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Pressure coefficient of the glass transition temperature in the thermodynamic scaling regime

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We report that the pressure coefficient of the glass transition temperature, dT_g/dp, which is commonly used to determine the pressure sensitivity of the glass transition temperature T_g, can be predicted in the thermodynamic scaling regime. We show that the equation derived from the isochronal condition combined with the well-known scaling, $TV^\gamma = \text{const}$, predicts successfully values of dT_g/dp for a variety of glass-forming systems, including van der Waals liquids, polymers, and ionic liquids.

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I. INTRODUCTION

The cooling of a liquid, at a constant pressure, is probably one of the most efficient and easiest ways to produce a solid phase. In general, there are two different scenarios. The first one takes place when a liquid turns into a crystalline solid at its freezing temperature. However, it is also possible that some liquids might be cooled below their freezing point without crystallization. On further cooling of the supercooled liquid, a transformation to an amorphous phase might occur. Both liquid-crystal and liquid-glass transitions can be easily identified by, e.g., measuring the temperature dependence of the specific volume $V(T)$. The first transition is manifested by an abrupt and discontinuous change of volume (the first order transition) at the crystallization temperature T_c, whereas the second one shows only a characteristic change in the slope of $V(T)$ at the glass transition temperature T_g. The nature of liquid vitrification has been a subject of great debate during the last decades [1]. Both thermodynamic and kinetic aspects of this transition have been quite extensively discussed in the literature [2]. However, most researchers are now inclined to think about the glass formation as a purely kinetic process and that no thermodynamic phase transition is involved at T_g.

The glass transition temperature alone is an important physical property used to characterize amorphous materials [3]. Beside volumetric measurements, as mentioned already above, there are also other experimental methods useful for determining of T_g. One of the most frequently exploited experimental techniques is differential scanning calorimetry (DSC). Using this technique, the glass transition point is usually defined as an intersection of the DSC curve with a median to the two heat capacity lines representing the glass and liquid behavior. On the other hand, taking into account the kinetic nature of the vitrification process, it is also valid to define T_g as an isochronal or isoviscosity state. According to this view, T_g has been frequently estimated as the temperature at which the structural relaxation time or viscosity is equal, let's say, to 100 s or 10^{12} Pas, respectively. However, it should be pointed out that the isochronal definition is affected by the experiment rate [4] and the isoviscosity one is often not held, e.g., by linear polymers and cross-linked polymers, which do not flow [5].

The glass transition can be induced by varying not only temperature but also pressure [6]. Over the past years much effort has been devoted to investigate the effect of pressure on the glass transition in various types of liquids [7]. From numerous experiments we have learned that the sensitivity of T_g to pressure depends on the nature and type of intermolecular interactions. For instance, a significant shift of T_g is usually observed for van der Waals liquids [8–12], whereas there is only a small pressure effect on the shift of T_g in the case of hydrogen bonded liquids [13,14]. The coefficient dT_g/dp is the most useful and convenient measure of this effect.

Although the glass transition is not a true thermodynamic phase transition, it has some properties of the second order transition. First derivatives of the Gibbs free energy (volume V and entropy S) are continuous, whereas the second ones (heat capacity c_p, thermal expansion coefficient α_p, and compressibility κ_T) change rapidly in the vicinity of T_g, showing a steplike behavior. The values of c_p, α_p, and κ_T are largest in the supercooled state and drop to lower values in the glassy state. For the mentioned above reason, numerous attempts have been made to describe the pressure coefficient of T_g in terms of Ehrenfest equations [15–18]:

$$\left(\frac{dT_g}{dp}\right) = \frac{\Delta\kappa_T}{\Delta\alpha_p}, \tag{1}$$

$$\left(\frac{dT_g}{dp}\right) = \frac{V_g T_g \Delta\alpha_p}{\Delta c_p}, \tag{2}$$

where Δ denotes the difference between the respective coefficients in the liquid and in the glass, and V_g is a specific volume at T_g. It should be stressed that the first equation incorporates the compressibility and the expansion coefficient also measured in the glassy phase, i.e., in the nonequilibrium state. This creates a difficulty in testing the validity of Eq. (1). Indeed, it has been experimentally verified that Eq. (1) is generally not fulfilled [3,19–25], whereas Eq. (2) seems to hold reasonably well for many systems, although not for all. Equation (1) is based on the free volume ideas, while Eq. (2) is based on the entropy approach [26]. Consequently, these results were interpreted as indicating that entropy theories describe the glass transition better than free volume ones [19].

Herein we provide a new equation for the pressure coefficient of the glass transition temperature. We test the proposed relationship using PVT data for several glass-forming liquids representing different groups, i.e, van der Waals liquids, polymers, hydrogen bonding, and ionic liquids.

II. THE PRESSURE COEFFICIENT—ITS FORMULATION, EXPERIMENTAL TEST, AND DISCUSSION

We begin our discussion of dT_g/dp with an analysis of experimental PVT data. Figure 1 shows the *V-T* dependences measured at various pressures (isobars) for glibenclamide and telmisartan (van der Waals liquids). All the details about PVT measurements can be found in Ref. [27]. PVT data for two other samples, i.e., verapamil hydrochloride (ionic liquid) and polystyrene (PS 168N) with $M_n = 354\,000$ g/mol (polymer) have been already presented in Refs. [27,28]. In order to parameterize the data collected in the supercooled liquid state, we used the following equation of state [29]:

$$\upsilon(T,p) = \frac{A_0 + A_1(T - T_0) + A_2(T - T_0)^2}{\{1 + (p - p_0)b_1 \exp[b_2(T - T_0)]\}^{1/\gamma_{EOS}}}, \quad (3)$$

where A_0, A_1, A_2, b_1, b_2, and γ_{EOS} are fitting parameters. The fixed parameters p_0 and T_0 are pressure and temperature in a chosen reference state defined herein by the glass transition temperature at ambient pressure.

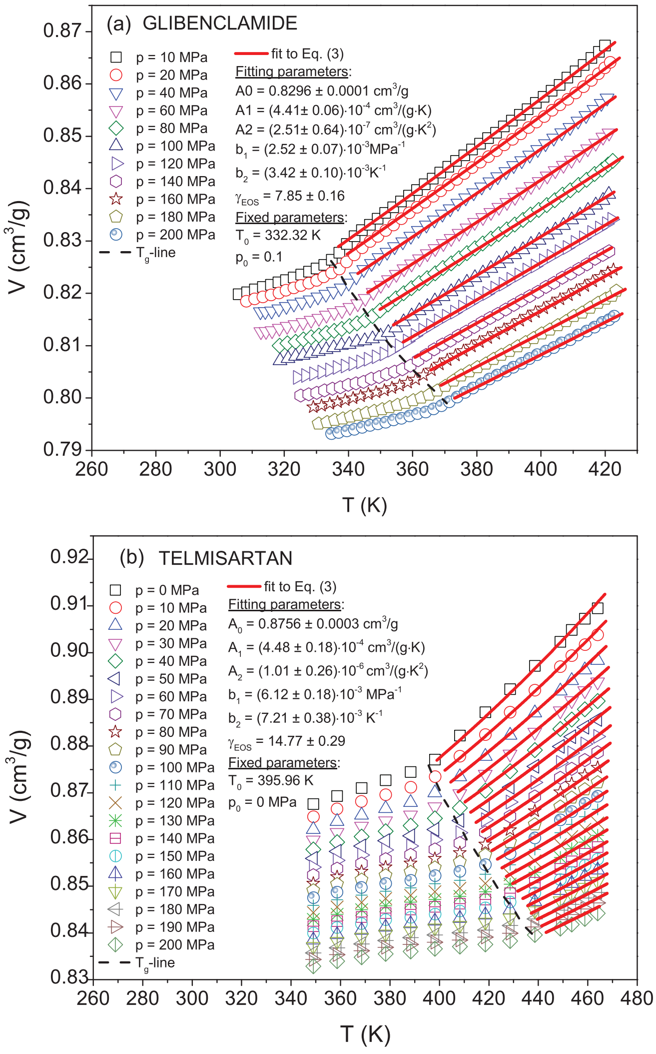

FIG. 1. (Color online) Plots of PVT data for (a) glibenclamide (measured at the cooling rate of 2.5 K/min) and (b) telmisartan (measured at the cooling rate of 1.0 K/min) with their fits to Eq. (3) in the liquid state.

For all analyzed samples, the excellent fits to the experimental data were achieved. The obtained fitting parameters are used next to calculate both the thermal expansion and the compressibility coefficients. The values of the glass transition temperature at various pressures were determined as the temperature of the intersection of two straight lines fitted to a portion of $V(T)$ data above and below the transition region. Determined in this way, values of T_g are plotted as a function of pressure in the insets in the Fig. 2. These experimental dependences were fitted to the phenomenological Andersson-Andersson equation [30]:

$$T_g(p) = T_g^0\left(1 + \frac{p}{k_1}\right)^{k_2}, \quad (4)$$

where k_1, k_2, and T_g^0 are fitting parameters. From this analysis, we were able to determine the values of the ratio of dT_g/dp in the limit of ambient pressure (see Table I).

As a starting point to find a new equation for the coefficient dT_g/dp, let's focus on the analysis of the experimental dependences of $\log_{10}T_g$ vs $\log_{10}V_g$ for systems studied here. These plots are displayed in Fig. 2. All the $\log_{10}T_g$ data exhibit a linear dependence on $\log_{10}V_g$. From the simple linear regression, one can determine the slope of the dependence, which we denote by the Greek letter γ. The values of the parameter γ are reported in Table I. In addition Fig. 2 also presents T_g determined from the high pressure dielectric measurements. For the considered glass formers, we find that these two different methods of measuring T_g provide consistent results, but not always exactly the same as can be seen in case of polystyrene [Fig. 2(c)]. Taking into account the fact that T_g determined from dielectric measurements was defined at a constant relaxation time, it is now obvious that the dependence $T_g(V_g)$ found for PVT data corresponds well to an isochronal line. However, it should be noted that an isochronal state along a $T_g(V_g)$ line should be in general regarded as an approximation due to the mentioned dependence of T_g on the experiment rate. Taking into account the Deborah number considered by Hodge for the glass transition temperature (Eq. (1) in [4]), one can see that the characteristic time scale for the glass transition, τ_g, can be evaluated more precisely by using the glass transition temperature T_g, the isobaric fragility parameter $m_p = \frac{d\log_{10}\tau}{d(T_g/T)}|_{T_g}$, and the cooling rate q_c in the following way: $\tau_g \approx T_g/(q_c m_p \ln 10)$. Assuming that the glass transition is approached at a constant cooling rate q_c in each isobaric state, the characteristic time scale for this transition depends mainly on the quotient T_g/m_p, which is pressure dependent. A typical behavior of glass forming materials under high pressure is characterized by an increase in T_g and a decrease in m_p with pressure [6]. It implies that T_g/m_p should increase with increasing pressure; however, this quotient established by using experimental data of glass formers is a slowly varying function of pressure, which usually results in the increase in τ_g by only a few seconds with increasing pressure from 0 to 200 to 300 MPa. For instance, the characteristic time scales τ_g of glibenclamide and a prototypical van der Waals liquid phenylphthalein-dimethylether increase by 7 and 9 s, respectively, if pressure increases from 0.1 to 200 MPa and $q_c = 3$ K/min. The pressure effect on the change in τ_g can be neglected especially in the limit of zero pressure in which

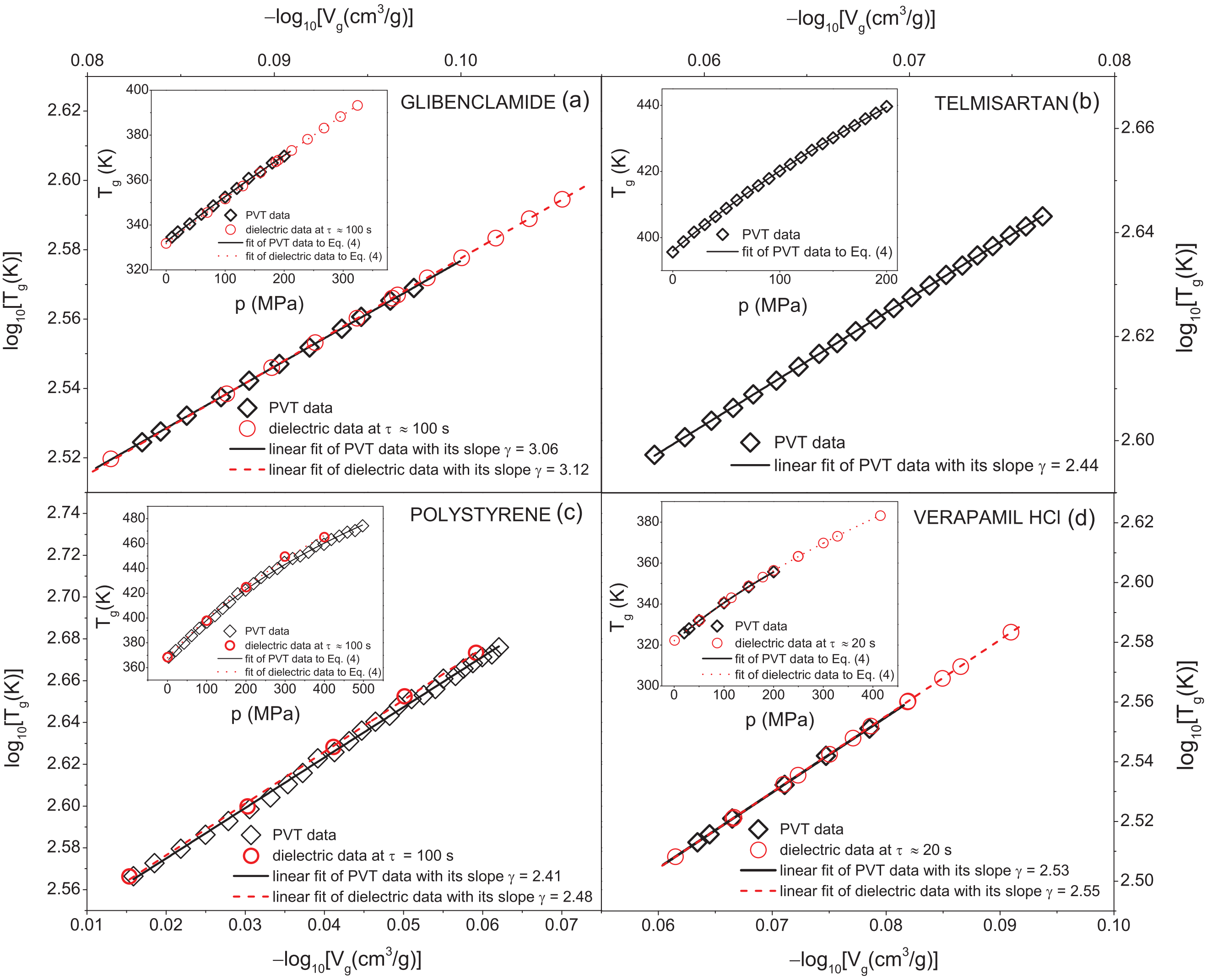

FIG. 2. (Color online) Plots of the dependences of $\log_{10} T_g$ vs $-\log_{10} V_g$ for (a) glibenclamide, (b) telmisartan, (c) polystyrene, and (d) verapamil hydrochloride, which are obtained from PVT and dielectric data (for telmisartan only PVT data are included). The PVT data for verapamile hydrochloride and polystyrene were reported in Refs. [27,28], respectively. All the used dielectric data were reported in Refs. [27,28,53], respectively. The corresponding pressure dependences of the glass transition temperature T_g are shown in the insets.

the pressure coefficient dT_g/dp is usually considered. Since a linear dependence of $\log_{10} T_g$ on $\log_{10} V_g$ has been revealed (Fig. 2), the relationship between T_g and V_g is expected to have the following form:

$$TV^{\gamma} = C \tag{5}$$

TABLE I. Values of the pressure coefficient dT_g/dp in K/MPa in the limit of ambient pressure and the scaling exponent γ, which are based on PVT data analysis.

Material	γ	dT_g/dp from Andersson-Andersson eq. [Eq. (4)]	dT_g/dp from Eq. (9)	dT_g/dp from Ehrenfest eq. [Eq. (1)]	dT_g/dp from Ehrenfest eq. [Eq. (2)]	dT_g/dp from Eq. (10)
Glibenclamide	3.06	0.21	0.21	0.32	0.15[b]	0.60
Telmisartan	2.44	0.28	0.27	0.21	0.30[b]	0.82
Polystyrene	2.41	0.39	0.40	0.51[a]	0.51[a]	1.30
Verapamil HCl	2.53	0.21	0.20	0.18	0.21[b]	0.64

[a] Taken from Ref. [28].

[b] Δc_p required by Eq. (2) has been calculated for glibenclamide, telmisartan, and verapamil HCl by using our unpublished heat capacity data obtained from the differential scanning calorimetry with stochastic temperature modulation.

where C is a constant. It should be noted that Eq. (5) considered for isochronal conditions is a simple consequence of the thermodynamic scaling with the scaling exponent γ [6,31,32].

The next step is to calculate the derivative of the Eq. (5) with respect to temperature that gives

$$\frac{d}{dT}C = V^{\gamma} + T\gamma V^{\gamma-1}\frac{dV}{dT}. \tag{6}$$

Assuming that an isochronal state is a good approximation of the glass transition or simply considering that the differentiation with respect to temperature is performed along the glass transition line in the PVT diagram, the above equation can be rewritten in the following way:

$$0 = V^{\gamma}\left\{1 + \gamma T V^{-1}\left[\left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial V}{\partial p}\right)_T \frac{dp}{dT}\right]\right\} \tag{7}$$

and transformed to the form:

$$0 = 1 + \gamma T V^{-1}\left(\frac{\partial V}{\partial T}\right)_p + \gamma T V^{-1}\left(\frac{\partial V}{\partial p}\right)_T \frac{dp}{dT}. \tag{8}$$

Finally, we arrive at the new relation describing the coefficient dT_g/dp:

$$\frac{dT_g}{dp} = \frac{\gamma T_g \kappa_T}{1 + \gamma T_g \alpha_p}. \tag{9}$$

It should be emphasized that the right side of the Eq. (9) includes thermodynamic coefficients in the equilibrium supercooled liquid state. Thus, there is no need to measure values in the nonequilibrium glassy phase as, for example, in the case of the Eq. (1).

In order to check a validity of the newly derived relationship we have calculated values of both thermal expansion and compressibility coefficients of supercooled liquid at T_g using fitting parameters previously found from the analysis of PVT data using the equation of state [Eq. (3)]. Having determined values of all the parameters in Eq. (9), we can calculate the value of the coefficient dT_g/dp. Comparison of the values of dT_g/dp determined from Eq. (9) and from the analysis of the $T_g(p)$ line shows a good agreement for systems studied here (Table I). On the other hand, the first Ehrenfest equation (1) does not give us correct values of dT_g/dp (Table I).

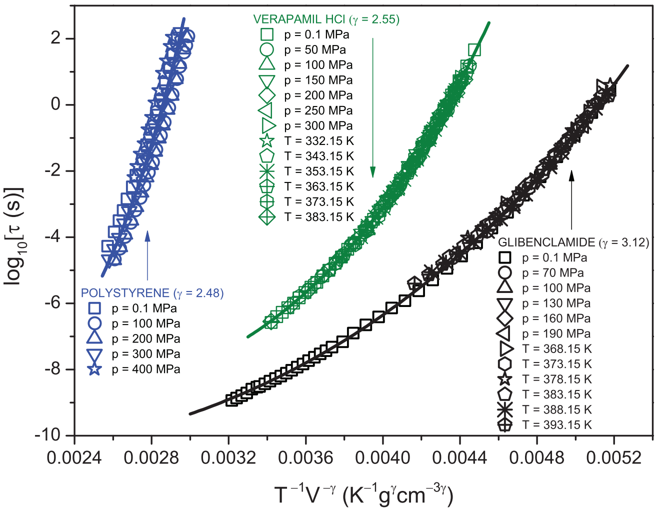

FIG. 3. (Color online) The TV^{γ}-scaling plot of structural relaxation times τ for glibenclamide, verapamil hydrochloride, and polystyrene. The used dielectric data were earlier reported in Refs. [27,28,53], respectively.

Next, we should answer the following question: What is the physical meaning of the exponent γ in Eq. (9). In the last decade, a new approach to the analysis and description of structural relaxation times and viscosity of glass-forming liquids, called thermodynamic scaling, was introduced [33–36]. According to this concept, the different isobaric and isothermal dependences of structural relaxation times/viscosity can be collapsed onto a single scaling curve if they are plotted as a function of TV^{γ}. Since it has been already pointed out that $T_g(V_g)$ is an isochronal line, the exponent γ in Eq. (9) can be identified with one appearing in the thermodynamic scaling law. This is confirmed when the dielectric relaxation times of each system examined here are plotted versus $T^{-1}V^{-\gamma}$ using the γ exponent value determined from its PVT data (see Fig. 3 and Table I). In order to answer the question we posed earlier, it should be noted that the scaling exponent γ has been related to the effective exponent m used to model the repulsive part of the intermolecular potential in dense systems, r^{-m}, $m = 3\gamma$. In a limiting case when the exponent tends to infinity, the hard sphere type of interaction becomes dominating. Then, the free volume is the key factor controlling the molecular dynamics. For this limiting case our new equation for the pressure coefficient of the glass transition temperature takes the following simple form:

$$\frac{dT_g}{dp} = \frac{\kappa_T}{\alpha_p}. \tag{10}$$

In this context, it should be mentioned that very recently, the same equation has been derived by Schmelzer [18]. Similarly to us, Schmelzer claims that Eq. (10) is valid only if molecular dynamics of glass-forming liquids can be described by the free volume concepts.

To demonstrate the general applicability of Eq. (9), we performed another test. Using the earlier reported dielectric and PVT data for commonly known glass formers, such as orthoterphenyl (OTP) [37,38], phenylphthalein-dimethylether (PDE) [39,40], 1,1′-bis (p-methoxyphenyl) cyclohexane (BMPC) [10,41], propylene carbonate (PC) [42,43], salol [12,44], and glycerol [43,45], we compared the values of dT_g/dp established from the dielectric data at ambient pressure to those determined from Eq. (9) with the scaling exponent γ also found from dielectric data. Table II presents a good agreement between the values of dT_g/dp predicted from the Eq. (9) and those found from the phenomenological relationships [e.g., Eq. (4)].

As mentioned the right hand side of the Schmelzer equation [Eq. (10)] can be also derived as the limiting case when our formula for dT_g/dp given by Eq. (9) tends to infinity. Then, the right hand side of Eq. (9) approaches its upper limit in terms of the possible values of the exponent γ. This implication of Eq. (9) explains why Eq. (10) yields the values of dT_g/dp (see Tables I and II), which are considerably larger than those predicted by using our equation for dT_g/dp [Eq. (9)] that are in a very good agreement with those determined directly from the experimental dependences $T_g(p)$. The overestimated

TABLE II. Values of the pressure coefficient dT_g/dp in K/MPa in the limit of ambient pressure and the scaling exponent γ, which are based on dielectric data analysis. Only the isobaric expansivity and the isothermal compressibility are calculated in Eqs. (9) and (10) from PVT data.

Material	γ	dT_g/dp from Andersson-Andersson eq. [Eq. (4)]	dT_g/dp from Eq. (9)	dT_g/dp from Eq. (10)
OTP	4.40[a]	0.26	0.26	0.61
PDE	4.38[a]	0.26	0.26	0.60
BMPC	7.84[a]	0.24	0.22	0.36
PC	4.20[b]	0.09	0.10	0.31
Salol	5.20[c]	0.20	0.19	0.42
Glycerol	1.40[b]	0.05	0.04	0.36

[a] From Ref. [52].

[b] From Refs. [43,45].

[c] From Ref. [7].

character of Eq. (10) found for the tested materials is a natural consequence of the fact that molecular dynamics of real glass formers is governed by both the thermal activations and the free volume changes, and the pure free volume is only one of the extreme ideal cases [6,7,34,46–51].

III. SUMMARY

In this paper, a new equation for the pressure coefficient of the glass transition temperature, dT_g/dp, is obtained and successfully tested for several glass-forming liquids. The derivative dT_g/dp is defined by thermodynamic coefficients characterizing solely the supercooled liquid state. Moreover, in the case when the free volume becomes a key factor governing molecular dynamics, our equation is transformed to the simpler form being consistent with the equation recently derived by Schmelzer.

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