

Kohn-Sham-Like Approach toward a Classical Density-Functional Theory of Inhomogeneous Polar Molecular Liquids: An Application to Liquid Hydrogen Chloride

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The Gordian knot of density-functional theories for classical molecular liquids remains finding an accurate free-energy functional in terms of the densities of the atomic sites of the molecules. Following Kohn and Sham, we show how to solve this problem by considering noninteracting molecules in a set of effective potentials. This shift in perspective leads to an accurate and computationally tractable description in terms of simple three-dimensional functions. We also treat both the linear- and saturation-dielectric responses of polar systems, presenting liquid hydrogen chloride as a case study.

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Introduction.—The importance of inhomogeneous polar molecular liquids, above all water, in the physical sciences can hardly be overstated: as solvents they are ubiquitous in soft condensed matter physics, biophysics, nanophysics, and chemical physics. The associated phenomena include hydrophobic interactions [1,2], protein folding [3,4], the behavior of colloidal suspensions [5], and phase transitions of confined liquids [6,7]. Because of the complex interplay of hydrogen bonding, long-range polar interactions, and short-range excluded volume effects, developing a tractable physical theory to describe the solvent in these systems remains a challenge [8].

Despite the importance, inherent interest, and extensive experimental study of polar liquids, most existing theories of the inhomogeneous molecular liquid either lack the accuracy to describe the above phenomena in a quantitatively satisfying way or become computationally prohibitive when applied to such complex problems. The description of liquids from first principles via *ab initio* methods may be accurate, but can only be applied to relatively small systems [9]. Even *classical* molecular dynamics requires rather long simulation times to sample phase-space sufficiently to extract meaningful thermodynamic averages [10]. This latter approach also suffers from the well-recognized difficulty of designing potentials to describe hydrogen-bonded liquids accurately [11].

An alternative approach is to start with the quantum mechanical free-energy functional for both electrons and nuclei and, by “integrating out” the electrons, to construct a density functional in terms of atomic site densities alone. These “classical” density-functional theories, which have been successfully applied to the study of simple liquids [12,13], provide a description of inhomogeneous physical systems that is founded on a number of exact theorems [14,15]. To apply this approach to the study of simple liquids, a hard sphere reference system is usually augmented by terms that capture weak long-range attractive forces [16]. Unfortunately, for most liquids of interest, a hard sphere reference system is a poor starting point because of the strong anisotropic short-range interactions

arising from the molecular structure and effects such as hydrogen bonding.

To remedy this, Chandler and co-workers [17–19] introduced a density-functional theory for molecular liquids in terms of a set of densities, one for each “interaction site” on the molecule (typically atomic centers). However, the construction of accurate free-energy functionals in such theories is challenging due to the “inversion problem”, the difficulty of using *only* atomic site densities to express the entropy associated with the geometric structure of the molecules. Below, we show how this inversion problem can be overcome by a Kohn-Sham-like change of variables from site densities to effective potentials and how the resulting functionals are both computationally tractable and can capture the basic underlying physics of molecular liquids, including dielectric screening effects.

Kohn-Sham approach.—The grand free-energy $\Omega^{(ni)}$ of a noninteracting gas of molecules is well known as a functional of the *relative potentials* $\psi_\alpha(\mathbf{r}) \equiv \phi_\alpha(\mathbf{r}) - \mu_\alpha$, where $\phi_\alpha(\mathbf{r})$ is the site-dependent external potential and μ_α is a site-specific chemical potential,

$$\Omega^{(ni)} = -k_B T n_r \int d^{3M} r s(\{\mathbf{r}_\alpha\}) e^{-\beta \sum_{\alpha=1}^M \psi_\alpha(\mathbf{r}_\alpha)}. \quad (1)$$

Here, n_r is the reference density at vanishing chemical potentials, M is the number of interaction sites on the molecule, and $s(\{\mathbf{r}_\alpha\})$, which describes the geometry of the molecule, is the intramolecular distribution function. For rigid molecules (zero internal energy), the entropy of the atomic site densities is easily extracted from $\Omega^{(ni)}$. Thus, to construct an *exact* density functional for the entropy, even for the *interacting* system, one only need express $\Omega^{(ni)}$ as a functional of the site densities. More generally, $\Omega^{(ni)}$ is a key part of the interacting functional directly analogous to the noninteracting kinetic energy functional $T_s[n]$ of Kohn and Sham [20]. Unfortunately, (1) only gives $\Omega^{(ni)}$ as a functional of the ψ_α . To express $\Omega^{(ni)}$ in terms of site densities requires solution of $n_\alpha^{(ni)}(\mathbf{r}) = \delta\Omega^{(ni)}/\delta\psi_\alpha(\mathbf{r})$ as a set of M coupled integral

equations for the $\psi_\alpha(\mathbf{r})$ in terms of the $n_\alpha^{(ni)}(\mathbf{r})$. This constitutes the “inversion problem” described above.

Chandler and co-workers have solved this inversion problem analytically in terms of an infinite continued fraction of convolutions for the *diatomic case only* [18]. The unwieldiness of this formal solution and its limitation to diatomics, however, has led actual calculations to be performed in the *united-atom approximation*, where, for the noninteracting part of the functional, all of the sites of a molecule are assumed to coincide at a single point [19]. Despite its crudeness, the resulting theory predicts quite well the correct stable ice structure at nearly the correct density [19]. However, by uniting the sites, this approximation cannot capture the dielectric response of an ideal gas of polar molecules and so provides a poor starting point for the study of dielectric effects.

The key observation which allows us to overcome the inversion problem is that the free-energy of a noninteracting molecular system, being a very complicated functional of the site densities, is a very simple functional of the relative potentials. This parallels the situation in electronic density-functional theory, where there is no known accurate functional for $T_s[n]$, the noninteracting (kinetic) energy, in terms of the density, but where this energy is easily written *exactly* in terms of single-particle orbitals. It was the transition from fully interacting electrons to a corresponding set of fictitious noninteracting particles, as proposed by Kohn and Sham [20], which allowed for the construction of accurate density functionals for the interacting electron gas. In the present case, the simplicity of evaluation of the grand free-energy of noninteracting molecules as a functional of the relative potentials suggests an analogous change of variables, now from the site densities to a set of effective relative potentials in which fictitious noninteracting molecules move.

Mathematically, a pair of Legendre transformations achieves this change of variables. Thermodynamically, the Legendre transform $\Omega^{(ni)} - \sum \int dr \psi_\alpha n_\alpha$ equals the intrinsic Helmholtz free-energy of the noninteracting system. Adding the internal energy U due to intermolecular interactions and the contribution of the *physical* external potentials ϕ_α yields the full Helmholtz free-energy of the *interacting* system. Finally, the second Legendre transformation subtracts $\sum \int dr n_\alpha \mu_\alpha$ to form the full *interacting* grand free-energy Ω as a functional of the *effective* potentials Ψ_α ,

$$\Omega = \Omega^{(ni)} - \sum_{\alpha=1}^M \int d^3r [\Psi_\alpha(\mathbf{r}) - \phi_\alpha(\mathbf{r}) + \mu_\alpha] n_\alpha(\mathbf{r}) + U[\mathbf{n}], \quad (2)$$

where $\mathbf{n} = \{n_1(\mathbf{r}), \dots, n_M(\mathbf{r})\}$, the set of densities, is explicitly a functional of the effective relative potentials $\Psi = \{\Psi_1(\mathbf{r}), \dots, \Psi_M(\mathbf{r})\}$ via $n_\alpha(\mathbf{r}) = n_\alpha^{(ni)}[\Psi](\mathbf{r}) \equiv \delta\Omega^{(ni)} / \delta\psi_\alpha(\mathbf{r})[\Psi]$. The effective relative potentials that minimize $\Omega[\Psi]$ then determine the equilibrium site densities and

allow for the calculation of the various equilibrium properties of the liquid. We mention that minimization with respect to the effective potential is known in the electron structure context as the optimized potential method [21].

Construction of approximate functionals.—As usual with density-functional theories, the construction of the internal energy U is difficult. Again, we follow the lead of Kohn and Sham and construct a free-energy functional that reproduces established results for the homogeneous phase in the limit of vanishing external fields. The Ornstein-Zernike (OZ) equation gives information about the analytic structure of U , in particular, it gives $\partial^2 U$, the Hessian of U with respect to the densities, as the difference between the inverses of the full and noninteracting correlation function matrices [22]. In the special case of the homogeneous phase, translational invariance then turns the OZ equation into a simple matrix equation in Fourier space, with one component for each field.

From now on, we will limit the discussion to a special class of liquids, which includes all diatomics and the liquid of most interest, water. The liquids in this class have the property that the lowest-order term in the long-wavelength expansion of the Hessian of $U[\mathbf{n}]$ has the form

$$K_{\alpha\gamma}(\mathbf{k}) = \left[\frac{\epsilon}{\epsilon - 1} - \frac{\epsilon^{(ni)}}{\epsilon^{(ni)} - 1} \right] \frac{4\pi}{\mathbf{k}^2} q_\alpha q_\gamma, \quad (3)$$

where q_α are the partial site charges, ϵ is the macroscopic dielectric constant and $\epsilon^{(ni)}$ is the dielectric constant of a system with intramolecular correlations only. This result may be derived by expanding the interacting and noninteracting correlation functions as $E + Fk^2 + \dots$, where there are no linear terms in k by rotational invariance, and E and F are matrices of coefficients, with one combination of coefficients from F giving the dielectric constant. In the cases of molecules described either by two sites or by three sites with a mirror plane symmetry, one can show that the *only* combination of the coefficients in F which enters the leading-order term in the OZ equation corresponds *exactly* to the bulk dielectric constant. All liquids composed of such molecules thus have the property that the long-wavelength dielectric response can be built into the free-energy functional without *any* knowledge of the long-wavelength limit of the experimental correlation functions (other than ϵ).

In general, we may view the internal energy U as expanded in a power series about the uniform liquid, with all terms, except the quadratic part (whose Hessian is given by (3) in the long-wavelength limit) gathered into an excess part, F^{ex} , which plays exactly the same role as the exchange-correlation functional of Kohn-Sham theory: it ensures proper bulk thermodynamic behavior and will ultimately be treated in some approximate way. We note that the constant term in the power series expansion of U determines the bulk thermodynamics (which we include in F^{ex}) and the linear term vanishes in the uniform equilibrium state of the system. Putting this all together gives

$$U[\mathbf{n}] = \frac{1}{2} \sum_{\alpha, \gamma=1}^M \int d^3r \int d^3r' n_{\alpha}(\mathbf{r}) \{ K_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') + C_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') \} n_{\gamma}(\mathbf{r}') + F^{\text{ex}}[\mathbf{n}], \quad (4)$$

where $C_{\alpha\gamma}$ describes those parts of the Hessian $\partial^2 U$ which K fails to capture.

To approximate F^{ex} , we first note that, in the case of zero external fields, all densities are equal and the first quadratic term (K) in (4) vanishes because of charge neutrality. Anticipating that the matrix function C will be constructed to vanish in the long-wavelength limit, F^{ex} then captures all the internal energy of the uniform phase and can be expressed as $F^{\text{ex}} = V f^{\text{ex}}(n)$, with V being the volume and n the average molecular density. Because of the presence of multiple density fields, generalizing this expression to the inhomogeneous case is more difficult than for the analogous exchange-correlation energy in electronic structure theory. Also, because of the strong correlations induced by excluded volume effects, *purely local* excess functionals fail to describe the liquid state [23]. We therefore approximate F^{ex} with a simplified *ansatz* in the spirit of weighted density-functional theory [23], but generalized to multiple species by allowing different weights b_{γ}^i for the various densities,

$$F^{\text{ex}}[\mathbf{n}] = \int d^3r \sum_i p_i f^{\text{ex}} \left(\sum_{\gamma=1}^M b_{\gamma}^i \bar{n}_{\gamma}(\mathbf{r}) \right), \quad (5)$$

where we introduce the weighted densities $\bar{n}_{\gamma}(\mathbf{r}) = \int d^3r' (\pi r_0^2)^{-3/2} \exp(-|\mathbf{r} - \mathbf{r}'|^2/r_0^2) n_{\gamma}(\mathbf{r}')$, with r_0 being a parameter ultimately fit to the experimental surface tension. To reduce to the correct form in the uniform case p_i and b_{γ}^i must fulfill $\sum_i p_i = 1$ and $\sum_{\gamma=1}^M b_{\gamma}^i = 1$.

To capture the behavior of the scalar function $f^{\text{ex}}(n)$, we use a polynomial fit to various bulk thermodynamic conditions. The condition that C vanishes in the long-wavelength limit subsequently fixes p_i and b_{γ}^i and ensures that C will be bandwidth limited and thus amenable to numerical approximation. For a given r_0 , this then completely specifies our approximation to F^{ex} . Next, relating $K + C + \partial^2 F^{\text{ex}}$ to the density-density correlation functions through the OZ relation then gives the matrix function C for a given r_0 . Finally, we can determine r_0 by adjustment until calculations of the liquid-vapor interface give the correct surface tension.

Hydrogen chloride.—We choose liquid hydrogen chloride as a model physical system exhibiting hydrogen bonding and for which detailed experimental data are available, including site-site correlation functions [24,25].

Assuming rigid intramolecular bonds, the distribution function becomes $s(\mathbf{r}_1, \mathbf{r}_2) = \delta(|\mathbf{r}_1 - \mathbf{r}_2| - B)/4\pi B^2$, with the gas phase bond length $B = 1.275 \text{ \AA}$ taken from experiment [25] and 1 and 2 referring to hydrogen and chlorine, respectively. We then select the partial charges to yield the experimental gas phase dipole moment [26],

resulting in $q_1 = -q_2 = 0.171e$ with e being the fundamental charge. Then, we approximate the simple bulk function $f^{\text{ex}}(n)$ by a fourth-order polynomial with coefficients adjusted to (a) reproduce the bulk modulus of the liquid phase and (b) to allow for coexistence of stable liquid and vapor phases at the appropriate densities, where the latter is treated as an ideal gas. Next, for the excess free-energy *functional*, the requirement that the matrix C vanishes in the long-wavelength limit fixes the integrand in (5) to be $[3f^{\text{ex}}(\bar{n}_1) + 4f^{\text{ex}}((\bar{n}_1 + \bar{n}_2)/2) + 3f^{\text{ex}}(\bar{n}_2)]/10$, under the assumption that the constant term (in an expansion in powers of k^2) of the inverse correlation function is proportional to that of the noninteracting case. Then, we determine C as described above using the partial structure factor data for the uniform liquid [24] and the macroscopic dielectric constant [27] as experimental inputs. Adjusting the smoothing parameter to give the experimental surface tension [28] yields $r_0 = 4.55 \text{ \AA}$.

Results.—As a test case, we study the behavior of liquid hydrogen chloride at $T = 194 \text{ K}$, $P = 4.5 \text{ bar}$ (chosen due to availability of experimental correlation functions [24]), which is in the liquid part of the phase diagram somewhere near the triple point. Figures 1(a) and 1(b) show the equilibrium density profiles which our theory predicts in a parallel plate capacitor (described as an infinite square-well potential for both species) in both moderate and strong applied fields, respectively. For comparison, the figure also shows the zero-field density profiles.

The zero-field profiles exhibit an extended gas phase region up to a distance of $\sim 1 \text{ nm}$ from the plates. This “lingering” gas phase region exists because molecules can minimize the influence of the repulsive walls by leaving the system and entering the reservoir at very little free-energy cost. As soon as a relatively weak external electric displacement D is applied, however, it becomes favorable for the dipolar molecules to enter the capacitor, largely destroying the gas phase region and resulting in an almost

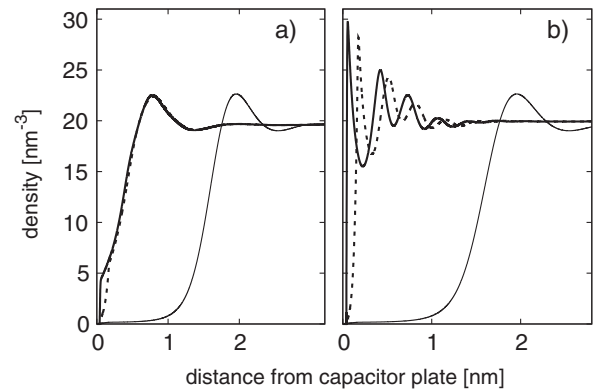


FIG. 1. Hydrogen- (thick dotted curves) and chlorine- (thick solid curves) site density versus distance from hard wall in (a) moderate and (b) high applied field. Reference results for zero field given in both panels (thin solid curves).

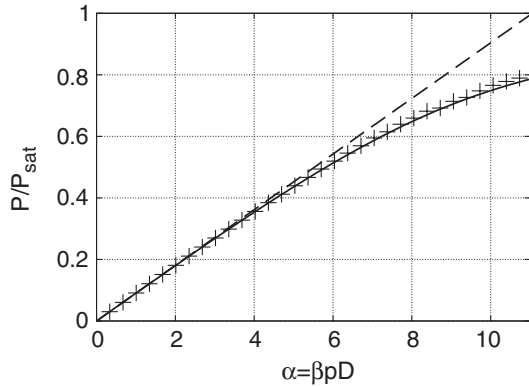


FIG. 2. Electric saturation fraction (P/P_{sat}) versus applied electric displacement (D): density-functional results (crosses), nonlinear electrostatics (solid line), linear response (dashed line).

rigid shift of the density profiles towards the capacitor walls for a large range of fields until the nonlinear dielectric response regime is reached. Figure 1(a) shows an example of this behavior for a relatively large field but where the dielectric response is still fairly linear ($\alpha \equiv \beta p D = 2.68$, where p is the molecular dipole moment). A dramatic qualitative change occurs in the strong field case. Figure 1(b), computed at $\alpha = 7.38$, shows the typical behavior in the high-field case. At large fields, the profile for each species exhibits a sharp peak followed by strong oscillations, where the peaks and oscillations are separated by one molecular bond length (~ 0.12 nm) indicating that they are the result of strong orientational ordering of the molecular dipoles. The oscillations of the site densities suggest an induced layering of molecules close to the surface, which results from the reorganization of the hydrogen-bond network in response to the increasing dipolar alignment of the molecules. The wavelength of the observed oscillations is about ~ 0.3 nm, corresponding to the length of the hydrogen bond [8].

The equilibrium site densities determine the induced polarization. Figure 2 compares the polarization, computed from our density-functional theory, to the result of self-consistently screened nonlinear electrostatics, computed by solving for the polarization P such that $P = P^{(ni)}(D - a_\epsilon 4\pi P)$, where $P^{(ni)}(E)$ is the response of a gas of non-interacting dipoles in a local field E and $a_\epsilon \equiv \epsilon/(\epsilon - 1) - \epsilon^{(ni)}/(\epsilon^{(ni)} - 1)$ ensures that for small D the correct linear response is recovered. Figure 2 shows that our density-functional theory not only reproduces the linear regime but also captures saturation effects.

In conclusion, we have shown how a Kohn-Sham-like change of variables yields a numerically efficient and accurate density-functional theory for molecular liquids. The resulting theory has the computational cost of the problem of a noninteracting gas of molecules in a self-consistent external potential. We have shown how to construct a functional in this approach which captures the

coexistence of liquid and vapor phases, the surface tension between these phases, and, for the liquid, the bulk mechanical properties, site-site correlation functions, linear dielectric response, and self-consistent dielectric saturation effects. Without modification, the current approach is ready to be developed for the liquid of greatest scientific interest: water.

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