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Efficient classical density-functional theories of rigid-molecular fluids and a simplified free energy functional for liquid water

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ABSTRACT

Classical density-functional theory provides an efficient alternative to molecular dynamics simulations for understanding the equilibrium properties of inhomogeneous fluids. However, application of density-functional theory to multi-site molecular fluids has so far been limited by complications due to the implicit molecular geometry constraints on the site densities, whose resolution typically requires expensive Monte Carlo methods. Here, we present a general scheme of circumventing this so-called inversion problem: compressed representations of the orientation density. This approach allows us to combine the superior iterative convergence properties of multipole representations of the fluid configuration with the improved accuracy of site-density functionals. Armed with the above general framework, we construct a simplified free-energy functional for water which captures the radial distributions, cavitation energies, and the linear and nonlinear dielectric response of liquid water. The resulting approach will enable efficient and reliable first-principles studies of atomic-scale processes in contact with solution or other liquid environments.

1. Introduction

The microscopic structure of liquids plays an important role in several biological processes and chemical systems of technological importance, and is the subject of continued scientific interest. Several computational techniques have been developed to study the bulk and inhomogeneous properties of liquids. (See [1] for a comprehensive review.)

Monte Carlo calculations and molecular dynamics simulations with a simplified Hamiltonian, often composed of additive pair-potentials, are the most popular techniques used to compute properties of inhomogeneous liquids. However these can be quite expensive due to the long equilibration times and extensive phase–space sampling necessary to compute thermodynamic averages with sufficiently low statistical noise.

Theories in terms of the equilibrium densities rather than individual configurations of molecules avoid this phase–space sampling and hence are much more efficient for the computation of equilibrium properties. Integral equation theories, based on approximations to the diagrammatic series of interactions, can be reasonably accurate but still prove relatively expensive and have only recently been applied to inhomogeneous systems in three dimensions [2].

All of the above methods require the construction of a simplified Hamiltonian, usually restricted to pair potentials. Many applications, such as the determination of chemical reaction pathways, also require estimation of free energies, which involves a coupling constant integration and hence incurs additional costs. Classical density-functional theories based on an exact variational theorem for the free energy of a liquid [3] avoid these restrictions, at least in principle. In practice, they involve directly approximating the free energy as a functional of the liquid density. They have the further advantage of being readily coupled to a quantum mechanical calculation of an electronic system within the framework of joint density-functional theory [4], which makes quantum treatment practical for much larger systems than possible with *ab initio* molecular dynamics [5].

Free-energy functional approximations for fluids of spherical particles often employ a thermodynamic perturbation about the hard sphere fluid described accurately by fundamental measure theory [6,7]. These may be extended to model polar fluids such as the Stockmeyer fluid [8], but the accuracy of such theories for real molecular fluids is not satisfactory.

Molecular fluids are best described within reduced interaction-site models (RISM) [9], which express the interactions in terms of a few sites on each molecule, usually on atomic centers constrained by a rigid, model molecular geometry. Free-energy functional descriptions in terms of these site densities, however, are complicated by the molecular geometry constraints: even the free-energy of an ideal gas of molecules is not expressible as an analytic, closed-form functional of the site-densities alone. An explicit functional can be written by introducing effective ideal-gas site potentials as auxiliary variables [10], but this still requires inversion of an integral equation to obtain these potentials from the site densities, a

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problem which can be solved explicitly only in some limits, such as reducing the molecule to a point [11], and requires a computationally demanding Monte Carlo integration for the general case.

The above inversion problem can effectively be avoided [12] by switching to the site potentials as the independent variables *instead* of the site densities. This method was applied successfully to fluids of hydrogen chloride [12] and water [13] in planar geometries with inhomogeneity in one dimension only. The convergence of free-energy minimization with respect to independent site-potential variables, however, turns out to be quite slow, particularly in the presence of strong electric fields.

This work presents a simple, general scheme of choosing independent variables that avoid the inversion problem by generating site densities for the free-energy functional treatment of molecular fluids. In Section 2, we demonstrate the site-potential solution as a special case of this general scheme and present other representations with better iterative convergence during free energy minimization. In Section 3, we construct a simplified semi-empirical excess functional for liquid water and in Section 4, we show that our overall approach captures to sufficient accuracy the properties most critical to successful *ab initio* treatment of solvation within the framework of joint density-functional theory.

2. Free energy of an ideal gas of rigid molecules

The site-density-functional theory of molecular fluids is based on approximations to the *in-principle* exact free-energy functional

$$\Phi[\{N_\alpha(\vec{r})\}] = \Phi_{\text{id}}[\{N_\alpha\}] + F_{\text{ex}}[\{N_\alpha\}], \tag{1}$$

where Φ is the grand free energy of the interacting fluid, Φ_{id} is the exact grand free energy for the ideal molecular gas, $N_\alpha(\vec{r})$ are the densities of distinct sites (indexed by α) in the molecule, and F_{ex} captures the effect of all the interactions and correlations. The equilibrium densities and free energy are obtained by minimizing the free energy over all allowed densities.

The heart of the inversion problem [10] lies in the fact that the site densities $N_\alpha(\vec{r})$ are not independent variables, but are constrained by the assumption of a rigid-molecular geometry. The most straightforward description that implicitly incorporates these constraints is in terms of the probability density, $p_\omega(\vec{r})$, of finding a molecule at location $\vec{r}$ with orientation $\omega \in SO(3)$. The free energy of the ideal molecular gas at temperature T in the presence of external site potentials V_α, with chemical potentials μ_α, is then

$$\Phi_{\text{id}} = T\int \frac{\mathrm{d}\vec{r}\,\mathrm{d}\omega}{8\pi^2} p_\omega(\vec{r}) \left(\log\frac{p_\omega(\vec{r})}{N_{\text{ref}}} - 1\right) + \sum_\alpha \int \mathrm{d}\vec{r} N_\alpha(\vec{r})(V_\alpha(\vec{r}) - \mu_\alpha), \tag{2}$$

with the site densities given by

$$N_\alpha(\vec{r}) = \sum_k \int \frac{\mathrm{d}\omega}{8\pi^2} p_\omega\left(\vec{r} - \omega\circ\vec{R}_{\alpha k}\right). \tag{3}$$

Here, the reference density N_{ref} sets the zero of chemical potential, $\omega\circ\vec{R}$ denotes the rotation of vector $\vec{R}$ by ω, and $\vec{R}_{\alpha k}$ are the site positions of a molecule at the origin in a reference orientation, with k indexing multiple symmetry-equivalent sites of each type α.[1]

Given the explicit expressions for the ideal-gas free energy (2) and site densities (3), $p_\omega(\vec{r})$ are suitable independent variables for *unconstrained* free-energy minimization and have recently been employed in molecular classical density functional calculations [14]. However, the number of discrete ω necessary to adequately sample the orientation integrals in (2) and (3) far exceeds the typical number of sites in a molecule. Consequently the memory requirements for the orientation density typically exceed those of the site densities by two orders of magnitude, and limit the direct orientation density approach to relatively small systems.

Storing the orientation density in its entirety is unnecessary, however, as we now show using a constrained-search approach [15]. First, we separate the explicitly p_ω-dependent entropy term from the remainder, expressing the overall free energy minimization as

$$\begin{aligned}\Phi &= \min_{p_\omega(\vec{r})}\left(\Phi_{\text{id}}[p_\omega(\vec{r})] + F_{\text{ex}}[\{N_\alpha\}]\right)\\ &= \min_{p_\omega(\vec{r})}\Bigg(T\underbrace{\int \frac{\mathrm{d}\vec{r}\,\mathrm{d}\omega}{8\pi^2} p_\omega(\vec{r})\log\frac{p_\omega(\vec{r})}{N_{\text{ref}}}}_{-S_{\text{id}}[p_\omega(\vec{r})]} + F_{\text{id-ex}}[\{N_\alpha\}]\Bigg),\end{aligned}$$

where S_{id} is the molecular ideal gas entropy. Next, the minimization over all $p_\omega(\vec{r})$ can be performed by minimizing over those $p_\omega(\vec{r})$ that yield a specific set of site densities $\{N_\alpha(\vec{r})\}$, and then minimizing over all $\{N_\alpha(\vec{r})\}$,

$$\Phi = \min_{\{N_\alpha(\vec{r})\}}\left(\min_{p_\omega(\vec{r})\mapsto\{N_\alpha(\vec{r})\}} T\int \frac{\mathrm{d}\vec{r}\,\mathrm{d}\omega}{8\pi^2} p_\omega(\vec{r}) \times \log\frac{p_\omega(\vec{r})}{N_{\text{ref}}} + F_{\text{id-ex}}[\{N_\alpha\}]\right).$$

Finally, using Lagrange multipliers $\psi_\alpha(\vec{r})$ for each $N_\alpha(\vec{r})$ constraint, the inner minimization over $p_\omega(\vec{r})$ yields

$$p_\omega(\vec{r}) = N_{\text{ref}}\prod_{\alpha,k} e^{-\psi_\alpha(\vec{r}+\omega\circ\vec{R}_{\alpha k})/T}, \tag{4}$$

a product of Boltzmann factors for each site, which leads to the interpretation of $\psi_\alpha(\vec{r})$ as ideal-gas effective potentials. Substituting (4) into (2) and (3) results in explicit expressions for the site densities and ideal gas free energy in terms of $\psi_\alpha(\vec{r})$, making them suitable independent variables for unconstrained free energy minimization. Moreover, the memory requirement for these site potentials equals that of the site densities and is thus quite manageable.

It is straightforward to verify that the free-energy minimization over site potentials $\psi_\alpha(\vec{r})$ derived above, reduces exactly to the ideal gas effective potential approach of [10,12]. (See [16] for details.) Fig. 1 compares the iterative convergence of the Polak–Ribiere nonlinear conjugate gradients algorithm [17] for minimizing the free-energy functional of liquid water with different choices for the independent variable. (The following sections include details of the excess functional approximation and the rationale for the test systems employed in this comparison.) Minimizing directly over $p_\omega(\vec{r})$ exhibits the best exponential convergence in both systems, whereas minimizing over the site potentials $\psi_\alpha(\vec{r})$ exhibits the poorest convergence.

The slow convergence of the ψ_α-minimization is particularly problematic in systems with strong electric fields. This arises because the nonlocal dependence of p_ω on ψ_α in (4) necessitates a global readjustment of ψ_α in order to reflect the rotation of a molecule at one point in response to the field. We next show that it is possible to minimize over other sets of independent variables, and that it is possible to retain the superior convergence of p_ω minimization while mitigating its memory requirements.

We begin by noting that the exact equivalence between minimization over $p_\omega(\vec{r})$ and minimization over $\{\psi_\alpha(\vec{r})\}$ holds only when the external potential takes the form of external site potentials $V_\alpha(\vec{r})$. In principle, we could go beyond the reduced-interaction site model and consider arbitrary orientation dependent external potentials $V_\omega(\vec{r})$ (of which site potentials $V_\alpha(\vec{r})$ are a special case). From this perspective, the minimization over $\{\psi_\alpha(\vec{r})\}$ can be interpreted as a minimization over only those $p_\omega(\vec{r})$ that maximize the molecular ideal-gas entropy $S_{\text{id}}[p_\omega(\vec{r})]$ subject to

[1] For example, in a 3-site water model with $\alpha \in \{O, H\}$, the sums run over $k = 1$ for $\alpha = O$ and $k \in \{1, 2\}$ for $\alpha = H$.