential. This yields the equilibrium time scale

$$\tau_{\mathrm{eq}}^{(\varepsilon)} = \frac{\sqrt{K^2+T^2/4}-T/2}{\sqrt{K^2+T^2/4}}\sqrt{\frac{\pi\beta B}{64}}\,e^{\beta B}. \tag{5.18}$$

For a nonlinear cooling process of the form (4.14), the results of Sec. IV B apply immediately. We consider cooling sequences with $R>1$, where the system goes from a paramagnet to a glassy state in a region around some $T_g \ll B$. Below the glassy transition one has an apparent specific heat

$$C = C_2 \left.\frac{\partial T_e}{\partial T}\right|_H . \tag{5.19}$$

This is of the general form (2.8), with background $C_1 = 0$, since there are no fast processes in the present model. It holds that

$$c_2 = \frac{C_2}{N} = \frac{1}{2} - \frac{T_e}{4\sqrt{K^2+T_e^2/4}} \approx \frac{1}{2} - \frac{T_e}{4K}. \tag{5.20}$$

The same universal line shapes of the oscillator model thus occur here, with nontrivial prefactor c_2. Between the right and left sides of the glassy transition region there is a difference $\Delta C = Nc_2(1-1/R)$.

Further on it will become clear that $m(t) - m_{\mathrm{eq}}(T_e)$ remains zero upon cooling at fixed field H. Therefore, one has

$$m = m_{\mathrm{eq}}(T_e) = \frac{H}{K} - \frac{H}{K^2}\varepsilon = \frac{H}{K^2}\left(\sqrt{K^2+\frac{T_e^2}{4}} - \frac{T_e}{2}\right). \tag{5.21}$$

This yields a magnetizability

$$\alpha = \frac{H}{2K^2}\left(1 - \frac{T_e}{\sqrt{4K^2+T_e^2}}\right)\frac{dT_e}{dT} \tag{5.22}$$

and, since $K^2 = \Gamma^2 + H^2$, a susceptibility $\chi = \chi_{11}$ of the form (2.28), with

$$\chi^{\mathrm{fluct}} = \frac{\Gamma^2 + T_e^2/4 + wT_e/2}{w(w+T_e/2)^2} \approx \frac{\Gamma^2}{K^3} - \frac{(\Gamma^2 - H^2)T_e}{2K^4}, \tag{5.23}$$

where $w = \sqrt{K^2 + T_e^2/4}$, and

$$\chi^{\mathrm{conf}} = -\frac{H}{w(2w+T_e)}\frac{\partial T_e}{\partial H} \approx -\frac{H}{2K^2}\left(1 - \frac{T_e}{2K}\right)\frac{\partial T_e}{\partial H}. \tag{5.24}$$

Around the glassy transition there occur smeared discontinuities in the apparent specific heat, magnetizability, and susceptibility,

$$\Delta c = c_2\left(1 - \left.\frac{\partial T_e}{\partial T}\right|_H\right), \tag{5.25}$$

$$\Delta\alpha = \frac{H}{K^2}c_2\left(1 - \left.\frac{\partial T_e}{\partial T}\right|_H\right), \tag{5.26}$$

$$\Delta\chi = \frac{H}{K^2}c_2\left.\frac{\partial T_e}{\partial H}\right|_T . \tag{5.27}$$

These results and Eq. (2.25) allow us to verify the first Ehrenfest relation (2.21).

From the identity $\mathcal{I} = S_{\mathrm{eq}}(T_e)$ and the expression (5.9) we obtain

$$\left.\frac{\partial\mathcal{I}}{\partial T_e}\right|_{T,H} = \frac{C_2}{T_e}, \quad \left.\frac{\partial\mathcal{I}}{\partial H}\right|_{T,T_e} = -\frac{HC_2}{K^2}. \tag{5.28}$$

We can now consider the modified second Ehrenfest relation (2.24). Due to Eqs. (5.25) and (5.26) it takes the form

$$\begin{aligned}
&\frac{c_2}{T_g}\left(1 - \left.\frac{\partial T_e}{\partial T}\right|_H\right) \\
&\quad = \frac{Hc_2}{K^2}\left(1 - \left.\frac{\partial T_e}{\partial T}\right|_H\right)\frac{dH_g}{dT} + \left(1 - \left.\frac{\partial T_e}{\partial T}\right|_H\right) \\
&\qquad \times \left(\frac{c_2}{T_g}\left.\frac{\partial T_e}{\partial T}\right|_H - \frac{Hc_2}{K^2}\frac{dH_g}{dT} + \frac{c_2}{T_g}\left.\frac{\partial T_e}{\partial H}\right|_T\frac{dH_g}{dT}\right).
\end{aligned} \tag{5.29}$$

After dividing out the common factor $1 - \partial T_e/\partial T$ and eliminating the remaining $\partial T_e/\partial T$ by use of the relation (2.25), it is seen that terms with and without dH_g/dT cancel separately. This implies that the modified second Ehrenfest relation is satisfied for any value of that parameter, as was to be expected.

Using Eq. (2.27) and the relation $T_g \approx A/\ln t_g$, the Prigogine-Defay ratio can now be expressed as

$$\Pi = \frac{\Delta C}{TN\Delta\alpha}\frac{dT_g}{dH} = \frac{K^2}{HT_g}\frac{dT_g}{dH} = 1 - \frac{K^2}{H\ln t_g}\frac{d\ln t_g}{dH}. \tag{5.30}$$

Contrary to what was long believed, the condition $\Pi<1$ is easily met. Indeed, in the case in which R is fixed, we may still choose the glassy transition line $T_g(H)$, or, equivalently, the glassy transition time scale $t_g(H)$. Values $\Pi<1$ thus occur when $dt_g/dH>0$, so in half of the sets of smoothly related cooling sequences. This analysis confirms our general argument that the Prigogine-Defay ratio can take any value between zero and infinity, and perhaps even negative values.

C. Aging regime and its thermodynamics

For temperatures in the aging regime we have, very analogous to Eq. (4.31),

$$\frac{d(e^{\beta_e B})}{dt}=\frac{2K^2}{(K-\varepsilon)^2}\sqrt{\frac{BT_e}{\pi}}(1-r^2),\tag{5.31}$$

where we again use the short hand $r=T/(2T_e-T)$. To leading order this relation even reduces to Eq. (4.31), the only change being $\exp(\beta_e A)\rightarrow\exp(\beta_e B)\approx\exp(\beta_e A+A/2K)$. Therefore, to leading order T_e again follows from Eq. (4.34), with $A\rightarrow A+AT_e/2K$.

Let us stress that we do not consider the regime $\Delta\gg1$, where a nonuniversal regime $1\ll\ln t\ll\Delta^2$ would occur. This is the subject of a recent work on a related model with fast and slow processes, in which a Kauzmann transition occurs [9].

In the next subsection it is made clear that $\mu_1=m_{\rm eq}-m$ is exponentially small in T_e. Therefore, the magnetization very closely follows its quasiequilibrium value set by T_e.

We can now check the thermodynamics. It holds that

$$U=N\left(-K+\frac{T_e}{2}-\frac{T_e^2}{8K}\right),\tag{5.32}$$

$$M=N\left(\frac{H}{K}-\frac{HT_e}{2K^2}+\frac{HT_e^2}{8K^2}\right),\tag{5.33}$$

$$\mathcal{I}=N\left(\frac{1}{2}\ln\frac{T_e}{K}+\frac{1}{2}-\frac{T_e}{4K}\right).\tag{5.34}$$

The first law (2.9) with $S_{\rm ep}=0$ reduces to $dU=T_e\,d\mathcal{I}-M\,dH$. At constant H it holds because one has replaced $T\rightarrow T_e$ in energy and entropy. Then one can take the difference between aging experiments at two nearby H's. The relation remains valid because M is essentially equal to its quasiequilibrium value $M_{\rm eq}(T_e,H)$.

In the modified Maxwell relation (2.15) the terms without explicit factor T cancel because of the first law (2.9) with $S_{\rm ep}=0$. The terms with explicit factor T cancel separately, because of the quasiequilibrium relation $\partial\mathcal{I}/\partial H|_{T,T_e}=-\partial M/\partial T_e|_{T,H}$ that follows from Eq. (2.11). Such a pairwise cancellation would, of course, not occur in less simple models. Indeed, in a glassy model with directed polymers [17] the modified Maxwell is also satisfied, but in a nontrivial manner [6].

D. Changing the external field and the need for an effective field

If also field H is changed in time, then we have to be more careful. The Monte Carlo dynamics now leads to

$$\dot m_a=\int dx\,W(\beta\tilde{x})\overline{y_a}p(x|\varepsilon),\tag{5.35}$$

where, again, $m_1=m$, $m_2=m_s$, and $\tilde{x}=x-\dot Hm$. We shall be interested in cases with logarithmically slow H, implying $\dot H\sim1/t$, where $\tilde{x}\approx x$.

From the definitions (5.12) we derive for the evolution of ε and μ_1

$$\begin{aligned}\dot\varepsilon&=\dot H\left(\frac{H}{K}-m\right)+\int dx\,W(\beta\tilde{x})xp(x|\varepsilon)\\&=\dot H\left(\frac{H}{K^2}\varepsilon+\mu_1\right)+\int dx\,W(\beta\tilde{x})xp(x|\varepsilon),\end{aligned}\tag{5.36}$$

$$\begin{aligned}\dot\mu_1&=-\dot H\left[-\frac{\Gamma^2}{K^3}+\varepsilon\frac{\Gamma^2-H^2}{K^4}+\left(\frac{H}{K}-m\right)\frac{H}{K^2}\right]-f\mu_1\\&\approx\dot H\frac{\Gamma^2}{K^3}-f\mu_1.\end{aligned}\tag{5.37}$$

So far we considered cooling at constant field. Then Eq. (4.39) says that $\mu_1(t)=\mu_1(t_0)h(t_0)/h(t)$ decays as a power law, namely $1/\sqrt{t}$ for $T>0$ and $1/t$ when $T=0$. Both behaviors are exponentially small in T_e, and much smaller than subleading powers of T_e that were neglected already. So to the accuracy considered we can set $M(t,H)$ equal to $M_{\rm eq}(T_e,H)$.

When the field is slowly changed in the course of time, the leading behavior of μ_1 is

$$\mu_1=\frac{\dot H\Gamma^2}{K^3f}.\tag{5.38}$$

As long as $|\mu_1|\ll HT_e/K^2$, the main change of $M(t)$ is still expressed by $M_{\rm eq}(T_e(t),H(t))$. Since $f\sim(1+r)/t$, this condition can be written as

$$\left|\frac{\partial H}{\partial\ln t}\right|\ll\frac{HKT_e(1+r)}{\Gamma^2}\quad\rightarrow\left|\frac{\partial H}{\partial T_e}\right|\ll\frac{AHK(1+r)}{\Gamma^2T_e}.\tag{5.39}$$

This condition is reasonable, and easily satisified near $T_e=0$.

When condition (5.38) is not fulfilled, it is not possible to describe $U(t)$ and $M(t)$ by $T_e(t)$ alone. One needs a second effective variable, namely the effective field $H_e(t)=H(t)+\delta H_e(t)$. Setting $K_e=\sqrt{\Gamma^2+H_e^2}$, we then have from quasiequilibrium formulas at (T_e,H_e)

$$u=-K_e+\frac{T_e}{2}\approx-K-\frac{H}{K}\delta H_e+\frac{T_e}{2},\tag{5.40}$$

$$m=\frac{H_e}{K_e}\left(1-\frac{T_e}{2K_e}\right)\approx\frac{H}{K}+\frac{\Gamma^2}{K^3}\delta H_e-\frac{H}{2K^2}T_e.\tag{5.41}$$

From the definitions (5.12) we can make the identifications

$$\varepsilon=\frac{T_e}{2}-\frac{H}{K}\delta H_e,\qquad\mu_1=-\frac{\Gamma^2-H^2}{K^3}\delta H_e,\tag{5.42}$$

or their inversion

$$T_e=2\varepsilon-\frac{2HK^2}{\Gamma^2-H^2}\mu_1,\qquad\delta H_e=-\frac{K^3}{\Gamma^2-H^2}\mu_1.\tag{5.43}$$

One can now consider any class of fields that change logarithmically slowly in time. After solving the dynamics, T_e and H_e follow. One can then also study fluctuations and the fluctuation-dissipation relation for this more general case, and look for universal behaviors. This matter is the subject of current research [9], which falls outside the scope of the present paper.

E. Fluctuations and fluctuation-dissipation relation

The energy fluctuations still follow from Eq. (3.22), and depend on H only through K. They are, to leading order, again given by Eq. (4.52),

$$\frac{1}{N}\langle \delta\mathcal{H}^2\rangle = C_{\varepsilon\varepsilon}(t,t) = \frac{T_e^3(t)}{A}\,\frac{1+r^3}{1-r^2}. \tag{5.44}$$

This allows us to solve the cross fluctuations from Eq. (3.25),

$$C_{\varepsilon m}(t,t) = -\frac{HT_e^3(t)}{AK^2}\,\frac{1+r^3}{(1-r)(2-r)}. \tag{5.45}$$

Finally, up to corrections of order T_e^2, the M fluctuations satisfy an equation very similar to Eq. (4.44). This yields

$$C_{mm}(t,t) = \frac{\Gamma^2 T_e(t)}{K^3}\left(1-\frac{T_e}{2K}\right) + \mathcal{O}(T_e^3), \tag{5.46}$$

where we notice that terms of relative order T_e/A have canceled on both sides of the equality sign. Considering the fluctuations in $M_1=M$, $M_2=M_s$, we have

$$C_{ab}(t,t) = \left(\frac{-H}{\Gamma}\right)^{a+b-2}\frac{\Gamma^2 T_e(t)}{K^3}\left(1-\frac{T_e}{2K}\right) + \mathcal{O}(T_e^3). \tag{5.47}$$

The difference with the oscillator model of the preceding section is which all four terms $(a,b=1,2)$ now have corrections of relative order T_e^2/A^2, which will be neglected from now on. They decay slower than the terms we keep, but we are not interested in the model-dependent very-long-time regime, where they dominate.

The time dependence of the $C_{mm}(t,t')$ follows from Eq. (3.34). In the interesting, not-very-asymptotic regime the term $C_{\varepsilon m}$ can be neglected. This implies finally that

$$C_{ab}(t,t') = C_{ab}(t',t')\,\frac{h(t')}{h(t)}, \tag{5.48}$$

which involves $h(t)$ defined as in Eq. (4.39), with, very analogous to Eq. (3.19),

$$\begin{aligned} f(t) &= \int_{-\infty}^{\infty} dx\, W(\beta x)\,\frac{4A - x(1-\varepsilon/K)}{2\varepsilon(t)(1-\varepsilon/(2K))}\,p(x|\varepsilon(t)) \\ &= 8Ap(0|\varepsilon)(1+r)\left(1+\frac{T_e}{2K}-\frac{r^2 T_e}{2A}\right). \end{aligned} \tag{5.49}$$

The equal-time correlators take the value

$$G_{ab}(t^+,t) = \frac{8A}{K^3}\left(\frac{-H}{\Gamma}\right)^{a+b-2} p(0|\varepsilon)\left(1-\frac{r^2 T_e}{2A}\right). \tag{5.50}$$

Both $C_{ab}(t,t')$ and $G_{ab}(t,t')$ have a time dependence $h(t)/h(t')$. The fluctuation-dissipation relation (2.34) again holds with the same effective temperature (4.51) as in the oscillator model,

$$\tilde{T}_e(t) = T_e(t) + \frac{\dot{T}_e(t)}{f(t)} = T_e - \frac{T_e^2}{A}\,\frac{2(T_e-T)}{2T_e-T}. \tag{5.51}$$

In deriving this result we noticed that terms of relative order T_e/K, as appearing in Eq. (5.47), have canceled. We can now redo the consistency check of Eq. (2.35) and verify that, up to relative order T_e^2,

$$\int_0^t dt'\, G_{mm}(t,t') = \beta_e C_{mm}(t,t) = \frac{\Gamma^2}{K^3}\left(1-\frac{T_e}{2K}\right). \tag{5.52}$$

Using that $T_e \approx \Delta^2 K/(8\ln t)$, we also find

$$\left.\frac{\partial T_e}{\partial H}\right|_{T,t} = \frac{\Delta^2 H}{8K\ln t} = \frac{HT_e}{K^2}. \tag{5.53}$$

As mentioned before, this is one order of magnitude smaller than Eq. (5.52). The relation (5.33) now implies $\partial m/\partial T_e|_{T,H} = -H/2K^2$, so that Eq. (2.31) becomes

$$\chi_{mm}^{\text{fluct}} = 0 + \frac{\Gamma^2}{K^3}\left(1-\frac{T_e}{2K}\right) - \left(-\frac{H}{2K^2}\right)\frac{HT_e}{K^2}. \tag{5.54}$$

In view of the prediction (5.23), this is the desired answer to the considered order.

Also the energy correlation and response function are essentially the same as in the oscillator model. This implies in particular the fluctuation-dissipation relation for energy fluctuations of the nonuniversal form (4.55) and (4.56).

Notice that when there are no random fields, $\Gamma=0 \rightarrow K=H$, the energy and the magnetization are proportional to each other, viz., $E=-HM$. For comparison with realistic glassy systems, the model becomes too poor. The above formula for the magnetization ceases to hold when $\Gamma < T_e$. For $\Gamma \rightarrow 0$ one finds the magnetization correlations from the energy correlations. One then finds the relations (4.55) and (4.56) both for energy and magnetization.

VI. DISCUSSION

In this paper we consider the question of whether the glass transition can be phrased in a thermodynamic framework. In a series of letters we have given already several arguments in favor of this possibility [7,6,10]. The present, admittedly long, paper is meant to explain enough details of this approach to make the picture and its various steps and assumptions transparent. We do this by working out in detail two simple models, which, in our feeling, are closer to reality than mean field spin glasses. We have pointed out there that a minimal thermodynamic description needs one more parameter to describe the situation, which could be the age of the glass or the cooling rate at which it was formed. We have discussed that for thermodynamics a more useful variable is the effective or fictive temperature T_e, introduced half a century ago by Tool [30]. In this paper we notice that the basic result for the change of heat in a glassy system,

$$đQ \leqslant T\, dS_{\mathrm{ep}} + T_e\, d\mathcal{I}, \tag{6.1}$$

immediately leads to a specific heat $C_p = C_1 + C_2\, \partial T_e/\partial T$, which was Tool's starting point for the analysis in the glass-formation region. In Sec. IV A we continue along his lines by studying in detail a certain nonlinear cooling traject, proposed recently by us in Ref. [10]. This cooling scheme is applicable to any glass-forming substance and expected to give universal scaling curves of $\partial T_e/\partial T$ in the glass-formation region, independent of the material considered, provided that the glass-transition region is narrow. It would be most interesting to test this idea on a realistic glass-forming liquid. One should first determine, once and for all, the equilibrium time scale $\tau_{\mathrm{eq}}(T)$ and then do glass experiments of the type (4.14) within the considered range. It contains two parameters: the glass-formation temperature T_g, where the cooling time scale becomes comparable to the equilibration time scale, and a ''speed'' parameter R. The resulting form for $\partial T_e/\partial T$ lies, after rescaling the width, on a universal scaling curve, which only depends on R.

We have worked out here the situation where the effective temperature shows up as an extra variable, though in principle it might be needed to consider as many effective parameters as there are macroscopic observables. We had already briefly considered the Ising chain with Glauber dynamics. In that model the nonequilibrium energy at zero field can be described by introducing the effective temperature. Its definition then coincides by equating the $\tau_{\mathrm{eq}}(T_e)$ with t. The behavior at nonzero field appears to be nonuniversal [7]. More or less the same happens in the backgammon model, for which the dynamics at zero field has been partly solved [18,19]. One could couple the system to a particle bath, and the chemical potential would play the role of an external field. So far this case remains to be worked out. We have, therefore, focused on very simple, exactly solvable models, namely the Bonilla-Padilla-Ritort model of Monte Carlo dynamics of uncoupled harmonic oscillators [20] and our recent model of Monte Carlo dynamics of uncoupled spherical spins in a random field [10]. At low temperature both models have an Arrhenius law for the equilibrium time scale. Upon cooling from high temperatures, they will sooner or later fall out of equilibrium. Though it may come as a surprise to some readers, we have shown that these oversimplified models with their unrealistic dynamics still share in their off-equilibrium phase universal properties of realistic glasses and models for glasses.

A description with only the effective temperature applies whenever the volume of the glass-forming liquid (or the magnetization of the glassy magnet) is close to its quasiequilibrium value set by the effective temperature obtained from fitting the energy. If this condition is fulfilled, the old objections against a thermodynamic description of the glassy phase can be inspected in detail. We have stressed that the most fundamental paradox, namely violation of the first Ehrenfest relation, is merely based on the misleading expectation that there is one ideal value for the compressibility. This notion has arisen from equilibrium considerations for the glassy state. They do not apply by definition, and have hindered progress until our recent works in this field. Indeed, from the knowledge of spin glasses, or from the solution of the present models (where $\chi_{\mathrm{ZFC}} = 0$), we know that the compressibility or the susceptibility can take a broad range of values immediately below the glassy transition. This means that no alternative determination is allowed, removing immediately the whole paradox: though half a century of research led to the general belief that the first Ehrenfest relation is always violated, it is actually satisfied automatically [6]. This point is underlined in Fig. 1, where we present a 3D plot of data for the glass transition in atactic polystyrene, collected in careful experiments by Rehage and Oels [5]. Though these authors claim that the first Ehrenfest relation is violated, and then continue to investigate a modified version, we explain that it is satisfied.

We have also pointed out that for glass-forming liquids the Maxwell relation between $\partial U/\partial p$ and $\partial V/\partial T$ is modified, which is not so surprising in view of the fact that equilibrium is not reached. The second Ehrenfest relation is then also modified, since it relies on the Maxwell relation. This fact implies that the Prigogine-Defay ratio can indeed be different from unity. We should recall that Davies and Jones [31] showed that $\Pi \geqslant 1$, while DiMarzio found that a deeper analysis of their equations leads to $\Pi = 1$ [37]. Both approaches, however, are based on the assumption that at the glass transition an unspecified number of order parameters freezes in, an assumption that was often made in the 1960s and 1970s. Such assumptions are invalid, however. What happens at the glass transition is that certain slow modes fall out of equilibrium, but on longer scales they may reach equilibrium again, even though other modes may then have fallen out of equilibrium. The upshot of this is that the Prigogine-Defay ratio can be different from unity. In contradiction to the standard belief, it can also be less than unity. We have pointed out before [6] that this already occurs in experiments on atactic polystyrene [5], though this was long not recognized.

It has been the important contribution of statistical physics to relate temporal fluctuations in macroscopic observables to their averages, the most known relation being $C = \beta^2\langle \delta H^2\rangle$. It is natural to investigate whether such relations have some universal-looking generalization in simple models for glasses. We have found that this is indeed the case for fluctuations in observables coupled to external fields [10]; see Sec. II E. These equations have been guessed with an eye on results from present models, in combination with some standard arguments on the short-time contributions.

Our progress was initially hindered by the fact that such a general formula appears not to hold for energy fluctuations. For the ferromagnetic Ising chain aging at $T=0$ from a random initial condition, we already realized which at zero field the energy defines an effective temperature $T_e = 2J \ln 4\pi t$, that coincides, to leading order, with the one following from equating the time scale with time, viz., $\tau_{\mathrm{eq}}(T_e) = t$ [7]. The energy correlations can be calculated from the Derrida-Zeitak spatial correlation function for the nonmeeting of two random walkers on a line. Indeed, the Ising chain is mapped to random walking of interfaces by setting $s_{i-1/2}s_{i+1/2}=1-2\rho_i$ with $\rho_i=1$ if an interface is present at i, and zero otherwise. It follows that $U/N=J(-1+2\rho)$, where $\rho=1/\xi$ is the average density of interfaces, with $\xi=\sqrt{4\pi t}\equiv\exp(2\beta_e J)$ the correlation length. It holds that

$$\frac{1}{N}\langle\delta U^2\rangle=4J^2(\rho-\rho^2)+8J^2\sum_{i>0}(C_{i,0}-\rho^2), \qquad (6.2)$$

where $C_{ij}=\langle\rho_i\rho_j\rangle=C(r_{ij})$ is the correlation function, given by Eq. (59) with $q=2$ in a paper by Derrida and Zeitak [40],

$$C(r)=\rho^2\left(1-e^{-2z^2}+2ze^{-z^2}\int_z^\infty e^{-u^2}du\right), \qquad (6.3)$$

where $z=\sqrt{\pi}\rho r$. One thus finds

$$\frac{1}{N}\langle\delta U^2\rangle=4J^2\rho(3-2\sqrt{2}). \qquad (6.4)$$

This differs from the naively expected quasiequilibrium result $T_e^2 dU/dT_e=4J^2\rho$ by a numerical prefactor $3-2\sqrt{2}=0.171\,572\,88$. We were informed by Luck that in the backgammon model a similar phenomenon occurs: the energy correlations are a factor 2 smaller than naively expected [41]. In the models of the present work the energy fluctuations are even smaller by an order of magnitude in T_e/A. These explicit examples show that there cannot exist a simple quasiuniversal formula relating energy fluctuations with the specific heat. The underlying reason here is that in the energy the leading fluctuations from different terms already cancel, leaving model-dependent, subleading effects only.

After completion of the original manuscript, Leuzzi verified that both in the harmonic-oscillator model and in the spherical spin model there holds the following relation between the specific heat and the energy fluctuations:

$$\left.\frac{\partial U}{\partial T}\right|_H=\frac{1}{T\,T_e^{(\varepsilon\,\varepsilon)}}\langle\delta\mathcal{H}^2\rangle-\left.\frac{\partial U}{\partial T_e}\right|_{H,T}\times\left(\left.\frac{dT_e}{\partial T}\right|_{H,t}-1\right)+\left.\frac{\partial U}{\partial T_e}\right|_{H,T}\left(\left.\frac{dT_e}{\partial T}\right|_H-1\right), \qquad (6.5)$$

where $T_e^{(\varepsilon\,\varepsilon)}$ is given by Eq. (4.56) for both models. The first two terms on the right-hand side cancel, and so do, of course, the ± 1 terms. In analogy with Eq. (2.28), we could interpret this relation as $C=C^{\text{fluct}}+C^{\text{loss}}+C^{\text{conf}}$, but the factor $1/T$ in the first term could imply that this attempted generalization is special to our present oscillator and spin models, as is already expressed by the fact that $T_e^{(\varepsilon\,\varepsilon)}\neq T_e$. It was also realized that for the cross derivatives $\partial U/\partial H$ and $\partial M/\partial T$ similar relations either do not occur or are much more complicated. The same holds for the fluctuation-dissipation relations connected to these two quantities.

Nevertheless, fluctuations in observables that couple to global external fields appear to behave in a universal way, at least to leading and dominant subleading order. These fluctuations are interrelated with the off-equilibrium fluctuation-dissipation relation (FDR). Originally observed by Sompolinsky [11], Horner [11,12,13] and then extended by Cugliandolo and Kurchan [14], this has become a popular test for glassiness of model systems [42,21,22,43]. For the models considered, the effective temperature showing up in the FDR is essentially the same as the one occurring in thermodynamics.

The absence of a universal relation between energy fluctuations and the specific heat is very welcome for gravitating systems, which often have a negative specific heat. We indeed showed that the present approach can immediately be applied to phrase the laws of black-hole dynamics in a nonequilibrium thermodynamic framework [38]. The role of bath temperature is played by the cosmic backgound temperature, that of the effective temperature by the Hawking temperature, that of the configurational entropy by Bekenstein's black hole entropy, while the short-time processes have no sizeable entropy. These ingredients bring a very close analogy with the picture discussed here, and are not even disturbed by the fact that the specific heat has the ''wrong'' sign. Let us mention, however, that negative specific heats are in no way limited to gravitation: they also occur in the present, extensive solid-state models, when one heats up the system in the glassy phase, as expressed by the negative values of $dT_e/dT=2C$ in Figs. 3–6.

Our picture for thermodynamics of the glassy state thus connects macroscopic observables via the first and second law, and relates their derivatives with respect to external fields with their fluctuations, thereby embedding the FDR-effective temperature in a larger thermodynamic framework. It is expected to be valid for a yet unknown class of glassy systems. Let us close this discussion by mentioning that very recently numerical data in the glassy phase of a binary Lennard-Jones system were interpreted in terms of an effective temperature, which dominates the (short-time) vibrational properties, in full agreement with the picture proposed above [44].

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