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Recent advances in classical density functional theory for associating and polyatomic molecules

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ABSTRACT

The function and stability of macromolecular systems, important in industrial and biological processes, are governed not only by molecular size and shape, but also by temperature-dependent hydrogen bonding forces and hydrophobicity of the system. Such processes can be found in many facets of chemistry and biology, most notably in self-assembly processes such as the formation of membranes and micelles in liquid or surfactant solutions, structuring in polymer/nanoparticle systems and the folding of proteins into stable, functional complexes.

We explore the range of capabilities to model such systems through classical density functional theory. Examples demonstrate capabilities of providing molecular insight into properties and structure of branched copolymer/nanoparticle systems, surfactant systems, and grafted polymers. Further opportunities to extend the theories to supramolecular assemblies and to create hybrid approaches with molecular simulation are discussed.

1. Introduction

Over the past thirty years, molecular modeling has largely been focused on understanding and explaining bulk homogeneous fluid behavior. For this reason, a significant increase in the number of approaches and accuracy of such approaches has been seen. The increase in both understanding and approaches came as the model complexity progressed from understanding simple hard spheres to associating hard spheres to non-spherical and polyatomic molecules. Provided these advances, there has been steady progress to further the understanding of inhomogeneous fluids, but this progress understandably lags behind bulk phase modeling as inhomogeneous theories are commonly perturbations to the homogeneous model. However, it is believed that this approach is the reason difficulties in modeling bulk fluid behavior still exist. That is, a complete and accurate picture of complex bulk fluid behavior (e.g., in the critical region or hydrogen bonding networks) is unattainable without a better understanding of the inhomogeneous fluid. In response to these sentiments, a shift in research and development emphasis toward molecular modeling of such inhomogeneous fluids has occurred. Accompanying the beliefs of many in this field is a wide-ranging scientific and industrial interest from technological processes involving interfaces, confined fluids, and self assembly. Thus, it is necessary to develop a theoretical tool capable of handling mixtures (potentially with trace components) where characteristics such as the size, shape, and hydrogen bonding of species are important.

Density functional (DF) methods serve as a valuable theoretical tool in the study of inhomogeneous fluids. Many of the interesting phenomena observed in biological and soft material systems involve time and length scales that are inaccessible by the more traditional methods such as experimentation and molecular simulation. DF methods have proven to be advantageous in providing information unavailable from these other methods. Experimental methods can often be difficult to apply and interpret on microscopic (or smaller) scales. This, in turn, makes it difficult to separate the effects of individual molecular forces on the system behavior meaning the relevance of competing effects is indiscernible. Molecular simulations are applicable on such scales; however, computational cost limits these approaches to systems of small to medium size molecules without significant coarse graining for short time periods while many times neglecting the solvent. Similar to experimental methods, results from molecular simulations typically require additional analytical methods to explain the underlying physics of the problem through indirect calculation from mechanical variables. On the other hand, density functional methods can take advantage of system symmetries to offer a less computationally demanding approach applicable to a wide range of problems where molecular level physics are included explicitly and thermodynamic properties are calculated directly from the free energy functional. Such systems include copolymers of varying lengths with nanoparticles or surfaces subject to

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a myriad of conditions and easily accounting for solvents explicitly. This advantage comes about because molecular simulations require detailed information about all of the constituent particles in a system while density functional methods focus on the direct connection between free energy and the density distributions of components. The theory incorporates enough molecular level detail to quickly and accurately provide physical insight to the system even in complex situations by calculating average properties directly without considering the detailed motions of individual particles.

The last two decades have seen the increased usage of density functional methods to predict the microstructure and thermodynamics of both simple atomic and complex polyatomic bulk and inhomogeneous fluids. The phrase density functional theory (DFT) refers to both the quantum approach developed by Hohenberg and Kohn [1] and Kohn and Sham [2] and the classical approach first applied by Ebner et al. [3]. The work of Kohn and co-workers is based in quantum chemistry, and their DFT was originally developed to explain the electronic structure of an inhomogeneous ground state electronic liquid. The evolution of DFT eventually led to its application to a classical system by Ebner et al. to model the interfacial properties of a Lennard–Jones (LJ) fluid. The classical approach forms the basis of the work presented here as it was a specific theoretical development to model inhomogeneous fluids. For this reason, any further mention of density functional theory refers to the classical version where the functionals apply to spatial distribution of molecules rather than electrons. For a detailed background and complete mathematical development, the reader is referred to the work by Evans [4].

Density functional theory has a statistical mechanics foundation with a motivation to express the free energy of an inhomogeneous system as a unique functional of the density of its constituent molecules $\rho(\mathbf{r})$ independent of any external potential. With this functional, DFT can be used to calculate the equilibrium structure and thermodynamic functions such as phase behavior, interfacial properties, surface forces, and molecular structure [5]. Developments have also been made to allow for dynamic and non-equilibrium problems to be solved by DFT [6]. Because density functional theory can be used to model a wide variety of physical systems, DFT is more of a framework to work within rather than simply a theory as its name implies. The remainder of this review outlines the basic structure of the theory, addresses approximations for the free energy functional, and discusses relevant recent developments within the theory. In addition, several applications to complex fluid systems are presented and the future direction of the field is discussed.

2. General formalism

The formalism presented here simply demonstrates the structural basics of a density functional theory. For this reason, it is presented for a simple, pure component monatomic fluid. In more complex cases, it is possible to generalize the DFT to accommodate polyatomic chains of like or unlike species; however, the general framework presented here is the same. One must simply make appropriate approximations of all the underlying physics of the problem and validate such approximations with experimental or molecular simulation data. This development presumes an adequate understanding of basic statistical mechanics (see standard texts by McQuarie [5] and/or Huang [6]).

Consider a monotonic fluid of n molecules, each of mass m at temperature T and volume V. The Hamiltonian of such a system has contributions due to kinetic energy (K), potential energy (U), and the external potential (E). The n molecule Hamiltonian is then defined as

$$\begin{aligned} H_n &= \sum_{\alpha=1}^{n}\frac{|\mathbf{p}_\alpha|^2}{2m}+\sum_{\alpha=1}^{n}\sum_{\beta=1}^{n}u_{\alpha\beta}(|\mathbf{r}_\alpha-\mathbf{r}_\beta|)+\sum_{\alpha=1}^{n}\nu_\alpha(\mathbf{r}_\alpha) \\ &= K+U+E \end{aligned} \tag{2.1}$$

where $\mathbf{p}_\alpha$ is the momentum of molecule α, $\mathbf{r}_\alpha$ is the coordinate vector for that molecule, $u_{\alpha\beta}$ is the intermolecular potential between molecules α and β at separation $|\mathbf{r}_\alpha-\mathbf{r}_\beta|$, and ν_α is the external potential acting on that molecule at position $\mathbf{r}_\alpha$. Given the definition of the system, the grand canonical ensemble proves to be the most appropriate as it has fixed V, T, and chemical potential (μ). The partition function in this ensemble is written in terms of the Hamiltonian as [7]

$$\Xi=\sum_{n=0}^{\infty}\frac{e^{\beta\mu n}}{n!h^{3n}}\int\prod_{\alpha=1}^{n}d\mathbf{p}_\alpha d\mathbf{r}_\alpha e^{-\beta H_n}. \tag{2.2}$$

In this definition, $\beta=1/k_bT$ is the inverse temperature with k_b and h being the Boltzmann and Plank constants, respectively. The definition of the grand potential, Ω, then follows as the natural logarithm of this partition function according to

$$\beta\Omega=-\ln\ \Xi. \tag{2.3}$$

The necessary conditions for phase coexistence in any ensemble are equivalent pressures (mechanical stability), temperatures (thermal stability), and chemical potentials (chemical stability) in all phases. Two of these conditions, equal temperature and chemical potential, are implicit by working in the grand canonical ensemble. The equal pressure condition is implied by further requiring a fixed grand potential.

In this development, the Hamiltonian and consequently the grand potential are a functional of $\nu_\alpha(\mathbf{r}_\alpha)$ making them a functional of the combined term

$$\phi(\mathbf{r})=\beta[\mu-\nu(\mathbf{r})]. \tag{2.4}$$

Using Eq. (2.4) in conjunction with the definition of the thermal de Broglie wavelength $\left(\Lambda=\sqrt{h^2/2\pi mk_bT}\right)$, the integration over the momentum coordinates in Eq. (2.2) can be carried out and simplified to give

$$\Xi=\sum_{n=0}^{\infty}\frac{1}{n!\Lambda^{3n}}\int e^{-\beta U_n}\prod_{\alpha=1}^{n}e^{\beta\sum_{\alpha=1}^{n}\phi(\mathbf{r}_\alpha)}d\mathbf{r}_\alpha. \tag{2.5}$$

It is now necessary to define the microscopic density operator

$$\hat{\rho}(\mathbf{r})=\sum_{\alpha=1}^{n}\delta(\mathbf{r}-\mathbf{r}_\alpha) \tag{2.6}$$

where δ is the multidimensional Dirac delta function. The equilibrium density profile is then defined by the ensemble average according to

$$\rho(\mathbf{r})=\langle\hat{\rho}(\mathbf{r})\rangle. \tag{2.7}$$

Combining these definitions allows one to redefine the potentials in terms of the density profile $\rho(\mathbf{r})$. Application to Eq. (2.5) reduces the expression to

$$\Xi=\sum_{n=0}^{\infty}\frac{1}{n!\Lambda^{3n}}\int e^{-\beta U_n}\prod_{\alpha=1}^{n}e^{\beta\int\phi(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}}d\mathbf{r}_\alpha. \tag{2.8}$$

Functional differentiation of this expression and application of the definition of the ensemble average leads to the conclusion

$$\rho(\mathbf{r})=\langle\hat{\rho}(\mathbf{r})\rangle=\frac{1}{\Xi}\frac{\delta\ \ln\ \Xi}{\delta\phi(\mathbf{r})}=-\frac{\delta\ \ln\ \Omega}{\delta\phi(\mathbf{r})}. \tag{2.9}$$