Effective temperatures in an exactly solvable model for a fragile glass

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A model glass is considered with one type of fast ($\beta$-type) of processes, and one type of slow processes ($\alpha$-type). On time-scales where the fast ones are in equilibrium, the slow ones have a dynamics that resembles the one of faciliated spin models. The main features are the occurrence of a Kauzmann transition, a Vogel-Fulcher-Tammann-Hesse behaviour for the relaxation time, an Adam-Gibbs relation between relaxation time and configurational entropy, and an aging regime. The model is such that its statics is simple and its (Monte-Carlo-type) dynamics is exactly solvable. The dynamics has been studied both on the approach to the Kauzmann transition and below it. In certain parameter regimes it is so slow that it sets out a quasi-equilibrium at a time dependent effective temperature. Correlation and Response functions are also computed, as well as the out of equilibrium Fluctuation-Dissipation Relation, showing the uniqueness of the effective temperature, thus giving support to the rephrasing of the problem within the framework of out of equilibrium thermodynamics.

1. INTRODUCTION

A glass can be viewed as a liquid in which a huge slowing down of the diffusive motion of the particles has destroyed its ability to flow on experimental time-scales. The slowing down can be expressed through the relaxation time, i.e. the characteristic time needed to have one inter-particle diffusion process of a particle while it is rattling between its neighbour particles, that form a cage around it. This relaxation time is proportional to viscosity. Cooling down from the liquid phase, at some point the system falls out of equilibrium: the slow liquid degrees of freedom are no more accessible and the relaxation time and the viscosity of the under-cooled melt grow suddenly by several orders of magnitude. The temperature at which this happens is defined as the glass transition temperature $T_g$ \([1]\). At $T_g$ the heat capacity decreases in a clear way going from liquid to glassy phase and also on reheating an abrupt, but different change shows up. (Some universal behavior in the cooling-heating process was pointed out by one of us \([2,3]\).) Moreover, discontinuities of this kind occur also in the compressibility and the thermal expansivity. This looks similar to a continuous phase transition, even though the analogy is not perfect, because of the smeared nature of the discontinuities and because the smaller specific heat value occurs below the glass transition, rather than above, as would normally occur in mean field phase transitions.

The above described transition is not a true thermodynamic phase transition, but it is strictly kinetic in origin: it takes place when the relaxation time becomes longer than the observation time and marks the transition from ergodic to non-ergodic behaviour. In general the location of this transition, the empirical glass transition temperature $T_g$, depends on the cooling rate, more precisely, on the cooling scheme. The absolute glass transition temperature is defined as the temperature where the viscosity equals $10^{13}$ Poise, and the equilibration time of the order of days. It is related to the slowest possible experiments one can realistically do. Cooling at higher rates there is a glass transition at a somewhat larger dynamical glass transition temperature.

The very slow relaxation of non-ergodic systems evolving towards equilibrium structures on time scales longer than the characteristic time scales of the experiments, depending on the history of the system (e.g. on the phase space region in which the initial conditions are chosen and on the cooling rate) is the so called regime of aging dynamics \([4,5]\).

Experimental data for the viscosity pattern of glass forming liquids are often fit to a Vogel-Fulcher-Tammann-Hesse (VFTH) behavior \([4,5]\): $\tau_{eq} \sim \exp[A (T - T_0)^\gamma]$, where the fitting parameter $T_0$ depends on the material and the range of temperatures in which the fit is performed. The exponent $\gamma$ is usually set equal to 1, and an argument for this choice was given by Adam and Gibbs \([1]\). However also exponents $\gamma \neq 1$ are compatible with data, merely affecting the width of the fitting interval. An analytic approach by Parisi \([10]\, on the other hand, using replica trick and field theory, gives $\gamma = 2$ in three dimensions. Here we shall consider $\gamma$ as a model parameter, that can be chosen below, equal to or above unity, and investigate the aspects of this standard picture.

Kauzmann \([11]\) pointed at the paradox that the difference between the liquid entropy and the crystal entropy (i.e. the entropy of the most organized state for the system) if naive extrapolated to zero temperature would become negative at some point. To circumvent this unphysical result he proposed the occurrence of a thermodynamic phase transition at the temperature (commonly denoted by $T_K$) where this entropy difference vanishes. Such a
A thermodynamic transition would be characterized by a discontinuity of the specific heat and by the exponential divergence of the relaxation time (VFTH for fragile glasses or Arrhenius for strong ones). Connected to this last feature is the usual assumption that the fitting parameter $T_0$ of the VFTH law coincides with the Kauzmann temperature $T_K$. We note that at this phase transition, the divergence of the relaxation time is not algebraic in temperature, as happens in ordinary continuous phase transitions, but it is exponential and no susceptibility diverges at the critical point.

The residual entropy given by the difference of the entropy of the undercooled liquid and the entropy of the vibrational modes of the crystal that could in principle be formed, is usually called complexity or configurational entropy. According to standard knowledge, the Kauzmann transition should be characterized by a vanishing, or minimal, configurational entropy. This prediction is very difficult to test experimentally, since the relaxation time is too long. The existence of a Kauzmann transition was nevertheless recently supported both by analytical and numerical results $[12-14]$. The configurational entropy is the entropy determined by the number of states that the system at temperature $T_K < T < T_g$ can visit.

At a given dynamic critical temperature $T_D$, generally greater than $T_g$, the separation of the time scales of slow ($\alpha$) and fast ($\beta$) processes starts to increase more rapidly than at higher temperature. Referring to the phase space we can say that structures get organized at two levels: some minima of the free energy are separated by very small barriers and between them $\beta$ processes take place; groups of those minima are contained in bigger basins separated by barriers requiring a greater free energy variation to be crossed. To make the system go from the configuration in one of these basins to another configuration in another basin, i.e. to have an $\alpha$ process, a longer time is needed. The time scale on which these processes are happening are, however, at $T_D$ and below (but above $T_g$), still very short in comparison with the observation time. In a cooling experiment the system is thus still in thermodynamic equilibrium.

Going on with cooling, the deepness of the local and global minima, appearing in the thermodynamic potential and corresponding to different metastable and stable states, grows: barriers between them become higher and higher until, at the glass transition temperature $T_g$, some states become impossible to reach during the time-scale we set for our system, i.e. the experimental time. The configurational entropy is the observable that counts the relevant states. As temperature decreases further the configurational entropy starts to decrease because the states available for the system are less and less. The Kauzmann temperature is reached when the system is stuck in one state and cannot move to any other, because, even asymptotically and even for short range systems where activated processes were present for $T_K < T < T_g$, the free energy barriers become infinite.

The configurational entropy density $s_c$ is usually connected directly to the relaxation time through the Adam-Gibbs relation $[13]$: $\tau_{eq} \sim \exp(1/s_c)$.

To recapitulate we have been referring basically to the following different regimes for a glass former.

- For $T > T_D$ the system is in a disordered phase. Diffusion processes have a very short relaxation time. At very high temperature the free energy describing the system has only one global equilibrium minimum and cooling towards the $T_D$ temperature small local minima show up.

- Around $T_D$ a dynamic transition takes place. The phase is still disordered but the free energy increases its roughness and some local minima become deeper: $\alpha$-$\beta$ bifurcation is qualitatively enhanced. In a simple mode coupling theory $[13]$ this is the temperature $T_{mc}$ at which a static transition is predicted with an algebraically diverging relaxation time. In the p-spin spin glass model $[16,17]$ this corresponds to the dynamic critical temperature $T_D$ at which the system goes to metastable states of energy higher than the minimum energy. For $T_g < T < T_D$ the dynamics of $\alpha$ processes has a huge slowing down but the temperature is high enough to reach equilibrium on the experimental time scales.

- Around $T_g$, that depends on the cooling rate, another transition takes place. Many other local minima appear and the free energy roughness is such that the deepest local minima, corresponding to metastable states, become ergodically separated on the time scales of the experiment. For $T_K < T < T_g$ the system has a very slow aging dynamics between the metastable states, proceeding by activated processes.

- At $T = T_K$ a thermodynamic phase transition shows up, with exponentially diverging relaxation time. The free energy barriers between deep local minima increase to infinite and the system gets stuck in one single minimum forever. Ergodicity is broken at any time scale. In the p-spin model this corresponds to the temperature at which the replica symmetry is broken $[18]$. The Kauzmann temperature $T_K$ is usually assumed to coincide with the fitting parameter $T_0$ of the VFTH law. Below the Kauzmann temperature the system evolves only through the configurations belonging to the ergodic component of the phase space where the dynamics brought it during the cooling.

- In a cooling experiment that goes below $T_K$, and in a quenching experiments to a temperature below $T_K$, the
agging dynamics visits only states with a free energy that is higher than the one in the static limit. Dynamics behaves as if occurring at a higher temperature.

The exponential divergence of time scale in glasses (opposed to the algebraic divergence in standard continuous phase transitions) might induce an asymptotic decoupling of the time-decades. The reasonable assumption can be made that, in a glassy system that has aged a long time \( t \), all processes with equilibration time much less than \( t \) are in equilibrium (the \( \beta \) processes), while those evolving on time scales much larger than \( t \) are still quenched, leaving the processes with time scale of order \( t \) (i. e. the \( \alpha \) processes), as the only interesting ones. Indeed this assumption was already tested successfully in models similar to, but even more idealized than, the one we are going to discuss in the present paper. Those models showed a glassy regime with an Arrhenius law (rather than VFTH), like a harmonic oscillator model \( \text{[13]} \) and a spherical spin model \( \text{[14]} \). The asymptotic decoupling of time scales that is the input for the present set of models could be the basic ground for a generalization of equilibrium thermodynamics to systems out of equilibrium \( \text{[2]} \). That approach involves systems where one extra variable is needed to describe the non-equilibrium physics, namely the effective temperature. One of our aims will be to test this picture in an exactly solvable model glass; we shall see that there are domains where it does apply (namely when the VFTH exponent \( \gamma \) exceeds unity) and where it does not apply (namely when \( \gamma \leq 1 \)). In this last case two extra variables will be needed making compulsory the introduction of an effective field besides the effective temperature.

In the present paper we are going to investigate an exactly solvable model glass that shows all of the features that we recalled above for the much more complicated real glasses. The model is introduced in section \( \text{[3]} \). It is built by processes evolving on two different, well separated time scales, representing the \( \alpha \) and \( \beta \) processes taking place in real glassy materials. In section \( \text{[3]} \) we introduce the dynamics that we apply to the model and we show the dynamic behaviour in the aging regime. We can implement the dynamics even below the Kauzmann temperature, thus getting insight in a regime where few analytic results are known. Even though the physics of our model is simple, we shall find general aspects of the results by formulating them in the thermodynamic language. The phrasing of the dynamic properties in terms of a generalized out-of-equilibrium thermodynamic frame is carried out in section \( \text{[4]} \), where we introduce effective parameters to take into account the history of the system. In section \( \text{[3]} \) we study two-time observables, such as correlation functions and response functions, and we look at the fluctuation dissipation ratio out of equilibrium \( \text{[20]} \).

2. MODEL

The model we study, that was firstly introduced in \( \text{[21]} \), is described by the following local Hamiltonian

\[
\mathcal{H}([x_i], \{S_i\}) = \frac{1}{2}K \sum_{i=1}^{N} x_i^2 - H \sum_{i=1}^{N} x_i - J \sum_{i=1}^{N} x_i S_i - L \sum_{i=1}^{N} S_i \tag{2.1}
\]

where \( N \) is the size of the system and \( \{x_i\} \) and \( \{S_i\} \) are continuous variables, the last satisfying a spherical constraint:

\[
\sum_{i} S_i^2 = N. \]

We will call them from now on harmonic oscillators and spherical spins, respectively. \( K \) is the Hooke elastic constant, \( H \) is an external field acting on the harmonic oscillators, \( J \) is the coupling constant between \( \{x_i\} \) and \( \{S_i\} \) and \( L \) is the external field acting on the spherical spins. As we will see in this paper the simple local form of (2.1) allows us to introduce an analytically solvable dynamics with glassy behaviour.

In our simple model we introduce by hand a separation of time scales where the spins represent the fast modes and the harmonic oscillators the slow ones. Separation of time scales is one of the most important and most general characteristics that glasses are supposed to hold. Indeed, we assume that the \( \{S_i\} \) evolve with time on a much shorter time scale than that of the harmonic oscillators. From the point of view of the spins the \( \{x_i\} \) are quenched random variables and the combination \( Jx_i \) can be seen as a random field exerted on spin \( i \). On the other hand, from the point of view of the motion of the \( \{x_i\} \) the spins are just a noise. To describe the long time regime of the \( \{x_i\} \) system we can average over this noise by performing the computation of the \( \{S_i\} \) partition function, yielding an effective Hamiltonian depending only on the \( \{x_i\} \), that will determine the dynamics of these variables.

Summing out fast variables is a standard technique in physics. For instance, in any Landau-Ginzburg-Wilson theory there occur coefficients, of which the temperature dependence arises from summing out fast processes. We now do the same in our model.

We perform the spin integration in the partition function using the saddle point approximation for large \( N \) and we get:

\[
Z_S([x_i]) = \int \left( \prod_{i=1}^{N} ds_i \right) \exp\left\{ -\beta \mathcal{H}([x_i], \{S_i\}) \right\} \delta \left( \sum_{i=1}^{N} S_i^2 - N \right) \tag{2.2}
\]
\[
\simeq \exp \left[ -\beta N \left( \frac{K}{2} m_2 - H m_1 - w + \frac{T}{2} \log \frac{w + \frac{T}{2}}{T} \right) \right]
\]

With \( \beta = 1/T \) and where we introduced the short-hands

\[
m_1 = \frac{1}{N} \sum_{i=1}^{N} x_i , \quad m_2 = \frac{1}{N} \sum_{i=1}^{N} x_i^2.
\]

and

\[
w \equiv \sqrt{J^2 m_2 + 2 J L m_1 + L^2 + \frac{T^2}{4}}.
\]

We can define the effective Hamiltonian \( \mathcal{H}_{\text{eff}}(\{x_i\}) \equiv -T \log Z_{\text{S}}(\{x_i\}) \), obtaining

\[
\mathcal{H}_{\text{eff}}(\{x_i\}) = \frac{K}{2} m_2 N - H m_1 N - w N + \frac{T}{2} \log \frac{w + \frac{T}{2}}{T}.
\]

(2.5)

This can also be written in terms of the internal energy \( U(\{x_i\}) \) and of the entropy of the equilibrium processes (i.e. the spins) \( S_{\text{ep}}(\{x_i\}) \):

\[
\mathcal{H}_{\text{eff}}(\{x_i\}) = U(\{x_i\}) - T S_{\text{ep}}(\{x_i\})
\]

(2.6)

\[
U(\{x_i\}) = N \left[ \frac{K}{2} m_2 - H m_1 - w + \frac{T}{2} \right]
\]

(2.7)

\[
S_{\text{ep}}(\{x_i\}) = N \left[ 1 - \log \frac{w + T/2}{T} \right]
\]

(2.8)

and it can indeed be verified that \( U \) is the Hamiltonian averaged over the spins and that \( S_{\text{ep}} \) is the entropy of the spins.

Another fundamental ingredient for the model is the introduction of a constraint on the phase space to avoid the existence of the single global minimum \( \{x_i = 0, \forall i\} \), thus implementing a large degeneracy of the allowable lowest states. The constraint is taken on the \( \{x_i\} \), thus concerning the long time regime. It reads:

\[
m_2 - m_1^2 \geq m_0
\]

(2.9)

where \( m_0 \) is a fixed but arbitrary, strictly positive constant. The now obtained model glass has no crystalline state. This constraint applied to the harmonic oscillators dynamics is a way to reproduce the behaviour of good glass formers, i.e. substances for which nucleation of the crystal phase is especially unlikely even at very slow cooling rates (e.g. network formers \( \text{B}_2\text{O}_3 \) and \( \text{SiO}_2 \), molecule organics such as glycerol and atactic polystyrene and different multicomponent liquid mixtures). These are substances for which there are non-crystalline packing modes for the particles composing them that have intrinsically low energy, thus favouring these disordered configurations. 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 be thermodynamically stable with respect to any crystal configuration [22].

As we will explain in detail in the next section, we impose a dynamics which satisfies this constraint and couples the otherwise non-interacting \( \{x_i\} \) in a dynamic way.

To shorten the notation for later purposes we define here the modified “spring constant” \( \tilde{K} \) and “external field” \( \tilde{H} \):

\[
\tilde{K} = K - \frac{J^2}{w + T/2}, \quad \tilde{H} = H + \frac{J L}{w + T/2}
\]

(2.10)

We stress that \( \tilde{K} \) and \( \tilde{H} \) are actually functions of the \( \{x_i\} \) themselves (through \( m_1 \) and \( m_2 \) that occur in \( w \)). We also define the constant

\[
D \equiv H J + K L
\]

(2.11)

Recalling the definitions (2.10) it is useful to note that

\[
\tilde{H} J + \tilde{K} L = H J + K L = D.
\]

(2.12)
1. Statics

The partition function of the whole system at equilibrium is:

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

(2.13)

The new object that appears in the exponent is the configurational entropy

\[
\mathcal{I} \equiv \frac{N}{2} \left( 1 + \log(m_2 - m_1^2) \right)
\]

(2.14)

which will be widely considered in section 4. It comes from the Jacobian of the transformation of variables $\mathcal{D}x \rightarrow dm_1 dm_2$, $\exp \mathcal{I}$, (see (2.3)). We can compute the large $N$ limit of this partition using once again the saddle point approximation. The saddle point equations are found minimizing the function

\[
\frac{\beta}{N} F(T, m_1, m_2) = \frac{1}{T} \left( \frac{K}{2} m_2 - H m_1 - w \right) + \frac{1}{2} \left[ + \log \frac{w + T/2}{T} - 1 - \log(m_2 - m_1^2) \right]
\]

(2.15)

Denoting the saddle point values of $m_1$ and $m_2$ as $\bar{m}_1$ and $\bar{m}_2$ the equations are:

\[
\bar{m}_1 = \frac{\tilde{H}(\bar{m}_1, \bar{m}_2)}{K(\bar{m}_1, \bar{m}_2)}
\]

(2.16)

\[
\bar{m}_2 = \bar{m}_1^2 + \frac{T}{K(\bar{m}_1, \bar{m}_2)}
\]

(2.17)

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. In terms of the equilibrium values $\bar{m}_k$ we find the following expression for the equilibrium free energy density:

\[
F(T, \bar{m}_1(T), \bar{m}_2(T)) = N \left\{ K \bar{m}_2 - H \bar{m}_1 - w (\bar{m}_1, \bar{m}_2) \right\} + \frac{T N}{2} \left[ \log \frac{w (\bar{m}_1, \bar{m}_2) + T/2}{T} - 1 - \log(\bar{m}_2 - (\bar{m}_1)^2) \right]
\]

(2.18)

\[
= U(T, \bar{m}_1, \bar{m}_2) - T S_{\text{eq}}(T, \bar{m}_1, \bar{m}_2) - T \mathcal{I}(T, \bar{m}_1, \bar{m}_2)
\]

(2.19)

For the Hessian of $\beta F(T, m_1, m_2)/N$ we find the following expressions

\[
H \equiv \frac{\partial^2}{\partial m_1 \partial m_2} F(T, m_1, m_2) = \begin{pmatrix} J^2 & \frac{J^3}{2w(w+T/2)} & \frac{J^3}{2w(w+T/2)} - \frac{m_1}{2w(w+T/2)} & -\frac{J^3}{2w(w+T/2)} - \frac{m_1}{2w(w+T/2)} \\ \frac{J^3}{2w(w+T/2)} & \frac{J^4}{2w(w+T/2)} & \frac{J^4}{2w(w+T/2)} - \frac{m_1}{2w(w+T/2)} & -\frac{J^4}{2w(w+T/2)} - \frac{m_1}{2w(w+T/2)} \\ \frac{J^3}{2w(w+T/2)} & \frac{J^4}{2w(w+T/2)} & \frac{J^4}{2w(w+T/2)} - \frac{m_1}{2w(w+T/2)} & -\frac{J^4}{2w(w+T/2)} - \frac{m_1}{2w(w+T/2)} \\ \frac{J^3}{2w(w+T/2)} & \frac{J^4}{2w(w+T/2)} & \frac{J^4}{2w(w+T/2)} - \frac{m_1}{2w(w+T/2)} & -\frac{J^4}{2w(w+T/2)} - \frac{m_1}{2w(w+T/2)} \end{pmatrix}
\]

(2.20)

\[
H \equiv \frac{\partial^2}{\partial m_1^2} F(T, m_1, m_2) = \frac{J^2}{2w(w+T/2)} \begin{pmatrix} 2L^2 & JL \frac{J^2}{2} & m_2 + m_1^2 - m_1 \\ JL \frac{J^2}{2} & (m_2 - m_1^2)^2 & -m_1 \frac{1}{2} \\ m_2 + m_1^2 - m_1 & -m_1 \frac{1}{2} & 0 \end{pmatrix}
\]

(2.21)

The determinant of the Hessian of $\beta F(T, m_1, m_2)/N$, computed at equilibrium, is

\[
\det(H) = \frac{1}{2(m_2 - m_1^2)^2} (1 + Q_\infty D + P_\infty)
\]

(2.23)

that is always positive. In the formula above we introduce the abbreviations

\[
Q \equiv \frac{J^2(HJ + KL)}{K^3 w(w + T/2)^2}, \quad Q_\infty \equiv \lim_{t \rightarrow \infty} Q(m_1(t), m_2(t)) = Q(\bar{m}_1, \bar{m}_2).
\]

(2.24)

\[
P \equiv \frac{J^4(m_2 - m_1^2)}{2K w(w + T/2)^2}, \quad P_\infty \equiv \lim_{t \rightarrow \infty} P(m_1(t), m_2(t)) = P(\bar{m}_1, \bar{m}_2).
\]

(2.25)
that we will often use in the following. The inverse matrix turns out to be

\[
C = H^{-1} = \frac{\overline{m}_2 - \overline{m}_1^2}{1 + Q_\infty D + P_\infty}
\begin{pmatrix}
1 + P_\infty & 2\overline{m}_1 - 2\frac{\beta}{\hbar}P_\infty \\
2\overline{m}_1 - 2\frac{\beta}{\hbar}P_\infty & 4\overline{m}_1^2 + 2(\overline{m}_2 - \overline{m}_1^2) + 4\frac{\beta^2}{\hbar^2}P_\infty
\end{pmatrix}
\]  

(2.26)

The elements of this matrix are the thermodynamic average of the fluctuations of \(m_1\) and \(m_2\) around their equilibrium values \(\overline{m}_1, \overline{m}_2\), times a factor \(N\), as we can immediately check expanding \(F\) to the second order around \(\overline{m}_1\) and \(\overline{m}_2\) in (2.13). This holds for temperature high enough where, asymptotically, the constraint (2.9) plays no role.

3. ANALYTICALLY SOLVABLE MONTE CARLO DYNAMICS WITH GLASSY ASPECTS

We assume as the dynamics a generalization of previously introduced parallel Monte Carlo dynamics for the harmonic oscillators. This kind of analytic Monte Carlo approach was first introduced in [23], and later applied in [19] to the simpler, exactly solvable harmonic oscillator model (which is just our model after setting \(J = L = 0\) and by one of us [2,3] also for a spherical spin model (which is the present model after setting \(H = K = 0\) and considering the \(\{x_i\}\) as quenched random variables). The thus obtained dynamical model with a very simple Hamiltonian and a contrived dynamics has the benefit of being not only programmable on a computer, but even being solvable analytically, which yields a much deeper insight in its properties. Moreover, in the long-time domain the dynamics looks quite reasonable in regard to what one might expect of any system with a VFT-law in its statics.

In a Monte Carlo step a random updating 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 \(\Delta^2\). We call \(x\) (without any subscript) the energy difference between the new and the old state, viz. \(x = \mathcal{H}(\{x'_i\}) - \mathcal{H}(\{x_i\})\). If the energy of the new configuration is higher than the energy of the initial configuration \((x > 0)\) the move is accepted with a probability \(W(\beta x) \equiv \exp(-\beta x)\); if the new energy is lower \((x < 0)\) it is accepted always \((W(\beta x) = 1)\).

The updating is parallel and it is this particular feature giving the collective behaviour leading to exponentially divergent time scales in a model with no interactions between particles such as ours. A sequential updating would not produce any glassy effect. In this sense there is an analogy with facilitated Ising models [24], and with the kinetic lattice-glass model with contrived dynamics of Kob and Andersen [25], where the transition probabilities depend on the neighboring configuration; this dynamics may induce glassy behavior in situations where ordinary Glauber dynamics [29] would not. Models of these types may give valuable insights in the long time dynamics, at least, within a class that exhibits some long-time universality.

In a Monte Carlo step the quantities \(Nm_1 = \sum_i x_i\) and \(Nm_2 = \sum_i x_i^2\) are updated. Let us denote their change by \(y_1\) and \(y_2\), respectively. Following [3] we get the distribution function of \(y_1\) and \(y_2\), for given values of \(m_1\) and \(m_2\):

\[
p(y_1, y_2|m_1, m_2) = \prod_i \frac{dr_i}{\sqrt{2\pi\Delta^2}} \exp\left(-\frac{r_i^2}{2\Delta^2}\right) \delta\left(\sum_i x'_i - \sum_i x_i - y_1\right) \delta\left(\sum_i x'^2_i - \sum_i x^2_i - y_2\right)
\]

\[
= \frac{1}{4\pi\Delta^2\sqrt{m_2 - m_1^2}} \exp\left(-\frac{y_1^2}{2\Delta^2} \frac{(y_2 - \Delta^2 - 2y_1m_1)^2}{8\Delta^2(m_2 - m_1^2)}\right)
\]  

(3.1)

We can express the energy difference as

\[
x = \frac{\dot{K}}{2} y_2 - \dot{H} y_1,
\]  

(3.2)

upon neglecting the variations of \(m_1\) and \(m_2\) that are of order \((y_k/N)^2 \sim \Delta^2/N\).

In terms of the energy difference \(x\) and of \(y = y_1\) the distribution function can be formally written as the product of two other gaussian distributions:

\[
p(y_1, y_2|m_1, m_2)dy_1dy_2 = \frac{p(x|m_1, m_2)}{\sqrt{2\pi\Delta_x}} \frac{p(y|x, m_1, m_2)}{\sqrt{2\pi\Delta_y}} \exp\left(-\frac{(x - \overline{x})^2}{2\Delta_x}\right) \exp\left(-\frac{(y - \overline{y}(x))^2}{2\Delta_y}\right) dx dy
\]  

(3.3)

where
Monte Carlo step: present model we let $\Delta$ component of the configuration space. At large enough temperatures, the combination is stuck forever. The system does not evolve anymore towards equilibrium but it is blocked in one single ergodic interpreted as activated dynamics. When the constraint is reached the $\Gamma$ becomes infinite and the system dynamics becomes, thus implying almost always a refusal of the proposed updating. In this way, in the neighborhood of the $\Delta_l^2$ $T$ remain strictly positive. The highest temperature, Kauzmann temperature $T_B$ where $\gamma$ is an exponent larger than zero that we discussed already as being used in practice to make the best VFTH-type fitting of the relaxation time in experiments [1,2]. In our model $\gamma$ is a constant; it has no prescribed value since we do not make any connection with a microscopic system. In the standard VFTH-law one would just take $\gamma = 1$. One of our results will be to see that there are three qualitatively different regimes: $\gamma > 1$, $\gamma = 1$ and $0 < \gamma < 1$, showing that the situation $\gamma = 1$ is actually non-generic.

We also define a quantity that we shall frequently encounter in the following,

$$\Gamma(t) = \left(\frac{B}{m_2(t) - m_1(t)^2 - m_0}\right)^\gamma.$$  

(3.7)

The nearer the system goes to the constraint (i.e. the smaller the value of $m_2 - m_1^2 - m_0$), the larger the variance becomes, thus implying almost always a refusal of the proposed updating. In this way, in the neighborhood of the constraint, the dynamics is very slow and goes on through very seldom but very large moves, a thing that can be interpreted as activated dynamics. When the constraint is reached the $\Gamma$ becomes infinite and the system dynamics is stuck forever. The system does not evolve anymore towards equilibrium but it is blocked in one single ergodic component of the configuration space. At large enough temperatures, the combination $m_2(t) - m_1^2(t) - m_0$ will remain strictly positive. The highest temperature, $T_0$, at which it can vanish for $t \to \infty$, is identified with the Kauzmann temperature $T_K$.

The question whether detailed balance is satisfied or not 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

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

(3.8)

but now, when we perform the inverse move $\{x_i\} \to \{x_i\}$ through $\Delta^2$ as defined in [3,4]. Thus the right hand side of the detailed balance consists of $p(-x|m_1, m_2; \Delta^2)$, $\neq p(-x|m_1, m_2; \Delta^2)$. Expanding this probability distribution in powers of $1/N$, however, we get that $p(-x|m_1', m_2'; \Delta^2) = p(-x|m_1, m_2; \Delta^2) + O(\Delta^2/N)$. Other terms of $O(\Delta^2/N)$ were already neglected in the approximation of $x$ done in [3,4]. So, inasmuch as the whole approach is valid only for $N \to \infty$, detailed balance is also satisfied; it would slightly be violated in a finite $N$ simulation. We work at very large $N$ and, even though $\Delta^2 \propto \Gamma(t)$ grows as the system approaches equilibrium (it even diverges at the Kauzmann temperature), we perform first the thermodynamic limit computing the dynamics equation and only eventually the limit $t \to \infty$. If we would do the opposite there would be a region around the Kauzmann temperature where the detailed balance is violated and the dynamics is not the one discussed here. However, this is not our aim since we are interested in the ergodicity breaking that takes place in systems with a large number (Avogadro like) of variables.

In the harmonic oscillator model and in the spherical spins model studied in [1,2] the dynamics was performed within this approach, but at fixed $\Delta$. Both cases showed a relaxation time diverging at low temperature with an Arrhenius law, typical of strong glasses. We could also study enhanced Arrhenius law by setting $m_0 = 0$ in the present model but here we want, instead, to develop a model representing a fragile glass with a Kauzmann transition at a finite temperature.

The Monte Carlo equations for the dynamics of $m_1$ and $m_2$ can now be derived according to the lines of [3]. They read:

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

(3.9)

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

(3.10)
Before performing the study of dynamics we define two new variables $\mu_1$ and $\mu_2$ depending on $m_1$ and $m_2$ and representing, respectively, the deviation from the equilibrium state and the distance from the constraint:

$$\mu_1 \equiv \frac{\hat{H}}{K} - m_1,$$

$$\mu_2 \equiv m_2 - m_1^2 - m_0.$$  \hspace{1cm} (3.11)  \hspace{1cm} (3.12)

When $\mu_1 = 0$ equilibrium is obtained and the equilibrium value of $m_1$ is given by the solution of the equation

$$\frac{\hat{H}(m_1, m_2)}{K(m_1, m_2)} = m_1.$$  \hspace{1cm} (3.13)

that is the saddle point equation (2.16), with $m_k$ being the equilibrium values of $m_k$, and it can be proven equivalent to a fourth order equation.

When $\mu_2 = 0$ the constraint is reached. This will happen if the temperature is low enough ($T \leq T_0$). $T_0$ is the highest temperature at which the constraint is finally reached by the system.

Above $T_0$ equilibrium will be achieved without reaching the constraint. The temperature is too high for the system to notice that there is a constraint at all on the configurations: $\lim_{t \to \infty} \mu_2(t) = T_0(T) > 0$.

At and below $T_0$ the system goes to configurations that become arbitrarily close to the constraint, and then stays there arbitrarily long.

When all system parameters are fixed (aging setup) the equations of motion (3.9)-(3.10) become in terms of $\mu_1$ and $\mu_2$

$$\dot{\mu}_1 = -JQ \int dx \ W(\beta x) \ x \ p(x|m_1, m_2) - (1 + QD) \int dx \ W(\beta x) \ \bar{\varphi}(x) \ p(x|m_1, m_2)$$  \hspace{1cm} (3.14)

$$\dot{\mu}_2 = \frac{2}{K} \int dx \ W(\beta x) \ \bar{x} \ (x|m_1, m_2) + 2\mu_1 \int dx \ W(\beta x) \ \bar{\varphi}(x) \ p(x|m_1, m_2)$$  \hspace{1cm} (3.15)

where we have used $D$ and $Q$ defined respectively in (2.11) and (2.24).

We also shorten the expression $\tilde{K}(m_2 - m_1^2)$ by the parameter

$$T_e \equiv \tilde{K}(m_2 - m_1^2),$$  \hspace{1cm} (3.16)

possibly depending on time through $m_1(t)$ and $m_2(t)$. For the moment this is just an abbreviation but in the next section we will show that an alternative description of the dynamics is possible where $T_e(t)$ turns out to be a mapping of the history of the system into an effective thermodynamic parameter. This effective temperature would be the temperature of a system at equilibrium visiting with the same frequency the same states that the actual - out of equilibrium - system at temperature $T$ is visiting on a given time-scale during its dynamics.

In the time regime where $\Gamma \gg x^2/T_e^2 \sim O(1)$ ($\mu_2(t) \ll 1$), the gaussian distribution of the $x$ can be approximated by

$$p(x|m_1, m_2) \simeq \exp\left(-\frac{\Gamma}{4T_e \sqrt{\pi}}\right) \exp\left(-\frac{x}{2T_e}\right) \exp\left(1 - \frac{x^2}{16T_e^2}\right) + \frac{x^4}{512T_e^4}\]$$ \hspace{1cm} (3.17)

and the equations (3.14), (3.15) become

$$\dot{\mu}_1 = 4\Upsilon \left[ JQ \tilde{K}(m_0 + \mu_2)r \left(1 - \frac{3(1 - 2r + 2r^2)}{\Gamma}\right) - \mu_1 (1 + QD) (\Gamma - (1 - 3r + 4r^2)) \right]$$  \hspace{1cm} (3.18)

$$\dot{\mu}_2 = -4\Upsilon \left[ 2(m_0 + \mu_2)r \left(1 - \frac{3(1 - 2r + 2r^2)}{\Gamma}\right) - \mu_2^2 (\Gamma - (1 - 3r + 4r^2)) \right]$$  \hspace{1cm} (3.19)

where $r$ is the normalized difference between the parameter $T_e$ and the heat-bath temperature $T$:

$$r \equiv \frac{T_e - T}{2T_e - T}$$  \hspace{1cm} (3.20)

and

$$\Upsilon \equiv \frac{\exp(-\Gamma)}{\sqrt{\pi \Gamma}} (1 - r).$$  \hspace{1cm} (3.21)
\( \Upsilon \) (upsilon) is the leading term of the expansion of the integral representing the acceptance rate of the Monte Carlo dynamics

\[
\int dx W(\beta x)p(x|m_1, m_2) \simeq \exp\left(\frac{-\Gamma}{\sqrt{\pi} \Gamma} \right) \left(1 - r\right) \left[1 - \frac{1}{2r} (1 - 2r + 4r^2) + \mathcal{O}(\mu_2^2)\right].
\] (3.22)

The solutions to the equations (3.18) and (3.19) depend on the relative size of \( \mu_1 \) and \( \mu_2 \), thus also on \( \gamma \), as well as on \( r \) that has a different behaviour above \( T_0 \), where \( T_e \) tends to \( T \) in the infinite time limit, and below, where \( T_e \) never equals the heat-bath temperature (see section 4).

The solution to the equation (3.19) can be easily found neglecting the second term, proportional to \( \mu_1^2 \). It is expressed in the implicit form

\[
2\pi \frac{\text{erf}(\Gamma(t))}{i} - 2\exp\left(\frac{\Gamma(t)}{\Gamma}\right) = \frac{8r_1 m_0 \gamma}{\pi} t + \text{const.}
\] (3.23)

where

\[
\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt.
\] (3.24)

To second order approximation this can be written as:

\[
\mu_2(t) \simeq \frac{1}{\log(t/t_0) + c \log \left(\log(t/t_0)\right)}^{1/\gamma}
\] (3.25)

The constants \( t_0 \) and \( c \) depend on the temperature phase as will be clarified in the following.

Above \( T_0 \) (3.25) is more precisely the behaviour of \( \delta \mu_2(t) \equiv \mu_2(t) - \mu_2(T) \). Since in this range of temperature \( T_e(t) - T \sim \delta \mu_2(t) \), the first order expansion of \( r \) is:

\[
r \simeq \frac{\delta \mu_2(t)}{m_0 + \mu_2(T)} \left(1 + \frac{P_\infty}{1 + Q_\infty D}\right) - \frac{2P_\infty D}{JK_{eq}(m_0 + \mu_2(T))(1 + Q_\infty D)}
\] (3.26)

where \( P_\infty \) and \( Q_\infty \) are given in (2.23)-(2.24). In this case in equation (3.23) \( c \) is equal to \( 1/2 \) and the expression of \( t_0 \) in terms of the parameters of the model is:

\[
t_0 \equiv \frac{\sqrt{\pi}}{8\gamma \Gamma(0)[1 + P_\infty/(1 + Q_\infty D)]}
\] (3.27)

where \( \Gamma(0) \) is the initial value of \( \Gamma(t) \).

\[ \text{FIG. 3.1. The difference between } \mu_2(t) \text{ and its asymptotic value } \mu_2(T) \text{ is plotted for heat bath temperature } T = 0.41, \text{ slightly above the Kauzmann temperature } T_0 = 4.00248. \text{ The case is plotted with } K = J = 1, H = L = 0.1, m_0 = 5. \text{ The upper two curves represent the exact solution (2.24) with two different initial conditions. The lower one is the approximated solution (2.25). In the inset the initial behaviour is shown: clearly the approximation is valid already after a few decades of the dynamics.} \]
Below $T_0$ the qualitative behaviour of $\mu_2(t)$ (in this case the $\overline{\mu}_2$ part is zero) is the same, but $T$ is never reached. This implies that $r$ goes to some asymptotic constant $r_\infty$. Concerning the solution (3.25) the only difference is in the values

$$c = \frac{2 + \gamma}{2\gamma}; \quad t_0 \equiv \frac{B\sqrt{\pi}}{8m_0\gamma r_\infty(1 - r_\infty)}.$$  

(3.28)

In figure (3.1) we show the exact solution, numerically computed, of equation (3.19) for a particular choice of the parameter values: $K = J = 1, H = L = 0.1, m_0 = 5, B = 1, \gamma = 2$. We can see that after a couple of decades the behaviour is the one given in (3.25).

The ratio of equations (3.18) and (3.19) brings the equation:

$$\frac{d\mu_1}{d\mu_2} = \frac{\mu_1(1 + QD)(\Gamma + 2 - 3r + 2r^2) - JQTe^{r^2}}{2r(m_0 + \mu_2) - \mu_1^2(\Gamma + 2 - 3r + 2r^2)}$$

(3.29)

With respect to the relative weight of $\mu_1$ and $\mu_2$ we can identify different regimes, where the solution has different behaviours.

1. $T > T_0$. The leading term of the solution is given by the stationary solution. We can also neglect the term of $O(\mu_1^3\Gamma)$ in the denominator. Using the expansion (3.26) for $r$ we get:

$$r \simeq \frac{1}{m_0 + \overline{\mu}_2} \frac{1 + P_\infty + Q_\infty D}{1 + Q_\infty D} \delta \mu_2$$

(3.30)

and

$$\mu_1(t) = \frac{TJQ_\infty(1 + P_\infty + Q_\infty D)}{(m_0 + \overline{\mu}_2)(1 + Q_\infty D)^2} \frac{\delta \mu_2(t)}{\Gamma} + O(\delta \mu_2^2) + O(\delta \mu_2^{2\gamma+1})$$

(3.31)

Here we have also expanded $\Gamma(t)$ as

$$\Gamma(t) = \overline{\Gamma} - \gamma \overline{\Gamma} \frac{\delta \mu_2(t)}{\overline{\mu}_2}.$$  

(3.32)

We are most interested in what happens next to the the Kauzmann temperature, i.e. for very big $\overline{\Gamma}$, at long but not extremely long times, that means $\delta \mu_2(t)$ small but not vanishing. A more detailed treatment, including an expansion in $T - T_0$ of $\overline{\mu}_2$ appearing in $P_\infty$ and $Q_\infty$, can also be done, looking carefully up to which extent $\overline{\mu}_2$ can be approximately neglected with respect to $\delta \mu_2(t)$. We can neglect $\overline{\mu}_2$ with respect to the whole $\mu_2(t)$ at temperatures very close to the Kauzmann temperature and for times that are not extremely long, so that we are far from the thermalization and the dynamics has still aging behaviour. In figure (3.2) we show the relative weight of $\overline{\mu}_2$ on the whole $\mu_2(t)$ for a specific case. As is clear from the figure, as soon as we go too far from $T_0$, we cannot neglect with respect to $\mu_2(t)$ its asymptotic value $\overline{\mu}_2$.

![FIG. 3.2. Ratio of $\overline{\mu}_2(T)/\mu_2(t)$ at different temperatures, at and above the Kauzmann temperature. Too far away from $T_0$ the contribution of $\overline{\mu}_2(T)$ to $\mu_2(t)$ becomes relevant. The case is plotted with $K = J = 1, H = L = 0.1, m_0 = 5$. For this set of parameters the Kauzmann temperature turns out to be $T_0 = 4.00248$](image-url)
2. $T < T_0$, $\gamma > 1$. In this and in the following cases the asymptotic value of $\mu_2(t)$ is $\overline{\mu}_2 = 0$ so that $\delta \mu_2(t) = \mu_2(t)$. Also in this dynamic regime the adiabatic approximation can be carried out and the second term in the denominator of (3.29) is again negligible. In this case the leading term of $r$ in its expansion in powers of $\mu_2$, $r_\infty$, is of $O(1)$. Therefore we get

$$\mu_1(t) = \frac{J \overline{T}_e r_\infty Q_\infty}{1 + Q_\infty D \overline{\Gamma}(t)} + O(\mu_2^{1+\gamma}),$$

(3.33)

where

$$\overline{T}_e \equiv \lim_{t \to \infty} \overline{K}(m_1(t), m_2(t))(m_0 + \mu_2(t)) = \overline{K}_0 m_0,$$

(3.34)

$$\overline{K}_0 \equiv \overline{K}(\overline{m}_1, \overline{m}_2),$$

(3.35)

$$r_\infty = \frac{\overline{T}_e - T}{2\overline{T}_e - T}.$$

(3.36)

3. $T < T_0$, $\gamma = 1$. In this case the adiabatic expansion is no more consistent. We have to solve the equation (3.29) taking $d\mu_1/d\mu_2$ into account. To leading order the equation takes the form:

$$\frac{d\mu_1}{d\mu_2} = \frac{\mu_1 \Gamma(1 + Q_\infty D) - J Q_\infty \overline{T}_e r_\infty}{2r_\infty m_0} + O(\mu_1) + O(\mu_2) + O(\Gamma \mu_1^2) + O(\Gamma \mu_1 \mu_2).$$

(3.37)

Defining the quantity $\epsilon \equiv \frac{B(1 + Q_\infty D)}{2r_\infty m_0}$ we identify other five sub-regimes in the case $\gamma = 1$.

(a) $\epsilon > 1$. The solution is

$$\mu_1(t) = \frac{J Q_\infty \overline{T}_e r_\infty}{2r_\infty m_0(\epsilon - 1)} \mu_2(t) - c_1 \frac{1}{\epsilon - 1} \mu_2^2(t).$$

(3.38)

The exponent $\epsilon$ is always positive, at least in cooling, because $\overline{T}_e > T$ making $r_\infty$ and $Q_\infty$ positive. $c_1$ is also positive because it is the exponential of the integration constant (the value of which depends on the initial conditions). Since $\epsilon > 1$, the second term in the right hand side can be neglected and $\mu_1 \sim \mu_2$.

(b) $\epsilon = 1$. We find:

$$\mu_1(t) = -\frac{J \overline{T}_e r_\infty Q_\infty \log \mu_2(t)}{1 + Q_\infty D \overline{\Gamma}(t)} + c_2 \mu_2,$$

(3.39)

where $c_2$ is the integration constant and can take any value. In the long time dynamics the logarithm term will take over and, independently from the initial conditions, will be $\mu_1 > \mu_2$ and positive.

(c) $1/2 < \epsilon < 1$. The second term in (3.38) is leading and the solution is

$$\mu_1(t) = c_1 \frac{1}{1 - \epsilon} \mu_2^2(t).$$

(3.40)

c_1 is a positive constant and $\mu_1 \gg \mu_2$ and positive.

(d) $\epsilon = 1/2$. When $\epsilon \leq 1/2$ the second term in the denominator, always neglected up to now, has to be taken into account. In this case the leading term in the denominator goes to zero and $J \overline{T}_e r_\infty Q_\infty$ can be neglected with respect to $\mu_1 \Gamma(1 + Q_\infty D)$ in the numerator. We can thus easily solve the equation:

$$\frac{d\mu_2}{d\mu_1} = \frac{2r_\infty m_0 - 2\mu_1^2 \Gamma}{\mu_1 \Gamma(1 + Q_\infty D)}.$$

(3.41)

For $\epsilon = 1/2$ we get

$$\mu_2(t) = -\frac{2}{1 + Q_\infty D} \mu_1^2(t) \log \mu_1(t) + c_2 \mu_1^2(t)$$

(3.42)

that is not invertible analytically. It is clear anyway that in this sub-regime $\mu_1 \gg \mu_2$. $c_2$ can take any value.
(e) $\epsilon < 1/2$. The solution is

$$
\mu_1(t) = \sqrt{\frac{m_0 r_\infty (1 - 2 \epsilon)}{\Gamma(t)}} \left( 1 + \frac{c_1}{2} \left( \frac{1 + Q_\infty D}{2} \right)^{1/\epsilon} \left( \frac{1 - 2 \epsilon}{\epsilon} \right)^{1/\epsilon - 1} \mu_2(t)^{1/2\epsilon - 1} \right)
$$

(3.43)

where $c_1 > 0$. It is still $\mu_1 \gg \mu_2$.

4. $T < T_0$, $\gamma < 1$. Considering also the term $\mu_1^2 \Gamma$ in the denominator of (3.29), the solution is now:

$$
\mu_1(t) = \sqrt{\frac{r_\infty m_0}{\Gamma(t)}} \left( 1 - \frac{1 + Q_\infty D}{2m_0 r_\infty} \mu_2(t) \Gamma(t) \right).
$$

(3.44)

In this low temperature regime is $\mu_1 \gg \mu_2$ once again.

For $\gamma = 1$, $\epsilon \leq 1/2$ and for $\gamma < 1$ the solution to equation (3.41) involves only the absolute value of $\mu_1$, thus giving two possible choices for the sign of the function $\mu_1(\mu_2)$. In order to guarantee continuity of $\mu_1$ at the parameters values at which the dynamics changes regime, we imposed to the $\mu_1$ in two contiguous regimes to have the same sign. That means that in (3.42), (3.43) and (3.44) we chose the plus sign.

The time dependent variables $\mu_1(t)$, $\mu_2(t)$ give the dynamic behaviour of every observable in the long, but not extremely long, time regime, i.e. in the aging regime. When the time increases further the dynamic will exponentially relax to equilibrium like $\exp(-t/\tau_{eq})$. We will see what $\tau_{eq}$ is in the next section.

4. OUT OF EQUILIBRIUM THERMODYNAMICS

The history of a system that is far from equilibrium can be expressed by a number of effective parameters, like the effective temperature or other effective fields, in order to recast the out of equilibrium dynamics in a thermodynamic approach. The number of effective parameters needed to make such a translation is, in principle, equal to the number quantities considered. For a certain class of systems, however, there is some effective thermalization and the approach to equilibrium becomes asymptotically equal to each other in time. Examples of out of equilibrium regimes governed by a single effective temperature have been considered in [28]. In computer glasses the approach applies with some success. [29,30].

Given the solution of the dynamics (thus the form of the functions $m_1(t)$ and $m_2(t)$) a quasi-static approach can be followed by computing the partition function $Z_e$ of all the macroscopically equivalent states (those having the same values for $m_{1,2}$) at the given time $t$. The measure on which this out of equilibrium partition function is carried on is not the Gibbs measure. In order to generalize the equilibrium thermodynamics we assume an effective temperature $T_e$ and an effective field $H_e$, and substitute the equilibrium measure by $\exp(-\mathcal{H}_{eff}(\{x_i\}, T, H_e)/T_e)$, where $\mathcal{H}_{eff}$ is introduced in (2.6) and the true external field $H$ in it has been substituted by an effective field $H_e$. $T_e$ and $H_e$ are at this step of the computation just fictitious parameters. However, as soon as we get the expression of the “thermodynamic” potential $F_e \equiv -T_e \log Z_e$ as a function of macroscopic variables $m_{1,2}$ and effective parameters, we can fix $T_e$ and $H_e$ as taking those values that make the potential as small as possible. We thus have to minimize $F_e$ with respect to $m_1$ and $m_2$ to determine $T_e$ and $H_e$ and evaluate the resulting analytic expressions at $m_1 = m_1(t)$ and $m_2 = m_2(t)$ given by the dynamics at the considered time $t$. Counting all the macroscopically equivalent states at the time $t$, at which the dynamical variables take values $m_1$ and $m_2$, we get:

$$
Z_e(m_1, m_2; T_e, H_e) = \int \mathcal{D}x \exp \left[ -\frac{1}{T_e} \mathcal{H}_{eff}(\{x_i\}, T, H_e) \right] \delta(Nm_1 - \sum_i x_i) \delta(Nm_2 - \sum_i x_i^2),
$$

(4.1)

From this partition function we can build an effective thermodynamic potential as a function of $T_e$ and $H_e$, besides of $T$ and $H$, where the effective parameters depend on time through the time dependent values of $m_1$ and $m_2$ solutions of the dynamics. They actually are a way of describing the evolution in time of the system out of equilibrium. The effective free energy takes the form:

$$
F_e(t) = U(m_1(t), m_2(t)) - TS_{ep}(m_1(t), m_2(t)) - T_e(t)I(m_1(t), m_2(t)) + [H - H_e(t)]Nm_1(t),
$$

(4.2)

with

$$
T_e(t) = \tilde{K}(t)(m_0 + \mu_2(t)),
$$

(4.3)

$$
H_e(t) = H - \tilde{K}_1(t).
$$

(4.4)
where the last term of $F_e$ replaces the $-HNm_1$ occurring in $U$ (see eq. (2.7)) by $-H_eNm_1$, and where
\[ I(t) = \frac{N}{2} \left[ 1 + \log |m_0 + \mu_2(t)| \right] \] (4.5)
is the configurational entropy and where $U$ and $S_{ep}$ are given in (2.7) and (2.8).

As we see from (1.3) and (1.4) in the dynamic regimes 1 and 2, reported in section 3, where $\mu_1 \ll \mu_2$, the effective temperature alone is enough for a complete thermodynamic description of the dominant physical phenomena ($H_e = H$), while in the regimes 3a, 3b ($\mu_1 \sim \mu_2$) and in 3c, 3d, 3e and 4 ($\mu_1 \gg \mu_2$), when $\mu_1$ becomes no more negligible, the effective field $H_e$ is also needed.

\[ a. \text{ Effective temperature from generalized first law} \]

Calling $M \equiv Nm_1$, and using (2.7), (2.8) and (2.14), the differential of the free energy (4.2) turns out to be:
\[ dF = -S_{ep}dT - \mathcal{I}dT_e - MdH_e , \] (4.6)
thus implying
\[ dU = TdS_{ep} + T_e d\mathcal{I} + (H_e - H)dM - MdH_e . \] (4.7)

Using this expression we are able to write down the first law of thermodynamics $dU = dQ + dW$, in the two temperature-two fields case, where the change in work done on the system is $\bar{d}W = \bar{d}H_e$. In order for the conservation of energy to be satisfied the heat variation has, then, to take the form
\[ dQ = TdS_{ep} + T_e d\mathcal{I} + (H_e - H)dM . \] (4.8)

This is the same expression obtained in the two temperature picture of [28] where the fields were absent. At equilibrium, where $H_e = H$ and $T_e = T$, this reduces to the usual expression for ideal reversible quasi-static transformations $dQ = TdS$, with the total entropy $S = S_{ep} + \mathcal{I}$.

From (1.8) the complete expression for the rate of change of the heat of the system turns out to be:
\[ \dot{Q} = \frac{TK^2(w + T/2)}{2DJ} N\tilde{\mu}_1 + \frac{\tilde{K}}{2} N\mu_2 + \frac{\tilde{K}\mu_1}{2} N + QD - \tilde{K}JQ \mu_1 \left( \tilde{\mu}_1 + \mu_2 \tilde{K}JQ \right) \] (4.9)

The heat flowing out of the system is $-\dot{Q}$. Referring to the aging regimes described in section 3 the quantity $\dot{Q}$ turns out to be proportional to $\mu_2$ in the regimes 1 ($T > T_0$) and 2 ($T < T_0, \gamma > 1$). In the dynamic regimes 3a and 3b ($T < T_0, \gamma = 1, \epsilon \geq 1$) is $\dot{Q} \propto \mu_1 + \mu_2$. For 3c, 3d, 3e ($T < T_0, \gamma = 1, \epsilon \leq 1$) and for regime 4 ($T < T_0, \gamma < 1$) $\dot{Q} \propto \mu_1$.

In every dynamic regime $\mu_1$ and $\mu_2$ are negative and this implies that the heat flow of the out of equilibrium system is positive in its approach to equilibrium, as it should, no matter the values of the parameters of the model.

Starting from the first law of thermodynamics, we can derive the effective temperature in yet another way, through a generalization of the Maxwell relation $T = \partial U/\partial S$ valid at equilibrium for a system of internal energy $U$ and entropy $S$, with the derivative taken at constant magnetization (or volume). We put for simplicity $H_e = H$ in the rest of this subsection. Out of equilibrium, together with the previous Maxwell relation for equilibrium processes (where $S$ has to be substituted by $S_{ep}$) also the following generalization holds:
\[ T_e = \left. \frac{\partial U}{\partial \mathcal{I}} \right|_{S_{ep}} . \] (4.10)

A more feasible identity, where the variable to be kept constant during the transformation is the bath temperature, rather than the entropy of the fast processes, can be obtained [31,32,12]. Let’s introduce with this aim the function $\Phi$:
\[ \Phi \equiv F_e + T_e \mathcal{I} \] (4.11)
inducing $d\Phi = T_e d\mathcal{I} - S_{ep}dT$. Through this auxiliary potential function $\Phi$ we can then rewrite the effective temperature as
\( T_e(t) = \frac{\partial \Phi}{\partial I} \bigg|_T \) \hfill (4.12)

This result is a firm prediction for systems that satisfy the assumption of a two temperature thermodynamics. For underlying mechanisms in specific cases see \[31,32,12\]. Writing the latter as \( \dot{\Phi}/\dot{I} \) and using (3.9) and (3.10) we get (neglecting terms of \( \mathcal{O}(\mu_1) \)):

\[ T_e(t) = \tilde{K}(m_1(t), m_2(t)) \left[ m_2(t) - m_1^2(t) \right] \] \hfill (4.13)

in agreement with (1.3).

1. Statics

\( T_0 \) is defined as the temperature at which the constraint is reached from above: some configurations become infeasible and the valleys of the free energy landscape are divided by infinite barriers. The breaking of the ergodicity in a landscape with many minima gives rise to a real thermodynamic phase transition \[11\].

When the constraint (2.9) on the phase space of the \( \{x_i\} \) is first reached, at \( T_0 \), in the infinite time limit, \( \mathcal{I} \) goes to its minimal value \( \mathcal{I}_0 \equiv \mathcal{I}(T_0) = 1 + \log m_0 \). Zero configurational entropy would mean that only one configuration is allowed for the system. Coming from high temperature there would thus be a transition from a many (meta-stable) states phase to a phase in which the system is stuck forever in one single minimum. This transition is what is thought to happen in real glasses, at the so called Kauzmann temperature. Since we are using the continuous variable \( \{x_i\} \), the entropy \( \mathcal{I} \) (as well as \( S_{\text{ep}} \)) is, in our case, ill defined at low temperature: it would diverge like \( \log T \) at zero temperature if no constraint would be present. Our value \( \mathcal{I}(T_0) \) is greater than zero, because this entropy counts all the multiple ways in which the continuous harmonic oscillators can arrange themselves in order to satisfy the constraint (2.9). Since we are dealing with classical variables we can bypass this inconvenience just subtracting from \( \mathcal{I} \) the constant \( \mathcal{I}_0 \) to make \( \mathcal{I}(T = T_0) = 0 \). The entropy value \( \mathcal{I}_0 \) is related to dynamics on time scales where all the degenerate minima are sampled. These are much longer than the scales of our interest, and for our purposes the constant \( \mathcal{I}_0 \) plays no role.

To see how the transition takes place we first look at the asymptotic behaviour of the effective temperature. When \( T \geq T_0 \) and \( t \to \infty \), \( T_e \) becomes the heat bath temperature \( T \). When \( T < T_0 \), instead, \( T_e \) never reaches such a temperature. It rather goes towards some limit value \( \overline{T}_e(T) \) that we can get from the equation (4.3). It may be rewritten for clearness in the explicit form

\[
(Km_0 - T_e + T)(Km_0 - T_e)(J T_e)^2 + D^2 m_0 (Km_0 - T_e)^2 - J^4 m_0 (T_e)^2 = 0 \] \hfill (4.14)

a quartic equation for the effective temperature in the infinite time limit. The same equation evaluated at \( T_e = T = T_0 \) gives us the value of the Kauzmann temperature \( T_0 \) as a function of the parameter of the model. In figure (4.1) we plot \( T_e \) versus \( T \) for a choice of parameter values.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{TeT.png}
\caption{In the static regime the effective temperature is shown as a function of the heat bath temperature. At high temperature they coincide but below the Kauzmann transition \( T_e \) does not reach \( T \), not even in the infinite time limit. The system remains out of equilibrium for ever. Values of the constants are \( K = J = 1, H = L = 0.1, m_0 = 5 \).}
\end{figure}
From (4.14) or Figure 4.1 we observe that \( \frac{dT_c}{dT} \Big|_{T_0^+} < 1 \) whereas, coming from above the Kauzmann temperature, one has, of course, \( \frac{dT_c}{dT} \Big|_{T_0^+} = 1 \). The derivative of \( T_c(T) \) shows thus a discontinuity at \( T = T_0 \). Any thermodynamic function, like \( U \) and \( m_1 \), will depend on the heat bath temperature both explicitly and through this effective temperature. For the specific heat we will have, for instance:

\[
C \equiv \left. \frac{1}{N} \frac{dU}{dT} \right|_H = \left. \frac{1}{N} \frac{\partial U}{\partial T} \right|_H + \left. \frac{1}{N} \frac{\partial U}{\partial T_c} \right|_{H,T} \left. \frac{dT_c}{dT} \right|_H. \tag{4.15}
\]

This is of the same form \( C = c_1 + c_2 (\partial T_c/\partial T)_p \) assumed originally by Tool [33] for the study of caloric behaviour in the glass formation region.

The discontinuity in \( \frac{dT_c}{dT} \big|_H \) causes a discontinuity in the specific heat and also in the quantity \( - \frac{\partial m_1}{\partial T} \big|_H \), called magnetizability in [2,3] (it is the analogue of a thermal expansivity for the model here described), because both of these quantities contains terms proportional to \( \partial T \). One could now discuss the Ehrenfest relations between these discontinuities, and the Prigogine-Defay ratio, as was done for related models by one of us [28,2,3]. Because of the close analogy between all these cases, we shall not go deeper into this at the present moment.

2. Dynamics

The relaxation time is the characteristic time on which the system initially out of equilibrium (because, for instance, of a sudden quench to low temperature) relaxes towards equilibrium. It can be defined, for instance, from the dynamical equations of the internal energy per harmonic oscillator \( u \equiv U/N \)

\[
\dot{u} = - \frac{u}{\tau_{eq}}, \tag{4.16}
\]

or, equivalently, from the equations of motion for \( m_1, m_2 \) as the time at which the quantity of interest goes to \( 1/e \) of its initial value. In any temperature regime comes out that the relaxation time has an exponential behaviour in \( \Gamma \):

\[
\tau_{eq} \sim e^{\Gamma} = \exp \left( \frac{B}{\mu_2} \right)^\gamma \tag{4.17}
\]

Making use of the solution (3.25) we find the following behaviour for the relaxation time versus the heat bath temperature:

1. \( T > T_0 \). \( \mu_2(t) \rightarrow \mu_2(T) \) and near enough to the Kauzmann temperature we can linearize the latter in \( T - T_0 \). For \( t \rightarrow \infty \) we get an exponential decay with relaxation time

\[
\tau_{eq} \propto \exp \left( \frac{A_0}{T - T_0} \right)^\gamma \tag{4.18}
\]

\[
A_0 = B \left. \left( \frac{\partial \mu_2(T)}{\partial T} \right)^{-1} \right|_{T_0} = \left. \frac{B \tilde{K} \delta K \delta K}{(K - \tilde{K})(1 + DQ) - \tilde{K} P} \right|_{T_0} \tag{4.19}
\]

This behaviour is a generalized Vogel-Fulcher-Tammann-Hesse (VFTH) law [6–8], where \( \gamma \) can have any value and in particular \( \gamma = 1 \). Looking at the configurational entropy, since at the first order expansion in \( \mu_2 \) we have \( \mathcal{I} - \mathcal{I}_0 \approx \frac{N}{2m_0 \mu_2} \), we also find from (4.17) the Adam-Gibbs relation [7]:

\[
\tau_{eq} \propto \exp \left[ \frac{NB}{2m_0 (\mathcal{I} - \mathcal{I}_0)} \right]^\gamma \tag{4.20}
\]

Far from equilibrium, in the aging regime where the relaxation is very slow, we can still define a time dependent “relaxation time” giving the characteristic time scale on which the \( \alpha \) processes are taking place. Always for \( T \) very near to \( T_0 \), in the aging regime, \( \bar{\mu}_2 \), the static part of \( \mu_2 \), is negligible with respect to the dynamic part \( \delta \mu_2 \) so that for the effective temperature we have the following expansion:

\[
T_c(t) \simeq T_0 + \frac{1 + DQ + P}{1 + QD} \tilde{K} \delta \mu_2(t) + \mathcal{O}(T - T_0). \tag{4.21}
\]
we get
\[ \tau(t) \propto \exp \left( \frac{A(T)}{T_e(t) - T} \right)^\gamma \simeq \exp \left( \frac{A(T_0)}{T_e(t) - T_0} \right)^\gamma \] (4.22)
\[ A(T) = \frac{B(1 + DQ_\infty + P_\infty)}{1 + Q_\infty D} \tilde{K}_\infty \] (4.23)

where \( A(T_0) < A_0 \), meaning that in the static \( \tau \) is more divergent.

2. \( T < T_0, \gamma > 1 \). For \( T < T_0 \) the relaxation time always diverges for \( t \to \infty \). However, as it was done in the case above \( T_0 \) for the relaxation in the aging regime, an instantaneous relaxation time can be considered and expressed in terms of the effective temperature using the first order expansion of \( T_e \) in \( \mu_2 \):
\[ T_e(t) = \bar{T} + \frac{1 + DQ_\infty + P_\infty}{1 + Q_\infty D} \bar{K}_\infty \mu_2(t). \] (4.24)
We find
\[ \tau(t) = \tau(T, T_e(t)) \propto \exp \left( \frac{A(T)}{T_e(t) - \bar{T}} \right)^\gamma \] (4.25)
where \( A(T) \) is the one written in (4.23). The aging behaviour just above and well below \( T_0 \) are thus intimately related. The expression (4.25) resembles a VFTH law where the heat bath temperature has been substituted by a time dependent effective temperature \( T_e(t) \) and the Kauzmann temperature by the asymptotic value \( \bar{T} \).
Such a relation for the time scale of the aging dynamics could hold very well in more general systems.

3. \( T < T_0, \gamma \leq 1 \). In these regimes, where \( \mu_1 \) cannot be neglected with respect to \( \mu_2 \), there is no simple expression for \( \tau \).

5. TWO-TIME VARIABLES: BREAKING OF TIME-TRANSLATION INVARIANCE AND THE FLUCTUATION-DISSIPATION RELATION

In this section we compute the correlation and response functions that, 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 (TTI) with respect to the case at equilibrium. The aim of computing such quantities is also to build a Fluctuation Dissipation relation and look at the meaning of the Fluctuation-Dissipation Ratio (FDR), \( \partial_t C(t, t')/G(t, t') \), far from equilibrium.

The correlation functions between the thermodynamic fluctuation of a quantity \( m_a(t) \) at time \( t \) and that of a quantity \( m_b(t') \) at a different time \( t' \) are defined like:
\[ C_{ab}(t, t') \equiv N \langle \delta m_a(t) \delta m_b(t') \rangle, \quad a, b = 1, 2 \] (5.1)
where \( \langle \ldots \rangle \) 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:
\[ G_{ab}(t, t') \equiv \frac{\delta \langle m_a(t) \rangle}{\delta H_b(t')}, \quad a, b = 1, 2 \] (5.2)

In our model \( H_1 = H \) and \( H_2 = K/2 \).

Since we will very often make use of the derivatives with respect to \( m_1 \) and \( m_2 \) of the integrals given by the Monte Carlo dynamics introduced in section 3 we show them in appendix explicitly computed and we shorten the notation defining the variables \( f_k \) and \( g_k, k = 0, 1, 2, 3 \) in (A.11)-(A.18).
First we analyze the case above the Kauzmann temperature. In this case the expansion of the \([A.11]-[A.18]\) in powers of \(\mu_2(t)\) becomes both an expansion in \(\delta \mu_2(t)\) and in \(\overline{\mu}_2\) (or equivalently in \(1/B' = (\overline{\mu}_2/B)^\gamma\)), because we are interested in studying what happens for large times and near the Kauzmann temperature \(T_0\), i.e. for small values of \(\delta \mu_2(t)\) and for small values of \(\overline{\mu}_2\) (or large values of \(\overline{\mu}\)). In the \(f_k\) and \(g_k\) written in appendix we left the notation without the bar meaning that an approximation for long times, i.e. an expansion in \(\delta \mu_2(t)\), or an expansion in \(\overline{\mu}_2\), has still to be done, depending on the kind of approximation that we need. For the sake of clearness we repeat here the expansion of \(\Gamma(t)\) in the aging regime:

\[
\mu_2(t) = \overline{\mu}_2 + \delta \mu_2(t); \quad \Gamma(t) = \Gamma - \gamma T \frac{\delta \mu_2(t)}{\overline{\mu}_2}.
\]  

(5.3)

The following exact relations hold:

\[
\partial_{m_1, \mu_1} = -1 - LQ \tilde{K}, \quad \partial_{m_2, \mu_1} = -\frac{J}{2}Q \tilde{K}
\]  

(5.4)

We stress that \(\partial_{m_1, \mu_1}\) and \(\partial_{m_2, \mu_1}\) are still functions of \(\mu_2\), through \(Q\) and \(\tilde{K}\), and that they can thus be expanded in powers of \(\delta \mu_2\), leading to corrections to the \(f_k\) and \(g_k\). Since in the end they will only appear in the combinations \(\partial_{m_1, \mu_1} + 2m_1 \partial_{m_2, \mu_1}\) and \(\partial_{m_1, \mu_1} - 2L/J \partial_{m_2, \mu_1}\) we just give the expressions of these ones:

\[
\partial_{m_1, \mu_1} + 2m_1 \partial_{m_2, \mu_1} = -(1 + QD) \simeq -(1 + Q_\infty D) - \delta \mu_2 Q_1 D, \quad \partial_{m_1, \mu_1} - 2L/J \partial_{m_2, \mu_1} = -1,
\]  

(5.5) \quad (5.6)

where

\[
Q_1 = \frac{Q_\infty}{(1 + Q_\infty D)(m_0 + \overline{\mu}_2)} \left[ \frac{J^2(m_0 + \overline{\mu}_2)(3\overline{\mu} + T/2)}{2\overline{\mu}^2(\overline{\mu} + T/2)} - 3P_\infty \right]
\]  

(5.7)

is the coefficient of \(\delta \mu_2(t)\) in the first order expansion of \(Q\):

\[
Q(t) = Q_\infty + Q_1 \delta \mu_2(t).
\]  

(5.8)

In the following formulae the derivatives of \(\mu_1\), as well as \(\mu_1\) itself, have to be considered as general, regular functions of \(\mu_2\).

Besides the expansion \([3.8]\) of \(Q\) we also give the expansions to first order in \(\delta \mu_2(t)\) of the quantities \(r\) (defined in \([3.20]\)), \(m_1\) \([2.10]\), \(\tilde{K}\) \([2.25]\) and \(Q\) \([2.24]\):

\[
r(t) = \frac{1}{m_0 + \overline{\mu}_2} \left( \frac{1 + Q_\infty D + P_\infty}{1 + Q_\infty D} \right) \delta \mu_2(t)
\]  

(5.9)

\[
\tilde{K}(t) = \tilde{K}_\infty + \frac{\tilde{K}_\infty P_\infty}{(1 + Q_\infty D)(m_0 + \overline{\mu}_2)} \delta \mu_2(t)
\]  

(5.10)

\[
m_1(t) = \overline{m}_1 - \frac{P_\infty D}{K_\infty J(1 + Q_\infty D)(m_0 + \overline{\mu}_2)} \delta \mu_2(t)
\]  

(5.11)

\[
P(t) = P_\infty + \frac{P_\infty}{(1 + Q_\infty D)(m_0 + \overline{\mu}_2)} \left[ 1 + Q_\infty D - P_\infty + \frac{J^2(m_0 + \overline{\mu}_2)(3\overline{\mu} + T/2)}{2\overline{\mu}^2(\overline{\mu} + T/2)} \right] \delta \mu_2(t)
\]  

(5.12)

where \(\overline{\mu} \equiv \sqrt{J^2\overline{\mu}_2 + 2JL\overline{m}_1 + L^2 + T^2/4}\). For what concerns the terms containing \(\Gamma_\mu_1\), from \([3.31]\) we saw that in this dynamic regime

\[
\Gamma_\mu_1 = \frac{JQ_\infty T}{m_0 + \overline{\mu}_2} \left( 1 + Q_\infty D \right)^2 \delta \mu_2 + \mathcal{O}(\delta \mu_2^2)
\]  

(5.13)

In \([3]\) equations of motion for simpler models were obtained. Our present model share the basic attributes that are needed to get those equations, namely the possibility of writing the transition probability \([6]\) of the Monte Carlo dynamics as the product of two gaussian probability distributions \([3.3]\), functions respectively of the energy variation \(x\) and of the variation \(y\) of the magnetization like quantity \(\sum_i x_i\).
We thus recall here the following equations holding for the equal time correlation functions:

\[
\frac{d}{dt} C_{ab}(t, t) = \int W(\beta x) \left\{ \mu_1 \frac{\nabla_x}{m_2 - b - \mu_1} \right\} + \Delta_y \left( \frac{H_1}{H_2} + \sum_{c=1,2} \frac{\partial}{\partial m_c} \left[ \mu_1 \mathcal{C}_c(t, t) \left( \mu_1 \right) \right] \right\} p(x|m_1, m_2) \, dx, \quad (5.14)
\]

where (recalling (3.2), (3.5) and using (3.6) and (4.3))

\[
\begin{align}
\bar{y}_1(x) &= \frac{\mu_1}{m_2 - b - \mu_1} \frac{x - \mathcal{F}}{K} = \left( 4\Gamma \mu_1 - \mu_1 \frac{x}{T_e} \right) + \mathcal{O}(\mu_1^2), \\
\bar{y}_2(x) &= \frac{2}{K} \left( x + \tilde{H} \bar{y}_1(x) \right) \\
\mathcal{F} &= \frac{\Delta^2 k}{2} = 4T_e \Gamma \\
\Delta_y &= \frac{\Delta^2 (m_2 - m_2)}{m_2 - \mu_1 - \mu_1} = 8(m_0 + \mu_2) \Gamma + \mathcal{O}(\mu_1^2) \quad (5.16)
\end{align}
\]

Expanding the integrals \( \int W(\beta x) \bar{y}_1(x) \bar{y}_2(x) p(x|m_1, m_2) \, dx \) and \( \Delta_y \int W(\beta x) p(x|m_1, m_2) \, dx \) up to order \( \mathcal{Y} \), the equations become:

\[
\begin{align}
\dot{C}_{11}(t, t) &= 8 \left[ m_0 + \mu_2(t) \right] \Gamma(t) \left[ 1 - \frac{1 - 2r + 4r^2}{\Gamma(t)} \right] \mathcal{Y}(t) + 2 f_1(t) C_{11}(t, t) + 2 g_1(t) C_{12}(t, t) \, , \quad (5.19) \\
\dot{C}_{12}(t, t) &= 16 m_1(t) \left[ m_0 + \mu_2(t) \right] \Gamma(t) \left[ 1 - \frac{1 - 2r + 4r^2}{\Gamma(t)} \right] \mathcal{Y}(t) + f_2(t) C_{11}(t, t) + \left[ f_1(t) + g_2(t) \right] C_{12}(t, t) + g_1(t) C_{22}(t, t) \, , \quad (5.20) \\
\dot{C}_{22}(t, t) &= 32 m_1(t)^2 \left[ m_0 + \mu_2(t) \right] \Gamma(t) \left[ 1 - \frac{1 - 2r + 4r^2}{\Gamma(t)} \right] \mathcal{Y}(t) + 32 \left[ m_0 + \mu_2(t) \right] f_2(t) C_{11}(t, t) + 2 g_2(t) C_{22}(t, t) \, . \quad (5.21)
\end{align}
\]

Due to the complicated form of the equations we are not able to find solutions valid at every time. We are obliged to find approximate solutions valid on given time scales. First we study the solutions in the aging regime, for times that are long but not longer than some given time-scale, \( t_g \), after which the system begins to thermalize. Afterwards we will study the dynamics of correlation and response functions for times much longer than \( t_g \), while the system is approaching to equilibrium.

\[ \textit{a. Dynamics in the aging regime} \]

In the aging regime, for temperature just above the Kauzmann temperature \( T_0 \), we can neglect \( \mathcal{F} \) with respect to \( \delta \mu_2(t) \). This means that in expressions (5.11)-(5.12) we have to put \( \mathcal{F} \) equal to zero everywhere, including the constants \( Q_\infty, P_\infty \) and \( \tilde{K}_\infty \) (defined respectively in (2.24), (2.25) and (3.35)) and we can write \( \delta \mu_2(t) = \mu_2(t) \).

To find the solutions to (5.19)-(5.21) we can firstly perform an adiabatic expansion neglecting the time derivatives of the correlation functions. Indeed, to first order of approximation \( \dot{C}_{ab} \) is proportional to \( \mu_2(t) \); they are of \( \mathcal{O}(\mu_2(t)) \), negligible with respect to the right hand side terms. We then compute the second order corrections. The solutions for the case \( T > T_0 \), in the aging regime with negligible \( \mathcal{F} \) and \( r \) proportional to \( \mu_2(t) \), turn out to be:

\[
\begin{align}
C_{11}(t, t) &= \frac{1}{1 + Q_\infty D} \left\{ m_0 + \mu_2(t) \left[ 1 - \frac{m_0 Q_1 D}{1 + Q_\infty D} \right] + \mathcal{O} \left( \frac{1}{1 + Q_\infty D} \right) + \mathcal{O}(\mu_2(t)) \right\} \\
C_{12}(t, t) &= \frac{1}{1 + Q_\infty D} \left\{ 2 m_1(t) m_0 + \mu_2(t) \left[ 2 m_1(t) - \frac{m_0 Q_1 D}{1 + Q_\infty D} - m_0 Q_\infty D \right] + \mathcal{O} \left( \frac{1}{1 + Q_\infty D} \right) + \mathcal{O}(\mu_2(t)) \right\} \\
C_{22}(t, t) &= \frac{1}{1 + Q_\infty D} \left\{ 4 m_1(t)^2 m_0 + \mu_2(t) \left[ 4 m_1(t)^2 - \frac{m_0 Q_1 D}{1 + Q_\infty D} - 4 m_0 m_1 Q_\infty D \right] + \mathcal{O} \left( \frac{1}{1 + Q_\infty D} \right) + \mathcal{O}(\mu_2(t)) \right\}
\end{align}
\]

To get these expressions it is enough to keep in \( f_1, g_1, f_2, g_2 \) (defined in (A.13)-(A.16)) only terms up to \( \mathcal{O}(1) \).
Once we have the equal time solutions we can solve the equations for the two times functions. Always following the approach of \[3\] we get the equations:

\[
\partial_t C_{ab}(t, t') = f_a(t) C_{1b}(t, t') + g_a(t) C_{2b}(t, t') \quad a, b = 1, 2.
\]

(5.25)

where \(f_a\) and \(g_a\) are defined in \([4.13]-[4.16]\). We introduce the function

\[
\dot{f} \equiv f_1 + \frac{2m_1 g_1}{g_2 - 2m_1 g_1} - g_2 - \frac{2m_1 f_1}{g_2 - 2m_1 g_1}
\]

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

(5.26)

where \(m_1\) is obtained from \([3.3]\) as

\[
m_1 \simeq 4 \mu_1 \Upsilon \Gamma - 4 \mu_1 (1 - 3r + 4r^2) = \mathcal{O}(\mu_2 \Upsilon)
\]

(5.27)

and is negligible with respect to the leading orders.

The decoupled equations for \(C_{11}\) and \(C_{12}\) that we get are, in this notation:

\[
\partial_t C_{1b}(t, t') = \dot{f}(t) \ C_{1b}(t, t'), \quad b = 1, 2.
\]

(5.28)

To the leading order the two correlation functions above are connected to \(C_{21}\) and \(C_{22}\) in the following way:

\[
C_{2b}(t, t') \simeq 2m_1(t) C_{1b}(t, t'), \quad b = 1, 2.
\]

(5.29)

Defining the time evolution function for the considered time-scale sector as

\[
\tilde{h}(\tau) \equiv \exp\left( - \int_0^\tau \dot{f}(t) dt \right)
\]

(5.30)

the solution of \([5.28]\) comes out to be

\[
C_{1b}(t, t') = \frac{\tilde{h}(t')}{\tilde{h}(t)} C_{1b}(t, t') + \mathcal{O}(\mu_1 \Upsilon)
\]

(5.31)

Following the approach of \[3\] we also derive the response function. Neglecting the terms of \(\mathcal{O}(\Upsilon^2)\) (called switch terms in \[3\]) they are:

\[
G_{11}(t, t') = -\beta \int dy_1 dy_2 W'(\beta x) y_1^2 p(y_1, y_2 | m_1, m_2) = -\beta \int dx W'(\beta x) \left[ \bar{y}_1(x)^2 + \Delta_y \right] p(x | m_1, m_2) = \]

\[
= -\beta \int dx W'(\beta x) \Delta_y p(x | m_1, m_2) + \mathcal{O}(\mu_2 \Upsilon) \simeq \frac{4 \Upsilon \Gamma}{K} - \frac{2 \Upsilon}{K} + \mathcal{O}(\mu_2 \Upsilon)
\]

(5.32)

\[
G_{12}(t, t') = -\beta \int dy_1 dy_2 W'(\beta x) y_1 y_2 p(y_1, y_2 | m_1, m_2) = \]

\[
= -\beta \frac{2 \Upsilon}{K} \int dx W'(\beta x) \left\{ x \bar{y}_1(x) + \hat{H} \left[ \bar{y}_1(x)^2 + \Delta_y \right] \right\} p(x | m_1, m_2) = \]

\[
= -2 \beta \frac{\hat{H}}{K} \int dx W'(\beta x) \Delta_y p(x | m_1, m_2) + \mathcal{O}\left(\frac{\mu_2 \Upsilon}{\Gamma} \right) \simeq \frac{8 \mu_1}{K} \Upsilon \Gamma - \frac{4 \mu_1 \Upsilon}{K} + \mathcal{O}(\mu_2 \Upsilon)
\]

(5.33)

\[
G_{22}(t, t') = -\beta \int dy_1 dy_2 W'(\beta x) y_2^2 p(y_1, y_2 | m_1, m_2) = \]

\[
= -\beta \frac{4}{K^2} \int dx W'(\beta x) \left( x^2 + 2 \hat{H} x \bar{y}_1(x) + \hat{H}^2 \left[ \bar{y}_1(x)^2 + \Delta_y \right] \right) p(x | m_1, m_2) = \]

\[
= -4 \beta \frac{1}{K^2} \int dx W'(\beta x) \left( x^2 + \hat{H}^2 \Delta_y \right) p(x | m_1, m_2) + \mathcal{O}\left(\frac{\mu_2 \Upsilon}{\Gamma} \right) \simeq \frac{16 \mu_1}{K} \Upsilon \Gamma - \frac{8 \mu_1^2 \Upsilon}{K} - 32 \Upsilon m_0^2 + \mathcal{O}(\mu_2 \Upsilon).
\]

(5.34)

The equations describing the evolution in \(t\) of the response to a perturbation at \(t'\) have the same shape of those for the correlation functions \([5.25]\). The solutions are then
\[ G_{ab}(t, t') = G_{ab}(t', t') \frac{\tilde{h}(t')}{h(t)}. \] (5.35)

With these results we can generalize the Fluctuation Dissipation Theorem (FDT) defining another effective temperature, \( T_e^{FD} \), by means of the ratio between the derivative with respect to the initial time (also called “waiting” time) \( t' \) of the correlation function \( C_{11} \) and the response function \( G_{11} \):

\[ T_e^{FD}(t, t') = \frac{\partial t C_{11}(t, t')}{G_{11}(t, t')} \] (5.36)

To compute it we need:

\[
\partial t C_{11}(t, t') = \left( \frac{\partial t C_{11}(t', t')}{h(t)} - \dot{f}(t') \frac{\tilde{h}(t')}{h(t)} \right) C_{11}(t', t') \approx -\dot{f}(t') \frac{\tilde{h}(t')}{h(t)} C_{11}(t', t')
\] (5.37)

\[
\simeq -4\Upsilon(t') \left\{ \left( 1 + Q_\infty D + Q_1 D \mu_2(t') \right) \Gamma(t') + O(1) \right\} \times \frac{1}{1 + Q_\infty D} \left[ m_0 + \mu_2(t) \left( 1 - \frac{m_0 Q_1 D}{1 + Q_\infty D} \right) \right] \frac{\tilde{h}(t')}{h(t)}
\]

\[
\simeq -4\Upsilon(t') \left\{ \left[ m_0 + \mu_2(t') \right] \Gamma(t') + O(1) \right\}
\]

Eventually we get

\[ T_e^{FD}(t, t') \approx T_e(t') \left[ 1 + O \left( \frac{1}{\Gamma(t')} \right) + O \left( \left( \mu_2(t') \right)^2 \right) \right] = T_e^{FD}(t') \] (5.38)

where \( T_e \) was first introduced in section 3 and later on derived in (4.3). We recall that \( \Gamma^{-1} \propto \mu_2^2 \). As we see here the above defined fluctuation dissipation effective temperature coincides, in the time-scale of our interest, with the effective temperature \( T_e \) that we got by the quasi static approach, only if 1/\( \Gamma \) is negligible with respect to \( \mu_2 \). This is true only if \( \gamma \), the exponent of the generalized VFTH law (4.18), is greater than one. Otherwise the last correction is no more sub-leading: already for \( \gamma = 1 \), \( T_e^{FD} \to T_e \) only in the infinite time limit, i. e. for time-scales longer than those of the considered aging regime. As already discussed in section 3, where we presented the results of the dynamics of the one-time observables, the value of the exponent \( \gamma \) discriminates between different regimes. For \( \gamma > 1 \) an out of equilibrium thermodynamics can be built in terms of a single additional effective parameter (the effective temperature \( T_e \)). For \( \gamma \leq 1 \), \( T_e \) alone does not give consistent results in the generalization of the equilibrium properties to the non equilibrium case and in order to cure this inconsistency more effective parameters are probably needed. This discrepancy was clear, from section 3, for the regimes below \( T_0 \) where already the one-time variables had different behaviours depending on the value of \( \gamma \) being greater, equal to or lesser than \( 1 \). For \( T > T_0 \) there was not such a difference at the one-time level. It shows up, instead, at the level of two-time observables, as we just saw.

b. Approach to equilibrium

For times longer than the aging regime time-scales the terms that are relevant in the equations (5.19)-(5.21) for the correlation functions and in the expressions (5.33)-(5.35) for the response functions are different. When \( t \gg t_g \) the equilibrium value \( \overline{\mu}_2 \) of the variable \( \mu_2 \) is no more negligible with respect to its time dependent part \( \delta \mu_2(t) \) (that is eventually going to zero as \( t \to \infty \)). We are in a regime where \( r \simeq 0 \) \( (T_e \simeq T) \). In the resolution of the equations (5.19)-(5.21) this means that all the terms of \( O(r \Upsilon \gamma / \mu_2) = O(\delta \mu_2 \Upsilon) \) are now sub-dominant with respect to those of \( O(\Upsilon) \) and of \( O(\Upsilon) \). To solve equations (5.19)-(5.21) we use the adiabatic expansion, as in the previous case. The solutions for very large time, with finite, though small \( \overline{\mu}_2 \) and a vanishing \( r \), are:

\[ C_{11}(t, t) = \frac{m_0 + \mu_2(t)}{1 + QD + P(1 + P)} (1 + P) + c_{11,r} r \] (5.39)

\[ = \frac{m_0 + \overline{\mu}_2}{1 + Q_\infty D + P_\infty} (1 + P_\infty) + c_{11,\delta \mu_2} \delta \mu_2(t) \]

\[ C_{12}(t, t) = C_{21}(t, t) \approx \frac{m_0 + \mu_2(t)}{1 + QD + P} \left( 2 \tilde{m}_1(t) - \frac{2L}{\overline{J}} P \right) + c_{12,r} r \] (5.40)
where

\[ c_{11,\mu} = \frac{1}{1 + DQ\gamma + P} \left( (m_0 + P_\gamma) P_0 Q_0 + Q_1 D(1 + P_\gamma) - \frac{8\gamma DQ\gamma \gamma O(1 + P_\gamma)(m_0 + P_\gamma)}{P_0(1 + DQ\gamma)^2} \right) \] (5.45)

and

\[ c_{12,\mu} = \frac{2}{1 + DQ\gamma + P} \left\{ \left[ m_1 \frac{L}{J} P_\gamma \left( 1 + \frac{D}{L DQ\gamma} (1 + DQ\gamma) \right) \right] - \frac{(m_0 + P_\gamma) P_0 (m_1 + \frac{L}{J}) (1 + DQ\gamma) + DQ_1 (m_1 - \frac{L}{J})}{1 + P_\gamma + DQ\gamma} \right. \]

\[ \left. + 4\gamma DQ \gamma \gamma O \left( 1 + P_\gamma \right) \left( 1 + \gamma DQ\gamma \gamma O \left( L + J P_\gamma - m_1 \right) \right) \right\} \] (5.46)

\[ c_{22,\mu} = \frac{2}{1 + DQ\gamma + P} \left\{ \left[ (m_0 + P_\gamma) \left[ 2m_1^2 + \frac{L^2}{J} P_\gamma \left( 1 + DQ\gamma \right) + DQ_1 \left( 2m_1^2 + \frac{L^2}{J} P_\gamma \right) + m_0 + P_\gamma \right] \right] \right. \]

\[ \left. - \frac{8\gamma DQ \gamma \gamma O \left( m_1 - \frac{L}{J} P_\gamma \right) \left( 1 + \gamma DQ\gamma \gamma O \left( L + J P_\gamma - m_1 \right) \right)}{JK_\gamma P_0(1 + DQ\gamma)^2} \right\} \] (5.47)

where \( Q_1 \) is defined in (5.17) and \( P_1 \) is the first order coefficient of \( P \) of its expansion in \( \delta\mu_2 \) (see 5.12).

To find the solutions to first order approximation in \( \delta\mu_2 \) it is enough to keep in each of the (5.13)-(5.16) only terms up to \( O(r\gamma) \) and \( O(r\gamma \gamma / (\Gamma \mu_2)) \). Whether or not the terms of \( O(r\gamma) \) or those of \( O(r\gamma \gamma / (\Gamma \mu_2)) \), with \( n = 1, 2, \ldots \) are the most important depends on the value of VFTH exponent \( \gamma \): if \( \gamma > 1 \), \( O(r\gamma \gamma / (\Gamma \mu_2)) \ll O(r\gamma) \), for large times; they are of the same order at \( \gamma = 1 \), while if \( 1/2 < \gamma < 1 \), \( O(r\gamma \gamma / (\Gamma \mu_2)) \gg O(r\gamma) \). Furthermore if \( \gamma \leq 1/2 \) also terms of order \( O(r\gamma \gamma / (\Gamma^2 \mu_2)) \) will be more important or as important as those of \( O(r\gamma) \). For yet smaller values of \( \gamma \) and more terms of the kind \( r\gamma \gamma / (\Gamma^2 \mu_2) \) will be much greater than \( O(r\gamma) \) in the aging regime.

As \( t \to \infty \) the solutions (5.33)-(5.42) coincides with the elements of the matrix (2.24), the inverse of the Hessian of the free energy of the model, i.e., they coincide with the average squared fluctuations at equilibrium.

Once we have the equal time solutions we can solve the equations (5.25) for the two times functions.

The function \( \tilde{f} \) is now:

\[ \tilde{f} = f_1 + \frac{2m_1 g_1}{g_2 - 2m_1 g_1} - g_1 \frac{f_2 - 2m_1 f_1}{g_2 - 2m_1 g_1} = \]

\[ = -4\gamma (1 + 1/QD + P) \left( 1 + P \right) - 4\gamma \frac{L^2}{\mu_2} \gamma (m_0 + \mu_2) \frac{QDP}{(1 + P)^2} + O\left( \frac{\gamma r}{\mu_2} \right) \] (5.48)
The decoupled equations for $C_{11}(t,t')$ and $C_{12}(t,t')$ that we get are always the (5.25). From them we can compute $C_{21}(t,t')$ and $C_{22}(t,t')$ as follows:

$$C_{21}(t,t') \simeq 2m_1(t) - P(t)L/J \frac{C_{11}(t,t')}{1 + P}$$

$$C_{22}(t,t') \simeq \frac{2m_1(t)^2 + 2P(t)L^2/J^2 + m_0 + \mu_2(t)}{m_1(t) - P(t)L/J} C_{12}(t,t')$$

Using the time evolution function $\tilde{h}$ for the considered time-scale sector as

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

the solution of (5.28) comes out to be

$$C_{1b}(t,t') = C_{1b}(t',t') \tilde{h}(t') \frac{\delta h(t')}{\delta h(t)} + O(\mu_1 Y)$$

In the leading terms of our expansion in $\delta \mu_2(t)$ and $\overline{\mu}_2$ the expressions for the $f$’s and $g$’s are given, for the case $T > T_0$ by (A.13)-(A.16).

Using (5.39), (5.40) and (5.48), we get

$$C_{11}(t,t') \simeq \frac{1 + P_\infty}{1 + Q_\infty D + P_\infty} [m_0 + \overline{\mu}_2 + O(\delta \mu_2(t))] \exp \left\{ -4 \int_{t'}^t \Gamma(t'')/(\Gamma(t'') - 1) \frac{1 + Q(t'')D + P(t'')}{1 + P(t'')} dt'' \right\}$$

$$C_{12}(t,t') \simeq \frac{2P_\infty L/J - \overline{\mu}_1}{1 + Q_\infty D + P_\infty} [m_0 + \overline{\mu}_2 + O(\delta \mu_2(t))] \exp \left\{ -4 \int_{t'}^t \Gamma(t'')/(\Gamma(t'') - 1) \frac{1 + Q(t'')D + P(t'')}{1 + P(t'')} dt'' \right\}$$

2. Low temperature case: $T < T_0$

Our approach allows also to study the regime below below the Kauzmann temperature $T_0$. In this last case, though, we have qualitatively different behaviours depending on the value of $\gamma$, i.e. on the relative weight of $\mu_1$ and $\mu_2$. We describe here the case $\gamma > 1$, where $\mu_1 \ll \mu_2$ (see (3.31)). For $\gamma > 1$, according to the results shown in section 4, it is, indeed, not necessary to introduce any effective thermodynamic parameter other than the effective temperature, and the analysis can be carried out in a way similar to the one of the previous case. In expanding the time dependent coefficients of $C_{ab}$ in the equations of motion (f1,2 and g1,2 given in equations (A.13)-(A.16)) we have now to take into account that $r$ never vanishes, while on the contrary the asymptotic value of $\mu_2(t)$, denoted by $\overline{\mu}_2$, is zero. The leading terms in the $f_k$ and $g_k$ ($k = 0, 1, 2, 3$) are in this case those of $O(Y \Gamma / \mu_2)$. The sub-leading terms are those of order $\Gamma \overline{\mu}_2 \gamma$ (coming always with $r$ as a multiplicative factor) and those of order $\Gamma$. All these terms are diverging terms, in the limit $t \to \infty$, and hence terms of $O(1)$ are now negligible with respect to them. They would lead to corrections to the FDR of order $1/\Gamma \ll \mu_2$.

The equations of motions for the equal time correlation functions are identical to the (5.17)-(5.21). What change are the time dependent coefficients $f_{1,2}$ and $g_{1,2}$ and $r = r_\infty + O(\delta \mu_2(t))$, where $r_\infty$ is defined in (3.36).

Solutions to these equations are obtained, as before, in the adiabatic approximation and expanding all the functions in powers of $\delta \mu_2(t)$ and $\overline{\mu}_2$:

$$C_{ab}(t) = [2m_1(t)]^{a+b-2} \left\{ \frac{1}{1 + Q_\infty D} \left[ m_0 + \mu_2(t) \left( 1 - \frac{m_0 Q_1 D}{1 + Q_\infty D} \right) \right] \right\} + O(\mu_2^2(t))$$

$$Q_1 \equiv \frac{Q_\infty}{(1 + Q_\infty D)m_0} \left[ \frac{J^2 m_0 (3w_\infty + T/2)}{2w_\infty (w_\infty + T/2)} - 3P_\infty \right]$$

(5.56)
\[\alpha_1 \equiv 1 + 3DQ(1 - 2P) + (DQ)^2(3 - 4P) + (DQ)^3,\]  
(5.57)

\[\alpha_2 \equiv 4(1 + DQ)[\tilde{K}LQ(1 + P) - DQ(1 - P)],\]  
(5.58)

\[\alpha_3 \equiv \frac{Jm_1}{K}Q(1 + DQ - m_0)(1 + \tilde{K}LQ)(5 - 12r + 12r^2).\]  
(5.59)

In the asymptotic limit this solutions do not coincide with \(\Delta^2\). That means that they are also different from the static limit of the correlation functions found in section 2 from the inverse of the Hessian matrix \([\tilde{2.26}]\). This is due to the fact that the static does not take into account the constraint \([\tilde{2.4}]\) on the configuration space. Above the Kauzmann temperature the dynamics never reaches this constraint so that, even if it is slowed down by its existence, it brings to the same static results. But as soon as we perform the dynamics at \(T > T_0\) or below it, the asymptotic regime will never coincide with the equilibrium one. The system will be stucked forever in one ergodic basin. But as soon as we perform the dynamics at \(T_0\) or below it, the asymptotic regime will never coincide with the equilibrium one. The system will be stucked forever in one ergodic basin.

We find the solutions of the equations \([\tilde{5.25}]\) for the two-time correlation functions following exactly the approach shown in the preceding section, with the following expressions for the functions \(\dot{m}_1\) and \(\dot{f}\):

\[\dot{m}_1 = 4\Gamma_1 T + O(\mu_2 T),\]  
(5.60)

\[\dot{f} = -4\Gamma(1 + QD) - 8\gamma QDP(1 - 3r + 2r^2) + O(\mu_2 T)\]  
(5.61)

The two-time correlation functions come out to be:

\[C_{1b}(t, t') \simeq \frac{[2m_1(t')D]^{b-1}}{1 + Q_\infty D} \left[m_0 + \mu_2(t') \left(1 - \frac{m_0Q_1D}{1 + Q_\infty D}\right) + O(\mu_1(t'))\right] \times\]
\[\times \left\{ \left[1 + Q(t')D\right] \Upsilon(t'')\Gamma(t'')dt'' \right\}, \quad b = 1, 2.\]  
(5.62)

\[C_{2b}(t, t') \simeq 2[m_1(t)D]^{b-1}C_{1b}(t, t') \quad b = 1, 2.\]  
(5.63)

For what concerns the response functions, from \([\tilde{5.33}]\) to \([\tilde{5.35}]\) we get

\[G_{11}(t, t^+) = \frac{4\Gamma_1 T}{K} - \frac{2\Upsilon(1 - 2r)^2}{K} + \frac{8\Upsilon(\Gamma_\mu)^2}{T_e},\]  
(5.64)

\[G_{12}(t, t^+) = \frac{8m_1\Upsilon}{K} - \frac{4m_1\Upsilon(1 - 2r)^2}{K} + \frac{16m_1\Upsilon(\Gamma_\mu)^2}{T_e} + \frac{16r\Gamma_\mu\Upsilon}{K},\]  
(5.65)

\[G_{22}(t, t^+) = \frac{16m_1^2\Upsilon}{K} - \frac{8m_1^2\Upsilon(1 - 2r)^2}{K} + \frac{32m_1^2\Upsilon(\Gamma_\mu)^2}{T_e} + \frac{64m_1r\Gamma_\mu\Upsilon}{K} + \frac{8m_0(1 - 2r)^2\Upsilon}{K}\]  
(5.66)

where this time the contributions \(\Gamma_\mu\) and \((\Gamma_\mu)^2\) are both of order \(\Upsilon\) and we take them into account.

The two-time behaviour of the response functions is as in \([\tilde{5.33}]\) with \(\dot{f}\) given by \([\tilde{5.61}]\).

The last thing that we need, before computing the \(T_e^{FP}\), is the derivative

\[\partial_{t'} C_{11}(t, t') = \frac{\dot{h}(t')}{h(t)} \partial_{t'} C_{11}(t, t') - \dot{f}(t') \frac{\dot{h}(t')}{h(t)} C_{11}(t, t') \simeq\]
\[\simeq 4\Upsilon(t') \frac{1}{1 + Q_\infty D} \left[m_0 + \mu_2(t') \left(1 - \frac{m_0Q_1D}{1 + Q_\infty D}\right)\right] \left[1 + Q(t')D\right] \Upsilon(t'')\Gamma(t'')dt'' \times\]
\[\times \exp\left\{ 4 \int_{t'}^{t} \left[1 + Q(t)D\right] \Upsilon(t'')\Gamma(t'')dt'' \right\}\]  
(5.67)

It follows
\[ T_{e}^{FD}(t,t') \simeq T_{e}(t') \left[ 1 + \mathcal{O}\left(\frac{1}{T}\right) + \mathcal{O}(\mu^{1+\gamma}_{2}) \right] = T_{e}^{FD}(t'). \] (5.68)

In this case \( \mathcal{O}(1/T) = \mathcal{O}(\mu_{1}) \) is always smaller than \( \mathcal{O}(\mu_{2}) \) because \( \gamma > 1 \): in the long time regime \( T_{e}^{FD}(t) \) coincides with \( T_{e}(t) \).

3. Effective temperature from the fluctuation formula

A self consistent picture with an effective temperature should also imply that the same effective temperature also governs other physical variables. From the expression of \( m_{1}(t;T) \) as function of \( H \) we can compute the quantity \( \chi^{(fl)} \equiv \frac{\partial m_{1}}{\partial H} \big|_{T,t} \) that is the contribution to susceptibility in a cooling-heating setup to a change in the field \( H \) at fixed time (also called fluctuation susceptibility). In a cooling experiment the whole susceptibility can, indeed, be written as

\[ \chi_{ab} = \frac{\partial m_{a}}{\partial H_{b}} \bigg|_{T,T_{e}} = \frac{\partial m_{a}}{\partial H_{b}} \bigg|_{T,H_{b}} \frac{\partial T_{e}}{\partial H_{b}} \bigg|_{T,T_{e}} \]

\[ = \frac{\partial m_{a}}{\partial H_{b}} \bigg|_{T,T_{e}} - \frac{\partial m_{a}}{\partial T_{e}} \bigg|_{T,H_{b}} \frac{\partial T_{e}}{\partial H_{b}} \bigg|_{T,T_{e}} \]

\[ = \chi^{\text{fluct}}_{ab}(t) + \chi^{\text{loss}}_{ab}(t) + \chi^{\text{conf}}_{ab}(t) \]

Here we are considering an aging situation, so only the first term is relevant. We can reasonably assume that the \( \chi^{\text{fluct}}_{ab}(t) \) can take the form

\[ \chi^{\text{fluct}}_{ab}(t) = \frac{\partial m_{a}}{\partial H_{b}} \bigg|_{T,T_{e}} = N \frac{\langle \delta m_{a}(t) \delta m_{b}(t) \rangle_{\text{fast}}}{T} + N \frac{\langle \delta m_{a}(t) \delta m_{b}(t) \rangle_{\text{slow}}}{T_{e}^{(fl)}(t)} \] (5.72)

where \( \langle \ldots \rangle_{\text{fast/slow}} \) is the average, respectively, over fast and slow processes. The fast ones being governed by the heat-bath temperature, the slow ones by some effective temperature \( T_{e}^{(fl)} \) depending on the time scale \( t \). Through \( \chi^{\text{fluct}}_{ab}(t) \) one can look at the connection between the fluctuation effective temperature \( T_{e}^{(fl)} \), introduced in \([2]\), and the other effective temperatures so far defined. To work it out we start from:

\[ \chi^{\text{fluct}}_{11}(t) \equiv \frac{\partial m_{1}}{\partial H} \bigg|_{T,t,t} = N \frac{\langle \delta m_{1}(t) \delta m_{1}(t) \rangle_{T_{e}^{(fl)}}}{T_{e}^{(fl)}} = C_{11}(t,t) \]

(5.73)

Using the following expression of \( m_{1} \) got from \([3.13]\):

\[ m_{1}(t;T,H) = -\frac{L}{J} + \frac{D}{JK (m_{1}(t;T,H),m_{2}(t;T,H);T)} \],

(5.74)

the fluctuation susceptibility \( \chi^{(fl)}_{11} \) turns out to be:

\[ \frac{\partial m_{1}}{\partial H} \bigg|_{T,t} = \frac{1}{K(1 + QD)} + \mathcal{O}(\mu_{1}) \].

(5.75)

Here we are neglecting terms like \( \partial \mu_{1}/\partial H \) and \( \partial \mu_{2}/\partial H \), of order \( \mu_{1} \) or higher (we deal with the regimes \( T > T_{0}, \forall \gamma \) and \( T < T_{0}, \gamma > 1 \) where \( \mu_{1} \ll \mu_{2} \)). Taking the expressions (5.22) and (5.53) we see that in both dynamic regimes that we are considering the leading term of \( C_{11} \) can be written as

\[ C_{11}(t,t) = \frac{m_{0} + \mu_{2}}{1 + QD} + \mathcal{O}(\mu_{2}) \]

(5.76)

and this leads to

\[ T_{e}^{(fl)} = \tilde{K}(m_{0} + \mu_{2}) + \mathcal{O}(\mu_{2}) \]

(5.77)

thus coinciding with (1.3) to the order of our interest, i.e. \( \mathcal{O}(\mu_{2}) \). At higher orders there will be non-universality. If \( \gamma \leq 1 \) the terms of \( \mathcal{O}(\mu_{2}) \) become dominant with respect to \( \mathcal{O}(\mu_{2}) \), leading to the same situation that we had for \( T_{e}^{FD} \) in (5.38), namely the thermodynamic description does not lead to a unique effective parameter.
In this paper we consider a model that owns all the basic properties of a fragile glass, built by processes evolving on two well separated time scales, representing the $\alpha$ and $\beta$ processes taking place in real glassy materials.

Also, the model is provided with a constraint applied to the harmonic oscillators dynamics, i.e. to the slow processes dynamics, in order to reproduce the behaviour of a good glass former.

Introducing a particular Monte Carlo dynamics and developing it analytically, thus having the opportunity of probing it in more detail with respect to a numeric study, we found equations of motion that are in all respect those typical of glass relaxation.

By means of the constrained dynamics we defined the Kauzmann temperature $T_0$ as the one at which the constraint is reached, asymptotically, for the first time in a cooling experiment from high temperature. There we showed how the real thermodynamic phase transition, taking place due to the breaking of the ergodicity in the landscape of our model, rich of degenerate minima, is characterized.

A detailed study of the dynamics was performed both above and below the Kauzmann temperature and for arbitrary values of the exponent $\gamma$ generalizing the typical VFTH behaviour, usually assumed for glasses, to $\tau_{eq} = \exp[A/(T - T_0)]$. The dynamics in the aging regime of both one time and two-time variables has been carefully analyzed, including the corrections to this regime, relevant at shorter times.

The decoupling of time scales is fundamental for a generalization of equilibrium thermodynamics to systems far from equilibrium. We tested on our exactly solvable model whether or not the generalized approach holds, involving one extra variable, namely the effective temperature, in 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 visiting with the same frequency the same states that the real - out of equilibrium - system at temperature $T$ is visiting on a given time-scale 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. In our work it has been first derived as the function of time (for given values of the heat bath temperature and of all the other parameters of the model) such that the evolving system out of equilibrium can be characterized by a probability measure of the configurations having a Boltzmann-Gibbs form with a factor $1/T$ instead of $1/T$ in front of the Hamiltonian.

Generally speaking, in order to recast the out of equilibrium dynamics, the history of a system that is far from equilibrium can be expressed by more than one effective parameter. This happens when more than one time-scale are involved in the dynamic evolution of a system. In those cases to every time-sector will correspond an effective temperature. Moreover the number of effective parameters needed to make such a translation into a thermodynamic view can, in principle, be equal to the number of relevant observables considered in every time sector. For certain dynamic regimes, determined by the temperature and by the VFTH exponent $\gamma$, however, the effective parameters pertaining to processes having the same time scale become equal to each other in time, for large times.

As we saw in section 3 in the dynamic regimes reported in section 4, when the variation $\mu_1(t)$ with respect to equilibrium of the variable $m_1$ is much greater than the distance from the constraint, $\mu_2(t)$, the effective temperature alone is enough for a complete thermodynamic description of the dominant physical phenomena (the effective field $H_e = H$), while in the regimes where $\mu_1(t)$ is no more negligible with respect to $\mu_2(t)$, the effective field $H_e(t)$ is also needed to map the dynamics on long time scales into a thermodynamic frame.

From the time behaviour of the slow varying observables in the aging regime we found in section 5 a VFTH relaxation time dependence on temperature above the Kauzmann transition and we derived the Adam-Gibbs relation between the relaxation time and the configurational entropy, that we can explicitly compute for our model.

We have been also able to study the dynamics of the system quenched to a temperature below the Kauzmann temperature. At long, finite time $t$ we see that it is possible to introduce an instantaneous relaxation time depending on the heat bath temperature in a non-trivial way but expressible in terms of the effective temperature. What we got in this way is actually a VFTH law where the heat bath temperature has been substituted by a time dependent effective temperature $T_e(t)$ and its asymptotic value $T_e$ takes the place of the Kauzmann temperature $T_0$. Such a relation for the time scale of the aging dynamics below $T_0$ could hold very well in more general systems.

At equilibrium the heat bath temperature enters many relations that can be rigorously proved and connected to each other in the frame of thermodynamics. Out of equilibrium we miss first principles to start with in the generalization of such a construction. We do not have any guaranty, for instance, that a given definition of effective temperature, done generalizing a given equilibrium formula, would match any other definition coming from the generalization of another equilibrium formula. At equilibrium the heat bath temperature enters the Boltzmann-Gibbs measure, the laws of thermodynamics, the fluctuation-dissipation theorem, different Maxwell relations, etc. However, out of equilibrium we have to check whether a single definition of effective temperature is compatible with any other. Since all effective temperatures have definite limits for long times, we should verify that these limits are identical (which happens always)
and that the leading approach to these limits coincide (which happens only for $\gamma > 1$). If that works out we find a way to completely recast the long time domain of the out of equilibrium dynamics into the language of thermodynamics, on a given time sector, of course, well separated from the other time sectors of the glassy dynamics. This behaviour may occur if the aging is so slow that the system has time enough to clearly set out an effective temperature before going to a lower value of it.

With this aim we also rederived the effective temperature from the fluctuation dissipation ratio and from the fluctuation formula connecting the susceptibility with the fluctuations of the slow variables of the system, namely $\sum_i x_i$. In section 4 we showed that the effective temperature $T_e^{FD}$ defined as the fluctuation dissipation ratio tends to the effective temperature $T_c$ that we got by the quasi static approach only if $\mu_2^2$ is negligible with respect to $\mu_2$. However, this is true, if $\gamma$ is greater than one. Otherwise the corrections of order $\mu_2^2$ are no more sub-leading and change significantly the time evolution of $T_e^{FD}$. Already for $\gamma = 1$, $T_e^{FD} \to T_c$ only in the infinite time limit, i. e. for time scales longer than those of the considered aging regime. Even above the Kauzmann temperature the value of the exponent $\gamma$ discriminates between different regimes. For $\gamma > 1$ an out of equilibrium thermodynamics can be built in terms of the single additional effective parameter $T_c$. For $\gamma \leq 1$, $T_c$ alone does not give consistent results in the generalization of the equilibrium properties to the non equilibrium case. In those cases one also needs an effective field $H_c$. However, no universal behaviour for the $T_c, H_c$ combination has been found.

We have seen that in case $\gamma > 1$ for temperatures above the Kauzmann temperature both the statics and the dynamics in the aging range can be described by Vogel-Fulcher-Tammann-Hesse laws, see eqs. (4.21), (4.22). Notice that these laws are not identical, the static one diverging more strongly, due to a larger prefactor of the divergent term in the exponent. We also noticed that in this situation $\gamma > 1$ the aging (well) below the Kauzmann temperature can be described in a form very analogous to the aging above it. For this reason it is meaningful to compare experiments in those two aging regimes, and in particular, to test whether the decay of measurable quantities, like the energy, the volume or the magnetization, has a common temporal law in the full aging regime.

Finally we checked the consistency of the widely mentioned thermodynamic picture by writing the first and second law using the effective temperature and we verified that it can be also computed from the generalization of the Maxwell relation at equilibrium giving the heat bath temperature as derivative of internal energy with respect to the entropy (see (4.12)), finding the same results we got from the other derivations in the same validity limits. However, we also found that, even within the solvable model of this paper, the applicability of the thermodynamic picture may or may not be valid, depending on the question how fast the relaxation time diverges.

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APPENDIX: MONTE CARLO INTEGRALS

Here we present the expressions of the integrals that we use in computing the dynamics of the observables following the Monte Carlo method explained in section 3. We recall that $x$, defined in 3.2, is the energy difference between the current configuration of the system and the one proposed for the updating. The variable $r$ (defined in 1.20) is instead the distance of the effective temperature $T_e$ from the heat-bath temperature (that is also the equilibrium value of $T_e$ in the dynamic regime above the Kauzmann temperature). First we define the abbreviation:

$$\Upsilon \equiv \frac{e^{-\Gamma (1-r)}}{\sqrt{\pi \Gamma}}, \quad (A.1)$$

that is the leading term of the acceptance ratio of the Monte Carlo dynamics given by:

$$\int dx W(\beta x) p(x|m_1,m_2) = \Upsilon \left( 1 - \frac{1 - 2r + 4r^2}{\Gamma} + \frac{3}{4\Gamma^2} \left( 1 - 4r + 16r^2 - 24r^3 + 16r^4 \right) + \mathcal{O}\left( \frac{1}{\Gamma^3} \right) \right). \quad (A.2)$$

Then we give the behaviour of the derivative with respect to time of the energy

$$\int dx W(\beta x) W(x|m_1,m_2) = -4r T_e \Upsilon \left( 1 - \frac{3(1 - 2r + 2r^2)}{\Gamma} + \frac{15}{4\Gamma^2} \left( 3 - 12r + 28r^2 - 32r^3 + 16r^4 \right) + \mathcal{O}\left( \frac{1}{\Gamma^3} \right) \right). \quad (A.3)$$
and of the variable $m_1$ (defined in \cite{2.3})

$$
\int dx W(\beta x) \mathcal{F}_1(x) p(x|m_1, m_2) = 4\mu_1 \Upsilon \left( \Gamma - (1 - 3r + 4r^2) + \mathcal{O} \left( \frac{1}{\Gamma} \right) \right). \tag{A.4}
$$

In section \cite{3} we compute the correlation and the response functions. In order to find their time dependence we need the following derivatives. In these formulae we show the derivatives with respect to $m_1$ and $m_2$, taken as independent variables, of the effective temperature $T_e$, the variable $r$ and the leading term of the Monte Carlo acceptance ratio $\Upsilon$. They are:

$$
\frac{\partial T_e}{\partial m_1} = 2K \left( P \frac{L}{J} - m_1 \right), \quad \tag{A.5}
$$

$$
\frac{\partial T_e}{\partial m_2} = K (P + 1); \quad \tag{A.6}
$$

$$
\frac{\partial r}{\partial m_1} = 2 \frac{1 - 3r + 2r^2}{m_0 + \mu_2} \left( P \frac{L}{J} - m_1 \right), \quad \tag{A.7}
$$

$$
\frac{\partial r}{\partial m_2} = \frac{1 - 3r + 2r^2}{m_0 + \mu_2} (P + 1); \quad \tag{A.8}
$$

and

$$
\frac{\partial \Upsilon}{\partial m_1} = - \Upsilon \left[ \frac{m_1 \gamma}{\mu_2} (2\Gamma + 1) + 2 \frac{1 - 2r}{m_0 + \mu_2} \left( P \frac{L}{J} - m_1 \right) \right], \quad \tag{A.9}
$$

$$
\frac{\partial \Upsilon}{\partial m_2} = \Upsilon \left[ \frac{\gamma}{2\mu_2} (2\Gamma + 1) - \frac{1 - 2r}{m_0 + \mu_2} (P + 1) \right]. \quad \tag{A.10}
$$

Furthermore, we show the extensive computation of the coefficients of equations \cite{5.15, 5.21} and \cite{5.25} for the dynamics of the two-time observables:

$$
f_0 \equiv \partial_{m_1} \int dx W(\beta x) p(x|m_1, m_2) \simeq -m_1 \gamma \frac{\Upsilon}{\mu_2} \left[ 2\Gamma - 1 + 4r - 8r^2 \right] + O \left( \frac{1}{\Gamma^2} \right) \tag{A.11}
$$

$$
+ O \left( \frac{\Upsilon}{\mu_2^2 \Gamma^2} \right) - 2 \frac{\Upsilon}{m_0 + \mu_2} \left( P \frac{L}{J} - m_1 \right) \left[ 1 - 2r + \frac{3 - 20r + 40r^2 - 32r^3}{\Gamma} \right] + O \left( \frac{\Upsilon}{\Gamma^2} \right).
$$

$$
g_0 \equiv \partial_{m_2} \int dx W(\beta x) p(x|m_1, m_2) \simeq \gamma \frac{\Upsilon}{2\mu_2} \left[ 2\Gamma - 1 + 4r - 8r^2 \right] + O \left( \frac{1}{\Gamma^2} \right) \tag{A.12}
$$

$$
+ O \left( \frac{\Upsilon}{\mu_2^2 \Gamma^2} \right) - \Upsilon \frac{1}{m_0 + \mu_2} (P + 1) \left[ 1 - 2r + \frac{3 - 20r + 40r^2 - 32r^3}{\Gamma} \right] + O \left( \frac{\Upsilon}{\Gamma^2} \right).
$$

$$
f_1 \equiv \partial_{m_1} \int dx W(\beta x) \mathcal{F}_1(x) p(x|m_1, m_2) \simeq -4m_1 \gamma \Upsilon \frac{\Gamma \mu_1}{\mu_2} \left[ 2\Gamma - 3 + 6r - 8r^2 \right] + O \left( \frac{\Upsilon \mu_1}{\mu_2} \right) \tag{A.13}
$$

$$
- 16 \Upsilon \frac{\Gamma \mu_1}{m_0 + \mu_2} \left( \frac{L}{J} P - m_1 \right) + 4 \Upsilon \partial_{m_1} \mu_1 \left( \Gamma - 1 + 3r - 4r^2 \right) + O(\mu_2 \Upsilon),
$$

$$
g_1 \equiv \partial_{m_2} \int dx W(\beta x) \mathcal{F}_1(x) p(x|m_1, m_2) \simeq 2\gamma \Upsilon \frac{\Gamma \mu_1}{\mu_2} \left[ 2\Gamma - 3 + 6r - 8r^2 \right] + O \left( \frac{\Upsilon \mu_1}{\mu_2} \right) \tag{A.14}
$$

$$
- 8 \Upsilon \frac{\Gamma \mu_1}{m_0 + \mu_2} (P + 1) + 4 \Upsilon \partial_{m_2} \mu_1 \left( \Gamma - 1 + 3r - 4r^2 \right) + O(\mu_2 \Upsilon),
$$

$$
f_2 \equiv \partial_{m_1} \int dx W(\beta x) \mathcal{F}_2(x) p(x|m_1, m_2) \simeq 2m_1 f_1 + \frac{2}{K} f_3 + 16 \Upsilon \frac{L}{J + QD} P \tag{A.15}
$$

$$
+ 16 \Upsilon \frac{L}{J + QD} \Gamma \mu_1 \mu_2 \left( \frac{L}{J} P - m_1 \right) + O(\mu_1 \Upsilon),
$$

$$
g_2 \equiv \partial_{m_2} \int dx W(\beta x) \mathcal{F}_2(x) p(x|m_1, m_2) \simeq 2m_1 g_1 + \frac{2}{K} g_3 + 8 \Upsilon \frac{P}{1 + QD} + O(\mu_1 \Upsilon), \tag{A.16}
$$

$$
f_3 \equiv \partial_{m_2} \int dx W(\beta x) p(x|m_1, m_2) \simeq 4m_1 \gamma \Upsilon T_e \frac{r}{\mu_2} \left[ 2\Gamma - 5 + 12r - 12r^2 - \frac{3}{\Gamma} (3 + 9r - 54r^2 + 140r^3 - 160r^4 + 80r^5) \right] \tag{A.17}
$$

$$
+ O \left( \frac{\Upsilon r}{\mu_2^2 \Gamma^2} \right) - 8 \Upsilon \frac{L}{J} P - m_1 \left[ 1 - 3r + 4r^2 \right] + O \left( \frac{\Upsilon}{\Gamma^2} \right),
$$

27
\[ g_3 \equiv \partial_{m_2} \int dx W(\beta x) x p(x|m_1, m_2) \simeq -2\gamma \Upsilon T e^r_{\mu_2} \left[ 2\Gamma - 5 + 12r - 12r^2 - \frac{3}{\Gamma} (3 + 9r - 54r^2 + 140r^3 - 160r^4 + 80r^5) \right] \quad (A.18) \]
\[ + \mathcal{O} \left( \frac{\Upsilon r}{\mu_2} \right) - 4\Upsilon \tilde{K} (P + 1) \left[ 1 - 3r + 2r^2 - \frac{3}{\Gamma} (1 - 5r + 12r^2 - 14r^3 + 8r^4) \right] + \mathcal{O} \left( \frac{\Upsilon}{T^2} \right) \quad (A.19) \]

All partial derivatives with respect to \( m_1 \) have been computed keeping \( m_2 \) fixed and vice-versa. At this stage time has not yet been introduced. Introducing it we are able to make an expansion of (A.11)-(A.18) in powers of \( \mu_2(t) \). In the formula we already performed such an expansion, breaking it at \( \mathcal{O}(\Upsilon/(\Gamma \mu_2)) \) that is more than sufficiently refined to derive the dynamics of the correlation and response functions in all the regimes of our interest.

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