Thermodynamic picture of the glassy state

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Abstract.   A picture for the thermodynamics of the glassy state is introduced. It assumes that one extra parameter, the effective temperature, is needed to describe the glassy state. This explains the classical paradoxes concerning the Ehrenfest relations and the Prigogine–Defay ratio. As a second feature, the approach connects the response of macroscopic observables to a field change with their temporal fluctuations, and with the fluctuation-dissipation relation, in a generalized non-equilibrium way.

1. Introduction

Thermodynamics for systems far from equilibrium has long been a field of confusion. A typical application is window glass, which is far from equilibrium: it is an undercooled liquid that, in the glass formation process, has fallen out of its metastable equilibrium.

Until recently, the general consensus reached after more than half a century of research was: *Thermodynamics does not work for glasses, because there is no equilibrium.* This conclusion was partly based on the failure to understand the Ehrenfest relations and the Prigogine–Defay ratio. It should be kept in mind that, so far, the approaches have leaned very heavily on equilibrium ideas. The well-known works are the 1953 Davies–Jones paper [1] and the 1958 Gibbs–DiMarzio paper [2], while a 1981 paper by DiMarzio has the title 'Equilibrium theory of glasses' and a subtitle 'An equilibrium theory of glasses is absolutely necessary' [3]. We shall stress that such approaches are not always applicable, due to the inherent non-equilibrium character of the glassy state. Actually, the above conclusion in italics is incorrect itself, the proper statement being that 'thermostatics does not work for glasses'. Let us stress that in the literature 'thermodynamics of glasses' usually refers to actual systems under laboratory conditions, i.e. far from equilibrium. These terminological issues show how regrettable it is that 'thermostatics' got lost as an expression for 'equilibrium thermodynamics'.

Thermodynamics is the most robust field of physics. Its failure to describe the glassy state is quite unsatisfactory, since up to 25 decades in time can be involved. Naively we expect that each decade has its own dynamics, basically independent of the other ones. We have found support on this point in models that can be solved exactly. Thermodynamics then means a description under smooth non-equilibrium conditions.

2. The thermodynamic picture for systems having an effective temperature

A system that, after a quench to a certain low temperature, slowly relaxes to equilibrium is characterized by the time elapsed since the quench, sometimes called the 'age' or 'waiting

time'. For glassy systems this is of special relevance. For experiments on spin glasses it is known that non-trivial cooling or heating trajectories can be described by an effective age [4]. Yet we do not wish to discuss spin glasses. They have an infinity of long timescales, or infinite-order replica symmetry breaking.

We shall restrict consideration to systems with one diverging timescale, having, in the mean-field limit, one step of replica symmetry breaking. They are systems with first-order-type phase transitions, having discontinuous order parameter, but usually no latent heat.

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

The picture to be investigated in this work applies to systems for which the non-equilibrium state involves two well-separated timescales. It can then be characterized by three parameters, T, p, and the *effective temperature $T_e(t)$*. For model systems to be discussed below, this quantity follows from analytically solving the dynamics of the system; for realistic (model) glasses that can be approximately described by a two-timescale picture, it could follow from appropriate (numerical) experiments [5]. For a set of smoothly related cooling experiments $T_i(t)$ at pressures p_i, one may express the effective temperature as a continuous function: $T_{e,i}(t) \to T_e(T, p)$. For the given set of experiments this sets a surface in (T, T_e, p) space. On combining with other experiments, such as cooling at a different rate, or first cooling and then heating, the surface becomes multi-valued. To cover the whole space one needs to perform many experiments, e.g., at different pressures and different cooling rates. The results should agree with findings from heating experiments and aging experiments. Thermodynamics amounts to giving differential relations between observables at nearby points in this space.

Of special interest is the thermodynamics of a thermal body at temperature T_2 in a heat bath at temperature $T_1 = T$. A basic assumption is separability of timescales, and consequent separability of phase space, allowing one to identify entropies S_1 and S_2. (For the energy, such a decomposition cannot be carried out.) This set-up allows one to maintain the difference in temperatures, and applies to mundane situations such as a cup of coffee, or an ice cream, in a room. The change in heat of such systems obeys $đQ \leqslant T_1 \, dS_1 + T_2 \, dS_2$.

A similar two-temperature approach proves to be relevant for glassy systems. The known exact results on the thermodynamics of systems can be summarized by the very same change in heat [6, 7]:

$$đQ = T \, dS_{ep} + T_e \, d\mathcal{I} \tag{1}$$

where S_{ep} is the entropy of the **e**quilibrium **p**rocesses, i.e. the fast or β-processes that have timescale less than the observation time. $\mathcal{I}$ is the configurational entropy of the slow or configurational processes (α-processes), also known as information entropy or complexity. In the standard definition [2], the configurational entropy S_c is the entropy of the glass minus that of the vibrational modes of the crystal. For polymers this still includes short-distance rearrangement, which is a relatively fast mode. It was confirmed numerically that S_c indeed does not vanish at any temperature, and it does not fit well to the Adam–Gibbs [8] relation $\tau_{eq} \sim \exp(C/T S_c)$ [9]. Our quantity $\mathcal{I}$ only involves long-time processes; the relatively fast ones are included in S_{ep}. To stress that in $\mathcal{I}$ only the slow modes of S_c contribute, it would deserve a separate name—the most natural one being *complexity*. The applicability of an Adam–Gibbs-type relation $\tau_{eq} \sim \exp(C/T\mathcal{I})$ remains an open issue, but it holds in a toy model for the standard 'folklore' of the glassy state [10].

If a system has a set of processes i with very different timescales τ_i and partial entropies S_i, one can define $\mathcal{I}$ as the sum of the S_i having $\tau_i > \tau_{eq}/10$, where $\tau_{eq} = \max \tau_i$ is the

equilibrium relaxation time. For a system quenched to a low temperature and aging there for a time t, the sum would be restricted to $\tau_i > t/10$.

2.1. First and second law

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

$$dU = T\,dS_{ep} + T_e\,d\mathcal{I} - p\,dV. \tag{2}$$

It is appropriate to define the generalized free enthalpy

$$G = U - T S_{ep} - T_e\mathcal{I} + pV. \tag{3}$$

This is not the standard free enthalpy, since $T_e \neq T$. It satisfies

$$dG = -S_{ep}\,dT - \mathcal{I}\,dT_e + V\,dp. \tag{4}$$

The total entropy is

$$S = S_{ep} + \mathcal{I}. \tag{5}$$

The second law requires $đQ \leqslant T\,dS$, leading to $(T_e - T)\,d\mathcal{I} \leqslant 0$, which merely says that heat goes from high to low temperatures.

Since $T_e = T_e(T, p)$, and both entropies are functions of T, T_e, and p, expression (1) yields the specific heat $C_p = \partial Q/\partial T\big|_p$. In the glass transition region all factors, except $\partial_T T_e$, are basically constant. This leads to

$$C_p = C_1 + C_2 \frac{\partial T_e}{\partial T}\bigg|_p. \tag{6}$$

Precisely this form was assumed half a century ago by Tool [11] as starting point for the study of caloric behaviour in the glass formation region, and it has often been used for the explanation of experiments [1, 12]. It is a direct consequence of equation (1).

For magnetic systems the first law gives

$$dU = T\,dS_{ep} + T_e\,d\mathcal{I} - M\,dH. \tag{7}$$

As above, one can define the generalized free energy $F = U - T S_{ep} - T_e\mathcal{I}$. It satisfies the relation $dF = -S_{ep}\,dT - \mathcal{I}\,dT_e - M\,dH$. In an aging system (fixed T and H) the rate of change $\dot{F} = -\mathcal{I}\dot{T}_e$ is usually positive. In the literature [8, 24], the 'experimental' or 'dynamical' free energy $F_{dyn} = U - T(S_{ep} + \mathcal{I})$ has also been considered. It evolves as $\dot{F}_{dyn} = (T_e - T)\dot{\mathcal{I}}$; thus it is related to entropy production, and always negative.

2.2. Modified Maxwell relation

For a smooth sequence of cooling procedures of a glassy liquid, equation (2) implies a modified Maxwell relation between macroscopic observables such as $U(t, p) \to U(T, p) = U(T, T_e(T, p), p)$ and V. This solely occurs since T_e is a non-trivial function of T and p for the smooth set of experiments under consideration.

For glass-forming liquids it reads

$$\frac{\partial U}{\partial p}\bigg|_T + p\frac{\partial V}{\partial p}\bigg|_T + T\frac{\partial V}{\partial T}\bigg|_p = T\frac{\partial \mathcal{I}}{\partial T}\bigg|_p \frac{\partial T_e}{\partial p}\bigg|_T - T\frac{\partial \mathcal{I}}{\partial p}\bigg|_T \frac{\partial T_e}{\partial T}\bigg|_p + T_e\frac{\partial \mathcal{I}}{\partial p}\bigg|_T. \tag{8}$$

In equilibrium $T_e = T$, so the right-hand side vanishes. For a glassy magnet one has

$$\frac{\partial U}{\partial H}\bigg|_T + M - T\frac{\partial M}{\partial T}\bigg|_H = T_e\frac{\partial \mathcal{I}}{\partial H}\bigg|_T + T\left(\frac{\partial T_e}{\partial H}\bigg|_T \frac{\partial \mathcal{I}}{\partial T}\bigg|_H - \frac{\partial T_e}{\partial T}\bigg|_H \frac{\partial \mathcal{I}}{\partial H}\bigg|_T\right). \tag{9}$$

2.3. Ehrenfest relations and the Prigogine–Defay ratio

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

Denoting the discontinuities as $\Delta O = O_{\text{liquid}} - O_{\text{glass}}$, we may follow Ehrenfest and take the derivative of $\Delta V(T, p_g(T)) = 0$. This yields the 'first Ehrenfest relation'

$$\Delta \alpha = \Delta \kappa \frac{\mathrm{d}p_g}{\mathrm{d}T} \tag{10}$$

while for a glassy magnet $\Delta \alpha = \Delta \chi \, \mathrm{d}H_g/\mathrm{d}T$.

The conclusion drawn from half a century of research on glass-forming liquids is that this relation is never satisfied [1, 13–15]. This has very much hindered progress on a thermo-dynamical approach. However, from a theoretical viewpoint it is hard to imagine that something could go wrong when just taking a derivative. McKenna [16] and, independently, also we [6] have pointed out that this relation is indeed satisfied automatically, but it is important say what is meant by κ in the glassy state.

Let us make an analogy with spin glasses. In mean-field theory they have infinite-order replica symmetry breaking. From the early measurements of Canella and Mydosh [17] on AuFe it is known that the susceptibility depends logarithmically on the frequency, and so on the timescale. The short-time value, called the zero-field-cooled (ZFC) susceptibility, is a lower bound, while the long-time value, called the field-cooled (FC) susceptibility, is an upper bound. Let us use the term 'glassy magnets' for spin glasses with one step of replica symmetry breaking. They are relevant for comparison with glass-forming liquids. For them the situation is worse, as the ZFC value is discontinuous immediately below T_g. This explains why already directly below the glass transition different measurements yield different values for κ. These notions are displayed in figure 1.

Previous claims about the violation of the first Ehrenfest relation can be traced back to the equilibrium idea that there is one, ideal κ, to be inserted in (10). Indeed, investigators always considered cooling curves $V(T, p_i)$ at a set of pressures p_i to determine $\Delta \alpha$ and $\mathrm{d}p_g/\mathrm{d}T$. However, $\Delta \kappa$ was always determined in another way, such as by measurement of the speed of sound, or by making pressure steps [18]. In equilibrium, such alternative determinations would yield the same outcome. For glasses this is not the case: the speed of sound is a short-time process, and additional pressure steps modify the glassy state. Therefore alternative procedures should be avoided, and only the cooling curves $V(T, p_i)$ should be used. They constitute a liquid surface $V_{\text{liquid}}(T, p)$ and a glass surface $V_{\text{glass}}(T, p)$ in (T, p, V) space. These surfaces intersect, and the first Ehrenfest relation is no more than a mathematical identity concerning the intersection line of these surfaces. It is therefore automatically satisfied [6]. The most careful data that we came across were collected by Rehage and Oels for atactic polystyrene [18]. In figure 2 we present those data in a three-dimensional plot, underlining our point of view.

The second Ehrenfest relation follows from differentiating $\Delta U(T, p_g(T)) = 0$. The relation obtained will also be satisfied automatically. However, one then eliminates $\partial U/\partial p$ by means of the Maxwell relation. We have already discussed the fact that away from equilibrium it is modified. The equality $T_e(T, p_g(T)) = T$ implies

$$\frac{\mathrm{d}T_e}{\mathrm{d}T} = \left. \frac{\partial T_e}{\partial T} \right|_p + \left. \frac{\partial T_e}{\partial p} \right|_T \frac{\mathrm{d}p_g}{\mathrm{d}T} = 1. \tag{11}$$
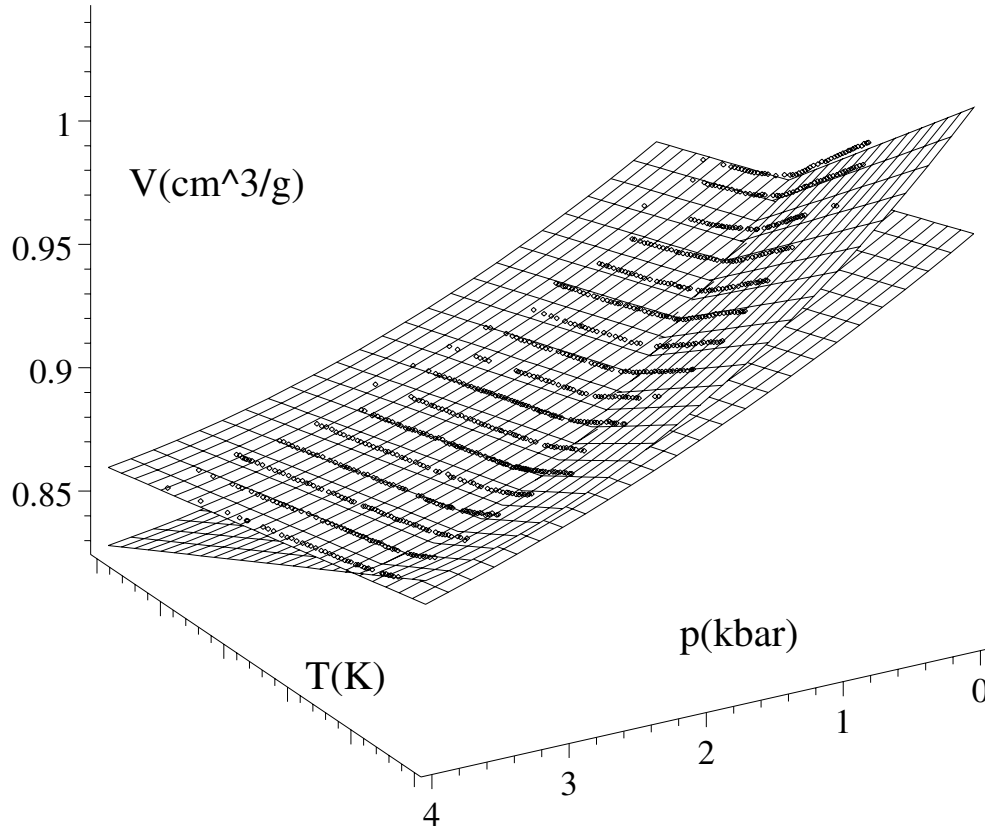
Figure 1. A schematic plot of the field-cooled (FC) and zero-field-cooled (ZFC) susceptibility in realistic spin glasses and in glassy magnets, as a function of temperature, in arbitrary units. In realistic spin glasses the infinite time or field-cooled susceptibility is larger than the short-time or zero-field-cooled susceptibility. In magnetic analogues of realistic glasses the short-time susceptibility even has a smeared discontinuity at the glass transition, yielding a value of χ that depends on the precise type of experiment which is performed. In glass-forming liquids the same happens for the compressibility.

Using equation (8) and inserting this relation, we obtain

$$\frac{\Delta C_p}{T_g V} = \Delta\alpha \frac{\mathrm{d}p_g}{\mathrm{d}T} + \frac{1}{V}\left(1 - \left.\frac{\partial T_e}{\partial T}\right|_p\right)\frac{\mathrm{d}\mathcal{I}}{\mathrm{d}T}. \tag{12}$$

The $\mathrm{d}\mathcal{I}/\mathrm{d}T$ term constitutes the total derivative along the glass transition line, $\partial\mathcal{I}/\partial T + (\partial\mathcal{I}/\partial p)\,\mathrm{d}p_g/\mathrm{d}T$. Its prefactor only vanishes at equilibrium ($T_e = T$), in which case the standard Ehrenfest relation is recovered. For glassy magnets one has similarly

$$\frac{\Delta C}{NT} = \Delta\alpha \frac{\mathrm{d}H_g}{\mathrm{d}T} + \frac{1}{N}\left(1 - \left.\frac{\partial T_e}{\partial T}\right|_H\right)\frac{\mathrm{d}\mathcal{I}}{\mathrm{d}T}. \tag{13}$$

The Prigogine–Defay ratio is defined by

$$\Pi = \frac{\Delta C_p \,\Delta\kappa}{TV(\Delta\alpha)^2}. \tag{14}$$

For equilibrium transitions it should be equal to unity. Assuming that at the glass transition a number of unspecified parameters undergo a phase transition, Davies and Jones derived that
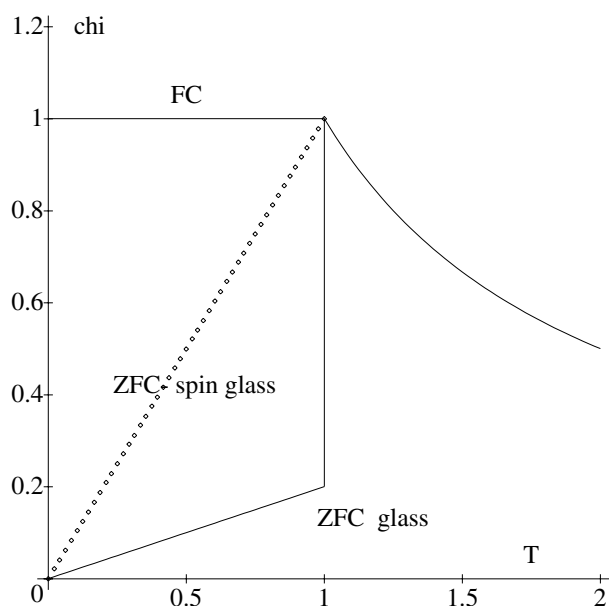
Figure 2. Data on the glass transition for cooling atactic polystyrene at the rate 18 K h^{-1}, scanned from the paper of Rehage and Oels [18]: specific volume V (cm^3 g^{-1}) versus temperature T (K) at various pressures p (kbar). As confirmed by a polynomial fit, the data on the liquid essentially lie on a smooth surface, and so do the data on the glass. The first Ehrenfest relation describes no more than the intersection of these surfaces, and is therefore automatically satisfied. The values for the compressibility derived in this manner will generally differ from results obtained via other procedures.

$\Pi \geqslant 1$ [1], while DiMarzio showed that in that case the correct value is $\Pi = 1$ [19]. For glasses, typical experimental values are reported in the range $2 < \Pi < 5$. It was therefore generally thought that $\Pi \geqslant 1$ is a strict inequality arising from the requirement of mechanical stability.

Since the first Ehrenfest relation is satisfied, it holds that

$$\Pi = \frac{\Delta C_p}{T V \, \Delta\alpha \, (\mathrm{d}p_g/\mathrm{d}T)} = 1 + \frac{1}{V \, \Delta\alpha} \left(1 - \left. \frac{\partial T_e}{\partial T} \right|_p \right) \frac{\mathrm{d}\mathcal{I}}{\mathrm{d}p}. \tag{15}$$

ΔC_p and $\Delta\alpha$ can be measured by cooling at a fixed pressure, but $\mathrm{d}p_g/\mathrm{d}T$ depends on cooling experiments at two pressures, or, more precisely, on the smooth set of cooling experiments. Therefore $\mathrm{d}p_g/\mathrm{d}T$ can be small or large, implying that Π *depends on the set of experiments*. As a result, it can also be below unity. Rehage and Oels found $\Pi = 1.09 \approx 1$ at $p = 1$ kbar, using a short-time value for κ. Reanalysing their data, we find from (15), where the proper long-time κ has been inserted, a value $\Pi = 0.77$. Notice that it is below unity. The commonly accepted inequality $\Pi \geqslant 1$ is based on the equilibrium assumption of a unique κ. Our theoretical arguments and the Rehage–Oels data show that this assumption is incorrect.

2.4. Fluctuation formula

The basic result of statistical physics is that it relates fluctuations in macroscopic variables to responses of their averages to changes in external field or temperature. We wondered whether such relations generalize to the glassy state.

In cooling experiments at fixed field it holds that $M = M(T(t), T_e(t, H), H)$. For a thermodynamic description one eliminates time, implying that $M = M(T, T_e(T, H), H)$. One may then expect three terms:

$$\chi \equiv \frac{1}{N} \frac{\partial M}{\partial H}\bigg|_T = \chi^{\text{fluct}}(t) + \chi^{\text{loss}}(t) + \chi^{\text{conf}}(t). \tag{16}$$

The first two terms add up to $(1/N)(\partial M/\partial H)\big|_{T,T_e}$. To find them separately, we switch from a cooling experiment to an aging experiment at the T, T_e, and H considered, by keeping, in *Gedanken*, T fixed from then on. The system will continue to age; this is expressed by $T_e = T_e(t; T, H)$. We may then use the equality

$$\frac{\partial M}{\partial H}\bigg|_{T,t} = \frac{\partial M}{\partial H}\bigg|_{T,T_e} + \frac{\partial M}{\partial T_e}\bigg|_{T,H} \frac{\partial T_e}{\partial H}\bigg|_{T,t}. \tag{17}$$

We have conjectured [20] that the left-hand side may be written as the sum of the fluctuation terms for fast and slow processes, defining the fluctuation contribution

$$\chi^{\text{fluct}}(t) = \frac{\partial M}{\partial H}\bigg|_{T,t} = \frac{\langle \delta M^2(t)\rangle_{\text{fast}}}{NT(t)} + \frac{\langle \delta M^2(t)\rangle_{\text{slow}}}{NT_e(t)}. \tag{18}$$

The first term is just the standard equilibrium expression for the fast equilibrium processes. Notice that the slow fluctuations enter with their own temperature, the effective temperature. This decomposition is confirmed by use of the fluctuation-dissipation relation in a form to be discussed below. From equation (17) then follows the 'loss' term

$$\chi^{\text{loss}}(t) = -\frac{1}{N} \frac{\partial M}{\partial T_e}\bigg|_{T,H} \frac{\partial T_e}{\partial H}\bigg|_{T,t}. \tag{19}$$

It is related to an aging experiment. In some models it is small [20, 21], but in another model [10] it is of order unity. There occurs in equation (16) also a configurational term

$$\chi^{\text{conf}} = \frac{1}{N} \frac{\partial M}{\partial T_e}\bigg|_{T,H} \frac{\partial T_e}{\partial H}\bigg|_T. \tag{20}$$

It originates from the difference in the system's structure for cooling experiments at nearby fields. This is the term that is responsible for the discontinuity of χ or κ at the glass transition. Its existence was anticipated by Goldstein and Jäckle [13, 14].

2.5. Fluctuation-dissipation relation

Nowadays quite a lot of attention is paid to the fluctuation-dissipation relation in the aging regime of glassy systems. It was put forward in works by Sompolinsky [22] and Horner [23,24], and generalized by Cugliandolo and Kurchan [25]; see [26] for a review.

In the aging regime there holds a fluctuation-dissipation relation between the correlation function $C(t, t') = \langle \delta M(t)\, \delta M(t')\rangle$ and $G(t, t')$, the response of $\langle M(t)\rangle$ to a short, small field-change $\delta H(t')$ applied at an earlier time t':

$$\frac{\partial C(t, t')}{\partial t'} = T_e(t, t') G(t, t') \tag{21}$$

with $T_e(t, t')$ being an effective temperature, also denoted as $T/X(t, t')$ [26].

We have observed that in simple models without fast processes, $T_e(t, t') = \tilde{T}_e(t')$ is a function of one of the times only [20, 21]. One then expects $\tilde{T}_e(t)$ to be close to the 'thermodynamic' effective temperature $T_e(t)$. We have shown that [21]

$$\tilde{T}_e(t) = T_e(t) - \dot{T}_e(t)\left(\frac{\partial \ln C(t, t')}{\partial t'}\bigg|_{t'=t}\right)^{-1} + \cdots. \tag{22}$$

So the effective temperatures T_e and $\tilde{T}_e$ are not identical. However, in the models analysed so far, the difference is subleading in $1/\ln t$.

Notice that the ratio $\partial_{t'} C(t, t')/G(t, t') = \tilde{T}_e(t')$ is allowed to depend on time t'. The situation with constant T_e is well known from mean-field spin glasses with one step of replica symmetry breaking [26], but we have not found such a constant T_e beyond mean-field theory [20, 21]. Only at exponential timescales does the mean-field spin glass behave as a realistic system [7].

2.6. Timescale arguments

Consider a simple system that has only one type of process (α-processes), which falls out of equilibrium at some low T. When it ages a time t at $T = 0$, it will have achieved a state with effective temperature $\overline{T}_e$, that can be estimated by equating time with the equilibrium timescale, $t = \tau_{eq}(\overline{T}_e)$. We have checked in solvable models that, to leading order in $\ln t$, it holds that $\overline{T}_e = T_e$. (The first non-leading order turns out to be non-universal.) This equality also is found in cooling trajectories, when the system is well inside the glassy regime. It says that the system basically has forgotten its history, and ages on its own, without caring about the actual temperature. Another way of saying this is that the dynamics in each new decade of time is basically independent of that in the previous decade.

This timescale argument, however, is not very strong. Though it works for simple model glasses, it does not work, for instance, for realistic spin glasses.

3. Solvable models

In the above, a variety of effective temperatures have been defined, and other definitions appeared also [27]. The most prominent one seems to us the 'thermodynamical' T_e, that appears in the second law $đQ \leqslant T\, dS_{\text{ep}} + T_e\, d\mathcal{I}$. If these effective temperatures are (basically) the same, then the above description leads to a coherent two-temperature picture. Let us now discuss models where this is or could be the case. (In principle also an effective field can occur [10]; we shall not consider that complication.)

The thermodynamic part of the above picture has been constructed from aging properties of the p-spin model [6, 24]. If the limit $N \to \infty$ is taken first, the aging dynamics starting from a random initial configuration follows from a set of equations very similar to the mode-coupling equations for glasses [24]. The long-time dynamical properties also follow from a replica calculation using the marginality condition [28]. Our first step has been to find the physical meaning of the marginal replica free energy. Hereto we analysed the Thouless–Anderson–Palmer (TAP) partition sum at zero field [29] and non-zero field [7]. In both cases we convinced ourselves that the replica free energy (the logarithm of the ordinary partition sum) does indeed coincide with the logarithm of the TAP partition sum. In other words, nothing went wrong on using replicas, and a physical interpretation should be anticipated. After the appearance of reference [27], we were convinced that T/x should be interpreted as a thermodynamic effective temperature [7], and it was already known that this combination appeared in the fluctuation-dissipation relation [25]. My studies with Sherrington and Hertz [30] on the p-spin model with a ferromagnetic coupling led to the insight that the fluctuation formula (16) is valid there without the loss term.

Similar results follow for a directed polymer model with glassy behaviour [6, 31]. In this model a directed polymer moves on a flat substrate with randomly located ridges. It prefers to lie in regions where ridges are widely separated. These Griffiths or Lifshitz singularities are the 'TAP states' of the problem. They occur often enough when the transverse width W

scales exponentially in the longitudinal width $W \sim \exp(L^{1/3})$. The statics of this model has a Kauzmann transition. The long-time dynamics involves hopping between these states. For an ensemble of non-interacting polymers starting from a random initial configuration, it has been argued that the motion involves a flow to states with decreasing complexity, as happens in the p-spin model at exponential timescales [7]. Nevertheless, the dynamics of the model deserves further attention.

Very informative are models with exactly solvable parallel Monte Carlo dynamics, such as independent harmonic oscillators [20, 21, 32] or independent spherical spins in a random field [20, 21]. In both cases the equilibrium timescale follows an Arrhenius law, which leads to glassy behaviour at low temperatures when cooling or when aging from a random initial configuration. Since these models are not mean-field-like, they have a proper dynamics, which satisfies the fluctuation formula (16). The effective temperatures decay as $1/\ln t$, with a common prefactor, but different $1/\ln^2 t$ corrections.

A model with a set of fast modes and a set of slow modes, that have a Vogel–Fulcher–Tammann–Hesse law for the divergence of the equilibrium timescale, has also been formulated. It allows one to study glassy dynamics below the Kauzmann temperature [10].

The two-temperature approach put forward here also explains why thermodynamics applies to black holes [33] and star clusters [34].

Acknowledgments

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