



# Isobaric and isochoric properties of decahydroisoquinoline, an extremely fragile glass-former

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## Abstract

Pressure–volume–temperature (PVT) measurements were obtained on decahydroisoquinoline (DHIQ). From the resulting equation of state in combination with previously reported dielectric relaxation data, an analysis of the volume contribution to the dynamics was carried out for this very fragile glass-former (isobaric fragility,  $m_P = 163$ ). We find that the ratio of the isochoric and isobaric fragilities equals  $0.71 \pm 0.02$ , reflecting a strong temperature effect, consistent with the large fragility. The relaxation times superpose when plotted versus temperature times the specific volume raised to the 3.55 power. This is a larger value of the exponent than expected based on the fragility of DHIQ. The implication is that for molecular glass-formers, the classical Lennard-Jones 6–12 repulsive potential may represent the limit for fragile liquids.

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## 1. Introduction

Although the art of glass-making dates to ancient times and glasses are part of everyday life, efforts to understand the phenomenon at the molecular level continue unabated. The most spectacular change, and thus a primary focus of research, is the dramatic slowing down (by more than 14 decades) of molecular motions in a liquid during vitrification, which transpires without change in molecular structure and only modest (a few percent) changes in thermodynamic parameters such as  $T$  and  $V$ . The lack of any signature of the glass transition in the structure means that without a temporal reference, the molecular motions of a glass cannot be differentiated from those of the corresponding supercooled liquid. In light of this, much of the effort to understand the glass transition is devoted to find-

ing correlations of the dynamics with other physical properties.

A popular metric for classifying the structural dynamics is the parameter  $m$ , referred to as the steepness index or the fragility [1,2]

$$m = \left. \frac{\partial \log(x)}{\partial (T_g/T)} \right|_{T=T_g} \quad (1)$$

Here  $T_g$  is the glass transition temperature, often defined as  $\tau(T_g) = 100$  s, and  $x$  can be the viscosity or a relaxation time  $\tau$ , with the latter measured by dielectric spectroscopy, photon correlation, neutron scattering, Brillouin scattering or other experimental techniques. The fragility at atmospheric pressure varies among small molecules and polymers in the range  $35 \leq m_P \leq 214$  [3–7], indicating the drastic differences in dynamics among different materials. The fragility has been shown to depend on pressure, generally decreasing with increasing pressure (except for strongly H-bonded materials) [8,9]. Using the equation of state (EOS) it is possible to calculate the fragility for isochoric

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conditions ( $m_V$ ). The ratio of  $m_V$  with the (more usual) isobaric fragility determined at atmospheric pressure ( $m_P$ ) gives a direct measure of the relative importance of volume to the dynamics at atmospheric pressure. If  $\tau$  is a unique function of volume, then  $m_V = 0$  (no change of  $\tau$  at constant  $V$ ); conversely,  $m_V = m_P$  if  $\tau$  depends only on  $T$ . It follows that  $0 \leq m_V \leq m_P$ .

The isochoric fragility  $m_V$  can be determined from  $m_P$  using the relation [10,11]

$$m_P = m_V(1 + \gamma\alpha_p T_g), \quad (2)$$

where  $\alpha_p$  is the isobaric volume expansion coefficient and  $\gamma$  is a material constant, obtained from the scaling relation

$$\tau(T, V) = \mathfrak{F}(TV^\gamma). \quad (3)$$

The superposition of relaxation times when expressed as a function of  $TV^\gamma$  has been verified for many glass-formers from dielectric relaxation and other measurements [10–18]. From data on various materials, including molecular and polymeric glass-formers, a correlation is found between  $m_V$  and  $m_P$ :  $m_P = (37 \pm 3) + (0.84 \pm 0.05)m_V$  [19]. An important consequence of this correlation is that large  $m_P$  is associated with large ratios of  $m_V/m_P$ ; thus, temperature exerts a stronger relative effect on more fragile materials than does volume.

The most fragile molecular glass-former is decahydroisoquinoline (DHIQ), for which  $m_P = 163$  [20,21]. DHIQ is a compact, rigid molecule having an amine group with a large dipole moment (see insert to Fig. 1). An unusual property of DHIQ is that despite its large fragility, the  $\alpha$ -dispersion in the dielectric spectrum is relatively narrow [20]. This is an exception to the usual correlation between the breadth of the relaxation peak and fragility [4,5] (although other such deviations are known [22]). Recently,

dielectric relaxation measurements of DHIQ under high pressure were published [21], showing that high pressure allows differentiation of the secondary relaxations in DHIQ. In this regard, the behavior of DHIQ is very similar to that of polypropylene glycol (PPG) trimer [23], in which the secondary relaxation, not having an intermolecular origin, can be identified through its very weak sensitivity to pressure (i.e. small activation volume) compared to the  $\alpha$  relaxation. In the case of PPG trimer this difference in activation volumes causes the process manifested as an excess wing at low pressure to become resolved from the overlapping  $\alpha$ -peak at high pressures.

Given its large  $m_P$ , it is of interest to determine  $m_V$  for DHIQ in order to test the previously found correlation between isobaric and isochoric fragilities. We can also test whether the scaling property (Eq. (3)) is valid for so fragile a glass-former. Herein, we present pressure-volume-temperature (PVT) data on DHIQ from which the EOS is obtained. Using the latter, the volume dependence of  $\tau$  for DHIQ is calculated, in order to assess the role of volume on the dynamics of this fragile liquid.

## 2. Experimental

The decahydroisoquinoline (>99% pure, mixed cis and trans) was obtained from Aldrich and degassed prior to the measurements. The change in specific volume ( $V = 1.0684 \text{ ml g}^{-1}$  at ambient conditions) was measured both isobarically as a function of temperature (cooling rate =  $0.5 \text{ }^\circ\text{C/min}$ ) over a range from  $25 \text{ }^\circ\text{C}$  to ca.  $100 \text{ }^\circ\text{C}$  at pressures from 10 to 200 MPa, and isothermally over the same range. These experiments were carried out using a Gnomix apparatus [24], which utilizes the confinement technique with mercury as the confining fluid.

## 3. Results and discussion

The isobaric (open symbols) and isothermal (solid symbols) measurements of the specific volume of DHIQ are shown in Fig. 1. The  $V(T, P)$  behavior can be described using the Tait EOS [25]

$$V(T, P) = V(T, 0)\{1 + C \ln[1 - P/B(T)]\}, \quad (4)$$

where  $C (= 0.0894$  by convention) is a constant,  $V(T, 0) = a_0 + a_1T + a_2T^2$  is the volume at zero pressure, and  $B(T) = b_0 \exp(-b_1T)$  describes the pressure dependence. Fitting the data in Fig. 1 yields:  $a_0 = 1.0465 \pm 1 \times 10^{-4} \text{ ml g}^{-1}$ ,  $a_1 = (7.81 \pm 0.02) \times 10^{-4} \text{ ml g}^{-1} \text{ }^\circ\text{C}^{-1}$ ,  $a_2 = (9.7 \pm 0.2) \times 10^{-7} \text{ ml g}^{-1} \text{ }^\circ\text{C}^{-2}$ ,  $b_0 = 183 \pm 0.2 \text{ MPa}^{-1}$ , and  $b_2 = (5.29 \pm 0.02) \times 10^{-3} \text{ }^\circ\text{C}^{-1}$ .

From the EOS the data measured at various pressures can be expressed as a function of  $V$  (Fig. 2). This plot shows that for the same average intermolecular distances (i.e. constant  $V$ ) the relaxation times can vary over many decades. This reflects the role of thermal energy, as clearly the dynamics are not strictly governed by the volume. As has been known for a long time [26,27], such behavior is

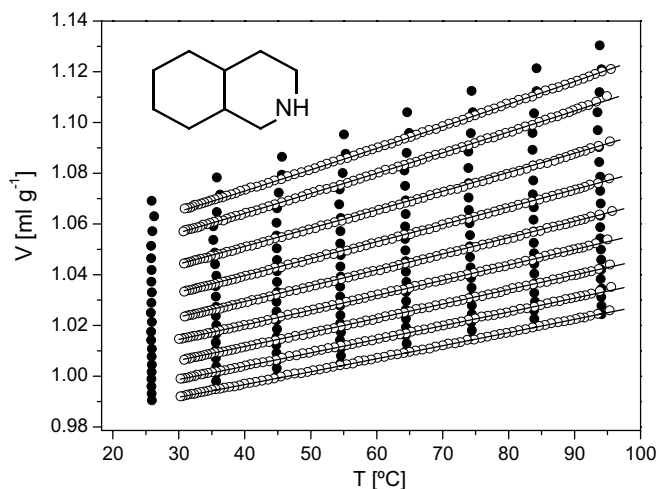


Fig. 1. Specific volume for DHIQ as a function of temperature. Open symbols are isobaric measurements at 10, 25, 50, 75, 100, 125, 150, 175 and 200 MPa (from top to bottom). Solid symbols are isothermal measurements from 0 to 200 MPa in increments of 10 K. Solid lines are the fit to the Tait equation (Eq. (4)) with the parameters given in the text. The insert shows the structure of DHIQ.

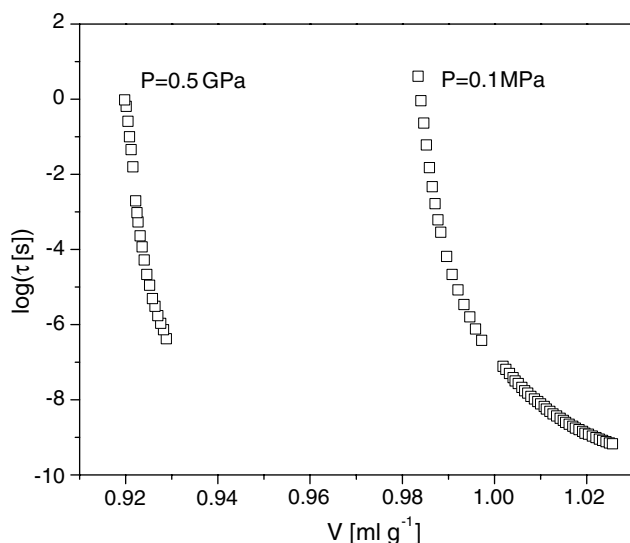


Fig. 2. Dielectric relaxation times at  $P = 0.1$  MPa (atmospheric pressure) and at  $P = 0.5$  GPa for DHIQ versus specific volume. The  $\tau$  data are from Ref. [21].

at odds with the underlying idea of free volume models, that the relaxation time is a function of the unoccupied volume [28,29]. To accommodate such results within a free volume approach, recourse must be made to a partitioning of free volume and occupied volume, each having distinct temperature coefficients [9].

For many materials, the relaxation time is found to be a unique function of the product  $TV^\gamma$  [10–18]. In Fig. 3 we see that DHIQ also conforms to this scaling behavior (Eq. (3)), with the relaxation times measured under different thermodynamic conditions collapsing to a master curve for  $\gamma = 3.55$ . This value is close to the exponent found for other molecular liquids, such as orthoterphenyl ( $\gamma = 4$ ) [15],

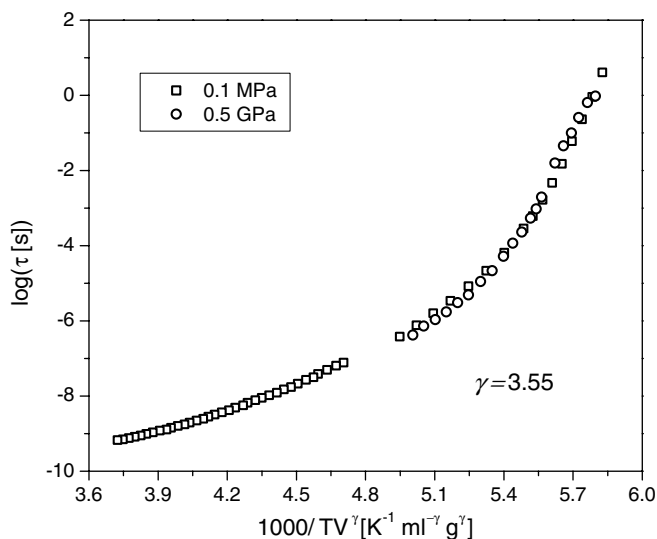


Fig. 3. Dielectric relaxation times at  $P = 0.1$  MPa (atmospheric pressure) and at  $P = 0.5$  GPa for DHIQ versus the product  $TV^\gamma$ . The  $\tau$  data are from Ref. [21].

propylene carbonate ( $\gamma = 3.7$ ) [30], cresolphthalein-dimethylether ( $\gamma = 4.5$ ) [13], and phenylphthalein-dimethylether ( $\gamma = 4.5$ ) [10].

Fitting the atmospheric pressure data over the entire range of  $T$  to the Vogel–Fulcher–Tammann–Hesse equation [31],  $\tau(T) = \tau_\infty \exp[DT_0/(T - T_0)]$ , yields  $D = 2.77 \pm 0.06$ ,  $\log(\tau_\infty) = -11.62 \pm 0.05$  and  $T_0 = 165.7 \pm 0.3$  K. We then obtain  $T_g = 180.4$  K (at which  $\tau = 100$  s) and  $m_P = 168 \pm 5$ , consistent with the previous determination [21]. Note that Richert et al. [20] reported a somewhat smaller value,  $m_P = 158$ ; the difference is probably within the experimental uncertainty, since for large  $m_P$  small errors in  $T$  propagate to large errors in  $\tau$ . In the following we use the average of the two values,  $m_P = 163$ . Jacobsen et al. [32] also carried out dielectric relaxation measurements on DHIQ, obtaining  $m_P = 154$  (and  $m_P = 143$  for mechanical measurements); however, this value was obtained by extrapolating to  $\tau = 10^3$  s and, given the consequent uncertainty, was not used in the following.

From the EOS we calculate  $\alpha_P(T_g) = 6.12 \times 10^{-4} \text{ C}^{-1}$ , whereby Eq. (2) gives  $m_V = 117$ . Thus,  $m_V/m_P$ , equal to the ratio of the isochoric and isobaric enthalpies,  $= 0.71 \pm 0.02$ . This is the highest value of the ratio found to date for any non-associated (strictly van der Waals) molecular glass-former. The ratio, a measure of the degree to which temperature governs  $\tau(T)$  relative to the effect of volume, varies from 0.38 to 0.64 for other molecular glass-formers [9,42]. A ratio of 0.71 implies that  $T$  exerts a stronger effect than  $V$ .

The isochoric and isobaric fragilities for DHIQ are displayed in Fig. 4, along with values for other liquids, polymers, and polymer networks [19,43]. A correlation between the two measures of fragility is evident. From linear fitting these data (both molecular and polymeric glass-formers collectively), we find  $m_P = (33 \pm 4) + (0.92 \pm 0.05)m_V$ , which is close to the relation suggested previously [19] (the present correlation is for 46 materials, ten more than in the prior work).

Fig. 5 is a plot of the scaling parameter  $\gamma$  versus the inverse isochoric fragility. While in general  $m_V$  decreases with increasing  $\gamma$  [19], DHIQ is an outlier. The implication is that for molecular glass-formers,  $\gamma \sim 4$  represents a lower limit, rather than  $\gamma = 0$ . This possibility requires further investigation on other fragile liquids.

The dependence of the relaxation time for DHIQ on volume and temperature shows some interesting features distinguishing it from other materials. The very high isobaric fragility is associated with a high isochoric fragility; however,  $m_V$  is somewhat less than expected from the correlation between  $m_V$  and  $m_P$  established for most glass-formers (solid line in Fig. 4). This implies that volume has a more important role than expected for this very fragile material. The importance of volume is also reflected in the magnitude of  $\gamma$ , which is large in comparison to the scaling exponents found for comparably fragile materials (which are polymers and associated liquids [9]). But there is an important difference: for polymers, the small values

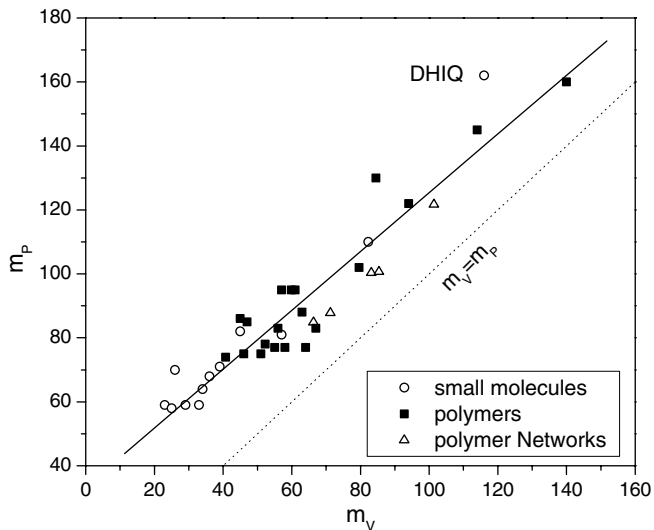


Fig. 4. Isobaric fragility  $m_p$  (at atmospheric pressure) versus isochoric fragility  $m_v$  for 33 materials (in order of increasing  $m_v$ ): PCB62 [8], 1, 1'-di(4-methoxy-5-methylphenyl)cyclohexane (BMMPC) [8], 1,1'-bis(*p*-methoxyphenyl)cyclohexane (BMPC) [33], PCB54 [34], PCB42 [34], cresolphthalein–dimethylether (KDE) [8], salol [8], phenylphthalein–dimethylether (PDE) [8], polypropylene oxide (PPO) [42], polymethylphenylsiloxane (PMPS) [35], *o*-terphenyl (OTP) [17], polyepichlorhydrin (PECh) [17], polymethyltolylsiloxane (PMTS) [36], polyvinylmethylether (PVME) [17], polyvinylacetate (PVAc) [42], polystyrene (PS) [37], PPG [38], PC [8], diglycidyl ether of bisphenol A (DGEBA) [42], 1,4-polyisoprene(PI) [39,12], poly[(phenol glycidyl ether)-co-formaldehyde] (PPGE) [42], PVAc(2) [17], polyvinylethylene (PVE) [40], 1,4-polybutadiene (PB) [17], polyethylacrylate (PEA) [37], polymethylacrylate (PMA) [17], methafluoaniline [41], PCGE [42], PMA(2) [37], polymethylmethacrylate (PMMA) [17] and polyvinylchloride (PVC) [37]. Polymer networks refer to PVE networks [43]. The solid line is a linear fit,  $m_p = (33 \pm 4) + (0.92 \pm 0.05)m_v$ .

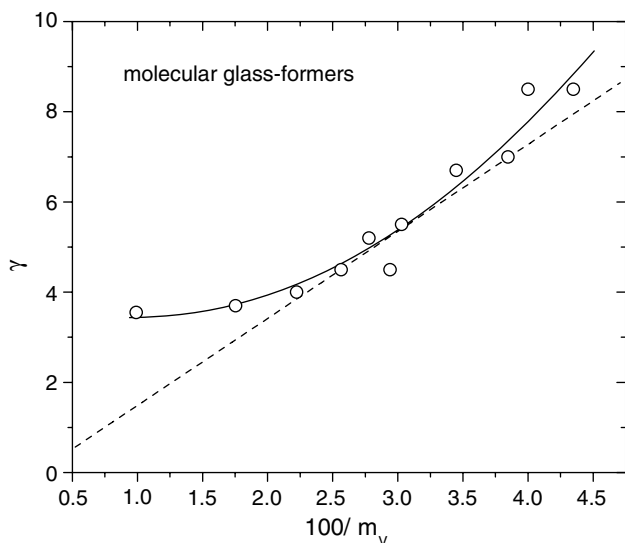


Fig. 5. Scaling exponent  $\gamma$  versus the inverse isochoric fragility for 25 amorphous materials. The small-molecule glass-formers (in order of increasing  $m_v$ ) are: PCB62, BMMPC, BMPC, PCB54, PCB42, KDE, salol, PDE, OTP, PC, and DHIQ. The dashed line is the fit of all data including polymers (Ref. [19]), while the solid line is only to guide to the eye regarding the behavior of molecular glass-formers.

of  $\gamma$  are due to the large number of intramolecular bonds per molecule which are insensitive to pressure, thus minimizing the effect of  $V$  [44]. On the other hand, for a simple molecule like DHIQ, the small magnitude of  $\gamma$  reflects directly the nature of the intermolecular interactions.

The idea of using Eq. (3) to analyze relaxation times arose from the notion that for local dynamics, the intermolecular potential could be approximated by an inverse repulsive power law [14,45]. Such a potential is most appropriate for spherically symmetric molecules with a dominant repulsive part, with the scaling exponent  $\gamma$  then interpreted in terms of the exponent  $3\gamma$  of the inverse power law potential. Certainly, molecular glass-formers lacking hydrogen bonds most closely approximate this idealized case, and we do find in Fig. 5 that the limiting value of  $\gamma$  approaches the value for the classical Lennard-Jones potential,  $3\gamma = 12$ .

A more general basis for the parameter  $\gamma$  can be developed. Starting from Eq. (3) we find

$$\left. \frac{\partial \log(\tau)}{\partial V} \right|_T = \left. \frac{\partial \log(\tau)}{\partial T} \right|_V \frac{T}{V} = - \left. \frac{\partial \log(\tau)}{\partial (1/T)} \right|_V \frac{1}{TV} \quad (5)$$

which can be rewritten as

$$\ln(10) \left. \frac{\partial \ln(\tau)}{\partial \ln V} \right|_T = - \gamma \left. \frac{\partial \log(\tau)}{\partial (1/T)} \right|_V. \quad (6)$$

At  $T = T_g$

$$\left. \frac{\partial \ln(\tau)}{\partial \ln(V)} \right|_{T_g} = - \gamma \frac{m_v}{\ln(10)}. \quad (7)$$

Since the isochoric fragility is a material constant [8], the volume dependence expressed on the left-hand side of Eq. (7) is directly proportional to  $\gamma$ .

Eq. (7) calls to mind the definition of the Grüneisen parameter  $\gamma_G$  [46]

$$\left. \frac{\partial \ln(\omega)}{\partial \ln(V)} \right| = - \gamma_G, \quad (8)$$

where  $\omega$  is the phonon frequency of the lattice (recognizing, of course, that  $\tau^{-1}$  has only the dimensions of frequency and does not represent any vibrational motion). Experimentally  $\gamma_G$  is approximately constant for temperatures well away from 0 K, having values in the range from 0.6 to 5 [47]. These equations suggest a possible correlation between  $\gamma$  and  $\gamma_G$ , as in fact can be derived from models of the dynamics of supercooled liquids [48,49].

Considering the expression for the free-volume [29]

$$\tau = \tau_0 \exp \left( a \frac{V_\infty}{V - V_\infty} \right), \quad (9)$$

where  $\tau_0$  and  $a$  are constants and  $V_\infty$  is the occupied volume, it can be seen that if  $V_\infty$  is a constant or only a function of  $T$ , then Eq. (7) cannot be satisfied, since it requires that  $V V_\infty / (V - V_\infty)^2 = \text{const}$ , which is satisfied only for  $V_\infty = 0$  or for a unique value of  $V$  (i.e.  $V = \text{const}$ ). Therefore,  $V_\infty$  has to be a function of  $V$ , implying that the fundamental idea behind Eq. (9) of free volume models cannot be correct.

#### 4. Conclusions

From PVT measurements on DHIQ in combination with previously published dielectric relaxation times, the relative contributions of temperature and volume (density) to the  $T$ -dependence of the structural relaxation dynamics were quantified. The ratio of the isochoric and isobaric activation enthalpies =  $0.71 \pm 0.02$ , which is the highest value of  $m_V/m_P$  found to date for a molecular glass-former. Since DHIQ is the most fragile molecular glass-former, this large value confirms the correlation that a large  $m_V/m_P$  ratio corresponds to large  $m_P$  (or that large  $m_V$  is associated with large  $m_P$ ). The value of  $m_V$ , however, is somewhat smaller than expected from the general correlation between  $m_V$  and  $m_P$ . This means that volume plays a more significant role than expected. Fitting data for a larger number of glass-formers (10 more than in Ref. [19]) gives slightly different values for the parameters of the linear correlation,  $m_P = (33 \pm 4) + (0.92 \pm 0.05)m_V$ .

The relaxation times are found to superpose onto a master curve when plotted as a function of  $TV^{3.55}$ . This exponent is larger than anticipated from the assumption that  $\gamma$  is inversely proportional to  $m_V$  (dotted line in Fig. 5). The suggestion is that for molecular glass-formers,  $\gamma$  tends to a limiting value  $\sim 4$  for large  $m_V$ ; further work is needed to confirm this. Assuming the exponent  $\gamma$  reflects the nature of the intermolecular repulsive potential, this limiting value of the exponent corresponds to the repulsive term in the classical Lennard-Jones 6–12 potential. Smaller values of  $\gamma$  have been found but only for polymers and hydrogen-bonded liquids.

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