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On the theoretical determination of the Prigogine-Defay ratio in glass transition

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In a recent analysis [J. W. P. Schmelzer and I. Gutzow, J. Chem. Phys. **125**, 184511 (2006)] it was shown for the first time that – in contrast to earlier belief arising from the works of Prigogine and Defay [*Chemical Thermodynamics* (Longman, London, 1954), Chap. 19; The first French edition of this book was published in 1950] and Davies and Jones [Adv. Phys. **2**, 370 (1953); Proc. R. Soc. London, Ser. A **217**, 26 (1953)] – a satisfactory theoretical interpretation of the experimentally observed values of the so-called Prigogine-Defay ratio Π, being a combination of jumps of thermodynamic coefficients at glass transition, can be given employing only one structural order parameter. According to this analysis, this ratio has to be, in full agreement with experimental findings, larger than one ($\Pi > 1$). Its particular value depends both on the thermodynamic properties of the system under consideration and on cooling and heating rates. Based on above-mentioned analysis, latter dependence on cooling rates has been studied in detail in another own preceding paper [T. V. Tropin, J. W. P. Schmelzer, and C. Schick, J. Non-Cryst. Solids **357**, 1303 (2011)]. In the present analysis, an alternative general method of determination of the Prigogine-Defay ratio is outlined, allowing one to determine this ratio having at ones disposal the generalized equation of state of the glass-forming melts under consideration and, in particular, the knowledge of the equilibrium properties of the melts in the glass transformation range. Employing, as an illustration of the method, a particular model for the description of glass-forming melts, theoretical estimates are given for this ratio being, again, in good agreement with experimental data. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3694531]

I. INTRODUCTION

Following the classical concepts as developed by Simon,[1,2] vitrification in the cooling of glass-forming melts is commonly interpreted as the transformation of a thermodynamically (meta)stable equilibrium system into a frozen-in, thermodynamically non-equilibrium system, the glass. Hereby it is assumed in a first approximation – suggested by F. Simon – that the transformation takes place at some well-defined sharp temperature, the glass transition temperature, T_g. Note that Simon was aware that the glass transition proceeds not at a sharp temperature value but in a certain temperature interval. He even stated – with reference to Tammann and Kohlhaas[3] and Parks and Huffmann[4] – explicitly that by varying the cooling rate different glasses can be obtained. However, he considered both the width of this interval and the effect of varying cooling rates as small and, by this reason, as to be of minor importance.[1] However, a more detailed experimental and theoretical analysis shows[5–7] – as discussed in detail explicitly already by Tammann[8] – that the transition to a glass via the cooling of a glass-forming liquid proceeds in a more or less broad temperature range, where the characteristic times of change of temperature, τ_T, and relaxation times of the system to the respective equilibrium states,

τ, are of similar magnitude.[9,10] In this transition interval, irreversible processes take place, resulting both in an irreversible increase of entropy of the whole system as well as finally with a further decrease of temperature in an entropy freezing-in in the glass as well as in significant changes of the temperature dependencies of all other thermodynamic parameters of the vitrifying systems.[2,7,9,11,12]

In particular, the glass transition is accompanied by qualitative changes of the response of the system to variations of the external control parameters like temperature and pressure. These qualitative changes of the response of the system are reflected in jumps of the thermodynamic coefficients like specific heat, thermal expansion coefficient, and compressibility. Treating the glass transition similarly to second-order equilibrium phase transitions – i.e., as proceeding in a singular point (Simon's model) – Prigogine and Defay (the results were first derived by Prigogine and Defay in 1950 in their first edition of their book,[13] cf., Chap. 19) and Davies and Jones[14] (in a different way) came to the conclusion that the so-called Prigogine-Defay ratio, Π,

$$\Pi = \frac{1}{VT} \frac{\Delta C_p \Delta \kappa}{(\Delta \alpha)^2} \bigg|_{T=T_g},\qquad(1)$$

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has to have in glass transition a value equal to one provided the system can be described comprehensively by introducing only one additional structural order parameter. Here V is the volume, T the absolute temperature, ΔC_p, $\Delta \kappa$, and $\Delta \alpha$ are the jumps of isobaric heat capacity, isothermal compressibility, and thermal expansion coefficient, respectively. A similar relation has been obtained earlier in second-order equilibrium phase transitions according to Ehrenfest's classification. Here a similar ratio,

$$\Pi_E = \frac{1}{VT} \frac{\Delta C_p \Delta \kappa}{(\Delta \alpha)^2} = 1, \qquad (2)$$

connecting the jumps of the thermodynamic coefficients in second-order equilibrium phase transitions, has shown to be always equal to one (for details see Refs. 2 and 7 and, in particular, Refs. 10, 12, 15–17). Since experimental analysis shows that the value of the Prigogine-Defay ratio in glass transition is larger than one, the results of Prigogine and Defay[13] and Davies and Jones[14] were treated as an indication that glass-forming melts have to be described by employing more than one structural order parameter. A detailed description of the state of affairs in this respect is given in the monographs[2,7] and in Refs. 15–17 where a reconsideration of the described theoretical approach is developed.

Indeed, applying the same method as employed by Prigogine and Defay, it was shown by us in Refs. 15–17 that – in contrast to the previous general belief – the experimental data on the value of the Prigogine-Defay ratio can be given a theoretical interpretation by introducing only one structural order parameter into the description. According to this analysis, this ratio has to be, in agreement with experimental findings, larger than one ($\Pi > 1$). Its particular value depends both on the thermodynamic properties of the system under consideration and on cooling and heating rates. Latter dependence – the dependence of the Prigogine-Defay ratio on cooling and heating rates – has been studied in detail – based on the approach developed by us in Refs. 15 and 16 – in preceding papers.[12,17] This discussion will be continued and extended in the present analysis.

In the present analysis, we give first (Sec. II) a brief sketch of the basic ideas of the approach of Prigogine and Defay[13] and Davies and Jones[14] in order to show why they came originally to a different opinion as compared to our conclusions. In Sec. III, we show then why the more correct interpretation of glass transition as proceeding in a certain temperature interval leads to a different result. In addition (in Sec. IV), an alternative general method of theoretical estimation of the Prigogine-Defay ratio is outlined, allowing one to determine this ratio having at one's disposal the generalized equation of state of the glass-forming melts under consideration. Employing here a particular model of glass-forming melts, theoretical estimates are given for this ratio being, again, in good agreement with experimental data. Note, that the method is general, it is applicable also to any alternative models considered eventually as more appropriate for a given system. A summary of the results and discussion (Sec. V) completes the paper.

II. CLASSICAL APPROACHES TO THE THEORETICAL DETERMINATION OF THE PRIGOGINE-DEFAY RATIO: PRIGOGINE AND DEFAY (1950) AND DAVIES AND JONES (1953)

A. Approach of Prigogine and Defay (1950)

In order to derive an expression allowing one to interpret theoretically the experimental data on the value of the Prigogine-Defay ratio utilizing only one structural order parameter, we follow here widely the thermodynamic approach as developed by De Donder,[18] employed and advanced by Prigogine and Defay.[13] We modify their derivation to some extent allowing us in a straightforward way to arrive at a generalization of their original conclusion. In order to proceed in this way, we summarize here first some of basic dependencies giving us the possibility to describe glass-forming systems and the process of vitrification (for details see Refs. 2, 7, 9, 15–17).

Introducing one structural order parameter, ξ, into the description of glass-forming melts, the change of the Gibbs free energy, G, in dependence on temperature, T, pressure, p, and structural order parameter, ξ, can be expressed as

$$dG = -S dT + V dp - A d\xi, \qquad (3)$$

where S is the entropy, V is the volume, and A is the affinity. The following relations hold

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{p,T} \cong -G_e^{(2)}(\xi - \xi_e),$$

$$G_e^{(2)} = \left(\frac{\partial^2 G}{\partial \xi^2}\right)\bigg|_{p,T,\xi=\xi_e} > 0. \qquad (4)$$

According to Prigogine and Defay,[13] changes of the affinity as a function of temperature, T, pressure, p, and structural order parameter, ξ, can be expressed as

$$dA = \frac{(A + h_{p,T})}{T} dT - v_{p,T} dp + a_{p,T} d\xi, \qquad (5)$$

$$a_{p,T} = \left(\frac{\partial A}{\partial \xi}\right)_{p,T}, \quad v_{p,T} = \left(\frac{\partial V}{\partial \xi}\right)_{p,T}, \quad h_{p,T} = \left(\frac{\partial H}{\partial \xi}\right)_{p,T}. \qquad (6)$$

Taking into account the definition of the Gibbs free energy, $G = H - TS$, we arrive with Eq. (4) at

$$h_{p,T} = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} + T\left(\frac{\partial S}{\partial \xi}\right)_{p,T} = -A + T\left(\frac{\partial S}{\partial \xi}\right)_{p,T}. \qquad (7)$$

If one considers not A but ξ as the dependent and T, p, and A as the independent variables, Eq. (5) may be rewritten as

$$d\xi = \frac{1}{a_{p,T}} dA - \frac{A + h_{p,T}}{T a_{p,T}} dT + \frac{v_{p,T}}{a_{p,T}} dp. \qquad (8)$$

Utilizing the assumption underlying Eq. (8), ξ is, in general, a function of A, T, and p. Its total differential has then the form

$$d\xi = \left(\frac{\partial \xi}{\partial A}\right)_{p,T} dA + \left(\frac{\partial \xi}{\partial T}\right)_{p,A} dT + \left(\frac{\partial \xi}{\partial p}\right)_{A,T} dp. \tag{9}$$

A comparison between Eqs. (8) and (9) yields

$$\left(\frac{\partial \xi}{\partial A}\right)_{p,T} = \frac{1}{a_{p,T}}, \quad \left(\frac{\partial \xi}{\partial T}\right)_{A,p} = -\frac{A + h_{p,T}}{T a_{p,T}},$$
$$\left(\frac{\partial \xi}{\partial p}\right)_{A,T} = \frac{v_{p,T}}{a_{p,T}}. \tag{10}$$

For closed systems in thermodynamic equilibrium, only two of the three thermodynamic state parameters (pressure, p, volume, V, and temperature, T) are independent variables and the structural order-parameter is an unambiguous function of these parameters independent on the prehistory of the system. For such equilibrium states, the thermodynamic coefficients (like thermal expansion coefficient, α, isothermal compressibility, κ, and isobaric heat capacity, C_p (Refs. 19 and 20))

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p, \quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{11}$$

can be expressed, consequently, as functions of pressure, p, and temperature, T, exclusively.

Above definitions retain their validity also in the more general case, when the system is in a thermodynamically non-equilibrium state characterized by one (or several) additional structural order-parameter(s), ξ, being not uniquely defined by pressure and temperature alone but depending also on the prehistory. Provided, as an example, we cool down the system with a given rate, $q = (dT/dt) < 0$. Then, we transfer the system into a glass along one of the possible trajectories of cooling giving rise to different dependencies, $\xi = \xi(p, T; q)$, and $A = A(p, T; q)$. Here $q = q(t)$ specifies the chosen cooling law.

For any of above defined trajectories, $\xi = \xi(p, T; q)$, of vitrification, the thermodynamic coefficients can be expressed as a sum of two terms.[13–15] For example, the change of the volume in dependence on pressure at constant temperature can be written in the form

$$\left(\frac{\partial V}{\partial p}\right)_T = \left(\frac{\partial V}{\partial p}\right)_{T,\xi} + \left(\frac{\partial V}{\partial \xi}\right)_{p,T}\left(\frac{\partial \xi}{\partial p}\right)_T. \tag{12}$$

With the definition of the isothermal compressibility κ (Eq. (11)), this equation can be transformed to

$$\kappa = \kappa_\xi - \frac{1}{V}\left(\frac{\partial V}{\partial \xi}\right)_{p,T}\left(\frac{\partial \xi}{\partial p}\right)_T. \tag{13}$$

The step-like change in the compressibility in glass transition can be expressed therefore as

$$\Delta\kappa = \kappa - \kappa_\xi = -\frac{1}{V}\left(\frac{\partial V}{\partial \xi}\right)_{p,T}\left(\frac{\partial \xi}{\partial p}\right)_T. \tag{14}$$

Similarly to Eq. (12), we can describe the isobaric heat capacity of the undercooled metastable melt as

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = C_{p,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T}\left(\frac{\partial \xi}{\partial T}\right)_p, \tag{15}$$

$$\Delta C_p = C_p - C_{p,\xi} = \left(\frac{\partial H}{\partial \xi}\right)_{p,T}\left(\frac{\partial \xi}{\partial T}\right)_p. \tag{16}$$

For the thermal expansion coefficient (defined by Eq. (11)), analogous relations

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left\{\left(\frac{\partial V}{\partial T}\right)_{p,\xi} + \left(\frac{\partial V}{\partial \xi}\right)_{p,T}\left(\frac{\partial \xi}{\partial T}\right)_p\right\}$$
$$= \alpha_\xi + \frac{1}{V}\left(\frac{\partial V}{\partial \xi}\right)_{p,T}\left(\frac{\partial \xi}{\partial T}\right)_p, \tag{17}$$

$$\Delta\alpha = \alpha - \alpha_\xi = \frac{1}{V}\left(\frac{\partial V}{\partial \xi}\right)_{p,T}\left(\frac{\partial \xi}{\partial T}\right)_p \tag{18}$$

can be derived easily. By a combination of Eqs. (14), (16) and (18), we obtain the following expression for the Prigogine-Defay ratio:

$$\Pi(T_g) = \frac{1}{VT}\left\{\frac{\Delta C_p \Delta\kappa}{(\Delta\alpha)^2}\right\}\bigg|_{T=T_g}$$
$$= -\frac{\left(\frac{\partial H}{\partial \xi}\right)_{p,T}\left(\frac{\partial \xi}{\partial p}\right)_T}{T\left(\frac{\partial V}{\partial \xi}\right)_{p,T}\left(\frac{\partial \xi}{\partial T}\right)_p}\bigg|_{T=T_g}$$
$$= -\frac{h_{p,T}}{T v_{p,T}}\frac{\left(\frac{\partial \xi}{\partial p}\right)_T}{\left(\frac{\partial \xi}{\partial T}\right)_p}\bigg|_{T=T_g}. \tag{19}$$

Applying these results to the interpretation of the glass transition, the differences in the thermodynamic coefficients and, consequently, the partial derivatives in Eq. (19) have to determined according to the approach employed for the glass transition temperature $T = T_g$. The particular way, how it has to be done in order to be able to employ the results for the interpretation of experimental data will be specified below.

In order to arrive first at some general model-independent conclusions, we determine now – employing the approach of De Donder[18] and Prigogine and Defay[13] – the derivatives $(\partial \xi/\partial p)_T$ and $(\partial \xi/\partial T)_p$ taking into account that the affinity along the chosen path (depending on cooling and heating rates) is defined uniquely via pressure and temperature similarly to the order parameter, ξ. Equation (8) yields then

$$d\xi = \frac{1}{a_{p,T}}dA - \frac{A + h_{p,T}}{T a_{p,T}}dT + \frac{v_{p,T}}{a_{p,T}}dp, \tag{20}$$

$$d\xi = \frac{1}{a_{p,T}}\left[\left(\frac{\partial A}{\partial T}\right)_p - \frac{A + h_{p,T}}{T}\right]dT$$
$$+ \frac{1}{a_{p,T}}\left[\left(\frac{\partial A}{\partial p}\right)_T + v_{p,T}\right]dp. \tag{21}$$

According to Eq. (5), the affinity A is in general a function of ξ, T, and p. Along the given path of cooling, the structural order parameter becomes a function of pressure and temperature. By this reason, the derivative of affinity with respect to pressure and temperature has to be computed similarly like the thermodynamic coefficients as given via Eqs. (12), (15) and (17).

The ratio $((\partial \xi / \partial p)_T / (\partial \xi / \partial T)_p)$, entering Eq. (19), can be written, consequently, as

$$\frac{\left(\frac{\partial \xi}{\partial p}\right)_T}{\left(\frac{\partial \xi}{\partial T}\right)_p} = \frac{\left(\frac{\partial A}{\partial p}\right)_T + v_{p,T}}{\left(\frac{\partial A}{\partial T}\right)_p - \frac{A + h_{p,T}}{T}}$$

$$= -\frac{T v_{p,T}}{A + h_{p,T}} \frac{\left[1 + \frac{1}{v_{p,T}}\left(\frac{\partial A}{\partial p}\right)_T\right]}{\left[1 - \frac{T}{A + h_{p,T}}\left(\frac{\partial A}{\partial T}\right)_p\right]} \quad (22)$$

and Eq. (19) yields (see also Refs. 15 and 17)

$$\Pi(T_g) = \frac{h_{p,T}}{A + h_{p,T}} \left. \frac{\left[1 + \frac{1}{v_{p,T}}\left(\frac{\partial A}{\partial p}\right)_T\right]}{\left[1 - \frac{T}{A + h_{p,T}}\left(\frac{\partial A}{\partial T}\right)_p\right]} \right|_{T=T_g}. \quad (23)$$

Utilizing, now, Simon's model, we have to follow the equilibrium curve up to the glass transition temperature. This assumption implies that both the affinity and the derivative of affinity with respect to pressure and temperature have to be set equal to zero. In such model approach, Eq. (23) yields $\Pi = 1$ independent on any additional assumptions concerning the system under consideration.

This result – that the Prigogine-Defay ratio is equal to one if one structural order parameter is employed for the description of glass-forming melts – was first derived by Prigogine and Defay in 1950 in the first edition of their book[13] (cf. Chap. 19). According to the analysis as sketched above, their conclusion is a direct result of this simplifying and in general not appropriate additional assumption that the glass transition proceeds suddenly at some well-defined temperature, T_g. The consequences with respect to the value of the Prigogine-Defay ratio, if one employs instead of Simon's model a more correct model of glass transition, will be discussed below.

B. Approach of Davies and Jones (1953)

1. Case of one structural order parameter

In their alternative approach to the determination of the Prigogine-Defay ratio (and a variety of other relationships describing the glass transition) not employing De Donder's thermodynamic method of description, Davies and Jones[14] went the following way. They introduced first a differentiable function $\varphi(x, y, \xi)$ of three independent variables x, y, and ξ. In addition, they consider a set of surfaces $u(x, y, \xi) = $ constant or in other words, a set of surfaces $\xi = \xi(x, y)$. One can then determine the derivatives of φ at constant ξ and constant u or for $\xi = \xi(x, y)$. In a next step, (i) the condition $u(x, y, \xi) = $ constant is connected with the equilibrium condition realized for the metastable liquid and (ii) constancy of the structural order parameter with the glassy state of the system under consideration. It is assumed in the analysis that – at the glass transition temperature – the equilibrium liquid and glass go over directly into each other in cooling or heating. Consequently, in the method of analysis of Davies and Jones, again, Simon's model is employed.

As the result of the analysis,[14] they obtained

$$\left. \frac{\partial \varphi(x, y, \xi)}{\partial x} \right|_u = \left. \frac{\partial \varphi(x, y, \xi)}{\partial x} \right|_{y,\xi} + \left. \frac{\partial \varphi(x, y, \xi)}{\partial \xi} \right|_{x,y} \left. \frac{\partial \xi}{\partial x} \right|_y. \quad (24)$$

For any fixed value of y, we have further

$$du = \left. \frac{\partial u(x, y, \xi)}{\partial x} \right|_{y,\xi} dx + \left. \frac{\partial u(x, y, \xi)}{\partial \xi} \right|_{x,y} d\xi = 0. \quad (25)$$

It follows

$$\left. \frac{\partial \xi}{\partial x} \right|_y = - \frac{\left. \frac{\partial u(x, y, \xi)}{\partial x} \right|_{y,\xi}}{\left. \frac{\partial u(x, y, \xi)}{\partial \xi} \right|_{x,y}}. \quad (26)$$

Equation (24) reads then

$$\Delta \left(\frac{\partial \varphi}{\partial x} \right) = \left. \frac{\partial \varphi(x, y, \xi)}{\partial x} \right|_u - \left. \frac{\partial \varphi(x, y, \xi)}{\partial x} \right|_{y,\xi} = -\varphi_\xi \frac{u_x}{u_\xi}, \quad (27)$$

with

$$\varphi_\xi = \left. \frac{\partial \varphi(x, y, \xi)}{\partial \xi} \right|_{x,y}, \quad u_x = \left. \frac{\partial u(x, y, \xi)}{\partial x} \right|_{y,\xi}, \quad (28)$$

$$u_\xi = \left. \frac{\partial u(x, y, \xi)}{\partial \xi} \right|_{x,y}. \quad (29)$$

These are the normal partial derivatives.

Equivalently to Eq. (27), we get

$$\Delta \left(\frac{\partial \varphi}{\partial y} \right) = \left. \frac{\partial \varphi(x, y, \xi)}{\partial y} \right|_u - \left. \frac{\partial \varphi(x, y, \xi)}{\partial y} \right|_{x,\xi} = -\varphi_\xi \frac{u_y}{u_\xi} \quad (30)$$

with

$$u_y = \left. \frac{\partial u(x, y, \xi)}{\partial y} \right|_{x,\xi}. \quad (31)$$

The equilibrium conditions at appropriate boundary conditions are given by the relation

$$u = f_\xi(x, y, \xi) = \left. \frac{\partial f(x, y, \xi)}{\partial \xi} \right|_{x,y} = 0. \quad (32)$$

With these conditions, we obtain from Eqs. (27) and (30)

$$u = f_\xi, \quad \varphi = f_x, \quad \Delta \left(\frac{\partial f_x}{\partial x} \right) = -\frac{f_{x\xi}^2}{f_{\xi\xi}}, \quad (33)$$

$$u = f_\xi, \quad \varphi = f_x, \quad \Delta\left(\frac{\partial f_x}{\partial y}\right) = -\frac{f_{x\xi} f_{y\xi}}{f_{\xi\xi}}, \quad (34)$$

$$u = f_\xi, \quad \varphi = f_y, \quad \Delta\left(\frac{\partial f_y}{\partial y}\right) = -\frac{f_{y\xi}^2}{f_{\xi\xi}}, \quad (35)$$

$$u = f_\xi, \quad \varphi = f_y, \quad \Delta\left(\frac{\partial f_y}{\partial x}\right) = -\frac{f_{y\xi} f_{x\xi}}{f_{\xi\xi}}. \quad (36)$$

From Eqs. (33) and (35), we arrive then at

$$\Delta\left(\frac{\partial f_x}{\partial x}\right)\Delta\left(\frac{\partial f_y}{\partial y}\right) = \left[\Delta\left(\frac{\partial f_x}{\partial y}\right)\right]^2 = \left[\Delta\left(\frac{\partial f_y}{\partial x}\right)\right]^2. \quad (37)$$

Now, let us treat in detail the situation that the system is kept at some given pressure, p ($x = p$), and some given temperature, T ($y = T$). In such case, the potential function, f, is the Gibbs free energy, G ($f = G$). Equation (37) yield then

$$\Delta G_{pp}\Delta G_{TT} = (\Delta G_{pT})^2 = (\Delta G_{Tp})^2. \quad (38)$$

With

$$dG = -SdT + Vdp \quad (39)$$

we obtain

$$\frac{\partial G}{\partial p} = V, \quad \frac{\partial^2 G}{\partial p^2} = \frac{\partial V}{\partial p}, \quad \frac{\partial^2 G}{\partial p \partial T} = \frac{\partial V}{\partial T}, \quad (40)$$

$$\frac{\partial G}{\partial T} = -S, \quad \frac{\partial^2 G}{\partial T^2} = -\frac{\partial S}{\partial T}, \quad (41)$$

and from Eq. (38)

$$\Delta\left(\frac{\partial V}{\partial p}\right)\Delta\left(-\frac{\partial S}{\partial T}\right) = \left(\Delta\frac{\partial V}{\partial T}\right)^2. \quad (42)$$

With the expressions for the thermal expansion coefficient, α, heat capacity at constant pressure, C_p, and isothermal compressibility, κ (cf. Eq. (11))

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right), \quad C_p = T\left(\frac{\partial S}{\partial T}\right), \quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right), \quad (43)$$

we get finally

$$\left.\frac{1}{VT}\frac{\Delta\kappa\,\Delta C_p}{(\Delta\alpha)^2}\right|_{T=T_g} = 1, \quad (44)$$

i.e., the above specified ratio is equal to one, again.

As already mentioned, this result is a consequence of the application of Simon's model. According to the assumption of Davies and Jones the system goes over from a metastable equilibrium state directly to the frozen-in state of a glass. In particular, note that dQ in Eq. (11) is replaced by TdS in Eq. (43). Such replacement is possible only if the system does not undergo in the glass transition any irreversible (relaxation) processes as in reality it is the case.

As evident and underlined by the authors,[14] the way of derivation of Eq. (44) as employed by Davies and Jones and described here briefly does not employ the application of

De Donder's method, however, the underlying the respective derivations assumptions are equivalent to the basic assumptions employed by Prigogine and Defay: by both groups of authors, the Simon model of the glass transition is essentially utilized.

2. Case of several structural order parameters

Davies and Jones[14] showed further already in 1953 that, for the case that more than one structural order parameter is required to appropriately describe the state of the glass-forming melt, the value of the Prigogine-Defay ratio may become larger than one. In the respective analysis, again, Simon's model is employed.

In this more general case (introducing into the description a set of structural order parameters $\{\xi_i\}$), Davies and Jones arrived at the following expressions:

$$\Delta C_p = \frac{1}{T}\sum_{i,j}\beta_{ij}\left(\frac{\partial H}{\partial \xi_i}\right)_{p,T}\left(\frac{\partial H}{\partial \xi_j}\right)_{p,T}, \quad (45)$$

$$\Delta\alpha = \frac{1}{TV}\sum_{i,j}\beta_{ij}\left(\frac{\partial H}{\partial \xi_i}\right)_{p,T}\left(\frac{\partial V}{\partial \xi_j}\right)_{p,T}, \quad (46)$$

$$\Delta\kappa = \frac{1}{V}\sum_{i,j}\beta_{ij}\left(\frac{\partial V}{\partial \xi_i}\right)_{p,T}\left(\frac{\partial V}{\partial \xi_j}\right)_{p,T} \quad (47)$$

leading to the result

$$\Delta\kappa\,\Delta C_p \geq TV(\Delta\alpha)^2. \quad (48)$$

It is noted then by these authors that for the case that the number of structural order parameters is equal to one, Eq. (44) is reestablished, again. However, it is further mentioned that Eq. (44) is fulfilled as well even for systems described by a set of structural order parameters, if for all structural order parameters the relations

$$\left(\frac{\partial H}{\partial \xi_i}\right)_{p,T} = k\left(\frac{\partial V}{\partial \xi_j}\right)_{p,T}, \quad i = 1, 2, \ldots, n \quad (49)$$

hold. So, the existence of more than one structural order parameters does not imply necessarily that the Prigogine-Defay ratio will be larger than one. DiMarzio stated later[21] that even in the case of several structural order parameters, the Prigogine-Defay ratio has to be equal to one provided the Simon model is employed in the description of the glass transition. This conclusion was, however, later refuted by Goldstein[22] and Gupta and Moynihan[23] (c.f. also Ref. 24).

C. A first conclusion

Summarizing these considerations, we can conclude: The assumptions underlying Simon's model of the glass transition have been employed by both Prigogine and Defay[13] and Davies and Jones[14] in their theoretical analysis of the value of the Prigogine-Defay ratio in glass transition. Both groups of authors came to the result that, provided only one structural order parameter governs the behavior of the system, the Prigogine-Defay ratio has to be equal to one. It is demonstrated here that it is really the already mentioned additional

assumption – the application of Simon's model of the glass transition in the analysis – that is leading to their result.

We will show further that an alternative approach and resolution of the deviations between theoretical predictions and experimental data on the Prigogine-Defay ratio is possible. This approach may lead – as shown as well – to correct results already in the case when only one structural order parameter is employed but not Simon's but the more realistic model of the glass transition as proceeding in a certain temperature interval is employed in the analysis.

III. PRIGOGINE-DEFAY RATIO: BEYOND SIMON'S MODEL

A. Application of De Donder's method

1. General results

As shown here earlier, the value of the Prigogine-Defay ratio can be estimated in terms of De Donder's approach (c.f. Eq. (23) and also Refs. 7, 12, and 17) as

$$\Pi(T_g) = \frac{h_{p,T}}{A + h_{p,T}} \frac{\left[1 + \frac{1}{v_{p,T}}\left(\frac{\partial A}{\partial p}\right)_T\right]}{\left[1 - \frac{T}{A + h_{p,T}}\left(\frac{\partial A}{\partial T}\right)_p\right]}\Bigg|_{T=T_g} . \quad (50)$$

Employing the model of glass-forming melts as discussed in detail in Refs. 2 and 7, estimates can be easily made of the derivatives $(\partial A/\partial p)$ and $(\partial A/\partial T)$. Utilizing such estimates, the terms containing derivatives of the affinity with respect to pressure and temperature in the square brackets in Eq. (50) can be shown to be small in comparison with one. By this reason, we can neglect them in a good approximation reconfirming the result obtained in Refs. 2, 7, 15, and 16, i.e.,

$$\Pi(T_g) \cong \frac{h_{p,T}}{A + h_{p,T}}\Bigg|_{T=T_g} . \quad (51)$$

Employing Simon's model for the estimation of the Prigogine-Defay ratio

$$\xi = \xi_e \quad \text{for} \quad T \geq T_g, \quad \xi = \xi_e(T_g) \quad \text{for} \quad T \leq T_g, \quad (52)$$

we arrive at

$$A = -G_e^{(2)}(\xi - \xi_e),$$
$$A(T_g) = -G_e^{(2)}(T_g)(\xi(T_g) - \xi_e(T_g)) = 0, \quad (53)$$

resulting in $\Pi = 1$, i.e., the value of the Prigogine-Defay ratio has to be equal to one in such cases independent on any particular assumptions concerning the system under consideration and the process conditions. In addition, no hysteresis effects occur, i.e., the value of the Prigogine-Defay ratio is the same for cooling and heating.

In terms of the generic model of vitrification and relaxation,[7] we have generally

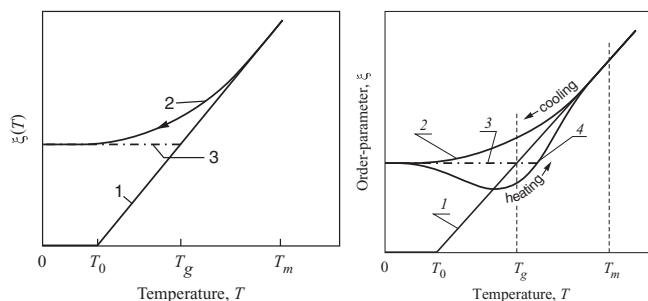$$A = -G_e^{(2)}(\xi - \xi_e), \quad G_e^{(2)} > 0, \quad h_{p,T} > 0, \quad A + h_{p,T} > 0. \quad (54)$$

FIG. 1. Dependence of the structural order parameter, ξ, in cooling and heating of a glass-forming melt: (1) Equilibrium value, (2) cooling curve, (3) Simon's approximation, and (4) heating curve. Treating vitrification in terms of Simon's model (curve (3) supplemented by the upper part of curve (1)), we get $\Pi = 1$ since under such assumption the state of the system in the metastable liquid coincides at T_g with the state of the glass. In contrast, considering the real cooling and glass transition as proceeding in a certain temperature interval, then we arrive at $\Pi > 1$ ($A < 0$) at cooling while for heating, $\Pi < 1$ ($A > 0$) is obtained.

For cooling, $\Pi > 1$, is obtained and for heating, $\Pi < 1$ (cf. Refs. 7 and 15). Treating vitrification in the way presented and going beyond Simon's model, one structural order parameter is sufficient to explain a value of $\Pi \neq 1$! The results of this analysis are illustrated on Fig. 1.

2. Interpretation of experimental data

Having arrived at these results, the question arises now which of the theoretically possible values of Π has to be chosen in order to interpret experimental data, i.e., to determine the ratio of the respective values of the thermodynamic coefficients as obtained by measurements and their interpretation. The procedure of the experimental specification of the value of the Prigogine-Defay ratio is discussed in detail in the caption to Fig. 2. As it follows from such analysis, in experiment not the current values of the ratio of the thermodynamic coefficients in cooling and/or heating are measured and, consequently, have to be treated theoretically but the jumps in the extrapolations of their equilibrium values as compared with the respective data obtained for the glass.

However, having a close look, for example, at the temperature dependencies of the structural order parameter and the configurational contributions to the specific heat as shown in Figs. 1 and 2, it is evident that – from the knowledge of the actual values of the thermodynamic coefficients along the **cooling curves** – one can make estimates of the experimentally determined values of the jumps of the thermodynamic coefficients in vitrification. Indeed, it can be assumed with a good accuracy[15] that the configurational specific heat determined for the cooling curve intersects the dashed Simon's model curve at nearly half of its jump at T_g ($\varphi \cong 2$) or some similar and identical for all thermodynamic coefficients factor φ. This assumption is based on the fact that the configurational contributions of all thermodynamic coefficients are essentially determined via the dependence of the structural order parameter on temperature. It will be discussed in more detail in Sec. III B. Employing such assumption, we get

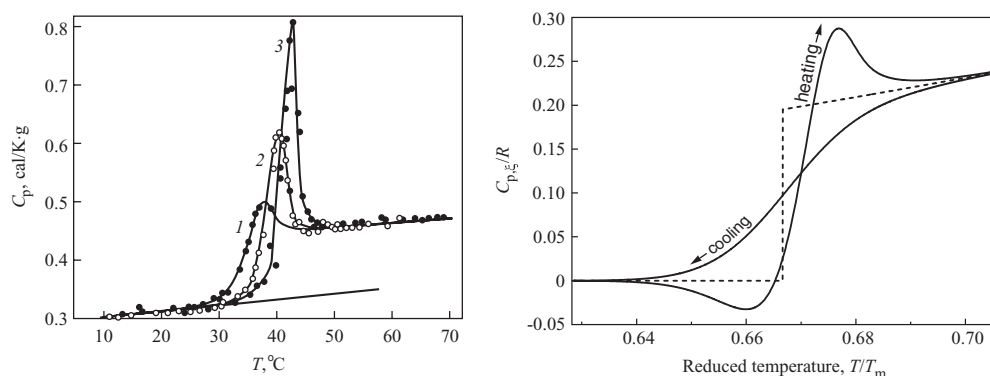$$\Delta C_p^{(exp)} = \varphi C_{p,conf}(T_g). \quad (55)$$

FIG. 2. (Top) $C_p(T)$-curves obtained in the process of heating of a glass-forming organic polymer melt (polyvinyl acetate) for different heating rates according to the measurements of Zhurkov and Levin (Ref. 29). Curve (1) corresponds to a heating rate of 0.1 K min^{-1}, curve (2) to 0.4 K min^{-1} and curve (3) to 1.5 K min^{-1}. (Bottom) Configurational contributions to the specific heat as determined theoretically. By a dashed curve, the construction is sketched how the jumps in the thermodynamic coefficients are determined experimentally. This approach corresponds in fact to a treatment of the glass transition corresponding to Simon's model (for further details see, e.g., Refs. 7, 9, and 15).

Assuming as mentioned that similar dependencies hold also for thermal expansion coefficient and compressibility

$$\Delta\alpha^{(exp)} = \varphi\alpha_{conf}(T_g), \quad \Delta\kappa^{(exp)} = \varphi\kappa_{conf}(T_g), \quad (56)$$

we get the following relation for the value of the Prigogine-Defay ratio, $\Pi^{(exp)}$, as it is determined experimentally:

$$\Pi^{(exp)} = \frac{1}{VT}\left\{\frac{\Delta C_p^{(exp)}\Delta\kappa^{(exp)}}{(\Delta\alpha^{(exp)})^2}\right\}\Bigg|_{T=T_g} = \Pi(T_g)^{\text{cooling}}$$

$$= \frac{h_{p,T}}{A + h_{p,T}}\Bigg|_{T=T_g}^{\text{Cooling}} > 1. \quad (57)$$

As already shown in Ref. 15 employing, again, the same model of glass-forming melts as utilized in the estimate of the dependence of the affinity on pressure and temperature (c.f. the discussion of Eq. (50)), we arrive at

$$\Pi = \frac{1}{1 - \left(\dfrac{G_e^{(2)}}{\chi RT_m}\right)(\xi - \xi_e)\Big|_{T=T_g}}$$

$$\cong \frac{1}{1 - \dfrac{\theta}{\chi}\left(\dfrac{\xi - \xi_e}{\xi_e}\right)\Big|_{T=T_g}}. \quad (58)$$

Thermodynamic properties of the system under consideration affect in this model the value of the Prigogine-Defay ratio via the parameter χ and the function $\xi_e = \xi_e(T)$ while the dynamics of the glass transition and the dependence on cooling rate is determined via the values of θ and ξ all of them taken at the appropriate for the cooling rate value of glass transition temperature. The results of computations of this dependence of Π on the cooling rate are shown on Fig. 3 (for the details see Ref. 17).

B. Test of the assumption underlying the analysis of experimental data

1. Model system: Basic dependencies

In order to test above employed assumption, we have to have at our disposal a model of glass-forming systems under consideration. For the specification of the thermodynamic properties of glass-forming melts, we employ here relations derived from a simple lattice-hole model of liquids discussed in detail in Refs. 2, 7, 9, 15, and 16 (a similar model has been employed recently by Johari in the analysis of the intensively discussed problem of configurational and residual entropies of defect crystals and the entropy's behavior on glass formation[25] and also by Goldstein[26]). The structural order parameter is connected in the framework of this model with the free volume of the liquid and defined via the number of unoccupied lattice sites (or holes), N_0, per mole of the liquid each of them having a volume, $v_0(p, T)$, identical to the volume occupied by a structural unit of the liquid at the same values of pressure and temperature. According to this model, the molar
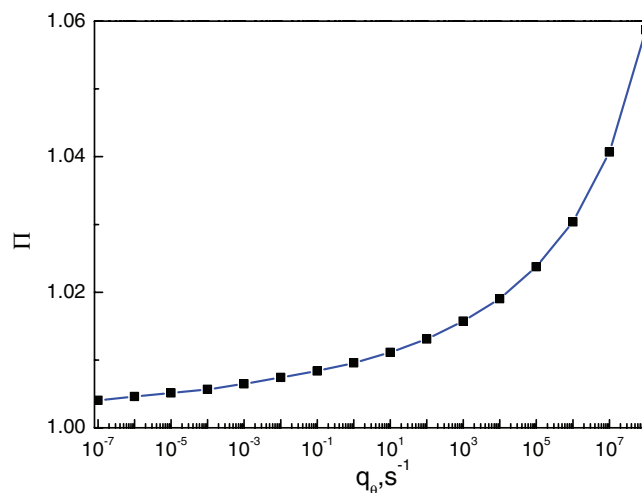

FIG. 3. Dependence of the Prigogine-Defay ratio of the given model system on cooling rates (for details see Refs. 12 and 17).

volume of the liquid is determined as[2]

$$V(p, T, \xi) = (N_A + N_0)v_0(p, T). \quad (59)$$

Here N_A is the Avogadro number. In the framework of this model, the fully ordered or crystalline state corresponds to a value of the structural order parameter equal to $\xi = 0$.[2]

The molar fraction of holes, ξ, in the system is given then by

$$\xi = \frac{N_0}{N_A + N_0}. \quad (60)$$

With

$$1 - \xi = \frac{N_A}{N_A + N_0}, \quad (61)$$

we can write the following expression for the configurational contributions to the volume of the system:

$$V_{conf} = N_0 v_0(p, T) = N_A v_0(p, T)\frac{\xi}{1 - \xi}. \quad (62)$$

The thermodynamic functions of the system are described in the framework of this model by the sum of contributions resulting from the thermal motion of the molecules of the liquid and, in addition, from the configurational contributions described by the structural order parameter, ξ. The configurational contribution to the molar volume (or the excess molar volume) is given, consequently, by Eq. (62).

The configurational part of the entropy per mole is described in this model via the conventional mixing term[2]

$$S_{conf} = -R\left(\ln(1 - \xi) + \frac{\xi}{1 - \xi}\ln\xi\right). \quad (63)$$

Introducing via ΔE_0 the energy of hole formation, the configurational contributions to the internal energy, U_{conf}, gets the form[2]

$$U_{conf} = \Delta E_0 \xi. \quad (64)$$

The configurational contribution to the enthalpy, H_{conf}, is given then by

$$H_{conf} = U_{conf} + pV_{conf} = \Delta E_0 \xi + N_0 v_0(p, T)\frac{\xi}{1 - \xi}. \quad (65)$$

The configurational contribution to the Gibbs free energy can be expressed, consequently, as

$$\begin{aligned} G_{conf} &= U_{conf} + pV_{conf} - TS_{conf} \\ &= \Delta E_0 \xi + N_0 v_0(p, T)\frac{\xi}{1 - \xi} \\ &\quad + RT\left(\ln(1 - \xi) + \frac{\xi}{1 - \xi}\ln\xi\right). \end{aligned} \quad (66)$$

The equilibrium conditions, $(\partial G_{conf}/\partial\xi) = 0$, yield in this case

$$\xi_e = \exp\left(-\frac{\Delta E_0(1 - \xi_e)^2 + pV_0}{RT}\right), \quad V_0 = N_A v_0. \quad (67)$$

For our purposes, a slightly modified version of this model[7,9,15,16] will be of major interest. It employs the normally fulfilled approximation $\xi \ll 1$ resulting in

$$V_{conf} \cong N_A v_0(p, T)\xi. \quad (68)$$

In the same approximation, the total volume is given by

$$V(p, T, \xi) \cong N_A v_0(p, T)(1 + \xi), \quad \xi = \frac{N_0}{N_A + N_0} \cong \frac{N_0}{N_A}. \quad (69)$$

In this modification of the model, primarily the configurational contribution to the enthalpy, H_{conf}, of one mole of the liquid is discussed. It is described in the framework of this modification of the lattice-hole model via the molar heat of evaporation, $\Delta H_{ev}(T_m)$, of the liquid at the melting temperature as

$$H_{conf} = \chi_1 \Delta H_{ev}(T_m)\xi.$$
$$\Delta H_{ev}(T_m) \cong \chi_2 RT_m \quad \text{with} \quad \chi_2 = 20. \quad (70)$$

With $H = U + pV$, we obtain for the configurational contribution to the internal energy the relation

$$U_{conf} = [\chi_1 \Delta H_{ev}(T_m) - pv_0(p, T)]\xi. \quad (71)$$

Finally, employing the definition of Gibbs' free energy, $G = U - TS + pV$, we arrive at

$$G_{conf} = \chi_1 \Delta H_{ev}(T_m)\xi + RT\left(\ln(1 - \xi) + \frac{\xi}{1 - \xi}\ln\xi\right). \quad (72)$$

The equilibrium value of the structural order parameter, $\xi = \xi_e$, is determined generally via the relation $(\partial G_{conf}/\partial\xi)$, again, resulting in this case in

$$\frac{\partial G_{conf}}{\partial\xi} = \chi_1 \Delta H_{ev}(T_m) + RT\frac{\ln\xi}{(1 - \xi)^2} = 0. \quad (73)$$

With Eqs. (70), (72) and (73), we obtain the following result

$$\frac{(1 - \xi_e)^2}{\ln\xi_e} = -\frac{1}{\chi}\left(\frac{T}{T_m}\right) \quad \text{where} \quad \chi = \chi_1\chi_2. \quad (74)$$

Knowing the value of χ_2 (cf. Eq. (70)), we determine the value of the parameter χ_1 demanding that at $T = T_m$ the value of ξ_e should be approximately equal to 0.05 (corresponding to experimentally observed density differences between liquid and crystal at the melting temperature, T_m[2]). In the computations performed here we set $\chi_2 = 20$ and $\chi_1 = 0.166$ resulting in $\chi = 3.32$.

In the vicinity of the state of configurational equilibrium, we obtain from Eq. (72) after performing a truncated Taylor expansion the result

$$G_{conf}(p, T, \xi)$$
$$\cong G_{conf}(p, T, \xi_e) + \frac{1}{2}\left(\frac{\partial^2 G_{conf}}{\partial\xi^2}\right)\Bigg|_{p,T,\xi=\xi_e}(\xi - \xi_e)^2. \quad (75)$$

The value of

$$G_e^{(2)} = \frac{\partial^2 G}{\partial \xi^2}\bigg|_{\xi=\xi_e} = RT \frac{\partial}{\partial \xi}\left[\frac{\ln \xi}{(1-\xi)^2}\right]_{\xi=\xi_e} > 0 \quad (76)$$

at equilibrium can now be easily calculated based on Eqs. (72) and (74). For physically reasonable small values of ξ, we get as an estimate[16]

$$G_e^{(2)} \cong \frac{RT}{\xi_e}. \quad (77)$$

2. Jumps of thermodynamic coefficients

Going over to the analysis of methods of theoretical determination of the value of the Prigogine-Defay ratio, in a first step we will analyze the behavior of the thermodynamic coefficients in vitrification in dependence on cooling rate. As an example, we consider here the configurational specific heat.

The specific heat along the path, given by $\xi = \xi(p, T; q)$, is a function of pressure, temperature, and the structural order-parameter, i.e., $C = C(p, T, \xi)$. Assuming the pressure to be kept constant, we have, by definition,

$$C_p(p, T, \xi) = \frac{dQ}{dT}. \quad (78)$$

From the first law of thermodynamics ($dU = dQ - pdV$) and the definition of the enthalpy, $H = U + pV$, we obtain

$$dH = dQ + Vdp \quad (79)$$

resulting, with the condition $p = \text{constant}$, in

$$dH = C_p(p, T, \xi)dT. \quad (80)$$

In a more extended form, Eq. (80) can be written as the sum of two terms (cf. Refs. 2, 7, 9, 13, and 14)

$$C_p(p, T, \xi) = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T}\frac{d\xi}{dT}. \quad (81)$$

The first term on the right hand side of above equation reflects the contribution to the specific heat due to thermal motion of the molecules (e.g., the phonon part), while the second term refers to configurational contributions.

Employing the model of glass-forming melts discussed above, the configurational contribution to the specific heat, $C_{p,\,conf}$, is given with Eq. (70) by

$$C_{p,conf} = \left(\frac{\partial H_{conf}}{\partial \xi}\right)_{p,T}\frac{d\xi}{dT} = \chi_1 \Delta H_{ev}(T_m)\frac{d\xi}{dT}. \quad (82)$$

In the model of vitrification, developed by Simon, the glass-forming system remains in a metastable state until a certain temperature, T_g, is reached in the cooling process (i.e., $\xi = \xi_e$ for $T \geq T_g$). At this temperature, the system becomes frozen-in and the structural order-parameter does not change any more in the further cooling process (i.e., $(d\xi/dT) = 0$ for $T \leq T_g$ or $\theta \leq \theta_g$). The configurational contribution, $C_{p,\,conf}$, to
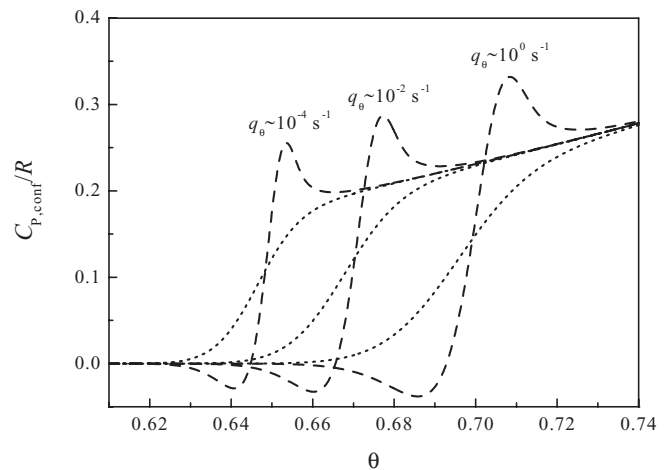

FIG. 4. Configurational contributions to the specific heats are shown for different values of the cooling and heating rates. Dotted curves refer to cooling and dashed curves to heating (for the details see Ref. 17).

the specific heat resulting from processes of structural reorganization, has then, consequently, the form

$$C_{p,conf}^{(Simon)} = \begin{cases} \chi_1 \Delta H_{ev}(T_m)\left(\dfrac{d\xi_e}{dT}\right) & \text{for} \quad T_g \leq T \leq T_m \\ 0 & \text{for} \quad 0 \leq T < T_g \end{cases} \quad (83)$$

with (cf. Eq. (74))

$$\frac{d\xi_e}{dT} = \chi\left(\frac{T_m}{T^2}\right)\frac{\xi_e(1-\xi_e)^3}{1-\xi_e+2\xi_e\ln\xi_e}, \quad (84)$$

$$\frac{d\xi_e}{d\theta} = \frac{1}{\chi}\frac{\xi_e(\ln\xi_e)^2}{(1-\xi_e+2\xi_e\ln\xi_e)(1-\xi_e)}, \quad \theta = \frac{T}{T_m}. \quad (85)$$

In contrast, considering vitrification as a continuous transition from a metastable to a frozen-in state, we have generally

$$C_{p,conf} = \chi_1 \Delta H_{ev}(T_m)\frac{d\xi}{dT} \cong \chi RT_m\frac{d\xi}{dT}, \quad T_0 \leq T \leq T_m. \quad (86)$$

In addition, the configurational contribution to the specific heat becomes also different in dependence on whether we consider cooling or heating processes.

Results of the theoretical computations of the configurational contributions to the specific heats are shown in Figs. 2 and 4. A comparison of experimental and theoretical results is given in Fig. 2. It is evident that the respective curves are widely, at least, qualitatively identical taking into account that in the experiments not only the configurational but the full specific heat is shown in dependence on temperature.

Similarly to the specific heat,

$$C_p(p, T, \xi) = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T}\frac{d\xi}{dT}, \quad (87)$$

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

one can define the configurational contributions to the thermal expansion coefficient, α

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \quad \alpha_{conf} = \frac{1}{V}\left(\frac{\partial V}{\partial \xi}\right)_{p,T}\frac{d\xi}{dT}\bigg|_p, \quad (88)$$

and the compressibility, κ

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T, \quad \kappa_{conf} = -\frac{1}{V}\left(\frac{\partial V}{\partial \xi}\right)_T\frac{d\xi}{dp}\bigg|_T. \quad (89)$$

It is evident from Eqs. (87) and (88) that the configurational contribution to the thermal expansion coefficient behaves in the same way as the configurational contribution to the specific heat. Consequently, the expressions for ΔC_p^{exp} and $\Delta \alpha^{exp}$ can be expected to be of similar form and can be given by Eqs. (55) and (56). The question thus remains to be answered how the derivative $(d\xi/dp)_T$ can be determined and, even more generally, what meaning has to be assigned to such derivative.

Above the vitrification range, this parameter is determined via $(d\xi_e/dp)_T$, below the vitrification range ξ does not change in dependence on pressure, consequently, the configurational contributions to the compressibility become there equal to zero again. Although the assumption that Eq. (56) holds for the compressibility as well seems to be well-founded, a final proof cannot be given here. By this reason, for the determination of the value of the Prigogine-Defay ratio in application to experiment, it is of interest to search for an alternative method of determination of this parameter not involving the detailed behavior of the order parameter in the glass transition interval but relying widely on equilibrium properties of the systems under consideration. The theoretical determination of the Prigogine-Defay ratio in such approach will be performed in Sec. IV.

IV. THERMODYNAMIC COEFFICIENTS AND PRIGOGINE-DEFAY RATIO: DETERMINATION VIA THE ANALYSIS OF THE EQUILIBRIUM PROPERTIES OF GLASS-FORMING MELTS

A. Basic equation

In the determination of the experimentally measured values of the Prigogine-Defay ratio as performed in Sec. III, the additional assumption as given by Eqs. (55) and (56) was employed supplementing the general results obtained via the application of the De Donder thermodynamic method. It has been shown that the Prigogine-Defay ratios have to be larger than one (qualitatively in full agreement with experiment) but quantitatively the mentioned approximations may introduce some uncertainty. By this reason, the analysis of alternative approaches is of interest.

Equations (14), (16), and (18) supply us with the configurational contributions to the thermodynamic coefficients both for the real course of vitrification and devitrification but also for the changes of the state of the metastable equilibrium melt. In latter case, the affinity A is equal to zero and earlier employed equations (Eqs. (3)–(10)) cannot be used. However, the configurational contributions to the equilibrium values of the thermodynamic coefficients can be determined directly knowing the configurational contributions to the enthalpy, the

volume, and the partial derivatives $(\partial \xi_e/\partial T)_p$ and $(\partial \xi_e/\partial p)_T$ for the respective metastable equilibrium states. Similarly to Eq. (19), we get

$$\Pi(T_g) = \frac{1}{VT}\left\{\frac{\Delta C_p \Delta \kappa}{(\Delta \alpha)^2}\right\}\bigg|_{T=T_g}$$

$$= -\frac{\left(\dfrac{\partial H}{\partial \xi}\right)_{p,T}\left(\dfrac{\partial \xi_e}{\partial p}\right)_T}{T\left(\dfrac{\partial V}{\partial \xi}\right)_{p,T}\left(\dfrac{\partial \xi_e}{\partial T}\right)_p}\bigg|_{T=T_g;\xi=\xi_e} \quad (90)$$

this time directly for the experimentally measured values of the Prigogine-Defay ratio. Indeed, the configurational contributions to the thermodynamic coefficients of the glass are equal to zero and above equation allows us to determine the value of the Prigogine-Defay ratio as obtained experimentally by extrapolation of the equilibrium behavior of the respective thermodynamic coefficients.

B. Application to model systems: First example

As the first example, we consider the model as developed in Ref. 2 and resulting into Eqs. (59)–(67) for the specification of the configurational contributions to the thermodynamic functions of the glass-forming melts. Let us assume first that both parameters of this theoretical model, ΔE_0 and v_0, do not depend on pressure and temperature. We get

$$\xi_e = \exp\left(-\frac{\Delta E_0(1-\xi_e)^2 + pV_0}{RT}\right), \quad (91)$$

$$\left(\frac{\partial \xi_e}{\partial T}\right)_p\left(1 - \frac{2\Delta E_0 \xi_e(1-\xi_e)}{RT}\right) = -\xi_e\frac{\ln\xi_e}{T}, \quad (92)$$

$$\left(\frac{\partial \xi_e}{\partial p}\right)_T\left(1 - \frac{2\Delta E_0 \xi_e(1-\xi_e)}{RT}\right) = -\xi_e\frac{V_0}{RT}. \quad (93)$$

These relations have to be substituted into Eq. (90). With

$$V_{conf} = V_0\frac{\xi}{1-\xi}, \quad V_0 = N_A v_0, \quad \frac{\partial V_{conf}}{\partial \xi} = \frac{V_0}{(1-\xi)^2} \quad (94)$$

$$H_{conf} = \Delta E_0 + pV_{conf}, \quad \frac{\partial H_{conf}}{\partial \xi} = \Delta E_0 + p\frac{\partial V_{conf}}{\partial \xi}. \quad (95)$$

we obtain after substitution into Eq. (90) the result $\Pi = 1$.

Considering the effect of the simplifying assumption of constancy of the parameters, ΔE_0 and v_0, for example, with respect to v_0, it follows immediately, that the assumption is not correct. It implies that the phonon contributions to the thermal expansion coefficient are assumed to be equal to zero. Equation (91) will not change if we employ the more general model approach considering these parameters as dependent on pressure and temperature, but already Eqs. (92) and (93)

have to be modified. Accounting for the pressure and temperature dependence of ΔE_0 and v_0, we can rewrite Eq. (91) as

$$\xi_e = \exp\left(-\frac{\Delta E_0(p,T)(1-\xi_e)^2 + pN_A v_0(p,T)}{RT}\right). \quad (96)$$

Taking the derivatives of ξ_e with respect to pressure and temperature, we get then instead of Eqs. (92) and (93)

$$\left(\frac{\partial \xi_e}{\partial T}\right)_p \left(1 - \frac{2\Delta E_0 \xi_e (1-\xi_e)}{RT}\right)$$
$$= -\xi_e \left(\frac{\ln \xi_e}{T} + \frac{(1-\xi_e)^2}{RT}\left(\frac{\partial \Delta E_0}{\partial T}\right)_p\right) + \frac{pN_A}{RT}\left(\frac{\partial v_0}{\partial T}\right)_p, \quad (97)$$

$$\left(\frac{\partial \xi_e}{\partial p}\right)_T \left(1 - \frac{2\Delta E_0 \xi_e (1-\xi_e)}{RT}\right)$$
$$= -\xi_e \left(\frac{V_0}{RT} + \frac{(1-\xi_e)^2}{RT}\left(\frac{\partial \Delta E_0}{\partial p}\right)_T + \frac{pN_A}{RT}\left(\frac{\partial v_0}{\partial p}\right)_T\right). \quad (98)$$

Employing now again Eq, (90), we arrive at

$$\Pi = -\frac{\left(\frac{\partial H}{\partial \xi}\right)_{p,T}\left(\frac{V_0}{RT}\right)}{\left(\frac{\partial V}{\partial \xi}\right)_{p,T}\ln \xi_e}$$
$$\times \left\{\frac{1 + \frac{(1-\xi_e)^2}{V_0}\left(\frac{\partial \Delta E_0}{\partial p}\right)_T + \left(\frac{\partial \ln v_0}{\partial \ln p}\right)_T}{1 + \frac{(1-\xi_e)^2}{R\ln \xi_e}\left(\frac{\partial \Delta E_0}{\partial T}\right)_p + \frac{pV_0}{RT\ln \xi_e}\left(\frac{\partial \ln v_0}{\partial \ln T}\right)_p}\right\}, \quad (99)$$

or

$$\Pi = \frac{1 + \frac{(1-\xi_e)^2}{V_0}\left(\frac{\partial \Delta E_0}{\partial p}\right)_T + \left(\frac{\partial \ln v_0}{\partial \ln p}\right)_T}{1 + \frac{(1-\xi_e)^2}{R\ln \xi_e}\left(\frac{\partial \Delta E_0}{\partial T}\right)_p + \frac{pV_0}{RT\ln \xi_e}\left(\frac{\partial \ln v_0}{\partial \ln T}\right)_p}. \quad (100)$$

In the framework of the original model,[2] the deviations of the Prigogine-Defay ratio from the value $\Pi = 1$ are, consequently, determined by the specific laws governing the temperature and pressure dependencies of the activation energy, ΔE_0, and the volume, v_0. For systems, where all these dependencies can be neglected, the result $\Pi = 1$ holds, for systems, where this is not the case, we get deviations from $\Pi = 1$.

This result reconfirms qualitatively our earlier obtained conclusions that one order parameter is sufficient in order to arrive at values of the Prigogine-Defay ratio not equal to one. The particular value of Π is determined basically by the thermodynamic properties of the systems under consideration. With respect to the model considered here, the question is, consequently, how to establish the dependence of the parameters on pressure and temperature. This task has been per-

formed in the framework of the alternative approach sketched already above. This more advanced model will be discussed in Sec. IV C.

C. Application to model systems: Second approach

In order to determine the value of the Prigogine-Defay ratios measured experimentally, we utilize here again a mean-field model discussed in the present paper already earlier. According to this model, the molar volume of the liquid is determined via the relation Eq. (69). The configurational contribution to the molar volume (or the excess molar volume) is given, consequently, by Eq. (68). The configurational contribution to the enthalpy, H_{conf}, of one mole of the liquid is described in the framework of this lattice-hole model via the molar heat of evaporation, $\Delta H_{ev}(T_m)$, of the liquid at the melting temperature via Eq. (70). The configurational part of the entropy per mole is described in this model via the conventional mixing term Eq. (63), the configurational contribution to the internal energy via Eq. (71), the Gibbs' free energy via Eq. (72). The equilibrium value of the structural order parameter, $\xi = \xi_e$, is determined via the relation $(\partial G_{conf}/\partial \xi)_{p,T} = 0$.

With above relations, we get with Eqs. (68) and (70)

$$\left(\frac{\partial V}{\partial \xi}\right)_{p,T} = N_A v_0(p,T), \quad \left(\frac{\partial H}{\partial \xi}\right)_{p,T} = \chi RT_m, \quad (101)$$

and, with Eq. (74) and assuming $\chi = $ constant,

$$\left(\frac{\partial \xi_e}{\partial T}\right)_p = -\frac{1}{\chi T_m}\frac{1}{\frac{\partial}{\partial \xi}\left[\frac{(1-\xi)^2}{\ln \xi}\right]_{\xi=\xi_e}},$$
$$\left(\frac{\partial \xi_e}{\partial p}\right)_T = \frac{T}{\chi T_m^2}\frac{1}{\frac{\partial}{\partial \xi}\left[\frac{(1-\xi)^2}{\ln \xi}\right]_{\xi=\xi_e}}\frac{dT_m}{dp}. \quad (102)$$

According to Eq. (76), here the inequality

$$\frac{\partial}{\partial \xi}\left[\frac{(1-\xi)^2}{\ln \xi}\right]_{\xi=\xi_e} < 0 \quad (103)$$

has to be fulfilled.

A substitution of Eqs. (101) and (102) into Eq. (90) yields

$$\Pi = \frac{\chi R}{N_A v_0(p_g, T_g)}\frac{dT_m}{dp}. \quad (104)$$

Employing the Clausius-Clapeyron equation[19,20] for the description of the change of the melting temperature with pressure

$$\frac{dT_m}{dp} = T_m \frac{\Delta V(T_m)}{\Delta H(T_m)}, \quad (105)$$

where ΔV and ΔH are the change of molar volume and of molar enthalpy in the liquid-solid phase transformation, we arrive finally at

$$\Pi = \frac{\chi RT_m}{N_A v_0(p_g, T_g)}\frac{\Delta V(T_m)}{\Delta H(T_m)}. \quad (106)$$

TABLE I. Data employed and results of computations via Eq. (106) of the Prigogine-Defay ratio for different systems.

Glass	T_g, K	T_m, K	$\Delta H(T_m)$ (kJ/mol)	$\Delta \rho(T_m)$ (g/cm³)	$\rho(T_g)$ (g/cm³)	Π (Theory)	Π (Expt.)
SiO$_2$ 60 g/mol	1200-1400[a]	2000[b]	9.6[b]	0.35[c,d]	2.1[d]	34.5	$10^3 - 2 \times 10^5$
B$_2$O$_3$ 70 g/mol	525[e]	750[c] 723[b]	24.56 [b,c]	0.9[c,d]	1.8[d]	1.7	4.7
Rubber 68 g/mol	473[f]	644–721	4.761	0.23	1.2	19.5–21.8	8.3[g]
Glycerol 92 g/mol	189.55, 190.9[h]	291.2 [b,c,h]	18.28[c] 18.3[i]	0.115[j]	1.325[j]	5.1	9.4
Glucose 180 g/mol	280, 275–330[i]	419[b]	34.2[k]	0.11[l]	1.53[l]	4.7	3.7[g]
Se 80 g/mol	305[f]	494[b]	6.69 [b,c]	∼0.72[m]	4.27[m]	12.1	2.4[g]
Polystyrene 104 g/mol	370[b,f]	513	5.9[n]	0.1	0.87[f]	21	16[g]

[a]Reference 30.
[b]Reference 31.
[c]Reference 33.
[d]Reference 34.
[e]Reference 32.
[f]Reference 35.
[g]Reference 14.
[h]Reference 36.
[i]Reference 37.
[j]Reference 38.
[k]Reference 39.
[l]Reference 40.
[m]Reference 41.
[n]Reference 42.

This relation can be employed in order to compute the Prigogine-Defay ratio for different systems of interest. As evident, its value is determined by thermodynamic properties of the system under consideration. The prehistory enters here only via the parameter $v_0(p_g, T_g)$ since glass transition temperature and pressure depend on prehistory according to the Bartenev-Ritland equation[27,28] and similar more general considerations.[7,10–12] Results of computations of the Prigogine-Defay ratio according to this equation are presented in Table I. Accounting for possible errors in the determination of the respective experimental values, the theoretical results are considered as quite satisfactory.

D. Possible generalizations

The basic relation for the determination of the Prigogine-Defay ratio in the employed here approach, Eq. (90), has been supplemented in Sec. IV C by Eqs. (101) and (102) resulting from model assumptions on the systems under consideration. Eq. (90) is, however, valid independent of such model assumptions and can be employed directly, if the partial derivatives of volume, enthalpy, and Gibbs free energy (latter relation determines ξ_e, cf. Eqs. (73) and (74)) can be determined. In this way, having at one's disposal the generalized equation of state of the systems under consideration, one can immediately determine the values of the Prigogine-Defay ratio. Since T_g depends on the cooling rate (or, more generally, on prehistory) the Prigogine-Defay ratio has to depend, in general, both on the thermodynamic properties of the systems under consideration and on the way the system is transferred to a glass.

V. RESULTS AND DISCUSSION

In the present analysis it is reconfirmed in an alternative way to discussed[10,15–17] previously by methods that the ex-

perimentally determined values of the Prigogine-Defay ratio being as a rule larger than one can be given a sound theoretical interpretation by employing only one structural order parameter. For this purpose, one has to go, however, beyond Simon's model and has to treat vitrification appropriately as proceeding in a certain transition interval. Indeed, as mentioned already by DiMarzio[43] in discussions of related problems with Gupta and Moynihan[44]: *In the simplest view of order parameter theory (SOPT) it is imagined that the freezing-in occurs abruptly. Above the transition line, the order parameters ...are free to relax to whatever values which will minimize the free energy, while below the transition line they attain a time independent value ... SOPT can be viewed only as a very crude approximation to the more general time-dependent order parameter theory*. In their reply, Gupta and Moynihan[44] noted: *We agree with DiMarzio that this (i.e., SOPT) is only a simple view on the glass transition and that deeper understanding will result from a detailed kinetic analysis of relaxation of internal parameters*. As it is shown here, the mentioned simplification in the description is indeed the origin why previous attempts in the determination of the Prigogine-Defay ratio advanced by Prigogine and Defay[13] and Davies and Jones[14] and their followers have led to an incorrect conclusion.

At part, in response to the comments to related problems made by Gundermann *et al.*[45] we would like to stress here once again the following points: (i) Our analysis shows that the classical expression for the Prigogine-Defay ratio can have values larger than one even for the case that only one structural order parameter is employed. Since in the classical Prigogine-Defay ratio differences of the metastable liquid and the resulting glass are discussed, non-equilibrium effects enter the theory only to a limited extent: As discussed already in Ref. 15 and also in even more detail here, in order to arrive at this result one has merely to avoid the consequences resulting from the very approximate in the considered context Simon's model approach. In Ref. 15, this analysis was performed based on the thermodynamics of irreversible

processes incorporating into the description the real course of the transition from the liquid to the glass. In the present analysis, we avoid this part and compute via Eq. (90) directly the Prigogine-Defay ratio comparing the thermodynamic coefficients of the metastable liquid and the glass. Of course, since the state of the glass can depend on the cooling rate, also the Prigogine-Defay ratio may depend on the cooling rate.[17] This effect is expressed in Eq. (90) by the choice of the value of pressure and temperature at which the Prigogine-Defay ratio is computed. (ii) The possibility to theoretically predict values of the Prigogine-Defay ratio larger than one already for the case of one structural order parameter does not employ necessarily that this value is always significantly larger than one. In particular, it can be also equal to one as discussed in one of the examples of the present analysis (the first simplified model). (iii) Here we concentrated the attention to demonstrate the possibility to develop an alternative to the analysis performed by us in Ref. 15 method showing that the Prigogine-Defay ratio can have values larger than one already in the case that the system can be described by only one structural order parameter. Qualitatively, the theoretical predictions are shown to be in agreement with experimental data. In order to improve the degree of agreement between theory and experiment quantitatively, one can either employ more correct models of the respective system or in case, when this is required (cf. Ref. 45), utilize models with several independent order parameters, $\{\xi_i\}$, $i = 1, 2, \ldots, f$, with their equilibrium values, $\xi_{i,e}$, determined by a set of equations similar to Eq. (73). In such more general case, instead of Eq. (90), we have to employ then the more general equation

$$
\Pi(T_g) = \frac{1}{VT} \left\{ \frac{\Delta C_p \Delta \kappa}{(\Delta \alpha)^2} \right\}\bigg|_{T=T_g}
$$

$$
= -\frac{\sum_{i=1}^{f} \left(\frac{\partial H}{\partial \xi_i}\right)_{p,T,(\xi_j, j \neq i)} \left(\frac{\partial \xi_{i,e}}{\partial p}\right)_T}{T \sum_{i=1}^{f} \left(\frac{\partial V}{\partial \xi_i}\right)_{p,T,(\xi_j, j \neq i)} \left(\frac{\partial \xi_{i,e}}{\partial T}\right)_p}\bigg|_{T=T_g; \{\xi_i = \xi_{i,e}\}}.
$$

(107)

Summarizing these considerations, we conclude: A method has been developed by us allowing one to determine the Prigogine-Defay ratio based on the knowledge of the equilibrium properties of the systems under consideration. It gives the possibility to compute this ratio provided the equilibrium thermodynamic properties of the system are known. It is shown that – employing a single structural order parameter and a simple but qualitatively correct lattice-hole model of the melts – the method allows one to derive estimates of the respective values being in qualitative and partly even quantitative agreement with experimental data. An extension of this analysis is possible by utilizing more appropriate models for the systems under consideration and employing if required more than one structural order parameters.

Finally, we would like to make the following general comments: The configurational contributions to the thermodynamic coefficients are determined essentially by the derivatives of the structural order parameter with respect to pressure, p, and temperature, T. Consequently, in the glass transition we are encountered, again, with a qualitative change of the

reaction of the system but this time going over from the response characteristic for a metastable equilibrium system to the response of the respective frozen-in non-equilibrium system, the glass, i.e.,

$$
\left(\frac{d\xi}{dT}\right) \neq 0 \quad \text{and} \quad \left(\frac{d\xi}{dp}\right) \neq 0
$$

$$
\Longleftrightarrow \quad \left(\frac{d\xi}{dT}\right) = 0 \quad \text{and} \quad \left(\frac{d\xi}{dp}\right) = 0. \quad (108)
$$

These characteristic features of the glass transition determine both the similarity and the difference of the glass transition as compared to second order equilibrium phase transitions and determine the specific value of the Prigogine-Defay ratio.

The dependence of the glass transition temperature on pressure, based on kinetic criteria of glass-formation, is analyzed theoretically in detail in Ref. 10. It is shown there why in some cases these dependencies have a similar form as the Ehrenfest relations in 2nd order equilibrium phase transformations and why, as a rule, deviations from such type of functional dependence is found. Based on such analysis, in this paper[10] a third as compared to Ref. 15 and the present paper independent proof of the conclusion is given that the values of the Prigogine-Defay ratio can be different from one even if only one structural order parameter is required for the description of the glass-forming system under consideration.

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