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Effect of entropy on the dynamics of supercooled liquids: new results from high pressure data

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We show that for arbitrary thermodynamic conditions, master curves of the entropy are obtained by expressing $S(T, V)$ as a function of TV^{γ_G}, where T is temperature, V specific volume and γ_G the thermodynamic Grüneisen parameter. A similar scaling is known for structural relaxation times, $\tau = \Im(TV^\gamma)$; however, we find $\gamma_G < \gamma$. We show herein that this inequality reflects contributions to $S(T, V)$ from processes, such as vibrations and secondary relaxations, that do not directly influence the supercooled dynamics. An approximate method is proposed to remove these contributions, S_0, yielding the relationship $\tau = \Im_1(S - S_0)$.

1. Introduction

If cooled fast enough to avoid crystallization, any liquid can assume a metastable "supercooled" state. Further cooling causes progressive increases of the structural relaxation time τ and viscosity η of the liquid, until a temperature, the glass temperature, is reached at which the η is so large as to be considered a solid (i.e. a glass), whereas τ exceeds the typical experimental timescale. Analogously, a glass can be formed by compressing a liquid under hydrostatic pressure while maintaining its temperature fixed. The study of the glass transition along these two pathways has proven fruitful for understanding the mechanisms underlying the glass transition, including resolving and quantifying the relative effect of T and V [1–3]. A key idea to progress in this area was the determination that at T_g (or some other characteristic temperature for which τ is constant [4–6]), the product of temperature times specific volume, with the latter raised to a power, was constant; i.e. $T_g V_g^\gamma = constant$ with γ a material-specific constant [7, 8]. Quite recently this has been generalized, with the

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discovery that the behaviour of $\tau(T,V)$ throughout the supercooled regime can be described as [9]

$$\tau(T,V) = \Im(TV^\gamma) \tag{1}$$

where $\Im$ is an unknown function. This behaviour has been verified by several groups using different techniques and finding comparable values of γ for the same material [6]. The original idea motivating this approach was the property of the inverse power law potential $U(r) \propto r^{-n}$ (with r the particle distance), for which $\tau(T,V) = \tilde{\Im}(TV^{n/3})$ [10]. Thus, for a 6–12 Lennard-Jones type potential, if the local properties are dominated by the repulsive part of the potential, equation (1) is expected with $\gamma = 4$. Such behaviour has been verified for OTP [11]. For other materials, γ assumes various values in the range $0.18 \leq \gamma \leq 8.5$ [6].

A still unresolved issue of the past half century is whether (and how) the dynamics of supercooled liquids and the consequent glass transition can be related to thermodynamic quantities, and even if there is an underlying thermodynamic transition [12]. The scaling law, equation (1), implies that if this process is dominated by a thermodynamic quantity, then the latter has to be a function of both T and V, satisfying the same scaling law. Recently, we have shown that under the approximations that (i) the isochoric heat capacity of a liquid, C_V, is constant with respect to T and (ii) the difference between isobaric and isochoric heat capacities, $C_P - C_V$, is constant with respect to V, than the entropy, S, for a supercooled liquid over typical experimental ranges satisfies a similar scaling law [13]

$$S(T,V) = \hat{\Im}(TV^{\gamma_G}) \tag{2}$$

where γ_G is the thermodynamic Grüneisen parameter given by

$$\gamma_G = \frac{V\alpha_P}{C_V\kappa_T} \tag{3}$$

with α_P the isobaric expansion coefficient and κ_T the isothermal compressibility. For the case of the inverse power law potential the entropy also scales as [14]

$$S \cong \Im_1(TV^{n/3}). \tag{4}$$

Therefore, in this particular case, $\gamma_G = n/3$, and τ should be a function of S alone.

In the following, we use experimental data to calculate the entropy in different conditions of T and V to confirm equation (2) and the consequent relation between τ and S.

2. Method

S at any condition of T and P can be calculated from thermodynamic data using

$$S(T,P) = S_{ref}(T_{ref},P=0) + \int_{T_{ref}}^{T} \frac{C_P}{T}\,dT - \int_0^P \frac{\partial V}{\partial T}\bigg|_P dP \tag{5}$$

where S_{ref} is the entropy at a reference temperature T_{ref} at atmospheric pressure ($P = 0$). According to the Tait equation of state (EOS) [15]

$$V(T,P) = V(T,P = 0)\{1 - C\ln[1 + P/(b_1 \exp(-b_2 T))]\} \tag{6}$$

where $C = 0.0894$ and b_1 and b_2 are constants. The integral of the thermal expansivity in equation (5) can be calculated as

$$\int_0^P \frac{\partial V}{\partial T}\bigg|_P dP = P\left[\frac{\partial V}{\partial T}\bigg|_{P=0}(1 + C) - V(T,0)Cb_2\right] \\ + CB(T)\ln\left(1 + \frac{P}{B(T)}\right)\left[V(T,0)b_2 - \left(1 + \frac{P}{B(T)}\right)\frac{\partial V}{\partial T}\bigg|_{P=0}\right]. \tag{7}$$

Therefore, after calculating S at atmospheric pressure from C_P, we calculate S at any T and P using equation (7) with the Tait parameters. This procedure is very similar to that used previously to test the Adam Gibbs model [16, 17].

3. Results and discussion

The insert to figure 1 shows the change of entropy, $S - S_{ref}$, for salol versus the specific volume V, taking as S_{ref} the entropy at $T = 220$ K and atmospheric pressure
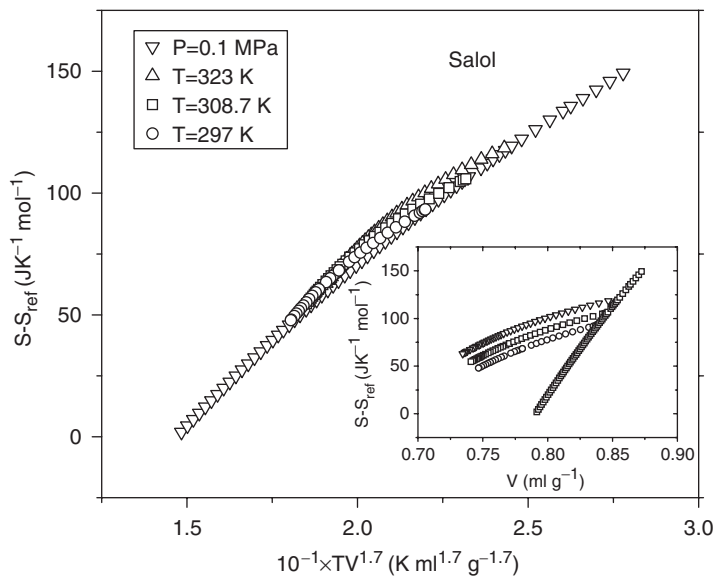

Figure 1. Entropy of salol at constant pressure and three constant temperatures minus $S_{ref} = S(T = 220$ K, $P = 0.1$ MPa) versus $TV^{1.7}$ and (insert) versus the specific volume. The entropy was calculated from C_P at atmospheric pressure [18, 19] and $V(T, P)$ data [18, 19].

(for which $\tau \sim 10$ s). The entropy at atmospheric pressure was calculated using data from the literature [18, 19]. To test equation (2), we plotted $S - S_{ref}$ versus the product of T and V with V raised to an exponent. There is a satisfactory collapse of the $S(T, V)$ data when the exponent is 1.7, as seen in figure 1. This empirical value of 1.7 is close to that previously determined for salol using equation (3) with thermodynamic data, $\gamma_G = 1.9$ [13].

A second example, polyvinyl acetate (PVAc), is shown in figure 2, for which the entropy was calculated using previously reported data [20, 21], S_{ref} is the entropy at $T = 313$ K and atmospheric pressure (again $\tau \sim 10$ s). These data collapse onto a master curve versus $TV^{0.9}$. Using equation (3), previously we found that $\gamma_G \approx 0.7$ [13]; therefore, equation (2) is verified to an acceptable degree of accuracy for PVAc.

Another case for which the data are not shown is propylene carbonate (PC). Using the data of Fujimori and Oguni [22] and Pawlus [23], we found super-positioning of the $S(T, V)$ versus TV^2. Equation (3) gives $\gamma_G = 1.4$ [13].

Thus the behaviour of $S(T, V)$ is described reasonably well as a function of TV^{γ_G}, equation (2), with the value of γ_G obtained from equation (3). This supports the approximations used to arrive at these expressions [13]. However, the value of the exponent γ_G yielding collapse of the $S(T, V)$ data is significantly smaller than the parameter γ in equation (1), used to superpose relaxation times: $\gamma = 5.2$ for salol [9], $\gamma = 2.5$ for PVAc [24] and $\gamma = 3.7$ for PC [22, 23]. This difference indicates that there is not a simple, direct connection between the
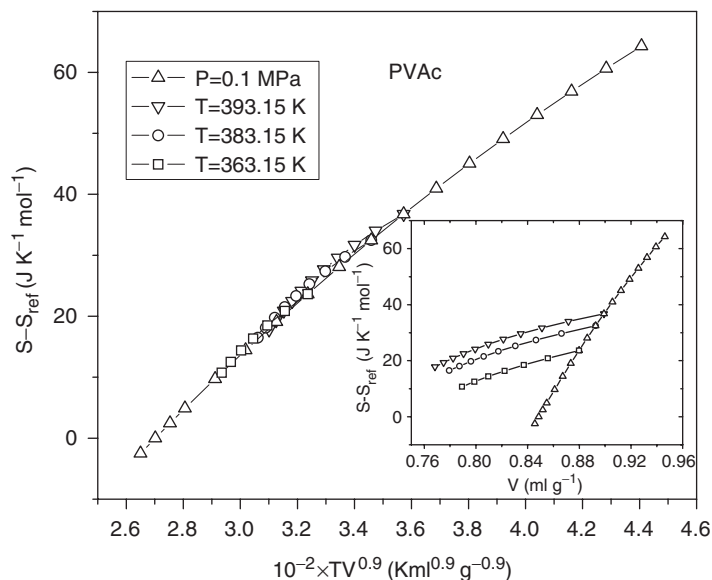

Figure 2. Entropy of polyvinyl acetate (PVAc) at constant pressure and three (constant) temperatures minus $S_{ref} = S(T = 313$ K, $P = 0.1$ MPa) versus $TV^{0.9}$ and (insert) versus the specific volume. The entropy was calculated from C_P at atmospheric pressure [21, 22] and $V(T, P)$ data [20, 21].
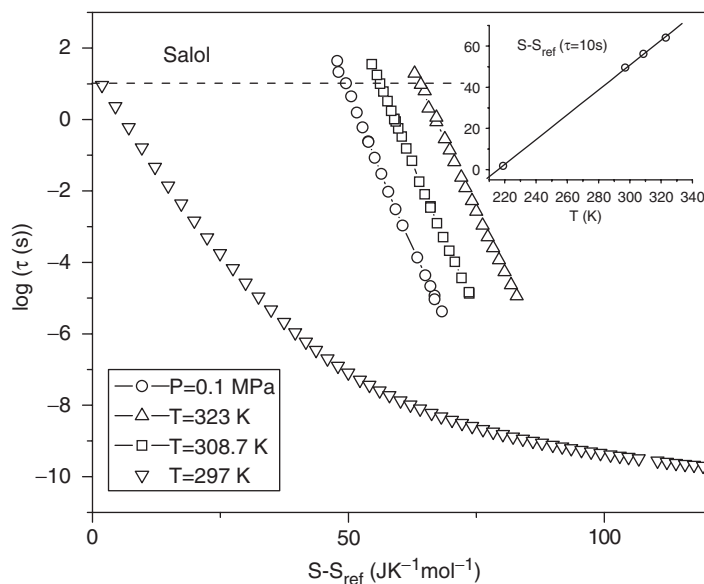
Figure 3. Dielectric relaxation times versus the entropy after subtraction of $S_{ref} = S(T = 220\,K,\ P = 0.1\,MPa)$, at atmospheric pressure and three fixed temperatures (using τ from the literature [27, 31]). In the insert are $S - S_{ref}$ at $\tau = 10\,s$ versus temperature as determined from the data in the main figure. The solid line is a linear fit.

relaxation times and the entropy changes accompanying vitrification. This is a well-known problem, arising from contributions to the entropy from other motions, such as vibrations and local secondary relaxations involving, for example, pendant moieties in polymers [25–27], which we refer to herein as S_0. The problem of subtracting S_0 is not straightforward, since these contributions in principle are both T- and V-dependent. However, the fact that the scaling exponent for $S(T, V)$ is roughly one-third of the value of γ for $\tau(T, V)$ is an indication that S_0 has a relatively weaker dependence on V. This is consistent with the observation that the characteristic times of local secondary motions are less sensitive to V compared to that of structural relaxation (which is not true for the activation energies)[1]. Therefore, as a first approximation we assume that as pressure varies, these extra contributions remain unchanged; that is, $S_0(T, V) \sim S_0(T)$. S_0 is taken as the value of $S(T_g)$ (corresponding to the dielectric α-relaxation time $= 10\,s$), for different T as a function of V. In figures 3 and 4, the respective dielectric relaxation times for salol [31] and PVAc [32, 33] are shown versus $S - S_{ref}$. In the inserts are plotted the values of $S - S_{ref}$ for which $\tau = 10\,s$ (i.e. $S_0 - S_{ref}$) versus T; the relationship is linear. Subtracting $S_0 - S_{ref}$ from

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[1]Secondary relaxations can be distinguished as one of two types: the so-called Johari–Goldstein (JG), which is coupled to the structural relaxation showing an activation volume $\Delta V_\beta \sim \beta_{KWW} \Delta V_\alpha$, and non-JG which have $\Delta V_\beta << \Delta V_\alpha$, as found for example in the case of PPG oligomers [28, 29] and for other cases, in agreement with the extended coupling model of Ngai [30].
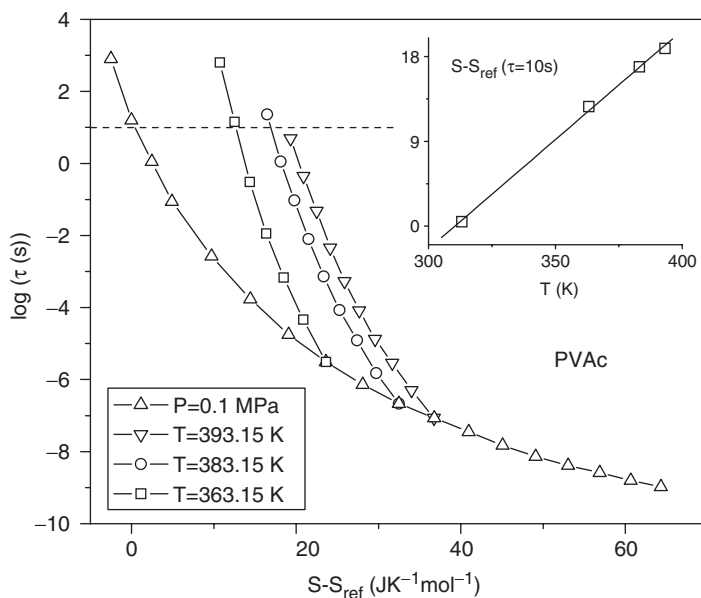
Figure 4. Dielectric relaxation times versus the entropy after subtraction of $S_{ref} = S(T = 313\,K,\ P = 0.1\,MPa)$, at atmospheric pressure and three fixed temperatures (using τ from the literature [28–33]). In the insert are $S - S_{ref}$ at $\tau = 10\,s$ versus temperature as determined from the data in the main figure. The solid line is a linear fit.

$S - S_{ref}$, we obtain the portion of the total entropy, $S - S_{ref}$, associated only with structural relaxation. In figure 5, $S - S_{ref}$ (open symbols) and $S - S_0$ (solid symbols) are shown for salol and PVAc. The T-dependences are similar and interestingly $S - S_0$ is about one-half $S - S_{ref}$ for both materials.

In figure 6 the dielectric relaxation times from figures 3 and 4 are plotted versus $S - S_0$. For both salol and PVAc the data essentially superpose to from a single curve. This demonstrates a direct correspondence between $S - S_0$ and τ, and thus rationalizes the TV^γ dependences of the dynamics and the entropy.

4. Conclusions

In the present paper we have investigated the behaviour of $S(T, V)$ using literature data to determine if the entropy is a function of TV^{γ_G}, equation (2), with γ_G given by equation (3). Our purpose is to determine whether the behaviour is related to the scaling relation of $\tau(T, V)$, i.e. equation (1). For three glass formers, salol, PVAc, and propylene carbonate, the entropy is found to vary uniquely with TV^{γ_G}, with values of the parameter γ_G consistent with equation (3). The differences between γ_G and γ are reconciled with the excess contribution to the total entropy from secondary processes that are not arrested at the glass
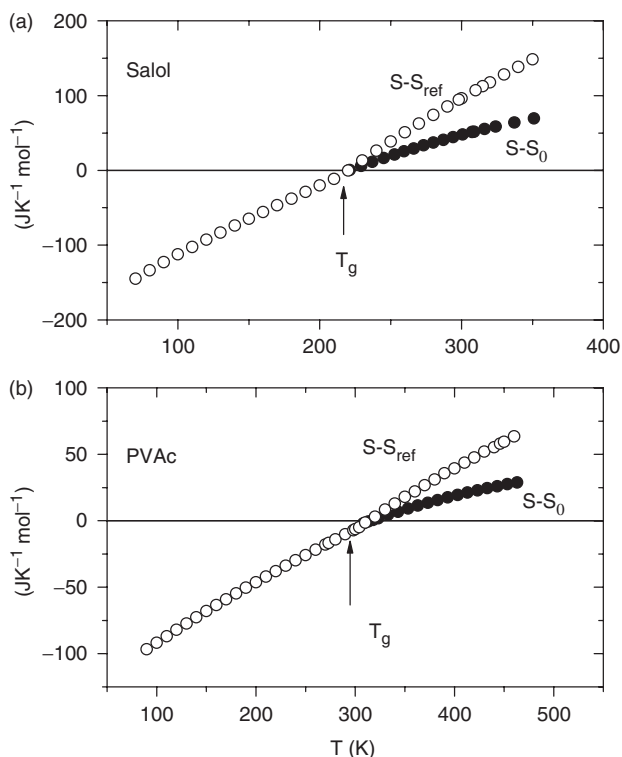
Figure 5. (a) Open symbols are *T*-dependence of entropy of salol at atmospheric pressure minus $S_{ref} = S(T = 220\,\text{K}, P = 0.1\,\text{MPa})$. Solid symbols are *S* minus $S_0 = S|_{\tau = 10s}$ determined from the fits of the data in the insert of figure 3. (b) Open symbols are *T*-dependence of entropy of PVAc at atmospheric pressure minus $S_{ref} = S(T = 313\,\text{K}, P = 0.1\,\text{MPa})$. Solid symbols are *S* minus $S_0 = S|_{\tau = 10s}$ determined from the fits of the data in the insert of figure 4.

transition and vibrations, which do not affect structural relaxation. We assume herein that this excess entropy, S_0, has a negligible dependence on *V*, which allows its direct determination from high pressure data. Specifically, we take the value of *S* for which $\tau = 10\,\text{s}$ at different *T* and *V*. After subtracting S_0 from the total entropy, τ is found to depend directly on the remaining part of the entropy, $\tau = \Im_1(S - S_0)$, as shown in figure 6. This implies that $S - S_0$ scales with the same exponent γ as does τ. As shown in figure 7, $S - S_0$ exhibits a linear variation on $1/TV^{\gamma}$; moreover, there is no suggestion of a thermodynamic divergence in the behaviour above absolute zero.

In conclusion, a possible interpretation of the scaling of the relaxation times, equation (1), in terms of the entropy is investigated. We verify that the entropy conforms to the scaling relation of the relaxation times; however, the same scaling exponent is obtained only if that portion of the entropy arising from other dynamical processes is subtracted. We also demonstrate a method to determine S_0.
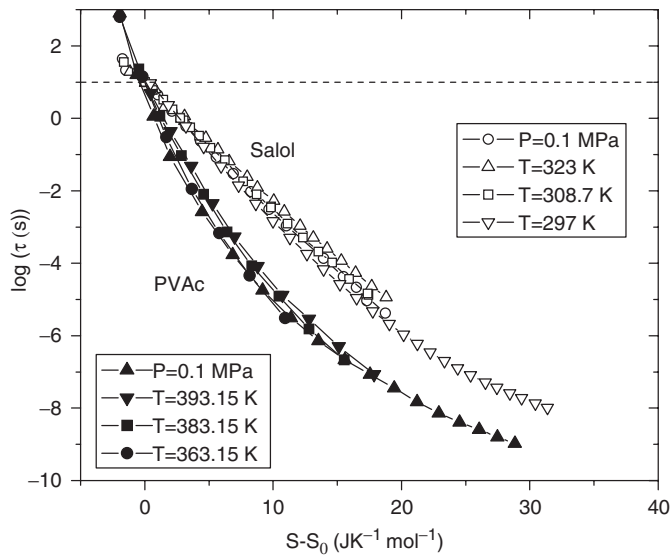
Figure 6.   Dielectric relaxation times for salol and PVAc (reported in figures 3 and 4, respectively) versus $S - S_0$.
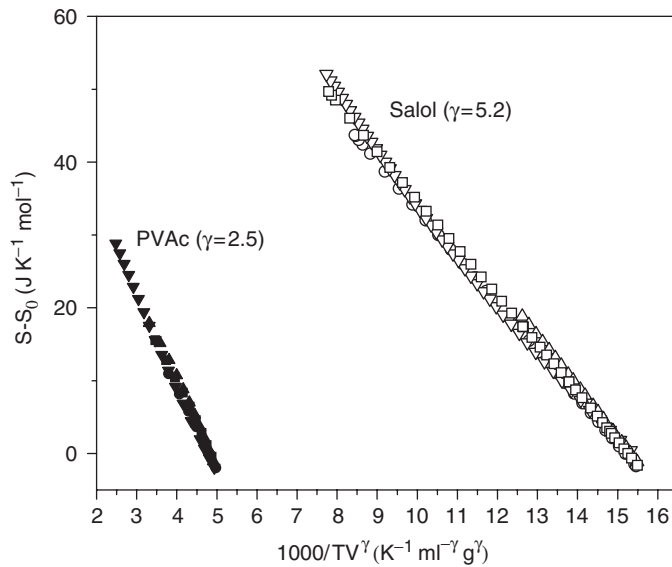

Figure 7. $S - S_0$ versus TV^γ with the value of γ for each material indicated in the figure. Symbols are the same as in figure 6.

Acknowledgements

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