Electronic Supplementary Information (ESI) for

"Combined Description of Polymer PVT and Relaxation Data using a Dynamic "TS2-SL" Mean-Field Lattice Model"

Valeriy V. Ginzburg

Department of Chemical Engineering and Materials Science,

Michigan State University,

428 S. Shaw Lane, Room 2100

East Lansing, Michigan 48824-1226

Email: vvg851966@gmail.com

Scaling and Universality

Here, we show how the combined TS2-SL model allows for the type of universality hypothesized by Casalini, Roland, Ngai, Paluch, and co-workers. We would like to re-phrase this universality in the following way:

1. The α-relaxation time and the Johari-Goldstein β-relaxation time – and by implication the whole dielectric relaxation spectrum – depend not on temperature T and pressure P separately, but rather on one combined "state variable" $Z = T_x(P)/T - 1$.
2. The equilibrium and supercooled liquid specific volume, $V_{sp}(T,P)$, the temperature T, and the α-relaxation time, τ_α, are related via, $\tau_\alpha(T,P) = f\left(T\left[V_{sp}(T,P)\right]^\gamma\right)$.
3. The relationship (2) above can be extended to the non-equilibrium, "glassy" branch if the cooling experiments for different pressures are done at the same cooling rate.

Below, we show that the conditions (1)—(3) provide a set of constraints that enables us to uniquely determine the model parameters as a function of pressure.

We begin by analyzing the TS2 equations for the relaxation times,

$$\tau_\alpha(T,P) = \tau_\infty \exp\left[\frac{E_1}{RT} + \frac{E_2 - E_1}{RT}\psi(T,P)\right] \qquad (S1)$$

$$\tau_\beta(T,P) = \tau_\infty \exp\left[\frac{E_1}{RT}\right] \tag{S2}$$

The variables ψ and ν are described by the coupled equations below (equations 6a and 6b of the main text; in eq 6b, we disregard the small $\overset{\circ}{P}$ term)

$$\ln\frac{\psi}{1-\psi} + \Delta\overset{\circ}{S} - \frac{\Delta\overset{\circ}{U} + \overset{\circ}{P}\Delta\overset{\circ}{V}}{\overset{\circ}{T}} = 0 \tag{S3}$$

$$\overset{\circ}{T}\left[\ln(1-\nu) + \nu\left\{1 - \frac{1}{\langle r\rangle}\right\}\right] + \nu^2 J = 0 \tag{S4}$$

In equation S3, $\Delta\overset{\circ}{S}$, $\Delta\overset{\circ}{U}$, and $\Delta\overset{\circ}{V}$ are functions of ψ and ν. To show that the scaling relationships hold (at least approximately), we first introduce the following auxiliary variables: the transition temperature $T_X(P)$, defined as the temperature where $\psi(T_x(P),P) = 0.5$, and the "state variable" Z, defined as $Z = \frac{T_X(P)}{T} - 1$. We now need to show that ψ and ν depend only on Z, and not on T and P separately.

Let us consider equation S4 first. It can be re-written as,

$$\frac{1}{1+Z}\frac{T_X(P)}{T^*(P)}\left[\ln(1-\nu) + \nu\left\{1 - \frac{1}{\langle r\rangle}\right\}\right] + \nu^2 J = 0 \tag{S5}$$

Clearly, as long as $\frac{T_X(P)}{T^*(P)} = const.$, the scaling is satisfied.

Now, consider eq (S3), re-written in original terms,

$$\ln\frac{\psi}{1-\psi} + \frac{\Delta S}{R} - \frac{\Delta U + P\Delta V}{RT} = 0 \tag{S6}$$

Substituting T in terms of Z, we obtain,

$$\ln\frac{\psi}{1-\psi}+\frac{\Delta S}{R}-\frac{1+Z}{T_X(P)}\frac{\Delta U+P\Delta V}{RT}=0 \qquad\qquad\text{(S7)}$$

For fragile glass-formers like PS and PMMA, ΔU can be considered nearly constant, $\Delta U \approx \Delta U_X$. Furthermore, $P\Delta V \ll \Delta U_X$. Thus, we can approximate

$$\Delta U+P\Delta V \approx \Delta U_X+P\Delta V \approx \Delta U_X\left(1+\frac{P\Delta V}{\Delta U_X}\right) \approx \Delta U_X \exp\left(\frac{P\Delta V}{\Delta U_X}\right).$$

Equation S7 can be now re-written as,

$$\ln\frac{\psi}{1-\psi}+\frac{\Delta S}{R}-\frac{1+Z}{T_X(P)}\frac{\Delta U_X \exp\left(\dfrac{P\Delta V}{\Delta U_X}\right)}{RT}=0 \qquad\qquad\text{(S8)}$$

Thus, to satisfy scaling and eliminate P, one needs to assume that,

$$T_X(P)=T_X(0)\exp\left(\frac{P\Delta V}{\Delta U_X}\right)\equiv T_X(0)\exp\left(\frac{P}{P_{0,T}}\right)$$

Thus, we have shown that ψ and ν depend only on Z, and not on T and P separately. Now let us consider τ_α and τ_β, given by equations S1 and S2. We can re-cast those equations as:

$$\ln\left(\frac{\tau_\alpha(Z)}{\tau_\infty}\right)=\left[\frac{E_1}{RT_x(P)}(1+Z)+\frac{E_2-E_1}{RT_x(P)}(1+Z)\psi(Z)\right] \qquad\qquad\text{(S9)}$$

$$\ln\left(\frac{\tau_\beta(Z)}{\tau_\infty}\right)=\left[\frac{E_1}{RT_x(P)}(1+Z)\right] \qquad\qquad\text{(S10)}$$

Thus, to eliminate the explicit P-dependence, one needs to set up the following conditions,

- $\dfrac{E_1(P)}{T_x(P)}$ is a constant (no P-dependence) $\qquad$ (S11a)

- $\dfrac{E_2(P)}{T_x(P)}$ is a constant (no P-dependence) $\qquad$ (S11b)

Now, let us consider the behavior of the specific volume in the equilibrium and supercooled liquid state. The specific volume, $V_{sp}(T,P)$, is given by,

$$v_{sp}(T,P) = \frac{v_0(P)\langle r \rangle}{M_{CRR}v}$$

$\qquad$ (S12)

The average length, $\langle r \rangle = \psi r_S + (1-\psi)r_L$, depends only on Z, and so does the occupancy, v.

Thus, $v_{sp}(T,P) = v_0(P)g(Z)$, where *g* denotes some unspecified function.

Let us now test the Casalini-Roland scaling, $\tau_\alpha(T,P) = f\left(T\left[V_{sp}(T,P)\right]^\gamma\right)$. The left-hand side is a function of Z alone – what about the right-hand side? We can write the right-hand side as,

$$RHS = f\left(T\left[V_{sp}(T,P)\right]^\gamma\right) = f\left(\frac{T_x(P)}{1+Z}\left[v_0(P)g(Z)\right]^\gamma\right) = f\left(T_x(P)\left[v_0(P)\right]^\gamma h(Z)\right)$$

$\qquad$ (S13)

where *h(Z)* is another unspecified function.

Thus, for the scaling to work, one requires that,

$$T_x(P)\left[v_0(P)\right]^\gamma = const.$$

$\qquad$ (S14a)

Or

$$\frac{v_0(P)}{v_0(0)} = \left[\frac{T_x(0)}{T_x(P)}\right]^{1/\gamma} \qquad\qquad \text{(S14b)}$$

The reduction in the specific volume of the material upon the increase in pressure is therefore related to the increase in the transition temperature, as one would expect. The parameter γ is material-dependent.

If – as discussed above -- we assume that the pressure dependence of the transition temperature, T_x, and the vacancy volume, v_0, is exponential (and we are only considering "small" pressures so that the functional form is only a matter of convenience), then,

$$\frac{v_0(P)}{v_0(0)} = \exp\left[\frac{P}{P_{0,v}}\right] \qquad\qquad \text{(S15a)}$$

$$\frac{T_x(P)}{T_x(0)} = \exp\left[\frac{P}{P_{0,T}}\right] \qquad\qquad \text{(S15b)}$$

It is straightforward to see that condition (S14b) means that,

$$P_{0,T} = \gamma P_{0,v} \qquad\qquad \text{(S16)}$$

The parameter $P_{0,v}$ or simply P_0 is the inverse of the zero-temperature compressibility of the material, or its bulk modulus, B.

Finally, let us consider the effect of cooling rate and determine the scaling and universality there. The equations of evolution for the solid fraction, ψ, and the dimensionless density, ν, are written as,

$$\frac{d\psi}{dt} = \frac{\psi^*(T(t),P) - \psi}{\tau_\psi(T(t),P)} \qquad\qquad \text{(S17a)}$$

$$\frac{dv}{dt} = \frac{v^*(\psi, T(t), P) - v}{\tau_v(T(t), P)} \qquad \text{(S17b)}$$

The temperature is a linear function of time,

$$T(t) = T_0 - kt \qquad \text{(S18)}$$

with k being the cooling rate and T_0 the initial temperature (note that its significance is negligible if it is sufficiently high in the equilibrium liquid zone, so that the initial portion of the cooling is fully equilibrated).

Once again, introducing the state variable Z and expressing time and temperature via Z, we obtain,

$$\frac{k}{T_x(P)}[1+Z]^2 \frac{d\psi}{dZ} = \frac{\psi^*(Z) - \psi}{\tau_\psi(Z)} \qquad \text{(S19a)}$$

$$\frac{k}{T_x(P)}[1+Z]^2 \frac{dv}{dZ} = \frac{v^*(\psi, Z) - v}{\tau_v(Z)} \qquad \text{(S19b)}$$

The solid-fraction and density relaxation times, τ_ψ and τ_v, are functions of the α- and β-relaxation times. Since τ_α and τ_β depend only on Z (not on T and P separately), so do τ_ψ and τ_v.

The initial conditions to equations (S19) reflect the fact that at the beginning of the cooling experiment, the material is fully equilibrated,

$$\psi(Z_0(P)) = \psi^*(Z_0(P)) \equiv \psi_{eq}(Z_0(P)) \qquad \text{(S20a)}$$

$$v(Z_0(P)) = v^*(\psi^*(Z_0(P)), Z_0(P)) \equiv v_{eq}(Z_0(P)) \qquad \text{(S20b)}$$

Suppose now that we obtained a numerical solution describing the solid fraction and density at P = 0 for a given cooling rate *k(0)* and a given initial temperature *T₀(0)*. The solution is denoted as

$\left(\psi\left(k\left(0\right),Z\right),v\left(k\left(0\right),Z\right)\right)$, with temperature back-calculated as $T = \dfrac{T_x\left(0\right)}{1+Z}$. Obviously, the same solution would also describe the cooling process at pressure P, provided that the cooling rate is rescaled to $k\left(P\right)=k\left(0\right)\dfrac{T_x\left(P\right)}{T_x\left(0\right)}$, and the temperature is now given by $T = \dfrac{T_x\left(P\right)}{1+Z}$. In practice, the required change in the cooling rate (5-10%) probably can be neglected, and one can say that the cooling dynamics are universal when described using the state variable Z, rather than time t or temperature T.