Ehrenfest Relations at the Glass Transition: Solution to an Old Paradox

Th. M. Nieuwenhuizen
Van der Waals-Zeeman Laboratorium, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

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In order to find out whether there exists a thermodynamic description of the glass phase, the Ehrenfest relations along the glass transition line are reconsidered. It is explained that the one involving the compressibility is always satisfied, and that the one involving the specific heat is principally incorrect. Thermodynamical relations are presented for nonergodic systems with a one-level tree in phase space. They are derived for a spin glass model, checked for other models, and expected to apply, e.g., to glass-forming liquids. The second Ehrenfest relation gets a contribution from the configurational entropy. [S0031-9007(97)03875-1]

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The glass transition is a dynamical freezing transition that occurs when a liquid is supercooled. The transition is smeared, but becomes sharper the slower one cools. For ideal, adiabatic cooling the transition will be sharp and occurs at the Kauzmann temperature T_K.

Experimentally it is known that second derivatives of the free energy, the specific heat, the compressibility, and the thermal expansivity, make a (smeared) jump from their liquid values to smaller values in the glass. Since many decades in time are involved, one might therefore wonder whether it can be described as a (smeared) second order phase transition. This idea has been put forward by Gibbs, DiMarzio, and Adam [1]. As thermodynamics amounts to system-independent laws, the approach leads to sine-qua-non relations along the glass transition line $p(T)$. They are the Ehrenfest relations

$$\Delta\kappa\,\frac{dp}{dT} = \Delta\alpha\,, \tag{1}$$

$$\frac{\Delta C_p}{TV} = \Delta\alpha\,\frac{dp}{dT}\,, \tag{2}$$

where $\Delta A \equiv A_{\text{liquid}} - A_{\text{glass}}$ for any A. From experiments it was concluded that the first relation is usually violated, while the second is closely satisfied in most cases, but not in all. (For reviews see [2,3].) The Prigogine-Defay ratio

$$\Pi \equiv \frac{\Delta C_p \Delta\kappa}{TV(\Delta\alpha)^2} \tag{3}$$

should be equal to $\Pi = 1$. Experimental values are typically found, however, in the range $2 < \Pi < 5$. It is generally believed that $\Pi = 1$ is a strict lower bound.

In an extension of the theory one assumes that at the transition a number of (unspecified) internal variables Z_i freeze in, and that the configurational entropy is constant along the transition line. This modifies (1) and (2) but keeps $\Pi = 1$ [4]. These negative results have prevented further development of a thermodynamic approach.

In this Letter we first explain that the first Ehrenfest relation is automatically satisfied (already in the reported measurements). By the same reasoning we shall conclude that the second relation must be incorrect. Analyzing model systems we shall then derive an extra contribution that arises from the configurational entropy.

Before discussing the meaning of the Ehrenfest relations, we first have to define the experiment, or, better said, the set of experiments, to be performed. Let us consider for definiteness cooling of a glass-forming liquid at a fixed pressure p_1 and cooling rate $Q = -dT/dt$. Starting from a high temperature one measures the specific volume $V(T; p_1)$. It is linear at large T and at low T and has a smooth crossover between these behaviors. This happens near the freezing temperature T_1. Let us then repeat the cooling experiment at a large set of different pressures p_i, with moderate steps $p_i - p_{i-1}$. This will lead to a set of freezing temperatures T_i, which define a smooth freezing line $p(T)$. The location of this line is by no means universal. It is defined by our set of measurements, here the set of p_i's and their common value Q of the cooling rate. Different smooth sets of experiments may involve a different cooling rate Q', nonuniform cooling by letting $Q \to Q_i$ depend smoothly on p_i, nonlinear cooling, or cooling where p also changes in time. All these sets of experiments will in principle lead to different transition curves $p(T)$. In practice this means that old works in literature, where the cooling procedure has not been specified, are not reproducible. Likewise, computer experiments, with their extremely high cooling rates, cannot yield realistic glass transition temperatures.

To test the first Ehrenfest relation (1) one needs $\kappa = -\partial \ln V/\partial p|_T$, which is difficult to determine from cooling curves at two consecutive pressures. Therefore it has become standard to measure κ_1 in the glass phase by cooling at p_1 down below T_1 and then making small pressure variations [5]. Such procedures, however, lead to a determination of dp/dT from an experiment at (essentially) p_1 only, *a contradictio inter terminis. No experiment at one pressure can fix the slope of the transition line,* because that depends on the conditions under which the set of experiments will be performed [6]. The hope that the compressibility could be obtained by small pressure variations is frustrated by the history dependence of the glassy state. A closely related phenomenon is known from experiments on spin glasses: the short-time ("zero-field cooled") susceptibility $\chi_{\rm ZFC} = (1 - q_{\rm EA})/T$ is lower than the long-time ("field cooled") susceptibility $\chi_{\rm FC} = [1 - \int_0^1 dx\, q(x)]/T$, where $q_{\rm EA}$ is the Edwards-Anderson order parameter and where $q(x) \leq q_{\rm EA}$ is the Parisi order parameter function. In the glass the short-time value of κ (measured by small pressure steps [5]) will also be too low, yielding the observed too large $\Delta\kappa$.

The correct procedure is obvious and comes from the meaning of the Ehrenfest relation. The continuity of the specific volume can be considered at two glass transition points (T_1, p_1) and (T_2, p_2), where $\Delta V = 0$. One may thus write $\Delta V(T_1, p_1) - \Delta V(T_1, p_2) = \Delta V(T_2, p_2) - \Delta V(T_1, p_2)$. [The terms at (T_1, p_2) do not vanish.] Dividing by $p_1 - p_2$ and taking the limit $p_2 \to p_1$ this, of course, leads to Eq. (1). However, we must use on both sides of the equality the same values of $p_1 - p_2$; it should not be taken "infinitesimal" on the left-hand side and only "small" on the right-hand side. In practice *the only way* is to determine κ from the curves $V(T; p_i)$. Modern computer graphics allows one to fit all the experimental data above and below the transition regions to high- and low-T surfaces in V-p-T space. Using all data should lead to reasonable fits. The intersection line of the surfaces will satisfy Eq. (1). This approach thus explains the old paradox: If properly interpreted, the first Ehrenfest relation is satisfied automatically. As there is no second procedure to produce the same glassy state, there is hardly a point in testing (1) experimentally.

By the same token the second Ehrenfest relation (2), relating dp/dT to measurements at one pressure only, cannot be correct. Likewise, the Maxwell relation $\partial U/\partial p + p\,\partial V/\partial p = -T\,\partial V/\partial T$ must be violated in the glass. We now show how unexpected behavior of the configurational entropy modifies it. Below we discuss the derivation for spin glasses, and then extend it to the glass transition in the hypernetted chain approximation. We believe that these relations are very general, and first formulate them for glass-forming liquids.

For glassy systems the entropy consists of two terms. $S_{\rm int}$ is the internal entropy, related to the glassy state the system condenses into; it lies well below the liquid entropy. $\mathcal{I}_c$ is the configurational entropy due to the number of equivalent glassy states. It is extensive at dynamical transitions, and becomes subextensive only for ideal adiabatic cooling. This part of the entropy is "lost" in the glass transition region. The quantity $T\,\partial S_{\rm int}/\partial T|_p$ will generally be smaller than the specific heat $C_p = \partial(U + pV)/\partial T|_p$. In spin glass models the configurational entropy contributes to the free energy as $-(T/x)\mathcal{I}_c$, where x is the weight $(0 \leq x \leq 1)$ occurring as the break point of the one-step replica symmetry breaking Parisi order parameter function. x also shows up dynamically as the factor by which the fluctuation-dissipation theorem is broken at long times [7]. $T_e \equiv T/x$ can be considered as effective temperature at which processes related to the configurational entropy thermalize [8].

It was shown that $C_p = T\,\partial S_{\rm int}/\partial T + T_e\,\partial \mathcal{I}_c/\partial T$ [9]. We are now in the position to take the first derivatives of the free enthalpy $G = U + pV - TS_{\rm int} - T_e\mathcal{I}_c$. This yields

$$\frac{\partial G}{\partial T} = -S_{\rm int} - \frac{\partial T_e}{\partial T}\,\mathcal{I}_c; \qquad \frac{\partial G}{\partial p} = V - \frac{\partial T_e}{\partial p}\,\mathcal{I}_c\,. \qquad (4)$$

Along the transition line G, $S_{\rm liq} = S_{\rm int} + \mathcal{I}_c$ and V are continuous with respect to the liquid. The standard assumption that the first derivatives of G are also continuous is seen to be incorrect [10]: the terms involving T_e are nontrivial in the glass $(\partial T_e/\partial T < 1,\ \partial T_e/\partial p \neq 0)$. The finite difference in slopes discussed here is due to unexpected behavior of the configurational entropy [10], neglected so far. It leads to the modified Maxwell relation

$$\frac{1}{T}\frac{\partial U}{\partial p} + \frac{p}{T}\frac{\partial V}{\partial p} + \frac{\partial V}{\partial T} = \left(\frac{T_e}{T} - \frac{\partial T_e}{\partial T}\right) \times \frac{\partial \mathcal{I}_c}{\partial p} + \frac{\partial T_e}{\partial p}\frac{\partial \mathcal{I}_c}{\partial T}\,. \qquad (5)$$

Along the freezing line one has $T_e[T, p(T)] = T$ and one may define the total derivative $d/dT = \partial/\partial T + (dp/dT)\partial/\partial p$. Equation (4) does not violate the balance: $d\Delta G/dT = 0$ since $dT_e/dT = 1$. Let us now consider Eq. (5) and subtract the values on the liquid side. Multiplying by dp/dT and using $dT_e/dT = 1$, $d\Delta U/dT = d\Delta V/dT = 0$ we obtain from (5) the modification of the second Ehrenfest relation [cf. Eq. (2)]

$$\frac{\Delta C_p}{TV} = \Delta\alpha\,\frac{dp}{dT} + \left(1 - \frac{\partial T_e}{\partial T}\right)\frac{1}{V}\,\frac{d\mathcal{I}_c}{dT}\,. \qquad (6)$$

This relation indeed connects dp/dT with another derivative along the transition line, namely, that of the configurational entropy. This term originates from the difference in slopes of the liquid and glass free enthalpies. The factor $1 - \partial T_e/\partial T > 0$ is a nontrivial weight. Since the first Ehrenfest relation is satisfied, measurement of κ is not needed for the Prigogine-Defay ratio: $\Pi = \tilde{\Pi}\,dT/dp$ with $\tilde{\Pi} = \Delta C_p/(TV\Delta\alpha)$ determined at one pressure. Π will be less than unity when $d\mathcal{I}_c/dT < 0$.

We now consider the data of Rehage and Oels for the glass transition of atactic polystyrene [11]. For cooling at a speed of 18 K/h at $p = 1$ bar they report $T = 361$ K, $\Delta C_p/V = 0.30$ J/g K, $\Delta\alpha = 3.5 \times 10^{-4}$ cm^3/g K, $dp/dT = 0.31$ bar/K, and $\Delta\kappa = 1.6 \times 10^{-5}$ cm^3/g bar. This was reported to yield $\Pi = 1.06 \approx 1.0$, and a violation of the first Ehrenfest relation. This violation has, however, already been traced back to the way κ was measured. Our Prigogine-Defay ratio $\Pi = \tilde{\Pi}\,dT/dp = 0.77$ *is less than unity.* The last term in Eq. (6) is negative and brings 23% of the value for the slope dp/dT, a large effect.

We have discussed how the configurational entropy modifies an Ehrenfest relation. This effect should be stronger for first order glass transitions, which occur, for instance, in water [3]. In the p-spin model [see Eq. (8)] this happens when the transversal field Γ exceeds a critical value [12]. Using that along the dynamical transition line $\Delta G = d\Delta G/dT = 0$ and Eq. (4) we obtain

$$\Delta V \frac{dp}{dT} = \frac{1}{T}(\Delta U + p\Delta V) + \left(\frac{T_e}{T} - \frac{\partial T_e}{\partial T}\right)\mathcal{I}_c, \qquad (7)$$

which deviates by the $\mathcal{I}_c$ term from the static Clausius-Clapeyron equation. Note that $x = T/T_e$ is below unity.

Let us now give the theoretical background of our relations. They have initially been derived within a spherical p-spin interaction spin glass. For a system of m-component spherical spins S_i^c ($i = 1, \ldots, N$, $c = 1, \ldots, m$), satisfying $\sum_{i,c} S_i^{c\,2} = N$, we consider the Hamiltonian in a transversal field

$$\mathcal{H} = -\sum_{i_1<\cdots<i_p} J_{i_1 i_2 \cdots i_p} S^z_{i_1} S^z_{i_2} \cdots S^z_{i_p} - \Gamma \sum_i S_i^x. \qquad (8)$$

The independent Gaussian quenched random couplings have average zero and variance $J^2 p!/2N^{p-1}$. The system has a multitude of states $a = 1, \ldots, \mathcal{N}$, each with its own free energy F_a that is a local minimum of a known Thouless-Anderson-Palmer (TAP)-free energy functional. The replica calculation with one-step replica symmetry breaking involves parameters μ, q_d, q_1, and x, leading to the free energy [12]

$$\begin{aligned}\frac{F}{N} = &-\frac{\beta J^2}{4}(q_d^p - \xi q_1^p) - \frac{T}{2x}\ln(q_d - \xi q_1) \\ &+ \frac{T\xi}{2x}\ln(q_d - q_1) + \frac{\mu}{2}(q_d - 1) \\ &- \frac{\Gamma^2}{2\mu} + \frac{(m-1)T}{2}\ln\frac{\mu}{T}, \end{aligned} \qquad (9)$$

where $\xi = 1 - x$. μ, q_d, and q_1 are determined by optimizing F. It was recently pointed out by us that the value of x is related to the time scale at which the system is considered [9]. Indeed, setting $\partial F/\partial x = 0$ [leading to Eq. (10) with $\eta \rightarrow \eta_{st} < 1$ independent of T and Γ] yields the static phase transition at the Kauzmann temperature T_K, related to the longest time scale. On the other hand, the marginality condition [Eq. (10) with $\eta = 1$] describes algebraic time scales, at which a transition occurs at a higher temperature T_A. This is reproduced by the mode-coupling equations, and is comparable to the sharp critical temperature occurring in mode-coupling equations for glasses. As this transition is absent in practice, we have considered the system at exponential time scales $t = t_0 \exp(N\tau)$ [9]. At given τ barriers with free energy height less than $N T\tau$ can be surpassed. η parametrizes the value of the free energies of the states a. As time evolves, the dominant lowest reached free energy $F_{\min}(t)$ has parameter $\eta(t)$. When, at fixed field Γ_1, the temperature $T(t)$ is also slowly lowered, we can eliminate t to obtain a function $\eta(T; \Gamma_1)$. Cooling trajectories at a large set of fields Γ_i define a set of experiments. If the set is "smooth" it will lead to a smooth function $\eta(T; \Gamma)$. This function should follow from solving the dynamical equations. We shall not do that, but remain on a quasistatic level, where the information of the cooling dynamics is coded in the function $\eta(T; \Gamma)$.

In our present analysis a freezing transition occurs when the temperature, below which the dominant lowest reached state will freeze, is equal to the actual temperature. We assume that we can still describe the situation by the Gibbs weight, which is the case when no relevant parts of phase have become inaccessible.

The free energy of the TAP states can be characterized by a parameter η ($\eta_{st} \leq \eta \leq 1$) that enters the condition

$$\frac{1}{2}\beta^2 p(p-1) q_1^{p-2} = \frac{\eta}{(q_d - q_1)^2}. \qquad (10)$$

In solving the saddle point equations for μ, q_d, and q_1, the above relation fixes $x = (p - 1 - \eta)(q_d - q_1)/\eta q_1$. One can calculate all quantities of interest. We have verified the following relations for $F(T, T_e(T, \Gamma), \Gamma)$:

$$F = U - TS_{\text{int}} - T_e \mathcal{I}_c; \qquad M = -\left.\frac{\partial F}{\partial \Gamma}\right|_{T,T_e}, \qquad (11)$$

$$S_{\text{int}} = -\left.\frac{\partial F}{\partial T}\right|_{T_e,\Gamma}; \qquad \mathcal{I}_c = -\left.\frac{\partial F}{\partial T_e}\right|_{T,\Gamma}, \qquad (12)$$

$$C \equiv \left.\frac{\partial U}{\partial T}\right|_{\Gamma} = T\left.\frac{\partial S_{\text{int}}}{\partial T}\right|_{\Gamma} + T_e \left.\frac{\partial \mathcal{I}_c}{\partial T}\right|_{\Gamma}. \qquad (13)$$

This implies the modified Maxwell relation

$$\begin{aligned}\frac{\partial U}{\partial \Gamma} + M - T\frac{\partial M}{\partial T} = &\left(T_e - T\frac{\partial T_e}{\partial T}\right)\frac{\partial \mathcal{I}_c}{\partial \Gamma} \\ &+ T\frac{\partial T_e}{\partial \Gamma}\frac{\partial \mathcal{I}_c}{\partial T}. \end{aligned} \qquad (14)$$

F, U, S_{int}, $\mathcal{I}_c$, M, and T_e only depend on the value of η in the point (T, Γ). Their temperature derivatives also depend on $\partial\eta/\partial T$, while their field derivatives involve $\partial\eta/\partial p$, the measure of variation between experiments at different fields.

The second Ehrenfest relation can be rederived by multiplying Eq. (14) by $(1/NT)d\Gamma/dT$. This yields generally

$$\begin{aligned}\frac{\Delta C}{NT} = &\Delta\alpha \frac{d\Gamma}{dT} + \left(1 - \frac{\partial T_e}{\partial T}\right)\frac{d\mathcal{I}_c}{NdT} \\ &- \left(1 - \frac{dT_e}{dT}\right)\frac{\partial \mathcal{I}_c}{N\partial T}, \end{aligned} \qquad (15)$$

while $\Delta\alpha = \Delta\chi\, d\Gamma/dT$ is again satisfied, where $\alpha \equiv -(\partial M/\partial T)/N$ and $\chi = (\partial M/\partial \Gamma)/N$. In comparing with (6) one should keep in mind that $dT_e/dT = 1$. Equation (15) also applies to the case where one starts cooling adiabatically below T_K. At freezing one then has $\mathcal{I}_c = d\mathcal{I}_c/dT = 0$, but the last term is nonzero.

$d\mathcal{I}_c/dT$ does not depend on $\partial\eta/\partial T$ but only on $d\Gamma/dT$. It holds that ΔC, $\Delta\alpha$, and $\Delta\chi$ are proportional to $1 - \partial T_e/\partial T$ (since near the transition $U_{\rm sg} - U_{\rm PM} \sim x - 1$).

The relations (11)–(15) are expected to be universal for dynamical glassy transitions with extensive configurational entropy. We have considered three other cases:

(1) In the case of a longitudinal field ($\Gamma \sum S_i^x \to H \sum S_i^z$) the same equations are satisfied; see also [9].

(2) The hypernetted chain equation of fluids is an approximate nonlinear integral equation for the pair-correlation function [13]. Mézard and Parisi [14] pointed out that in a certain region it has many solutions, describing a glass phase. By weakly coupling different copies (replicas) of the system, they introduced a replica calculus. The main difference with the above spin glass is that the spin-spin overlap is replaced by the pair-correlation function. The static transition again follows from the relation $\partial F/\partial x = 0$. Dynamically this relation is not satisfied, and there is an extensive configurational entropy. We now can make the same assumptions as in the above spin glass and will rederive Eq. (6).

(3) Recently we have introduced a model of a directed polymer on a square lattice with a correlated random potential, consisting of randomly located parallel ridges (repulsive potentials) [15]. The polymer prefers to lie in broad lanes (width ℓ) in between ridges, of which there occur a lot when the transversal width scales as $W = \exp(\lambda L^{1/3})$ in the parallel width L. The free energy reads

$$F = Lf_B(T) + \frac{\Gamma(T)LT}{2\ell^2} - \nu\ell - T\mathcal{I}_c\,, \qquad (16)$$

where $f_B(T)$ is an uninteresting bulk free energy density, Γ is the interface stiffness, $\exp(-\mu)$ is the chance for having no ridge at a given height, and ν is a chemical potential favoring ($\nu > 0$) or disfavoring ($\nu < 0$) wide lanes, and $\mathcal{I}_c = \log W - \mu\ell$ is the complexity. At some T_K, where $\gamma(T;\nu) \equiv (\mu/\lambda)[T\Gamma(T)/(T\mu - \nu)]^{1/3}$ equals $\gamma(T;\nu) = 1$, there occurs a static "Kauzmann" transition from a high-temperature phase, where the polymer lies in the broadest lane ($\ell = \ell_{\max} \equiv \lambda L^{1/3}/\mu$), to a low-temperature phase, where it spends most of the time in a set of narrower lanes ($\ell^* = \gamma\ell_{\max}$ with $\gamma < 1$).

Starting from a large set of uniformly distributed independent polymers, we are interested in the dynamical (short time) regime A, where (16) is valid with ℓ increasing logarithmically with time [15]. In order to make contact with previous theory, we replace $T\mathcal{I}_c$ in (16) by $T_e\mathcal{I}_c$ where $T_e(t) = LT\Gamma(T)/[\mu\ell(t)]^3 + \nu/\mu$. A minimum will then occur at $\ell = \ell(t)$. In the polymer model one has a reversed role of heating and cooling [15]. A set of experiments can be introduced by specifying smoothly related heating trajectories at a large number of ν_i's. For each of them a dynamical phase transition can occur at any $T < T_K(\nu_i)$, where the dominant width $\ell(t)$ reached so far equals its freezing value $\ell^*[T(t)]$. This transition is very similar to the ones above. Equations (11)–(15) are satisfied with $\Gamma \to \nu$. As before, $\mathcal{I}_c$ is large at the transition. The second term in the right-hand side of Eq. (15) is finite, while the last one vanishes. A related transition can occur at any $T > T_K$. Then the transition line is $\ell(t) = \ell_{\max}$, where $\mathcal{I}_c = 0$. Now the last term in (15) is nonvanishing [16].

In conclusion, we have pointed out that the present understanding of the Ehrenfest relations is incorrect. We have explained that the first one is satisfied automatically and that the second one must be modified. From quasistatic model calculations we have shown that it gets an extra contribution from the configurational entropy. This explains that the Prigogine-Defay ratio is smaller than unity in the experiments or Ref. [11].

We have also presented the generalization of the standard thermodynamical laws to nonergodic situations with a one-level tree in phase space. This is given in Eqs. (11)–(14), where T_e is an effective temperature, that depends slowly on time. Along the transition line the modified Maxwell relation Eq. (14) leads to a new form (6) and (15) of the second Ehrenfest relation. We have checked the predictions in several model systems.

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Note added.—We have checked our Ehrenfest relations for cooling in the backgammon model, which has no disorder but entropic barriers [17].

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