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Comment regarding “On the theoretical determination of the Prigogine-Defay ratio in glass transition” [J. Chem. Phys. 136, 124502 (2012)]

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Generally, experimentally determined values of the Prigogine-Defay (PD) ratio are different from unity. This can be explained if one considers that more than one single order parameter are involved in the thermodynamics of the glass transition process. Against the consensual view, Tropin *et al.* demonstrated that PD ratios can be different from unity even if one single order parameter is involved. This “Comment” aims to discuss fundamental mistakes leading to this conclusion in the recent article “On the theoretical determination of the Prigogine-Defay ratio in glass transition” [J. Chem. Phys. 136, 124502 (2012)] by Tropin *et al.*

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In a recent paper by Tropin *et al.* “On the theoretical determination of the Prigogine-Defay ratio in glass transition” [1], several important errors are made that invalidate the principal conclusions. Since some of these errors are systematically reproduced in several papers published these last years by the same group, we feel obliged to draw attention to them. [2–4]

In the seminal papers of Davies and Jones on the irreversible approach to equilibrium in glasses [5], or on the thermodynamic and kinetic properties of glasses [6], the notion of structural order parameter ξ was used to describe the non-equilibrium behavior of systems undergoing a glass transition. Particularly, it is nowadays admitted that, since the experimentally determined values of the Prigogine-Defay (PD) ratio at the glass temperature are generally different from unity, then more than one structural order parameter are involved in the thermodynamics of the glass transition [6].

Against the consensual view, Tropin *et al.* demonstrated that PD ratios can be different from unity even if one single order parameter is involved. Although we do not discuss on the eventuality of such a conclusion, we argue that the expression of the PD ratio under which the authors based their reasoning is inexact. Firstly, we argue that this expression is not a PD ratio. Secondly, we state that this expression cannot be related to the glass transition, because important contributing terms are missing. Furthermore, we demonstrate that the alternative approach proposed in the last part of Ref. [1], allowing comparison between theory and experimentally determined values of the PD ratio, is also erroneous.

Such as originally demonstrated by Garden *et al.* [7], and published recently [8], a general expression can be derived when the configurational contributions of the three thermodynamic coefficients C_p , α_p and κ_T , are used in order to define a non-equilibrium configurational PD ratio:

$$\Pi^{conf} = \frac{1}{VT} \frac{C_p^{conf} \kappa_T^{conf}}{(\alpha_p^{conf})^2} \quad (1)$$

$$= \frac{\left(\frac{\partial H}{\partial \xi}\right)_{p,T} \left[\left(\frac{\partial V}{\partial \xi}\right)_{T,p} + \left(\frac{dA}{dp}\right)_T\right]}{\left(\frac{\partial V}{\partial \xi}\right)_{T,p} \left[A + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} - T \left(\frac{dA}{dT}\right)_p\right]} \quad (2)$$

where A is the affinity, $\left(\frac{\partial H}{\partial \xi}\right)_{p,T}$ is the heat of transformation and $\left(\frac{\partial V}{\partial \xi}\right)_{T,p}$ is the volume change involved in the process. $\left(\frac{dA}{dp}\right)_T$ and $\left(\frac{dA}{dT}\right)_p$ are the temperature and pressure derivatives of the affinity at constant temperature and constant pressure respectively. This expression above, and the associated exact calculations have only been recently used by Tropin and co-workers [4], and shown again in the Ref. [1]. Unfortunately, the authors systematically neglected the temperature and pressure derivatives of the affinity $\left(\frac{dA}{dp}\right)_T$ and $\left(\frac{dA}{dT}\right)_p$ as compared to their neighboring terms. Consequently, the following expression that the authors identified to a PD ratio is:

$$\Pi = \frac{\left(\frac{\partial H}{\partial \xi}\right)_{p,T}}{A + \left(\frac{\partial H}{\partial \xi}\right)_{p,T}} \quad (3)$$

This approximated expression was originally provided *ad hoc* in previous works because at this time the two affinity derivative contributions were simply omitted [2, 3, 9]. No proof is given in Ref. [1] and in previous works that suggest neglecting the two affinity derivatives in Eq. (2) to yield to Eq. (3). Actually, this assumption cannot be related to the glass transition since the expression (3) corresponds to a glass transition process occurring at constant affinity ($dA = 0$).

On the contrary, Garden *et al.* demonstrated recently that the two affinity-derivative contributions are of fundamental importance in the phenomenological description of the glass transition (see Fig. (5) and Fig. (9) in Ref. [10]). They are both involved in the thermodynamics describing the temperature and pressure behaviors of the coefficients C_p , κ_T , and α_p and thus in their changes at T_g [10]. For non-equilibrium systems ($A \neq 0$), it is obvious that the expression (3) above is different from unity. The question now arises whether this departure from unity has something in common with the classical question on measured PD ratios of glasses such as claimed by the authors. The departure from unity of such expression (3) is very small and has nothing to do with the classical problem of glass science on the non-unity of measured PD ratios (such as for example shown in Fig. 3 of Ref. [1] with only few percent of departure from unity).

In a further step, Tropin *et al.* proposed an alternative approach of the non-unity of the PD ratio [1]. This way was totally different from the previous one although the authors claimed that it reconfirmed previous conclusion. Indeed, the authors based now their demonstration on exact expressions relying on equilibrium properties of the system under consideration, i.e. now $A = 0$, in total contradiction with the PD ratio defined by the expression (3) above. Indeed, in the first part they attributed the departure from unity on the departure from equilibrium of the system. Now, in the paragraph IV, the authors used the fundamental equation (90) of Ref. [1]:

$$\Pi(T_g) = - \frac{\left(\frac{\partial H}{\partial \xi}\right)_{p,T} \left(\frac{\partial \xi_e}{\partial p}\right)_T}{T \left(\frac{\partial V}{\partial \xi}\right)_{T,p} \left(\frac{\partial \xi_e}{\partial T}\right)_p} \quad (4)$$

considering, this time, equilibrium transformations only, to allow comparison between the theory and experimentally determined values of the PD ratio. In a first step, they used the lattice-hole model of liquid to demonstrate that $\Pi(T_g) = 1$ (see paragraph IV.B: “Application to model systems: First example”). Next, in the same paragraph, the authors derived a new expression for the PD ratio (Eq. (100)). This time, the temperature and pressure dependence of the model parameters $\Delta E_0(p, T)$ and $v_0(p, T)$ were taken into account to discuss on the departure from unity of the PD ratio. As they did not know explicitly this temperature and pressure dependence, a very crude approximation was used in the following paragraph (see paragraph IV.C: “Application to model systems: Second example”) leading to an other expression of the PD ratio containing the Clausius-Clapeyron equation (Eq. (104)). The authors wanted to convince us that their approximate expressions (102) were in fact rather equivalent to the exact expressions (97) and (98) for the temperature and pressure derivatives of the equilibrium order parameter. We point out

that using too rough expressions (102), a wrong value for $\Pi(T_g)$ is achieved. To demonstrate that, it is sufficient to calculate the expressions $\left(\frac{\partial \xi_e}{\partial p}\right)_T$ and $\left(\frac{\partial \xi_e}{\partial T}\right)_p$ independently of the model used. Nevertheless, we agree that the parameters ΔE_0 and v_0 can be temperature and pressure dependent. Starting from the total differential of affinity (Eq. (5) of Ref. [1]), considering equilibrium only (i.e. $A = 0$; $dA = 0$; $\xi = \xi_e$), we then obtain the model independent expressions for the pressure and temperature derivatives of the equilibrium value of the order parameter (see for example Eq. (19.14), p. 293 of Ref. [11]):

$$\left(\frac{\partial \xi_e}{\partial p}\right)_T = \frac{\left(\frac{\partial V}{\partial \xi}\right)_{T,p}}{\left(\frac{\partial A}{\partial \xi}\right)_{T,p}}, \quad \left(\frac{\partial \xi_e}{\partial T}\right)_p = - \frac{\left(\frac{\partial H}{\partial \xi}\right)_{p,T}}{T \left(\frac{\partial A}{\partial \xi}\right)_{T,p}} \quad (5)$$

Substituting these expressions into (4) yields to unity. The question is: how these approximate expressions (102) can lead to $\Pi(T_g) \neq 1$, while the exact expressions above lead to $\Pi(T_g) = 1$? The answer is that the expressions (102) are truly too approximate and consequently this alternative second approach is also irrelevant.

In conclusion, the exact general expression (2) is not a classical PD ratio [7, 8]. Therefore, the expression (3) does not represent a classical PD ratio. More importantly, if it can be demonstrated that the general expression (2) is related to experimentally determined PD ratios (which has not been demonstrated by the authors), the expression (3) cannot be used, because important thermodynamic contributions are arbitrarily neglected. Eventually, the alternative approach based on equilibrium properties of the system allowing comparisons with experiments is also wrong.

Finally, at the present time it has not been demonstrated by Tropin *et al.* that, if only one single underlying order parameter is supposed to be involved in the thermodynamics of the glass transition, then the Prigogine-Defay ratio should be very different from unity like in experiments.

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