New theory may shed light on dynamics of large-polymer liquids

August 23 2011

This is Illinois professor Kenneth S. Schweizer. Credit: L. Brain Stauffer

A new physics-based theory could give researchers a deeper understanding of the unusual, slow dynamics of liquids composed of large polymers. This advance provides a better picture of how polymer molecules respond under fast-flow, high-stress processing conditions for plastics and other polymeric materials.

Kenneth S. Schweizer, the G. Ronald and Margaret H. Professor of materials science and engineering at the University of Illinois, and graduate student Daniel Sussman published their findings in the journal Physical Review Letters.

"This is the first microscopic theory of entangled polymer liquids at a fundamental force level which constructs the dynamic confinement potential that controls slow macromolecular motion," said Schweizer,

who also is a professor of chemistry and of chemical and biomolecular engineering and is affiliated with the Frederick Seitz Materials Research Laboratory at the U. of I. "Our breakthrough lays the foundation for an enormous amount of future work relevant to both the synthetic polymers of plastics engineering and the biopolymers relevant to cell biology and mechanics."

Polymers are long, large molecules that are ubiquitous in biology, chemistry and materials, from the stiff filaments that give cells their structure to plastics. Linear polymers fall into two classes: rigid rods like uncooked spaghetti or flexible strands like al dente noodles.

When in a dense solution, linear polymers become entangled like spaghetti in a pot, intertwining and crowding each other. Each polymer is hemmed in by its neighbors, so that the liquid behaves like an elastic, viscous rubber. Given enough time, the liquid will eventually flow slowly as polymers crawl along like snakes, a movement called reptation. Researchers have long assumed that each polymer's reptation is confined to a tube-shaped region of space, like a snake slithering through a pipe, but have had difficulty understanding how and why the polymers behave that way.

Schweizer and Sussman's new theory, based on microscopic physics, explains the slow dynamics of rigid entangled polymers and quantitatively constructs the confining dynamic tube from the forces between molecules. The tube concept emerges as a consequence of the strong interactions of a polymer with its myriad of intertwining neighbors. The theory's mathematical approach sheds greater light on entanglement and better explains experimental data.

"Our ability to take into account these crucial physical effects allows us to predict, not assume, the confining tube concept, identify its limitations, and predict how applied forces modify motion and

elasticity," Schweizer said.

Not only does the new theory predict tube confinement and reptative motion, it reveals important limitations. The researchers found that the "tubes" weaken as applied forces increase, to the point where the tube concept fails completely and the liquid loses its rubbery nature. This is particularly important in plastics processing, which exposes polymer liquids to high stress conditions.

Next, the researchers plan to continue to study how external stress or strain quantitatively determine the driven mechanical flow behavior of entangled polymer liquids. They also hope to develop a theory for how attractive forces can compete with entanglement forces to result in soft polymer gels.

More information: The paper, "Microscopic Theory of the Tube Confinement Potential for Liquids of Topologically Entangled Rigid Macromolecules," is available online.

Provided by University of Illinois at Urbana-Champaign