Configurational Prigogine-Defay ratio

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Classically, the Prigogine-Defay (PD) ratio involves differences in isobaric volumic specific heat, isothermal compressibility and isobaric thermal expansion coefficient between a super-cooled liquid and the corresponding glass at the glass transition. However, determining such differences by extrapolation of coefficients that have been measured for super-cooled liquid and glassy state, respectively, poses the problem that it does not take into account the non-equilibrium character of the glass transition. In this paper, we assess this old question by taking into account the gradual change of configurational contributions to the three thermodynamic coefficients upon varying temperature and pressure. Macroscopic non-equilibrium thermodynamics is applied to obtain a generalized form of the PD ratio. The classical PD ratio can then be taken as a particular case of this generalization. Under some assumptions, a configurational PD ratio (CPD ratio) can be expressed in terms of fictive temperature and fictive pressure what, hence, provides the possibility to experimentally verify this formalism. Noteworthy and differing from previous approaches towards the PD ratio, here, the glass transition is considered as non-isoaffine.
I. INTRODUCTION

Upon vitrification, some of the thermodynamic properties of a glass former undergo a jump which can be observed experimentally. Classically, the Prigogine-Defay (PD) ratio was defined as the ratio of the jumps of the following thermodynamic quantities:

\[
\Pi = \frac{1}{V T_g} \left\{ \frac{\Delta C_p \Delta \kappa_T}{(\Delta \alpha_p)^2} \right\}_{T=T_g}
\]

(1)

where \(\Delta C_p\), \(\Delta \kappa_T\) and \(\Delta \alpha_p\) are the differences taken at the glass temperature, \(T_g\), of the extrapolated measured isobaric heat capacity, isothermal compressibility and isobaric thermal expansion coefficient as observed in liquid and glassy states, respectively. \(V\) is the volume of the system.

The PD ratio has initially been derived by Prigogine and Defay, using classical thermodynamics of irreversible processes and De Donder’s order parameter framework [1]. In their original definition, the sign “\(\Delta\)” represents a difference between a state at constant affinity (isoaIfine state) and a state at constant order parameter (that is, the glassy state). Indeed, since the affinity and the order parameter are thermodynamically conjugated, in analogy to the well-known expression of the difference between isobaric and isochoric heat capacity (\(C_p - C_V\)), an expression of the difference between isoaIfine and iso-order-parameter heat capacity (\(C_A - C_\xi\)) can be derived. So, in allowing the affinity to tend towards zero, the sign “\(\Delta\)” represents the super-cooled liquid-to-glassy difference and, hence, the common definition of the PD ratio is obtained. If applied to second order phase transitions, simple equilibrium thermodynamic arguments show that this quantity is equal to unity. This can be demonstrated by expressing the continuity of volume and entropy (first order derivatives of the Gibbs free energy) following Ehrenfest’s classification, when the system undergoes a phase change [2].

For the case of glass transitions, however, numerous experiments have revealed that this ratio may differ from unity. That is, in some cases, \(\Pi < 1\) has been observed, but more often, experimental value of \(\Pi \approx 1\) are obtained (as an extreme example, for the case of vitreous silica, classical experimental approaches yield a value of \(\Pi \approx 10000\)). In a pioneering study, Davies and Jones were transferring De Donder’s nomenclature to the classical field of glass science[3]. They interpreted the experimental observation of \(\Pi \neq 1\) as an evidence that multiple (more than one) order parameters must be introduced to completely describe the glass transition in a real system. Over the following decades, the so-called “order parameter approach” has then been applied and

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refined by Moynihan, DiMarzio, Goldstein, Gupta and others [4–8] and became widely accepted. A more general approach towards the PD ratio was undertaken by Lesikar and Moynihan. In their consideration, the value of the PD ratio results from a thermodynamic stability condition, and can be generalized to unconventional thermodynamic parameters such as electric polarisation [9]. It was assumed that each thermodynamic variable is governed by its corresponding order parameter, what generally implies \( \delta \neq 1 \). They also have derived a particular condition for which the PD ratio is equal to unity even if several order parameters are taking part in the glass transition [9].

The topic has been reviewed in a very complete form by Nemilov [10]. In further studies, also, Gutzow and Schmelzer have discussed the PD ratio mostly from viewpoint of its genuine definition [11].

During the last decade, however, with the publication of several new papers, the debate has been reopened. Similar to Ritland’s original concept of the fictive temperature [12, 13], a phenomenological “two temperature thermodynamic approach” was developed by Nieuwenhuizen in which he reconsiders various classical problems of the glass transition [14, 15]. Among them is counted the non-unity of the PD ratio. It was shown that by taking into account the configurational entropy of a supercooled system, one of the two Ehrenfest relations is modified what, consequently yields \( \delta \neq 1 \). The problem was approach from another angle by Ellegaard and al. [16]. In their study, they are introducing a dynamic PD ratio where only the imaginary parts of the involved complex thermoviscoelastic coefficients are taken into account. They demonstrate rigorously that under such assumptions PD may become unity at all frequencies even when only a single order parameter is taken into account. Experimental and theoretical works have confirmed this for volume-enthalpy correlated glass-formers [17, 18]. Eventually, in 2006, Schmelzer and Gutzow, in re-formulating a thermodynamic description by means of classical thermodynamics of irreversible processes, derived a new expression of the PD ratio [19]. A new expression of the P.D. ratio was derived. Their expression highlights the role of thermodynamic affinity, explicitly stating that the considered system is out of thermodynamic equilibrium, and that the glass transition does not follow Ehrenfest’s original definition of a phase transition (where a discontinuity in some derivative of Gibbs free energy occurs at a precise temperature or pressure). More precisely, the transition process takes place over a definite temperature or pressure range. Within this range, the system starts to deviate from thermodynamic equilibrium. Thus, in their formulation, the difference “\( \Delta \)” attains its genuine formulation: a difference between a state at constant affinity and a state at constant order parameter. In the present study, based on these considerations, a
simple expression of the PD ratio is derived, based solely on enthalpy and affinity. Subsequently, it is demonstrated within this formulation, that PD can differ from unity, independently on the number of involved order parameters.

Under the "single order parameter assumption", we provide a generalization of Schmelzer and Gutzow’s expression of the PD ratio, and we extend the approach to other than isoaffine transformations. The configurational parts of the three thermodynamic coefficients, $C_p$, $κ_T$ and $α_p$ are used directly in order to define a configurational Prigogine-Defay (CPD) ratio. The classical expression of the PD ratio as well as the expression of Schmelzer and Gutzow become particular cases of this definition, where the creation of affinity occurs as a direct result of changes in temperature or pressure. This demonstrates the complexity of the phenomenological behaviour of the glass transition as a thermodynamically irreversible process.

The paper is written as follows: In section 2, the non-equilibrium thermodynamic approach of the glass transition is briefly exposed. In section 3, the CPD ratio is proposed. A tri-dimensional diagram is then depicted and the glass transition is seen as a path in this diagram. A simple expression of the CPD ratio is then provided, revealing only the isobaric heat capacity and the isothermal compressibility coefficient. Then, this last expression is simply transformed to make apparent the fictive temperature and the fictive pressure. In section 4, the unity of the CPD ratio is discussed.

II. NON-EQUILIBRIUM THERMODYNAMIC APPROACH OF THE GLASS TRANSITION

A. The order parameter model

A physical system at thermodynamic equilibrium is characterized by variables or parameters defining the thermodynamic state of the system. These variables $\{x_i\}$ obey an equation of state. This equation of state connect them together. Generally, it is difficult to attribute precise variables to a thermodynamic system under observation, and sometimes the choice seems subjective. From De Donder’s work on irreversible chemical reactions, it is known that a supplementary thermodynamic variable is necessary to completely describe, thermodynamically, a system which has been brought out of equilibrium [20, 21]. This variable, denoted $ξ$, was called the degree of advance of the chemical reaction. Subsequently, it has been generalized by Prigogine, Defay and van Rysselberghe to any irreversible process. In this generalization, $ξ$ characterizes the advance of
the process. This approach has been used until the emergence of the thermodynamic concept of internal variables [22, 23]. While in chemical reactions, $\xi$ can be well-defined, in other irreversible processes, its nature is more difficult to precise. In the glass community, $\xi$ has been called the degree of order or the order parameter[46]. Following De Donder, the variation of entropy of a system undergoing a thermodynamic transformation is given by:

$$dS = d_eS + d_iS$$  \hfill (2)

where $d_eS$ is the reversible exchange of entropy between the system and its surrounding (exchange of heat, work or matter) and $d_iS$ is the positive generation of entropy produced within the system itself when it is relaxing towards its equilibrium state. The entropy production term and the order parameter are connected by the following equality:

$$d_iS = \frac{Ad\xi}{T} \geq 0$$  \hfill (3)

$T$ is the temperature of the system and $A$ the affinity of the process. $A$ is the intensive conjugated thermodynamic variable associated to the order parameter $\xi$. In the $\{p, T\}$ state ensemble, the affinity is defined as:

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{p,T}$$  \hfill (4)

where $G$ is the Gibbs free energy of the system. The affinity is the thermodynamic force of the process exactly like gradients of intensive variables for other processes. From the definition of the state function $G$ ($G = H - TS$), the Berthelot-De Donder formula is obtained:

$$A = T\left(\frac{\partial S}{\partial \xi}\right)_{p,T} - \left(\frac{\partial H}{\partial \xi}\right)_{p,T}$$  \hfill (5)

where $H$ is the enthalpy. A system out of thermodynamic equilibrium is consequently characterized by the variables $\{p, T, \xi\}$ or $\{p, T, A\}$ and not only by $\{p, T\}$ variables. The order parameter obviously has an equilibrium value for any values of the couple $\{p, T\}$. In this case, this equilibrium value $\xi_{eq}(p, T)$, defines the condition of thermodynamic equilibrium for the system with the necessary and sufficient condition that $A = 0$ at any instant. But in the case of the glass transition, if the system is (for a certain time) brought out of thermodynamic equilibrium, the three latter variables must completely define the instantaneous state of the system. The system is not anymore constrained to remain in the $\{p, T\}$ equilibrium plane. Instead, it leaves this plane to follow the value of the affinity and order parameter, which become now time-dependent. $\xi$ and $A$ depend of time and of the instantaneous time course of $p$ or $T$. For example, if the system is suddenly
brought out of thermodynamic equilibrium by means of quick pressure or temperature jumps then after the arrest of these perturbations, the variables $\xi$ and $A$ continue to evolve until they reach their equilibrium values ($\xi_{eq}$ for the order parameter and 0 for the affinity). This time evolution is expressed in the physical ageing process of glasses. A glass is a system for which the order parameter has not any possibilities to reach such equilibrium values, because experimentally the system is brought in a range where the relaxation time becomes too high and $\xi$ is frozen. During the vitrification process, the heat capacity and other thermodynamic coefficients become the sum of two separated contributions due to time-scale separation. The first contribution is concerned by the rapid degrees of freedom (phonon’s bath) as compared to the speed of variation of the temperature. The internal exchanges of energy which follow a temperature perturbation can occur between these rapid modes. In other words, the modes of vibration are thermalized. They define the temperature $T$ of the system. The other heat capacity contribution involves the slow internal degrees of freedom as compared to the speed of variation of the temperature (it is assumed that these are connected to the configurational changes inside the system). They are driven by the variable $\xi$, and this heat capacity contribution is called the configurational contribution\[47]:

$$C_p = \left(\frac{dH}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} \left(\frac{d\xi}{dT}\right)_p = C_{p,\xi} + C_{p,conf}$$

Upon this decomposition, the glass transition is the thermodynamic transformation represented by the gradual freezing of these configurational modes when the pressure or the temperature vary. That is to say that the second contribution of the right hand side of Eq. (6) is progressively lost during the time course of $p$ or $T$. The adjective “progressively” or “gradual” means that this loss of configurational contribution occurs in given pressure or temperature intervals, and not only at a definite temperature or pressure (like in a phase transition) \[19, 24\]. If the principal characteristic of the glass transition is a continuous freezing of the configurational degrees of freedom, then the variable $\xi$ which is associated to these modes is progressively slow down until total arrest. In this case, the velocity of $\xi$ is completely neglected over the temperature time rate ($\left(\frac{d\xi}{dT}\right)_p = 0$ and thus $C_{p,conf} = 0$). Consequently, a glassy state is a state defined by a heat capacity (idem for the other coefficients) at constant order parameter $C_\xi = \left(\frac{\partial H}{\partial T}\right)_\xi$ where only the phonon contribution is measured. Contrary, the heat capacity of a liquid or a supercooled liquid contains, in addition to the latter, the order parameter contribution which in this case is maximum ($\{p\}\wedge\{conf\} = Max\}$). In this case, the internal exchange of energy that follows the temperature variation allows the system to adapt its structure to the new temperature. This maximal contribution for each thermodynamic coefficient can be exactly calculated as a function of the thermodynamic derivatives such as $\{see
following sections). We will see that these maximal contributions, that are also named $ are those that in fact are computed in the expression of the classical PD ratio.

B. Working assumptions: single order parameter, single relaxation time and linearity

Here we briefly assess the important assumptions used in the following:

- Firstly, we suppose that one single order parameter is sufficient to explain most of the basic features of the glass transition. An important consequence of such an assumption is that the configurational contributions of the three thermodynamic coefficients are all driven by the same order parameter $\xi$:

$$C_{p}^{\text{conf}} = \left( \frac{\partial H}{\partial \xi} \right)_{p,T} \left( \frac{d\xi}{dT} \right)_{p}$$

$$k_{T}^{\text{conf}} = -\frac{1}{V} \left( \frac{\partial V}{\partial \xi} \right)_{T,p} \left( \frac{d\xi}{dp} \right)_{T}$$

$$\alpha_{p}^{\text{conf}} = \frac{1}{V} \left( \frac{\partial V}{\partial \xi} \right)_{p,T} \left( \frac{d\xi}{dT} \right)_{p}$$

Let us also indicate that in the following, others relaxational effects are not taken into account. Secondary $\beta$-relaxation processes or anharmonicity effects are not tackled because they are not accessible by $C_{p}$, $k_{T}$ and $\alpha_{p}$ measurements.

- The second assumption requests that the order parameter relaxes with one well-defined relaxation time $\tau$, although it is known that a distribution of relaxation times is in fact implied for a more adequate description of the glass transition. We can, however, suppose that $\tau$ is the average upon all the $\tau_{i}$ implied in the distribution. With the first assumption, this implies that enthalpy and volume evolve along time following the same $\tau$ after temperature or pressure disturbances.

- Eventually, we suppose that the glass transition can be well depicted using linear physics of irreversible processes. This is the case if temperature or pressure time rates imposed on the system are so slow that the system never departs too far from equilibrium. This latter assumption leads up to important mathematical consequences:

1. affinity and the time rate of the order parameter are proportional:

$$\frac{d\xi}{dt} \sim L \frac{A}{T}$$

(10)
where $L$ is the so-called Onsager coefficient. It is sometimes discussed in the literature that such a relation can hold even for high departures from equilibrium. For example, the Fourier law remains valid even upon high temperature gradients. Prigogine and co-workers have experimentally validate such relations in the case of particular chemical reactions where the assumption comes back to neglect $A$ as regard to $RT$ ($R$ is the ideal gas constant) [25]. Now, discussing the validity of such linear relation for the case of the glass transition is a problem beyond the scope of this article. This has been well investigated by Möller and al. and Gutzow and al. [24, 26, 27].

2. -the isobaric and isothermal heat and volume advancements of the transformation (derivatives of the first order with respect to $\xi$ of the enthalpy and the volume) have always constant values, i.e their values at equilibrium:

\[
\begin{align*}
\left(\frac{\partial V}{\partial \xi}\right)_{p,T} & \sim \left(\frac{\partial V}{\partial \xi}\right)_{p,T}^{eq} \\
\left(\frac{\partial H}{\partial \xi}\right)_{p,T} & \sim \left(\frac{\partial H}{\partial \xi}\right)_{p,T}^{eq}
\end{align*}
\] (11)

3. -the second order derivative of the Gibbs free energy with respect to $\xi$ has also its value at equilibrium:

\[
\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T} \sim \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T}^{eq}
\] (12)

4. -the order parameter relaxes towards its equilibrium value following a simple first order linear differential equation:

\[
\frac{d\xi}{dt} \sim -\frac{(\xi - \xi_{eq})}{\tau}
\] (13)

The equilibrium value of the order parameter $\xi_{eq}$ is exclusively and instantaneously driven by the temperature or the pressure.

5. -The last consequence is certainly the most difficult to justify. It states that close to equilibrium the affinity is negligible as compared to the isothermal heat of the transformation:

\[
A \ll \left(\frac{\partial H}{\partial \xi}\right)_{p,T}^{eq}
\] (14)

In Appendix A, we show briefly that this last assumption comes to neglect the heat of friction due to the entropy production term as compared to the heat released or supplied due to the advance of the order parameter at a given temperature. In other words, this means that the amount of heat involved in the structural change is greater than the heat produced by
internal dissipation. This implies also that the fictive temperature $T_f$ can be, to a first order, close to the temperature $T$ of the system in the linear regime (but bear in mind that $dT_f \neq dT$ to a first order).

All these assumptions have been discussed in classical non-equilibrium thermodynamics books [28–30].

III. CONFIGURATIONAL PRIGOGINE-DEFAY RATIO

A. Derivation of the configurational Prigogine-Defay ratio for general out of equilibrium transformations

A thermodynamic transformation occurs out of equilibrium if the system of interest is, over a certain time, departed from its state of equilibrium. This means that the order parameter $\xi$ is deviated from its equilibrium value $\xi_{eq}$ whereas it evolves along time following the equation (13). The flux of the order parameter is driven by the thermodynamic force of the process which corresponds to its conjugated affinity. Since the affinity is a state function, it can be differentiated with respect to the three state variables, namely $\{p, T, \xi\}$. This yields the total differential of affinity [1]:

\[ dA = \left( \frac{\partial A}{\partial T} \right)_{p,\xi} dT + \left( \frac{\partial A}{\partial P} \right)_{T,\xi} dp + \left( \frac{\partial A}{\partial \xi} \right)_{p,T} d\xi \]  \hspace{1cm} (15)

The first and second partial derivatives involved in this equation can be transformed using Maxwell relations at constant pressure and temperature respectively. With the help of Eq. (5) this yields:

\[ \left( \frac{\partial A}{\partial T} \right)_{p,\xi} = \left( \frac{\partial S}{\partial \xi} \right)_{p,T} = \left( \frac{\partial H}{\partial \xi} \right)_{p,T} + \frac{A}{T} \]  \hspace{1cm} (16)

\[ \left( \frac{\partial A}{\partial P} \right)_{T,\xi} = - \left( \frac{\partial V}{\partial \xi} \right)_{T,p} \]  \hspace{1cm} (17)

Using the definition of affinity, the third partial derivative is simply (with an opposite sign) equal to the second order derivative with respect to $\xi$ of the Gibbs free energy at constant pressure and temperature:

\[ \left( \frac{\partial A}{\partial \xi} \right)_{p,T} = - \left( \frac{\partial^2 G}{\partial \xi^2} \right)_{p,T} \]  \hspace{1cm} (18)

The thermodynamic stability of the system requires that $\left( \frac{\partial^2 G}{\partial \xi^2} \right)_{p,T}$ must be strictly positive. From the total differential of the affinity (Eq. (15)), it is now possible to extract the isobaric temperature
derivative of the order parameter and the isothermal pressure derivative of the order parameter involved in the three configurational contributions (Eq. (7), (8) and (9)):

\[
\left( \frac{d\xi}{dT} \right)_p = A + \left( \frac{\partial H}{\partial \xi} \right)_{p,T} - T \left( \frac{dA}{dT} \right)_p \quad (19)
\]

\[
\left( \frac{d\xi}{dp} \right)_T = -\left[ \left( \frac{\partial V}{\partial \xi} \right)_{T,p} + \left( \frac{dA}{dp} \right)_T \right] \left( \frac{\partial^2 G}{\partial \xi^2} \right)_{p,T} \quad (20)
\]

These two temperature and pressure derivatives reveal the affinity production due to temperature perturbation under isobaric conditions and due to pressure perturbation under isothermal conditions respectively, which are the signatures of irreversible processes taking place during such perturbations. Now, from these three configurational contributions (Eq. (7), (8) and (9)):

\[
\Delta C_p = C_p^{conf} 
\]

\[
\Delta \kappa_T = \kappa_T^{conf} 
\]

\[
\Delta \alpha_p = \alpha_p^{conf} 
\]

a configurational Prigogine-Defay ratio can be derived:

\[
\Pi^{conf} = \frac{1}{VT} \frac{\Delta C_p \Delta \kappa_T}{(\Delta \alpha)^2} = -\frac{1}{T} \left( \frac{\partial H}{\partial \xi} \right)_{p,T} \left( \frac{d\xi}{dp} \right)_T \left( \frac{\partial V}{\partial \xi} \right)_{T,p} \quad (24)
\]

Here the sign “\(\Delta\)” signifies a difference between thermodynamic coefficients corresponding to the effective state of the system measured during the glass transition and those of the corresponding glassy state (iso-order-parameter state). With Eq. (19) and (20) the CPD ratio can be expressed as the following:

\[
\Pi^{conf} = \frac{\left( \frac{\partial H}{\partial \xi} \right)_{p,T} \left[ \left( \frac{\partial V}{\partial \xi} \right)_{T,p} + \left( \frac{dA}{dp} \right)_T \right]}{\left( \frac{\partial V}{\partial \xi} \right)_{T,p} \left[ A + \left( \frac{\partial H}{\partial \xi} \right)_{p,T} - T \left( \frac{dA}{dT} \right)_p \right]} 
\]

(25)

This is the general expression of the CPD ratio during a non-equilibrium glass transition. Some comments are necessary at this point. Firstly, the CPD ratio is defined over the whole transformation interval (temperature and pressure intervals) within which the glass transition takes place,
and not only at a predetermined temperature such as \( T_g \) or a characteristic pressure within the glass pressure range. This remark has already been outlined by Schmelzer and Gutzow [19, 24]. Secondly, due to the time dependence of affinity (and its derivatives), \( \Pi^{\text{conf}} \) can be time dependent. However, time dependent quantities in Eq. (25) can vary in such a way that the ratio remains fixed and time independent. The notion of time dependent PD ratio has already been envisaged by Havlicek [31, 32]. Let us, for closing this part, indicate that the assumptions previously mentioned have not been used for the moment. Now, from the general expression of the CPD ratio, different cases can be envisaged.

1. **Ideal glass transition: usual Prigogine-Defay ratio for an equilibrium thermodynamic transformation**

A transformation which takes place at thermodynamic equilibrium is a transformation for which the control parameters (pressure or temperature) vary so slowly that the system has enough time to restore its equilibrium state. In other words, when \( \xi_{eq}(p,T) \) moves, \( \xi \) follows it instantaneously, or in practises, \( \xi \) moves more rapidly than the variations of the control parameters. Consequently, it is impossible to observe an equilibrium glass transition. If it would be the case, the liquid must remain a super-cooled liquid during all the pressure or temperature courses until the liquid becomes a solid. The heat capacity of the super-cooled liquid can be extrapolated to a characteristic temperature for which the liquid and glassy states are the same. This temperature is the Kauzman temperature, \( T_K \), for which the relaxation time is infinite. To the best of our knowledge, nobody has never been able to perform experiments in order to approach sufficiently close to this characteristic temperature. As of today, it is unknown whether or not at this temperature a phase transition occurs, or whether there a discontinuity in the derivatives of the Gibbs free energy. During a real glass transition, eventually, the relaxation time of the order parameter becomes so high that it is impossible for the system to adapt its structure to the new temperature and pressure, respectively, in the experimental time scale. Thus, a glass transition occurs outside thermodynamic equilibrium. Anyway, let us suppose for instance that such an ideal glass transition is possible at the limit of infinitely slow temperature and pressure rates: \( dT/dt \to 0 \) and \( dp/dt \to 0 \). In that case, the three configurational contributions \( \Delta C_p, \Delta \kappa_T \) and \( \Delta \alpha_p \) are at their maximum and always equal to the difference between the equilibrium liquid and the glass at each temperature and pressure (the glass being the state of matter obtained for infinitely fast temperature and pressure rates: \( dT/dt \to \infty \) and \( dp/dt \to \infty \)). On Figure 1, a schematic diagram shows how the heat capacity behaves during different thermodynamic transformations, i.e during an equilibrium transformation (liquid), during
a perfect non-equilibrium transition (ideal glass) and during a real glass transition (viscous glass).

At this point, one can ask whether measuring such differences in the thermodynamic coefficients does make sense for the study of a real glass transition. Indeed, even in the presence of a real glass transition (for which \(dT/dt\) takes a defined value different from zero), if the difference between the super-cooled liquid and the glass is taken at \(T_g\) by extrapolation of the heat capacity of the liquid and the glass at this temperature, this comes back to take \(\Delta C^\text{eq}_p\) for determining the PD ratio. Anyway, we can calculate these maximal configurational contributions by means of the total differential of affinity in putting \(A = 0\) and \(dA = 0\). In this situation, temperature and pressure derivatives of the equilibrium value of the order parameter become (Eq. 19,20):

\[
\left( \frac{d\xi}{dT} \right)_p^\text{eq} = \frac{\left( \frac{\partial H}{\partial \xi} \right)^\text{eq}}{T \left( \frac{\partial^2 G}{\partial \xi^2} \right)^\text{eq}}_{p,T} \tag{26}
\]

\[
\left( \frac{d\xi}{dp} \right)_T^\text{eq} = -\frac{\left( \frac{\partial V}{\partial \xi} \right)^\text{eq}}{V \left( \frac{\partial^2 G}{\partial \xi^2} \right)^\text{eq}}_{p,T} \tag{27}
\]

The equilibrium configurational contributions (Eq. 7, 8, 9) are as follows:

\[
\Delta C^\text{eq}_p = \left[ \frac{\left( \frac{\partial H}{\partial \xi} \right)^\text{eq}}{T \left( \frac{\partial^2 G}{\partial \xi^2} \right)^\text{eq}}_{p,T} \right]^2 \tag{28}
\]

\[
\Delta \kappa^\text{eq}_T = \left[ \frac{\left( \frac{\partial V}{\partial \xi} \right)^\text{eq}}{V \left( \frac{\partial^2 G}{\partial \xi^2} \right)^\text{eq}}_{p,T} \right]^2 \tag{29}
\]

\[
\Delta \alpha^\text{eq}_p = \frac{\left( \frac{\partial V}{\partial \xi} \right)^\text{eq}}{V T \left( \frac{\partial^2 G}{\partial \xi^2} \right)^\text{eq}}_{p,T} \left( \frac{\partial H}{\partial \xi} \right)^\text{eq}_{p,T} \tag{30}
\]

We can compute these three equilibrium contributions in the formula of the PD ratio (or simply in putting \(A = 0\) and \(dA = 0\) in Eq. (25)) in order to obtain a PD ratio, in its usual meaning, which is strictly equal to unity. The conclusion is that, under the single order parameter assumption, during an ideal glass transition the PD ratio is equal to unity like in the case of a second order phase transition. During this equilibrium transformation, the PD ratio is measured over a given temperature or pressure interval and not only at a critical temperature or pressure. Now a pertinent question could be to know if, under the single order parameter assumption, the non-unity of the PD ratio could be due to the real out of equilibrium nature of the glass transition.
2. Isoaffine glass transition

The isoaffine transformation is a very particular case of non-equilibrium transformation. The fact that this type of transformation can well-describe a glass transition is, in our point of view, questionable. Indeed, it must be very improbable that all the partial derivatives in the equation (15) are connected in such a manner that \( dA \) equals zero at any time during the transformation while \( A \) is different from zero. Moreover, since we know that the glass transition is a transformation starting from an equilibrium state (super-cooled liquid) for which \( A = 0 \) to a glassy state for which \( A \neq 0 \), then the isoaffine glass transition is, in fact, impossible. Nevertheless, it seems that this has been the way which was initially followed by Prigogine and Defay, and that this way was also recently reconsidered by Schmelzer and Gutzow [1, 19]. A critical lecture of the famous paper of Davies and Jones (Ref. [3]) reveals that most of the mathematical thermodynamic derivations are also made under the assumption of iso-affinity. Indeed, in making \( dA = 0 \) in equation (25) then the expression of the PD ratio derived by Schmelzer and Gutzow is found:

\[
\Pi^{conf} = \frac{\left( \frac{\partial H}{\partial \xi} \right)_{p,T}}{A + \left( \frac{\partial H}{\partial \xi} \right)_{p,T}}
\]

(31)

Under the assumption of linearity (close to equilibrium transformation) then for the isoaffine glass transition, \( \Pi^{conf} \) is very close to unity because in this case the inequality \( A << \left( \frac{\partial H}{\partial \xi} \right)_{p,T} \) holds (see Eq. 14, see also more precision on this assumption in Appendix A).

3. A three dimensional diagram of the glass transition

The state of a material out of thermodynamic equilibrium is given by three independent thermodynamic variables \((p, T, A)\). Thus the state of a glassy material can be represented in a diagram with three axes representing the values of \( p, T \) and \( A \) as in Figure 2. The order parameter is a function of these three variables alone: \( \xi = \xi(p, T, A) \) while at equilibrium, the equilibrium order parameter \( \xi_{eq} = \xi_{eq}(p, T, A = 0) \) is fixed by the condition \( A = 0 \) and is a function of \( p, T \) only. Upon cooling at constant pressure \( p = p_0 \) but with different temperature rates \( \gamma_1 \) and \( \gamma_2 \), the system is driven out of equilibrium by the temperature variation rate and enters into the slowly relaxing states at different temperatures \( T_a \) and \( T_b > T_a \). Upon further cooling, the system enters a true glassy state with a fixed order parameter \( \xi_a \) and \( \xi_b \). These evolutions are represented as trajectories (a) and (b) on the Figure 2. Although glass 1 and glass 2, represented by the point (a)
and (b), are at the same temperature and pressure, it is clear that they are not in the same states since they have different affinities. Nevertheless if these two glassy materials were still within the glass transition interval, they would relax toward the $A = 0$ and eventually reach identical equilibrium states. The fictive temperature concept is also a measure of the structure of the system like $\xi$ (cf. following paragraphs). According to the definitions given by Davies and Jones [3], the fictive temperature $T_f$ of the materials can be deduced in the linear regime by the intercept of the tangent of the trajectories in the $(p_0, T, A)$ plane with the $(p_0, T, A = 0)$ axis. In the glass transition interval, the fictive temperature is varying and follows the control temperature although with some delay, its value at a particular point within the glass transition range of trajectory (b) has been represented on the diagram of figure 2. As soon as the system is in a glassy state but still in the linear regime, the fictive temperature is constant and noted $T'_f$ and necessary the trajectory in $(p_0, T, A)$ plane becomes rectilinear. The final fictive temperatures ($T'_f$) have been marked on the diagram for trajectories (a) and (b). Next we perform a cooling of the material under pressure $p_1$ at a rate $\gamma_2$ as represented by trajectory (c). We explicitly supposed in the diagram that $dT_g/dp > 0$ (where $T_g$ is the glass temperature). In the case of a true first order transition, this would be equivalent to supposing that the molar volume of the glass is smaller than the molar volume of the liquid for a positive melting latent heat. In other words, this means that under pressure for a given temperature rate, the system is driven out of equilibrium at higher temperature than under atmospheric pressure [33–35]. This can be re-phrased in terms of fictive temperature: for a given cooling rate, the fictive temperature of a sample cooled under high pressure will be higher than the fictive temperature of a sample cooled under atmospheric pressure. This has been recently observed experimentally [33–35]. The final fictive temperature has also been marked for this glass. Finally we perform an experiment in which the system is maintained in equilibrium ($A = 0$) at constant temperature $T_0$. The pressure is then increased at a given rate yielding the trajectory (d) pictured on figure 2. If the pressure variation drives the system out of thermodynamic equilibrium, then above a vitrifying pressure $p_g$, the system enters first a glass transition range in pressure and if the pressure is further increased, the system becomes totally glassy and increasing the pressure does not change significantly the value of the order parameter $\xi$. So, if the cooling rate of trajectory (c) and the increasing pressure rate of trajectory (d) are well chosen, it is possible that the two trajectories intercept as pictured by point (d) in the diagram. A fictive pressure of the glassy material (d) can be defined in the same manner as the fictive temperature. From this diagram, it can be seen that the system can be set into an identical glassy state by using
either temperature variation at constant pressure or pressure variation at constant temperature. This naturally provides a link and equivalence between the fictive pressure and fictive temperature concepts and the order parameter approach introduced by De Donder. Figure 3 provides an experimental illustration of above arguments. It shows the dependence of a structural parameter, the relative amount of tetrahedrally coordinate boron, $BO_4$, in a borosilicate glass as a function of fictive pressure and fictive temperature [33]. Here, $[BO_4]$ may be taken as related to the order parameter, and different $(T, p)$ paths may lead to different structural states of the final glass. In the following, a formalism is developed that will help to translate future physical experiments in the framework of the CPD ratio.

**B. Expression of the Configurational Prigogine-Defay ratio as a function of the isobaric heat capacity and isothermal compressibility coefficient**

From now, the assumptions described in paragraph 2.2 will be used in order to simplify the general expression (25) of the CPD ratio. This will allow to connect its value to measurable quantities in a different, novel fashion. Firstly, let us re-formulate expression (25) in the form of a ratio of two adimensional quantities that involve only thermal and mechanical variables, respectively:

$$
\Pi_{conf} = \frac{\Pi_{calo}}{\Pi_{meca}}
$$

where we have for the two terms of the ratio:

$$\Pi_{calo} = \frac{\left(\frac{\partial H}{\partial \xi}\right)_{p,T}}{A + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} - T \left(\frac{dA}{dT}\right)_p}$$

$$\Pi_{meca} = \frac{\left(\frac{\partial V}{\partial \xi}\right)_{T,p}}{\left(\frac{\partial V}{\partial \xi}\right)_{T,p} + \left(\frac{dA}{dp}\right)_T}$$

Using the assumptions of paragraph 2.2, we obtain:

$$\Pi_{calo} \sim \frac{\left(\frac{\partial H}{\partial \xi}\right)_{p,T}^{eq}}{\left[\left(\frac{\partial H}{\partial \xi}\right)_{p,T}^{eq} - T \left(\frac{dA}{dT}\right)_p^{eq}\right]}$$

$$\Pi_{meca} \sim \frac{\left(\frac{\partial V}{\partial \xi}\right)_{T,p}^{eq}}{\left[\left(\frac{\partial V}{\partial \xi}\right)_{T,p}^{eq} + \left(\frac{dA}{dp}\right)_T^{eq}\right]}$$
It could be easily demonstrated that the two previous quantities can be expressed as a function of the heat capacity only for $\Pi_{calo}$ and as a function of the compressibility only for $\Pi_{meca}$ (see Appendix B):

$$\Pi_{calo} \sim \frac{\Delta C_p^{eq}}{\Delta C_p} = \frac{\Delta C_p^{eq}}{C_p^{conf}} \quad (37)$$

$$\Pi_{meca} \sim \frac{\Delta \kappa_T^{eq}}{\Delta \kappa_T} = \frac{\Delta \kappa_T^{eq}}{\kappa_T^{conf}} \quad (38)$$

$\Delta C_p^{eq}$ is the equilibrium contribution as classically involved in the usual PD ratio although $\Delta C_p$ is the difference between the effectively measured heat capacity during the glass transition (viscous state) and the glassy state. The same arguments hold for the measured isothermal compressibility. Thus, the CPD ratio now depends only on the isobaric heat capacity and the isothermal compressibility (the isobaric thermal expansion coefficient does not now play a role anymore):

$$\Pi^{conf} \sim \frac{\Delta C_p^{eq} \Delta \kappa_T}{\Delta C_p \Delta \kappa_T^{conf}} \quad (39)$$

Let us remark that $\Pi_{calo}$ is what is known in the glass literature as the inverse of the normalised heat capacity which is equal to unity only when the system is in the liquid state. In letting time to the material to adjust its configuration at each pressure and temperature, respectively, we observe that $\Pi_{calo}$ and $\Pi_{meca}$ tend directly toward unity. The question is whether this attainment holds on such a manner that $\Pi^{conf}$ remains equal to one at each instant. This could be envisaged in developing the latter expression of $\Pi^{conf}$ using the fact that $\Delta C_p$ and $\Delta \kappa_T$ involved temperature rate and pressure rate, respectively:

$$\Delta C_p = \left( \frac{\partial H}{\partial \xi} \right)_{p,T} \frac{d\xi}{dt} \frac{dT}{dt} \sim \left( \frac{\partial H}{\partial \xi} \right)_{p,T}^{eq} \frac{d\xi}{dt} \frac{dT}{dt} \quad (40)$$

$$\Delta \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial \xi} \right)_{T,p} \frac{d\xi}{dt} \frac{dp}{dt} \sim -\frac{1}{V} \left( \frac{\partial V}{\partial \xi} \right)_{T,p}^{eq} \frac{d\xi}{dt} \frac{dp}{dt} \quad (41)$$

With these previous equations, in assuming that near equilibrium, a temperature variation under isobaric condition induces the same order parameter disequilibrium as does a pressure variation under isothermal condition, with the help of (Eq. (28) and (29)) we obtain for $\Pi^{conf}$ the following value:

$$\Pi^{conf} \sim -\frac{1}{T} \left( \frac{\partial H}{\partial \xi} \right)_{p,T}^{eq} \frac{dT}{dt} \frac{dp}{dt} \quad (42)$$
This provides a condition for the unity of the CPD ratio under relaxation involving mechanical and thermal variables and temperature and pressure time rates:

$$\frac{dT}{dt} = \frac{dp}{dt} = -T \left( \frac{\partial V}{\partial \xi} \right)_{eq}^{T,p} = -T \left( \frac{\partial H}{\partial \xi} \right)_{eq}^{\phi,T}$$

(43)

This is a prerequisite for experiments in order to obtain a CPD ratio equal to unity. The experimental challenge is to be able to follow this requirement for being at the same point in the three dimensional diagrams of figures 2 and 3 after temperature and (or) pressure perturbations. Noteworthy, as mentioned before, if enthalpy and volume relax towards equilibrium with different relaxation times for equivalent thermodynamic perturbations, the ratio of the two relaxation times ($\tau_H$ and $\tau_V$) must appear in the previous equation. In other words, if thermal and mechanical variables are driven by different order parameters, then experimentally, we must adapt the rate of variations of $T$ in one experiment and the rate of variation of $P$ in another one in order to fulfil the unity condition for the CPD ratio. Wondraczek and colleagues have performed experiments in order to probe such $P,T$ influences on the structure of glasses [33–35].

C. Expression of the configurational Prigogine-Defay ratio as a function of the fictive temperature and the fictive pressure

Tool has originally defined a concept, called the fictive temperature, adapted to a phenomenological description of calorimetric experiments on glasses [36, 37]. In short, this quantity represents the temperature of the slow relaxing modes during a glass transition. Moynihan and co-workers have used the fictive temperature concept for a description of the glass transition and ageing processes, and have connected it to heat capacity data [38–40]. By means of a systematic conformity between the “two temperatures thermodynamics” developed by Nieuwenhuizen and the order parameter approach of De Donder, we have recently demonstrated that the fictive temperature of Tool can in fact represent a real thermodynamic temperature for systems undergoing irreversible processes [41]. For instance, the fictive temperature of Tool is equivalent to the effective temperature of Nieuwenhuizen. Davies and Jones have however already established such a direct link between the fictive temperature and the order parameter [3]. In the same way, they also have defined a fictive pressure. Close to equilibrium, the affinity can be developed as a function of the fictive temperature departure from the classical one (under isobaric condition) and also as the function
of the fictive pressure departure from the pressure (under isothermal condition):

\[ A \sim (T - T_f) \left( \frac{\partial A}{\partial T} \right)_{p, \xi}^{eq} \]  

(44)

\[ A \sim (p - p_f) \left( \frac{\partial A}{\partial p} \right)_{T, \xi}^{eq} \]  

(45)

With equations (16) and (17) and neglecting the affinity as compared to the heat of the transformation, we obtain:

\[ A \sim \left( \frac{\partial H}{\partial \xi} \right)_{p,T}^{eq} \frac{(T - T_f)}{T} \]  

(46)

\[ A \sim - \left( \frac{\partial V}{\partial \xi} \right)_{T,p}^{eq} (p - p_f) \]  

(47)

Using linear relation (10) this yields to a new expression for \( \Pi_{con_f} \) from Eq. (42):

\[ \Pi_{con_f} \sim \frac{(p - p_f)}{(T - T_f)} \frac{dT/dt}{dp/dt} \]  

(48)

Using the well-know differential equation of Tool and a similar one for the fictive pressure in the linear regime we have:

\[ \frac{dT_f}{dt} = \frac{(T - T_f)}{\tau} \]  

(49)

\[ \frac{dp_f}{dt} = \frac{(p - p_f)}{\tau} \]  

(50)

When \( T \) or \( p \) are stopped, these two linear differential equations give an exponential decay for the fictive temperature and the fictive pressure which are linked to enthalpy and volume relaxation. As we are placed in the assumption of one single order parameter (\( \tau \) is the same in the two equations), this leads to a simple expression for the CPD ratio:

\[ \Pi_{con_f} \sim \frac{dp_f}{dT_f} \frac{dT}{dT_f} \]  

(51)

It is straightforward to remark that a result obtained a long time ago by Moynihan, connecting the normalised heat capacity with the temperature derivative of the fictive temperature has been re-found [38, 40]:

\[ \Pi_{calo} \sim \frac{\Delta C_p^{eq}}{\Delta C_p} = \frac{dT}{dT_f} \]  

(52)

Here \( \Delta C_p^{eq} \) is taken at \( T \) while in the original derivation of Moynihan \( \Delta C_p^{eq} \) is taken at \( T_f \) in the normalised heat capacity expression. The two ways are equivalent upon the linear assumption.
because $T \sim T_f$ (see Appendix A for details). The conclusion of this paragraph is that the CPD ratio can involve only fictive temperature and fictive pressure along with the classical temperature and pressure. Notwithstanding its simplicity, this sort of connection can be a good way to establish the link between this theoretical approach and physical experiments. Relation (51) can however indicate to us how, firstly the CPD ratio must be equal to unity or not, and secondly, how the classical PD ratio, which is the long-term average of $\Pi^{\text{conf}}$, can also be equal to unity or not. This is briefly discussed now.

IV. ON THE UNITY OF THE CONFIGURATIONAL PRIGOGINE-DEFAY RATIO

At infinitely long time-scale, i.e. for infinitely slow cooling rate or pressure variations, the system has enough time to restore its internal equilibrium. It behaves like a liquid. The fictive temperature and pressure vary exactly like their corresponding temperature and pressure driving variables. Eq. (51) states that $\Pi^{\text{conf}}$ is equal to unity. But as already mentioned, under these circumstances, no glass transition does occur. In real situations, even for very slow variations of the driving variables, there exists an instant at which the relaxation time of the system $\tau(T, p)$ will reach a value for which the system cannot anymore restore its long range configuration. From this instant, the experimenter begins to observe a fall in the measured thermodynamic coefficients ($C_p$, etc.). This fall is not sudden. It occurs over a definite interval (temperature or pressure). During this collapse, the system looses its configurational entropy which is observable by a smooth jump in the heat capacity. This being, there is also relaxational effect which becomes small due to the importance of the relaxation time. There is however an irreversible generation of entropy. This entropy gain due to friction during slow internal configurational readjustments is generally small. In the linear regime, the entropy production term is indeed negligible (see Appendix A). This has already been discussed by Davies and Jones [3]. From this situation, the fundamental question arises as to whether the departure of the fictive temperature from the equilibrium temperature of the system reaches a value in such a fashion that the fictive pressure attains a value different from the pressure of the system such that the Eq. (51) leads to unity for $\Pi^{\text{conf}}$. Indeed, from Eq. (48), considering that only one single order parameter is implied, $\Pi^{\text{conf}}$ is unity if the scanning temperature or pressure rates (under isobaric and isothermal conditions respectively) are in proportion with the departure of the fictive temperature and pressure respectively from their driving variables:

$$\frac{dT/dt}{dp/dt} = \frac{T - T_f}{p - p_f}$$

(53)
Here, the requirement obtained in paragraph 3.2 (Eq. (43)) is found as a function of the fictive temperature and the fictive pressure directly, which are measurable quantities. The discussion made after the Eq. (43) is still valuable. The fact that the CPD ratio should be equal to unity only if this type of statement is fulfilled is an argument in favour of researchers (see for example McKenna [2]) who argue that the departure from unity for $\Pi$ remarked in the literature is probably due to a erroneous consideration of the different histories in the measurement of the three thermodynamic coefficients $C_p$, $\kappa_T$ and $\alpha_p$. However, the statement that “$\Pi$ different from unity” is due to the presence of more than one single order parameter is also true as we have shown that in this paper. But, to our point of view, if we suppose that “$\Pi$ different from unity” is probably due to a bad consideration of the history of a glass sample in the measurement of the thermodynamic coefficients, then “$\Pi$ different from unity” is not a definitive proof in favour of a multi-order parameters description of the glass transition.

V. CONCLUSION

In this paper, we have shown that, when the configurational parts of the three thermodynamic coefficients involved in the expression of the PD ratio are considered, a general expression can be derived for this ratio. We have called this general expression, the configurational PD ratio. The classical PD ratio usually discussed in the literature, and experimentally measured by extrapolation of the properties of the super-cooled liquid and the glass at $T_g$, is a limiting case of this expression for infinitely high time scales of observation (or identically for infinitely slow temperature and pressure time variations), i.e when only thermodynamic equilibrium is considered. We have questioned the pertinence of the classical expression of the PD ratio for the characterization of the glass transition since it is known that the glass transition is by essence an out of equilibrium transformation. Since when classical PD ratios are measured, the obtained values are generally different from unity, we have discussed that it could be due to the out of equilibrium nature of the glass transition. Indeed, in a real glass transition the configurational parts of the three coefficients $C_p$, $\kappa_T$ and $\alpha_p$ vanish gradually upon temperature decrease or by varying the pressure. Some classical and some more recent studies have tackled this issue in discussing the PD ratio in terms of difference of the thermodynamic coefficients between a state at constant affinity and a state at constant order parameter. We have also criticised this point of view, because during the out of equilibrium phase transformation there is a permanent creation of affinity and the isoaffine case is not typical for the glass transition. If the out of equilibrium character of the glass transition must
be correctly taken into account then we must construct a PD ratio with thermodynamic coefficients effectively recorded during the glass transition, i.e. by taking into account a difference between an out of equilibrium state during the transition (measured \( C_p, \kappa_T \) and \( \alpha_p \)) and a state at constant order parameter (the glass: \( C_{p,\xi}, \kappa_{T,\xi} \) and \( \alpha_{p,\xi} \)). When taking into account such time dependent variations of the three thermodynamic coefficients, under the single order parameter assumption and under the assumption of identical thermodynamic histories, the unity for the CPD ratio is always confirmed. Our conclusion at this level joins that which can be found in the literature on this topics, i.e., that the non unity of the classical PD ratio is either due to the presence of several order parameters for a complete description of the glass transition, or because in most of the cases \( \Delta C_p, \Delta \kappa_T \) and \( \Delta \alpha_p \) are measured on sample for which thermodynamic history have not seriously be taken into account [2]. For the moment the debate is not closed. Under linearity conditions, we have also given an expression for the CPD ratio where the number of relevant coefficients have been reduced from three to two, and where only normalised isobaric heat capacity and normalised isothermal compressibility play a role. From this last expression the CPD ratio can be expressed as a function of not only the temperature and the pressure but also as a function of the fictive temperature and the fictive pressure. All these properties are experimentally accessible, and a future challenge will be to correlate the present formalism to experimental situations.

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[46] Certainly this appellation comes from Landau general theory on phase transitions, where order parameter and degree of order have been defined. The order parameter being a particular case of degree of order for continuous transition for which third order terms in the series expansion of the Gibbs free energy does not appear (pure second order phase transition). In our case, for the sake of simplicity we call the variable $\xi$ the order parameter, despite that for glass transition the term degree of order, or degree of advance of the process (cf. De Donder) must be more rigorously used.

[47] These two contributions are experimentally accessible with difficulties, and some sub-decompositions can take place (see for example references [44, 45]).
Figure 1: On this schematic graph $C_P$ as a function of temperature upon cooling ($\beta = dT/dt$) is shown in different situations. An equilibrium transformation occurs when the cooling ramp is so slow that equilibrium is maintained all the time, i.e the measured heat capacity is that of a super-cooled liquid. A completely non-equilibrium transformation occurs when the cooling ramp is infinitely fast. The system becomes instantaneously frozen, i.e the measured heat capacity is that of a glass. A real transformation takes place when a liquid is cooled following a determined scanning rate where it undergoes a measurable jump in the heat capacity. The difference $\Delta C_P^{eq}$ which is computed in the classical PD ratio is taken between the hypothetically equilibrium and completely non-equilibrium state taken at the glass temperature $T_g$ of the real glass transition.
Figure 2: Diagram in the $(p, T, A)$ space representing the state of an out of equilibrium system. Different hypothetical trajectories yielding glasses are represented: (a) $p = p_0; \frac{dT}{dt} = \gamma_1$; (b) $p = p_0; \frac{dT}{dt} = \gamma_2 > \gamma_1$; (c) $p = p_1 > p_0; \frac{dT}{dt} = \gamma_1$; (d) $T = T_0; \frac{dp}{dT} \neq 0$. The corresponding glass states are marked by the letters (a), (b), (c) and (d). The equilibrium state from which the glasses are formed is marked by the letter (e).are connected by equilibrium (reversible) trajectories in the $(p, T, A = 0)$ plane.
Figure 3: \(\{P_f, T_f, \{BO_4\}\}\) tri-dimensional graph showing the dependence of a structural parameter, the relative amount of tetrahedrally coordinate boron, \(BO_4\), in a borosilicate glass as a function of fictive pressure and fictive temperature [33]. The concentration of boron \([BO_4]\) is the structural order parameter in these experiments.
Appendix A:

One assumes that sufficiently close to equilibrium the affinity obeys the inequality:

\[ A << \left( \frac{\partial H}{\partial \xi} \right)_{eq}^{p,T} \]  \hspace{1cm} (54)

Dividing by \( T \) and multiplying by \( d\xi/dt \) the two members yields:

\[ \frac{A}{T} \frac{d\xi}{dt} << \frac{\left( \frac{\partial H}{\partial \xi} \right)_{eq}^{p,T}}{T} \frac{d\xi}{dt} \]  \hspace{1cm} (55)

The left-hand-side is the so-called entropy production term and the right-hand-side the configurational entropy rate:

\[ \frac{dS}{dt} = \frac{dS^{conf}}{dt} \]  \hspace{1cm} (56)

The configurational entropy rate is defined thanks to the configurational heat capacity such as follows:

\[ \frac{dS^{conf}}{dt} = \frac{C_{p}^{conf}}{T} \times \frac{dT}{dt} \]  \hspace{1cm} (57)

Thus neglecting the affinity as compared to the heat of reaction at constant temperature and pressure is equivalent to neglect the entropy production as compared to the configurational entropy change.

Davies and Jones have shown that close to equilibrium the affinity can be written simply as follows [3]:

\[ A \sim (T - T_f) \left( \frac{\partial A}{\partial T} \right)_{eq}^{p,\xi} \]  \hspace{1cm} (58)

This comes simply from a Taylor series expansion with an arrest to a first order in the departure of the fictive temperature to the temperature. Using Maxwell relation and the Berthelot-De Donder formula (Eq. 5), this last equation becomes:

\[ A \sim \frac{(T - T_f)}{T} \left[ \left( \frac{\partial H}{\partial \xi} \right)_{eq}^{p,T} + A \right] \]  \hspace{1cm} (59)

Let us first observe that if the inequality (54) is fulfilled then the affinity can be written:

\[ A \sim \frac{(T - T_f)}{T} \left( \frac{\partial H}{\partial \xi} \right)_{eq}^{p,T} \]  \hspace{1cm} (60)

Secondly, if we develop further the previous equation (59), without using the inequality (54), we arrive easily to the following equation:

\[ A \sim \frac{(T - T_f)}{T_f} \left( \frac{\partial H}{\partial \xi} \right)_{eq}^{p,T} \]  \hspace{1cm} (61)
In comparing the two previous equations, we conclude that neglecting the affinity before the heat of reaction in the linear regime is also equivalent to state that the fictive temperature remains close to the real temperature of the system to a first order:

\[ T_f \sim T \]  \hspace{1cm} (62)

Let us be aware, such as shown in the paper, that it is not true for the first order derivative of these two temperatures even to a first order:

\[ dT_f \neq dT \]  \hspace{1cm} (63)

Knowing this fact, we can start from the expression of the PD ratio recently derived by Schmelzer and Gutzow for isoaffine case [19]:

\[ \Pi_{A=\text{cste}}^{\text{conf}} = c\text{ste} \sim \frac{T_f}{T} \]  \hspace{1cm} (64)

And using the equality (61) we obtain easily that:

\[ \Pi_{A=\text{cste}}^{\text{conf}} \sim \frac{T_f}{T} \]  \hspace{1cm} (65)

which, as demonstrated, in the linear regime is close to the unity. Such an expression for the PD ratio has already been obtained by Ottinger by another way [42]. If we start mostly from the equality (60), that we have derived recently [41], we obtain for the isoaffine PD ratio the other expression:

\[ \Pi_{A=\text{cste}}^{\text{conf}} \sim \frac{T}{2T - T_f} \]  \hspace{1cm} (66)

which is also very close to the unity in the linear regime.

A last remark can be made: in using the Eq. (61) in place of Eq. (60) in the Eq. (42) then, a more exact expression is found for the expression (51) which becomes now:

\[ \Pi_{A=\text{cste}}^{\text{conf}} \sim \frac{T_f}{T} \frac{d\ln T}{d\ln T_f} = \frac{dp_f}{dp} \frac{dT}{dT_f} \]  \hspace{1cm} (67)

Upon the assumption used, this is equivalent to the expression (51).
Appendix B:

Firstly, let us rewrite the exact expressions of $\Pi_{\text{calo}}$ and $\Pi_{\text{meca}}$:

\[
\Pi_{\text{calo}} = \frac{\left(\frac{\partial H}{\partial \xi}\right)_{p,T}}{A + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} - T \left(\frac{dA}{dT}\right)_{p}}
\]

\[
\Pi_{\text{meca}} = \frac{\left(\frac{\partial V}{\partial \xi}\right)_{T,p}}{\left[\left(\frac{\partial V}{\partial \xi}\right)_{T,p} + \left(\frac{dA}{dp}\right)_{T}\right]}
\]

For the equation (68), in multiplying the numerator and denominator by the ratio $\left(\frac{\partial H}{\partial \xi}\right)_{p,T}/T \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T}$, we obtain the expression:

\[
\Pi_{\text{calo}} = \frac{\left[\left(\frac{\partial H}{\partial \xi}\right)_{p,T}\right]^2}{T \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T}}
\]

where we recognize for the numerator an expression close to the maximum contribution of the configurational heat capacity $\Delta C^e_{p}$ (see Eq. 28). Upon the assumptions used, where it is admitted that $\left(\frac{\partial H}{\partial \xi}\right)_{p,T} \sim \left(\frac{\partial H}{\partial \xi}\right)_{p,T}^{eq}$ and $\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T} \sim \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T}^{eq}$, then it is equivalent to $\Delta C^e_{p}$. For the denominator, we recognize $\Delta C_p$ expressed in function of the affinity and the temperature derivative of the affinity (see Ref. [43]). Indeed, in using the total differential of the affinity under isobaric condition, we can easily replaced $(d\xi/dT)_p$ in the classical expression of the heat capacity:

\[
C_p = \left(\frac{dH}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} \left(\frac{d\xi}{dT}\right)_p
\]

in order to obtain for $\Delta C_p = C_p - C_{p,\xi}$, which is the desired expression. In conclusion, close to equilibrium there is:

\[
\Pi_{\text{calo}} \sim \frac{\Delta C^e_{p}}{\Delta C_{p}}
\]

Starting from the equation (69), the same reasoning can be done. Let us start from the definition of the compressibility coefficient:

\[
\kappa_T = -\frac{1}{V} \left(\frac{dV}{dT}\right)_T - \frac{1}{V} \left(\frac{\partial V}{\partial \xi}\right)_{T,p} \left(\frac{d\xi}{dp}\right)_T
\]

In using the total differential of the affinity under isothermal condition we have obtained:

\[
\left(\frac{d\xi}{dp}\right)_T = -\left[\left(\frac{\partial V}{\partial \xi}\right)_{T,p} + \left(\frac{dA}{dp}\right)_{T}\right]
\]
which included in the preceding equality yields to:

$$\Delta \kappa_T = \frac{\left[ \left( \frac{\partial V}{\partial \xi} \right)_{T,p} \right]^2 + \left( \frac{\partial V}{\partial \xi} \right)_{T,p} \left( \frac{dA}{dp} \right)_T}{V \left( \frac{\partial^2 G}{\partial \xi^2} \right)_{p,T}}$$  \hspace{1cm} (75)

We observe that such expression appears directly if we multiply the numerator and denominator of the equation (69) by \( \left( \frac{\partial V}{\partial \xi} \right)_{T,p} / V \left( \frac{\partial^2 G}{\partial \xi^2} \right)_{p,T} \), and in this case the maximal contribution of the configurational compressibility coefficient (in the linear regime) appears directly:

$$\Delta \kappa_{eq}^T = \frac{\left[ \left( \frac{\partial V}{\partial \xi} \right)_{T,p} \right]^2}{V \left( \frac{\partial^2 G}{\partial \xi^2} \right)_{p,T}}$$  \hspace{1cm} (76)

Consequently:

$$\Pi_{meca} \sim \frac{\Delta \kappa_{eq}^T}{\Delta \kappa_T}$$  \hspace{1cm} (77)