Brownian Dynamics Simulation Methods for Polymer Solutions

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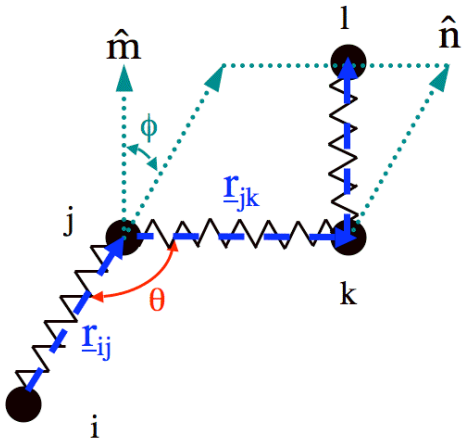
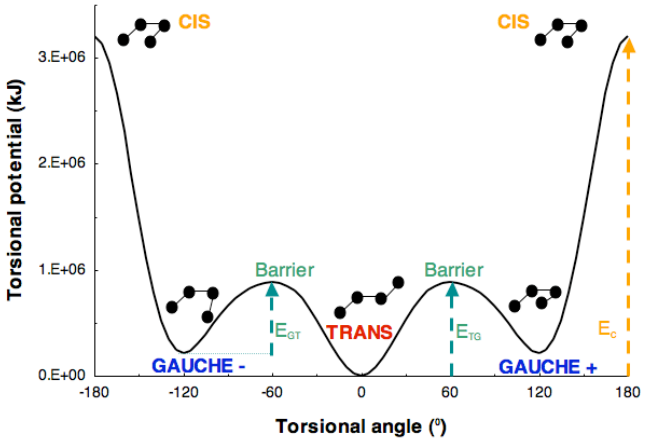
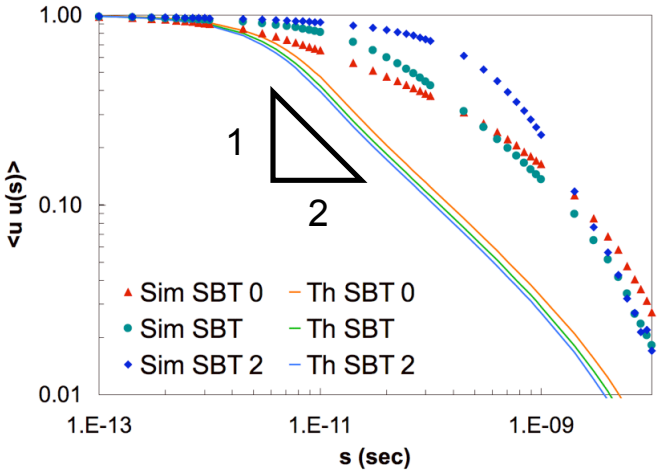
Viscoelastic measurements show that the fast relaxation modes expected from local motions of polymer backbone bonds are not evident in the viscoelastic spectrum. We have carried out accurate Brownian dynamics simulations on a polymer chain with locally realistic bond-bond bending and torsional potentials, and have found that the relaxation of fast local modes are slowed down by energy barriers to torsion and bending, to the extent that the relaxation rates of the local modes overlap those of longer-ranged "spring-like" modes encompassing motions of many bonds.







Locally realistic model for polymer chain shows **beads** held together by **stretching forces** which maintain polymer backbone bond lengths close to 1.53 $\overset{0}{A}$, realistic **bending forces** retain tetrahedral bond angle, and realistic **torsional forces** maintain the 3-D chain configuration.

Ryckaert-Bellemans torsional potential establishes **potential barriers** between **trans** (least energy), **gauche** (intermediate energy), and **cis** (maximum energy) states controlling the probability with which bonds transition between states.

With increasing E_{TG} (**0**, **base**, **2 x base**), theory (Th) predicts unit vector autocorrelation, $\langle uu(s) \rangle$, relaxes faster for smaller coils (**SBT 2** faster than **SBT 0**). Simulation (S) shows faster modes are suppressed with increasing barrier height but long time behavior is eventually recovered.