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How glasses explore configuration space

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Abstract

We review a statistical picture of the glassy state derived from the analysis of the off-equilibrium fluctuation-dissipation relations. We define an ultralong-time limit where 'one-time quantities' are close to equilibrium while the response and correlation can still display ageing.

In this limit it is possible to relate the fluctuation response relation to static breaking of ergodicity. The resulting picture suggests that even far from that limit, the fluctuation-dissipation ratio relates to the rate of growth of the configurational entropy with the free-energy density.

1. Introduction

Glassy systems spend long periods of time out of equilibrium, i.e. in regions of configuration space which have vanishing Boltzmann probability. The evolution towards more and more optimized regions of phase space is so slow that the fast degrees of freedom react on short timescales as if they were in equilibrium against the frozen background of the slow variables. On longer timescales, however, the off-equilibrium nature of the glassy phase shows up in the phenomenon of ageing: the responses to small perturbations, as well as the correlation functions, depend on the 'age' of the glass, i.e. the time spent in the low-temperature phase [1, 2]. The dynamics becomes slower and slower as the age becomes greater; nevertheless, even on the largest scales observed, there is no tendency to stop: the system eventually wanders away from any finite region of phase space.

In the last few years, following some developments in spin-glass mean-field theory [3–5], many theoretical [6], numerical [7] and more recently experimental papers [8–10] have focused on the study of off-equilibrium fluctuation-dissipation relations. In [11], it has been shown that the fluctuation-dissipation relation found in mean-field analysis of glassy relaxation can be used to define effective temperatures, higher than that of the heat bath governing the heat exchanges between slow degrees of freedom.

The analysis of the fluctuation-dissipation relation has revealed deep relationships between ageing dynamics and the nature of the free-energy landscape [12]. In this paper we would like to review a picture of glassy dynamics based on the analysis of these relations [13].

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Two kinds of glassy system emerge from experimental and theoretical analysis. One can identify two kinds of glassy behaviour:

- A first class, for which spin glasses provide an example, where the asymptotic values of extensive quantities, such as internal energy and magnetization, seem not to depend on the cooling rate or other differences in cooling procedure.
- A second class, that of structural glasses, in which the apparent asymptotic values of these quantities depend strongly on the cooling rate, and remain strongly different from the equilibrium values for the largest timescales which can be probed.

Ageing phenomena are common to both families. During ageing the linear response to external perturbations displays age-dependent behaviour and anomalies with respect to equilibrium, which is in conformation with the fluctuation-dissipation theorem. Many efforts have been devoted to relating these anomalies to the properties of the underlying energy or free-energy landscapes [12–17].

A first step towards the comprehension of this relationship can be achieved by idealizing the first situation, assuming that for long times *all* extensive 'one-time observables' (1TO), or more precisely the ones that can be written as sums of local quantities, are close to equilibrium. We call this situation the *ultralong-time limit* and observe that in principle:

(a) this limit does not imply the absence of ageing in two time observables such as responses and correlation functions;
(b) usual nucleation arguments imply that in systems with regular short-range interactions this limit is achieved in a finite, i.e. volume-independent, time.

Of course this last observation remains a matter of principle in structural glasses, where this equilibration time is exceedingly long, and one needs to understand dynamics on much shorter timescale.

For notational simplicity, in the theory that we are going to expose, we will use the language of magnetic systems. Our considerations, however, will very general and can be immediately applied, e.g. to glass-forming systems of classical particles in interaction. In order to illustrate the ideas, we discuss a spin-glass system where the spins S_x interact through a Hamiltonian

$$H(\boldsymbol{S}) = -\sum_{x<y} J_{x,y} S_x S_y \tag{1}$$

on the D-dimensional square lattice with short-range interactions $J_{x,y}$. The spins will be, for simplicity, assumed to be Ising variables $S_x = \pm 1$. We will consider the dynamical setting of a fast quench from high to low temperature at an instant marking the origin of the time axes.

2. Ageing in the ultralong-time limit

The classical ageing experiments concentrate on the study of the response of the system to an external perturbation in the linear regime. Consider the effect of an external magnetic field h, corresponding to a perturbation term in the Hamiltonian $H^{(1)}(\boldsymbol{S}) = -h\sum_x S_x$, acting from the quenching time 0 to a waiting time t_w. At linear order in h, the magnetization $M(t, t_w) = \frac{1}{N}\sum_x \langle S_x(t)\rangle_h$ at later times t can be written as $M(t, t_w) = h\chi(t, t_w)$, where, introducing the instantaneous response $R(t, s) = \frac{\delta\langle M(t)\rangle}{\delta h(s)}$, the susceptibility can be written as $\chi(t, t_w) = \int_0^{t_w} \mathrm{d}s\, R(t, s)$. This is a quantity usually measured in ageing experiments and exhibits scaling, non-time-translation-invariant behaviour. In usual equilibrium regimes, this function is related to the correlation function $C(t, t_w) = \frac{1}{N}\sum_{x,y}\langle S_x(t)S_y(t_w)\rangle$ by the

fluctuation-dissipation relation $\chi(t - t_w) = \beta C(t - t_w)$. Off-equilibrium, the same relation has in general no reason to be valid. One usually defines the fluctuation-dissipation ratio (FDR)

$$\beta\tilde{x}(t, t_w) = \frac{\partial\chi(t, t_w)/\partial t_w}{\partial C(t, t_w)/\partial t_w} \tag{2}$$

or $x(t, C)$ defined by the relation $x(t, C(t, t_w)) = \tilde{x}(t, t_w)$. In equilibrium conditions the FDR is equal to unity and $\chi(t, t_w) = \beta C(t - t_w)$. Spin-glass mean-field theory [3–5] has suggested that in ageing systems $x(t, C)$ tends to a non-trivial limit $x(C)$, taking the limit $t, s \to \infty$ for fixed values of $C(t, s)$. In these systems the FDR appears to have some universal character. It is independent of the particular response/correlation function probed. The function $x(C)$ appears to have mathematically the properties of a probability function. The ratio $T/x(C)$ can be considered an effective temperature governing heat exchanges with degrees of freedom reacting on the timescales specified by the value of the correlation [11]. Such non-generic behaviour can be understood in the ultralong-time limit, resulting in a rather detailed statistical description on how glassy systems visit configurational space in ageing dynamics. In the limit in which the FDR becomes time independent, 1TO (e.g. energy and magnetization) become asymptotically close to their final value. We will call this limit the 'ultralong-time limit' in reference to the fact that structural glasses are always observed on much shorter timescales. Let us stress that in short-range systems with regular interactions the asymptotic values of the 1TO must be the equilibrium one. The ultralong-time limit could be appropriate in spin glasses, where the values of 1TO seem not to depend on the cooling procedure, but it is certainly not an appropriate description for structural glasses, where the 1TO are strongly out of equilibrium. In this context we can still think of this limit as a useful conceptualization for studying ageing in a simplified situation and getting hints as to the statistical principles that govern glassy dynamics even far from this ideal situation.

3. Equilibrium ergodicity breaking

We would like to discuss how a non-trivial FDR in the ultralong-time limit relates to the phenomenon of ergodicity breaking in the equilibrium distribution. Breaking of ergodicity, or absence of ergodicity at equilibrium, means that the weight of the equilibrium distribution is concentrated on more than one disjoint phase space region (these are called ergodic components), in which the ergodic property holds separately. If the system is prepared in one of these regions, it will never get out from it. A familiar example is provided by systems in the presence of a first-order phase transition, where different phases are equally dynamically stable. In that case, a suitable 'external field' can be used to project on the different phases. The situation that we would like to describe, that of an ideal glass, can be expected to be different. In disordered systems, the possible different ergodic components dominating at low temperature can be expected to be as disordered as the configurations of the high-temperature phase and no external field is available to select any of them. A suitable description of that situation has been provided by spin-glass mean-field theory [18] where ergodicity breaking is characterized statistically through the comparison of the different ergodic components. One first defines a measure of similarity among configurations, and then studies its statistical distribution induced by the canonical measure and the eventual quenched disorder. For spin glasses it is natural to define the overlap between two spin configurations $\boldsymbol{S} = (S_1, \ldots, S_N)$ and $\boldsymbol{S}' = (S'_1, \ldots, S'_N)$ as the normalized scalar product:

$$q(\boldsymbol{S}, \boldsymbol{S}') = \frac{1}{N}\sum_i S_i S'_i. \tag{3}$$

The overlap probability function (OPF) is defined as

$$P(q) = \overline{\frac{1}{Z^2}\sum_{\boldsymbol{S},\boldsymbol{S}'} \exp(-\beta(H(\boldsymbol{S}) + H(\boldsymbol{S}')))\delta(q - q(\boldsymbol{S}, \boldsymbol{S}'))} \tag{4}$$

where the overline denotes the average over the quenched variables of the system (if any). If ergodicity holds, the OPF is equal to a single delta function. Any difference from this simple form is a sign of ergodicity breaking. Conversely, a single delta function is not necessarily associated with ergodicity. The different components $\alpha = 1, 2, 3, \ldots$ appear in the equilibrium distribution, each with a probability weight w_α reflecting its free-energy difference from the lowest state. It turns out that the OPF can be non-trivial only if the participation ratio $\sum_\alpha w_\alpha^2$ is non-vanishing in the thermodynamic limit. This excludes e.g. the case of an extensive number of ergodic components where $w_\alpha \sim \exp(-N\Sigma)$.

Despite its origin in the context of spin glasses, the concept of overlap, and the corresponding probability function, can be suitably applied in more general glassy systems. A possible definition in the case of structural glasses and some applications are discussed in [19, 20].

4. How ageing relates to equilibrium

Linear response theory allows one to relate the OPF of the canonical probability and the FDR according to the relation [12]

$$P(q) = \frac{\mathrm{d}x(q)}{\mathrm{d}q}. \tag{5}$$

The argument that leads to (5) is rather formal, and consists in finding a family of observables, expressed as sums of local quantities, whose average values relate in equilibrium and in dynamics respectively to the moments of the OPF and the derivative of the FDR with respect to the correlation. As the dynamical averages should tend to the equilibrium ones, one deduces the identity between the OPF and the derivative of the FDR. The argument runs as follows. Let us consider a set of operators which translate the lattice along a direction $\hat{\imath}$ parallel to one of the coordinate axes:

$$\mathcal{T}_k^{(p)}(x) = x + \frac{kL}{p}\hat{\imath}; \qquad k = 1, \ldots, p-1. \tag{6}$$

We denote by $\mathcal{S}_1$ the set in which the coordinate in the direction $\hat{\imath}$ takes the values $1, 2, \ldots, L/p$. We define our family of perturbations to have the form

$$H_p(\boldsymbol{S}) = \sum_{x\in\mathcal{S}_1} J_x^{(p)} S_x S_{\mathcal{T}_1^{(p)}(x)} \cdots S_{\mathcal{T}_{p-1}^{(p)}(x)}, \tag{7}$$

where the couplings $J_x^{(p)}$ are independent, identically distributed Gaussian variables, with zero mean and variance $E_J J_x^2 = p$. Despite the apparent long-range character of the interactions, the perturbations H_p can be seen as short-range observables in a folded space, and as such they belong to the class of observables whose long-time-limit values tend, according to our hypothesis, to the equilibrium ones. Let us consider now a system evolving with Hamiltonian $H + hH_p$. These perturbations can be seen as short-range perturbations and one can expect their effect to be described by linear response theory for small h. If we consider the expected values, in off-equilibrium dynamics and at equilibrium of the perturbation H_p, following simple mathematical manipulations implied by linear response theory and by self-averaging properties

with respect to the variables $J_x^{(p)}$, one finds respectively for the dynamic and equilibrium averages

$$\langle H_p(t)\rangle_{dyn} = -\beta h \int_0^1 \mathrm{d}q\; pq^{p-1}x(t,q) \tag{8}$$

$$\langle H_p\rangle_{eq} = -\beta h\left(1 - \int_0^1 \mathrm{d}q\; q^p P(q)\right). \tag{9}$$

In the ultralong-time limit, $\langle H_p(t)\rangle_{dyn} \to \langle H_p\rangle_{eq}$ for all p. Correspondingly, $x(t,q) \to x(q)$ and integrating (8) by parts we find the relation (5). This relation relates the possibility of a persistent non-trivial FDR in the ageing dynamics to ergodicity breaking in the equilibrium measure, and, as we will discuss, can be taken as the starting point for an analysis of how ageing systems visit configuration space. The relation can be generalized to other important features which have been identified theoretically as possible in ageing dynamics. One of these features is ultrametricity which, at equilibrium, implies a hierarchical organization of the ergodic components. In dynamics, this property means that the times $t(C, t_w)$ necessary for the correlation $C(t, t_w)$ to take the value C and defined by the relation $C(t(C, t_w), t_w) = C$ verify for $C_1 < C_2$ the relation $t(C_2, t_w)/t(C_1, t_w) \underset{t_w\to\infty}{\longrightarrow} 0$; in other words, that decreasing values of the correlation correspond to increasingly long relaxation times. Reasoning similar to that leading to (5) allows us to conclude that, surprisingly, in a given system, static ultrametricity and dynamic ultrametricity are either both present or both absent. Recently, the relation (5) has also been generalized to local quantities in [21]. A more complete discussion of the relation (5) should prove the validity of using the linear response in the presence of ergodicity breaking, which involves the commutation of the thermodynamic limit and $h \to 0$ in statics, as well as the long-time limit and $h \to 0$ in dynamics. This property has been called 'stochastic stability', in reference to the fact that the commutation of limits is possible whenever the introduction of weak random perturbations of the kind (7) does not have major effects on the statistical distribution of the states relevant for the equilibrium probability and the long-time off-equilibrium dynamics. On physical grounds, one expects stochastic stability to be valid and linear response theory to have a range of validity in glassy systems. Violation of these properties should result in dynamical crossovers for $t \to \infty$ and $h \to 0$, which are in principle experimentally observable. So if in some systems one could measure the asymptotic value of the FDR, this would provide information on the equilibrium free-energy landscape.

5. Physical picture

The relation (5), which links the off-equilibrium dynamics to the properties of the free-energy landscape relevant at equilibrium, has been discussed in the previous section on a purely formal basis: we have supposed equilibration of 1TO together with validity of long-range theory, and obtained the relation from straight mathematical analysis. The scope of this section is discussion of its physical origin. In order to simplify the discussion, we will consider the simplest model of ageing dynamics with a non-trivial FDR. We will suppose that the dynamics will consist in a short-time equilibrium-like part and a long-time ageing part characterized by a unique age-dependent relaxation time $\tau(t_w)$ which grows and tends to infinity for large t_w. Notice that this is the assumption commonly used to fit ageing response data both in structural glasses [1] and in spin glasses [2]. In this picture the correlation functions can be decomposed into a stationary short-time part and an ageing long-time part as

$$C(t, t_w) = C_{st}(t - t_w) + C_{ag}\left(\frac{t - t_w}{\tau(t_w)}\right). \tag{10}$$

As usual, we define q_{EA} as the value that separates the stationary from the ageing part of the correlation, so $C_{st}(t-t_w) = C^*_{st}(t-t_w) - q_{EA}$ is a monotonically decreasing function equal to $1-q_{EA}$ for $t-t_w = 0$ and tending to zero for $t-t_w \to \infty$, while $C_{ag}\left(\frac{t-t_w}{\tau(t_w)}\right)$ is equal to q_{EA} for $\frac{t-t_w}{\tau(t_w)} = 0$ and tends to 0 for $\frac{t-t_w}{\tau(t_w)} \to \infty$. Correspondingly, we will assume that the FDR will take the value 1 in the stationary domain ($q_{EA} \leqslant C(t,t_w) \leqslant 1$) and the constant value $x < 1$ in the ageing regime $C(t,t_w) \leqslant q_{EA}$, so the linear susceptibility takes the form

$$\chi(t,t_w) = \beta C_{st}(t-t_w) + \beta x C_{ag}\left(\frac{t-t_w}{\tau(t_w)}\right). \tag{11}$$

The relation between correlation and response is often visualized by plotting parametrically $\chi(t,t_w)$ versus $C(t,t_w)$ for fixed t_w. The present case corresponds to having for large t_w two straight lines respectively of slope β for $q_{EA} < C(t,t_w) \leqslant 1$ and βx for $0 \leqslant C(t,t_w) < q_{EA}$. These forms of the correlation and response are the ones found in models of the p-spin model family [3]. Numerical simulations of glass-forming systems indicate that the two-regime behaviour is a good approximation for the finite t_w-behaviour of the response not too close to the estimated value of q_{EA}, although in that case the parameter x depends on t_w [22]. In these cases, however, 1TO are far from equilibrium, at variance with what we suppose here.

The form (11) corresponds to an equilibrium distribution where the function $P(q)$ has the simple form

$$P(q) = (1-x)\delta(q-q_{EA}) + x\delta(q). \tag{12}$$

A straightforward computation shows that the observables H_p of the previous section are expressed according to (9) as

$$\langle H_p \rangle = -\beta h(1 - q^p_{EA} + x q^p_{EA}). \tag{13}$$

The equilibrium regime at short times implies that the system spends its time in regions of the configuration space where it has the time to approximately equilibrate before relaxing further on a much longer scale. This observation can be attributed to decomposition, where the dynamical variables, say the instantaneous values of the spins, are written as sums of fast and slow contributions:

$$S_x(t) = [S_x(t) - m_x(t)] + m_x(t), \tag{14}$$

where $[S_x(t) - m_x(t)]$ is the fast component and the slow component $m_x(t)$ can be simply defined as

$$m_x(t) = \frac{1}{\tau(t_w)} \int_t^{t+\tau(t_w)} \mathrm{d}u\, S_x(u). \tag{15}$$

The sets of fast variables corresponding to the same slow variables define metastable regions of configuration space, called 'quasi-states', that have lifetimes of the order of $\tau(t_w)$. This notion can be related to the potential energy landscape notions of basins or, more precisely, metabasins [23] in the inherent structure picture [24], with which the quasi-states could be identified.

We can at this point rather naturally define thermodynamic quantities: to each quasi-state labelled by the values of the slow variables $\boldsymbol{m} = (m_1, \ldots, m_N)$ we can associate a free energy $f(\boldsymbol{m})$, and we can define a 'configurational entropy' $\Sigma(f)$ as the logarithmic multiplicity of quasi-states as a function of their free energy f.

For long but finite times, the quasi-states dominating the dynamics will present a small but extensive free-energy difference from the lowest state. The parameter q_{EA} has the meaning of a self-overlap within a quasi-state: $q_{EA} = \frac{1}{N}\sum_x m_x^2(t)$. The equilibrium distribution, on the other hand, concentrates on the ergodic components, or true states, which have finite free-energy differences from the ground state and infinite lifetimes. As we have stressed, if the

function $P(q)$ is non-trivial, the multiplicity of such states grows less than exponentially with N. On the other hand, for the number of quasi-states with free-energy difference $N\,\Delta f$ from the ground state, one can expect $\mathcal{N}(f) \sim \exp(N\rho\,\Delta f)$.

Let us discuss the effect on the system of a small perturbation and concentrate for simplicity on the case of $p = 1$, corresponding to an external magnetic field. As discussed first in [25], the effect of the field on the equilibrium distribution will be twofold. On one hand, within any given ergodic component, with given average magnetization M_{av}, higher weight will be given to configurations with higher magnetization differences from the average $M - M_{av}$. On the other, in the selection of the components, higher weight will be given to components with higher average magnetization. The actual value that the magnetization will take can then be understood as a two-step free-energy-minimization process. The first step is a single-component free-energy minimization. This is done according to the usual equilibrium relation within a component: $\beta h(M - M_{av}) = \frac{1}{N}\beta[\langle H_1^2\rangle_{sc} - \langle H_1\rangle_{sc}^2] = -\beta h(1 - q_{EA})$, where by $\langle\ \cdot\ \rangle_{sc}$ we have denoted the average over a single component. The second step is the choice of the components with the appropriate average magnetization. The probability that a given unperturbed component has average magnetization M_{av} is, for small values of M_{av}, Gaussian with zero average and variance Nq_{EA}. Taking then into account the independence of the perturbation from the original Hamiltonian, we have that the number of quasi-states with free-energy difference Δf with respect to the unperturbed ground state and average magnetization M_{av} is given by

$$\mathcal{N}(f, M_{av}) \sim \exp(N[\rho\,\Delta f - M_{av}^2/2q_{EA}]). \tag{16}$$

In the presence of the perturbation, the actual value of M_{av} will be the one minimizing $\Delta f - hM_{av}$, respecting the constraint that the number of states is higher than zero: $\rho\,\Delta f - m^2/2(1 - q_{EA}) \geqslant 0$. One finds that the minimization is achieved in fact for $\rho\,\Delta f - M_{av}^2/2(1 - q^p) = 0$, thus finding, by comparing with (13), that $\rho = \beta x$.

The equivalence (9) tells us that the same selection criteria should be valid asymptotically in off-equilibrium dynamics. The way in which the energy distributes among the different degrees of freedom in dynamics is asymptotically the same as that at equilibrium. Free energy not only governs equilibrium, but also the dynamics: quasi-states of equal free energy are selected asymptotically with equal probability. Notice that this conclusion does not depend on the observables that we have considered in the analysis; according to our line of reasoning, the same factor x appears in the anomalous response to any perturbation. Under these circumstances, one may wonder how the system can always be microscopically far from the true equilibrium components as the off-equilibrium behaviour of correlation and response implies. This relates to the abundance of quasi-states with extensive free-energy differences $N\,\Delta f$, which in order to have a non-trivial FDR must be exponentially large. In that case, a small Δf, while it implies small differences for the 1TO from the equilibrium values, implies big microscopic differences between the quasi-states visited and the ergodic components.

These considerations, based on timescale separation and the closeness of the 1TO to their equilibrium values, do not of course directly apply to structural glasses. However, on the basis of the analysis of the case of the p-spin model, where the 1TO adopt values different from the equilibrium ones [13], one can hypothesize that the previous quasi-state selection principle could also be valid far from the ultralong-time limit. This is supported by numerical simulations, which have reported the existence of well defined FDR very far from equilibrium which are fairly constant in the ageing regime [22] and do not appear to depend on the different quantities which have been studied [26].

In this regime, we probe a region of parameters corresponding to finite configurational entropy, and as 1TO are strongly out of equilibrium, no connection can be made between the

measurable values of the FDR and the equilibrium OPF. However, thanks to equiprobability, in this case also the FDR can be related to some static characterization of the configuration space. At a given time, corresponding to a quasi-state free energy f, the system will have reached with equal probability one of the $\mathcal{N}(f) \sim \exp(N\Sigma(f))$ possible quasi-states, where the configurational entropy $\Sigma(f)$ is an increasing function of f. In order to rationalize the relation (13), one has just to suppose that the dynamics is dominated by the relaxation of the configurational entropy towards smaller values, and that a small perturbation in the Hamiltonian does not change its rate of reduction. In other words, at a given time t_w, the configurational entropy will take the same value $\Sigma(t_w)$ in the absence and in the presence of the perturbation. Writing then the total free energy as an unperturbed term f plus a perturbation term $-\beta h M_{av}$, one can write that $\Sigma(t_w) = \Sigma(f) - M_{av}^2/2(1 - q_{EA})$. Minimizing the total free energy $f = f - \beta h M_{av}$ with this constraint, one recovers the formula (13) with the relation

$$\beta x = \frac{\partial \Sigma}{\partial f}. \tag{17}$$

During ageing, the effective temperature $1/(\beta x)$ and the configurational entropy obey the same relation with the total thermodynamic entropy as the true temperature follows at equilibrium. This kind of relation has been recently used to argue in favour of the 'Edwards measure' for lattice gas systems [16] and granular material under shear [27]. Let us note that even if it is not indicated explicitly in the notation, the various parameters (f, q_{EA}, etc) are now slow functions of time. The equiprobability hypothesis, which in the ultralong-time limit arises rather naturally from 1TO equilibration, is much harder to justify when these quantities are out of equilibrium. At present, the physical principles that would explain equiprobability are not clear, although it has been tentatively associated with a chaotic property related to the thermal noise [28]: two 'clones' generated by doubling a given system at the time t_w but evolving later with different realizations of the thermal noise would give rise to divergent trajectories.

We would like to stress that the analysis that we have presented implies equivalence between the relaxation of field-induced perturbations after removal of the field and the regression of spontaneous fluctuation [13] in a way that generalizes the classical Onsager argument for equilibrium systems [29]. Conditions of both kinds in fact imply free-energy minimization with a configurational entropy constraint, and, within the two-step relaxation model that we have considered, lead to the relation (11).

Up to now we have considered as a reference setting a simple quench from high to low temperature. We can generalize the present dynamical picture to more complex thermal histories retaining equiprobability of quasi-states with equal free energy. We would get in this case a dynamical picture in agreement with the multi-temperature thermodynamics described in [30], where the macroscopic state of a glass is specified by a suitable number of history-dependent effective temperatures. The model discussed here corresponds to just an effective temperature in addition to the external one. According to direct numerical measurement of the FDR in glass-forming models, this corresponds, to a good approximation, to the situation found in model liquid systems [22]. Good indications in favour of the present picture come from numerical simulations of glass-forming liquids. In [31] the relation (17) has been tested and found to hold good, starting from a direct measure of the FDR and an estimate of the configurational entropy as the logarithmic number of inherent structures with given energy. Other interesting numerical evidence has been found within the Kob–Andersen kinetic model in [16] and in the related problem of granular materials under shear in [27]. Experimentally, there is clear evidence that violations of fluctuation-dissipation theory are present on long timescales [8–10], but whether these correspond to effective temperatures is not clear at the present stage.

6. Conclusions

In this paper we have discussed a possible picture of how glassy systems visit configuration space based on the analysis of the fluctuation-dissipation relations during ageing. The ultralong-time limit, possibly relevant for the case of spin glasses, gives us a case where we can understand in considerable detail the meaning of the anomalous response and effective temperatures defined on the basis of off-equilibrium fluctuation-dissipation relations. The asymptotic value of the anomalous response is related to the existence of a non-trivial equilibrium OPF $P(q)$, which in turn implies ergodicity breaking in the equilibrium distribution. The meaning of the equivalence can be found in a dynamical principle of selection of the quasi-states in the asymptotic limit: quasi-states with equal free energy are selected with equal probability in the dynamical process. Under these circumstances, where the system is macroscopically close to equilibrium, the possibility of always being microscopically far from equilibrium and continuing to age relates to the abundance of states, which, in order for there to be a non-trivial FDR, must become exponentially large as soon as the free-energy difference Δf becomes finite.

This leads to a dynamical picture that can be generalized to the case in which the system is macroscopically out of equilibrium, assuming equiprobability of quasi-states of equal free energy, and a rate of decrease of the configurational entropy independent of possible small perturbations. This hypothesis predicts the existence of FDR (effective temperatures) related to the growth of the configurational entropy with the quasi-state free energy and therefore independent of the particular correlation and response measured. The experimental verification of this property, and the clarification of the physical principles leading to it, remain open problems requiring future research.

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