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Exactly solvable model glass with facilitated dynamics

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Abstract

A model glass with fast and slow processes is studied. The statics is simple and the facilitated slow dynamics is exactly solvable. The main features of a fragile glass appear: Kauzmann transition, Vogel–Fulcher law, Adam–Gibbs relation and aging. The time evolution can be so slow that a quasi-equilibrium occurs at a time-dependent effective temperature. The same effective temperature is derived from the fluctuation-dissipation ratio, which supports the applicability of out-of-equilibrium thermodynamics.

1. Introduction

We present the outcome of our investigation of an exactly solvable model glass that shows all of the basic features of much more complicated real glasses, such as aging [1, 2], diverging relaxation time to equilibrium (Vogel–Fulcher–Tammann–Hesse-like (VFTH-like) [3]), configurational entropy satisfying the Adam–Gibbs relation [4], Kauzmann transition [5] and violation of the fluctuation-dissipation theorem [2, 6].

In studying the model we make use of a particular parallel Monte Carlo (MC) dynamics that retains the fundamental collective nature of the glassy dynamics and that can be carried out analytically in our model. We will see how this dynamics undergoes a huge slowing down as the system is cooled down and which kind of aging dynamics the system acquires. We can implement such dynamics even below the Kauzmann temperature, thus getting information in a regime where few analytical results are known.

The main motivations for this work are twofold. Firstly we want to get more insight into glassy dynamics in its various aspects, exploiting the analytical solvability of our model. Indeed, every feature of glassy behaviour that we find can be linked in a direct correspondence with the given elements of the model, thanks to its simplicity. We can even switch certain properties or certain kinds of dynamic behaviour on and off, by tuning the model parameters or implementing the facilitated dynamics in alternative ways. Furthermore, the configurational entropy is exactly computable (see section 2) as a function of the dynamic variables of the model.

The second goal is to check the generality of the concept of *effective temperature*, very often discussed in the literature within many different approaches (see for instance [2, 6–13]) and to see whether it is possible to use such a parameter in the construction of a consistent out-of-equilibrium thermodynamic theory. Even though the physics of our model is simple, we shall find general aspects of the results by formulating them in the language of thermodynamics (see section 5).

In glasses, the exponential divergence of timescales (as opposed to the algebraic divergence in standard continuous phase transitions) might induce an asymptotic decoupling of the time decades [14]. Exploiting this, we build the dynamics of our model on the reasonable assumption that, in a glassy system that has aged for a long time t , all processes with equilibration time much less than t (the β -processes) are in equilibrium, while those evolving on timescales much larger than t are still quenched, leaving the processes with timescale of order t (i.e. the α -processes) as the only interesting ones. To model this, we will introduce by hand two different kinds of variable, evolving on two very different (decoupled) timescales.

Such an asymptotic decoupling of timescales, which is the input for the present model and for a set of other models in the same class [10, 15–18], could be the basis for a generalization of equilibrium thermodynamics to systems out of equilibrium [10].

In section 2 we introduce the model and in section 3 the facilitated dynamics that we apply to it. The dynamical behaviour of the one-time observables will be shown in section 4. In section 5 an out-of-equilibrium formulation of the thermodynamics is proposed. From the study of two-time variables (in section 6) we show that, quite reasonably since we are not at equilibrium, the fluctuation-dissipation theorem is no longer valid. We will also see in section 6 that from the fluctuation-dissipation ratio (FDR) we can derive an independent definition of effective temperature.

2. The model and its static properties

2.1. The Hamiltonian and the constraint on the configuration space

The model displaying fragile glass behaviour was introduced in [20] and comprehensively studied in [19]. It is described by the following local Hamiltonian:

$$\mathcal{H}[\{x_i\}, \{S_i\}] = \frac{1}{2}K \sum_{i=1}^N x_i^2 - H \sum_{i=1}^N x_i - J \sum_{i=1}^N x_i S_i - L \sum_{i=1}^N S_i \quad (1)$$

where N is the size of the system and $\{x_i\}$ and $\{S_i\}$ are continuous variables, the latter satisfying a spherical constraint: $\sum_i S_i^2 = N$. We will call them respectively harmonic oscillators and spherical spins. K is the Hooke elastic constant, H is an external field acting on the harmonic oscillators, J is the constant of coupling between $\{x_i\}$ and $\{S_i\}$ on the same site i , L is the external field acting on the spherical spins. A separation of timescales is introduced by hand: the spins represent the fast modes and the harmonic oscillators the slow ones. We assume that the $\{S_i\}$ relax to equilibrium on a timescale much shorter than that of the harmonic oscillators. From the point of view of the motion of the $\{x_i\}$, the spins are just noise. To describe the long-time regime of the $\{x_i\}$, we can average over this noise by performing the computation of the $\{S_i\}$ partition function, obtaining an effective Hamiltonian depending only on the $\{x_i\}$ that determines the dynamics of these variables. Using the saddle-point approximation for large N we find

$$Z_S(\{x_i\}) = \int \left(\prod_{i=1}^N dS_i \right) \exp\{-\beta\mathcal{H}[\{x_i\}, \{S_i\}]\} \delta\left(\sum_{i=1}^N S_i^2 - N\right) \simeq e^{-\beta\mathcal{H}_{\text{eff}}(\{x_i\})} \quad (2)$$

where we introduce the effective Hamiltonian $\mathcal{H}_{\text{eff}}(\{x_i\}) \equiv -T \log Z_S(\{x_i\})$ —that is, the free energy for a given configuration of $\{x_i\}$ —as

$$\mathcal{H}_{\text{eff}}(\{x_i\}) = \frac{K}{2} m_2 N - H m_1 N - w N + \frac{TN}{2} \log \frac{w + T/2}{T}. \tag{3}$$

Here we have defined

$$m_1 \equiv \frac{1}{N} \sum_{i=1}^N x_i \quad m_2 \equiv \frac{1}{N} \sum_{i=1}^N x_i^2 \quad w \equiv \sqrt{J^2 m_2 + 2JLm_1 + L^2 + \frac{T^2}{4}}. \tag{4}$$

The effective Hamiltonian, equation (3), can also be written in terms of the internal energy $U(\{x_i\})$ and the entropy $S_{\text{ep}}(\{x_i\})$ of the equilibrium processes (i.e. the spins):

$$\mathcal{H}_{\text{eff}}(\{x_i\}) = U(\{x_i\}) - T S_{\text{ep}}(\{x_i\}) \tag{5}$$

$$U(\{x_i\}) = \frac{K}{2} m_2 N - H m_1 N - w N + \frac{TN}{2} \quad S_{\text{ep}}(\{x_i\}) = \frac{N}{2} - \frac{N}{2} \log \frac{w + T/2}{T}. \tag{6}$$

The model is additionally characterized by a constraint on the phase space, introduced to avoid the existence of a single global minimum, and implementing a large degeneracy of the allowable lowest states. The constraint is imposed on the $\{x_i\}$, thus concerning the long-time regime. It reads

$$m_2 - m_1^2 \geq m_0 \tag{7}$$

where m_0 is a model parameter. It is a fixed, but arbitrary, strictly positive constant. This constraint, applied to the harmonic oscillator dynamics, is a way of reproducing the behaviour of good glass formers, i.e. substances for which nucleation of the crystal phase is extremely unlikely even at very slow cooling rates (e.g., network formers B_2O_3 and SiO_2 , molecular organics such as glycerol and atactic polystyrene, and different multicomponent liquid mixtures). These are substances for which there are non-crystalline packings of the particles that have intrinsically low energy. The amorphous configurations are thus favoured. In general the crystal state still exists, at lower energy, but the probability of nucleating a crystal instead of a glass is negligible. In specific cases (binary solutions) the glassy state can even be lower in energy than the crystalline one and is thermodynamically stable with respect to any crystal configuration [21].

In the next section we will impose a MC dynamics [15, 22] which satisfies this constraint and couples the otherwise non-interacting $\{x_i\}$ in a dynamic way. We will then study the resulting dynamics analytically.

To reduce the notation we define the modified ‘spring constant’ \tilde{K} and ‘external field’ \tilde{H} :

$$\tilde{K} = K - \frac{J^2}{w + T/2} \quad \tilde{H} = H + \frac{JL}{w + T/2}. \tag{8}$$

We stress that \tilde{K} and \tilde{H} are actually functions of the $\{x_i\}$ themselves (through m_1 and m_2 , occurring in w).

2.2. Statics at heat bath temperature T

Before describing the facilitated dynamics employed, we sketch very briefly the statics of the model. The partition function of the whole system at equilibrium is

$$\begin{aligned} Z(T) &= \int \mathcal{D}x \mathcal{D}S \exp[-\beta \mathcal{H}(\{x_i\}, \{S_i\})] \delta\left(\sum_i x_i^2 - N\right) \\ &= \int dm_1 dm_2 \exp\left\{-\beta N \left[\frac{K}{2} m_2 - H m_1 - w \right. \right. \\ &\quad \left. \left. + \frac{T}{2} \log\left(\frac{w + T/2}{T}\right) - \frac{T}{2} (1 + \log(m_2 - m_1^2))\right]\right\}. \end{aligned} \tag{9}$$

The new object (with respect to equation (2)) appearing in the exponent of the above expression is the configurational entropy

$$\mathcal{I} \equiv \frac{N}{2} [1 + \log(m_2 - m_1^2)]. \quad (10)$$

The saddle-point equations are found by minimizing the expression in square brackets in (9) with respect to m_1 and m_2 . This yields

$$\frac{\tilde{H}(\bar{m}_1, \bar{m}_2)}{\tilde{K}(\bar{m}_1, \bar{m}_2)} = \bar{m}_1 \quad \bar{m}_2 - \bar{m}_2^2 = \frac{T}{\tilde{K}(\bar{m}_1, \bar{m}_2)}. \quad (11)$$

The form of the solutions $\bar{m}_1(T)$, $\bar{m}_2(T)$ is quite complicated because each of these equations is actually a fourth-order equation, but they can be explicitly computed.

3. Facilitated Monte Carlo dynamics

We assume as the dynamics a parallel MC dynamics for the harmonic oscillators. This kind of analytical MC approach was first introduced in [22], and later applied to the exactly solvable harmonic oscillator model [15] (which is just our model with $J = L = 0$) and to the spherical spin model [10, 16] (which is the present model with $H = K = 0$ and considering the $\{x_i\}$ as quenched random variables). The dynamical model that we obtain, with a very simple Hamiltonian and a contrived dynamics, has the benefit of being analytically solvable, which yields a much deeper insight into its properties than numerical simulations. Moreover, in the long-time domain the dynamics looks quite reasonable compared to what one might expect for any system with a VFTH law in its approach to equilibrium.

In a MC step a random update of the variables is performed ($x_i \rightarrow x'_i = x_i + r_i/\sqrt{N}$) where the $\{r_i\}$ have a Gaussian distribution with zero mean and variance Δ^2 . We define $x \equiv \mathcal{H}_{\text{eff}}(\{x'_i\}) - \mathcal{H}_{\text{eff}}(\{x_i\})$ as the energy difference between the new and the old state. If $x > 0$ the move is accepted with a probability $W(\beta x) \equiv \exp(-\beta x)$; otherwise it is always accepted ($W(\beta x) = 1$). The updates for all x_i are done in parallel. It is the parallel nature of the updates that allows for collective behaviour, leading to exponentially divergent timescales in models such as ours with no interactions between particles. Sequential updating would not produce any glassy effects. This dynamics may induce glassy behaviour in situations where ordinary Glauber dynamics [23] would not. In our model the parallel dynamics mimics the presence of interactions between atoms in realistic glasses, where a large internal cooperativity occurs. In this respect the constraint is not essential. A version of MC dynamics with parallel updates that does not take into account the constraint on the $\{x_i\}$ still retains glassy behaviour (see [17] for the study of such a dynamical version of our model). Here, however, we will only look at the dynamics with a built-in constraint. For different examples of dynamics implying non-trivial collective behaviour, the reader can consult, for instance, studies of the n -spin facilitated kinetic Ising model [24, 25] or of the kinetic lattice-gas model [21, 26].

In this section we will show the basic steps leading to dynamical equations. For further details we refer the reader to [10, 15, 17, 19]. In a MC step the quantities $\sum_i x_i = Nm_1$ and $\sum_i x_i^2 = Nm_2$ are updated. We denote their changes by y_1 and y_2 , respectively. Their distribution function is, for given values of m_1 and m_2 ,

$$\begin{aligned} p(y_1, y_2 | m_1, m_2) &\equiv \int \prod_i \frac{dr_i}{\sqrt{2\pi\Delta^2}} e^{-r_i^2/(2\Delta^2)} \\ &\times \delta\left(\sum_i x'_i - \sum_i x_i - y_1\right) \delta\left(\sum_i x'^2_i - \sum_i x^2_i - y_2\right) \\ &= \frac{1}{4\pi\Delta^2\sqrt{m_2 - m_1^2}} \exp\left(-\frac{y_1^2}{2\Delta^2} - \frac{(y_2 - \Delta^2 - 2y_1m_1)^2}{8\Delta^2(m_2 - m_1^2)}\right). \end{aligned} \quad (12)$$

Neglecting the variations of m_1 and m_2 of order Δ^2/N , we can express the energy difference as

$$x = \frac{\tilde{K}}{2}y_2 - \tilde{H}y_1. \quad (13)$$

In terms of x and $y = y_1$ the distribution function can be formally written as the product of two Gaussian distributions:

$$\begin{aligned} p(y_1, y_2|m_1, m_2) dy_1 dy_2 &= dx p(x|m_1, m_2) dy p(y|x, m_1, m_2) \\ &= \frac{dx}{\sqrt{2\pi}\Delta_x} \exp\left(-\frac{(x-\bar{x})^2}{2\Delta_x}\right) \frac{dy}{\sqrt{2\pi}\Delta_y} \exp\left(-\frac{(y-\bar{y}(x))^2}{2\Delta_y}\right) \end{aligned} \quad (14)$$

where

$$\bar{x} = \Delta^2 \tilde{K}/2 \quad \Delta_x = \Delta^2 \tilde{K}^2(m_2 - m_1^2) + \Delta^2 \tilde{K}^2(m_1 - \tilde{H}/\tilde{K})^2 \quad (15)$$

$$\bar{y}(x) = \frac{m_1 - \tilde{H}/\tilde{K}}{m_2 - m_1^2 + (m_1 - \tilde{H}/\tilde{K})^2} \frac{x - \bar{x}}{\tilde{K}} \quad \Delta_y = \frac{\Delta^2(m_2 - m_1^2)}{m_2 - m_1^2 + (m_1 - \tilde{H}/\tilde{K})^2}. \quad (16)$$

To represent a fragile glass, the dynamics that we assume for the system is a generalization of the analytical treatment of MC dynamics introduced in [22]. The dynamical model with this generalized dynamics can still be analytically solved. We let Δ^2 , the variance of the random updates $\{r_i\}$, depend on the distance from the constraint, i.e. on the whole $\{x_i\}$ configuration before the MC update:

$$\Delta^2(t) \equiv 8[m_2(t) - m_1^2(t)] \left[\frac{B}{m_2(t) - m_1^2(t) - m_0} \right]^\gamma \quad (17)$$

where B , m_0 and γ are constants. The exponent γ also enters the VFTH relaxation law, as we will see later on. In the literature it is usually set equal to 1, and an argument for this choice was given by Adam and Gibbs [4]. An exact explanation for it was provided by Kirkpatrick *et al* [27] and further quantitative analysis was reported in [28]. However, these studies do not exclude exponents $\gamma > 1$, which are always compatible with the data and merely affect the width of the fitting interval. Analytical approaches [29, 30] give $\gamma = 2$ in three dimensions. Here we consider γ as a model parameter which can be chosen to be below, equal to, or above unity, and investigate aspects of this standard picture.

The VFTH law that we obtain is a direct consequence of the special choice (17) for the MC update. In the harmonic oscillator model and in the spherical spin model studied in [10, 15, 16], the dynamics was performed within the same approach, but at fixed Δ . Both cases showed a relaxation time diverging at low temperature with an Arrhenius law, typical of *strong* glasses. The same is found by setting $m_0 = 0$ and $\gamma = 1$ in the present model [17] but here we instead want to develop a model representing a *fragile* glass with a Kauzmann transition at a finite temperature.

The question of whether detailed balance is satisfied is also non-trivial in our model. Indeed, it happens to be satisfied for this kind of dynamics only for large N . For exact detailed balance we should have

$$p(x|m_1, m_2) \exp(-\beta x) = p(-x|m_1, m_2) \quad (18)$$

but now, when we perform the inverse move $\{x'_i\} \rightarrow \{x_i\}$, the probability distribution also depends on the $\{r_i\}$ through Δ^2 as defined in equation (17). It can be verified that the violation is of order $1/N$.

The MC equations for the dynamics of m_1 and m_2 derived from this construction read

$$\dot{m}_1 = \int dy_1 dy_2 W(\beta x) y_1 p(y_1, y_2 | m_1, m_2) = \int dx W(\beta x) \bar{y}(x) p(x | m_1, m_2) \quad (19)$$

$$\dot{m}_2 = \int dy_1 dy_2 W(\beta x) y_2 p(y_1, y_2 | m_1, m_2) = \frac{2}{\tilde{K}} \int dx W(\beta x) (x + \tilde{H} \bar{y}(x)) p(x | m_1, m_2). \quad (20)$$

4. Single-time dynamical observables

The dynamics of the system can be expressed in terms of two combinations of m_1 and m_2 . The first one, defined as

$$\mu_1 \equiv \frac{\tilde{H}}{\tilde{K}} - m_1 \quad (21)$$

represents the distance from the instantaneous equilibrium state. By instantaneous equilibrium state we mean that \tilde{H} and \tilde{K} depend on the values of m_1 and m_2 at a given time t . For $t \rightarrow \infty$, at the true equilibrium, one has $\mu_1 = 0$.

The second dynamical variable is defined as the distance from the constraint (7):

$$\mu_2 \equiv m_2 - m_1^2 - m_0. \quad (22)$$

When $\mu_2 = 0$ the constraint is reached. This will happen if the temperature is low enough ($T \leq T_0$) and the time large enough. T_0 is the highest temperature at which the constraint is asymptotically ($t \rightarrow \infty$) reached by the system; it is identified with the Kauzmann temperature [19].

The closer the system gets to the constraint (i.e. the smaller the value of $m_2 - m_1^2 - m_0$), the larger the variance Δ^2 , implying almost always a rejection of the proposed update. In this way, in the neighbourhood of the constraint, the dynamics is very slow and proceeds through very rare but very large moves, which can be interpreted as activated processes. When the constraint is reached the variance Δ^2 becomes infinite and the dynamics gets stuck. The system no longer evolves towards equilibrium, but is blocked in one single ergodic component of the configuration space.

In terms of μ_1 and μ_2 , the equations of motion (19), (20) become

$$\dot{\mu}_1 = -JQ \int dx W(\beta x) x p(x | m_1, m_2) - (1 + QD) \int dx W(\beta x) \bar{y}(x) p(x | m_1, m_2) \quad (23)$$

$$\dot{\mu}_2 = \frac{2}{\tilde{K}} \int dx W(\beta x) x p(x | m_1, m_2) + 2\mu_1 \int dx W(\beta x) \bar{y}(x) p(x | m_1, m_2) \quad (24)$$

where D and Q are given by

$$D \equiv HJ + KL = \tilde{H}J + \tilde{K}L \quad Q \equiv \frac{J^2 D}{\tilde{K}^3 w (w + T/2)^2}. \quad (25)$$

Above T_0 , ordinary equilibrium will be achieved without reaching the constraint. The temperature is, then, too high for the system to ‘notice’ that there is a constraint on the configurations at all (we are speaking about the asymptotic time regime), and this implies

$$\lim_{t \rightarrow \infty} \mu_2(t) = \bar{\mu}_2(T) = \frac{T}{\tilde{K}_\infty(T)} - m_0 > 0 \quad (26)$$

where

$$\tilde{K}_\infty(T) \equiv \lim_{t \rightarrow \infty} \tilde{K}(m_1(t), m_2(t); T) = \tilde{K}(\bar{m}_1(T), \bar{m}_2(T)). \quad (27)$$

\bar{m}_1 and \bar{m}_2 are the solutions of the static self-consistent equations (11), if $T \geq T_0$.

For $T < T_0$ the second equation in (11) should be replaced by

$$\bar{m}_2 - \bar{m}_1^2 = m_0 \quad \forall T < T_0. \tag{28}$$

Below T_0 the system visits configurations arbitrarily close to the constraint, and then stays there for arbitrarily long times. By definition of T_0 , we can write

$$m_0 = \frac{T_0}{\tilde{K}_\infty(T_0)}. \tag{29}$$

The equations of motion (23) and (24) can be solved in the long-time regime, for fixed parameters (aging set-up). We note that the value of the VFTH exponent γ discriminates between different dynamic regimes given by $\gamma > 1$, $\gamma = 1$ and $0 < \gamma < 1$ [19] (the situation $\gamma = 1$ remains model dependent even in the long-time limit). We find, to the leading orders of approximation for large times, the following behaviour for μ_2 [19]:

$$\mu_2(t) \simeq \frac{B}{[\log(t/t_0) + c \log(\log(t/t_0))]^{1/\gamma}}. \tag{30}$$

For $T \geq T_0$ the parameters c and t_0 are

$$c = \frac{1}{2} \quad t_0 \equiv \frac{\sqrt{\pi}(1 + Q_\infty D)}{8\gamma(1 + P_\infty + Q_\infty D)}. \tag{31}$$

Here t_0 is $O(1)$ for a large range of parameter values and Q_∞ is given by equation (25) computed at $m_1 = \bar{m}_1(T)$ and $m_2 = \bar{m}_2(T)$. The other function of temperature appearing in the above expression, P_∞ , is defined as the infinite-time limit of

$$P \equiv \frac{J^4(m_2 - m_1^2)}{2\tilde{K}w(w + T/2)^2}. \tag{32}$$

That means that P is evaluated for $m_1 = \bar{m}_1(T)$ and $m_2 = \bar{m}_2(T)$. The solution (30) is valid in the aging regime, where $t_0 \ll t \ll \tau_{\text{eq}}(T)$.

Below T_0 the qualitative behaviour of $\mu_2(t)$ is the same, but T is never reached. Compared to the solution (30) the only difference is in the values

$$c = \frac{2 + \gamma}{2\gamma} \quad t_0 \equiv \frac{B\sqrt{\pi}}{8\gamma} \frac{(2\tilde{K}_\infty(T)m_0 - T)}{m_0^2\tilde{K}_\infty(T)(\tilde{K}_\infty(T)m_0 - T)}. \tag{33}$$

The dynamical behaviour of μ_1 depends not only on the temperature (above or below T_0) but also on γ being greater, equal to or less than one. With respect to the relative weight of μ_1 and μ_2 , we can identify different regimes [19]. In this presentation we just state that for the regime with $T \geq T_0$ and for the one with $T < T_0$ and $\gamma > 1$, one has $\mu_1(t) \ll \mu_2(t)$ and a unique effective thermodynamic parameter can be properly defined in various independent ways (see the next section).

What we said up to now concerns the aging regime. If we consider even larger timescales, finally approaching equilibrium in the temperature regime $T \geq T_0$, the equations of motion for any one-time observable $o(t)$ (magnetization, energy, distance from the constraint etc) take the form

$$\dot{o}(t) \simeq -\frac{o(t)}{\tau_{\text{eq}}}. \tag{34}$$

From the study of the dynamics for very large times [19, 20] we get a characteristic time of relaxation to equilibrium which depends on temperature according to a generalized VFTH law:

$$\tau_{\text{eq}} \sim \exp\left(\frac{A}{T - T_0}\right)^\gamma. \tag{35}$$

When $t \sim \tau_{\text{eq}}(T) \sim \exp[A/(T - T_0)]^\gamma$ the ‘distance’ μ_2 becomes

$$\bar{\mu}_2(T) \simeq B / \left[\left(\frac{A}{T - T_0} \right)^{1/\gamma} \right]^\gamma \propto T - T_0. \quad (36)$$

The parameter T_0 in the VFTH law is identified with the Kauzmann temperature, i.e. the temperature such that $\mathcal{I}(T_0) \equiv \mathcal{I}_0$ is the minimum of the configurational entropy (and for any $T < T_0$, $\mathcal{I}(T) = \mathcal{I}_0$ persists). Moreover, the specific heat displays a discontinuity at T_0 : at that temperature the model undergoes a real thermodynamic phase transition. The Adam–Gibbs relation between relaxation time and configurational entropy density (equation (10)) is also obtained, in the form [19]

$$\tau_{\text{eq}} \sim \exp\left(\frac{N}{\mathcal{I} - \mathcal{I}_0}\right)^\gamma. \quad (37)$$

5. Effective temperature and out-of-equilibrium thermodynamics

In this section we introduce effective parameters in order to rephrase the dynamics of the system out of equilibrium within a thermodynamic description (for a complete derivation see [10]).

In [19] we obtained, by different methods, various expressions for the effective temperature T_e as a function of the interaction parameters of the model and of the time evolution of its observables. All of them coincided in the regime with $T > T_0$ and $\gamma > 1$.

We want to recall briefly one particular derivation of T_e . Knowing the solution of the dynamics at a given time t , a quasi-static approach can be taken by computing the partition function Z_e of all the macroscopically equivalent states at the time t . In order to generalize equilibrium thermodynamics, we assume an effective temperature T_e and an effective field H_e , and replace the Boltzmann–Gibbs equilibrium measure by $\exp(-\mathcal{H}_{\text{eff}}(\{x_i\}, T, H_e)/T_e)$, where \mathcal{H}_{eff} is given in (5) and the true external field H has been replaced by the effective field H_e . Since we then get the expression for the ‘thermodynamic’ potential $F_e \equiv -T_e \log Z_e$ as a function of the macroscopic variables $m_{1,2}$ and the effective parameters, we can determine T_e and H_e by minimizing F_e with respect to m_1 and m_2 and evaluating the resulting analytical expressions at $m_{1,2} = m_{1,2}(t)$.

The partition function of the macroscopically equivalent states is

$$Z_e \equiv \int \mathcal{D}x \exp\left[-\frac{1}{T_e} \mathcal{H}_{\text{eff}}(\{x_i\}, T, H_e)\right] \delta\left(Nm_1 - \sum_i x_i\right) \delta\left(Nm_2 - \sum_i x_i^2\right). \quad (38)$$

From this we construct the effective thermodynamic potential as a function of T_e and H_e , in addition to T and H , where the effective parameters depend on time through the time-dependent values of m_1 and m_2 that are obtained as solutions of the dynamics:

$$F_e(t) = U - TS_{\text{ep}} - T_e(t)\mathcal{I} + [H - H_e(t)]Nm_1(t) \quad (39)$$

with

$$T_e(t) = \tilde{K}(m_1(t), m_2(t)) [m_0 + \mu_2(t)], \quad (40)$$

$$H_e(t) = H - \tilde{K}(m_1(t), m_2(t))\mu_1(t). \quad (41)$$

T_e and H_e are actually a way of describing the evolution in time of the system out of equilibrium. U is the internal energy of the whole system, S_{ep} is the entropy of the fast or equilibrium processes (the spherical spins)—see equation (6)—while \mathcal{I} is the entropy of the slow, ‘configurational’, processes (the harmonic oscillators; see equation (10)). The last term of F_e replaces the $-HNm_1$ occurring in U by $-H_eNm_1$. U , S_{ep} and \mathcal{I} are ‘state’ functions, in the sense that they depend on the state described by T , T_e , H and, if needed, H_e . In the case

where only one relevant effective parameter T_e remains, these functions do not depend on the path along which its value has been reached.

As we already mentioned, for our VFTH relaxing model at $T \geq T_0$, and at $T < T_0$ with $\gamma > 1$, the effective temperature alone is enough for a complete thermodynamic description of the dominant physical phenomena ($H_e = H$).

6. Two-time variables: breaking of time-translation invariance and the fluctuation-dissipation relation

In this section we compute the correlation and response functions which, unlike the energy and the quantities $m_1(t)$ and $m_2(t)$, depend in a non-trivial way on two times when the system is out of equilibrium, thus showing directly the loss of time-translation invariance compared to the equilibrium case. The aim of computing such quantities is also to construct a fluctuation-dissipation relation and look at the meaning of the FDR, $\partial_{t'} C(t, t')/G(t, t')$, far from equilibrium, and to compare it with the effective temperature derived in other ways, e.g., as in (40).

The correlation functions relating the thermodynamic fluctuation of a quantity $m_a(t)$ at time t to that of a quantity $m_b(t')$ at a different time t' are defined as

$$C_{ab}(t, t') \equiv N \langle \delta m_a(t) \delta m_b(t') \rangle \quad a, b = 1, 2 \quad (42)$$

where $\langle \dots \rangle$ is the average over the dynamic processes, i.e. the harmonic oscillators.

The response of an observable m_a at time t to a perturbation in a conjugate field H_b at some previous time t' takes the form

$$G_{ab}(t, t') \equiv \frac{\delta \langle m_a(t) \rangle}{\delta H_b(t')} \quad a, b = 1, 2. \quad (43)$$

In our model, $H_1 = H$ and $H_2 = -K/2$.

In order to be concise, we will in the following only give results without derivation; moreover, we will concentrate on the FDR for fluctuations of $\sum_i x_i = Nm_1$ coupled to the external field H , i.e. we only consider $a = b = 1$. For the complete derivation we refer the reader to [19].

Once the evolution of the two-time observables is known, we can generalize the fluctuation-dissipation theorem to define another effective temperature, T_e^{FD} , as the ratio between the derivative with respect to the initial time (also called the ‘waiting’ time) t' of the correlation function C_{11} and the response function G_{11} :

$$T_e^{\text{FD}}(t, t') \equiv \frac{\partial_{t'} C_{11}(t, t')}{G_{11}(t, t')}. \quad (44)$$

The dynamics depends strongly on whether T is above or below the Kauzmann temperature and this dependence produces different equations for the leading terms in the correlation and response functions. Therefore, we present the results for the two cases separately.

6.1. High-temperature case: $T > T_0$, arbitrary γ

First of all we define the time evolution function for the timescale sector considered as

$$\tilde{h}(\tau) \equiv \exp\left(-\int_0^\tau \tilde{f}(t) dt\right) \quad (45)$$

and the acceptance rate of the MC dynamics

$$\Upsilon = \frac{\exp(-\Gamma)}{\sqrt{\pi\Gamma}} \frac{T_e}{2T_e - T}. \quad (46)$$

T_e is, in the above expression, just an abbreviation for $\tilde{K}(m_0 + \mu_2)$, as given in equation (40). We will look at its relation with $T_e^{\text{FD}}(t, t')$. The function \tilde{f} in equation (45) is, in this regime,

$$\tilde{f} = -4\Upsilon \left\{ (1 + QD)\Gamma - \left[1 + QD - \frac{2DQP}{1 + QD} - \frac{DP(1 + QD)}{\gamma(1 + P + QD)} \right] + O\left(\frac{1}{\Gamma}\right) \right\} \quad (47)$$

with D , Q and P given respectively by (25) and (32).

The correlation function turns out to be

$$C_{11}(t, t') = C_{11}(t', t') \frac{\tilde{h}(t')}{\tilde{h}(t)} + O(\mu_2^{1+\gamma} \Upsilon) \quad (48)$$

with

$$C_{11}(t', t') \simeq \frac{m_0 + \mu_2(t')}{1 + Q(t')D}. \quad (49)$$

Following the approach of [10] we also derive the response function:

$$G_{11}(t, t') = G_{11}(t', t') \frac{\tilde{h}(t')}{\tilde{h}(t)} + O(\mu_2^{1+\gamma} \Upsilon) \quad (50)$$

with

$$G_{11}(t', t') = -\beta \int dy_1 dy_2 W'(\beta x) y_1^2 p(y_1, y_2 | m_1, m_2) \quad (51)$$

$$= -\beta \int dx W'(\beta x) \Delta_y p(x | m_1, m_2) + O(\mu_2^2 \Upsilon)$$

$$= \frac{4\Upsilon(t')\Gamma(t')}{\tilde{K}(t')} - \frac{2\Upsilon(t')}{\tilde{K}(t')} + O(\mu_2 \Upsilon). \quad (52)$$

Eventually we get

$$T_e^{\text{FD}}(t, t') \simeq T_e(t') [1 + O(\mu_2(t')^\gamma) + O(\mu_2(t')^2)]. \quad (53)$$

For $\gamma > 1$ this is equal to T_e in the aging regime ($\mu_2(t')^\gamma$ goes to zero faster than $\mu_2(t') \sim T_e(t') - T$), while as soon as the VFTH exponent equals one, the correspondence breaks down and only the asymptotic limits of the two effective temperatures will be equal to each other (and to the heat bath temperature).

6.2. Low-temperature case: $T < T_0$, $\gamma > 1$

Our approach also allows us to study the regime below the Kauzmann temperature. In this last case, though, we have qualitatively different behaviours depending on the value of γ , i.e. on the relative weight of μ_1 and μ_2 . We describe here the case $\gamma > 1$, where $\mu_1 \ll \mu_2$ [19].

We find the solutions of the equations for the two-time correlation functions with the following expressions for the function \tilde{f} :

$$\tilde{f} = -4\Upsilon\Gamma(1 + QD) - 8\Upsilon \frac{QDP}{1 + QD} (1 - 3r + 2r^2) + O(\mu_2 \Upsilon) \quad (54)$$

where r is an abbreviation for the normalized difference between the effective temperature (40) and the heat bath temperature:

$$r \equiv \frac{T_e - T}{2T_e - T}. \quad (55)$$

The two-time correlation function turns out to be

$$C_{11}(t, t') \simeq \frac{1}{1 + Q(t')D} [m_0 + \mu_2(t') + O(\mu_2^\gamma(t'))] \frac{\tilde{h}(t')}{\tilde{h}(t)}. \quad (56)$$

For the response function, we have

$$G_{11}(t, t') \simeq \left[\frac{4\Upsilon(t')\Gamma(t')}{\tilde{K}(t')} - \frac{2\Upsilon(t')(1-2r(t'))^2}{\tilde{K}(t')} + 8\Upsilon(t')T_e(t') \left(\frac{Jr(t')Q(t')}{1+Q(t')D} \right)^2 \right] \frac{\tilde{h}(t')}{\tilde{h}(t)}. \quad (57)$$

It follows that

$$T_e^{FD}(t, t') \simeq T_e(t')[1 + O(\mu_2(t')^\gamma) + O(\mu_2(t')^{1+\gamma})]. \quad (58)$$

In this case $O(\mu_2^\gamma)$ is always smaller than $O(\mu_2)$: in the long-time regime, $T_e^{FD}(t)$ coincides with $T_e(t)$.

With this outcome we have demonstrated that it is possible to identify an effective temperature that, coupled to the configurational entropy, is able to map the dynamics of a system out of equilibrium into a thermodynamic framework. In our model, either above or below the Kauzmann transition, such a construction seems to be well founded, provided that the VFTH exponent γ is bigger than one. In this case the time evolution is so slow that a quasi-equilibrium occurs at a time-dependent effective temperature. For γ below one, instead, the time evolution is too fast to allow for such a straightforward translation into thermodynamics.

7. Conclusions

In this paper we have been studying a particular model glass that has all the basic attributes of a real glass and whose dynamics can be analytically solved.

An important assumption for our study has been the decoupling of timescales of the processes taking place in the glassy dynamics. The decoupling of timescales is also fundamental for a generalization of equilibrium thermodynamics to systems far from equilibrium.

From the temporal behaviour of the slowly varying observables in the aging regime we found a VFTH relaxation time above the Kauzmann transition and we derived the Adam–Gibbs relation between the relaxation time and the configurational entropy, which can be explicitly computed for our model. It is also possible to study the dynamics of the system quenched to a temperature below the Kauzmann temperature. For such an analysis we refer the reader to [19].

We proposed an out-of-equilibrium thermodynamic formulation and we tested on our exactly solvable model whether or not such a generalized approach holds, having one extra variable, namely the *effective temperature*, for the description of the non-equilibrium thermodynamics. By ‘effective temperature’ we mean a thermodynamic quantity that would be the temperature of a system at equilibrium which visits with the same frequency the same states as the real—out-of-equilibrium—system at temperature T visits on a given timescale during its dynamics. This kind of parameter appears in the thermodynamic functions together with the heat bath temperature and the fields coupled to the system’s observables and is coupled to the configurational entropy.

Generally speaking, in order to recast the out-of-equilibrium dynamics in a thermodynamic framework, the history of a system that is far from equilibrium may be expressed by more than one effective parameter. This happens when more than one long timescale is involved in the dynamic evolution of a system. In those cases to every time sector there will correspond an effective temperature [31]. Moreover, in a given time sector, the number of effective parameters needed to make such a translation to a thermodynamic framework may, in principle, be equal to the number of relevant observables considered. In our model, however, for certain dynamic regimes determined by the temperature and by the VFTH exponent γ , the effective parameters

pertaining to processes having the same timescale become equal to each other for large times. When the distance $\mu_1(t)$ from equilibrium is much smaller than the distance from the constraint, $\mu_2(t)$, a single effective temperature alone is enough for a complete thermodynamic description of the dominant physical phenomena; this happens when $\gamma > 1$.

In many models the concept of effective temperature is used in an attempt to give a thermodynamic description of the glassy phase. There are several analytical and numerical works defining the effective temperature as the FDR (among others [32–34]) and also glassy models in which the effective temperature can be measured by coupling the system to a slowly relaxing thermometer [18, 35]. Even in granular systems, such an approach has been used with some success [36]. However, as far as we know, either no comparison is made between alternative (equally well founded) definitions of effective temperature or, when such a comparison is carried out, very often no coincidence is found [34, 35, 37]. Nevertheless, in the p -spin model the fluctuation-dissipation effective temperature coincides with the thermodynamic effective temperature; both are equal to T/x where x is the break point of the Parisi function [38, 39].

The coincidence of effective temperatures for the present model (in those parameter regions where it does take place) appears to be connected to a sufficiently slow relaxation dynamics. In order to understand what could happen in other models a very general analysis should be performed in order to identify what the minimal requirements are for producing an equilibration of different degrees of freedom within a single timescale (for a contribution in this direction see, for instance [40]).

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