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Thermodynamics of the Glassy State: Effective Temperature as an Additional System Parameter

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A system is glassy when the observation time is much smaller than the equilibration time. A unifying thermodynamic picture of the glassy state is presented. Slow configurational modes are in quasiequilibrium at an effective temperature. It enters thermodynamic relations with the configurational entropy as a conjugate variable. Slow fluctuations contribute to susceptibilities via quasiequilibrium relations, while there is also a configurational term. Fluctuation-dissipation relations also involve the effective temperature. Fluctuations in the energy are nonuniversal, however. The picture is supported by analytically solving the dynamics of a toy model. [S0031-9007(98)06195-X]

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Thermodynamics is an old but powerful subject. After the invention of the steam machine it was needed for understanding their optimal efficiency. It applies to a wide variety of systems, ranging from ideal gases to black holes. Equilibrium thermodynamics is a well understood subject. Important contributions were made by Carnot, Clausius, Kelvin, Boltzmann, and Gibbs.

Thermodynamics for systems close to equilibrium was worked out in the middle of this century. Applications are systems with heat flows, electric currents, and chemical reactions. A basic assumption is the existence of local thermodynamic equilibrium, and the task is to calculate the entropy production. Important contributions were made by de Donder, Prigogine, de Groot, and Mazur.

Thermodynamics for systems far from equilibrium has long been a field of contradiction and confusion. A typical application is a window glass. A cubic micron of glass is not a crystal; it is an undercooled liquid which has fallen out of equilibrium. In a glassy system the relaxation time $\tau_{\rm eq}(T)$ of the slow or so-called α processes has become larger than the observation time, while the fast or β processes are still in equilibrium. Waiting long enough might bring the system back to its equilibrium state. In glasses one often assumes the Vogel-Tamman-Fulcher law $\tau_{\rm eq} \sim \exp[A/(T - T_K)]$. In many other systems one encounters an Arrhenius law $\tau_{\rm eq} \sim \exp(A/T)$. As we shall demonstrate on a toy model, such systems display the same glassy behavior.

We shall consider glassy transitions for liquids as well as for random magnets. The results map onto each other by interchanging volume V, pressure p, compressibility $\kappa = -\partial \ln V/\partial p$, and expansivity $\alpha = \partial \ln V/\partial T$, by magnetization M, field H, susceptibility $\chi = (1/N)\partial M/\partial H$, and "magnetizability" $\alpha = (-1/N)\partial M/\partial T$, respectively.

A glass forming liquid exhibits near the glass transition smeared discontinuities in quantities such as the heat capacity C_p, the expansivity, and the compressibility. This defines a smeared glass transition line $T_g(p)$ or $p_g(T)$, with behavior similar to continuous phase transitions of classical type, i.e., with specific heat exponent $\alpha = 0$. Since the 1920s quite some attention has been paid to introduce a thermodynamic description; see, e.g., [1–3]. It was investigated, in particular, whether the discontinuities satisfy the two Ehrenfest relations (the analogs for second order transitions of the Clausius-Clapeyron relation of a first order transition), and whether the Prigogine-Defay ratio [see Eq. (23)] equals unity. Very recently we have explained the experimental observations [4].

A state that slowly relaxes to equilibrium is characterized by the time elapsed so far, the "age" or "waiting time." For glassy systems this is of special relevance. In spin glass experiments nontrivial cooling-heating cycles can be described by an effective age [5]. One thus characterizes a nonequilibrium state by three parameters, T, H, or p, and the age t or the cooling rate $\dot{T} = dT/dt$. For thermodynamics a more suitable third variable is the *effective temperature* $T_e(t)$, introduced half a century ago by Tool [6,7]. $T_e \neq T$ will describe the best quasiequilibrium the α processes could reach so far; it follows in simple cases by equating $\tau_{\rm eq}(T_e) = t$.

For a set of smoothly related cooling experiments $T_i(t)$ at fields H_i one may express the effective temperature as a continuous function: $T_{e,i}(t) \rightarrow T_e(T,H)$. This sets a surface in (T, T_e, H) space that becomes multivalued if one first cools, and then heats. To map out the whole space many sets of experiments are needed, e.g., at different cooling rates. Thermodynamics amounts to give, for a certain class of systems, universal relations between state variables at nearby points in this space.

Within this framework some new results were obtained for a spin glass model with one step of replica symmetry breaking [4,8,9]; such models are related to systems without disorder that have one, and only one, diverging time scale. The fast and slow modes do not have only their own temperature, they also have their own entropy: the entropy of equilibrium processes $S_{\rm ep}$ and the "configurational" or "information" entropy or "complexity" $\mathcal{I}$, respectively. The total entropy is $S = S_{\rm ep} + \mathcal{I}$. Previous results can be summarized by setting $\text{đ}Q = TdS_{\mathrm{ep}} + T_e d\mathcal{I}$. In the course of time the system will satisfy $(T - T_e)d\mathcal{I} \geq 0$, as required by the second law. In combination with the first law, the thermodynamic relations can then be represented as

$$dU = TdS_{\mathrm{ep}} + T_e d\mathcal{I} + \text{đ}W\,, \tag{1}$$

$$F = U - TS_{\mathrm{ep}} - T_e \mathcal{I}\,, \tag{2}$$

$$dF = -S_{\mathrm{ep}}dT - \mathcal{I}dT_e + \text{đ}W\,, \tag{3}$$

where $\text{đ}W = -pdV$ for liquids and $-MdH$ for magnets. Equation (1) immediately leads to the form $C_p = C_1 + C_2 \partial T_e/\partial T|_p$ used in practice [2,6,10].

Out of equilibrium the Maxwell relation between $U(T(t), t, H) \to U(T, T_e(T, H), H)$ and M is, of course, not satisfied; however, the above implies that its violation is related to the change of configurational entropy:

$$\frac{\partial U}{\partial H} + M - T\frac{\partial M}{\partial T} = \left(T_e - T\frac{\partial T_e}{\partial T}\right)\frac{\partial \mathcal{I}}{\partial H} + T\frac{\partial T_e}{\partial H}\frac{\partial \mathcal{I}}{\partial T}\,. \tag{4}$$

Here we wish to add to this scheme the nonequilibrium susceptibilities. We will derive the results in a toy model with fields H_a and magnetizations M_a $(a = 1, 2)$. As could be guessed from $M_a \equiv M_a(T, T_e(T, H), H)$, there appear two terms:

$$\chi_{ab} \equiv \frac{1}{N}\frac{\partial M_a}{\partial H_b}\bigg|_T = \chi_{ab}^{\mathrm{fluct}}(t) + \chi_{ab}^{\mathrm{conf}}(t)\,. \tag{5}$$

First there is the expected fluctuation contribution

$$\chi_{ab}^{\mathrm{fluct}}(t) = \frac{\langle \delta M_a(t)\delta M_b(t)\rangle_{\mathrm{fast}}}{NT(t)} + \frac{\langle \delta M_a(t)\delta M_b(t)\rangle_{\mathrm{slow}}}{NT_e(t)} - \frac{1}{N}\frac{\partial M_a}{\partial T_e}\bigg|_{T,H}\frac{\partial T_e}{\partial H_b}\bigg|_t\,. \tag{6}$$

Notice that fast and slow processes again enter with their own temperature while the third term is small. Since $T_e \neq T$, there occurs a new, configurational term

$$\chi_{ab}^{\mathrm{conf}} = \frac{1}{N}\frac{\partial M_a}{\partial T_e}\bigg|_{T,H}\frac{\partial T_e}{\partial H_b}\bigg|_T\,. \tag{7}$$

It originates from the difference in the system's structure for cooling experiments at nearby fields [11]. Such universal relations would not hold for energy fluctuations.

We shall also see in the toy model that the correlation function $C_{ab}(t, t') = (1/N)\langle \delta M_a(t)\delta M_b(t')\rangle$ and the response function $G_{ab}(t, t') = (1/N)\delta M_a(t)/\delta H^b(t')$ satisfy the fluctuation-dissipation relation

$$\frac{\partial C_{ab}(t, t')}{\partial t'} = T_e(t')G_{ab}(t, t') \tag{8}$$

in the aging regime, while in the equilibrium or short-time regime T replaces T_e. This has been confirmed numerically for a soft sphere glass [12]. Equation (8) is consistent with (6): in performing $\int_0^t G_{ab}(t, t')\,dt'$ one uses that $\partial_{t'}C$ changes much faster than $T_e(t')$, allowing one to replace $T_e(t')$ by $T_e(t)$ in the aging regime, and by T in the equilibrium regime $t' \approx t$.

Note that the ratio $\partial_{t'}C/G$ depends on time. The situation with constant T_e is well known from mean-field spin glasses [13]. However, this time independence is an artifact of the mean-field approximation [9].

Finally, one estimates scaling in the aging regime of two-time quantities as

$$C(t, t') \approx C\left[\frac{t - t'}{\tau_{\mathrm{eq}}(T_e(t'))}\right] \approx C\left(\frac{t - t'}{t'}\right) = C\left(\frac{t}{t'}\right), \tag{9}$$

showing immediately the familiar t/t' scaling; there may be logarithmic scaling corrections.

The full picture [Eqs. (1)–(9)] shows that slow modes are at a quasiequilibrium at T_e. As in a plasma, slow and fast modes equilibrate at their own temperature.

In a number of simple models there occurs a dynamical glassy state when cooling near $T = 0$. If there is only one time scale, there remain only slow processes in the frozen phase (only α, no β processes). This implies that U has no explicit dependence on T, and that $S_{\mathrm{ep}} = 0$.

In order to corroborate our statements, we consider a toy model involving free spherical spins $\sum S_i^2 = N$. The Hamiltonian contains two parts, a "self-interaction" term involving quenched random fields $\Gamma_i = \pm\Gamma$ with average zero, and a coupling to an external field H

$$\mathcal{H} = -\sum_{i=1}^N \Gamma_i S_i - H\sum_{i=1}^N S_i\,. \tag{10}$$

In terms of the "staggered" magnetization $M_s \equiv (1/\Gamma)\sum_i \Gamma_i S_i$ one simply has $\mathcal{H} = -\Gamma M_s - HM$.

In equilibrium at low T the internal energy reads $U_{\mathrm{eq}}/N = -K + \frac{1}{2}T$, the entropy $S_{\mathrm{eq}}/N = \frac{1}{2}\ln(eT/K)$, the magnetizations $M_{\mathrm{eq}}/N = H/K - \frac{1}{2}HT/K^2$, and $M_{s;\mathrm{eq}}/N = \Gamma/K - \frac{1}{2}\Gamma T/K^2$, where $K \equiv \sqrt{\Gamma^2 + H^2}$.

This model gets glassy behavior when it is subject to Monte Carlo dynamics with parallel update, which couples the spins dynamically. The time evolution can be solved exactly, since it maps closely on the dynamics for uncoupled harmonic oscillators, introduced by Bonilla, Padilla, and Ritort [14], when extended to include a field.

Per time step $1/N$ one makes parallel Monte Carlo moves, $S_i \to S_i' = S_i + r_i/\sqrt{N}$, with Gaussian noise having $\langle r_i\rangle = 0$ and $\langle r_i^2\rangle = \Delta^2$. Next one makes a global rescaling of the length of the spins in order to keep $\sum S_i'^2 = N$. This leads to the final update

$$S_i' = S_i + \frac{r_i}{\sqrt{N}} - S_i\sum_j\left(\frac{r_j S_j}{N\sqrt{N}} + \frac{r_j^2}{2N^2}\right) + \cdots\,. \tag{11}$$

Denoting $\mathcal{H}$ by E, it is simple to calculate the joint transition probability of $x \equiv E' - E$ and $y \equiv M' - M$,

$$p(x, y\,|\,E, M) = p(x\,|\,E)p(y\,|\,x, E, M)\,, \tag{12}$$

where both factors are Gaussian. In terms of

$$\varepsilon = K + \frac{E}{N}; \qquad m = \frac{M}{N}; \qquad \tilde{m} = m - \frac{H}{K} + \frac{H}{K^2}\,\varepsilon\,, \tag{13}$$

the centers of the Gaussians are

$$x_0 = \frac{1}{2}\Delta^2(K - \varepsilon); \qquad y_0 = -\frac{Hx}{K^2} - \tilde{m}\,\frac{\Delta^2K^2 - 2Kx + 2x\varepsilon}{2\varepsilon(2K - \varepsilon)}, \tag{14}$$

while their variances read

$$\Delta_x = \Delta^2\varepsilon(2K - \varepsilon); \qquad \Delta_y = \frac{\Delta^2\Gamma^2}{K^2} - \frac{\Delta^2K^2\tilde{m}^2}{\varepsilon(2K - \varepsilon)}, \tag{15}$$

respectively. Following Metropolis, a move $E' = E + x$, $M' = M + y$ is accepted with probability $W(\beta x)$, where $W = 1$ if $x < 0$, while $W = \exp(-\beta x)$ if $x > 0$. The dynamics is now fully specified. The average energy evolves according to a closed equation for $\varepsilon(t)$ [14],

$$\frac{d\varepsilon}{dt} = \int_{-\infty}^{\infty} dx\, W(\beta x)xp(x|\varepsilon). \tag{16}$$

We find that the average magnetization satisfies similarly

$$\frac{dm}{dt} = \int_{-\infty}^{\infty} dx\, W(\beta x)y_0p(x\,|\,\varepsilon). \tag{17}$$

At low T there occur Arrhenius laws for the equilibrium relaxation times viz. $\tau_{\mathrm{eq}} \equiv \tau_{\mathrm{eq}}^{(E)} = \frac{1}{2}\beta A\tau_{\mathrm{eq}}^{(M)} = (\pi A/64T)^{1/2}\exp(A/T)$ with $A \equiv \Delta^2K/8$, responsible for nonequilibrium behavior in typical cooling procedures.

We first consider the situation at $T = 0$. Starting from a random initial condition, the system will slowly evolve towards the ground state. It is this evolution that we now wish to capture within a thermodynamic framework. Equating $U(t) = U_{\mathrm{eq}}(T_e, H)$ leads to [14]

$$T_e(t) \approx \frac{A}{\ln 2t/\sqrt{\pi} + \ln\ln 2t/\sqrt{\pi}}. \tag{18}$$

As asserted above, the same T_e is obtained via the relaxation time:$t = \tau_{\mathrm{eq}}(\tilde{T}_e(t)) \rightarrow \tilde{T}_e(t) = T_e(t) + \mathcal{O}(T_e^2)$.

In equilibrium it holds that $\tilde{m} = 0$. The result $\tilde{m} \sim 1/t \sim \exp(-\beta_eA)$ proves that the magnetization very closely follows its quasiequilibrium value $m_{\mathrm{eq}}(T_e, H)$.

To test the thermodynamics we need the configurational entropy. It is defined as the logarithm of the number of states leading to $U(t, H) = U_{\mathrm{eq}}(T_e, H)$. Since $S_{\mathrm{int}} = 0$ it simply holds that $\mathcal{I} = S_{\mathrm{eq}}(T_e(t), H)$. We can now verify the relation $dU = T_e d\mathcal{I} - MdH - M_s d\Gamma$. At constant H and Γ it is valid, because one has replaced $T \rightarrow T_e$ in energy and entropy. Then one can take the difference of two evolution experiments at two nearby H's. The relation remains satisfied since $M(t) \approx M_{\mathrm{eq}}(T_e, H)$. The modified Maxwell relation (4) is also obeyed. Finally one can change H in the course of time. Then $\tilde{m} \ll HT_e/K^2$ as long as $\partial H(t)/\partial T_e(t) \ll \beta_e(t)H(t)\Delta^2$. This is a mild condition. If H is changed quicker, or if it goes to zero too rapidly, the system will not be able to reach a quasiequilibrium described by T_e alone.

We have also considered the fluctuation formula. They are too lengthy to be reproduced here. We found

$$\frac{\langle\delta M^2\rangle}{N} = \frac{\Gamma^2T_e}{K^3} - \frac{\Gamma^2T_e^2}{2K^4} + \mathcal{O}(T_e^3) \qquad \frac{\langle\delta\mathcal{H}^2\rangle}{N} = -\frac{K^2\langle\delta\mathcal{H}\,\delta M\rangle}{HN} = \frac{T_e^3}{A}. \tag{19}$$

The latter two relations imply that $\Gamma^2\langle\delta M_s^2\rangle \approx H^2\langle\delta M^2\rangle \approx -\Gamma H\langle\delta M\delta M_s\rangle$. Since there are no fast processes, it immediately follows that the quasiequilibrium relation (5) is satisfied for all four cases, to leading order in T_e. In contrast, for $M_a \rightarrow \mathcal{H}$, $H_a \rightarrow \beta$ or β_e the corresponding relations are violated.

The two-time correlation functions $C_{ab}(t, t')$ and response functions $G_{ab}(t, t')$ exhibit related behavior. These functions decay as $C_{ab}(t, t') = C_{ab}(t', t')h(t')/h(t)$ with $h(t) = \exp(\beta_eA) \sim t(\ln t)^2$ and satisfy the fluctuation-dissipation relation (8) for any nonzero value of H and Γ [15]. (For the oscillator model at zero field these relations were derived in [14].)

Now we consider a cooling experiment from high temperatures. A glass transition will occur when the cooling time scale $T/|\dot{T}|$ becomes comparable to the equilibration time scale $\tau_{\mathrm{eq}}(T_e(t))$. Let us assume that it happens at a low temperature $T_g \ll A$, so at an exponential time scale $t_g = \tau_{\mathrm{eq}}(T_g) \sim \exp\beta_gA$. This will imply that the width of the transition region is small: $\Delta T_g \sim T_g^2/A \ll T_g$. Assuming in that region a nonlinear cooling process of the form $T(t) = (1 - \tilde{Q})T_g + \tilde{Q}\tau_{\mathrm{eq}}^{-1}(t)$, we derive from (16)

$$\frac{\partial T_e}{\partial T} = \frac{T - T_e}{\tilde{Q}}\,\frac{\tau'_{\mathrm{eq}}[T_g + (T - T_g)/\tilde{Q}]}{\tau_{\mathrm{eq}}(T_e)}. \tag{20}$$

This equation is similar to but different from earlier proposals [6,10], and might be universal for narrow glassy transitions. It covers three cases: (a) $\tilde{Q} > 1$, normal cooling towards or in the glass; (b) $0 < \tilde{Q} < 1$, cooling in a glassy state so slowly that equilibrium is achieved later; (c) $\tilde{Q} < 0$, heating up in the glassy state. The apparent specific heat $c = \frac{1}{2}\partial T_e/\partial T$ decreases if cooling is not too slow. In a heating experiment it is negative, but it produces near T_g the well known overshoot $c > \frac{1}{2}$, with height and shape depending solely on $\tilde{Q}$.

In a cooling experiment from large T Eq. (20) yields initially $T_e(t) = T(t)$, up to exponential corrections, describing thermodynamic equilibrium at the instantaneous temperature. Below the glass transition region one has $T_e \approx T_g + (T - T_g)/\tilde{Q} \approx \tau_{\mathrm{eq}}^{-1}(t)$. This agrees with (18) and shows that the actual temperature and the cooling history are irrelevant: to leading order the energy just evolves as if the system had been quenched to zero temperature, and aged there. It can be checked that all relations linear in T_e remain as at $T = 0$, thus supporting the picture (1)–(9).

This solution allows us to check the Ehrenfest relations along the glass transition line $H_g(T)$ in cooling procedures ($\tilde{Q} > 1$). Below the transition region one has $c = 1/2\tilde{Q}$, $\alpha = H/2K^2\tilde{Q}$, and $\chi = \Gamma^2/K^3 - (H/2K^2)\partial T_e/\partial H$. Comparing with the paramagnet and using that along the transition line the equality $T_e = T$ implies that $\partial T_e/\partial T + (\partial T_e/\partial H)(dH_g/dT) = 1$, we find that the jumps in α and χ satisfy the first Ehrenfest relation

$$\Delta\alpha = \Delta\chi\,\frac{dH_g}{dT}\,. \tag{21}$$

Until very recently, it was widely believed that this relation is violated at the glass transition. We pointed out that experimentalists had inserted some short-time value of χ or κ [4], like the "zero-field-cooled" (ZFC) susceptibility χ_{ZFC}, i.e., the first term of χ^{fluct} in Eq. (6). In spin glasses with one step replica symmetry breaking χ_{ZFC} is strictly smaller than the χ of the paramagnet [16]. In the present model, there are no β processes, so χ_{ZFC} even vanishes. On the other hand, the long-time or field-cooled value $\chi_{\mathrm{FC}} = \chi^{\mathrm{fluct}}$ is continuous at T_g. The correct discontinuity, $\Delta\chi = -\chi^{\mathrm{conf}}$ arises from Eq. (7). As $\Delta\alpha = (\partial m/\partial T_e)(\partial T_e/\partial T - 1)$, this explains in detail why the first Ehrenfest relation is satisfied automatically [4].

It was also shown in [4] that the modified Maxwell relation (4) leads to the modified second Ehrenfest relation

$$\frac{\Delta C}{NT_g} = \Delta\alpha\,\frac{dH}{dT} + \frac{1}{N}\left(1 - \frac{\partial T_e}{\partial T}\right)\left(\frac{\partial \mathcal{I}}{\partial T} + \frac{dH_g}{dT}\,\frac{\partial \mathcal{I}}{\partial H}\right). \tag{22}$$

We can now verify that it is also satisfied. The new last term needed for validity beyond equilibrium.

The Prigogine-Defay ratio may be expressed as

$$\Pi \equiv \frac{\Delta C\Delta\chi}{NT_g(\Delta\alpha)^2} = 1 + \frac{1}{N\Delta\alpha}\left(1 - \frac{\partial T_e}{\partial T}\right)\frac{d\mathcal{I}}{dH}\,. \tag{23}$$

The definition looks as an equilibrium relation, and it was shown that Π must be larger than unity for mechanical stability [2]. This was based, however, on the invalid assumption of thermodynamic freezing of a set of unspecified order parameters. The equivalent relation $\Pi = (\Delta C/NT_g\Delta\alpha)dT_g/dH$ allows $\Pi < 1$ if dT_g/dH, which depends on $d\tilde{Q}/dH$, and is small enough. We realized that already in the classic experiment of Rehage and Oels [17] on the glass transition in atactic polystyrene there occurs a value $\Pi = 0.77$ [4]. In our present model $\Pi = (K^2/HT_g)dT_g/dH$ becomes less than unity whenever dt_g/dH is positive. This condition occurs in half of the smoothly related sets of cooling trajectories.

In conclusion, we have proposed a unifying thermodynamic picture of the glassy state. It does not apply to ideally slow experiments, but to conditions that are typically met. As in a plasma, slow and fast modes equilibrate at their own temperature. On long-time scales and under mild conditions, global thermodynamical quantities, like the energy and volume or magnetization(s), go to quasiequilibrium values at a certain effective temperature $T_e(t)$. Slow fluctuations contribute to susceptibilities with factor $1/T_e$. For cooling trajectories at two nearby external fields (pressures), the difference of the magnetization (volume) involves the usual fluctuation susceptibility (compressibility), and a new structural contribution that arises from the difference in effective temperatures. Correlation and response functions exhibit t/t' scaling, and satisfy a fluctuation-dissipation relation involving T_e.

We have verified our picture in the glassy phase of the low-temperature dynamics of an exactly solvable toy model that contains two external fields. We expect that the fields may also stand for other "mechanical" forces, such as pressure or chemical potential.

The picture has the right signs to be valid for a class of glassy systems. For verifying it in glass forming liquids it is desirable to map out the full (T, T_e, p)-space by cooling experiments, and to check that against aging experiments.

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