Supplementary Materials for

Fast equilibration mechanisms in disordered materials mediated by slow liquid dynamics

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Supplementary Text

Sharpness of the SAP peak
In the frequency domain, the slow Arrhenius process peak is sharper (full width at half height \( \approx 1.1 \text{ decades} \)) than the \( \alpha \)- (\( \approx 2.5 \text{ decades} \)), and by far less broad than secondary relaxations in the glassy state (> 5 decades). In the text, we mention that SAPs can be associated to the spectral response of a Debye process, a molecular mechanism with a single relaxation time \( \sim (1 + 2\pi ft_{mol})^{-1} \), corresponding to a simple exponential decay in the time domain \( \exp(-t/t_{mol}) \).

Simple exponential decays are a limiting case of stretched exponential decays, often referred to as Kohlrausch-Williams-Watt function \( \exp(-t/t_{mol})^{\beta_{KWW}}, \) commonly used to describe relaxation processes in the time domain.(59) To verify if the SAP could be described by a Debye process, meaning \( \beta_{KWW} = 1 \), we determined the stretching exponent \( \beta_{KWW} \) from the isothermal dielectric spectra, via the relation\( (60) \beta_{KWW}^{1.23} = a_{SAP} \). In Figure S3 we show the temperature dependence of \( \beta_{KWW} \) for all the polymers investigated. A histogram of the experimental values is also provided. The results support our assumptions, within experimental errors \( \beta_{KWW} = 1 \).

Finally, we remark that the deviations from errors \( \beta_{KWW} = 1 \) on the determination of \( \beta_{KWW} \) come from the difficulties in deconvolving the genuine response of the SAP from that of other processes (including the electronic background of the measuring cell) in the frequency domain.

Thickness and molecular weight dependence of the SAP
We investigated the role of thickness (sample size) and molecular weight (macromolecular size, chain length) on the dynamics of the slow Arrhenius process. As we show in Figure S5 for P2ClS, P4ClS and PS, chain length does not affect the activation energy of the slow Arrhenius process.

No impact of film thickness on the activation energy of the SAP was observed, see Figure S6. On the contrary, sample size affected the intensity of the slow Arrhenius process, following the same trend usually observed for the \( \alpha \)-process, see Figure S7. The intensity of the segmental relaxation peak decreases upon thickness reduction due to the smaller number of molecular units participating in the relaxation process. This trend is due to the presence of a layer of chains irreversibly immobilized onto the metallic surfaces, which has a dielectric strength much smaller than that in bulk.(2)

The observation that the dielectric strength of the SAP peak follows the same thickness dependence of the intensity of the \( \alpha \)-peak implies that the volume fraction of the molecular units responsible for the two processes are the same.

Analysis of the adsorption kinetics
Considering that every monomer contacting the substrate results in the attachment of the whole chain, the adsorbed amount is given by the product of the molecular rate responsible for the contact between monomer and substrate, \( q \), the number of available monomers and the polymerization degree \( N \). The number of available monomers is established by the monomer density, \( \rho \), and the number of chains making a contact with a flat wall per unit surface \( (N^{-1/2}) \). The number of monomers adsorbed per units of surface at any given time is thus proportional to \( N^{1/2} \). The adsorbed amount is expressed, therefore, as

\[ \Gamma = q\rho N^{1/2} t \] (S1)
Neglecting the changes in density (< 2% in 20 nm thick films)(48), in this regime the adsorbed thickness $h_{ads}$ increases with time as

$$h_{ads} = v t$$  \hspace{1cm} (S2)

The zero-order reaction mechanism becomes less efficient with crowding, as the presence of previously adsorbed chains limits further adsorption. The apparent adsorption rate progressively decreases; in such regime the adsorbed amount increases logarithmically with time. The timescale separating the two regimes (linear vs logarithmic) is indicated with the crossover time, $t_{\text{cross}}$. At this point, attachment of new chains can only occur through the formation of loops that over time become increasingly longer as the density of available sites decreases. Finally, the adsorbed amount and the thickness of the adsorbed layer saturates.

Considering this adsorption model, and for all investigated temperatures, we fitted the data range corresponding to $t_{\text{cross}}$ to a linear function, while to a logarithmic function for the second regime (see left panel of Figure S8). Due to the weak temperature dependence of density, the adsorption velocity $v$, that we get from experiments, has the same activation energy as the monomer adsorption rate, $q$. An example of the outcome of isothermal experiments to determine the adsorption rate in the first linear regimes is given in the right panel of Figure S8. In Figure S9, we show the corresponding values of $v$ as a function of the temperature of the experiments.

For all the polymers investigated, we found that the absolute value of the activation energy of $v$ corresponds to that of the characteristic time of the SAP. To provide a visual representation of the adsorption results in a relaxation/equilibration map (log time vs inverse temperature), we considered a characteristic time of the process and plotted $t_{\text{cross}} = n v^{-1}$. This procedure was also possible in those cases where, because of the ultraslow kinetics of adsorption, the crossover time was not reached, considering that previous work(51, 53) has proven that $h_{\text{cross}} = v t_{\text{cross}}$ is a constant. Therefore, by measuring the value of $h_{\text{cross}}$ at temperatures where the crossover was clearly observed we could obtain $t_{\text{cross}}$ also at other temperatures. For example, the equilibration data of Figure 2.g were obtained by converting $v$ into $t_{\text{cross}}$, by using the experimentally determined value of $h_{\text{cross}} = 5$ nm. Finally, we remark that our rationale on the relation between relaxation and equilibration processes would hold also in case of the wrong choice of the value of $h_{\text{cross}}$. The only requirement to test the validity of our assumptions is using a temperature invariant value of the crossover thickness.

### Comparison of molecular and equilibration activation energies

The values of the activation energies of the SAP ($E_{\text{SAP}}$) and the equilibration processes ($E_A$) are given in Table S2. The $R^2$ column includes the determination coefficient obtained by fitting equilibration data to the equation

$$\log(t_{eq}) = a + E_{\text{SAP}} \frac{1}{k_B T}$$  \hspace{1cm} (S3)

where $a$ is the only free parameter.

#### Empirical methods to estimate the high temperature limit of the activation energy based on $T_g$

To determine the activation energy of the segmental process in the limit of high temperature, we considered the reasoning developed by Wang and Porter for the activation energy of viscous flow at temperatures well above $T_g$. In their work,(58) they describe the flow activation energy at $T_g + \varepsilon$ (e.g. $\varepsilon = 150 K$) by means of a description of viscosity based on a generalized polymer model, while explicitly considering the expansion coefficient of the melt, $\alpha_T$. They obtained:

$$E_{\text{flow}} = \frac{R}{\alpha_T} \frac{(T_g + \varepsilon)^2}{(1-K) T_g + \varepsilon}$$  \hspace{1cm} (S4)
where \( R \) is the gas constant and \( K = T_0 / T_g \), \( T_0 \) is the temperature at which the viscosity of system would diverge. \( K=0.77 \) in the generalized model considered by Wang and Porter, that is, a constant dynamic fragility was considered.

To derive our expression for segmental mobility, we start from the activation energy of the \( \alpha \)-relaxation time expressed through the VFT equation. We are aware the VFT equation is the most common, but only one of the possible equations describing the temperature dependence of the relation time. Equations like those we derived can be obtained by means of other models for the segmental mobility. For the VFT expression, we have

\[
E_A(T) = RT^2 \frac{DT_0}{(T-T_0)^2} \tag{S5}
\]

Under the same assumptions made by Wang and Porter, the activation energy of the segmental process in the limit of high temperature can be expressed as

\[
E_A(T_g + \varepsilon) = RDK T_g \left( \frac{(T_g+\varepsilon)^2}{(1-K)T_g+\varepsilon} \right) \tag{S6}
\]

We used equation S6 to build up the green shadowed area of the inset of Figure 3, indicating the most probable values of activation energy as a function of \( T_g \). These approaches are limited by the assumption that each glass-formers should be described by the same dynamic fragility, that is by the same values of D and K. This is obviously a rough approximation. We used the spread over the D and K data of the systems we measured to account for the possible deviations from a unified glass model (that is, at constant D and K values).

Finally, while we understand that such approaches should be considered as simple guidelines, we noticed that strong glass formers tend to be in the upper limit of the shadowed curve, while fragile glassformers lie in the lower limit. See for example the case of PIB, one of the strongest systems, whose expected activation energy is lower than that measured experimentally in both equilibration (rheology) and molecular mobility (SAP) experiments. This trend is expected from previous work stating an inverse correlation between fragility and high temperature activation energy.
**Deconvolution of dielectric spectra.** Examples of fits of the dielectric loss (open squares) of PTBuA (a), PMMA (b) and P4ClS (c) to equation (2). The experimental data were analyzed as the sum of contributions of the different dielectric processes (dashed lines): conductivity (black), SAP process (red), α- segmental relaxation (green), an RC parasitic circuit peak, due to the nonzero resistivity of the electrodes at high frequencies (blue).
Examples of 3D plots 3-dimensional plots of the dielectric loss, as a function of frequency and temperature, for films of the polymers listed in the panels b-i of Figure 2. In case of excessive contribution of the conductivity, we obtained the dielectric loss from the real part of the dielectric function, via the approximate relation $\varepsilon''_{\text{der}} \approx -\pi/2 (\partial \varepsilon'/\partial \ln f)$.
**Analysis of the stretching exponent $\beta_{KWW}$.** (a) Values of $\beta_{KWW}$ obtained from the fits of the SAP of different polymers, via the relation $\beta_{KWW}^{1,2,3} = \alpha \cdot \beta$, where $\alpha$ and $\beta$ are the shape parameters of the HN equation. (b) Histogram of the obtained values of $\beta_{KWW}$ shown in panel a), revealing that a distribution centered around 0.95. This value is close to 1, hinting that the SAP is a Debye process.
Relaxation and equilibration maps for additional polymers. These plots complement the results of Figure 2. For each system, the logarithm of the molecular times ($t_{\text{mol}}$) on the left axes, and the logarithm of the equilibration times ($t_{\text{eq}}$) on the right axes are given as a function of the inverse temperature. This representation provides a direct access to the activation energy of the processes ($= R \frac{\partial \ln t}{\partial T^{-1}}$ where $R$ is the gas constant). For each polymer we identify two molecular processes, the segmental relaxation (white symbols), the slow Arrhenius process (red symbols). Equilibration data from adsorption experiments are indicated with blue star.
Lack of molecular weight dependence of the SAP. Relaxation times of the slow Arrhenius process of (a) P2CLS, (b) P4CLS and (c) PS thin samples with different molecular weight, showing the invariance of their activation energy and with respect to changes in $M_w$. In the case of PS, the low $M_w$ data corresponds to the bulk data reported by Lupascu et al. [Macromolecules 2006, 39, 5152-5158].
Lack of thickness dependence of the SAP. Activation energy of the SAP as a function of thickness for a) PC, b) P4CLS, c) PVAC and d) PVK. For PC, we also show, for comparison, the impact of thickness on the segmental dynamics.
**Thickness dependence of the intensity of the SAP and segmental peaks.** Dielectric strength of the SAP (red) and segmental relaxation (green) as a function of thickness for (a) PC, (b) PVAC, showing the generalized decrease of strength when decreasing the thickness.
**Fig. S8.**

**Time evolution of the adsorbed thickness for PTBMA at different annealing temperatures.** Linear fits of experimental data in the early stage of adsorption provides the values of adsorption rate $v$, shown in Figure S9. In panel a, the horizontal arrow indicates the values of the crossover thickness, while the crossover time is indicated by the vertical arrow.
Fig. S9.

Temperature dependence of the adsorption rate of PTBMA.
Impact of $T_g$ on the parameters of equation S6. Parameters K and D, obtained from VFT fits to the experimental data, as function of the glass transition temperature. Dashed lines indicate the mean values of the two parameters.
| Polymer                                | Acronym | $M_w$ [kDa] | PDI  | Manufacturer         |
|----------------------------------------|---------|-------------|------|----------------------|
| Polycarbonate                          | PC      | 43          | 1.9  | Polymer Source Inc.  |
| Polystyrene                            | PS      | 955         | 1.08 | Polymer Laboratories |
| Poly(ethyl methacrylate)               | PEMA    | 344         | 2.70 | Sigma-Aldrich        |
| Poly(4-tert-butylstyrene)              | PTBS    | 156         | 1.08 | Polymer Source Inc.  |
| Poly(vinyl acetate)                    | PVAc    | 100         | -    | Sigma-Aldrich        |
| Poly(vinyl acetate)                    | PVAc    | 243         | 2.7  | Sigma-Aldrich        |
| Poly(methyl methacrylate)              | PMMA    | 350         | -    | Sigma-Aldrich        |
| Polyisobutylene                        | PIB     | 838         | 1.19 | Polymer Source Inc.  |
| Poly(2-chlorostyrene)                  | P2CIS   | 376         | 1.6  | Polymer Source Inc.  |
| Poly(2-chlorostyrene)                  | P2CIS   | 1312        | 1.28 | Polymer Source Inc.  |
| Poly(4-chlorostyrene)                  | P4CIS   | 75          | -    | Sigma-Aldrich        |
| Poly(4-chlorostyrene)                  | P4CIS   | 6000        | 4    | Polymer Source Inc.  |
| Poly(tert-butyl acrylate)              | PTBuA   | 132         | 1.2  | Polymer Source Inc.  |
| Poly(vinylbenzyl chloride)             | PVBCl   | 100         | -    | Sigma-Aldrich        |
| Poly(4-methylstyrene)                  | P4MS    | 112         | 1.02 | Polymer Source Inc.  |
| Poly(tert-butyl methacrylate)          | PTBMA   | 267         | 1.5  | Polymer Source Inc.  |
| Poly(tert-butyl methacrylate)          | PTBMA   | 690         | 1.13 | Polymer Source Inc.  |
| Poly(benzyl methacrylate)              | PBzMA   | 100         | -    | Sigma-Aldrich        |
| Poly(n-propyl methacrylate)            | PNPMA   | 480         | 1.5  | Polymer Source Inc.  |
| Poly(N-vinyl carbazole)                | PVK     | 380         | 1.6  | Polymer Source Inc.  |

**List of materials**
Table S2.

| Polymer | $E_{\text{SAP}}$ (kJ mol$^{-1}$) | $E_A$ (kJ mol$^{-1}$) | equilibration methods | $R^2$ (fitted by fixing $E_{\text{SAP}}$) |
|---------|-------------------------------|----------------------|----------------------|----------------------------------------|
| PS      | 91±10                         | 76±13, 74±10, 86±5   | adsorption, dewetting,(18) aging(57, 61) | 0.907, 0.911, 0.992                   |
| PEMA    | 118±10                        | 119±16               | adsorption           | 0.954                                  |
| PTBS    | 88±10                         | 90±5, 88±20          | adsorption, aging(14) | 0.967, 0.968                           |
| PVAc    | 57±5                          | 67±5                 | adsorption           | 0.980                                  |
| PMMA    | 120±10                        | 127±12               | adsorption           | 0.981                                  |
| PIB     | 80±10                         | 82±15, 79±15         | reentanglement(30), shear(30) | 0.969, 0.998                          |
| P4ClS   | 124±5                         | 135±10               | adsorption           | 0.985                                  |
| PTBuA   | 86±5                          | 85±10                | adsorption           | 0.989                                  |
| PVBCl   | 147±6                         | 154±15               | adsorption           | 0.992                                  |
| P4MS    | 95±5                          | 120±15               | adsorption           | 0.942                                  |
| PTBMA   | 92±5                          | 96±10                | adsorption           | 0.989                                  |
| PNPMA   | 114±5                         | 119±15               | adsorption           | 0.994                                  |
| PMPS    | 40±20                         |                      |                      |                                        |
| PC      | 98±5                          |                      |                      |                                        |
| PBzMA   | 87±5                          |                      |                      |                                        |

**List of activation energies.** No $E_A$ value was listed for those systems where we could not find literature data on equilibration processes, nor we could perform equilibration experiments over a temperature range large enough to obtain reliable data.