

Entropy basis for the thermodynamic scaling of the dynamics of *o*-terphenyl

C M Roland¹ and R Casalini^{1,2}

¹ Naval Research Laboratory, Chemistry Division, Code 6120, Washington, DC 20375-5342, USA

² Chemistry Department, George Mason University, Fairfax, VA 22030, USA

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Abstract

Structural relaxation times and viscosities for non-associated liquids and polymers are a unique function of the product of temperature, T , times specific volume, V , with the latter raised to a constant, γ_τ . Similarly, for both neat *o*-terphenyl (OTP) and a mixture, the entropy for different T and pressure, P , collapses to a single curve when expressed versus TV^{γ_s} , with the scaling exponent for the entropy essentially equal to the thermodynamic Grüneisen parameter. Since the entropy includes contributions from motions such as vibrations and secondary relaxations, which do not affect structural relaxation, $\gamma_s < \gamma_\tau$. We show herein that removal of these contributions gives a satisfactory account of the magnitude of γ_τ . Moreover, the relaxation times of OTP are found to be uniquely defined by the entropy, after subtraction from the latter of a V -independent component.

1. Introduction

Understanding the origin of the dramatic change in the dynamics of liquids and polymers as the glass transition is approached from the equilibrium state remains a central issue in soft condensed matter, notwithstanding more than 50 years of research. Various interpretations have been proposed, based variously on configurational entropy, energy landscapes and free volume; however, no consensus has emerged. The problem remains unsolved, in part due to the diversity of glass-forming materials and the wealth of experimental data that must be addressed. One significant recent finding is that relaxation times measured under different conditions of T and P superpose to form a single curve when plotted versus TV^{γ_τ} [1, 2]; that is

$$\tau = f(TV^{\gamma_\tau}) \quad (1)$$

where f represents an unknown function, V is the specific volume, and γ_τ is a material constant. The motivation for equation (1) derives from simulations by Hansen and co-workers [3, 4] on a Lennard-Jones 6-12 fluid showing that the glass transition occurs at a constant value of $T_g V_g^4$. Subsequently, from NMR measurements Hollander and Prins [5]

found that $T_g V_g^2$ is a constant for polypropylene, while Tölle *et al* [6] obtained a similar result for the crossover temperature of mode coupling theory in *o*-terphenyl (OTP) with the exponent equal to 4. These results indicate that a characteristic temperature associated with a given value of the relaxation time occurs at a fixed structure factor. Generalizing this result to any relaxation time [1] leads to equation (1), whose validity has now been demonstrated for more than 50 liquids, including results from dielectric spectroscopy [1, 7–12], neutron [13] and light scattering [14, 15], viscosity measurements [14, 16] and simulations [17, 18]. Equation (1) has also been found to be valid for the normal mode in polymers [19, 20] and for the component dynamics in polymer blends [21, 22] (although a problem in analysing blend dynamics is uncertainty in the relationship between component volume and the total volume). A breakdown of the scaling can be expected wherever the material itself changes (chemically) with T or P —an example being strongly hydrogen bonded materials such as water and glycols [16].

The idea underlying equation (1) is that for local properties the intermolecular potential can be represented by a two-body repulsive power law [23–25]

$$U(r) \sim r^{-3n} \quad (2)$$

where r is the intermolecular separation and n a constant related to the steepness of the potential. To the extent that equation (2) is accurate, thermodynamic properties in general will depend only on the scaled variable TV^n [23, 24]. This scaling breaks down for the equation of state, due to neglect of the longer range attractions [26]. However, we have shown for three glass-forming materials, propylene carbonate, salol and polyvinylacetate (PVAc), that the entropy is well represented by [27]

$$S = f(TV^{\gamma_S}) \quad (3)$$

with the scaling exponent numerically equal to the Grüneisen parameter, γ_G . This result, $\gamma_S = \gamma_G$, can be derived from equation (2) [26] or from thermodynamics using

$$\gamma_G = \frac{V\alpha_P}{C_V\kappa_T} \quad (4)$$

where α_P is the isobaric thermal expansivity, κ_T the isothermal compressibility and C_V the isochoric heat capacity. If γ_G is independent of V (or equivalently $\frac{\partial P}{\partial T}|_V \propto \frac{1}{V}$ [28]) it follows that the entropy is

$$S(T, V) = C_V \ln(TV^{\gamma_G}) + S_{\text{ref}}. \quad (5)$$

The condition $TV^{\gamma_G} = \text{const}$ corresponds to an adiabatic transformation reminiscent of an ideal gas. Interestingly, the scaling exponent for the relaxation times, γ_τ , is about threefold larger than γ_S [27].

In this paper we test equation (3) for a prototypical liquid, OTP, and for a mixture of OTP with *o*-phenyl phenol (OPP). This mixture has a substantially larger value of γ_τ than OTP [29], and as we show herein, the scaling exponent for the entropy is correspondingly larger. We also examine a means to correct the Grüneisen parameter for contributions from motions not involved in structural relaxation, whereby consistency between γ_τ and γ_G (and thus γ_S) is achieved.

2. Results

2.1. OTP

Quasielastic neutron scattering [13], transverse Brillouin dynamic light scattering [14] and viscosity measurements [14] all indicate a value of $\gamma_\tau = 4.0$ for OTP, consistent with $n = 4$

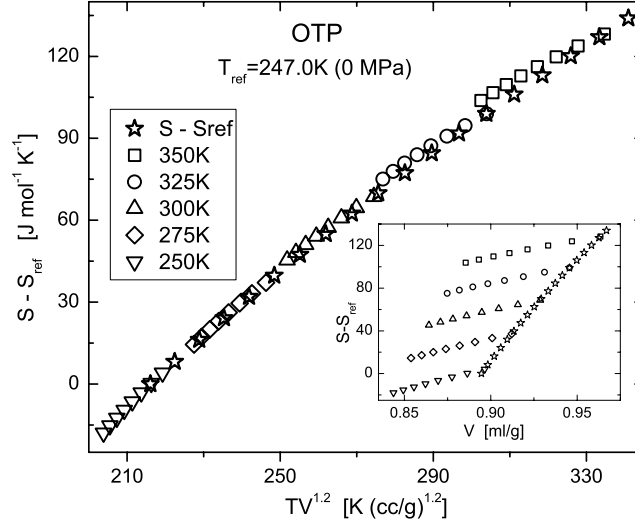


Figure 1. Scaled plot of the total entropy minus the entropy at the ambient pressure T_g for OTP (five isotherms and one isobar). The inset shows the same data versus specific volume. The entropies were calculated at $P = 0.1$ MPa from the heat capacity [31] and at higher pressures from the equation of state [32] using equation (6).

in equation (2) [30]. (The reported value for dielectric relaxation times is slightly larger, $\gamma_\tau = 4.25$ [14].) To evaluate the dependence of the entropy on T and V , we calculate S using

$$S(T, P) = S_{\text{ref}}(T_{\text{ref}}, P = 0) + \int_{T_{\text{ref}}}^T \frac{C_P}{T} dT - \int_0^P \left. \frac{\partial V}{\partial T} \right|_P dP \quad (6)$$

where C_P is the isobaric heat capacity and S_{ref} the entropy at a reference temperature T_{ref} and $P = 0$. Thus we determine $S(T, 0) - S_{\text{ref}}$ at zero pressure using the atmospheric heat capacity data for OTP reported by Chang and Bestul [31]. The results are shown as a function of volume over the range from $T_g \sim 247$ K to $T = 355$ K in the inset to figure 1. Using the reported equation of state data for OTP [32], we evaluate the third term in equation (6) for five temperatures spanning this range, with the obtained values of $S(T, P) - S_{\text{ref}}$ included in the inset.

Next we replot these data as a function of TV^{γ_S} with the exponent adjusted to give collapse of the $S(T, P) - S_{\text{ref}}$ onto a single master curve. Superposition is achieved for $\gamma_S = 1.2$, which is substantially smaller than the value of 4 for γ_τ . We compare this exponent to γ_G , based on the connection between these quantities (equation (5)) [26, 28]. Whereas the scaling exponent γ_S is constant, γ_G is a strong function of temperature close to 0 K and well below T_g ; however, at higher temperature it becomes approximately constant [33, 34]. The thermodynamic Grüneisen parameter is defined in equation (4) [33], with the isochoric heat capacity obtained from C_P using the thermodynamic relation

$$C_V = C_P - \frac{TV\alpha_P^2}{\kappa_T}. \quad (7)$$

The result is $\gamma_G = 1.2$ for OTP at T_g and zero pressure, in agreement with the scaling exponent for the entropy.

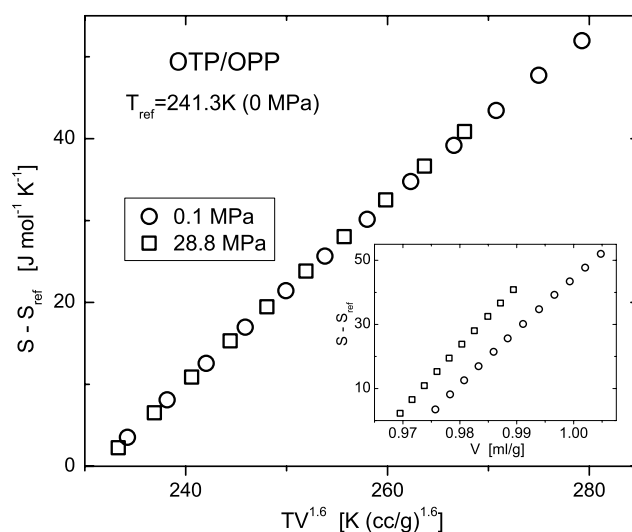


Figure 2. Scaled plot of the total entropy minus the entropy at the ambient pressure T_g for a 2:1 mixture of OTP and OPP (two isobars). The inset shows the same data versus specific volume. The entropies were calculated from the heat capacity at the two pressures as reported in [35].

2.2. OTP/OPP

Dielectric relaxation times for a mixture of OTP and OPP (2:1 weight ratio) were found to scale for a value of the exponent $\gamma_\tau = 6.2$ [29]. Takahara *et al* [35] reported heat capacity, thermal expansivity and compressibility measurements at both ambient and $P = 28.8$ MPa for this same mixture, enabling the entropy to be determined directly for these two pressures. The results are shown in the inset of figure 2. (Note that both data sets are isobars, whereas figure 1 for OTP shows an isobar and five isotherms.) When replotted versus $TV^{1.6}$, the data collapse to a single curve. The entropy scaling exponent is smaller by a factor of almost 4 than γ_τ . From equation (4) the Grüneisen parameter for the mixture is calculated to be 1.30 at T_g , close to the value of γ_S for the mixture.

2.3. Excess contributions to γ_G and S

The superpositioning of the entropy for the two materials supports identification of the scaling exponent γ_S with the Grüneisen parameter; however, for both liquids γ_S is three to four times smaller than the scaling exponent for the relaxation times. This difference is due to the contribution to the entropy from motions not involved in structural relaxation, i.e. vibrations and local secondary processes. This is a problem common to assessments of configurational entropy models of the glass transition [36–39]. The configurational entropy is usually unavailable, so the total entropy is used after subtraction of the crystal entropy. This subtraction assumes equivalent T and P dependences for the excess contributions to the total and the crystal entropies, with the expectation that the resulting ‘excess’ entropy is at least proportional to the configurational entropy [40, 41].

We have recently proposed a different approach to determine the configurational entropy, S_c , from the total entropy, which obviates the need to subtract the crystal entropy [27]. The small value of the scaling exponent for the entropy connotes a relatively weak volume dependence; thus, to a first approximation that portion of the entropy not involved in structural

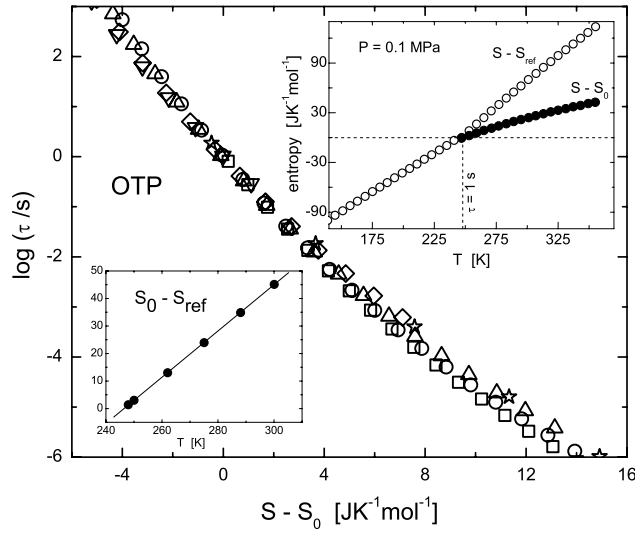


Figure 3. OTP relaxation times [42] versus the total entropy minus the contribution from motions not involved in structural relaxation (symbols as in figure 1). This contribution, S_0 , was taken to equal the value of the entropy at $T_g(P)$ (with $S_0(T)$ assumed to be volume independent). The top inset compares $S - S_0$ and $S - S_{\text{ref}}$ (with S_{ref} a constant equal to $S(T_g, 0.1 \text{ MPa})$). The lower inset shows the linear dependence of $S_0 - S_{\text{ref}}$ on T (parameters given in the text).

relaxation (which we designate S_0) can be taken to have a negligible dependence on V ; that is, $S_0(T, V) \sim S_0(T)$. This implies that for constant τ , and presumably constant configurational entropy, $S_0 \sim S(T_g)$ (where T_g is the temperature corresponding to a fixed value of τ). For salol and PVAc it has indeed been shown that their respective $\tau(T, V)$ are essentially a single function of $S(T, V) - S_0(T)$, with the latter defined as described herein [27].

We test this idea for OTP using the dielectric relaxation times reported by Naoki and co-workers [42], who measured τ over the range $257 < T \text{ (K)} < 290$ for P from ambient to 79 MPa. Their data were well described by a generalized Vogel–Fulcher equation having the form [42]

$$\tau = 8.907 \times 10^{-22} \exp\left(\frac{3779 + 3.43P}{T - 170 - 0.19P}\right). \quad (8)$$

Using this equation, the T and P for which $\tau = 1\text{s}$ were determined and the corresponding values of $S(\tau = 1\text{s}) - S_{\text{ref}} (= S_0 - S_{\text{ref}})$ were obtained (lower inset to figure 3). The data exhibit a linear temperature dependence, $S_0 - S_{\text{ref}} = -207.1 \pm 0.3 + (0.84 \pm 0.001)T$. The configurational entropy, $S_c = S - S_0$ is then obtained by subtracting from $S - S_{\text{ref}}$ the linear fit of $S_0 - S_{\text{ref}}$ (solid symbols in the upper inset to figure 3). In the main part of figure 3, the relaxation times for OTP are plotted versus $S - S_0$. It can be seen that the τ for different thermodynamic conditions (varying T at constant P or varying P at constant T) fall on a single curve; that is, the relaxation times are uniquely defined by the entropy, after subtraction of the V -independent component of S .

This approach is equivalent to considering that in the liquid state during an isothermal compression or expansion, the entropy change is purely configurational; that is, the unoccupied or ‘free’ volume has to be removed before vibrational or local intramolecular motions are

Table 1. Scaling exponents and Grüneisen parameters.

	γ_τ	γ_S	γ_G	γ_G^{exc}
OTP	4.0 [13, 14]	1.2	1.2	3.7
OTP/OPP	6.2 [29]	1.6	1.3	6.9 ^a
Salol	5.2 [1]	1.7 [27]	1.9 [28]	6.2

^a Glass values used since there is no crystalline state.

affected. Thus,

$$\left. \frac{\partial S_c}{\partial V} \right|_T = \left. \frac{\partial S^{\text{liq}}}{\partial V} \right|_T - \left. \frac{\partial S_0}{\partial V} \right|_T \approx \left. \frac{\partial S^{\text{liq}}}{\partial V} \right|_T. \quad (9)$$

We therefore calculate S_c as the entropy in excess to the glass, starting from the differential form

$$dS_c = \left(\left. \frac{\partial S^{\text{liq}}}{\partial T} \right|_V - \left. \frac{\partial S_0}{\partial T} \right|_V \right) dT + \left(\left. \frac{\partial S^{\text{liq}}}{\partial V} \right|_T \right) dV = \frac{\Delta C_V}{T} dT + \left. \frac{\partial P}{\partial T} \right|_V^{\text{liq}} dV \quad (10)$$

where we have used equation (9) together with one of the Maxwell relations, with $\Delta C_V = C_V^{\text{liq}} - C_V^{\text{xtal}}$. Defining an ‘excess’ Grüneisen parameter γ_G^{exc} as

$$\gamma_G^{\text{exc}} = \frac{V \alpha_P^{\text{liq}}}{\Delta C_V \kappa_T^{\text{liq}}} \quad (11)$$

equation (10) can be rewritten as

$$dS_c = \Delta C_V \left(\frac{dT}{T} + \gamma_G^{\text{exc}} \frac{dV}{V} \right). \quad (12)$$

Integration of equation (12) requires two assumptions, both of which add negligible error: (i) γ_G^{exc} is independent of V . Although strictly speaking the Grüneisen parameter and γ_G^{exc} are weakly dependent on volume, previously we showed for other liquids that the change is less than 5% over the supercooled range [28]. (ii) ΔC_V is independent of T . Calculating C_V for OTP using equation (7) and the data of Change and Bestul [31] and Naoki [32], we find that from 303 to 247 K, the isochoric heat capacity changes by less than 1.3%. Thus, these assumptions are verified and equation (12) is integrated, yielding an expression similar to equation (5)

$$S_c = \Delta C_V \ln(T V \gamma_G^{\text{exc}}) + \text{const.} \quad (13)$$

Therefore S_c should scale when plotted as a function of the variable $T V \gamma_G^{\text{exc}}$. In table 1 we list the value of γ_G^{exc} calculated according to equation (11) (using crystal data for OTP from [31] and [32]). The result is only 7% smaller than γ_τ , whereas there is a factor of 3.3 difference between γ_G and γ_τ .

We cannot extend this exact procedure to the OTP/OPP mixture because it does not crystallize (indeed, OPP is added in order to suppress crystallization of the OTP). Therefore, instead we calculate the excess heat capacity with respect to the glass rather than the crystal. The result is $\gamma_G^{\text{exc}} = 6.9$, which is only 10% larger than γ_τ .

The requisite data for this calculation are also available for salol. Previously it was found that the Grüneisen parameter defined by equation (4), while essentially equal to γ_S , was about threefold smaller than the scaling exponent for the relaxation times of salol [27]. Using crystal data from [43], equation (11) gives for the excess Grüneisen parameter, $\gamma_G^{\text{exc}} = 6.2$, which compares favourably to the scaling exponent for the relaxation times, $\gamma_\tau = 5.2$ [1].

3. Conclusions

We have shown herein that the total entropy of both OTP and its mixture with OPP is a function of TV^{γ_S} with $\gamma_S \sim \gamma_G$. The values of γ_S for the two liquids differ substantially from the respective scaling exponents for the relaxation times γ_τ . This difference is due to the additional contributions to the entropy, S_0 , from vibrations and secondary processes. For OTP and salol, we carry out a correction to the Grüneisen parameter, using values of the expansivity, compressibility and heat capacity of the crystalline state, while for OTP/OPP we use values for the glassy state. The obtained γ_G^{exc} are in quite good agreement with the reported values for γ_τ .

A method is also illustrated to correct the entropy for the excess contribution by assuming that S_0 has a negligible dependence on V , whereby $S_0(T) \sim S(T_g)$ with the latter obtained from measurements at elevated pressure. It can then be shown that τ for OTP depends only on $S - S_0$, a result previously found for salol and PVAc [27]. This in turn means that $S - S_0$ conforms to equation (1) with the same exponent γ_τ . These results affirm that the thermodynamic scaling of the relaxation times (equation (1)) has an entropic origin, supporting the idea that models of the supercooled dynamics of liquids should be based on the configurational entropy.

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