

# Simple Ratio for Testing a Supercooled Liquid's Relaxation Time–Entropy Relation

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Variation of a supercooled liquid's viscosity and relaxation time with temperature is currently related to the liquid's excess entropy over the crystal phase value, instead of its configurational entropy. This assumes that a liquid's nonconfigurational entropy is either equal to or proportional to the crystal's entropy. To examine its validity, we define an exact ratio  $R_{TS}$ , which is equal to 2 if the assumption is valid, and then determine  $R_{TS}$  from the available data on 10 liquids. Its value is close to 2 for *o*-terphenyl and glycerol and deviates from 2 for eight liquids. This shows that the nonconfigurational entropy of most liquids is not proportional to the crystal's entropy, which has consequences for the current use of the excess entropy in developing theories of vitrification and for computer-simulation of the entropy–diffusivity relations by using the inherent structure model.

## 1. Introduction

When a liquid is supercooled, its viscosity and relaxation time continuously increase and the self-diffusion coefficient, volume, entropy, and enthalpy continuously decrease. When the magnitude of its viscosity exceeds  $10^{13}$  dPa·s, the liquid vitrifies and its thermal expansion coefficient and heat capacity decrease over a narrow temperature range. In a theory of viscosity known as the entropy theory,<sup>1</sup> this occurrence is explained in terms of the loss of a liquid's configurational entropy,  $S_{\text{conf}}$ . According to this theory,<sup>1</sup> molecules in a viscous liquid rearrange cooperatively, and the probability of this cooperative rearrangement rapidly decreases as a liquid is cooled.<sup>1</sup> Accordingly, the viscosity of a liquid varies as  $\exp[C/TS_{\text{conf}}]$ , where  $C$  is a constant and  $T$  is the temperature. The intuitive appeal of this theory has led to its wider use in correlating the variation of a supercooled liquid's molecular relaxation time with its entropy. However, the relation between the viscosity and  $S_{\text{conf}}$  seems to have remained unexamined.

Although the entropy theory does not lead to the inference that an internally equilibrated state of a liquid would undergo a second order thermodynamic transition to another disordered state at a temperature above 0 K, this inference has been seen as a part of the theory. Recently, it has been pointed out that such an inference is implausible<sup>2,3</sup> and, further, that studies which had tested the entropy theory and found it to be valid had used  $S_{\text{exc}}$ , the excess entropy of a liquid over that of its ordered crystal state, instead of the required  $S_{\text{conf}}$ , simply because  $S_{\text{conf}}$  values are not available. This use implies that the nonconfigurational part of a viscous liquid's entropy,  $S_{\text{nonconf}}$ , is equal to the entropy of its ordered crystal,  $S_{\text{crys}}$ , over the range of temperatures being studied. More recently, it has been concluded that  $S_{\text{conf}}$  cannot be equal to  $S_{\text{exc}}$ , because  $S_{\text{nonconf}}$ , which is the sum of the vibrational and anharmonic force contributions and any contribution from the ability of molecules to rearrange in the  $\beta$ -relaxation process of a viscous liquid, would not be equal to  $S_{\text{crys}}$ .<sup>4</sup> However, if  $S_{\text{conf}}$  is found to be proportional to  $S_{\text{exc}}$  over the relevant temperature range,  $S_{\text{exc}}$  may be used in place of  $S_{\text{conf}}$  in testing the entropy theory. This

proportionality too has been questioned,<sup>5</sup> but no numerical test for resolving this issue was proposed.

Here we define a ratio,  $R_{TS}$ , which can be determined from dielectric relaxation and entropy measurements. If  $S_{\text{conf}}$  is proportional to  $S_{\text{exc}}$ ,  $R_{TS}$  will be found to be equal to 2. But if  $S_{\text{conf}}$  is not proportional to  $S_{\text{exc}}$ ,  $R_{TS}$  will deviate from 2, and  $S_{\text{exc}}$  may not be useful for testing the merits of the entropy theory. From the available data, we determine  $R_{TS}$  for 10 liquids and find that this ratio is equal to 2 only for two liquids. For the other eight, it deviates from 2. Thus, it seems that, generally speaking,  $S_{\text{conf}}$  is not proportional to  $S_{\text{exc}}$  or that  $S_{\text{nonconf}}$  is considerably different from  $S_{\text{crys}}$ .

## 2. Use of the Entropy–Viscosity Relation

According to the entropy theory,<sup>1</sup> the viscosity,  $\eta$ , and the relaxation time,  $\tau$ , of a viscous liquid vary with the temperature,  $T$ , such that

$$\eta \quad \text{and} \quad \tau = A \exp\left[\frac{C}{TS_{\text{conf}}}\right] \quad (1)$$

where  $C$  is a (temperature-independent) material's constant,  $S_{\text{conf}}$  is as defined earlier here, and  $A$  is an empirical parameter which has been assumed to be negligibly dependent on  $T$ .<sup>1</sup> Equation 1 has no inference for a second order thermodynamic transition at a temperature  $T_2$  or  $T_k$ . This inference had been accommodated by making three approximations: (i) the difference between the extrapolated heat capacities of an equilibrium liquid and its glass at  $T_g$ ,  $\Delta C_p(T_g)$ , remains constant over the temperature range from  $T_g$  to  $T_2$ , as in eqs 25–27 of ref 1; (ii)  $S_{\text{conf}}$  is equal to  $S_{\text{exc}}$ , that is,  $S_{\text{nonconf}}$  is negligibly different from  $S_{\text{crys}}$ ; and (iii) the residual entropy  $S_0^\circ$  ( $S_{\text{exc}}$  at 0 K) of a glass is equal to  $S_{\text{exc}}$  at  $T_g$ , as in eqs 34 and 35 of ref 1. Thus, according to approximation i,

$$S_{\text{conf}}(T_g) = \Delta C_p(T_g) \ln\left(\frac{T_g}{T_2}\right) \quad (2)$$

where  $\Delta C_p = (C_{p,\text{liq}} - C_{p,\text{glass}})$  and  $T_2$  is the second order transition temperature, which is 70–80% of  $T_g$ .

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Approximations ii and iii have led to

$$\left[ \frac{S_{\text{exc}}(T_g)}{\Delta C_p(T_g)} \right] = \ln \left( \frac{T_g}{T_2} \right) \quad (3)$$

or

$$T_g = T_2 \exp \left[ \frac{S_{\text{exc}}(T_g)}{\Delta C_p(T_g)} \right] \quad (3a)$$

where

$$S_{\text{exc}}(T_g) = S_0^\circ + \int_0^{T_g} [C_{p,\text{glass}} - C_{p,\text{crys}}] d \ln T \quad (4)$$

or

$$S_{\text{exc}}(T_g) = \Delta S_m - \int_{T_g}^{T_m} [C_{p,\text{liq}} - C_{p,\text{crys}}] d \ln T \quad (4a)$$

where  $S_0^\circ$  is the residual entropy of a glass,  $\Delta S_m$  is the entropy of its crystal-melting, and  $T_m$  is the melting point.

Goldstein<sup>6</sup> had noted that a geometrical construction within the above-given three approximations leads to the ratio  $[S_{\text{exc}}(T_g)/\Delta C_p(T_g)] \approx 0.2$ . This ratio is also obtained from eq 3 when  $T_2$  is equal to  $0.8T_g$  or  $(T_g/T_2) = 1.22$ . Hence, eq 3a relates the  $T_g$  determined from measurements of a molecular transport property to an unobservable thermodynamic transition temperature  $T_2$  through the use of  $S_{\text{exc}}$  and  $\Delta C_p$  values at  $T_g$ . Since  $\ln(T_g/T_2)$  for various liquids is within the range 0.16–0.28 ( $T_g = 1.17T_2$  to  $T_g = 1.33T_2$ ),  $S_{\text{exc}}(T_g)$  should be 16% to 28% of the value of  $\Delta C_p(T_g)$  for different liquids. This suggests that if the  $\Delta C_p(T_g)$ ,  $T_2$ , and  $T_g$  values of a liquid are known,  $S_{\text{exc}}(T_g)$  can be estimated without performing the heat capacity measurements on its crystal phase. Also, if the cooling rate of a liquid, or the heating rate of a glass, is decreased, the  $T_g$  observed by calorimetry would decrease.

Since  $\Delta C_p$  of a viscous liquid over a range of temperature between  $T_g$  and  $T_2$  is taken to remain constant in the entropy theory,<sup>1</sup> eq 3 may be written as

$$S_{\text{exc}}(T_g) = \Delta C_p(T_g) \ln T_g - \Delta C_p(T_g) \ln T_2 \quad (4b)$$

Now, if  $T_g$  is measured by heating a glass of a fixed composition at different heating rates, its value would vary, but  $T_2$  will remain constant. Therefore, according to eq 4b,  $S_{\text{exc}}(T_g)$  would vary linearly with  $\ln T_g$ . We suggest, therefore, that the two consequences of eq 3, (i) the magnitude of  $S_{\text{exc}}(T_g)/\Delta C_p(T_g)$  remaining within 0.16 to 0.28 and (ii) linear variation of  $S_{\text{exc}}(T_g)$  with  $\ln T_g$  of a liquid according to eq 4b, can be examined by using the available data. In an unrelated discussion of the properties of supercooled liquids, Hodge<sup>7</sup> has used the consequences of eq 3 for modeling the  $C_p$ 's variation with  $T$ .

Recent studies<sup>2,4</sup> have shown that approximations i–iii made in ref 1 are neither theoretically nor experimentally justifiable. Despite that, approximate values of  $z^*(T_g)$ , the minimum size of the cooperatively rearranging region at  $T_g$ , have been determined for different liquids by taking the pre-exponential term of eq 1 to be equal to the pre-exponential term of the Vogel–Fulcher–Tammann equation.<sup>8</sup> These  $z^*(T_g)$  values of different liquids have been found to be in the range 2.4–14.3,<sup>8</sup> and the consequences of these values for the observed decrease in the relaxation time and in the  $T_g$  of liquids confined to nanometer size pores have been described.<sup>8</sup> Ngai and co-workers,<sup>9,10</sup> and others<sup>11,12</sup> have tested the approximate relations based upon the Adam–Gibbs equation<sup>1</sup> by using newly obtained

data of  $S_{\text{exc}}$  and heat capacity in some cases.<sup>11,12</sup> These studies<sup>9–12</sup> have concluded that the entropy theory may not be valid.

### 3. Ratio for Testing the Entropy Approximation

The dielectric relaxation time of the  $\alpha$ -relaxation process,  $\tau_{\text{diel}}$ , has been frequently used in the study of molecular kinetics of supercooled liquids. This choice is mainly due to the facts that procedures for determining  $\tau_{\text{diel}}$  over the range  $10^{-9}$  to  $10^4$  s are relatively simple and the equipment needed for such measurements has been commercially available. But when the merits of the entropy theory are tested by using a correlation between  $\tau_{\text{diel}}$  (or  $\eta$ ) and thermodynamic quantities,  $\Delta C_p(T_g)$  and  $S_{\text{exc}}(T_g)$ , the conclusions that are drawn become questionable for at least three experimental reasons: (i) The  $\Delta C_p(T_g)$  value is not determined with sufficient accuracy because the glass softening endotherm is spread over the 5–25 K range, requiring, therefore, that the magnitude of  $\Delta C_p(T_g)$  be determined by extrapolating the measured  $C_p$  values to  $T_g$  from both sides of the sigmoid shaped  $C_p$  increase, one from  $T > T_g$  and the second from  $T < T_g$ .<sup>12</sup> (ii) The  $\Delta C_p(T_g)$  value depends on the measurements' time scale, the distribution of relaxation times, and the nonlinearity parameter.<sup>7,12</sup> (iii) The  $S_{\text{exc}}(T_g)$  value depends on the measured  $T_g$ , which in turn depends on the heating rate. For these reasons, we avoid using  $\Delta C_p(T_g)$  and  $S_{\text{exc}}(T_g)$  values and thereby also eliminate the use of approximations i, ii, and iii described in section 2. We also avoid the practice<sup>14</sup> of using the plot of  $\log(\tau)$ , or  $\log(\eta)$ , against  $T_g/T$ ,<sup>13</sup> and the related quantity,  $m$  [ $=d \log \tau/d(T_g/T)$ ].<sup>14</sup> The reason for doing so is that the quantity  $m$  is estimated by drawing a tangent at  $T_g/T = 1$ , an extreme data point in such plots, and its value is, therefore, subject to errors.

To determine whether  $S_{\text{nonconf}}$  is equal to  $S_{\text{crys}}$ , or if  $S_{\text{conf}}$  from molecular arrangements that produce the  $\alpha$ -relaxation process is proportional to  $S_{\text{exc}}$ , we rewrite eq 1 as a ratio,  $(T_a/T_b)[S_{\text{conf}}(T_a)/S_{\text{conf}}(T_b)]$ , where  $T_a$  and  $T_b$  are two arbitrarily chosen temperatures at which the transport property and entropy data are available, and  $S_{\text{conf}}(T_a)$  and  $S_{\text{conf}}(T_b)$  are the configurational entropy at those two temperatures. When the dielectric relaxation time of the  $\alpha$ -process,  $\tau_{\text{diel}}$ , is taken as a measure of a liquid's molecular kinetics, we select these two temperatures such that  $\tau_{\text{diel}}$  is 1  $\mu\text{s}$  at  $T_a$  and  $\tau_{\text{diel}}$  is 100 s at  $T_b$ . Hence, the ratio obtained from eq 1 is given by

$$R_{\text{TS}} = \left( \frac{T_a}{T_b} \right) \frac{S_{\text{conf}}(T_a)}{S_{\text{conf}}(T_b)} = \frac{(2 - \log A)}{(-6 - \log A)} \quad (5a)$$

Equation 5 is exact within the precepts of the Adam–Gibbs equation,<sup>1</sup> and all quantities in eq 5a are accurately measurable by calorimetry, except for the parameter  $A$ . The value of  $A$  can be determined by vibrational spectroscopy, but this is rarely done. Instead, its value is taken to represent the phonon time scale. Since  $A$  may differ for different liquids, we need to first ascertain the effect of different  $A$  values on the calculated  $R_{\text{TS}}$ . When  $A$  in eq 5a is taken to be equal to  $10^{-14}$  s, as in earlier studies,<sup>14</sup>  $R_{\text{TS}}$  is equal to 2.

$$R_{\text{TS}} = \left( \frac{T_a}{T_b} \right) \frac{S_{\text{conf}}(T_a)}{S_{\text{conf}}(T_b)} = \frac{(2 + 14)}{(-6 + 14)} = 2 \quad (5b)$$

If  $A$  is instead taken to be less than  $10^{-14}$  s,  $R_{\text{TS}}$  becomes less than 2, and if  $A$  is taken to be greater than  $10^{-14}$  s,  $R_{\text{TS}}$  becomes greater than 2. Since  $A$  is seen to represent the phonon time scale, its magnitude cannot be taken to be greater than  $10^{-13}$  s.

**TABLE 1: Measured Values of the Kinetic and Thermodynamic Quantities of Several Supercooled Liquids<sup>a</sup>**

liquid	$T_b$ (K)	$S_{\text{exc}}(T_b)$ (J/mol·K)	$T_a$ (K)	$S_{\text{exc}}(T_a)$ (J/mol·K)	$R_{\text{TS}}$
ethanol <sup>b</sup>	98	14.9	138	27.3	2.58
<i>n</i> -propanol <sup>c</sup>	97	18.5	134	32.7	2.44
1,3-propanediol <sup>d</sup>	167	29.4	230	48.8	2.29
glycerol <sup>d</sup>	190	26.9	235	44.5	2.05
salol <sup>c</sup>	220	28.3	257	44.5	1.84
2-methyltetrahydrofuran <sup>c</sup>	91	23	105	33.2	1.66
toluene <sup>e</sup>	115	5.8	132	12.6	2.49
<i>o</i> -terphenyl <sup>f</sup>	246	21.5	283	38.1	2.04
3-bromopentane <sup>g</sup>	108	21.6	136	32	1.86
propylene carbonate <sup>h</sup>	158	18.5	182	26.1	1.62

<sup>a</sup>  $T_a$  is the temperature at which  $\tau_{\text{diel}} = 1 \mu\text{s}$ , and  $T_b$  is the temperature at which  $\tau_{\text{diel}} = 10^2 \text{ s}$ . ( $T_b$  thus defined has also been taken as equal to calorimetric  $T_g$  in some studies.<sup>18</sup>) <sup>b</sup>  $T_a$  and  $T_b$  were determined from the parameters for the Vogel–Fulcher–Tamman equation given in ref 19 and  $S_{\text{exc}}$  from ref 20. Parameters for the  $\alpha$ -relaxation process in Table 1, ref 25, yield  $T_a = 141 \text{ K}$ . With the correspondingly high value of  $S_{\text{exc}}(T_a)$ ,  $R_{\text{TS}}$  for ethanol would be higher than 2.6. <sup>c</sup>  $T_a$  and  $T_b$  were determined from eq 13 and Table 2 values in ref 18.  $S_{\text{exc}}$  taken from ref 18. <sup>d</sup>  $T_a$  and  $T_b$  were determined from eq 13 and Table 2 values in ref 18.  $S_{\text{exc}}$  from ref 21. <sup>e</sup>  $T_a$  and  $T_b$  were determined from the  $m$  and  $T_0$  values in ref 22.  $S_{\text{exc}}$  taken from ref 23. <sup>f</sup>  $T_a$  and  $T_b$  were determined from eq 13 and Table 2 values in ref 18.  $S_{\text{exc}}$  taken from ref 17. <sup>g</sup>  $T_a$  and  $T_b$  were determined from eq 13 and Table 2 values in ref 18.  $S_{\text{exc}}$  taken from ref 23. <sup>h</sup>  $T_a$  and  $T_b$  were determined from eq 13 and Table 2 values in ref 18.  $S_{\text{exc}}$  taken from ref 24.

Therefore, the value of 2.14 calculated by using  $A = 10^{-13}$  in eq 5 becomes the maximum  $R_{\text{TS}}$  for a liquid. For the sake of self-consistency, as well as for plausibility in the use of the phonon time scale, we keep  $A$  equal to  $10^{-14} \text{ s}$  for all liquids.

On the assumption that  $S_{\text{conf}}$  of a viscous liquid is proportional to  $S_{\text{exc}}$ , eq 5 becomes

$$R_{\text{TS}} = \left( \frac{T_a}{T_b} \right) \frac{S_{\text{exc}}(T_a)}{S_{\text{exc}}(T_b)} = 2 \quad (6)$$

where

$$S_{\text{exc}}(T_a) = \Delta S_m - \int_{T_a}^{T_m} [C_{p,\text{liq}} - C_{p,\text{crys}}] d \ln T \quad (7a)$$

and

$$S_{\text{exc}}(T_b) = \Delta S_m - \int_{T_b}^{T_m} [C_{p,\text{liq}} - C_{p,\text{crys}}] d \ln T \quad (7b)$$

Thus, a criterion may be obtained for determining whether  $S_{\text{conf}}$  is proportional to  $S_{\text{exc}}$ : if  $R_{\text{TS}}$  calculated from eq 6 is equal to 2,  $S_{\text{conf}}$  is proportional to  $S_{\text{exc}}$ , and if it is not equal to 2, then  $S_{\text{conf}}$  is not proportional to  $S_{\text{exc}}$ , within the limits of the theory.<sup>1</sup>

#### 4. Experimental Test for the Use of $R_{\text{TS}}$

We use the  $\tau_{\text{diel}}$  and  $C_p$  data from the literature and determine  $S_{\text{exc}}$  at two temperatures,  $T_a$ , at which  $\tau_{\text{diel}} = 1 \mu\text{s}$ , and  $T_b$ , at which  $\tau_{\text{diel}} = 100 \text{ s}$ . (Note that, in some studies,  $T_b$ , at which  $\tau_{\text{diel}} = 100 \text{ s}$ , has been taken as  $T_g$ .) Values of  $T_a$ ,  $T_b$ ,  $S_{\text{exc}}(T_a)$ , and  $S_{\text{exc}}(T_b)$  are listed in Table 1 along with the source of the data. From eq 6, we calculate  $R_{\text{TS}}$  and list its value also in Table 1. It is seen that  $R_{\text{TS}}$  varies from 1.62 for propylene carbonate to 2.58 for ethanol. Its value is close to 2 for glycerol and *o*-terphenyl. Since  $S_{\text{exc}}$  has been determined with an accuracy better than 2% and  $T_a$  and  $T_b$  have been determined to an accuracy better than 0.5%, the maximum variation in  $R_{\text{TS}}$  owing to this inaccuracy will be  $\pm 0.04$ . However, the discrepancy from

the expected value of 2 for  $R_{\text{TS}}$  in Table 1 is  $\pm 0.40$ , which is about ten times the above-calculated uncertainty of  $\pm 0.04$ . There can be a further uncertainty in the  $R_{\text{TS}}$  value if the samples used for  $C_p$  and  $\tau_{\text{diel}}$  measurements differed in purity, but this uncertainty cannot be determined here because information on the purity of the samples used is not available. With that as a caution, we conclude either that  $S_{\text{conf}}$  is not proportional to  $S_{\text{exc}}$  for eight out of the 10 liquids listed in Table 1 or that the use of eq 1 here is inappropriate.

It should be noted that one's choice of  $A$  value has an effect on the merits of the calculated  $R_{\text{TS}}$ . For that reason, we first inquire what value of  $A$  in eq 6 would make a liquid's  $R_{\text{TS}}$  equal to 2, and then we examine if that (forced)  $A$  value is physically plausible for that liquid. Now, to lower  $R_{\text{TS}}$  of toluene from 2.49 in Table 1 to 2.0, the  $A$  value in eq 6 would have to be increased from  $10^{-14}$  to  $10^{-11.37} \text{ s}$ . But an  $A$  value of  $10^{-11.37} \text{ s}$  indicates an implausibly long time for phonon modes. On the other extreme, to raise  $R_{\text{TS}}$  of propylene carbonate from 1.62 in Table 1 to 2.0, the magnitude of  $A$  in eq 6 would have to be decreased from  $10^{-14}$  to  $10^{-18.9} \text{ s}$ . But an  $A$  value of  $10^{-18.9} \text{ s}$  indicates an implausibly short time for phonon modes. Moreover, use of an  $A$  value other than  $10^{-14} \text{ s}$  would put all those analyses in question that have used the quantity  $m$  determined by using  $\tau_{\text{diel}} = 10^{-14} \text{ s}$  at  $T_g/T = 0$  and  $\tau_{\text{diel}} = 10^2 \text{ s}$  at  $T_g/T = 1$ . (Reference 14 may be read for further details.) We conclude that if  $R_{\text{TS}}$  of the eight liquids in Table 1 is forced to become equal to 2, it can be done only by choosing an implausible value of  $A$ .

For comparing  $R_{\text{TS}}$  of different liquids, we may keep  $A = 10^{-14} \text{ s}$  in eq 6 and consider why the  $R_{\text{TS}}$  value for some liquids deviates from 2. To do so, we express  $S_{\text{exc}}$  as

$$S_{\text{exc}} = \chi S_{\text{conf}} + \chi (S_{\text{nonconf}} - S_{\text{crys}}) \quad (8)$$

where the quantity  $(S_{\text{nonconf}} - S_{\text{crys}})$  is positive and  $\chi$  is the proportionality constant. Thus, we rewrite eq 6,

$$R_{\text{TS}} = \frac{T_a}{T_b} \frac{S_{\text{conf}}(T_a) + [S_{\text{nonconf}}(T_a) - S_{\text{crys}}(T_a)]}{S_{\text{conf}}(T_b) + [S_{\text{nonconf}}(T_b) - S_{\text{crys}}(T_b)]} = 2 \quad (9)$$

For eq 9 to be valid,  $S_{\text{conf}}$ ,  $S_{\text{nonconf}}$ , and  $S_{\text{crys}}$  should decrease in the same proportion when a liquid is cooled from  $T_a$  to  $T_b$ . To discuss the implications of  $R_{\text{TS}} \neq 2$ , for eight liquids in Table 1, we consider both cases, (i) when  $R_{\text{TS}} < 2$  and (ii) when  $R_{\text{TS}} > 2$ . When  $R_{\text{TS}} < 2$ , the implication is that as the liquid is cooled from  $T_a$  to  $T_b$ , its  $(S_{\text{nonconf}} - S_{\text{crys}})$  decreases proportionately *less* than its  $S_{\text{conf}}$ . In contrast, when  $R_{\text{TS}} > 2$ , the implication is that as the liquid is cooled from  $T_a$  to  $T_b$ , its  $(S_{\text{nonconf}} - S_{\text{crys}})$  decreases proportionately *more* than its  $S_{\text{conf}}$ . In either case, the finding that  $R_{\text{TS}}$  is not equal to 2 shows that  $(S_{\text{nonconf}} - S_{\text{crys}})$  is finite and that it does not vary in proportion to  $S_{\text{conf}}$ . We recall that  $(S_{\text{nonconf}} - S_{\text{crys}})$  is a reflection of the difference in the phonon frequencies, excess anharmonic forces in a liquid over a crystal's, and any contribution from a liquid's  $\beta$ -relaxation process.

The finding that  $(S_{\text{nonconf}} - S_{\text{crys}})$  does not vary in proportion to  $S_{\text{conf}}$  has two consequences for the current efforts in computer simulations of the entropy from the inherent structure model:<sup>15,16</sup> (i)  $S_{\text{nonconf}}$  of a liquid is not the same as  $S_{\text{crys}}$ , and (ii) the difference  $(S_{\text{nonconf}} - S_{\text{crys}})$  does not vary in proportion to  $S_{\text{conf}}$ . Differences arising from this assumption may be small in some cases and therefore may be excluded. But this would not be generally true, and therefore, by using this approximation, we might be excluding an important aspect of molecular dynamics. We conclude that the validity of eq 1 is yet to be demonstrated.



This may be done only when  $S_{\text{conf}}$  becomes available. The ratio  $R_{\text{TS}}$  seems to be helpful in determining whether the data analysis based on the use of  $S_{\text{exc}}$  is reliable. Its use seems also desirable for relating the thermodynamic and molecular kinetic changes observed on supercooling a liquid.

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## Appendix A

Data on 7 of the 10 liquids reported in Table 1 have also been analyzed earlier.<sup>14</sup> Since our conclusion differs from theirs,<sup>14</sup> we need to examine the reasons for the difference. The equation used was<sup>14</sup>

$$\left(\frac{m}{m_{\text{min}}}\right) = 1 + \left[\frac{\Delta C_p(T_g)}{S(T_g)}\right] \quad (1A)$$

where  $m$  is the slope of the  $\log \tau_{\text{diel}}$  against  $T_g/T$  plot in the limit  $T_g/T = 1$  and  $m_{\text{min}}$  (=16) is the slope of a straight line between two limits,<sup>14</sup> one at  $\tau_{\text{diel}} = 10^{-14}$  s where  $T_g/T = 0$  and the second at  $\tau_{\text{diel}} = 10^2$  s where  $T_g/T = 1$ . When  $m = 16$ , the temperature dependence of  $\tau_{\text{diel}}$  is Arrhenius. The quantity  $S(T_g)$  in eq 1A has been defined as<sup>14</sup> “the total entropy of the liquid that includes both configurational and vibrational contributions”. However, we find that the data plotted in Figure 1 of ref 14 had been calculated by using  $S_{\text{exc}}(T_g)$ , and not  $S(T_g)$ , in eq 1A. To elaborate, from the data in Table 2 in ref 17 we obtain  $S(T_g) = 262$  J/mol·K,  $\Delta C_p(T_g) = 109.3$  J/mol·K, and  $S_{\text{exc}}(T_g) = 21.5$  J/mol·K for *o*-terphenyl. From these values, we obtain  $[1 + (\Delta C_p(T_g)/S(T_g))] = 1.41$  and  $[1 + (\Delta C_p(T_g)/S_{\text{exc}}(T_g))] = 6.08$ . The latter value agrees with  $\sim 6.2$  plotted in Figure 1 of ref 14. Therefore, eq 3 had been used earlier,<sup>14</sup> but its  $\ln[T_g/T_2]$  term was replaced by  $m$  and  $m_{\text{min}}$  parameters. Since  $m$  is determined from the slope at  $T_g/T = 1$ , its accuracy is low. We suggest that this may be the reason for the difference between our conclusions and theirs.<sup>14</sup>

We also note a limitation of eq 1A. It implies that as  $m$  approaches 16,  $[\Delta C_p(T_g)/S_{\text{exc}}(T_g)]$  would approach zero. This can occur only if  $\Delta C_p(T_g) \rightarrow 0$  or else  $S_{\text{exc}}(T_g) \rightarrow \infty$ . However, such low values of  $\Delta C_p(T_g)$  and high values of  $S_{\text{exc}}(T_g)$  seem physically implausible. In practice, a zero value of  $\Delta C_p(T_g)$  (for

a liquid with  $m = 16$ ) means that there is no thermodynamic manifestation of the liquid's vitrification at its  $T_g$ , but since  $\Delta C_p(T_g)$  is usually finite, we conclude that  $m$  cannot be equal to 16 in eq 1A. Evidently, as long as a decrease in  $C_p$  is observed on vitrification,  $\tau_{\text{diel}}$  would not vary according to the Arrhenius equation over the entire temperature range of the  $\log \tau_{\text{diel}}$  against  $T_g/T$  plots. For the same reason, the occasionally suggested change from the Adam–Gibbs temperature dependence to an Arrhenius temperature dependence of  $\log \tau_{\text{diel}}$  with  $m = 16$  would be inconsistent with the observation of change in  $C_p$  of the liquid at  $T_g$ .

## References and Notes

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