419i Off-Lattice Dynamic Monte Carlo Simulations of Aggregation and Gelation

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Several different approaches have previously been taken to study the dynamics of gelation and to model the structures formed during this process. At one extreme is Brownian Dynamics (BD), which is based on actual microscopic interatomic potentials. While this method can be made very accurate and requires only microscopic information, it can access only very short times and therefore cannot be used to treat conditions where the characteristic reaction probabilities are low or diffusion times are long. At the other extreme are coarse-grained methods such as Diffused-Limited-Cluster-Aggregation (DLCA), which uses a very simplified fast dynamics. DLCA does not reproduce the actual dynamics of the gel formation but does produce, within some limitations, gels of reasonable fractal structure.

We propose an intermediate approach (Salazar and Gelb, Physica A (2005), in press): a way to reproduce the actual dynamics of the gel formation and track the growing gel structure, taking into account the microscopic inter-particle interactions, but using a simplified fast dynamics. Based in the Dynamic Monte Carlo method (DMC), which has been successfully used to model on-lattice reaction-diffusion systems, we develop an off-lattice realistic stochastic time evolution which include diffusion and reaction random steps based in the original proposal of Gillespie (Gillespie, J. Comput. Phys. (1976) 22, 403), while including the inter-particle potential interaction. The off-lattice diffusion step is computed by using first collision time distributions. Our method also corresponds to an extension (by additional of spatial inhomogeneity) of a DMC-type approach to solution of the kinetic equations of polymer growth in perfectly homogeneous solutions (Rankin et al, Macromolecules (2000) 33, 7639)

The method is applied to 1D aggregation by contact or by using a double-well interaction potential to describe both weak aggregation and intermolecular bonding. A comparison of BD, DLCA, and DMC is made in terms of the time evolution of the mean cluster size and cluster size distribution. We then discuss necessary modifications for extension to two and three dimensions and present results from trial 2D and 3D calculations.