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POLYMER DYNAMICS:

Chance Encounters

Thomas P. Russell*

When long, flexible chain molecules are tethered to a surface, they can form an exceptionally large number of conformations. However, the probability that a configuration exists depends on an associated energy, which accounts for the stretching of the chain at the interface and the interactions between the chain and the surrounding medium. Consequently, not all configurations are equally probable. It is tempting to think that configurations with a low probability are unimportant, but as Jeppesen *et al.* demonstrate on page 465 of this issue (1), some of the least probable configurations nevertheless play an important role in recognition.

As we know from classical rubber elasticity, as a chain is stretched, the chain configuration becomes energetically unfavorable, and the retractive force increases rapidly as the elongation of the chain increases. In the presence of a good solvent, the osmotic pressure counteracts this retractive force. Compressed configurations are then not favored, and the chains will extend from the surface to maximize favorable interactions between the chain segments and the solvent.

If we replace the solvent with a polymer, as is the case at the interface between two polymers, a similar situation exists, although the entropic contribution to the free energy of mixing is reduced because of the high molecular weights of both components. At equilibrium, the balance between these forces causes the polymer chains to assume an average configuration.

Numerous studies have evaluated the equilibrium properties of polymer interfaces, polymer brushes, polymer stabilized suspensions, adhesion promoters, and filled polymer systems, which all depend on the average configuration of the chains at the interface (2-7). For example, the interfacial width between two polymers describes the average interpenetration between two polymer layers. The interpenetration in turn dictates adhesion between the polymers, that is, the force required to pull the layers apart. In the case of colloidal suspensions, the average configuration of chains anchored to a particle surface defines a minimum separation distance between the particles, which prevents aggregation or precipitation.

Polymer chains at interfaces are not static but dynamic and are constantly probing different ensembles of configurations. We know that excursions of the chains into very high-energy states must exist, but these events are exceptionally difficult to detect, because they are so infrequent and short-lived. However, although the equilibrium states of polymeric systems depend largely on the average configuration of the chains, the ability of chains to test and adopt energetically unfavorable states is manifest in many kinetic processes. In the case of surface reconstruction, for example, a system is driven from one equilibrium state to another by a change in the surface or interfacial energy (8). The pathway by which the reconstruction occurs may require the diffusion of chains through domains where unfavorable segmental interactions occur, but overall reduction in the free energy allows these excursions to occur.

Similarly, if a long chain molecule must diffuse through a pore having a diameter comparable to that of a segment, the entropy of the chain poses a substantial barrier to this diffusion. Even though only a few configurations of the chain will allow passage of the macromolecule through the pore, eventually, after countless attempts, a configuration occurs where there is sufficient penetration to allow complete passage of the chain through the pore (9).

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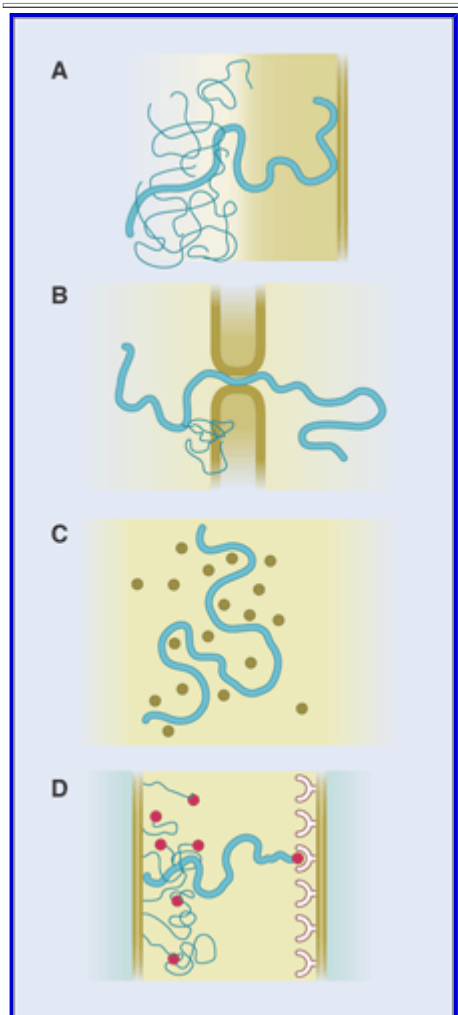
there is sufficient penetration to allow complete passage of the chain through the pore (27).

Conversely, macromolecules may be prevented from sampling all possible configurations, for example, in a gel or a medium with fixed obstacles. This causes an entropic confinement of the chains, which increases with the length of the chain. Such restrictions of configurational states forms the basis of several molecular separations processes (10, 11).

But what occurs when there is no applied force that drives the chains to high-energy configurations? In principle, the macromolecules must sample all configurational states, even those that cost a large amount of energy, but proving this point has been difficult.

Jeppesen *et al.* (1) have devised a very clever, quantitative means of probing the configurational dynamics of long chain molecules at equilibrium anchored to a surface, the ability of the chains to sample rare, high-energy configurations, and the importance of these configurations to recognition processes. The authors placed ligands on the ends of chains anchored to one surface and introduced a second surface to which receptor sites are attached. They found a strong attractive force between the surfaces. This force occurred abruptly when the separation distance between the surfaces is much larger than the average radius of gyration of the anchored chains, which defines the average volume occupied by a chain.

The probability that the tethered chains stretch to such distances without application of an external force is miniscule. Nonetheless, by combining direct force measurements as a function of separation distance for chains of different length with simulations and theory, Jeppesen *et al.* (1) have been able to see the effects of the rare, highly extended chain configurations and the chance encounters of the chain ends with the adjacent surface (see the figure). With sufficiently strong binding sites on the ends of the chains, the highly extended configurations are trapped, and the elastic, retractive force of the chains that span between the two surfaces pulls the surfaces together at distances far greater than the equilibrium radius of gyration.



Chains in motion. (A) A polymer chain diffuses through a second polymer during a surface reconstruction in response to a change in surface interactions, (B) a single chain diffuses through a narrow pore, (C) a polymer is entropically trapped by physical barriers, and (D) one of many end-functionalized polymers anchored to a surface samples a high-energy configuration and interacts with a surface decorated with complementary functional groups.

The beauty of this work lies in its simplicity and the absence of any applied external force to achieve the highly extended configurations. Nature dictates that these configurations must occur, however infrequently or energetically unfavorable. Not only do Jeppesen *et al.* (1) demonstrate that these chance events occur, but they also show how such rare excursions of the tethered chains may play an important role in long-range biological recognition processes. In many ways, the encounters between the chain ends and the recognition sites are "as vessels starting from ports thousands of miles apart pass close to each other in the naked breadths of the ocean, nay, sometimes even touch in the dark (12, p. 353)."

References

1. C. Jeppesen *et al.*, *Science* **293**, 465 (2001).
2. E. Helfand, Y. Tagami, *J. Chem. Phys.* **56**, 3592 (1972).
3. S. Anastasiadis *et al.*, *J. Chem. Phys.* **92**, 5677 (1990) [ADS].
4. J. W. Smith, E. J. Kramer, P. J. Mills, *J. Polym. Sci.* **32**, 1731 (1994).
5. K. Char, H. R. Brown, V. R. Deline, *Macromolecules* **25**, 4164 (1993).
6. L. Leger, E. Raphael, H. Hervet, *Adv. Polym. Sci.* **138**, 185 (1999).
7. J. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, London, 1993).
8. K. Senshu *et al.*, *Langmuir* **15**, 1754 (1999).
9. M. Muthukumar, *J. Chem. Phys.* **111**, 1037 (1999) [ADS].
10. D. A. Hoagland, M. Muthukumar, *Macromolecules* **25**, 6696 (1992).
11. J. Han, H. G. Craighead, *Science* **288**, 1026 (2000).
12. O. W. Holmes, *The Professor at the Breakfast Table* (Atlantic Monthly Company, Boston, 1858).

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