

Derivative-based analysis for temperature and pressure evolution of dielectric relaxation times in vitrifying liquids

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The derivative-based analysis for detecting regions of the validity of the Vogel-Fulcher-Tammann (VFT) dependence for superpressed and supercooled liquids is discussed. For the temperature (T) path the analysis introduced by Stickel *et al.* [J. Chem. Phys. **104**, 2043 (1996); **107**, 1086 (1997)] is recalled. For the pressure (P) path the derivation based on the counterpart of the VFT dependence proposed in Paluch *et al.* [J. Phys.: Condens. Mater. **10**, 4131 (1998)] is presented. The appearance of two ideal glass temperatures (T_0) or pressures (P_0), fragility strength coefficients (D_T, D_P), and prefactors (τ_0^T, τ_0^P) for VFT equations in following dynamical domains, i.e., high-temperature (ΔT_{high}) and low-temperature (ΔT_{low}) or low-pressure (ΔP_{low}) and high-pressure (ΔP_{high}), is stressed. It is noteworthy that the values of $T_0(\Delta T_{high}) > T_0(\Delta T_{low}), D_T(\Delta T_{high}) \ll D_T(\Delta T_{low})$, and $\tau_0^T(\Delta T_{high}) \gg \tau_0^T(\Delta T_{low})$. Analogous behavior was noted for isothermal ΔP_L and ΔP_H dynamic domains. A similar derivative-based approach is also applied to test the validity of the mode coupling theory (MCT) critical-like equation $\tau(T) \propto (T - T_X)^{-\gamma}$. It yields the temperature T_X and the MCT power (“critical”) exponent γ exclusively from the simple linear regression. The extension of such an analysis for the pressure path is also given. The hardly discussed question of the error of estimations of γ and T_X is emphasized. The relation between the derivative based behavior mentioned above and the apparent activation enthalpy (temperature path) or the apparent activation volume (pressure path) is indicated. The presented analysis was applied to discuss the dynamic crossovers in supercooled and superpressed diethyl phthalate, based on experimental data supplemented by those given in Pawlus *et al.* [Phys. Rev. E **68**, 021503 (2003)].

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I. INTRODUCTION

One of the important concepts added to the physics of glassy liquids within the last decade is the qualitative change of dynamics above glass transition [1–42]. It was noted that on passing the dynamic crossover temperature T_B , located well above the glass temperature T_g , a set of phenomena occurs. For instance (i) the change in the Vogel-Fulcher-Tammann (VFT) relation [1–5,7,10,11,14,17,18,25–33,37,39,40], (ii) the split of the secondary relaxation from the primary α relaxation [1,3–5,23,27,28,35,37,41], (iii) decoupling of DC-conductivity from the α -relaxation time [1–5,13,17,18,21,24,29,30], (iv) decoupling between rotational and translational diffusion [1,3,5,8,9,13,20,24], and (v) the emerging universality of the relaxation time at the crossover, namely, $\tau(T_B) \approx 10^{-7}$ s [3–5,31,36,39–41].

For detecting T_B temperature Stickel *et al.* [10,11] proposed the derivative analysis of experimental data followed by the linearized plot $\phi_T'(1/T) = [-d \log \tau / d(1/T)]^{-1/2}$ vs $1/T$. For such a plot the Arrhenius domain is manifested as a constant function (a nonsloped line) and the VFT domain as the sloped line [11].

Recently, Casalini *et al.* [28] extended the above analysis to detect crossovers between dynamical regimes for isothermal, pressure dependences of dynamic properties. They claimed [28] “Since the pressure dependence of τ can be described by a similar equation, with T replaced by inverse pressure, an analogous derivative function for pressure data is $\phi_P' = [d \log_{10} \tau / dP]^{-1/2}$.” Next, basing on the plot $\phi_P'(P)$, as the natural extension of the $\phi_T'(1/T)$ plot, they identified

VFT based dynamic domains as regions of validity of the pressure-related linear behavior of transformed experimental data for an impressive set of vitrifying liquids ([28] and next in Refs. [30,35–39]).

It is noteworthy that intersections of straight lines representing different dynamic domains in the above analysis constituted the basic tool for determining crossover temperatures T_B [3,4,10,11,17,18,25–30,33,37] and pressures P_B [28–30,35–39]. The emerging universality of the dielectric relaxation time and the viscosity at the crossover, namely, $\tau(T_B, P_B) \approx 10^{-7}$ s [5,31,35,39,40] stress the significance of the above analysis.

The VFT based derivation of the above distortion-sensitive transformation of experimental data has been clearly shown for the temperature evolution of dynamic properties [27–29,33–37]. To the best of the authors knowledge, no such derivation for the pressure path has been proposed so far, including the mentioned Refs. [28–30,35–40].

This paper presents the comprehensive description of the derivative-based linearized transformation of temperature and pressure dependences of relaxation time on approaching the glass transition. The VFT based temperature paths analysis recalls results of Refs. [2,4,10,11]. This created the background for discussing the isothermal, pressure behavior which starts with the pressure counterpart of the VFT equation introduced in Ref. [14]. The omitted absolute of the consequent appearance of two qualitatively different ideal glass temperatures or pressures and fragility strength coefficient prefactors is emphasized. Further, the application of the derivative-based analysis of data with the linear function output for the solely two-parameter fitting of the basic mode-

coupling theory (MCT) critical-like dependence [1,3] for both T and P paths is shown. The relationship between the discussed derivative-based behavior and the evolution of the apparent activation energy or the apparent activation volume for both paths is raised.

Results above are applied to test the dynamical regimes in supercooled and superpressed diethyl phthalate, based on experimental data and those given in Ref. [30].

II. EXPERIMENT

The analysis presented in this paper is applied for discussing temperature and pressure evolution of the primary dielectric relaxation time in diethyl phthalate (DEP), for which the glass temperature $T_g=179$ K and the fragility taken as the steepness index $m_T=69$ are declared [3,30,40]. The analysis is based on data from Ref. [30] supplemented by measurements aimed at the extension of the range of tested temperatures and pressures, namely for (i) $T>300$ K ($P=0.1$ MPa isobar) and (ii) $P<300$ MPa ($T=293$ K isotherm). Measurements were carried out using the experimental setup applied in the authors earlier studies [35,42]; the Novocontrol BDS 80 impedance analyzer (0.01 Hz–1 GHz) with Quattro temperature unit (± 0.1 K) and the high pressure setup for linear and nonlinear dielectric studies. The limitation of dielectric measurements to frequencies $f<3$ MHz is one of the still unsolved experimental problems and is still an unsolved basic problem of dielectric pressure studies. Hence, loss curves for higher temperatures matched with lower pressures are often outside the “experimental window.” To overcome this problem, values of relaxation times can be estimated from the behavior of DC conductivity [30]. In this way the mentioned additional values of dielectric times were obtained. Data were analyzed using ORIGIN 7.0 software. All errors are given as three standard deviations. This paper focuses only on the temperature or pressure evolution of relaxation time in DEP. The distribution of dielectric relaxation times, the appearance of the secondary relaxation, and the breaking of the (DSE) law is presented in Ref. [30]. The analyzed experimental data are shown in Figs. 1 and 2 for the temperature and pressure paths, respectively. They also include results of the VFT based analysis for following dynamical domains as discussed below.

III. RESULTS AND DISCUSSION

The VFT dependence constitutes one of the basic tools for portraying the non-Arrhenius temperature dependence of dielectric relaxation time [3]

$$\tau(T) = \tau_0^T \exp\left[\frac{C}{T-T_0}\right] = \tau_0^T \exp\left[\frac{D_T T_0}{T-T_0}\right], \quad (1)$$

where T_0 is related to the hypothetical, extrapolated, ideal glass transition and the value of the strength parameter D_T describes the fragility strength coefficient. For the prefactor usually $\tau_0=10^{-14\pm 2}$ s is declared [1–5].

However, the temperature dependence of the primary relaxation in glass-forming liquids can also be portrayed by the Arrhenius-like dependence with the apparent, temperature-

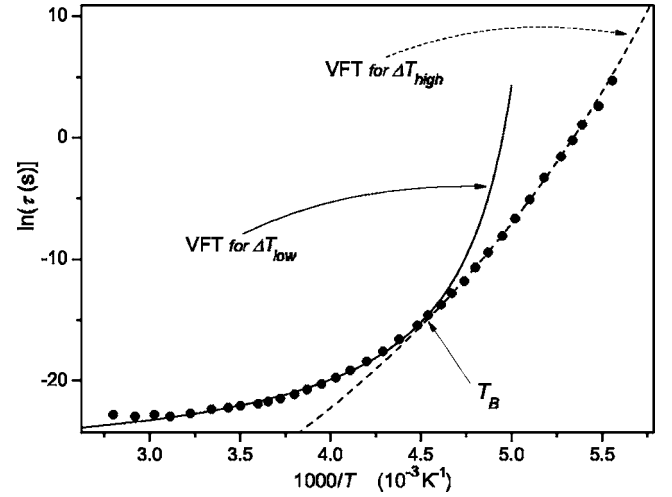


FIG. 1. Dielectric relaxation time in supercooled diethyl phthalate as a function of temperature presented in the form of the Arrhenius plot showing regions of the validity of the simple linear dependence as a linear function. The solid and the dashed curves are portrayed by VFT dependences with $D_T=2.2$, $T_0=188$ K, which resulted in $\tau_0^T \approx 4.7 \times 10^{-12}$ s for ΔT_{high} domain and $D_T \approx 32$, $T_0 \approx 111$ K, and $\tau_0^T = 7 \times 10^{-22}$ s for ΔT_{low} domain.

dependent, activation energy $E_a(T)$, namely [3,4],

$$\tau(T) = \tau_0^T \exp\left(\frac{E_a(T)}{RT}\right). \quad (2)$$

For the case of the simple Arrhenius behavior $E_a(T)=\text{const.}$

Recalling next the first law of thermodynamics and applying the resulting differential relation for the apparent activation behavior one can obtain $dE_a = TdS + V_a dP$ (V_a denotes the activation volume, P is for pressure, and S for entropy)

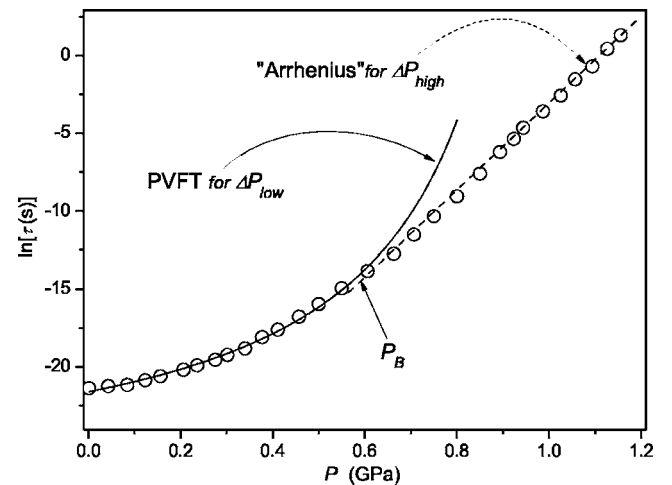


FIG. 2. Dielectric relaxation time in superpressed diethyl phthalate as a function of pressure presented in the form of the Arrhenius plot showing regions of the validity of the simple linear dependence as a linear function. The solid curve portrays the VFT dependence (ΔP_{low}) and the dashed line is for the Arrhenius description (ΔP_{high}).

[43,44] which for $P=\text{const}$ yields $dH_a/d(1/T) = TdS/d(1/T)$, one can obtain for the $\ln \tau$ vs $1/T$ derivative of relation (2):

$$\begin{aligned} \frac{d \ln \tau(T)}{d(1/T)} &= \frac{d[E_a(T)/RT]}{d(1/T)} \\ &= \frac{d\{[H_a(T) - TS(T)]/RT\}}{d(1/T)} \\ &= \frac{H_a(T)}{R} + \frac{1}{R} \left[\frac{dH_a(T)}{d(1/T)} - T \frac{dS(T)}{d(1/T)} \right] = \frac{H_a(T)}{R}. \end{aligned} \quad (3a)$$

Combining this with the analogous derivative of the VFT relation (1) one can obtain

$$H'_a(T) = \frac{H_a(T)}{R} = \frac{d \ln \tau}{d(1/T)} = D_T T_0 \left(\frac{T}{T - T_0} \right)^2. \quad (3b)$$

The most common measure of fragility is the steepness index at T_g , namely [3,7],

$$m = m_{T_g} = \left[\frac{d \log_{10} \tau}{d(T_g/T)} \right]_{T=T_g}. \quad (4)$$

Taking $T=T_g$ in last term of relation (3) and multiplying both sides of this relation by $1/T_g$ one can obtain

$$\begin{aligned} \frac{H'_a(T_g)}{T_g} &= \frac{H_a(T_g)}{RT_g} = \frac{m_{T_g}}{\log_{10} e} \\ &= \left[\frac{d \ln \tau}{d(T_g/T)} \right]_{T=T_g} = \frac{D_T T_0 T_g}{(T_g - T_0)^2} \\ &= \frac{DT(T_0/T_g)}{(1 + T_0/T_g)^2}. \end{aligned} \quad (5)$$

The last term in Eq. (5) is the same as the one derived for fragility m in Ref. [15]. Following relations (4) and (5) the evolution of the activation enthalpy is reflected by the changes of the steepness index $m(T)=m_T$, namely,

$$\frac{d \ln \tau}{d(1/T)} = H'_a(T) = \frac{Tm_T}{\log_{10} e}. \quad (6)$$

The plot of $[d \ln \tau/d(1/T)]^{-1/2}$ vs $1/T$ should yield a linear dependence in the region of the validity of the VFT equation, namely

$$\begin{aligned} \left[\frac{d \ln \tau}{d(1/T)} \right]^{-1/2} &= [H'_a(1/T)]^{-1/2} \\ &= \left(\frac{Tm_T}{\log_{10} e} \right)^{-1/2} \\ &= [(D_T T_0)^{-1/2}] - \frac{[T_0(D_T T_0)^{-1/2}]}{T} = A - \frac{B}{T}. \end{aligned} \quad (7)$$

This yields $T_0=|B/A|$ and $D_T=1/|AB|$ for the VFT domain and the nonsloped dependence for the Arrhenius region.

The above analysis recalls the derivative-based transformation of experimental data introduced in Refs. [2,4,10,11], stressing its relation with the evolution of the apparent activation energy and the steepness index. Such analysis, first proposed by Stickel *et al.* in the 1980s [11], applies $\log_{10} \tau$ instead of $\ln \tau$, which introduces the $\log_{10} e$ multiplier. To avoid this factor the natural logarithm is used in this paper.

For discussing the isothermal pressure behavior of the dielectric relaxation time we recall the pressure analog of the VFT relation (1), first proposed in Ref. [14]

$$\tau(P) = \tau_0^P \exp \left[\frac{D_P P}{P_0 - P} \right], \quad T = \text{const}, \quad (8)$$

where D_P is the pressure related fragility strength coefficient and P_0 is the extrapolated pressure for the ideal glass transition at given temperature $T=\text{const}$.

For very high P_0 values, i.e., strong glassformers, the condition $P \gg P_0$ is always fulfilled for experimentally accessible values of pressures. It reduces the above equation to the Arrhenius case, $\tau(P) = \tau_0^P \exp(V_a P/R)$ where V_a is the constant activation volume. If the value of P_0 is relatively small, relation (8) is reduced to $\tau(P) = \tau_0^P \exp[\text{const}/(P_0 - P)]$, enabling the portraying of $\tau(P)$ behavior for very fragile glass-forming liquids [44]. However, there is a strong difference regarding prefactors τ_0^T and τ_0^P in relations (1) and (8). For the pressure-related case [relation (8)] τ_0^P can be taken from $\tau(T)$ measurements under atmospheric pressure and therefore $\tau_0^P \gg \tau_0^T$.

The pressure dependence of the primary relaxation time in glassforming liquids can also be portrayed by the Arrhenius-like dependence but with the apparent, pressure-dependent, activation volume $V_a(T)$, namely [3],

$$\tau(P) = \tau_0^P \exp \left[\frac{PV_a(P)}{RT} \right], \quad T = \text{const}. \quad (9)$$

Hence, the derivative $d \ln \tau(P)/dP$ yields the “normalized” apparent activation volume $V'_a = V_a/RT$, where $T=\text{const}$ is the isotherm temperature. Relating this to the derivative of the pressure analog of the VFT dependence (PVFT relation) one can obtain

$$V'_a(P) = \frac{d \ln \tau}{dP} = \frac{D_P P_0}{(P_0 - P)^2}, \quad T = \text{const}. \quad (10)$$

Recalling the pressure-related definition of the steepness index [22]

$$m_{P_g} = \left[\frac{d \ln \tau}{dP/P_g} \right]_{P=P_g} \quad (11)$$

and next substituting $P=P_g$ in last term of relation (11) and finally multiplying both sides of this equation by P_g one can obtain

$$P_g V'_a = \frac{V_a(P_g)}{RT_g} = \frac{m_{P_g}}{\log_{10} e} = \frac{D_P P_0}{(P_0 - P_g)^2} = \frac{D P_g / P_0}{\left(1 - \frac{P_g}{P_0}\right)^2}. \quad (12)$$

The last term in the above relation is the same as the one obtained for m_P in Ref. [22]. Following relation (10) the plot $d \ln \tau / dP$ vs P should yield a linear dependence in the region of validity of the VFT-like relation (8), namely,

$$\left[\frac{d \ln \tau}{dP} \right] = [V'_a]^{-1/2} = (D_P P_0)^{-1/2} P_0 - (D_P P_0)^{-1/2} P = A + BP. \quad (13)$$

This enables the estimation of parameters in relation (8): $P_0 = A/B$ and $D_P = 1/AB$. Hence, the plot $\phi_P = d(\ln \tau) / d(P)$ proposed by Casalini *et al.* [28] shows the underlying linear evolution of the reduced apparent activation volume V_a / RT or the steepness index related quantity $m_P / P \log_{10} e$.

The distortion-sensitive, derivative analysis can also be applied to test the validity of the MCT critical-like behavior on approaching the ergodic—nonergodic crossover temperature $T_X = (1.3 \pm 0.1) T_g$ [1,3,6], namely,

$$\tau(T) = \tau_0^{T-MCT} \left(\frac{T - T_X}{T_X} \right)^{-\gamma}. \quad (14)$$

In Refs. [1,3,4,6] the symbol “ γ ” is used for the MCT “critical” exponent in relation (14). However, such a symbol has already been reserved for the critical exponent of compressibility [43,45]. The notation applied in relation (14) avoids the consequent confusion possible for some glassy systems [33,42].

Our survey of reference experimental data for various supercooled liquids suggests that $\tau_0^{T-MCT} = \tau(T = 2T_X) = 10^{-10 \pm 1}$ s [3,4,6,12,16,42]. In practice, experimental data are portrayed by the above relation for $T - T_X > 15$ K.

To test the validity of relation (14) the plot $[\tau(T)]^{-1/\gamma}$ vs T is most frequently referred to [3,4,6,12,19]. Recently, an analysis analogous to the one applied in the case of critical phenomena [42,45], based on the $\ln[\tau(T)]$ vs $\ln(T - T_X)$ plot, was also used [40]. Both procedures involve one “hidden,” adjustable parameter, namely, exponent γ or temperature T_X , followed by linear regression. However, the question of the reliability of such an analysis arises. In this respect the so-called pseudospinodal analysis is worth recalling [45–47]. It was introduced for the estimation of the position of the spinodal curve in binary mixtures of limited miscibility basing on measurements in the stable, high temperature (homogeneous) phase. Specific heat [45], light scattering [46], and nonlinear dielectric effect [47] dependences were analyzed by equations resembling relation (14) but with $T_X = T_{spinodal}$ for $T > T_{binodal} = T_{spinodal} + \Delta T$. Even if the discontinuity was very small ($\Delta T \approx 1$) the experimental errors for the estimated $T_{spinodal}$ and the critical exponents were considerably high [45–47]. This clearly suggests that for supercooled liquids, where the “discontinuity” $\Delta T > 15$ K, the estimation error of γ and T_X parameters is obviously high, although usually avoided ([2–4,6,12,16,42] and references therein).

Combining relation (2) for the Arrhenius-like dependence with the apparent activation enthalpy and the MCT critical-like relation (14) one can obtain

$$H'_a(T) = \frac{H_a(T)}{R} = R \left(\frac{d \ln \tau}{d(1/T)} \right) = \frac{\mathcal{J} T^2}{T - T_X}. \quad (15)$$

Hence, $T^2 / H'_a(T) = T^2 / \{d[\ln \tau(T)] / d(1/T)\} = A + BT$ plot yields a linear dependence in the region of the validity of the MCT critical-like description. Thus the simple linear regression, without any “hidden,” adjustable coefficients gives the desired parameters, namely, $T_X = |A/B|$ and $\mathcal{J} = |B^{-1}|$. In our opinion the distortion-sensitive characteristic of the derivative analysis and the simplification mentioned above also yields the true error of T_X and \mathcal{J} estimations.

In the case of critical phenomena temperature and pressure are isomorphic variables, i.e., isomorphic relations with the same universal critical exponents describe the behavior of given physical magnitudes both as a function of temperature and pressure [45]. Hence, the question arises whether the critical-like behavior predicted by the MCT for the temperature behavior may occur for the pressure paths in glassy liquids, namely,

$$\tau(P) = \tau_0^{P-MCT} \left(\frac{P_X - P}{P_X} \right)^{-\gamma'}. \quad (16)$$

Combining relations (8) and (16) and applying the derivative analysis one can obtain

$$\begin{aligned} \left[\frac{d \ln \tau(P)}{dP} \right]^{-1} &= \left(\frac{V_a}{RT} \right)^{-1}_{T=const} \\ &= (V'_a)^{-1} = \mathcal{J}'^{-1} P_X - \mathcal{J}'^{-1} P = A - BP. \end{aligned} \quad (17)$$

Therefore, one may estimate $\mathcal{J} = B^{-1}$ and $P_X = A/B$ in relation (16) from a simple linear regression, without any “hidden,” additional parameters.

The application of the above analysis for supercooled and superpressed diethylphthalate (DEP) is presented in Figs. 3 and 4. Figure 3 shows the VFT-based $[H'_a]^{-1/2}$ vs $1/T$ plot, which is the clear analog of the Stickel *et al.* plot [2,4,10,11]. Despite the extension of the range of temperatures the dynamic crossover $T_B \approx 230$ K is approximately the same as in Ref. [30]. However, we would like to clarify the factor hardly discussed so far, namely, the fact that each of the following dynamical domains is described by a different set of parameters (D_T, T_0, τ_0) or (D_P, P_0, τ_0^P) . For instance from the temperature test in DEP we obtained $D_T \approx 2.4$, $T_0 \approx 184$ K, and $\tau_0^T \approx 4.7 \times 10^{-12}$ s for $T > T_B$ and $D_T \approx 30$, $T_0 \approx 111$ K and $\tau_0^T = 7 \times 10^{-22}$ s for $T < T_B$. Hence, the value of $T_0 \approx 130$ K given in Refs. [30,40] can be considered as the average of the above values, depending on the range of temperatures applied for the VFT-based estimation. The obtained in Fig. 3 values of the fragility strength coefficient D_T show that on passing T_B the crossover from a fragile to a less fragile (stronger) glass former occurs, associated with the decrease of the fictitious temperature T_0 . Analogous behavior occurs for the pressure path, as shown in Fig. 4.

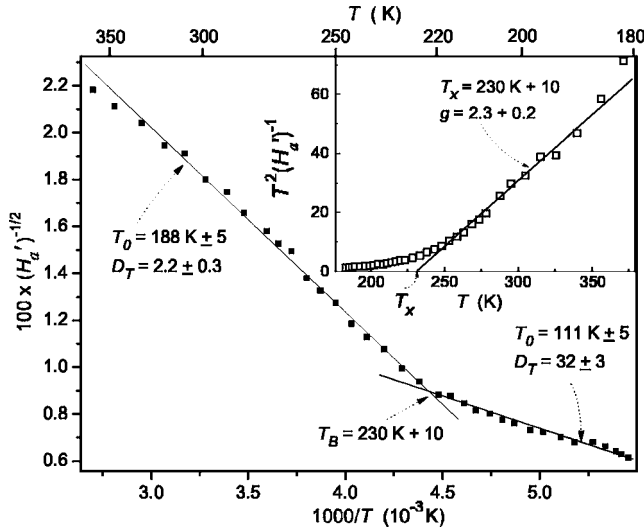


FIG. 3. The linearized plots of the temperature dependences of the reduced apparent activation energy in supercooled diethyl phthalate focused on the validity of the VFT relation (1). The inset shows results of analysis focused on testing the validity of the MCT critical-like relation [Eqs. (14) and (15)]. Values of fitted parameters are given in the figure. The relaxation time at dynamic crossovers is as follows: $\tau(T_B) = \tau(T_X) \approx 0.5 \times 10^{-7}$ s.

The inset in Fig. 3 presents $T^2[H'_a(T_X)]^{-1}$ vs T plot of the same data. In this case the region of the validity of the MCT critical-like dependence (15) is manifested as a straight line.

It is noteworthy that T_X can be determined from condition $T^2[H'_a(T_X)]^{-1} = 0$, based solely on simple extrapolation of the linear dependence, without any additional “hidden” adjustable parameters. This also enables an unequivocal estimation of errors of basic parameters in relation (15), namely, ± 10 K for T_X and ± 0.2 for g .

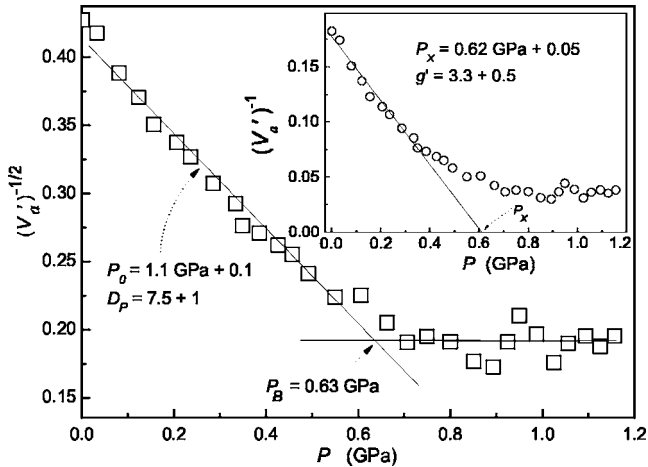


FIG. 4. The linearized plot of the pressure dependence of the reduced apparent activation volume in superpressed diethyl phthalate focused on the validity of the VFT-like relation (9). The inset shows results of the linearized, derivative focused on testing the validity of the MCT critical-like relation [Eqs. (16) and (17)]. Values of fitted parameters are given in the figure. Regarding relaxation time at dynamic crossovers, $\tau(P_B) \approx 1.1 \times 10^{-6}$ s and $\tau(P_X) \approx 9 \times 10^{-7}$ s.

Figure 4 presents $[V'_a]^{-1/2}$ vs P plot based on the derivative analysis of the isothermal ($T=293$ K), pressure evolution of the dielectric relaxation time. As stated above it is equivalent to the Casalini *et al.* [28] transformation of dielectric relaxation time data $\phi'_p(P)$. The dynamic crossover is clearly seen at $P_B \approx 0.6$ GPa. Also for the pressure case the dynamics for $P > P_B$ becomes “stronger,” showing the Arrhenius behavior (nonsloped line) within the limit of the experimental error.

The analysis presented in the inset in Fig. 4 seems to support the conclusion that the critical-like dependence predicted by MCT [relation (15)] can be extended for the pressure path [relation (17)]. Noteworthy is the coincidence of P_B and P_X in Fig. 3 as well as T_B and T_X in Fig. 4. The latter coincidence is strongly suggested in Refs. [31,32,40]. The parametrization of experimental data using VFT and PVFT dependences with the above set of parameters is shown via solid and dashed curves in Figs. 1 and 2.

IV. CONCLUSIONS

It has been shown that the derivative-based, VFT focused, analysis with the linear function output of dielectric relaxation times reflects the evolution of the apparent activation energy and the apparent activation volume for the temperature and pressure paths, respectively. The following dynamical domains are characterized by different sets of VFT parameters. Particularly noteworthy is the shift from a “fragile” (small D_T and D_P) to a “strong” (high values of D_T and D_P) pattern on passing T_B or P_B on cooling or pressuring. Dynamical domains are associated with two fictitious ideal glass temperatures and/or pressures, strongly different fragility strength coefficients, and VFT prefactors. The set of “Stikel *et al.*” [9,10] plots in Refs. [2–4,10,11,17,18,25–29,33,36,39,42] may indicate the universality of such behavior. It has also been suggested that the derivative-based plots $T^2[H'_a(T)]^{-1}$ or $[V'_a(P)]^{-1}$ enable a simple and reliable estimation of parameters describing the critical-like MCT behavior. It is noteworthy that values of exponents g for the temperature path [relation (14)] and g' for the pressure path [relation (16)] are different. This nonuniversality of the power exponent in relations (14) and (16) agrees with recent tests based on the high frequency light scattering susceptibility in orthoterphenyl, where the pressure and temperature shift of the frequency minimum was analyzed [48]. Noteworthy is also the coincidence between P_B and P_X as well as T_B and T_X values. The latter one is strongly recommended in studies carried out up to now ([31,40] and references therein). Values of relaxation times at $T_B \approx 230$ K and $P_B \approx 0.62$ GPa are equal to the same “magic,” universal relaxation time $10^{-7 \pm 1}$ s. This agrees with the suggestion of Ref. [36] that the relaxation time at the dynamic crossover may be independent of temperature and pressure and thus can serve as the control variable of the crossover.

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