Overview

In a famous paper, "*More is different*," P. W. Anderson (1972) highlighted the "hierarchical structure of science." Even though we understand the fundamental laws of basic particles or objects, the physical behavior of aggregates of these entities, usually associated with strong interactions and correlations, cannot be "understood from simple extrapolations from the properties of a few of these particles." More is different, and more leads to emergent phenomena as a result of increasing complexities as length and time scales increase. For this very reason, chemical and biological sciences, which study essentially physical phenomena from the nanometer scale up to the macroscopic scale of our living world, call upon their own principles, rather than the microscopic quantum mechanic theory.

This viewpoint is further supported by the multitude of complex behaviors of soft and biological matter, which typically involve objects of large spatial extensions, such as long polymers or membranes, and a confluent of energy and time scales of different interactions (Phillips and Quake, 2006). A key feature of mesoscopic organization in soft and biological matter is that competing interactions at different length scales can interplay with each other and result in sophisticated self-assembly. This new paradigm, which extends the classical "symmetry breaking" picture of Landau, is referred to as the "Middle Way" (Laughlin et al., 2000).

In this thesis I study two problems related to the self-assembly of soft matter as a result of competing interactions at different length scales.

In Part I, we study the physics of reversible gelation. Reversible gel is a class of materials which are macroscopic networks formed by reversible associations. Compared to irreversible gel with permanent connections, such as rubber, reversible gel is characterized by both solid-like elasticity and liquid-like relaxations. These features are characteristic of structural glasses. We choose the model of associating polymer solutions, which is a prototype for reversible gelation, and analyze the thermodynamics and phase transitions in the system. We find that gelation is intimately related to the micro-structural order-disorder transition in this system and gelation to order-disorder transition is an analog of glass transition to crystallization.

To further corroborate our conjecture regarding the nature of gelation, in particular, its relation to the microphase transition, we study the phase transitions in diblock copolymer melts, which are

characterized by the microphase spinodal as in associating polymer solutions. Using a thermodynamic replica approach, we find a micro-structural glass transition in the system which results from self-assembly due to competitions between monomer interactions and polymer chain flexibility. In particular, we find that in the mean field limit (infinitely long chains), this glass transition becomes identical to the microphase spinodal, suggesting that the microphase spinodal can be regarded as the signature for glass transitions in this class of systems. In this calculation we also propose a systematic treatment of fluctuations due to the cubic coupling term that appears in asymmetric copolymers, which is missing in the Brazovskii-Leibler-Fredrickson-Helfand theory (Brazovskii, 1975; Leibler, 1980; Fredrickson and Helfand, 1987). Chapter 3 is adapted from our paper, C.-Z. Zhang and Z.-G. Wang, *Phys. Rev. E***73**, 031804 (2006). Copyright (2006) by the American Physical Society.

In Part II we study two problems related to ligand-receptor interactions between surfaces, which is a central motif in cell adhesion and signaling. In Chapter 4[1] we analyze the thermodynamics of interactions between flat surfaces mediated by receptors that are tethered by polymer chains. This model is widely used in bioengineering applications (Garcia, 2006) and biophysical measurements (Wong et al., 1997; Jeppesen et al., 2001). From statistical thermodynamics calculations we obtain an effective two-dimensional binding constant reflecting contributions from the microscopic binding affinity as well as from stretching of the polymer tether. In addition, we distinguish between different scenarios as a result of different receptor mobilities relative to the biological process or experimental measurements. These results clarify the persistent confusion about the interpretation of experimental measurements of binding affinity (Dustin et al., 1996; Orsello et al., 2001). We also demonstrate the versatile control over surface interactions by several examples that combine different types of ligand-receptor interactions, which have both biological and bioengineering relevance.

In Chapter 5[2] we study the interplay between specific ligand-receptor binding and membrane deformations. We offer a systematic analysis of the dynamics of the first-order adhesion typical for cell and membrane adhesion mediated by specific receptors (Bruinsma et al., 2000; Bruinsma and Sackmann, 2002; Sackmann and Goennenwein, 2006). We find that the evolution of membrane deformations along the adhesion pathway is governed by the characteristic length associated with the adhesion potential, while the energetics is governed by the potential depths of the adhesion potential. The dependence of the critical radius and the energy barrier on relevant parameters, including the bending rigidity, the barrier height of the potential, and the separation of the potential minima, are obtained by scaling arguments, and verified by numerical calculations. For completeness we also give a scaling analysis of the scenario when adhesion is a weak first-order transition; this is done by a Peierls argument which accounts for the entropic corrections of irregular boundary shapes.

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