

Coupling between the microscopic dynamics of solute and solvent: Universal picture of the dynamical transition

Aim of the Proposed Experiment and Scientific Background

The view that the microscopic dynamics of biomolecules (proteins, but also RNA, DNA) is enslaved to the solvent (water) is fairly well accepted [1-3]. The famous dynamical transition in hydrated proteins at about 220 K is arguably related to a singularity in the microscopic dynamics of the hydration water, whether the latter is a resolution effect [4] or a resolution-independent transition [5-7]. Following extensive debates on the importance of the dynamical transition for protein function, with numerous pro [8-11] and contra [12-14] arguments presented, we argue that the protein dynamical transition is merely a specific case of a universal, solvent-driven transition in the solute dynamics. As such, it does not require an aqueous solvent, or hydrogen bonding between the solute and solvent. Whenever there is a glass transition in the solvent dynamics, there will be the corresponding transition in the solute dynamics, provided that the two are coupled (that is, the solvent wets the solute). Furthermore, a dynamical transition in the solvent (and, therefore, in the solute) requires a certain minimal hydration or solvation level [15]. We argue that this fact, empirically well-known from the experiments on protein hydrated powders, is actually deeply rooted in the universal laws governing the dynamics of interfacial fluids. We have carried out a systematic molecular dynamics (MD) simulation study on polystyrene (PS) solvated with toluene, intentionally chosen as a model system with non-aqueous solvent and the absence of hydrogen bonds. Even though dry polystyrene is characterized by a high glass transition temperature of 373 K, we postulated that polystyrene in contact with the sufficient number of toluene molecules will exhibit a dynamical transition related to the transition in the solvent toluene, closer to the glass transition temperature of toluene of 116 K. Our preliminary analysis of trajectories support our postulates, in order to validate this experimentally, we would like to carry out Quasielastic neutron scattering (QENS) measurements on a PS solvated with toluene. **The aim of the proposed experiment is to probe the dynamical transition of PS (solute) and its correlation with toluene (solvent).**

Results of Preliminary Work

A series of molecular dynamics (MD) simulation were carried out on 8 PS chains, each made of 32 styrene units, and solvated with different toluene concentrations (toluene/styrene ratios of 0.0, 0.5, and 2.0). Initial systems were prepared and minimized with Materials Studio[1] and the cvff[2] force-field. The LAMMPS[3] MD package was used for subsequent equilibration (5ns, NPT) and production runs (10ns, NPT) at a series of temperatures and atmospheric pressure. With different loading of toluene started from no toluene per styrene (desolvated PS) to 128 toluene per styrene (~infinite diluted solution) at 20 different temperatures starting from 30 to 410 K using ORNL computing facilities. Average mean square displacement (MSD) for hydrogens corresponding to PS has been calculated for each temperature. It is found that with no toluene i.e. desolvated PS, MSD of hydrogens belongs to PS undergo transition around ~373 K which is glass transition of PS and very same behavior is observed up to 0.5 toluene per styrene (~threshold loading). However, with addition of 2 toluene molecules per styrene this transition is shifted towards the glass transition temperature of toluene i.e. 116 K. MSDs of hydrogens of PS for three cases i.e. zero, 0.5 and two toluene per styrene are shown in Fig.1a. It is evident that addition of toluene (solvent) beyond a threshold loading greatly affects the transition temperature of PS and follow very similar to toluene solvent ($T_g \sim 116$ K). This provides an indication that the

dynamical transition of solute (PS) is purely salved by solvent (toluene) and is also true for other glass forming liquids such as toluene.

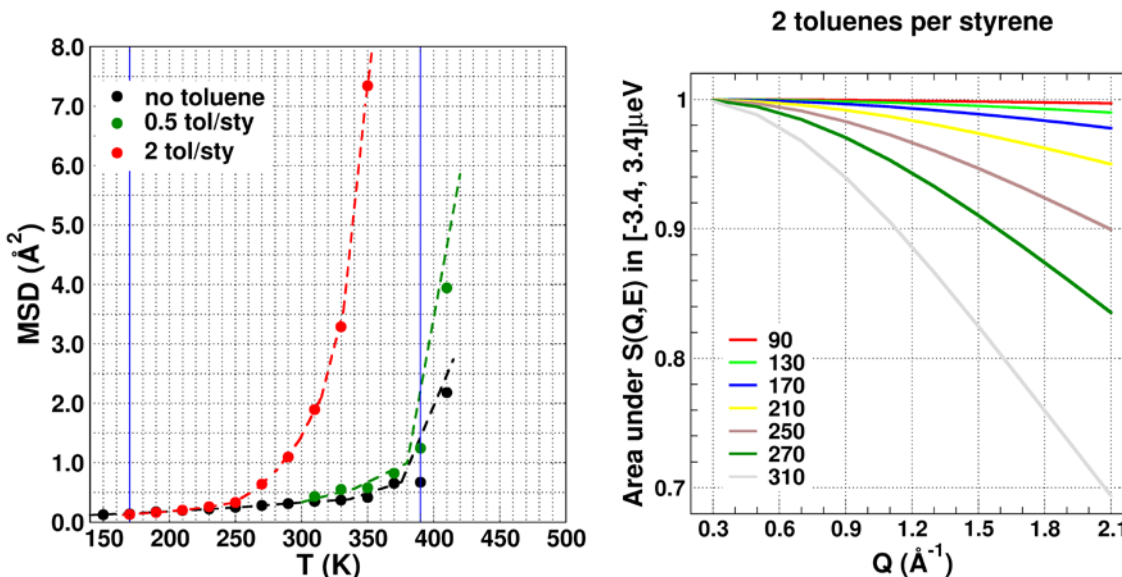


Fig. 1 (a) Temperature dependence of mean square displacement of hydrogens correspond to polystyrene (PS) for three different loadings namely zero, 0.5 and 2 toluene molecules per styrene. It is evident that dynamic of PS (solute) is salved by toluene (solvent). (b) Variation of elastic intensity as obtained by integrating calculated $S(Q,E)$ within -3.4 to $+3.4 \mu\text{eV}$ with Q as well as temperature for 2 toluene per styrene.

(Jose: need to modify Figs , please make wider the range of temperature in Fig 1a starting from 30 K, any better suggestion for Fig 1b)

Dynamic structure factor $S(Q,E)$ have been calculated from simulation trajectories. Elastic intensity is obtained similar as obtained from fixed window scan experiment by integrating $S(Q,E)$ within a selective energy transfer range centered at zero energy transfer for example -3.4 to $+3.4 \mu\text{eV}$. Elastic scan also show very similar results and consistent with obtained MSD. For example variation of elastic intensity for 2 toluenes per styrene is shown in Fig. 1b.

Proposed Experiments

The high energy resolution ($\sim 3.4 \mu\text{eV}$) backscattering spectrometer BASIS, will be best suited to observe the mean square displacement of polystyrene as well as the toluene. We plan to carry out fixed window scan on solvated polystyrene powder with deuterated toluene at three different loading same as our MD simulation namely 0.0, 0.5 and 2 toluene molecules per styrene on three set of PS, (i) fully hydrogenated, (ii) PSd3 (deuterated main chains) and (iii) PSd5 (deuterated phenyl ring) in a temperature range from 30 K to 450 K covering the glass transition temperature (~ 373 K) of pure PS. We also need to carry fixed window scan on pure hydrogenated toluene and hydrogenated toluene with fully deuterated PS with 0.5 and 2 toluene molecule per styrene as a reference. We thus have a total of 12 (3×3 (three samples at three loadings) + 3 reference samples = 12 samples) fixed windows scan with on an average ~ 9 hrs

each. Therefore, we would need a total of **5 days of beam time on BASIS spectrometer** including time for sample changes.

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