Reply to "Comment on 'Vibrational and configurational parts of the specific heat at glass formation' "

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The premise of the Comment is questionable in three respects: (i) the C_p integral needed to determine the entropy cannot be zero, (ii) configurational entropy is not equal to the excess entropy of a polymer melt over its crystal state, and (iii) entropy associated with the secondary relaxation in a melt is part of its configurational entropy and is not to be subtracted from the excess entropy.

The Comment[1] provides an argument to indicate that the finding of Tombari *et al.*[2] is consistent with $S_{exc,\beta}/S_{exc}$ being 0.5 to 0.9, where $S_{exc,\beta}$ is the contribution to entropy from fast molecular dynamics that appears as β or secondary relaxations and S_{exc} is the difference between the entropy of the polymer melt and its ordered (100%) crystalline state.

We disagree with the argument[1] and briefly explain why. First, perhaps it would be helpful to note that:

(1) The argument relies on fitting the equation,[3]

$$\tau = \tau_0 \exp\left[\frac{C}{T(S_{exc} - \text{constant})} \right], \tag{1}$$

with τ as the dielectric relaxation time of the α process. Equation (1) itself was obtained by arbitrarily replacing TS_{conf} in the Adam-Gibbs equation[4] by $T(S_{exc} - \text{constant})$,[3] where S_{conf} is the configurational entropy of a melt.[4] The value of the constant that linearized a plot of $\ln \tau$ against $[T(S_{exc} - \text{constant})]^{-1}$ was termed $S_{exc,\beta}$, and it was concluded: "As can be noticed, $S_{exc,\beta}/S_{exc}$ increases with decreasing temperature due to the constancy of $S_{exc,\beta}$."[3] Since $(\partial S/\partial T)_p = C_p/T$, this constancy of $S_{exc,\beta}$ with changing T means that $C_{p,exc,\beta}/T$ is zero. Its corollary is used as an argument:[1] if $C_{p,exc,\beta}/T$ is found to be zero, $(\partial S_{exc,\beta}/\partial T)_p$ would be zero, i.e., $S_{exc,\beta}$ would be constant, and $S_{exc,\beta}/S_{exc}$ would be large. As had been known for glasses in general, Tombari *et al.*[2] found that $C_{p,exc,\beta}$ is small in relation to the vibrational C_p. Cangialosi *et al.*[1] took this finding to mean that $C_{p,exc,\beta}/T=0$, and on that basis they argue that $S_{exc,\beta}/S_{exc}$ is large.

In general, the difference between the entropy of a melt at two temperatures is determined by measuring the area under the C_p against $\ln T$ plot (or the C_p/T against T plot) confined by the two temperatures. The rate of change in the entropy with T is then equal to this area divided by the temperature difference. The constancy of the entropy with changing T would require that this area (between two temperatures) be zero. That can occur only if C_p is formally zero, which cannot be true when $T > T_g$. Therefore, formally speaking, whatever low value of $C_{p,exc,\beta}$ is found to be and howsoever high T is, it would not mean that the area—a measure of

$S_{exc,\beta}$—would remain constant with changing T. No experiment has shown that the entropy contribution from a thermally activated process in a melt remains constant with changing T.

(2) The premise of the comment—namely, Eq. (1)—was obtained by adding an adjustable parameter arbitrarily to the Adam-Gibbs equation,[4] which already had used several approximations. Since its suggestion for molecular liquids in 1965, it has been variously pointed out that it does not account for certain characteristic features of the α relaxation of polymers. The one feature that is relevant here is the distribution of relaxation times, as pointed out by Ngai,[5] whose tail contributes to C_p and entropy at T below T_g.[6] Consequently, *not* all configurational entropy of a melt is lost on cooling to $T < T_g$.

Briefly, C_p of a melt has contributions from at least three sources:[6] (i) change in the liquid's structure with T, as a result of both the α relaxation and the β or secondary relaxation dynamics, (ii) change in the phonon frequencies with T, and (iii) change in the anharmonic force contribution. In the glassy state at T just below T_g, only the tail of the α-relaxation dynamics contributes, and the magnitudes of (ii) and (iii) decrease. All of these contributions make it difficult to use the Adam-Gibbs equation[4] and the Kauzmann's extrapolation of S_{exc} to zero at $T < T_g$ for understanding the physics of ultraviscous liquids.

Others may examine the details of fitting Eq. (1) and the data itself. We point out that: (a) Equation (1) contains three adjustable parameters, τ_0, C, and a "constant," none of which can be determined independently; (b) S_{exc} in Eq. (1) is not equal to S_{conf} of the Adam-Gibbs equation, and since high molecular weight polymers do not 100% crystallize to an ordered state (most atactic polymers do not even crystallize), their S_{exc} is not accurately estimated.

Finally, $S_{exc,\beta}$ of a melt is due to the availability of different local configurations by faster dynamics. It is seen as part of the melt's configurational entropy and, therefore, should not be subtracted from the overall S_{conf} approximated as S_{exc} to obtain Eq. (1).

To conclude, the findings of Tombari *et al.*[2] do not support the argument[1] that $S_{exc,\beta}$ remains constant with changing T.

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[1] D. Cangialosi, A. Alegria, and J. Colmenero, preceding paper, Phys. Rev. B **78**, 176301 (2008).

[2] E. Tombari, C. Ferrari, G. Salvetti, and G. P. Johari, Phys. Rev. B **77**, 024304 (2008).

[3] D. Cangialosi, A. Alegria, and J. Colmenero, Europhys. Lett. **70**, 614 (2005).

[4] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).

[5] K. L. Ngai, J. Phys. Chem. B **103**, 5895 (1999).

[6] G. P. Johari, J. Chem. Phys. **112**, 7518 (2000), see Eq. (7), and references therein.