

Rotaxanes as Entropy-Dominated Molecules

Yongxiang Gao

University of Illinois, Department of Materials Science, Urbana, IL, U.S.A.

Edie Sevick

Australian National University, Research School of Chemistry, Canberra, ACT, Australia

David Williams^{C, S}

Australian National University, Research School of Physical Sciences & Engineering, Canberra, ACT, Australia
drw110@physics.anu.edu.au

Rotaxanes are molecules that are architecturally similar to some baby rattles: one or more ring-like molecules threaded onto a molecular axle that is capped on both ends with stoppers to prevent the rings from falling off. These materials were first synthesized only 40 years ago and today there is an active and vibrant synthetic community. One of the most interesting features of these rotaxanes is the ability of a ring to slide along the axle. For example, by selectively tuning strong enthalpic interactions within the molecule, researchers can entice a ring to cover specific portions of the axle - this can be used to shield particular chemical groups to impart a changeable molecular hydrophobicity or reactivity. The synthetic literature is huge, but only a few consider properties that arise from strong, tunable enthalpic interaction. However, these molecules can potentially be synthesized to be entropy-dominated molecules, in many ways similar to (but different from) a polymer chain. The rings that are threaded on the axle have significant translational entropy and behave very much like a gas confined to one dimension. This entropy is not particularly interesting unless we can access it through some control of the fluctuations of the rings. One way to do this is to fix one end of the axle to a surface and manipulate the topmost ring using an attached piston: this molecular architecture is referred to as a piston-rotaxane (Sevick & Williams, Langmuir (2010)). If the piston is moved towards the surface the free rings are compressed; if the piston is moved away from the surface the axle length available to the rings is expanded. In this way, the piston alters the molecule's entropy and, if the rings are few in number over a long axle, imparts a long molecular relaxation time. This piston-rotaxane behaves as a scaled-down version of an automobile shock-absorber. A version of this piston-rotaxane has already been synthesized and its force-extension profile measured using AFM (Bough et al, PNAS (2006)); however, that version contained no free rings and as such, is missing the essential gas, needed for entropic response. Using equilibrium and non-equilibrium statistical mechanics, we predict interesting properties of this new soft molecule.