Supplementary Information for "A Simple Mean-Field Model of Glassy Dynamics and Glass Transition"

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The supplementary information describes the TS2 contribution to the heat capacity of polymers using polystyrene as an example. It is shown that this contribution is negligible compared to the overall (phonon-determined) heat capacity.

The TS2 internal energy per unit mass of material is given by,

$$U = \frac{1}{m_0}\left[\psi\varepsilon_S + (1-\psi)\varepsilon_L\right] \qquad \text{(S1)}$$

where ψ is the solid element volume fraction, m_0 is the mass of the lattice element (which is taken to be equal to the cooperative rearrangement region or CRR), and $\varepsilon_{S(L)}$ is the TS2 enthalpy of a solid (liquid) element. The temperature dependence of ψ is given by,

$$\psi = \left(1 + \exp\left\{\frac{\Delta S}{R}\left[1 - \frac{T^*}{T}\right]\right\}\right)^{-1} \qquad \text{(S2)}$$

By differentiating eq (S1) with respect to T, we obtain the heat capacity (in units of J/(g K)),

$$C_P = \frac{R}{m_0}\left[\frac{\Delta U}{RT}\right]^2 \psi\left(1-\psi\right) \quad \text{(S3)}$$

Here, $\Delta U = T^{*}\Delta S$ is the enthalpy difference between the liquid and solid states. The estimated model parameters ΔU and ΔS for polystyrene are given in Table 4 of the main text. To evaluate *m₀*, we can use the film dynamics analysis (section 2.7 of the main text), stipulating that,

$$m_0 \cong \rho v_0 \cong \rho \frac{4}{3}\pi h_0^3 \quad \text{(S4)}$$

In writing equation (S4), we neglected the difference between the liquid and the solid densities (~10-15% error). To evaluate h_0, we use the following expression (based on equation 15 of the main text),

$$b = h_0 \frac{2T_\infty^* - T_{top}^* - T_{bottom}^*}{T_\infty^*} = h_0 \frac{2\left(\Delta T^*\right)}{T_\infty^*} \quad \text{(S5)}$$

In equation (S5), the left-hand-side is known – *b = 0.7 nm* (see Table 5 of the main text). To estimate h_0, we need to guess the value of ΔT^* -- the difference between the transition temperatures for the bulk polystyrene and the PS-air boundary layer. Taking $\Delta T^* = 70\ K$ and $T_\infty^* = 366\ K$, we obtain h_0 = 1.8 nm. Then, taking ρ = 1 g/cm^3, we obtain the mass of an element, $m_0 \cong 15.4$ *kg/mol* (or about 145 PS repeat units). Substituting all the numbers into equation (S3), we obtain the TS2 contribution to heat capacity as function of temperature (Figure S1).

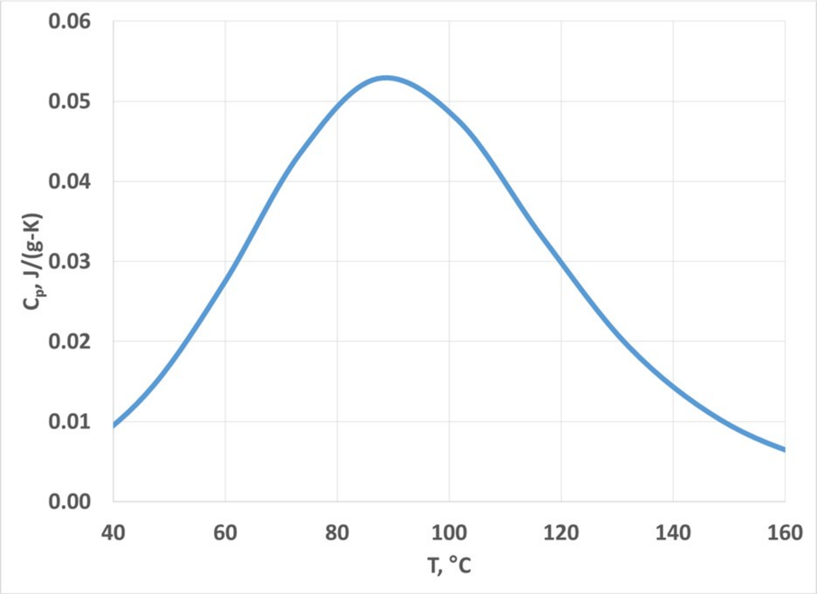

Figure S1. The TS2 contribution to the heat capacity of PS, as function of temperature.

Let us now compare the calculated TS2 contribution to experimental data on PS heat capacity. In Figure S2, we re-plot the data shown above, together with the experimental data of Simon and co-workers (DSC measurements at 2 K/min cooling rate)[1, 2]. It can be clearly seen that the TS2 effect is negligible compared to the overall heat capacity (mainly due to the phonon contributions). The heat capacity upon cooling, shown here, differs from the heat capacity upon heating, where a characteristic overshoot (heat capacity maximum) can often be seen, depending on the rate of prior cooling and the rate of subsequent heating. Those effects are beyond the scope of the current model and likely require a comprehensive investigation of the interactions between phonons and the CRR boundaries.

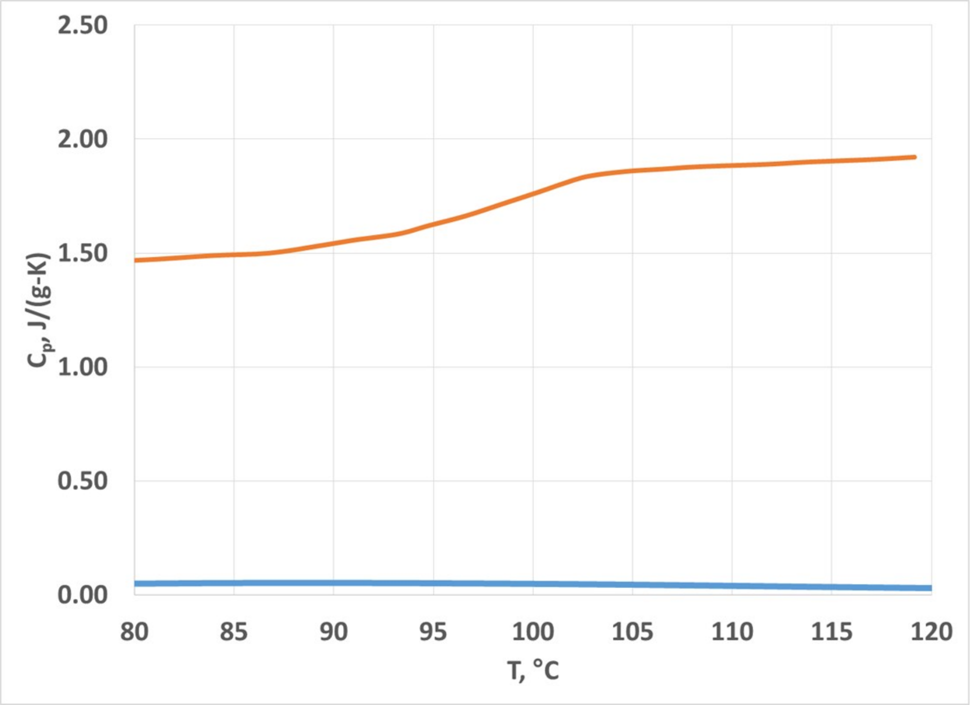

Figure S2. The experimental heat capacity of PS (orange line; DSC on cooling, cooling rate 2 K/min) and the calculated TS2 contribution to the heat capacity of PS (blue line).

1. P. Badrinarayanan, W. Zheng, Q. Li and S. L. Simon, *Journal of Non-Crystalline Solids*, 2007, **353**, 2603-2612.
2. G. B. McKenna and S. L. Simon, *Macromolecules*, 2017, **50**, 6333-6361.