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Confinement effects on the Slow Arrenhius Processes (SAP) observed in polymer melts

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The rate at which a nonequilibrium system decreases its free energy is commonly ascribed to molecular relaxation processes, arising from spontaneous rearrangements at the microscopic scale. While equilibration of liquids usually requires density fluctuations at timescales quickly diverging upon cooling – known as the α-modes –, growing experimental evidence indicates the presence of different pathways of weaker temperature dependence. Such equilibration processes exhibit a temperature-invariant activation energy on the order of 100 kJ/mol. Based on a large series of molecular dynamics and equilibration experiments, we identified the underlying molecular process responsible for this class of Arrhenius equilibration mechanisms with a slow mode (SAP), universally present in the liquid dynamics [1]. While in bulk samples the SAP can be masked by conductivity and electrode polarization, measurements in thin films permitted us to directly access the relaxation spectra of these slow modes. By analyzing polymer chains of different molecular weight and films of different thickness, we verified that this process is present also in bulk melts and that the activation energy and the characteristic molecular time of the SAP are not affected by either the macromolecular or the sample size. On the contrary, the large sensitivity of the intensity of the SAP dielectric peak to film thickness indicates that this process extends for length scales much larger than those of the α-modes. The SAP, which we show is intimately connected to high temperature flow, can efficiently drive melts and glasses towards more stable, less energetic states. Our results show that measurements of liquid dynamics can be used to predict the equilibration rate in the glassy state.

[1] Song et al., Science Advances 8, eabm7154 (2022)

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