

## I-Q 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, liquids at surfaces, and surface-induced phenomena.

### I-Q-1 Peptide Conformations in Alcohol and Water: Analyses by the Reference Interaction Site Model Theory

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It is experimentally known that alcohol induces peptides to form  $\alpha$ -helix structures much more than water. Though the  $\alpha$ -helix structure formed is independent of the alcohol species, degree of the induction increases as bulkiness of the hydrocarbon group in an alcohol molecule increases. In this article we investigate conformations of peptides (Met-enkephalin and the C-peptide fragment of ribonuclease A) in methanol, ethanol, and water using the reference interaction site model theory. Molecular models are employed for the solvents. Our theoretical results show the following. Alcohol indeed facilitates peptide molecules to form the secondary structures with intramolecular hydrogen bonds such as the  $\alpha$ -helix. In alcohol a solvophobic atom of a peptide is *less solvophobic* than in water while a solvophilic atom is *less solvophilic*. The solvation free energy in alcohol thus becomes considerably less variable against conformational changes than in water, with the result that the conformational stability in alcohol is governed by the conformational energy. The peptide molecule tends to take a conformation with the lowest conformational energy such as the  $\alpha$ -helix, which is independent of the alcohol species. Moreover, these trends are enhanced as bulkiness of the hydrocarbon group in an alcohol molecule increases. In the text, the microscopic origin of the differences between alcohol and water in solvation of peptide molecules, which cannot be obtained by analyses treating the solvent as a dielectric continuum, is discussed in detail.

### I-Q-2 Binary Fluid Mixture Confined between Macroparticles: Surface-Induced Phase Transition and Long-Range Surface Forces

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A binary fluid mixture of components 1 and 2, which is confined between two macroparticles separated by distance  $L$ , is analyzed by the RISM theory. Particles of component 1 interact through attractive potential, and those of component 2 and those of different components interact through hard-sphere potential. The macroparticle-fluid particle potential is the hard-sphere one. Component 2, the minor component, is enriched near each macroparticle. When the concentration of component 2 in the bulk  $Y_2$  is sufficiently high, the following is observed. As  $L$  decreases component 2 is even more enriched in the confined domain, and at the threshold value  $L_T$  the theory exhibits a signal of the surface-induced phase transition, appearance of the second phase of component 2 in the confined domain. This phenomenon can occur even when the bulk mixture is stable as a single phase. As  $Y_2$  increases  $L_T$  becomes larger. ( $L_T - d_M$ ) can be far longer than the molecular scale, and the attractive interaction induced between macroparticles becomes correspondingly long range.

### I-Q-3 Solvent Effects on Conformational Stability of Peptides: RISM Analyses

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We describe features of our methodology for predicting tertiary structures (*i.e.*, conformations) of proteins in solvent just from the amino-acid sequences and molecular models for the solvent. The methodology, which is a combination of the Monte Carlo simulated annealing technique and the reference interaction site model theory, is illustrated for the small peptides, Met-enkephalin and C-peptide. Important roles played by water are discussed, and the alcohol effects on peptide conformations are newly analyzed.

### I-Q-4 Effects of a Trace Amount of Hydrophobic Molecules on Phase Transition for Water Confined between Hydrophobic Surfaces: Theoretical Results for Simple Models

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The author has analyzed the phase transition phenomenon for a hydrophilic fluid containing a hydrophobic component at low concentration, which is confined between hydrophobic surfaces, using the RISM-HNC theory with a simple model. Among various hydrophilic fluids, water is doubtlessly the most important one. Water molecules interact through strongly attractive potential, and apolar particles or hydrophobic molecules are soluble only at extremely low concentrations. However, presence of even a trace amount of those molecules affects the phase transition behavior to a drastic extent. Even when the surface separation is far larger than the molecular scale, the wetting of the hydrophobic molecules and the drying of water can occur in the domain confined. The attractive interaction induced between the surfaces become correspondingly long range. As the concentration of the hydrophobic component becomes higher, the wetting/drying transition occurs at a larger surface separation and the induced interaction becomes longer range. The hydrophobic molecules, which are contained in water within biological systems at very low concentrations, have caught little attention so far but should play essential roles in a variety of surface-induced phenomena.

#### **I-Q-5 Methodology for Predicting Approximate Shape and Size Distribution of Micelles**

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We propose a methodology for predicting the approximate shape and size distribution of micelles with all-atom potentials. A thermodynamic theory is combined with the Monte Carlo simulated annealing technique and the reference interaction site model theory. Though the methodology can be applied to realistic models of surfactant and solvent molecules with current computational capabilities, it is illustrated for simplified models as a preliminary step.