DYNAMICS OF POLYMER SOLUTIONS

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Both dilute polymer solutions and polymer melts were active research areas in the mid-1970's, and interest in properties over the full range of concentrations from coil overlap ($\phi = \phi^*$) to the melt state ($\phi = 1$), was growing. Screening and scaling methods had already proven fruitful in that range for static properties such as osmotic pressure $\pi(\phi)$ and coil dimensions $R_g(\phi)$. In 1976 de Gennes extended them to dynamic properties, first in good solvents and later at the theta condition.

Choosing coil overlap ϕ^* as the reference concentration for both statics and dynamics, arguing for equality of dynamic and static screening lengths, taking the solvent viscosity as the time scale reference, *e.g.*, $\eta(\phi) \propto \eta_s$, and using his reptation mechanism to express chain entanglement contributions, de Gennes developed expressions for viscosity, diffusion coefficient, relaxation time and modulus. For $\phi > \phi^*$ in good solvents, he further assumed that both modulus and osmotic pressure are directly proportional to binary chain contact density, implying $G_N^{\circ}(\phi) \propto \pi(\phi)$. He thereby provided the first comprehensive framework for organizing dynamic data at finite concentrations and stimulated a myriad of new studies.

Some of his predictions and inferences about solutions have stood the test of time. As frequently happens in such pioneering efforts, however, the new data has also called many of the original proposals into question. Nonetheless, further advances evolved from those early beginnings, and the entire subject blossomed. For example, use of the de Gennes screening ideas made clear that volume exclusion has a much weaker effect than thought originally. This, together with the inadequacy of solvent scaling for all but the minutest of concentrations, established the limits for the theory, $\phi^* \lesssim \phi \lesssim 0.1$. Despite the harsh testing requirements this imposed, careful and extensive studies by Adam and coworkers (theta solvents in 1984 and good solvents in 1995) clearly revealed a need for additional changes, in particular the existence of two distinct dynamic regimes in the $\phi^* < \phi < 1$ domain. The Adam work also showed the undiluted melt to be a more appropriate reference state for dynamics, a result used by Milner (2005) to derive a quantitative relationship between $G_N^{\mathrm{o}}(\phi)$ and $\pi(\phi)$ in good solvents. In addition, the unexpected similarity of $G_N^{\mathrm{o}}(\phi)$ in good and theta solvents over wide ranges of concentration was explained by the Colby-Rubinstein scaling theory (1990).

Among outstanding questions, viscosity and modulus exhibit unexplained differences in entanglement-concentration relationships, and the variation among solvent species in dynamics at finite concentration—the free volume effect—remains a vexing problem.