ME – PhD Thesis Colloquium

In Silico Study on Equilibrium Dynamics of Macromolecules in Dilute Solutions

Prabeen Kumar Pattnayak, Department of Mechanical Engineering, IISc Bengaluru

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ABSTRACT

Brownian motion serves as a connecting link between the physical and biological sciences, observed in phenomena ranging from the random jittery movements of simple pollen grains in water to the intricate thermal motion of complex macromolecules within living systems. The diffusion dynamics of long-chain molecules is one of the fundamental problems in soft matter physics with broad scientific importance, for example, in DNA dynamics, protein folding, polymer nanocomposites, polymer-dispersed liquid crystals, and drug delivery.

A polymer chain in solution adopts fluctuating conformations due to its large number of internal degrees of freedom and is commonly characterized by its average size, shape, and intramolecular topological constraints. The dependence of polymer diffusion on size is well understood and is conveniently described using the hydrodynamic radius R_h . According to Zimm theory, the translational diffusion coefficient D_t scales with R_h through the Stokes–Einstein relation, while the rotational diffusion coefficient D_r follows the Stokes–Einstein–Debye relation. However, the explicit influence of molecular shape and topology on macromolecular diffusion, independent of size, has received comparatively limited attention. In this thesis, the diffusion dynamics of polymers in dilute solution are investigated using a hybrid molecular dynamics–multi-particle collision dynamics (MD–MPCD) framework, which explicitly incorporates hydrodynamic interactions and thermal fluctuations of the solvent.

The first part of this thesis investigates the effect of polymer shape on diffusion dynamics in dilute solution. Using star polymers with varying functionality but approximately identical hydrodynamic radii, the role of shape anisotropy is delineated. The relative shape anisotropy κ^2, defined from the traceless deviatoric part of the gyration tensor, is employed as a quantitative measure of shape. While translational diffusion is found to be insensitive to shape at fixed R_h , in agreement with Zimm theory, rotational diffusion exhibits a strong inverse dependence on κ^2 . This dependence is well described by a rectangular hyperbola, indicating that shape anisotropy plays a decisive role in rotational mobility of the macromolecules.

The second part of the thesis focuses on the effect of intramolecular topological constraints on polymer diffusion. Seven topologically distinct macromolecules: linear chain, ring, different types of catenanes, trefoil knot, and Borromean ring are studied at approximately constant hydrodynamic radius. The translational diffusion coefficients of these systems are found to be nearly identical, demonstrating the robustness of Zimm scaling even for topologically complex polymers. In contrast, the rotational diffusion coefficients show systematic deviations from the rectangular hyperbola relationship between D_r and κ^2 observed for star polymers at constant R_h . These deviations provide clear evidence that intramolecular topological constraints introduce additional dynamical restrictions that cannot be captured by the relative shape anisotropy alone.

The final part of the thesis examines how rotational diffusion influences the reaction kinetics of macromolecular self-assembly. Using linear and star polymers as model systems, assembly pathways are analyzed through the rotational diffusion ratio $f_{SE}^2 = D_r R_h^2 / 3D_t$. The dynamical mechanisms of self-assembly are elucidated using reactive path density analysis, revealing how variations in rotational mobility reshape the pathways connecting unbound and bound states. Together, these results demonstrate that shape and topology play a central role in controlling rotational diffusion and, consequently, the dynamical pathways of macromolecular assembly.

ABOUT THE SPEAKER

Prabeen Kumar Pattnayak is a PhD student in the Mechanical Engineering Department working with Prof. Aloke Kumar and Prof. Gaurav Tomar. He joined in August 2019. He holds a B.Tech in Mechanical Engineering from Centurion University (Odisha) and an M.Tech in Mechanical Engineering (Marine) from Defence Institute of Advanced Technology, Pune. His research focuses on microscale transport processes in soft matter.