Classical density-functional theory for water

Sahak A. Petrosyan, David Roundy, Jean-François Brière and Tomás A. Arias

Department of Physics, Cornell University, Ithaca, NY 14853
(Dated: in press)

We introduce a new computationally efficient and accurate classical density-functional theory for water and apply it to hydration of hard spheres and inert gas atoms. We find good agreement with molecular dynamics simulations for the hydration of hard spheres and promising agreement for the solvation of inert gas atoms in water. Finally, we explore the importance of the orientational ambiguity in state-of-the-art continuum theories of water, which are based on the molecular density only.

INTRODUCTION

Water is the most abundant liquid on earth and is essential for life. Water is a called a universal solvent for its ability to dissolve both acids and bases, as well as polar and non-polar molecules.

Despite its importance to a wide range of problems in chemistry and biology, it is still an open challenge to build a first principles theory of the microscopic structure of water and its interaction with solutes\[1\]. The underlying reason for this is the complex interplay between the kinetic energy of molecules and the the orientation dependent potential energy of inter-molecule interactions.

For the study of liquids and their interactions with external systems, two general classes of theoretical methods have been developed. The first treats the liquid as a collection of molecules treated either \textit{ab initio} within density-functional theory or with a model interatomic potential, such as the simple point charge (SPC) model [2] or the 4-site transferable intermolecular potential TIP4P [3], and then uses molecular dynamics (MD) or Monte Carlo numerical methods to perform statistical averaging over the thermal phase space [4–6]. These methods are intuitively simple to understand and also relatively straightforward to implement numerically. However, because they involve statistical averaging of many molecules over an exponentially growing configuration phase space, these methods are numerically very demanding. The second class of methods treats the liquid as a continuous medium [7–11]. Without the need for thermal averaging or to represent molecules individually, these latter methods are much more efficient computationally. However, such models are generally built in an empirical way and, generally, there is no systematic way to improve them. Nonetheless, significant progress has been made in understanding the interaction of water with external environments using this approach, such as the work of Pratt and Chandler [12] on the theory of the hydrophobic effect and the Lum, Chandler, Weeks (LCW) theory of hydrophobicity [13].

In this work, we explore the nature of the interaction of water with external environments using a somewhat different approach than that of Chandler and coworkers and work in a classical density-functional theory framework. There are two main advantages of working in this framework. First, the classical density-functional theory of liquids is a continuous theory of the liquid state which is exact in principle. Moreover, this framework gives the free energy and the density profile of the liquid in any external potential \(V(\vec{r})\) in terms of a single density-functional\[1\], so that study of the hydrophobic effect (liquid in contact with either an impenetrable wall or an impenetrable hard sphere) and of the interaction of the liquid with any solute can be carried out in a single, unified framework. A number of approximate density-functional theories have been developed for water and applied to the hydrophobic effect [14–15]. Much more demanding theories which go beyond the average molecular density to consider explicitly the distribution of molecular orientations in water have also been developed [13, 16]. All of these density functional theories, however, prove to be either quite computationally demanding or provide an over-simplified description.

We begin this work by introducing a new, computationally efficient density-functional theory for water which accurately reproduces the hydrophobic effect near hard boundaries. We then present the first application of a classical density-functional theory to realistic \textit{ab initio} potential energy surfaces of solutes, applying our theory to the solvation of the inert gas sequence. This latter study allows us to address directly the question of whether explicit orientation dependence, with all of the concomitant computational demands, is necessary to provide an accurate description of the solvation of even the simplest solutes.

CLASSICAL DENSITY-FUNCTIONAL THEORY

Classical density-functional theory for liquids follows from a variational principle which was first established by Hohenberg and Kohn [17] for the inhomogeneous electron gas at zero temperature and later generalized to finite temperature by Mermin [18].

The theorem states that the equilibrium grand potential \(\Omega_0\) of a liquid at chemical potential \(\mu\) in any exter-
nal potential $V(\vec{r})$ can be found by minimizing, over all possible thermally averaged molecular densities $\rho(\vec{r})$, the sum of a universal functional and the interaction of that density with the potential,

$$\Omega_0 = \min_{\rho(\vec{r})} \left\{ F[\rho(\vec{r})] + \int (V(\vec{r}) - \mu) \rho(\vec{r}) \, d\vec{r} \right\},$$

(1)

with the density profile $\rho(\vec{r})$ which minimizes the free-energy giving the exact average density at thermal equilibrium. $F[\rho(\vec{r})]$ is said to be a universal functional of density $\rho(\vec{r})$ in the sense that it does not depend whatsoever on the external potential $V(\vec{r})$ but only upon the nature of the solvent itself. This yields the significant advantage that once a good approximation is found for the universal functional $F[\rho(\vec{r})]$, it can be used to study the interaction with any possible external potential $V(\vec{r})$, such as that representing one solute or another.

Even though $F[\rho(\vec{r})]$ is exact in principle, its analytical form is not known and approximations must be developed. Generally, one begins by separating the functional as

$$F[\rho(\vec{r})] = F_{id}[\rho(\vec{r})] + F_{ex}[\rho(\vec{r})],$$

(2)

where $F_{id}[\rho(\vec{r})]$ is the free energy of ideal gas whose analytic form is known exactly,

$$F_{id}[\rho(\vec{r})] = kT \int \rho(\vec{r}) \ln(\rho(\vec{r})) \, d\vec{r},$$

(3)

and where $F_{ex}[\rho(\vec{r})]$ is defined as the excess free energy beyond that of the ideal gas and contains all the other terms responsible for correlations among the molecules.

Our density-functional theory is inspired by a class of weighted-density functionals\[10\]. Our method, however, is computationally much simpler in that it does not require computationally demanding self-consistent calculations of the weighted density. On the other hand, our form does allow us to incorporate much of the same physics as \[7\] and thus find a form which is competitive computationally but more accurate than other, more simplified functionals\[11\].

**CONSTRUCTION OF CLASSICAL DENSITY-FUNCTIONAL THEORY FOR WATER**

The form we choose to consider is

$$F[\rho(\vec{r})] = F_{id}[\rho(\vec{r})] + \int f_{ex}(\bar{\rho}(\vec{r})) d\vec{r}$$

$$+ \int \int \rho(\vec{r}) \chi(\vec{r} - \vec{r}')(\bar{\rho}(\vec{r}')) d\vec{r} d\vec{r}'$$

(4)

where $F_{id}[\rho(\vec{r})]$ is given by Eq. \[3\] and $f_{ex}(\bar{\rho}(\vec{r}))$ is a local function of $\bar{\rho}(\vec{r})$, a Gaussian smoothed density,

$$\bar{\rho}(\vec{r}) = (2\lambda^2\pi)^{-\frac{3}{2}} \int \rho(\vec{r}') e^{-\frac{|\vec{r} - \vec{r}'|^2}{2\lambda^2}} \, d\vec{r}',$$

(5)

and $\chi(\vec{r})$ is an interaction kernel which integrates to zero. The first term in Eq. \[4\], which is known exactly, ensures that the short length-scale properties (to which $F_{ex}$ does not couple) are treated properly. The second term in Eq. \[4\] ensures that a large-scale phase separation between vapor and liquid is treated correctly and, often, can capture exactly the experimental two-particle correlation functions in the bulk liquid\[2\] for an appropriate convolution kernel in Eq. \[5\]. However, we find that, for the experimentally observed two-particle correlation function in liquid water, the equation for the kernel has no real solutions. The solutions have small imaginary parts and thus cannot be used directly. The real parts of the solution, however, closely resemble a Gaussian. Thus, we employ a Gaussian in Eq. \[5\] and add the last term in Eq. \[4\] to ensure that the experimental two-particle correlation function in the bulk liquid is reproduced.

To construct the functions and parameters needed in Eq. \[4\], we begin by noting that, for the uniform liquid, the last term gives zero ($\chi$ has zero integral) and $\bar{\rho}(\vec{r}) = \rho(\vec{r})$, so that $f_{ex}(\rho)$ can be constructed to reproduce the properties of the uniform liquid exactly. In practice, we parameterized $f_{ex}(\rho)$ as a sixth-order polynomial

$$f_{ex}(\rho) = a\rho^6 + b\rho^5 + c\rho^4 + d\rho^3 + e\rho^2 + f\rho + g.$$  

(6)

with parameters chosen to reproduce, for bulk water at standard ambient temperature and pressure (SATP), the density and bulk modulus of both the liquid and vapor (four parameters), the derivative of the bulk modulus of the liquid with respect to pressure $\partial B/\partial P$, and phase coexistence of the liquid and vapor (equality of grand potential). Table \[I\] gives both the fit data and the resulting parameters, and Figure \[I\] presents the final function $F(\rho)$. Note that in this work we employ mostly atomic units (a.u.) so that Planck’s constant, the electron mass and the fundamental charge all have numerical value unity ($\hbar = m_e = e = 1$), implying that energies are measured in units of 1 hartree=27.21 eV and distances in units of 1 bohr=0.5291 Å.

To construct $\chi(\vec{r})$, we work in the Fourier representation. As noted above, $\chi(\vec{r})$ integrates to zero so that

| a | $6.630 \times 10^5$ |
| b | $-1.277 \times 10^5$ |
| c | $9.200 \times 10^5$ |
| d | $-2.602 \times 10^5$ |
\( \tilde{\chi}(\vec{k} = \vec{0}) = 0 \). For \( \vec{k} \neq \vec{0} \), we fit to the experimental pair distribution function \( g(r) \) of bulk uniform water at SATP [19]. Finally, the Gaussian width parameter \( \lambda = 0.4415 \) a.u. has been fit to the surface tension of bulk water 70 mN/m or \( 4.5 \times 10^{-5} \) a.u. We emphasize that in constructing this functional we used only the macroscopic properties of water.

APPLICATION TO HYDRATION OF HARD SPHERES

To test the accuracy of this approximation we use it to calculate the free energy of a spherical cavity in water, a standard test case used in the literature [10, 13, 20, 21] to explore density variations in water over all possible length scales. The interaction potential with a hard sphere is over-idealized because it depends only on the distance of the water molecule to the hard sphere and does not depend on the orientation. For instance, for a real water molecule it is unclear even what point to take to represent the location of the molecule. The position of the oxygen nucleus is most often taken.

Figure 2 compares our results for the surface tension (free energy change per unit area) of a spherical cavity with results of molecular simulations for SPC/E water [22]. The figure verifies that the surface tension approaches the macroscopic value in the limit of large radii and show the, for smaller radii, the surface tension has a strong dependence on radius. Our results are in agreement with Lum-Chandler-Weeks [13] theory. The good agreement with explicit molecular dynamics simulations suggests that this model gives good quantitative description of the hydrophobic effect, a central problem of theoretical chemistry.

APPLICATION TO HYDRATION OF INERT GAS ATOMS

The ultimate motivation for inhomogeneous continuous theories of bulk water is to understand solvation of real solutes, not artificial hard boundaries. Within the density-functional framework of Eq. (1), one can simply and rigorously incorporate the effects of any external potential \( V(\vec{r}) \) acting on the liquid, making treatment of real solutes simple in principle, provided a static potential \( V(\vec{r}) \) accurately describes the interaction of water with the solute. For our next test, we treat a simple but challenging problem for which there is experimental data, the solvation of inert gas atoms.

The experimental solubilities of the inert gases in water give the corresponding solvation free energies directly. In the dilute limit, the free energy of solvation \( \Delta \Omega \) relates to the mole fraction solubility through the relation

\[
\Delta \Omega = k_B T \log \left( \frac{n_{\text{gas}}}{X_1 n_w} \right) = k_B T \log \left( \frac{1 \text{atm}}{k_B T X_1 n_w} \right) \tag{7}
\]

where \( X_1 \) is the mole fraction solubility in water and \( n_w \) is the number density of liquid water.

The experimental data, which Table II summarizes, show an interesting trend. Although the solvation energies of hard spheres increase with size, the solvation energies of inert gas atoms tend to decrease. (Note that for helium, the worst possible case, we estimate quantum zero-point effects to be quite small, on the order of 0.005 eV, so that this must be purely an effect of the interactions.) Thus, a simple cavity model for solvation of inert gas atoms is not a good approximation and one must use a more realistic interaction potential \( V(\vec{r}) \).
We determined the potential energy of interaction between a water molecule and an atom of each of the inert gases in Table II directly through \textit{ab initio} density-functional theory calculations within the generalized gradient approximation (GGA) \cite{5}. For these calculations we take \( \vec{r} \) to be the displacement between the nucleus of the inert gas and the nucleus of the oxygen atom and considered one hundred different orientations for the water molecule, with these orientations optimized to sample the angular dependence evenly according to the procedure of Womersley and Sloan \cite{2}. Figure 3 summarizes the results for argon, which was typical of all of the inert gasses considered in this work.

The scatter in the interaction energy at each distance \( r \) shows a strong dependence on the orientation of the water molecule, particularly at closer distances. The question then immediately arises of how to couple to any continuum theory based solely on the molecular density \( N(\vec{r}) \) with no information about the orientations of the solute. As the coupling in such \textit{density-only} functional theories takes the form \( \int V(\vec{r})n(\vec{r})d\vec{r} \), a choice must be made to define a unique value for the potential \( V(\vec{r}) \) for each point \( \vec{r} \). One approach would be to assume that each water molecule independently assumes its most favored orientation for a given distance, thereby defining \( V(r) \) as the minimum energy envelop (\( V_{\text{min}} \)) of the data in Figure 3. Another approach would be to take the thermal average interaction under the assumption that the water molecules choose their orientations independently of each other, thereby defining \( V(r) \) as the Boltzmann weighted average (\( V_{\text{KT}} \)) of the data at each distance.

Table II summarizes the results of the minimum free energy of our functional for both of these approaches. For helium and neon experimental and theoretical results agree quite well. Also the difference between using \( V_{\text{min}} \) and \( V_{\text{KT}} \) is less than 0.04eV. As the size of atoms gets bigger the discrepancy also increases suggesting that orientational ordering of water molecules around the atoms is playing an important role and a density-only description is not enough.

### CONCLUSIONS AND FUTURE DIRECTIONS

This work presents a simple density-functional theory for water which gives reasonable overall agreement with molecular dynamics simulation data for the solvation of hard spheres in water, with quite good agreement for smaller spheres (radius less than 2.5Å). However, as we move to look at simple solutes, such as inert gasses, we find mixed results. While we are able to reproduce the counter-intuitive trend of decreasing energy with increasing size in the inert gas sequence when going from He to Ne, we fail to do so for the larger atoms. Thus, although solvation of hard spheres, whose interaction with water molecules is generally taken to involve only the location of the oxygen nucleus and thus contains no orientation dependence, may be well described by density-only theories, such theories do not necessarily describe well the solvation of even simple solutes such as inert gases. It thus appears that treatment of orientation in some form is needed to attain results approaching chemical accuracy for realistic solutes. This work was funded by NSF GRANT #CHE–0113670.

| Exp. (eV) | \( V_{\text{KT}} \) (eV) | \( V_{\text{min}} \) (eV) |
|----------|-----------------|-----------------|
| Helium   | 0.12            | 0.12            | 0.09            |
| Neon     | 0.12            | 0.11            | 0.07            |
| Argon    | 0.09            | 0.22            | 0.17            |
| Krypton  | 0.07            | 0.25            | 0.18            |

Table II: Solvation energies of inert gas atoms

---

[1] J. P. Hansen and I. R. McDonald, \textit{Theory of Simple Liquids} (Academic Press, 1989).
[2] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, and J. Hermans, \textit{Intermolecular Forces} (Reidel, Dordrecht, 1981).
[3] W. Jorgensen, J.Chandrasekhar, J. Madura, R. Impey, and M. Klein, J. Chem. Phys. 79, 926 (1983).
[4] P. Kollman, Chem. Rev. 93, 2395 (1993).
[5] G. M. Torrie and J. Valleau, J. Comput. Phys. 23, 187 (1977).
[6] E. A. Carter, G. Cicotti, J. T. Hynes, and R. Kapral, Chem. Phys. Lett. 156, 472 (1989).
[7] W. Curtin and N. W. Ashcroft, Phys. Rev. A 32, 2909 (1985).
[8] J. Tomasi and M. Persico, Chem. Rev. 94, 2027 (1994).
[9] B. Roux and T. Simonson, Biophys. Chem. 78, 1 (1999).
[10] S. X. Sun, Phys. Rev. E 64, 021512 (2001).
[11] J. D. Thompson, C. J. Cramer, and D. G. Truhlar, J. Chem. Phys. 119, 1661 (2003).
[12] L. Pratt and D. Chandler, J. Chem. Phys. 67, 3683 (1977).
[13] K. Lum, D. Chandler, and J. D. Weeks, J. Phys. Chem. 103, 4570 (1999).
[14] T. F. Meister and D. M. Kroll, Phys. Rev. A 31, 4055 (1985).
[15] R. Ramirez and D. Borgis, J. Phys. Chem. 109, 6754 (2005).
[16] K. Ding, D. Chandler, S. J. Smithline, and A. D. J. Haymet, Phys. Rev. Let. 59, 1698 (1987).
[17] P. Hohenberg and W. Kohn, Phys. Rev. B 136, 864 (1964).
[18] N. Mermin, Phys. Rev. A 137, 1441 (1965).
[19] P. A. Machin and J. Woodhead-Galloway, Molecular Physics 31, 233 (1976).
[20] D. M. Huang, P. L. Geissler, and D. Chandler, J. Phys. Chem. B 105, 6704 (2001).
[21] G. Hummer, S. Garde, A. E. Garcia, A. Pohorille, and L. R. Pratt, Proc. Natl. Acad. Sci. USA 93, 8951 (1996).
[22] P. R. ten Wolde, S. X. Sun, and D. Chandler, Phys. Rev. E 65, 011201 (2001).
[23] J. P. Perdew, K. Burke, and M. Ernzerhov, Phys. Rev. Lett. 78, 3865 (1997).
[24] R. S. Womersley and I. H. Sloan, Adv. in Comp. Math. 114, 195 (2001).