I-N Theoretical Analyses on Nonlinear Behavior of Complex Systems

When material A and material B form a complex system, for example, an interface (or an interface region) newly appears between the two materials. Structure and properties of the interface are often totally different from those of the bulk materials, with the result that the complex system exhibits highly nonlinear behavior that can never be understood by superposition of the behaviors of the individual materials. We deal with a complex system in which liquid solvent or aqueous solution is one of the constituents. The integral equation theories are applied to the liquid solvent and combined with theoretical methods or computer simulation techniques for the other constituents. Some of the complex systems considered are biomolecules in aqueous solution, molecular assemblies formed by self-organization of surfactant molecules in solvent, metal-liquid interface, solvent-mediated interaction between colloidal particles, surface-induced phase transition phenomena, and entropic excluded-volume effects in colloidal and biological systems.

I-N-1 Long-range Interaction between Hydrophilic Surfaces Immersed in a Hydrophobic Fluid Containing a Hydrophilic Component at Low Concentration

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Behavior of a hydrophobic fluid containing a hydrophilic component at low concentration, which is confined between macroparticles separated by distance L, is analyzed using the RISM-HNC theory. When the hydrophilicity of the macroparticle surface is sufficiently high, the following is observed. A layer within which particles of the hydrophilic component are enriched is formed around each macroparticle. As L decreases the two enriched layers within the confined domain continue to grow, eventually leading to a phase transition. The range of the macroparticle interaction induced can be far longer than the molecular scale.

I-N-2 Statistical-Mechanical Analysis on Entropically Driven Formation of Ordered Structure

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Phase separation in a mixture of small and large colloidal particles and the interaction induced between a macromolecule (a large particle) and a cell membrane (a surface) immersed in smaller molecules (small particles), have been analyzed using an integral equation theory. Simplified models are employed to study the entropically driven formation of ordered structure, which is ascribed to the excluded volume effects (forces of increasing the system entropy by reduction of the total excluded volume for the small particles). In the analysis on the induced interaction, attention is focused on effects due to the packing fraction of the small particles, the diameter of the large particle, the surface curvature, presence of a small amount of particles slightly larger than the small particles, and attractive interaction between the small particles. A significant result is that great specificity is provided between the diameter of the large particle and the surface curvature. Works concerning the roles of the excluded volume effects on the "lock and key" steric interactions between macromolecules and protein folding in the biological systems, which are in progress in our group, have also been discussed.

I-N-3 Depletion Effects on the Lock and Key Steric Interactions between Macromolecules

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The hypernetted-chain (HNC) equations solved on a three-dimensional cubic grid are employed to calculate the spatial distribution of the depletion potential between a big solute of *arbitrary geometry* and a big sphere immersed in small spheres forming the solvent. Effects of the step edge on the lateral depletion force along a wall surface are analyzed and shown to be in qualitatively good agreement with a recent experimental observation. Simple model calculations are performed for the *lock and key* steric interactions between macromolecules, and it is found that the depletion effects provide the interactions with remarkably high selectivity.

I-N-4 Improvement of the Reference Interaction Site Model Theory for Calculating the Partial Molar Volume of Amino Acids and Polypeptides

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We propose a simple, efficient bridge correction of the one-dimensional reference interaction site model (RISM) theory. By combining the modified RISM method with the Kirkwood-Buff theory, the partial molar volume is calculated for the 20 amino acids and

for oligopeptides of glutamic acids in extended and a-helix conformations. The bridge correction drastically improves agreement between the calculated values and the experimental data.

I-N-5 Spatial Distribution of Depletion Potential between a Big Solute of Arbitrary Geometry and a Big Sphere Immersed in Small Spheres

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The hypernetted-chain integral equations are solved on a three-dimensional cubic grid to calculate the spatial distribution of the depletion potential between a big solute of *arbitrary geometry* and a big sphere immersed in small spheres forming the solvent. By analyzing the potential along a specific trajectory of the big sphere, effects due to the geometric feature of the big solute (step edges, trenches, corners, changing curvature, *etc.*) can be examined in detail. As an illustration, effects of the step edge on the lateral depletion potential along a wall surface are analyzed. Along the trajectory considered, the big sphere moves at constant height, starting on the center of the wall surface and moving horizontally past the edge. The potential minimum occurs not on the center but at a location much closer to the edge. The big sphere is repelled from the edge into the wall surface, and to escape to the bulk it must overcome a significantly high free-energy barrier. A positive peak of the potential occurs near the edge on the bulk side. As another illustration, simple model calculations are performed for the *lock and key* steric interaction between macromolecules. The potential at contact (*i.e.*, the stabilization free energy) for the key that exactly fits the lock is far larger than for smaller and larger keys and considerably in excess of the value predicted by the Asakura-Oosawa (AO) theory. A very high free-energy barrier features the potential for a smaller key, preventing its access to the lock. The depletion effects on the interaction are substantially large, and the selectively given is remarkably high. The physical origin of the failure of the AO theory is discussed in detail.