A rheological model of the calorimetric glass transition

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Abstract. The connection between phase transitions (PTs) and calorimetric glass transitions (CGTs) is considered, first with reference to second order PTs as described by Ehrenfest, then by comparison with a rheological approach. This results in connecting the partition functions of the 'ideal' liquid with that of the 'ideal' glass, by means of a 'real' partition function, explicitly depending on the cooling (heating) rate. By requiring the entropy and heat capacity at any cooling rate in the rheological model to be positive, it turns out that the CGT sharpens with decreasing difference between the two ideal free energies, and not simply with decreasing cooling rate. In addition, it is impossible to make the two ideal free energies join at arbitrary low cooling rates without singularities, if their difference is non-vanishing at zero temperature. If this is not the case, a lower limiting critical cooling rate is predicted, at which a *secondary* (or β) relaxation toward the glass becomes a *true* PT. Under special conditions, the primary (or α) relaxation can *simulate* a true PT, in which case one may speak of a 'false' PT. A classification of glass-forming materials is possible, based on the difference between false PTs simulating first-order PTs (class (A) materials), or second-order PTs (class (B) materials). The rheological model is also discussed in connection with the mode-coupling theory of the glass transition.

1. Introduction

The possible linkage between the glass transition (GT) and some kind of phase transition (PT) is one of the most debated problems in the theory of liquid and glassy systems. There is at present an increasing deal of experimental evidence [1–5] supporting the existence of a true (though non-conventional) PT in the undercooled liquid, as predicted by the mode-coupling theory [6–11]. This PT marks the transition from a liquid phase governed by cooperative motions, all related to a *single* time scale decreasing with temperature, to a different liquid phase, whose behaviour is still ergodic, but essentially due to thermally activated processes, and evolving with *different* scaling times [12]. The critical temperature T_{MC} of this process (MC stands for mode coupling) is in general 10–20% higher than the temperature T_g around which the so called 'calorimetric' glass transition (CGT) occurs. The latter process is macroscopically marked by the increase of the shear viscosity up to solid-like values, by smoothed discontinuities in the heat capacity, compressibility and expansivity, and by the dependence of the whole process on the thermal history of the sample. On this basis, the identification of the CGTs with the *dynamical* PT predicted by the mode-coupling theory is quite unlikely [13], but the possible connection between CGTs and *thermodynamical* PTs is still an open question which will be discussed in the present paper. Surveys on the same topics have been given by Owens [14], Jäckle [15] and Sethna *et al* [16].

As opposed to the thermodynamical models suggesting a PT picture for the CGT [16–19], the 'rheological' approach [20] puts more emphasis on the divergence of the relaxation

times typical of the viscous flow, without special attention to any 'underlying' PT. This approach points to a purely kinetic picture of the CGT, in which all the relevant phenomena can be interpreted as a consequence of the structural arrest of the viscous flow, when the corresponding relaxation time exceeds the measurement time scales.

In the present paper, we discuss the PT–CGT linkage starting from the rheological approach just outlined. First we consider the following question:

(i) can the CGT be linked to a second-order thermodynamical PT as described by Ehrenfest?

which naturally arises when considering the jumps observed in many cases at the CGT in second-order susceptibilities. Arguments for a negative answer are usually found from the violation of the Ehrenfest theorems connecting the rate of change of T_c (the PT temperature) with pressure, to the discontinuities of the thermal quantities at a second-order PT [21, 22]. Very recently, Hunt [23] has discussed the question (i) in the same context, with special attention to the dependence of the CGT temperature T_g on the measurement time, which is also the starting point of the present paper. However, the negative answer we shall give in what follows to question (i) is not based on the Ehrenfest theorems, but on a much more elementary argument (see section 2) which, to our knowledge, has never been reported explicitly in the preceding literature, apart from a short mention given by ourselves without formal details [22]. Gupta and Moyninhan [21] seem to allude to a closely related problem, but with different aims and methods. The present approach to question (i) (section 3) will also introduce some aspects of the CGT–PT linkage which will be useful for the second part of the paper (sections 4–6), where the rheological model is discussed. By the rheological model (section 4) we mean a semi-empirical approach to the 'real' partition function, which includes the cooling-rate effects. The 'concavity' of the free energy, which is necessary and sufficient for the entropy and heat capacity to be positive, will turn out to be a very stringent condition (section 5). In particular, it will be shown that the CGT sharpens with the difference in modulus between the ideal-liquid and ideal-glass free energy, and not simply with the cooling rate [15, 24–26]. In addition, if the difference between the ideal-liquid and the ideal-glass free energy is non-vanishing for vanishing temperature, the rheological model predicts the following alternative: either a *true* second-order PT occurs at low cooling rates, which should describe the *secondary* (β) relaxation, or the secondary relaxation itself is absent. In section 6 all these aspects will be compared with recent experimental data [24–26]. We also consider the possible coexistence of the true PT with a 'false' PT at higher temperatures, marked by a fairly abrupt change of the heat capacity, and describing the primary (α) relaxation. Finally we discuss the connection and the compatibility between the rheological approach and the mode-coupling theory (MCT) of the glass transition.

2. Odd-order and even-order phase transitions according to Ehrenfest

According to the old classification due to Ehrenfest, a PT is only characterized by the fact that some derivative of the free energy G is discontinuous at some critical point. To avoid irrelevant complications, we shall refer in the following only to jth-order *thermal* susceptibilities, that is, derivatives such as $\partial^j G / \partial T^j$ (which we write as $\partial^j G$ for brevity), with a discontinuity at some critical *temperature* T_c. Implicit in the Ehrenfest classification is the possibility of defining a low-temperature and a high-temperature phase, in equilibrium at T_c, each characterized by its own free energy G_L and G_H respectively. By distinguishing

between left-hand side (−) and right-hand side (+) limits, the discontinuity condition thus reads

$$\lim_{T \to T_c^+} \partial^j G_H(T) = \lim_{T \to T_c^-} \partial^j G_L(T) \qquad (j < n)$$

$$\lim_{T \to T_c^+} \partial^n G_H(T) \neq \lim_{T \to T_c^-} \partial^n G_L(T). \qquad (1)$$

If one of the two phases (or both) can be physically extended, as a *metastable* state, in the region where the other is *stable*, we say that the two phases *coexist*. In this case, a second condition is to be accounted for defining G_L and G_H as the stable free energies for $T < T_c$ and $T > T_c$ respectively:

$$G_L(T) < G_H(T) \qquad \text{for } T < T_c \text{ (if the two phases coexist } below \ T_c)$$

$$G_L(T) > G_H(T) \qquad \text{for } T > T_c \text{ (if the two phases coexist } above \ T_c). \qquad (2)$$

From the conditions (1) and (2) it readily follows that

(ii) only if n in (1) is *odd* can T_c be an *internal* point of the interval in which the two phases coexist.

In fact, from condition (1) one should write $\Delta G = G_L - G_H = A(T - T_c)^n$ (A is a constant), in a sufficiently small *open* interval containing T_c, but from condition (2), ΔG must change sign when crossing T_c, so that n is necessarily odd. Hence the qualitative feature which distinguishes odd from even-order PTs as described by Ehrenfest is that the critical temperature of the latter is necessarily a *border* point of the coexistence interval of the two phases. In more physical language,

(iii) if n is even, then one of the two phases cannot be *physically* extended across T_c.

3. Calorimetric glass transition and second-order phase transitions following Ehrenfest

The special feature which we need to stress about the CGT is that by changing the cooling rate Q, it is possible to shift the glass-transition temperature T_g. In fact, it is experimentally shown that T_g increases logarithmically with the cooling rate. Two functional forms have been suggested: in [27]

$$T_g(Q) = T_m/[1 + C \ln(Q_M/Q)] \qquad (3)$$

and in [24]

$$T_g(Q) = T_g^0 + T_A/\ln(Q_M/Q) \qquad (4)$$

which we shall discuss in what follows. Equations (3) and (4) should not be extended to $Q = 0$, since a *finite* lower limiting cooling rate Q_m will certainly exist, larger than or equal to the critical cooling rate below which the system crystallizes. However, from (3) and (4) one must conclude that the glassy and the liquid 'phases' do coexist in a temperature interval at least as large as that spanned by $T_g(Q)$, when Q varies in the range of experimentally accessible values. Sometimes it is assumed for theoretical speculations that the (undercooled) liquid and the glass ideally coexist in the whole interval between the Kauzmann temperature T_K and the melting temperature T_m. The argument in section 2 leads one to exclude the possibility that any even-order PT can describe the CGT, if the critical temperature has to fall *inside* this coexistence interval. Some consequences are as follows:

(a) In any model describing the CGT as a second-order PT as described by Ehrenfest the critical temperature T_c coincides necessarily with the limiting value $T_g(Q_m)$.

In fact only under this condition is one granted that T_c is at the border of the liquid–glass coexistence interval, as required by the even-order condition. According to this argument

(b) it is quite misleading to support the PT picture for CGTs with the *experimental* evidence that many glass formers exhibit a 'discontinuity' in the heat capacity, as expected from a second-order PT.

If one refers to an experimentally observed GT, the cooling rate Q_{exp} falls manifestly between Q_m and Q_M, so that the critical temperature at which the heat capacity exhibits a jump certainly does fall inside the liquid–glass coexistence interval. This however excludes any even-order PT.

A further consequence of statements (ii) and (iii) is that

(c) the only way to connect a CGT occurring at a non-critical cooling rate with a *thermodynamical* PT is to assume that the latter is odd order.

It is worth stressing that the present criticism of the linkage between CGTs and *thermodynamical* PTs has a common aspect with Jäckle's criticism [13] concerning the *dynamical* PT predicted by MCT. In both cases, the crucial point is the cooling rate. In particular, Jäckle points out that MCT is not able to account for cooling-rate effects. In the conclusive part of the paper, we will show that the rheological model of the CGT is compatible with MCT, so both pictures can be used in parallel, to fill in the gap between the rheological effects and MCT.

4. A 'rheological' picture of the undercooled melt

In the next part of the paper we will attempt to formulate a model, based on the rheological picture of the CGT, in which the cooling-rate effects are included *ab initio*. The results will be used both to support the applicability of the model itself to realistic situations, and to make further comparisons with the PT picture.

In the rheological approach to the CGT the relevant quantity in the problem is the ratio (whose reciprocal is denoted as the *Deborah number* [28]

$$\sigma = \tau_{meas}/\tau_{visc} = \Delta T/Q\tau_{visc} \tag{5}$$

where τ_{meas} is the measurement time and τ_{visc} is the relaxation time for the viscous flow. The second equation (5) is obtained for a specific process, that is, a cooling (heating) occurring at a mean rate $Q = \Delta T/\tau_{meas}$, ΔT being the *finite* change of temperature occurring in the real process of cooling/heating [15]. We stress that, if $T(t)$ describes a *monotonic* change of the temperature T with the time, than $Q = dT/dt$ can be expressed as an explicit function of T itself. Hence (5) is rather general, though we will refer in the next only to processes at *constant* cooling rate. The ratio σ is a measure of the ergodicity of the system, with respect to the slow degrees of freedom which describe the viscous flow of the liquid: $\sigma = \infty$ means that the system is ergodic (ideal liquid) and the free energy is given by an average over all modes. In contrast, $\sigma = 0$ means that the slow degrees of freedom are completely 'frozen in' (ideal glass) and the free energy is obtained by a *non-ergodic* thermal average, performed only over the 'fast' modes (typically, the oscillatory motions), by taking fixed

values for the slow ones [15, 29]. A possible way to connect these two extreme situations, for any value of σ, is to write the 'real' Q-dependent partition function as

$$Z_\sigma = \int \frac{d\{q_f\}d\{v_f\}}{\Omega_F} \int d\{q_s\}d\{v_s\} G_\sigma(\{q_s\}, \{v_s\}) \exp[-\beta H(\{q_f, v_f\}|\{q_s, v_s\})] \tag{6a}$$

($\beta = 1/\kappa T$), where $\{q_a\}$ and $\{v_a\}$ are suitable Lagrangian parameters and velocities respectively, split into fast ($a = f$) and slow ($a = s$) components, which determine the energy H. Ω_F is an elementary volume of the fast-mode phase space, and the function G_σ satisfies the following conditions:

$$\lim_{\sigma \to 0} G_\sigma = \delta(\{q_s\} - \{X_g\})\delta(\{v_s\}) \qquad \lim_{\sigma \to \infty} G_\sigma = 1/\Omega_S. \tag{6b}$$

The first relation (6b) accounts for the non-ergodic limit, in which the slow modes are frozen in a single glassy configuration $\{X_g\}$, with zero velocity. The second relation (6b) accounts for the ergodic limit in which the whole phase space of the slow modes becomes available with uniform probability (Ω_S is an elementary volume of the 'slow' phase space). The basic assumption underlying (6) is that even in a non-equilibrium process such as that envisaged, a partition function can be defined by integration over the phase space, provided that a suitable weighting factor depending on the thermal process is introduced. Probably, this assumption should not be applied *tout court* to all non-equilibrium processes, but it looks reasonable in a case such as the CGT, in which the temperature is operatively defined during all the process, and thermal equilibrium is certainly achieved (on the measurement time scale) for both the initial and final states. From (5) and (6a) one should notice that on the temperature scale the 'sharpness' of the CGT is greatly influenced by the rate of change of τ_{visc} with the temperature. In particular it is possible to deduce (3) and (4) from the expressions

$$\tau_{visc} = \tau_0 e^{(\beta E_{act})} \tag{7a}$$

($\beta = 1/\kappa T$), and

$$\tau_{visc} = \tau_0 \exp[T_A/(T - T_g^0)] \tag{7b}$$

respectively [15, 23, 24]. (7a) is experimentally verified for most glass-forming materials, close enough to the CGT temperature T_g [30], while (7b), denoted the Vogel–Fulcher law, is more controversial. For example, Brüning and Samwer [24] stress that the best-fit value T_g^0 in (7b), estimated from the experimental data on $T_g(Q)$ (4b), turns out to be significantly higher than the same value best fitted to the viscosity data. In any case, (4b) introduces a finite-temperature divergence of some characteristic time scale, which is suggestive of a possible critical behaviour at T_g^0. For the rheological picture in itself, the choice between (4a, 7a) and (4b, 7b) is not crucial, and can be assumed as an external input.

In order to evaluate the integral over the slow modes, we introduce the total number of 'slow' states

$$M_\sigma = \int d\{q_s\} d\{v_s\} G_\sigma \stackrel{def}{=} (m_\sigma)^N \tag{8}$$

which contribute to the thermal average for a given value of σ. We also define the average number m_σ of states per particle (in a total number of N). According to (6b), M_σ ranges

between $M_0 = 1$ (the ideal glass) and a maximum value M_∞ for the ideal liquid. As discussed elsewhere [29], one expects the liquid energy to be the sum of a fast- and a slow-mode contribution

$$H = H_f(\{q_f\}, \{v_f\}) + H_s(\{q_s\}, \{v_s\}|T) \tag{9}$$

where the latter may depend explicitly on T. In fact, the analogy with the Born–Oppenheimer approximation suggests that the slow effective Hamiltonian H_s does also depend on the *thermal* average $\langle H_f \rangle_T$ performed over the fast modes. After multiplying and dividing ($6a$) by M_σ, one notices that $G_\sigma(\ldots)/M_\sigma$ is a probability distribution, normalized to unity. Hence a certain value $H_s^*(T, \sigma)$ will exist such that, on account of (9), ($6a$) becomes

$$Z_\sigma = M_\sigma \int \frac{\mathrm{d}\{q_f\}\mathrm{d}\{v_f\}}{\Omega_F} \exp[-\beta H_f(\{q_f\}, \{v_f\}) - \beta H_s^*(T, \sigma)]. \tag{10}$$

Recalling that the integral in (10), multiplied by $\exp[-\beta H_s(\{X_g\}, 0|T)]$, coincides with the ideal-glass partition function Z_0 ($6b$), we can take the logarithm of (10), divide it by the number N of particles, and then use the second equation (8) to write the Helmholtz free energy per particle

$$\Phi_\sigma = \Phi_0 + \Delta\Phi_\sigma = \Phi_0 + h_s^*(T, \sigma) - h_s(\{X_g\}, 0|T) - \kappa T \ln[m_s(\sigma)] \tag{11}$$

where Φ_0 is the ideal-glass free energy and h_s, h_s^* are energies per particle. The usefulness of (11) is related to the possibility that the mean number m_s of slow states per particle is *finite* and relatively small in the thermodynamical limit. Otherwise the quantity $\Delta\Phi_\sigma$ would result from the (finite) difference of two divergingly large terms, and (11) would provide an unsuitable representation. Assuming *indistinguishable* particles, which is the correct position, even in the non-degenerate limit, it easy to see that the existence of an upper limiting value in the single-particle energy is the crucial condition to avoid the divergence of the number of states per particle. Indeed, an upper limiting value for the slow-mode energy ($\cong 0.16$ eV in Se) has been introduced even for the ideal liquid [31], so we may expect $m_s(\infty) < \infty$. In any case, for the present purposes we need only to discuss (11) close to the CGT point, where $m_s(\sigma)$ is expected to be not only finite, but also close to unity (see ($6b$)).

5. The rheological model at the calorimetric glass transition

In (11) it is possible to distinguish between the contribution

$$\Delta h_s = h_s^*(T, \sigma) - h_s(\{X_g\}, 0|T) \tag{12}$$

and the contribution $-\kappa T \ln(m_s)$. The quantity (12) is a sort of local energy carried by the slow modes, and we expect it to be positive at any temperature (see below). The term 'local' is used here to indicate that Δh_s is only related to the shape of the probability distribution $G_\sigma(\ldots)/M_\sigma$, which describes the *local* freezing in of the slow motions, as opposed to the quantity M_σ which describes the *global* shrinking of the phase-space volume available. The latter effect (which is essentially entropic) is accounted for by the term $-\kappa T \ln(m_s)$ in (11). This distinction suggests further insights into the rheological behaviour of the

system, described by the function G_σ. For example, we may assume that close to the CGT point the quantity M_σ numerates the glassy *configurations* $\{X_g\}$ which can be explored during the measurement time, while the probability density $G_\sigma(\ldots)/M_\sigma$ describes the residual freezing in of the slow modes, which can still relax after *one* or a few glassy configurations remain available. In this way the rheological model can account for the so called α relaxation $(M_\sigma \to 1, -\kappa T \ln(m_s) \to 0)$, followed by the so called β relaxation $(G_\sigma(\ldots)/M_\sigma \to \delta(\{q_s\} - \{X_g\})\delta(\{v_s\}))$, which concludes the stabilization process. One will then identify two characteristic temperatures $T_\alpha > T_\beta$ (both in general depending on the cooling rate), marking the vanishing of $-\kappa T \ln(m)_s$ and Δh_s respectively:

$$\Phi_\sigma = \Phi_0 + \Delta h_s(\sigma\, T) - \kappa T \ln[m_s(\sigma)] \qquad \text{for } T > T_\alpha \tag{13a}$$

$$\Phi_\sigma \cong \Phi_0 + \Delta h_s(\sigma, T) \qquad \text{for } T_\beta < T < T_\alpha \tag{13b}$$

$$\Phi_\sigma \cong \Phi_0 \qquad \text{for } T < T_\beta. \tag{13c}$$

Whether T_α and T_β are sharply defined or not is not a crucial problem, provided that they have, as we assume, an operative definition (see also the appendix). Accordingly, the condition $M_\sigma = 1$ for the α relaxation can be replaced by the condition that M_σ decreases rapidly to values of the order of unity below T_α, being much larger above. The positiveness of Δh_s can be justified by taking a *Gaussian* $G_\sigma(\ldots)/M_\sigma$ around each glassy configuration:

$$\frac{G_\sigma(\{q\}, \{v\})}{M_\sigma} = \pi^D (\det\Lambda_q \det\Lambda_v)^{1/2} \frac{1}{M_\sigma} \sum_{g=1}^{M_\sigma} \exp[-\{q - X_g\}\Lambda_q\{q - X_g\} - \{v\}\Lambda_v\{v\}] \tag{14}$$

where $\Lambda_{q,v}(\sigma)$ are $D \times D$ positive definite matrices (D is the dimension of the $\{q\}$ space), whose eigenvalues tends to zero (infinity) for σ going to infinity (zero) (see (6b)). We have removed the index s from the variables for the sake of brevity. By assuming that $\{X_g\}$ is a local-equilibrium configuration for the energy h_s, we may expand h_s close to the GT point as

$$h_s \cong \{q - X_g\}\Gamma_q\{q - X_g\} + \{v\}\Gamma_v\{v\} \tag{15}$$

where $\Gamma_{q,v}(T)$ are, in turn, positive definite matrices. Inserting (14) and (15) into (6a) for $M_\sigma \to 1$, it follows that

$$\Delta h_s \cong \tfrac{1}{2}\kappa T \ln[\det(\Lambda_q + \beta\Gamma_q)\det(\Lambda_v + \beta\Gamma_v)/\det\Lambda_q\det\Lambda_v] \tag{16}$$

which is manifestly positive. (13b), with the positiveness of Δh_s (16), implies that $\Phi_\sigma(T) > \Phi_0(T)$ for $T < T_\alpha$. However one also expects $\Phi_\sigma(T) \cong \Phi_\infty(T) < \Phi_0(T)$ in the high-temperature limit, in which σ is very large and the ideal-liquid phase is certainly stable against any other phase (including the crystalline one). Hence there will be a temperature $T_0(\sigma) > T_\alpha$ at which the 'real' free energy $\Phi_\sigma(T)$ crosses the ideal-glass free energy $\Phi_o(T)$ and becomes *larger* than $\Phi_0(T)$ at lower temperatures. One may again use (14) in (10), by taking the high-temperature limit, which leads to expand the exponentials in (14) in a power series. At the first order one verifies that this yields a *positive* contribute to the free energy of the ideal liquid, so that $\Phi_\sigma(T) > \Phi_\infty(T)$ in the high-temperature limit. All these features are sketched in figure 1, where it is seen that the passage from the two free-energy curves representing the ideal liquid ($\Phi_\infty(T)$) and the ideal glass ($\Phi_0(T)$) is far from trivial and does not display any close resemblance to a thermodynamical PT. In particular, in the
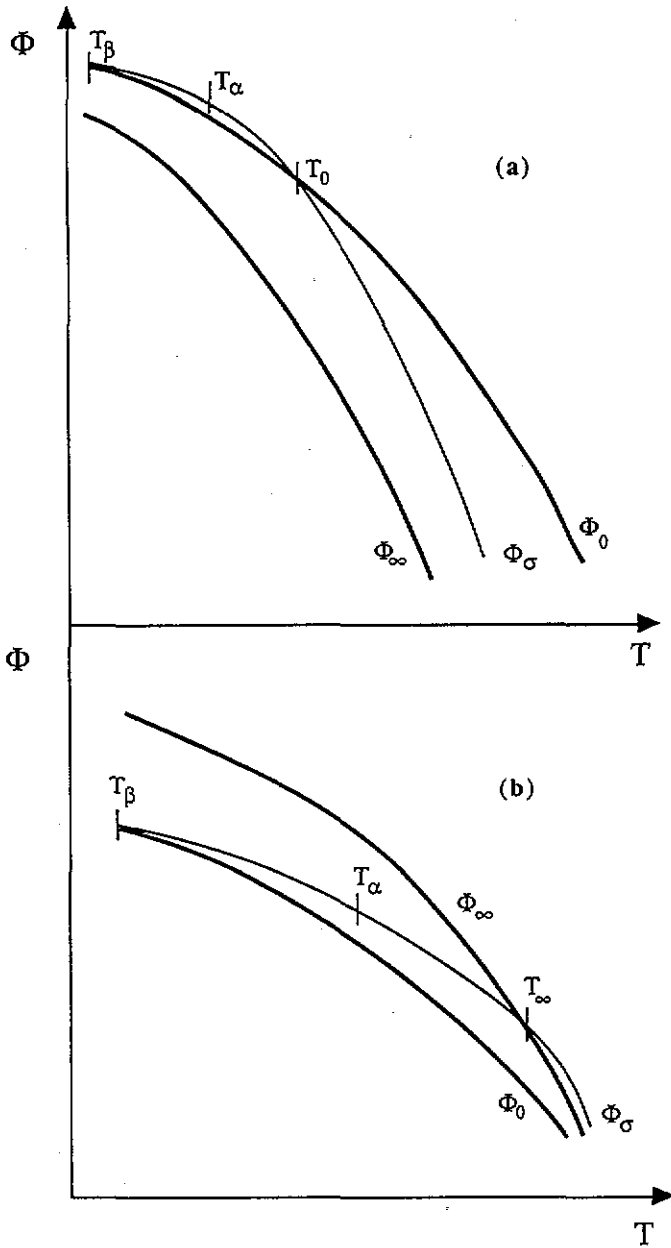
Figure 1. Sketch of the real free energy Φ_σ (fine curve), interpolating the two limiting functions Φ_∞, Φ_0 (bold curves) in the cases $\Phi_\infty < \Phi_0$ (a), and $\Phi_\infty > \Phi_0$ (b). All the functions satisfy the conditions (17).

interval T_β–T_0 the real system looks unstable against the ideal glass (figure 1(a)), because $\Phi_\sigma(T) > \Phi_0(T)$, while at high temperatures, the real system looks unstable against the ideal liquid (figure 1(b)), because $\Phi_\sigma(T) > \Phi_\infty(T)$. In both cases the notion of 'instability' is of course misleading, since the 'excess' free energy in the present model is a cooling-rate effect and can be removed *at any temperature* by a suitable choice of the cooling process.

Some relevant consequences for the rheological model follow from requiring that $\Phi_\sigma(T)$
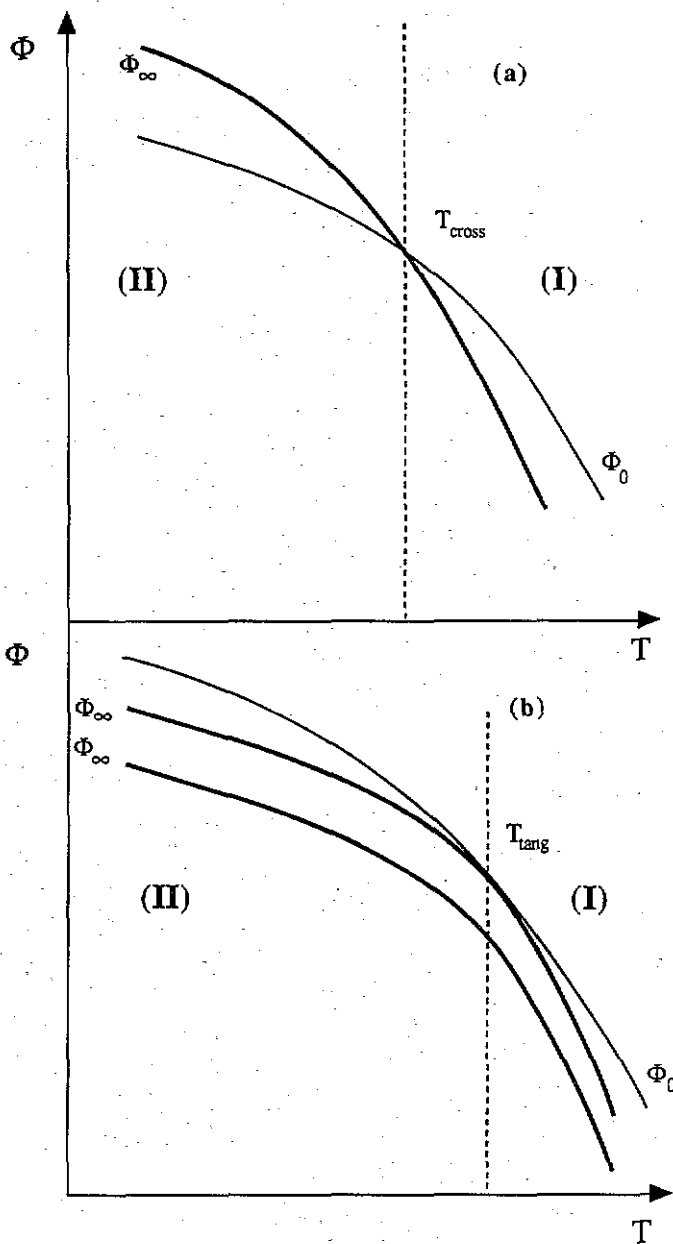
Figure 2. Two possible cases for the limiting free energies: (a) Φ_∞ (bold curve) crosses Φ_0 (fine curve) at a point T_{cross}; (b) Φ_∞ and Φ_0 are tangential at point T_{tang}. Also included in (b) is the case $\Phi_\infty < \Phi_0$ everywhere (T_{tang} now indicates the point at which the two free energies are closest to each other). The broken line divides the region (I) in which $|\Phi_\infty - \Phi_0|$ increases with T, from that (II) in which $|\Phi_\infty - \Phi_0|$ decreases with T.

behaves as a 'concave' function of T, that is

$$\partial \Phi_\sigma / \partial T < 0 \qquad \text{(positiveness of the entropy)}$$
$$\partial^2 \Phi_\sigma / \partial T^2 < 0 \qquad \text{(positiveness of the heat capacity).} \qquad (17)$$

This is assumed to hold even for the limiting values of σ, so that the conditions (17) apply to $\Phi_0(T)$ and $\Phi_\infty(T)$ as well. Since $\Phi_0(T)$ and $\Phi_\infty(T)$ must be connected by a function $\Phi_\sigma(T)$ satisfying (17), it can be argued (see the appendix) that the temperature interval marking the passage from $\Phi_0(T)$ to $\Phi_\infty(T)$, which we call the CGT interval, *increases* as the *square root* of $|\Delta\Phi| = |\Phi_\infty - \Phi_0|$, calculated in some internal point of the interval. However, the CGT interval determines the sharpness of the CGT, so that when $|\Delta\Phi(T)|$ increases with T (zone (I) in figure 2), the CGT tends to become sharper and sharper with *decreasing* cooling rate, since the decrease of the cooling rate shifts the CGT interval to lower values. Similarly, when $|\Delta\Phi(T)|$ decreases with T (zone (II) in figure 2), the CGT tends to sharpen when the cooling rate *increases*.

The case (I) ($|\Delta\Phi(T)|$ increasing with T) seems to be the rule, from the experimental viewpoint (see, for example, [15, 23, 24]). However, it is difficult to decide whether this happens because (I) holds at *all temperatures*, or because the cooling rates corresponding to (II) ($|\Delta\Phi(T)|$ decreasing with T) are not accessible in practice (one should not forget that a *minimum* cooling rate is necessary to avoid crystallization). In addition, there are old [25] and very recent [26] experimental results (which we discuss below), supporting the possibility of the opposite behaviour (II), hence we will discuss some theoretical consequences of combining the two cases, (I) and (II), as sketched in figure 2. In particular we can prove a fairly reasonably (but not so easy to show) aspect of the CGT, that is

(iv) the sharpest CGT occurs at the temperature at which the two ideal free energies Φ_∞ and Φ_0 are as close as possible.

In fact, let there exist a temperature T_{cross} (*independent* of the cooling rate) such that $\Phi_\infty(T_{cross}) = \Phi_0(T_{cross})$ (figure 2(*a*)), and let Q_{cross} be the cooling rate which yields $T_g = T_{cross}$ (T_g being the measured CGT temperature, which can be identified with the middle point of the CGT interval, for the present aims). From the arguments above, for $Q > Q_{cross}$, the CGT interval *decreases* with Q (case (I)), while for $Q < Q_{cross}$, the CGT interval *increases* with Q (case (II)). Hence the *sharpest* CGT should occur at $T_g = T_{cross}$, which proves the assertion (iv). Furthermore, the square-root dependence on $|\Delta\Phi(T)|$ suggests that the CGT interval should *vanish* for $Q = Q_{cross}$, but in this case the situation sketched in figure 2(*a*) would correspond to a first-order PT as described by Ehrenfest, since $\Delta\Phi(T)$ changes sign at T_{cross}. In figure 2(*b*) the ideal-glass free energy is always *larger* than that of the ideal liquid, except at the *tangent* point T_{tang} (if any), where $\Phi_\infty(T_{tang}) = \Phi_0(T_{tang})$. The same arguments as used for figure 2(*a*) can be applied to the present case too, in order to prove the assertion (iv). In particular, for the optimal cooling rate Q_{tang} such that $T_g = T_{tang}$, the CGT is as similar as possible to a second-order PT as described by Erhenfest, if one limits the analysis to the heat capacity behaviour. In fact the difference $\Phi_\infty(T) - \Phi_0(T)$ is proportional to $(T - T_{tang})^2$, around T_{tang}, which gives a discontinuity of the heat capacity. Of course, there is no real underlying PT, since the condition $\Phi_\infty < \Phi_0$, even *below* T_{tang}, makes it clear that the transition does not involve any 'equilibrium' process connecting the two phases, as already stressed in section 3.

The rheological model has other relevant consequences if the cooling rates can be chosen so small as to shift the CGT below T_{cross} (in figure 2(*a*)), or below T_{tang} (in figure 2(*b*)). In the latter case, for the sake of brevity we indicate with the same symbol T_{tang} the temperature at which Φ_∞ and Φ_0 are as close as possible, no matter if they are really tangent or not. The important point is that if the difference $|\Phi_\infty(T) - \Phi_0(T)|$ is non-vanishing at zero temperature, there will certainly be a critical cooling rate Q_c below which the real free energy $\Phi_\sigma(T)$ cannot connect Φ_∞ and Φ_0 without displaying singularities, or without violating one of the two conditions (17). For the case in figure 2(*a*), the proof is elementary.

If $\Phi_\infty(0) = \Phi_0(0) > 0$, it is possible to find a strictly positive temperature T_c such that $\Phi_\infty(T_c) = \Phi_0(0)$. Now, for the CGT to occur below T_{cross} in figure 2(a), there must exist a temperature T_∞ at which $\Phi_\infty(T_\infty) = \Phi_\sigma(T_\infty)$ (see figure 1(b)). In fact we have already shown that $\Phi_\sigma(T) > \Phi_\infty(T)$ at high temperature, while now $\Phi_\sigma(T)$ must approach $\Phi_0(T)$ in a region where the latter is *lower* than $\Phi_\infty(T)$. It is clear that for cooling rates below the critical value Q_c, such that $T_\infty = T_c$, the real free energy Φ_σ cannot join the ideal-glass limit without decreasing with *decreasing* T, in contrast with the *first* condition (17). For the case in figure 2(b), the proof is based on the violation of the *second* condition (17), and looks a little less elementary. The mathematical details for the calculation of T_c and Q_c are therefore given in the appendix. The conclusion is that, avoiding a negative measured entropy or heat capacity in the rheological model, leads one to consider the following alternatives:

(v) there is a temperature $T_{PT} \geqslant T_c$, below which the ideal liquid phase, though mathematically sound, does not make physical sense; or

(vi) the β-relaxation temperature $T_\beta(Q)$ (13) becomes negative for $Q < Q_c$, so that Φ_σ never joins Φ_0 for $Q < Q_c$.

6. Comparison with experimental data and with the mode-coupling theory

The possibility (v) is consistent with a second-order PT in the *modern* sense, even though it is not possible, in the present context, to be more specific about its features, which depend on the details of the function G_σ (6). From the preceding analysis, we may try to separate glass formers of class (A), referring to figure 2(a), from those of class (B), referring to figure 2(b). For the former one expect a 'false' *first-order* PT from liquid to glass, at high cooling rates (high temperature) and a true second-order PT (in the modern sense) at low cooling rates (low temperatures). For systems of class (B) the true PT is less distinguishable from the 'false' one, since the latter too looks like a second-order PT. However, for systems of class (B) there could be a remarkable possibility. If Q_{tang} and Q_{PT} are not too different, one could identify, at the *same* cooling rate $Q_{exp} = Q_{PT} \cong Q_{tang}$, a smoothed but well displayed jump in the heat capacity both around T_{tang} (the false PT) and the true PT, at a slightly lower temperature T_{PT}. Hence for class (B) glass formers, it is possible to reconcile the kinetic picture of the CGT [20–22] with the PT picture [16–19]. The former should be true for the higher-temperature process which yields the heat-capacity jumps. For practical purposes, this could be identified with the *primary* (or α) relaxation. The PT picture should instead apply to the lower-temperature process which could be identified with the *secondary* (or β) relaxation, leading the system to achieve a complete stabilization. Relevant to these points are the experimental results obtained by Brüning and Samwer [24], for different glass-forming samples. The width ΔT_g of the GT interval is shown to scale linearly with $\ln Q$, that is

$$\Delta T_g(Q) = \Delta T_0 \ln(Q/Q_0) \qquad Q \geqslant Q_0. \tag{18}$$

We can now connect (7b) and (18) to the expression

$$[\Delta T_g(T_g)]^2 \propto |\Delta\Phi(T_g)| \stackrel{\text{def}}{=} |\Phi_0(T_g) - \Phi_\infty(T_g)| \tag{19}$$

as obtained in the appendix (A4). Indeed, (A4) connects a lower limiting value of ΔT_g to $|\Delta\Phi|$ calculated at a suitable internal point of the CGT interval. However we may reasonably

expect that the square-root dependence (19) is correct at least for small CGT intervals. From (7b), (18) and (19) it follows that

$$\Delta\Phi(T) \propto [\ln(Q_M/Q_0) - T_A/(T - T_g^0)]^2 \tag{20}$$

on replacing T_g with any value T of the temperature. Close to the value

$$T_{tang} = T_g^0 + T_A/\ln(Q_M/Q_0) \tag{21}$$

at which the right-hand side of (20) vanishes, one gets

$$\Phi_0(T) - \Phi_\infty(T) \propto T_A^2(T - T_{tang})^2/(T_{tang} - T_g^0)^4. \tag{22}$$

Thus we may conclude that the glass formers considered by Brüning and Samwer are likely to belong to class (B), with Φ_0 and Φ_∞ tangent at the temperature T_{tang}. In the case of B_2O_3 (for which the data are reported with the least uncertainty) one gets, for example

$$T_{tang} - T_g^0 \cong 18 \pm 5K. \tag{23}$$

If T_g^0 in (7b) ($\cong$ 491 K in B_2O_3) corresponds to some critical process, a reasonable possibility is to take $T_g^0 = T_{PT}$ (the true PT temperature) in which case (23) is a practical realization of our guess that the false PT temperature is slightly higher than T_{PT}. The optimal cooling rate Q_{tang} at which $T_g = T_{tang}$ follows from (18), which yields $Q_{tang} = Q_0 \cong 10^{-5.3}$ K s^{-1} in B_2O_3. The only point of disagreement between the rheological model and the conclusions drawn by Brüning and Samwer from their data is that the former predicts ΔT_g *increasing* again for $Q < Q_0$ (as if, for example, the logarithm in (18) were replaced by its modulus). Instead, Brüning and Samwer suggest the possibility that ΔT_g 'saturates' to a lower limiting value (not necessarily zero), and becomes independent of the cooling rate. An experimental answer on this point would be interesting, but it is not clear whether crystallization can be avoided or not with cooling rates as low as $10^{-5.3}$ K s^{-1} (in B_2O_3). However, let us recall the measurements of Thomas and Parks [25], on account of the comments of Rajeswari and Raychaudhuri [26]. In [25] it is shown that the value of ΔT_g obtained from heat capacity measurements on B_2O_3 by reheating after *slow* cooling or simply by cooling, is *larger* than ΔT_g obtained by reheating after *fast* cooling (figure 3(a)). In [26] it is argued that the heat-capacity measurement obtained by cooling is the slowest one, so that figure 3(a) gives support to the possibility that in B_2O_3 the GT interval ΔT_g increases again with *decreasing* cooling rate, after having reached a minimum. Even more suggestive of this possibility are the data, reported in [26], on the heat-capacity measurements in glycerol (see figure 3(b)). It is clearly seen that the value of ΔT_g decreases, reaches a minimum, then increases again, for *decreasing* cooling rates, that is, for measurements times increasing from about 6×10^{-4} s to about 4×10^3 s. From figure 3(b), we have derived a logarithmic relation between τ_{meas} and ΔT_g (that is, between Q and ΔT_g):

$$\Delta T_g = \delta T_g |\ln(\tau_{meas}/\tau_0)| + \Delta T_{min} \tag{24}$$

where in glycerol, $\delta T_g \cong 1.55$ K, $\Delta T_{min} \cong 24.44$ K, $\tau_0 \cong 1.53$ s. Of course, the quantitative estimate of the parameters entering (24) has a certain degree of arbitrariness, depending on the criterion adopted to define the GT interval (see figure 3). However, our guess that the dependence on Q (or τ_{meas}) occurs via the *modulus* of the logarithm is indeed well supported. An additional feature, contrasting with the case of B_2O_3 [24], is the existence
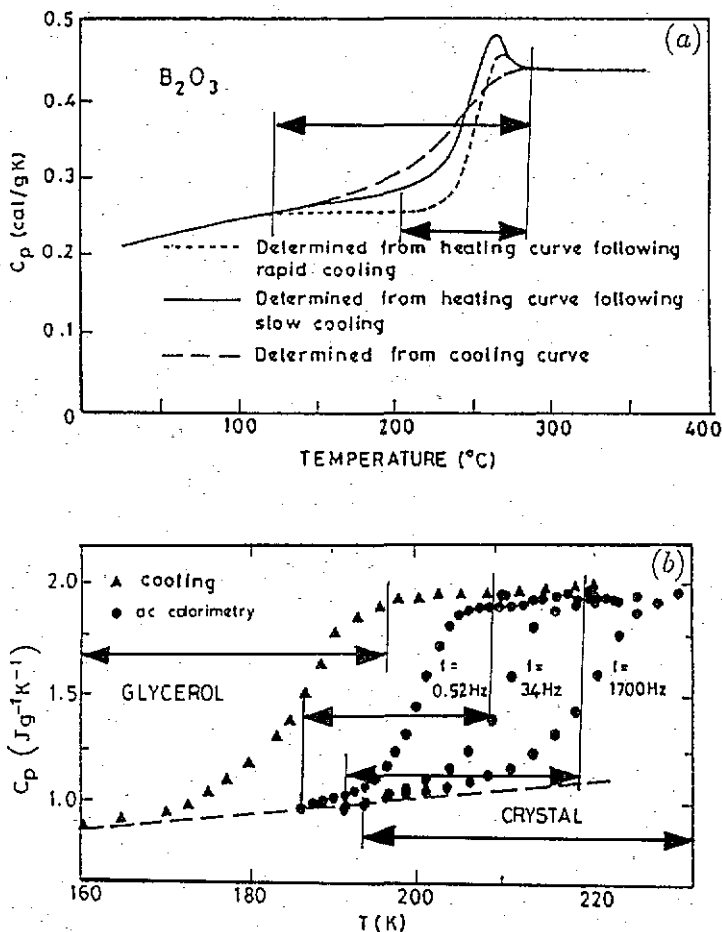
Figure 3. Heat capacity in B_2O_3 (a) and in glycerol (b), taken from [25] and [26] respectively. Double headed arrows indicate the GT intervals. To derive the parameter in (24), the measurement times have been estimated as the reciprocals of the frequencies reported in (b), from AC calorimetry. The measurement time for the pure cooling process (filled triangles) is reported in [26] as 4×10^3 s.

of a minimum GT integral ΔT_{min}, which indicates that the ideal free energies in glycerol should never be tangent (see the lower bold curve in figure 2(b)).

Coming back to [24], we can conclude that the application of the rheological model to the data reported therein leads to a fairly general conclusion: the false PT in B_2O_3 looks like a second-order PT as described by Ehrenfest, as expected for class (B) materials, while the true PT, though very close to the false one on the temperature scale, can be only ideally attained, since from (7b) $T_g = T_g^0$ means that $Q = 0$.

The possibility (vi) does not require (but does not exclude) any underlying PT. It simply suggests that some glass formers could have no *secondary* (or β) relaxation if the cooling rate is too small. In this case the glass could be cooled down to arbitrary low temperatures, after freezing in a single glassy configuration (*primarily* or α relaxation), without complete arrest of the residual slow modes. The best candidates for this class, which we denote as (C), should be the *silicates* (and in particular SiO_2), which do not display β relaxation in ordinary conditions [32]. According to the rheological model, however, the absence of

β relaxation should also correspond to particularly *slow* processes of cooling, so that one expects the silicates to be very good glass formers, which tend to glassify with very small cooling rates in ordinary condition. This is indeed observed experimentally.

In order to discuss the compatibility of the rheological model with MCT, we come back to (6). These equations postulate that the phase space of the slow degrees of freedom is not equiprobably accessible, except for diverging measurement time, and that the non-uniform occupancy of this space can be accounted for by a weighting function G_σ, depending only on the reciprocal Deborah number (5). It is this function which contains all the dynamical information, and is thereby determined by the specific dynamical model (such as the MCT) chosen to describe the liquid phase. In particular, two effects are expected from the application of MCT to the rheological model. According to Richert and Bässler [33] and Rössler [34], the critical temperature T_{MC} in MCT (which *does not* depend on the cooling rate) should mark the transition of the viscous time scale τ_{visc} from (7b) at $T > T_{MC}$ to (7a) for $T < T_{MC}$, so that one expects a similar change to reflect on G_σ through the definition (5). Another possible effect is related to the transition from a *single* scaling law ruling all relaxation processes ($T > T_{MC}$), to a regime of *different* scaling times ($T < T_{MC}$) for different classes of processes [12]. In the rheological model, the latter effect can be accounted for by partitioning the phase space of the slow degrees of freedom into different subspaces, each referring to the relaxation process (or class of relaxation process) whose scaling times τ_{visc}, τ', $\tau'' \ldots$ will split from one another below the critical temperature. Assuming for simplicity that those subspaces are non-intersecting, one can associate with each of them a weighting function of the type (6), and take for G_σ the product of those functions. In summary, from MCT one expects that equations (6) hold for $T > T_{MC}$, with a single functional form and with a single time scale τ_{visc} given by (7b). On the other hand, for $T < T_{MC}$, one expects a product $G_\sigma G_{\sigma'} G_{\sigma''} \ldots$ of several functions, each referring to a subspace of the slow degrees of freedom, in which the degree of ergodicity is marked by $\sigma' = \tau_{meas}/\tau'$, $\sigma'' = \tau_{meas}/\tau'', \ldots$, in addition to the fundamental ratio σ (5), with τ_{visc} now given by (7a). In this case, one expects many CGT temperatures T_g, $T_{g'}$, $T_{g''}, \ldots$, depending on the specific processes observed. It should be clear from the preceding discussion that the CGT and the PT predicted by MCT are quite different, albeit quite compatible processes. If the cooling rate is *large* enough, however, one may expect that the rise of the CGT temperature and the broadening of the CGT intergal lead to the critical temperature T_{MC} being included in the CGT interval itself. Hence for the two processes to be observed separately on the same temperature scale, one needs in general sufficiently low cooling rates.

7. Conclusions

The aim of this paper is to discuss the long-standing problem of the CGT–PT linkage from the rheological viewpoint. First we have made reference to the Ehrenfest classification, not because of its relevance for a modern approach to the PTs, but because a certain deal of confusion is still present, concerning the experimental 'resemblance' of the CGT to a second-order PT as described by Ehrenfest. One of the relevant points of the present paper is to stress how ambiguous and misleading it could be to take this resemblance too seriously (statement (b)). As a general message, the paper shows that merely in the framework of Ehrenfest's classification, one should be very careful in 'extrapolating' the behaviour of one phase in the stability region of another phase, and then defining the 'jump' of any thermodynamical quantity F as the difference $\Delta F = F_L - F_H$. Even-order PTs are examples in which ΔG (the jump of the free energy) looks mathematically innocuous, but the above-mentioned procedure is completely wrong.

The second part of the paper illustrates the rheological model and some of its consequences. The approach is quite descriptive and phenomenological. The form assumed in (6) is a reasonable way to interpolate two limiting cases (the ideal liquid and the ideal glass) with a partition function depending on the reciprocal Deborah number (5). The special form (14) of the interpolating function G_σ is suggested by the phenomenological evidence that α and β relaxations are distinct processes, while the choice of a Gaussian shape for the probability distribution of the slow modes follows from a standard procedure in most statistical problems. The concavity conditions (17) are thus the only first-principle ingredients in the model. It is worth stressing that it is only conditions (17) which are crucial for the results obtained.

A first non-trivial result is the relationship between the CGT sharpness and the cooling rate. One might suppose that the observed sharpening of the CGT with *decreasing* cooling rates [15] provides support for the existence of an underlying PT. In fact the decrease of the cooling rate makes the CGT closer and closer to an *equilibrium* process, which simultaneously becomes more and more 'critical' (sharp). This might suggest the wrong conclusion that at a lower limiting cooling rate the GT must *necessarily* become a true, sharp PT, and that the smoothness of the CGT is simply a non-equilibrium effect. In contrast, the rheological picture indicates that the CGT tends to sharpen not directly with the cooling rate, but with the difference between the ideal free energies. Hence the CGT will sharpen with *decreasing* cooling rates, in the region (I) (figure 2) where that difference increases in modulus with the temperature, but it will sharpen with *increasing* cooling rates in the region (II) (figure 2) where the difference decreases in modulus with the temperature. This means that in the rheological model the abrupt change of, say, the heat capacity, is not to be taken as an indication that the CGT is very close to an equilibrium process, but simply that the ideal free energies are very close at T_g. Recent [24, 26] and less recent [25] experimental data seem to point to the same direction, in stressing that the relation between ΔT_g and the cooling rate could be not as elementary as the assumption 'increasing sharpness = increasing equilibrium' would suggest (see figure 3 and (24)). Numerical simulation could provide significant insights on the dependence of T_g and ΔT_g on the cooling rate. At present, we recall the results of [35], where the problem is considered for T_g, and for other relevant structural parameters, but without explicit reference to ΔT_g.

The second non-trivial result which follows from the rheological model is the alternative between (v) a true PT at low cooling rates, that is, below T_{cross} or T_{tang}, and (vi) the absence of the β relaxation, when $|\Phi_\infty(0) - \Phi_0(0)| > 0$. Again, the crucial point here are the conditions (17), which prevent the CGT occurring at too low temperatures, without singularities. A remarkable possibility is that a fairly sharp CGT, reminiscent of a second order PT as described by Ehrenfest (*false* PT), can be observed in parallel with a *true* second-order PT, at a slightly lower temperature. For this to occur, the system must be of class (B), that is, it must behave as in figure 2(b), with $\Phi_\infty(T_{tang}) = \Phi_0(T_{tang})$ (which makes it possible to realize the steepest jump in the heat capacity), and the optimal cooling rate Q_{tang}, for which $T_g \cong T_{tang}$, must be comparable with the critical cooling rate Q_{PT} at which T_g is equal to the critical temperature T_{PT} of the true PT. This description supports both the arguments against the GT–PT linkage, and those in favour of it, provided the former are referred to the α relaxation, and the latter to the β relaxation.

Two other classes of systems have been identified, one of which, denoted as (A), corresponds to figure 2(a), and differs from class (B) in that the higher-temperature transition is reminiscent of a first-order PT. To the authors' knowledge, there is not at present any clear experimental evidence for the existence of such systems.

The third class, denoted as (C), may correspond to figure 2(a) or 2(b). Systems

belonging to this category should not display β relaxation at low cooling rates. It is argued that the silicates could be good candidates for class (C).

We have also discussed the compatibility between the rheological model and MCT, by stressing what influence MCT should have on the occupancy function (6).

As a concluding remark, concerning the true PT predicted by the rheological model, we stress that the existence of a critical *temperature* now follows from the existence of a critical *cooling rate*. Hence the special feature marking the difference between 'rheological' PT discussed in the present paper, and the conventional equilibrium PTs, is the possibility that the true order parameter is the cooling rate. This may open new perspectives to the study of non-equilibrium phase transitions, which have not been explored so far.

Acknowledgments

Appendix

In this appendix we first illustrate the relation between the sharpness of the CGT and the difference (in modulus) between the two ideal free energies. We assume as a phenomenological input that a CGT interval can be operatively defined, in which the real free energy $\Phi_\sigma(T)$ passes from values very close to that of the ideal liquid ($\Phi_\infty(T)$), to values very close to that of the ideal glass ($\Phi_0(T)$). It follows that two temperatures $T_\alpha^* > T_\beta^*$ can be operatively defined (see figure A1), at which $\Phi_\sigma(T) = \Phi_\infty(T)$ for $T > T_\alpha^*$ and $\Phi_\sigma(T) = \Phi_o(t)$ for $T < T_\beta^*$. The width of the GT interval will be given by $T_\alpha^* - T_\beta^*$. In the case sketched in figure A1, the transition is assumed to occur in a region in which $\Phi_\infty(T) < \Phi_0(T)$, while in figure A1 the opposite case $\Phi_\infty(T) > \Phi_0(T)$ is taken into account. The cases in which the GT 'starts' as in figure AI (at higher temperature) and 'ends' as figure A1 (at lower temperatures) simply correspond to the 'optimal' cooling rate, that is, to the sharpest GT. Let us consider the two linear functions $S_\infty(T)$ and $S_0(T)$, representing the tangent lines to $\Phi_\infty(T)$ and $\Phi_0(T)$ at the points T_α^* and T_β^* respectively:

$$S_\infty(T) = \Phi_\infty(T_\alpha^*) + (T - T_\alpha^*)[\partial_T \Phi_\infty]_{T_\alpha^*} \tag{A1a}$$

$$S_0(T) = \Phi_0(T_\beta^*) + (T - T_\beta^*)[\partial_T \Phi_0]_{T_\beta^*}. \tag{A1b}$$

The concavity conditions (17) imply necessarily that $\Phi_\sigma(T) < S_\infty(T)$ for $T < T_\alpha^*$ and $\Phi_\sigma(T) < S_0(T)$ for $T > T_\beta^*$. This means that $T_0^* < T_\beta^*$ and $T_\infty^* > T_\alpha^*$ for the two temperatures T_0^* and T_∞^* at which the straight lines in figure (A1a) and (b) intersect $\Phi_0(T)$ and $\Phi_\infty(T)$ respectively. Then it follows that

$$T_\alpha^* - T_\beta^* > T_\alpha^* - T_0^* \qquad \text{(figure A1)} \tag{A2a}$$

and

$$T_\alpha^* - T_\beta^* > T_\infty^* - T_\beta^* \qquad \text{(figure A1)}. \tag{A2b}$$

Of course, we are concerned with relatively narrow CGT intervals, so that we may reasonably approximate $\Phi_0(T)$ and $\Phi_\infty(T)$ by the quadratic forms

$$\Phi_\infty(T) \cong \Phi_\infty(T_0^*) - A_\infty(T - T_0^*) - \tfrac{1}{2}B_\infty(T - T_0^*)^2 \tag{A3a}$$

$$\Phi_0(T) \cong \Phi_0(T_\infty^*) - A_0(T - T_\infty^*) - \tfrac{1}{2}B_0(T - T_\infty^*)^2 \tag{A3b}$$

where the A and B coefficients are positive on account of (17). The conditions $S_\infty(T_0^*) = \Phi_0(T_0^*)$, $S_0(T_\infty^*) = \Phi_\infty(T_\infty^*)$, with the aid of (A1) and (A2), yield, from (A3)

$$T_\alpha^* - T_0^* = \{[\Phi_0(T_0^*) - \Phi_\infty(T_0^*)]/B_\infty\}^{1/2} \tag{A4a}$$

$$T_\infty^* - T_\beta^* = \{[\Phi_\infty(T_\infty^*) - \Phi_0(T_\infty^*)]/B_0\}^{1/2} \tag{A4b}$$

showing that the lower limiting value for the GT interval (A2), in both cases sketched in figure A1, *increases* with the *square root* of the difference in modulus between the two ideal free energies, calculated in a point *internal* to the GT interval.
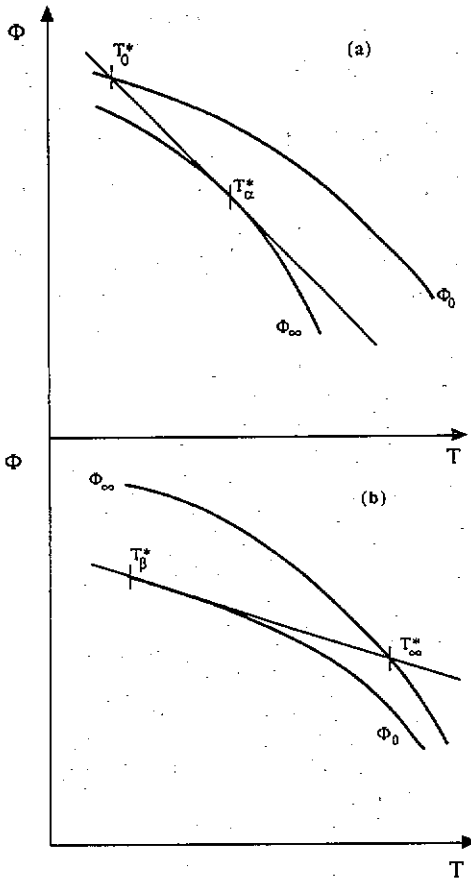

Figure A1. The same as in figure 1, with the straight lines S_∞ and S_0 (A1) replacing Φ_σ.

The second point to be discussed in the present appendix is the impossibility for $\Phi_\sigma(T)$ to approach $\Phi_0(T)$, in the case in figure 2(b), at too low temperatures (too low cooling rates), if $\Phi_0(0) - \Phi_\infty(0) > 0$. Once can again make use of figure A1, by setting $T_0^* = 0$, and by noticing that in this case the temperature T_α^* is a lower limiting value, below which it is impossible for $\Phi_\sigma(T)$ to approach $\Phi_0(T)$ starting from values arbitrary close to $\Phi_\infty(T)$, without violating the second condition (17). Hence the critical temperature T_c which we refer to in the text is given, on account of (A1a), with $T_0^* = 0$, by the equation

$$\Phi_\infty(T_c) - T_c[\partial_T\Phi_\infty]_{T_c} = \Phi_0(0). \tag{A5}$$

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