

Density Functional Theory for Phase-Ordering Transitions

PI: Jianzhong Wu

A. A brief description of accomplishments.

The proposed research aims to develop new density-functional methods to describe microscopic structure and phase ordering transitions in colloidal dispersions and other complex molecular systems. In addition to theoretical developments, the computational methods have been used to address a number of fundamental questions related to solvation, colloidal and surface forces, and formation of nanoparticles. The following summarizes key accomplishments from the activities of the ongoing project (ER46296).

1) Colloidal structure and thermodynamic properties

Understanding the equilibrium structure and thermodynamic properties of complex fluids such as colloids, protein solutions and micelles often relies on model systems where drastically simplified potentials are used to describe the solvent-mediated potential of mean force. Among such model systems, the square-well (SW) potential is a popular choice because it provides a succinct description of the molecular excluded-volume effects as well as the strength and the range of solvent-mediated interactions. Despite its simplicity, accurate prediction of the properties of SW fluids remains a theoretical challenge for systems with long-range attractions and/or at inhomogeneous conditions.

We have been developing a perturbative density functional theory for quantitative description of the structural and thermodynamic properties of model systems applicable to the bulk as well as inhomogeneous conditions. The free-energy functional combines a modified fundamental measure theory to account for the short-range repulsion and a quadratic density expansion for the long-range attraction. The long-correlation effects are taken into account by using analytical expressions of the direct correlation functions of bulk fluids recently obtained from the first-order mean-spherical approximation. The perturbative density functional theory has been calibrated by extensive comparison with simulation data from this work and from the literature. The theory yields good agreement with simulation results for the radial distribution function of bulk systems and for the density profiles of square-well fluids near the surfaces of spherical cavities or in slit pores over a broad range of the parameter space and thermodynamic conditions.

2) Colloidal dynamics

Existing theoretical methods for nonequilibrium systems are mostly hinged on the assumption of local equilibrium, i.e., thermodynamic concepts and relationships introduced for equilibrium systems are presumed applicable to nonequilibrium conditions. While the generalized thermodynamics methods have been useful for describing transport processes such as heat conduction and mass diffusion in macroscopic systems, their broader application is often

questioned, in particular for small systems and for activation processes where the dynamic processes are dominated by fluctuation and non-local correlation effects.

In this work, we introduced a generic procedure for statistical-mechanical description of the dynamic properties of non-equilibrium colloidal systems by using hierarchical multi-body correlation functions and the maximum entropy principle. We demonstrated that the generic procedure is theoretically self-consistent within given macroscopic information for a non-equilibrium system yet fully complies with the dynamics of individual particles at the microscopic limit. Because the new concepts introduced in this work complement with those used in statistical thermodynamics, the generic procedure enables us to treat equilibrium and time-dependent phenomena within a unifying theoretical scheme. We have illustrated connections of the hierarchical method to a number of conventional non-equilibrium statistical-mechanical methods and to various phenomenological dynamic equations. While for the sake of simplicity the discussion in this work is mainly focused on one-component colloidal systems, we expect that a similar self-consistent procedure can be derived for more complicated non-equilibrium systems.

3) A hybrid MC-DFT for entropic forces

An entropic force arises in a solution or a colloidal dispersion when the local distribution of solvent (or co-solvent) molecules is disrupted due to the presence of the solute. Because it is affiliated with the solvent configuration rather than a specific microscopic energy, the microscopic origin of an entropic force appears obscure and sometimes it is misinterpreted. Even in its simplest form induced by the excluded-volume effects, current understanding is mostly limited to interaction between colloidal particles in the presence of polymer chains dissolved in a good solvent. Whereas existing theoretical methods are adequate to quantify entropic force in colloidal systems with relatively simple geometry, their extension to multi-dimensional interactions such as those important for biological systems is challenging.

In this work, we proposed a hybrid method for computation of entropy forces by using MC simulation to predict the density distributions of solvent molecules and the fundamental measure theory for free-energy calculations. Whereas the DFT is formulated in terms of the density profiles, direct minimization of the free energy functional with respect to a three-dimensional density is unrealistic for most anisotropic systems. This is because the DFT calculation often entails lengthy iterations and requires an extremely small grid (~ 0.002 molecular diameter) to capture the density profiles. On the other hand, simulation of the solvation free energy is in general very time-consuming but simulation of the solvent density at a fixed solute configuration is not a computationally demanding task. For calculating the solvent density, simulation on the time scale comparable to that corresponding to the relaxation dynamics is often sufficient. Besides, simulation is not limited by the dimensionality and much larger grids (~ 0.1 molecular diameter) can be used to sample the solvent density profile. While extension of molecular simulation for simple colloidal systems to those with solutes of more complicated shape requires essentially no increase of the computational cost, DFT provides an efficient link between the microscopic structure and thermodynamic potentials. A combination of simulation and DFT takes advantages of the good features of both methods.

4) Nanoparticle stability and colloidal lock-and-key interactions

A conventional wisdom for controlling nanoparticle size and shape during the synthesis is that particle growth favors the direction of a facet with the highest surface energy. However, the particle solvation free energy, which dictates the particle stability and growth, depends not only on the surface area/free energy but also on other geometric measures such as the solvent excluded volume and the surface curvatures and their affiliated thermodynamic properties. In this work, we have studied the geometrical effects on the solvation free energies of non-spherical nanoparticles using morphometric thermodynamics and density functional theories. For idealized systems that account for only molecular excluded-volume interactions, morphometric thermodynamics yields a reliable solvation free energy when the particle size is significantly larger than the solvent correlation length. However, noticeable deviations can be identified in comparison with the microscopic theories for predicting the solvation free energies of small nanoparticles. The conclusion holds also for predicting the potential of mean force underlying the colloidal “key and lock” interactions. In comparison with the microscopic theories, morphometric thermodynamics requires negligible computational cost and thereby is very appealing for broad practical applications.

5) An efficient algorithm for calculation of the direct correlation functions of molecular systems

Direct correlation function (DCF) plays an important role in liquid integral-equation theories and non-mean-field applications of the classical density functional theory (DFT). While for a simple fluid, the DCF can be easily calculated from the radial distribution function via the Fourier transform and/or, for special cases, can be derived from analytical expressions, computation of the site-site DCFs of a molecular fluid is more challenging due to numerical issues affiliated with solving the matrix integral equations. In this work, we developed a new theoretical method for accurate evaluation of the site-site DCFs of molecular fluids by combination of molecular simulation and analytical asymptotic analysis. The computational procedure entails four steps: 1) molecular simulation is used to calculate the site-site total correlation functions (TCFs) in real space; 2) the reference-interaction-site model (RISM) is used to calculate the site-site DCFs in Fourier space at large wave numbers; 3) asymptotic expressions are derived for the TCFs and DCFs in the limit of small wavenumbers; and 4) the site-site DCFs over the entire range are obtained by interpolation of the asymptotic results. The numerical procedure has been illustrated by application to bulk SPC/E water. Accurate evaluation of the site-site DCFs for water prepares a foundation for future applications of DFT to aqueous systems with atomic details.

6) Molecular driving forces of crystal growth

A perennial challenge for crystal engineering is identification of thermodynamic conditions favoring crystal growth with controlled size and morphology. While experimental investigations are instrumental to understanding the effects of macroscopic variables on the kinetic processes, analysis and utilization of the experimental data toward a rational design require a fundamental knowledge linking molecular driving forces to thermodynamic variables dictating crystallization. In this work, the crystal growth rates are calculated from NVT molecular dynamics simulations based on the fluctuation-dissipation theorem. Special attention is given to the effect of

intermolecular forces on the interfacial behavior and the kinetics of crystallization. By calculating of crystal growth rates at the (001) direction of model fluid-solid systems over a broad range of the parameter space, we find that crystal growth in protein solutions or in colloids can be qualitatively different from that in simple fluids and that the kinetics of colloidal crystallization can be achieved by an effective control of the potential of mean force in addition to thermodynamic conditions.

7) Atomistic density functional theory and its application to solvation

We have been developing an atomistic density functional theory (ADFT) as an alternative to molecular simulation for rapid and accurate computation of solvation free energies in an aqueous solvent. In the DFT calculation, the free-energy functional is formulated within the framework of the reference interaction site model (RISM) with a closure that accounts for multi-body correction effects based on the hypothesis of the universality of the bridge functional. With the site-site direct correlation functions of the pure water obtained from molecular simulation and the bridge functional derived from the modified fundamental measurement theory, ADFT enables rapid prediction of the solvation free energies from the atomic density profiles of the solvent molecules around the solute obtained from molecular simulation or from direct free-energy minimization. The new computational procedure is fully compatible with conventional force fields and can be easily integrated with standard simulation packages.

8) Single-chain Monte Carlo simulation

The structural and thermodynamic properties of polymer in solvent are important to many soft materials. The conformational properties of polymer in solvent are strongly dependent on the polymer-solvent interaction and internal chain correlations. However, the conventional computer simulations are usually hindered by expensive computational cost in particular for high solvent densities and implicit solvent models cannot fully capture the polymer-solvent interactions. In this work, we combined the Monte Carlo simulation and the modified fundamental theory to introduce so-called single-chain simulation to study the conformational properties of single hard sphere chain in hard sphere solvent. Within the framework of single-chain simulation, the Monte Carlo moves are only applied to polymer segments, while we use accurate free energy functional to account for the fluctuating density distributions of solvent molecules and polymer-solvent interactions. We compared the radius of gyration and end-to-end distance of polymer in solvent with direct simulation which explicitly considers the solvent molecules. The overall agreement between our single-chain simulation and direct simulation is very good. The good agreement ensures promising applications of single-chain simulation to more realistic systems.

9) Time-dependent density functional theory for electrode charging kinetics

We introduced a new microscopic theory that is capable of describing both the equilibrium and kinetics of electric double layer from a molecular perspective. Numerical examples are given to illustrate its application to model electrochemical chemical systems that retain the essential features. The theoretical predictions are compared with results from conventional electrochemical methods. Whereas the latter predict erroneous dependence of the surface charge and energy density on the separation between the electrodes, it yields the relaxation time in

remarkable agreement with the microscopic theory. We expect that the microscopic theory will be useful, as demonstrated in application of the equilibrium DFT, for understanding the performance novel electrochemical devices including supercapacitors.

10) Density functional theory for interfacial properties of ionic liquids

Ionic liquids have attracted much recent theoretical interest for broad applications as environmentally-friendly solvents in separation and electrochemical processes. Because of the intrinsic complexity of organic ions and strong electrostatic correlations, the electrochemical properties of ionic liquids often defy the descriptions of conventional mean-field methods including the venerable, and over-used, Gouy-Chapman-Stern (GCS) theory. Classical density functional theory (DFT) has proven to be useful in previous studies of the electrostatic properties of aqueous electrolytes but until recently it has not been applied to ionic liquids. Here we report predictions from the DFT on the interfacial properties of ionic liquids near neutral and charged surfaces. By considering the molecular size, topology, and electrostatic correlations, we have examined major factors responsible for the unique features of electric-double layers of ionic-liquids including formation of long-range and alternating structures of cations and anions at charged surfaces. We have also investigated the dependence of the surface-area-normalized capacitance on the pore size for ionic liquids and a model organic electrolyte inside nanopores of supercapacitors.

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