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Geometry-based density functional theory: an overview

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Abstract

An overview of recent developments and applications of a specific density functional approach that originates from Rosenfeld's fundamental measure theory for hard spheres is given. Model systems that were treated include penetrable spheres that interact with a step function pair potential, the Widom–Rowlinson model, the Asakura–Oosawa colloid–polymer mixture, ternary mixtures of spheres, needles, and globular polymers, hard-body amphiphilic mixtures, fluids in porous media, and random sequential adsorption that describes non-equilibrium processes such as colloidal deposition and random car parking. In these systems various physical phenomena were studied, such as correlations in liquids, freezing and demixing phase behaviour, the properties of fluid interfaces with and without orientational order, and wetting and layering phenomena at walls.

1. Introduction

Density functional theory (DFT) [1] is a powerful tool for studying many phenomena in condensed matter including freezing, and surface and interface behaviour. For most systems of interest the central quantity of DFT, the excess free energy functional that arises from interactions between particles, is unknown and one uses approximations to it. Hence having reliable approximative functionals is the essential prerequisite for studying any of the above phenomena.

For the generic model in the field, hard spheres (HS) and their mixtures, the Rosenfeld functional [2] plays a central role, due to its intrinsic structure that unifies earlier theories (Percus–Yevick and scaled-particle theory) and, more importantly, due to the high quality of the results when compared to those of computer simulations. A brief summary of some of the relevant work [2–9] that led to the present-day formulation of the Rosenfeld functional is given below. One essential step was the observation that by imposing the correct dimensional crossover, the HS functional can be constructively obtained [5]. Subsequently, it was realized

that this is not restricted to the HS case. Provided that the model features well-defined single-particle shapes, from its zero-dimensional (0D) free energy one can construct systematically a genuine DFT for the specific model. In the following an overview of such recent developments is given.

The paper is organized as follows. In section 2 the general structure of the theory is briefly outlined. The models for which such functionals were constructed are summarized in section 3 along with physical applications. We finish with concluding remarks in section 4.

2. Structure of the theory

2.1. Input

The first substantial building block of the theory is a geometrical representation of the particle shapes using four characteristic measures, namely the volume, surface, integral mean curvature, and Euler characteristic of the particles. As an example, the volume measure is a function that is unity inside and zero outside the particle shape. These functions are used to obtain weighted densities by convolutions with the actual density profile. In particular, the weight functions are constructed to obtain the Mayer bonds, $\exp(V_{ij}) - 1$, where V_{ij} is the pair potential between species i and j , by convoluting weight functions.

The second building block is the so-called 0D limit, a situation where all particles present in the system are forced to sit on top of each other. This is a well-defined limiting case that allows for an exact (in many cases analytic) solution of the many-body problem. The 0D limit can be viewed as a small cavity of particle size. As all particles present in the cavity overlap, the configurational integral becomes trivial and one can obtain the exact excess free energy F_{0D} . One then imposes that the functional, when applied to a corresponding situation, recovers this solution, i.e. $F_{\text{exc}}[\{\eta_i \delta(\mathbf{r})\}] = F_{0D}(\{\eta_i\})$, where η_i is the average particle number of species i .

2.2. Output

Applying the functional to constant-density profiles, the properties of the homogeneous bulk fluid are an output of the theory. This in contrast to many other approximations that require information about the fluid as an input. This implies that e.g. the fluid demixing phase diagram is an output of the theory. Pair correlation functions can be obtained via two routes. One is via the Ornstein–Zernike relation and obtaining the direct correlation functions from the second functional derivative of the excess free energy (evaluated for constant density distributions). This provides a severe test of the theory, as taking the derivatives will in general enhance any inaccuracies on the level of the free energy. The other, more powerful, approach is via the so-called test-particle route where one minimizes the grand potential in the presence of an external potential that is generated by a test particle fixed at the origin. Furthermore, as the 0D limit is described correctly, which is crucial for freezing [3, 4], one believes fluid–solid coexistence to be described correctly, although this has not been investigated in detail for systems other than pure HS yet.

3. Models and applications

3.1. Hard spheres

Rosenfeld’s original work [2] was already formulated for HS mixtures. Subsequently this was empirically modified for improved dimensional crossover [3, 4], and a good account of

the HS freezing transition obtained. Reversing the line of thought, Tarazona and Rosenfeld demonstrated that a HS density functional can be systematically *generated* from the 0D limit by considering multi-cavity distributions [5], and following this principle improved versions were obtained [6, 7]. Current work is devoted to the study of the dimensional crossover in HS mixtures. It turns out that a rank-three weight function is required to fulfil the 1D limit for mixtures [8]. Further progress is the implementation of the Carnahan–Starling equation of state for pure HS [7] and for mixtures [9]. High spatial dimensionalities have also been considered [10].

3.2. Penetrable spheres

Particles that interact with a step function pair potential share geometrical properties with HS, but feature an additional non-trivial energy scale $\epsilon/k_B T$, where ϵ is the step height, k_B is the Boltzmann constant, and T is the temperature. Due to the close relationship of the geometrical properties of this system with those of pure HS, the solution for the 0D free energy was the essential requirement for constructing a DFT for this system [11]. Fluid pair correlation functions (obtained by test-particle calculations) were shown to be in good agreement with simulation results, and the freezing phase diagram was obtained, indicating stabilization of the fluid upon decreasing $\epsilon/k_B T$. Subsequently, the penetrable sphere system was used to study the degree of universality of the bridge functional [12].

3.3. Colloid–polymer mixtures

The DFT for the Asakura–Oosawa (AO) colloid–polymer mixture (where colloids are HS and polymers are ideal spheres) was shown to recover free volume theory in bulk [13]; many details and an investigation of the bulk fluid phases can be found in [14]. This theory was applied to the free interface between demixed fluid phases and to the behaviour induced by a hard wall [15, 16] where entropic wetting (by colloidal liquid) and a novel scenario of a finite sequence of layering phase transitions was found.

Subsequent work was devoted to a more realistic description of colloid–polymer mixtures than that provided by the AO model. The influence of poor solvent quality [17] was modelled by assuming a two-component solvent: one component, the primary solvent, provides a homogeneous background and is (as usual) not explicitly treated. A further cosolvent component is a poor solvent for the polymer, and by tuning its density the overall solvent quality can be modified. In this simple model the cosolvent is assumed to be an ideal gas of point particles that cannot penetrate the polymers, hence generating an effective depletion attraction between the polymer spheres that was shown to stabilize fluid–fluid coexistence.

Actual polymers possess a flexible shape, and this will be influenced by the presence of colloidal particles. To account for such size fluctuations, a polydisperse (in polymer radii) AO model was proposed and treated within DFT [18], finding colloid-induced polymer compression. As a simple model for investigating the effects caused by polymer non-ideality, the polymer–polymer interaction was assumed to be a step function (like in the penetrable sphere model above) [19]. By matching the step height with estimates for the strength of the polymer–polymer repulsion, improved agreement with experimental results was obtained. In particular the liquid branch of the fluid demixing binodal moves toward higher polymer concentrations compared to the case for ideal polymer.

For large polymers the hard-core interaction between polymer and colloids in the AO model is no longer justified, as a small (compared to the radius of gyration of the polymer) colloidal particle may penetrate the open coil structure of a polymer. Assuming a finite interaction between colloid and polymer, whose strength is determined from known field theoretical

results, a penetrable AO model [20] was proposed. For polymer-to-colloid size ratios as large as 10, this greatly enhances the mixed region in the phase diagram.

Recently, in colloid–polymer mixtures exposed to a plane-wave external potential that models the influence of a standing laser field, so-called laser-induced condensation was found [21].

3.4. Spheres, needles, lollipops

Remedying a deficiency of Rosenfeld’s original DFT for non-spherical hard bodies [22, 23] a mixture of HS and hard, vanishingly thin needles that may represent stretched polymers or colloidal rods was treated [24]. The interface between demixed fluid phases in this model was studied [25] by investigating density and orientational order parameter profiles as well as the surface tension. In particular, interesting orientational order of the needles was found: on the needle-rich side of the interface the needles preferentially lie parallel to the interface plane, similar to the behaviour near a wall. On the sphere-rich side the needles align perpendicular to the wall; the particles stick through the voids in the first sphere layer. The DFT was also extended to the case of interacting rods (in the Onsager limit) [25] by introducing orientational convolutions into the framework. For vanishing sphere density, this functional is a reformulation of the Onsager functional for rods in terms of single-particle geometries. Reference [25] also gives many explicit expressions for weight functions in simple geometries relevant for wall and test-particle calculations. With a similar approach, Roth and co-workers [26] calculated the entropic torque exerted on a spherocylinder (with finite width) in a sea of HS near a hard wall.

A further study was devoted to the phase behaviour of a colloidal suspension upon adding globular polymers *and* needles as depletion agents. In this ternary mixture, interesting fluid demixing phase behaviour with various critical points and a triple point was calculated for different needle–polymer interactions [27]. Particularly interesting is the case of hard-core repulsion between polymers and needles, where these two species *compete* to generate depletion interaction between the spheres.

Using the sphere–needle mixture as a generic model to study demixing that is solely driven by the particle shapes, a third component with an amphiphilic character was added. A hybrid shape of sphere and needle where the needle is attached rigidly to the sphere constitutes a minimal model for an amphiphilic molecule [28]. The equation of state derived within the DFT framework was found to be in good agreement with computer simulation results over a wide range of densities and compositions of the three species.

3.5. Fluids in porous media

To study the adsorption of fluids in porous media, i.e. disordered, amorphous solids, commonly one uses a model description for the matrix, assuming ‘frozen’ liquid configurations where the particles are immobilized. Such a random matrix is then brought into contact with a fluid that is allowed to equilibrate. Such systems are usually referred to as being quenched–annealed, where the quenched component constitutes the matrix and the annealed component constitutes the fluid. For such systems a new density functional approach that treats the matrix on the level of its density profile(s) was proposed [29]. As an application, the AO colloid–polymer mixture adsorbed in matrices of different kinds was considered [30]. Comparing to phase diagrams obtained from the optimized random phase approximation and replica OZ equations, quantitative agreement was found.

3.6. Miscellaneous

Further applications include the Widom–Rowlinson model which is a mixture where particles of the same species are assumed to be non-interacting, but particles from different species experience HS repulsion. Again this model features well-defined particle shapes and non-trivial 0D statistical properties that were used to obtain a DFT [31]. The predictions of the partial pair correlation functions compare well with simulation results, and the result for the phase diagram possess comparable quality to those from other theories, but also fails to give the precise location of the critical point.

Furthermore, the non-equilibrium process of random sequential adsorption of hard bodies onto a d -dimensional substrate was treated [32]. In 1D one usually refers to the random car-parking problem, and in 2D to (irreversible) colloid deposition. The DFT approach allows one to treat an adsorption probability that is non-uniform in space according to the Boltzmann factor of a prescribed external potential. For the simple test case of a hard boundary of the adsorption region, good agreement with simulation results was found. In particular, it was shown that considerably less structure is built up as compared to the case for the corresponding equilibrium model. This behaviour could be traced back to the smaller (by about a factor of 1/2) contribution of the excess free energy to the total grand potential.

4. Conclusions

Summarizing, geometry-based DFT has been shown to predict phase behaviour, structural correlations, and surface and interface behaviour for a (restricted) range of model systems. Comparison with computer simulation results and to those from other theories indicate the good quality of the results. Moreover, numerous predictions of interesting physical phenomena have been made.

Despite attempts to treat arbitrary soft interactions [33–38], from the existing studies one can conclude that the principal method for obtaining a geometry-based DFT works reliably if (at least) two conditions are fulfilled. First, the model under consideration needs to feature well-defined particle *shapes* that allow one to express the (pair) interactions naturally—the Lennard-Jones model may serve as a counter-example, where the two-particle interaction is clearly defined but the notion of the shape of a single particle is at least not immediate. Second, the 0D statistics (i.e. the stacking of particles on top of each other) needs to retain some of the essential physics of the model under consideration.

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