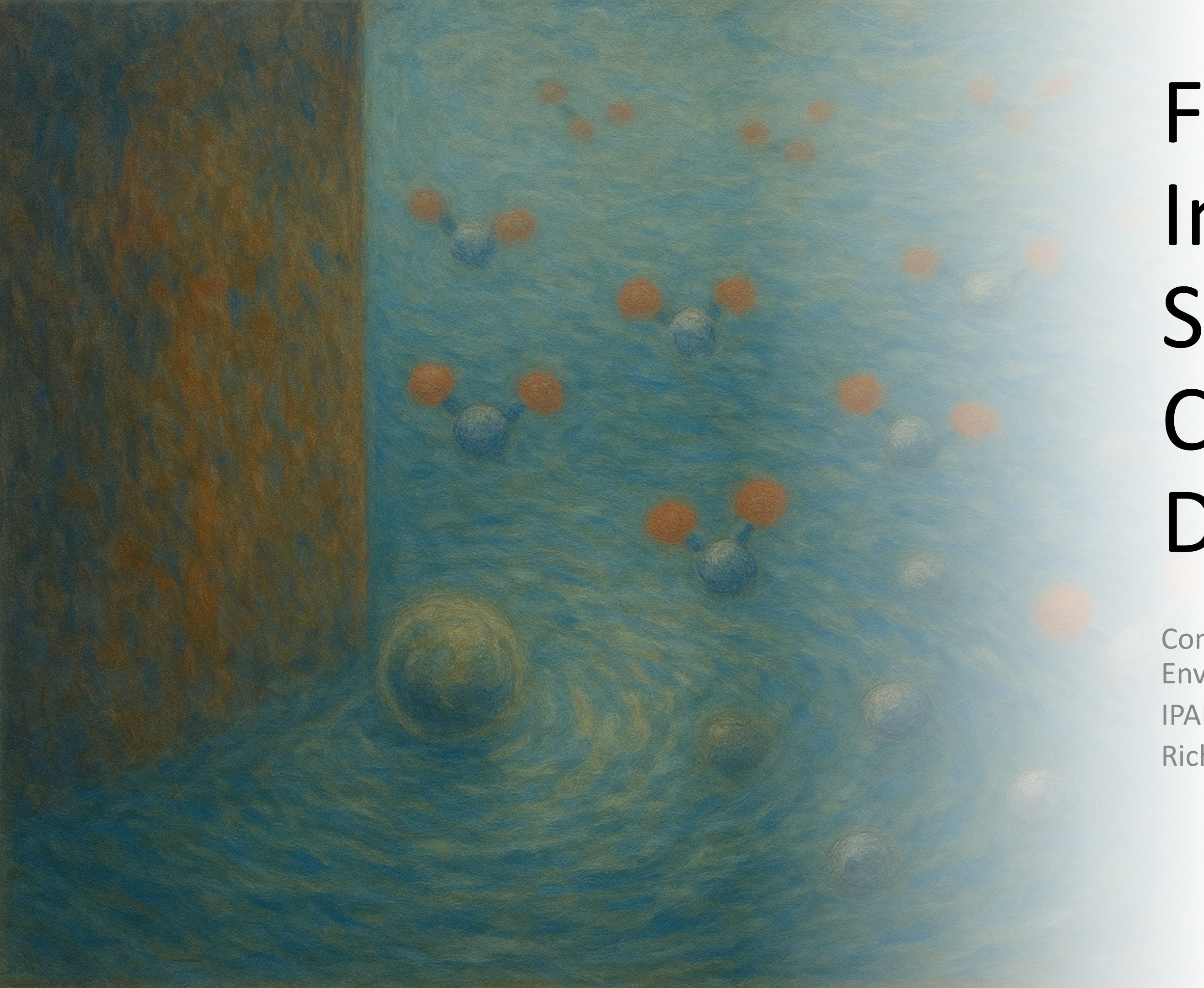


From Implicit Solvation to Classical DFT

Continuum Descriptions of Liquid Environments

IPAM Tutorial – Fall 2025

Richard G. Hennig, University of Florida

Part I: Implicit Solvation Models

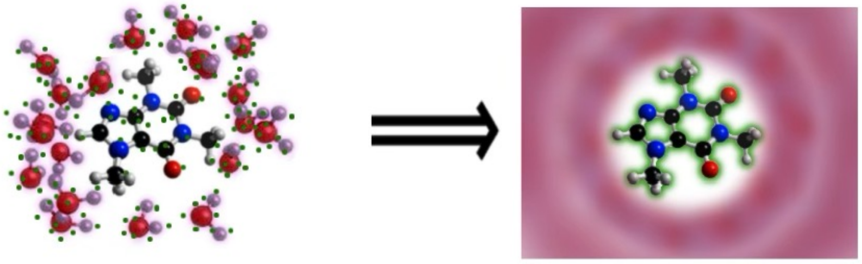


Image courtesy of Shankar (2013)

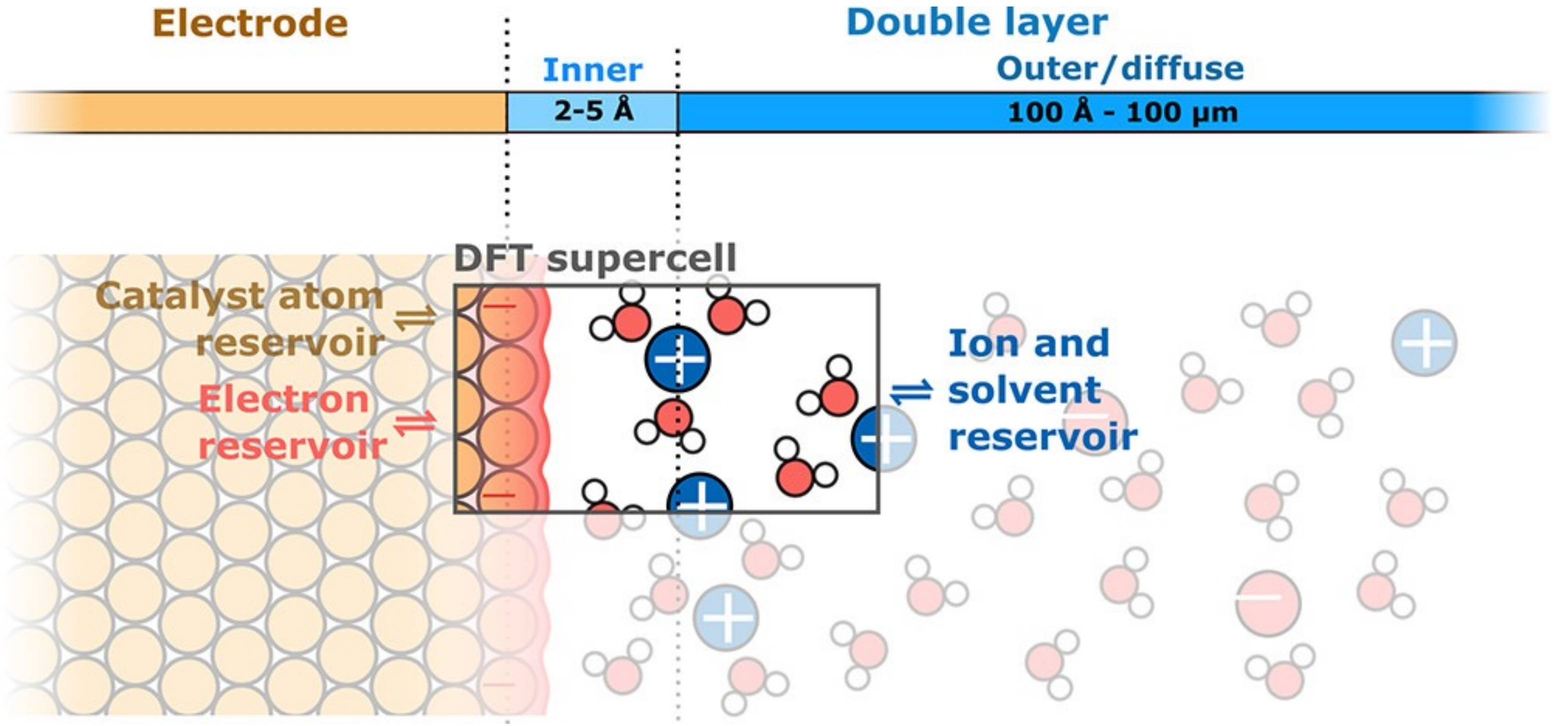
Motivation

- Electrochemical and catalytic processes at solid-liquid interfaces are controlled by solvent effects.
- **Explicit solvent models** are accurate but computationally expensive due to the need for extensive sampling.
- **Implicit solvation models** offer a **computationally efficient** alternative by treating the solvent as a continuous polarizable medium.

Goal

- Efficiently simulate electrochemical interfaces
- Replace explicit solvent molecules with dielectric continuum
- Models widely used in DFT codes:
  VASPsol, JDFTx, SALSA, CANDLE

Spatial Decomposition



Solute region, explicitly described by DFT | Interface region | Electrolyte region, Implicitly described by Poisson-Boltzmann equation

Chem. Rev. 2022, 122, 10777

Key Concepts

Continuum Representation:

- Solvent is modeled as a dielectric continuum, removing the need for explicit solvent molecules.

Electrostatic & Non-Electrostatic Energy Contributions:

- **Electrostatic contribution** via solution of the Poisson or Poisson–Boltzmann equations.
- **Non-electrostatic terms** (e.g., cavitation, dispersion, repulsion) treated empirically or semi-empirically.

$$\nabla \cdot [\varepsilon(\mathbf{r})\nabla\phi(\mathbf{r})] = -\rho(\mathbf{r})$$

$$\nabla \cdot [\varepsilon(\mathbf{r})\nabla\phi(\mathbf{r})] = -\rho_{\mathrm{solute}}(\mathbf{r}) - \rho_{\mathrm{ion}}(\mathbf{r})$$

Cavity Formation:

- A solute-shaped cavity is defined, typically based on electron density or atom positions.

Energy Functional Perspective of Implicit Solvation

Why Use an Energy Functional?

- The implicit solvent model describes a **thermodynamic system**: Solute (quantum-mechanical), interface, and continuum solvent.
- The **Gibbs free energy** $G[\rho,\phi]$ serves as a **variational functional**.
- All governing equations follow from minimizing this energy:

$$\delta G[\rho,\phi] = 0 \quad \Rightarrow \quad \text{Euler–Lagrange equations}$$

2. Total Energy Functional (General Form)

$$G[\rho,\phi] = E_{\mathrm{DFT}}[\rho] + G_{\mathrm{solvent}}[\rho,\phi]]$$

$$\text{with } \; G_{\mathrm{solvent}}[\rho,\phi] = E_{\mathrm{electr}}[\rho,\phi] + G_{\mathrm{cav}} + G_{\mathrm{disp}} + G_{\mathrm{rep}} + G_{\mathrm{ion}}[\phi]$$

Hierarchy of Energy Contributions

$$G[\rho, \phi] = E_{\mathrm{DFT}}[\rho] + G_{\mathrm{solvent}}[\rho, \phi]]$$

$$\text{with } G_{\mathrm{solvent}}[\rho, \phi] = E_{\mathrm{electr}}[\rho, \phi] + G_{\mathrm{cav}} + G_{\mathrm{disp}} + G_{\mathrm{rep}} + G_{\mathrm{ion}}[\phi]$$

- Each term corresponds to a physically motivated energy component

Contribution	**Description**	**Impact**
E_{electr}	Electrostatic energy	Solvent polarization
G_{ion}	Ionic entropy, screening	Double-layer formation
G_{cav}	Cavity formation work	Solute–solvent boundary
G_{disp}	Dispersion	van der Waals attraction
G_{rep}	Repulsion	Short-range solvent exclusion

- Systematic inclusion and adjustment improves fidelity and transferability.
- Advanced models (e.g. SaLSA, CANDLE) adjust or improve these components.

Inhomogeneous Poisson Equation

- Start with the electrostatic energy:

$$E_{\text{electr}}[\phi] = \frac{1}{2}\int \varepsilon(\mathbf{r})|\nabla\phi(\mathbf{r})|^2 \; d\mathbf{r}$$

- To minimize this energy with respect to the electrostatic potential, we take the functional derivative with respect to $\phi(\mathbf{r})$ and set this to zero

$$\frac{\delta E_{\text{electr}}}{\delta\phi(\mathbf{r})} = -\nabla\cdot[\varepsilon(\mathbf{r})\nabla\phi(\mathbf{r})] - \rho(\mathbf{r}) = 0$$

- The resulting equation is the Poisson Equation

$$\boxed{\nabla\cdot[\varepsilon(\mathbf{r})\nabla\phi(\mathbf{r})] = \rho(\mathbf{r})}$$

- Boundary conditions and numerical solution depend on code

Inhomogeneous Poisson-Boltzmann Equation

- Add the **ideal entropy** of mixing term for the ions:

$$G_{\text{ion}} = -TS_{ion} \quad \text{with} \quad S_{\text{ion}} = -k_{\text{B}} \int_V \sum_i c_{\text{i}} \ln\left(\frac{c_i}{c_i^0}\right) \mathrm{d}\mathbf{r}$$

and Boltzmann distribution for $c_i = c_i^0 \exp\left(-\frac{z_i\, e\, \phi}{k_B T}\right)$

and ionic charge density $\rho_{\text{ion}} = \sum_i e\, z_i\, c_i$

- Minimization with respect to $\phi(\mathbf{r})$ leads too the Poisson-Boltzmann Equation

$$\boxed{\nabla \cdot [\varepsilon(\mathbf{r}) \nabla \phi(\mathbf{r})] = -\rho_{\text{solute}}(\mathbf{r}) - \rho_{\text{ion}}(\mathbf{r})}$$

Free Energy of Solute-Solvent System

- Linear approximation: polarization proportional to the external field

$$\mathbf{P} = \{\epsilon(\mathbf{r}) - 1\}\mathbf{E}$$

- Energy of solvated system

$$E[n(r), \phi(r)] = \underbrace{E_{\mathrm{TXC}}[n(r)]}_{\text{kinetic + exchange correlation}} + \int_V \phi(r)(\rho_{\mathrm{solute}} + \rho_{\mathrm{ion}}(r))\, d^3r$$

$$- \int_V \underbrace{\frac{\epsilon(r)}{8\pi} |\vec{\nabla}\phi(r)|^2\, d^3r}_{\text{Bound charge interaction}} + \underbrace{\tau A}_{\text{Cavitation energy}}$$

$$- \underbrace{kTS_{\mathrm{ion}}}_{\text{Entropy of mixing}}$$

Energy Minimization

- Total energy functional *E*[*n*(**r**), ϕ(**r**)] of charge density *n*(**r**) and the electrostatic potential ϕ(**r**)
- Minimization with respect to *n*(**r**) ⇒ Modified Kohn-Sham Hamiltonian

$$\Bigg[\frac{-\nabla^2}{2} + \underbrace{V_{\text{vac}}(r)}_{\text{vacuum potential}} + \Delta\phi(r) - \frac{d\epsilon(r)}{dn}\frac{|\nabla\phi|^2}{8\pi} + \tau\frac{\delta A_{\text{cav}}}{\delta n} + kT\frac{\delta S_{\text{ion}}}{\delta n}\Bigg]\psi_i = \epsilon_i\psi_i$$

Advantages of the Energy Functional Approach

- Provides a **first-principles rationale** for model construction.
- Enables **self-consistent coupling** to electronic DFT.
- Framework aligns with **variational methods**, enabling mathematically rigorous improvements.
- Supports **extension to dynamics, fluctuations, and nonlocal effects**.

Evolution of Implicit Solvation Models

1. Classical Foundations (1920s - 1980s)

- **Born Model (1920):** Ion as a charged sphere in a dielectric continuum.
  Max Born, *Z. Phys.* 1920, 1, 45–48.

$$\Delta G_{\text{Born}} = -\frac{1}{8\pi\varepsilon_0}\left(1 - \frac{1}{\varepsilon_r}\right)\frac{q^2}{R}$$

- **Onsager Model (1936):** Reaction field theory for polar solutes in spherical cavities.
  Lars Onsager, *J. Am. Chem. Soc.* 1936, 58, 1486.

$$\Delta G_{\text{Onsager}} = -\frac{\mu^2}{a^3} \cdot \frac{(\varepsilon_r - 1)}{(2\varepsilon_r + 1)}$$

- **Kirkwood-Onsager Theory (1939):** Statistical mechanical accounts for the orientational correlation in polar solvents,.
  John Gamble Kirkwood, *J. Chem. Phys.* 1939, 7, 911.

$$\varepsilon_r = 1 + \frac{4\pi N_A \rho \mu^2}{9 k_B T} \cdot \left[1 + \sum_{i \neq j} \langle \cos\theta_{ij} \rangle\right]$$

Evolution of Implicit Solvation Models

2. Polarizable Continuum Models - PCM (1980s–1990s)

- **IEF-PCM and CPCM (Gaussian codes)**: Surface charge-based solvation in fixed atom-centered cavities. J. Tomasi & M. Persico, *Chem. Rev*. 1994, 94, 2027.
- **Limitations**: Sharp boundaries; not compatible with plane-wave DFT; limited for charged or asymmetric systems.

3. Density-Based Dielectric Models (2002-2003)

- **Methodological Origin:** Fattebert and Gygi
- Introduced smooth dielectric cavity as local function of electron density $n(\mathbf{r})$.
- Avoids discontinuities and enables variational derivation of the electrostatic equation.
- Introduced functional minimization framework leading to the modified Poisson equation:

$$\nabla \cdot \left(\varepsilon[n(\mathbf{r})]\nabla\phi(\mathbf{r})\right) = -n(\mathbf{r})$$

- Fattebert & Gygi, *J. Comput. Chem*. 2002, 23, 662–666.
  Fattebert & Gygi, *Int. J. Quantum Chem*. 2003, 93, 139–147.

Evolution of Implicit Solvation Models

4. Self-Consistent Continuum Solvation and Major Code Implementations

- Andreussi, Dabo, I.; Marzari, N. J. Chem. Phys. 2012, 136, 064102:
  - Improved switching function for numerical robustness.
  - Formulated a variational functional ensuring accurate forces and stresses.
  - **Quantum Espresso** implementation
- **JDFTx** (formulation as joint DFT)
  Sundararaman, Gunceler, Arias, JCP 2014, 140, 144504.
- **VASPsol**
  Mathew, Sundararaman, Letchworth-Weaver, Arias, Hennig, JCP 2014, 140, 084106 and Mathew, Kolluru, Mula, Steinmann, Hennig, JCP 2019, 151, 234101
- **VASPsol++** (adds Stern layer, constant potential, and improved numerical implementation)
  Islam, Khezeli, Ringe, Plaisance, JCP 2023, 159, 234117

Beyond Local Dielectrics – Spherically Averaged Liquid Susceptibility Ansatz

Motivation

- Traditional implicit solvation models rely on **local dielectric functions** $\varepsilon[n(r)]$, which:
  - Assume local response to electric fields.
  - Are symmetric with respect to cation/anion solvation.
- But **real solvents exhibit nonlocal correlations** and **asymmetric response**, especially at charged interfaces.

Starting Point: Linear Response Theory of the Solvent

- Derived from classical DFT.
- Solvent response is written in terms of a **nonlocal susceptibility kernel** $\boldsymbol{\chi}(\mathbf{r}, \mathbf{r}')$:

$$\rho_{\mathrm{ind}}(\mathbf{r}) = \int \chi(|\mathbf{r} - \mathbf{r}'|)\phi(\mathbf{r}')\, d\mathbf{r}'$$

- Induced charge density produces dielectric screening effect.

Sundararaman & Goddard, *J. Chem. Phys.* 2015, 142, 064107

Beyond Local Dielectrics – Spherically Averaged Liquid Susceptibility Ansatz

Effective Dielectric Operator

- Rather than defining a scalar dielectric function $\varepsilon(\mathbf{r})$, SaLSA uses an operator form of the dielectric response.
- The screened electrostatic potential satisfies a generalized Poisson equation:

$$\nabla \cdot [\varepsilon_0 \nabla \phi(\mathbf{r})] + \rho_{\text{ind}}[\phi] = -\rho_{\text{solute}}(\mathbf{r}))$$

with

$$\rho_{\text{ind}}(\mathbf{r}) = \int \chi(|\mathbf{r} - \mathbf{r}'|)\, \phi(\mathbf{r}')\, d\mathbf{r}'$$

- χ is spherically averaged nonlocal susceptibility kernel.
- Obtained from classical DFT of solvent.

Sundararaman & Goddard, *J. Chem. Phys.* 2015, 142, 064107

Beyond Local Dielectrics – Spherically Averaged Liquid Susceptibility Ansatz

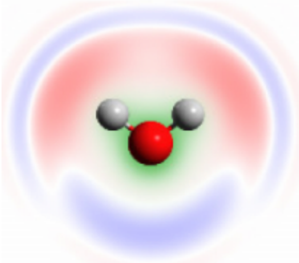
Cavity Definition in SaLSA

- Instead of defining a cavity using a critical electron density n_c, SaLSA constructs solvent response as:

$$\rho_{\text{solv}}(\mathbf{r}) = \int n_{\text{solv}}(\mathbf{r} - \mathbf{r}') \cdot s(\mathbf{r}')\, d\mathbf{r}'$$

where:

- n_{solv}: Solvent molecule’s charge distribution (electrons and nuclei), spherically averaged.
- $s(\mathbf{r}')$: Shape function indicating solvent accessibility around the solute (often derived from convolution of solute’s density with a kernel)
- Cavity emerges naturally via overlap of solvent and solute charge densities No longer requiring a sharp boundary or switching function.
- Parameter-free physically-motivated model.



SaLSA

LinearPCM

Sundararaman & Goddard, *J. Chem. Phys.* 2015, 142, 064107

Benchmarks of Solvation Models

Oğuz, Vassetti, Labat, Theor. Chem. Accounts 2021, 140, 99.

Units: kcal/mol	Mean Absolute Error	Mean Signed Error	Root Mean Squared Error
SMD	1.21	0.80	1.70
VASPsol	1.27	0.14	1.68
FDPB	0.74	0.02	1.05

- Compares three continuum solvation models:
  - Solvation Model Density (SMD)
  - VASPsol
  - Finite-Difference Poisson Boltzmann (FDPB)
- Hydration energies of molecules, polymers and semiconductor surfaces
- 630 neutral molecules of the FreeSolv test shown on the right
- Accuracy of SMD similar to VASPsol with improved accuracy for FDPB
- FDPB solves the Poisson equation on a 3D grid with a sharp dielectric interface and atomic charges taken from a force-field and distributed on the 3D grid to represent the solute charge density
- All models use cacity surface energy and solvent permittivity as parameters.
- FDPB also uses atomic charges and radii for each solvent atom type, SMD uses atomic radii and many other solvent parameters. VASPsol uses only two parameters (n_c and σ for interface)

Benchmarks of Solvation Models

MNSol – experimental solvation energy dataset by Don Truhlar

- https://comp.chem.umn.edu/solvation
- 274 aqueous + 679 non-aqueous solutions, 19 unique solvents, 392 neutral solutes
- Benchmark on 274 $\Delta G_{\mathrm{sol}}^{\mathrm{exp}}$ from MNSol

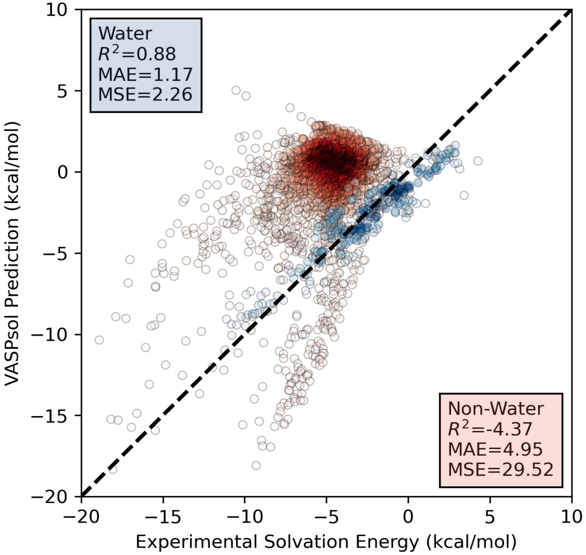
Solvation Models	**MAE (kcal/mol)**
COSMO-RS (GAUSSIAN)*	0.5
SM8 (Q-CHEM)*	0.6
VASPsol (VASP)	1.2
FDPB	1.3
C-PCM (GAMESS)	1.6
COSMO (GAUSSIAN)	2.2

VASPsol performs well for **aqueous solutions**, on par with other models.

Benchmarks of Non-Aqueous Solutions

MNSol – experimental solvation energy dataset by Don Truhlar

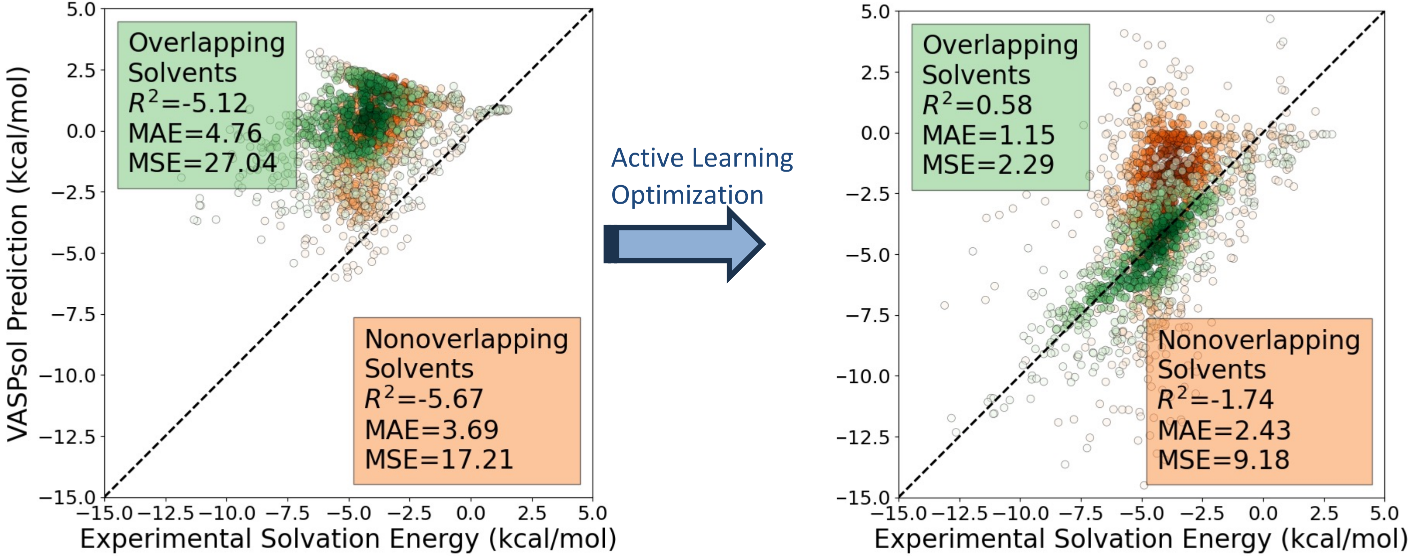
- https://comp.chem.umn.edu/solvation
- 274 aqueous + 679 non-aqueous solutions, 19 unique solvents, 392 neutral solutes
- Benchmark on 274 ΔG_{sol}^{exp} from MNSol



Do not just update ε and use default parameters for non-aqueous solutions.

Machine Learning of VASPsol Parameters

- Machine learning on data from MNSol
- Testing on Solv@TUM, https://mediatum.ub.tum.de/1452571
- 67 non-aqueous solvents, 5952 Experimental solvation energies from partition coefficients
- Used 1801 solutions of 48 non-aqueous solvents and 351 solutes



Some solvents have consistent underpredictions

Combined:
MAE: 1.92 kcal/mol
R^2: -0.5

AI model for VASPsol can generalize to unseen solvents and parameterize them

Implicit Solvation Models

Implicit Solvation Models – Key Takeaways

- Why: Capture solvent effects efficiently for electrochemistry & catalysis.
- How: Replace explicit molecules with dielectric continuum + empirical corrections.
- Strengths: Self-consistent, variational framework; implemented in major DFT codes; robust for aqueous systems.
- Limitations: Local, mean-field, static response → miss solvent structure & dynamics.
- Frontiers: Machine learning, nonlocal kernels, explicit-implicit hybrids.
- Vision: Toward predictive, transferable solvation models bridging atomistic DFT and experimental observables.

Assumptions and Limitations

- Locality: $\varepsilon(\mathbf{r})$ depends on $n(\mathbf{r})$ or $\phi(\mathbf{r})$, no spatial kernel.
- Mean-field treatment of ions (Boltzmann distributions).
- Static response: no time dependence or memory.
- Implicit models miss solvent structure and fluctuations.

Part II: Classical Density Functional Theory (cDFT)

From Hohenberg-Kohn to Solvation Models

Motivation

- Fluids & electrolytes: inhomogeneous, correlated, hard to atomistically simulate
- Continuum solvation models: fast but structureless
- Classical DFT: statistical mechanics reformulated in density space
- Goal: equilibrium density $\rho(\mathbf{r})$, solvation free energies, interfacial structure.

Fundamental Theorems & Variational Principles

Quantum DFT (Hohenberg–Kohn, 1964)

Theorem:

- Ground-state electron density $n_0(\mathbf{r})$ uniquely determines external potential $V_{\text{ext}}(\mathbf{r})$ (up to a constant).

Consequence:

- All observables are unique functionals of $n_0(\mathbf{r})$.

Energy functional:

- $E[n] = F[n] + \int v_{\text{ext}}(\mathbf{r})\; n(\mathbf{r})\, d\mathbf{r}$, where $F[n]$ is the **universal functional** (kinetic + interactions).

Variational principle:

- Ground-state density minimizes total energy functional $E[n] \geq E[n_0]$, with equality for the true ground-state density $n_0(\mathbf{r})$.

References:

- P. Hohenberg & W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- W. Kohn & L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

Classical DFT (Evans, 1979)

Theorem (Evans):

- Equilibrium one-body density $\rho_{\text{eq}}(\mathbf{r})$ uniquely determines external potential $V_{\text{ext}}(\mathbf{r})$ (up to a constant).

Consequence:

- All equilibrium properties are unique functionals of $\rho(\mathbf{r})$.

Grand potential functional:

- $\Omega[\rho] = F[\rho] + \int (V_{\text{ext}}(\mathbf{r}) - \mu)\, \rho(\mathbf{r})\, d\mathbf{r}$, where $F[\rho]$ is the **intrinsic Helmholtz free energy functional**.

Variational principle:

- Equilibrium density minimizes grant potential energy functional $\Omega[\rho] \geq \Omega\left[\rho_{\text{eq}}\right]$, with equality at the equilibrium density.

Reference:

- R. Evans, *Adv. Phys.* **28**, 143–200 (1979).
- N. D. Mermin, *Phys. Rev.* **137**, A1441 (1965).
  (finite-T HK, precursor to cDFT form)

Decomposition of Functionals in Classical DFT

General Structure

- **Grand potential functional** written as $\Omega[\rho] = F[\rho] + \int dr\ (V_{\text{ext}}(r) - \mu)\,\rho(r)$, with $F[\rho] = F_{\text{id}}[\rho] + F_{\text{ex}}[\rho]$.

1. Ideal Gas Term (known exactly)

- Captures configurational entropy of non-interacting particles: $F_{\text{id}}[\rho] = k_B T \int dr\ \rho(r)\left[\ln\left(\Lambda^3 \rho(r)\right) - 1\right]$, where Λ is the thermal de Broglie wavelength.
- *Analogy:* with non-interacting kinetic energy $T_s[n]$ in quantum DFT.

2. Excess Free Energy Term (unknown / approximated)

- Encodes all particle interactions and correlations:

$$F_{\text{ex}}[\rho] = \text{repulsions} + \text{attractions} + \text{electrostatics} + \ldots$$

- **Hard-sphere repulsion:** Fundamental Measure Theory (FMT).
- **Dispersion/attraction:** mean-field or Weighted-Density Approximation (WDA).
- **Electrostatics:** primitive ion models, mean spherical approximation (MSA).
- **Molecular orientation:** Molecular DFT (MDFT).

Decomposition of Functionals in Classical DFT

General Structure

- **Grand potential functional** written as $\Omega[\rho] = F[\rho] + \int dr\ (V_{\text{ext}}(r) - \mu)\,\rho(r)$, with $F[\rho] = F_{\text{id}}[\rho] + F_{\text{ex}}[\rho]]$.

3. External Potential Term

- Interaction of the fluid with boundaries, fields, solutes: $\int V_{\text{ext}}(r)\ \rho(r)\ dr$.
- Examples:
  - solid wall → steric confinement
  - solute molecule → solvation shell
  - charged electrode → electrostatic double layer
- Analog to $\int v_{\text{ext}}\ n(\mathbf{r})\,d\mathbf{r}$ in quantum DFT.

Analogy with quantum DFT

Concept	**Quantum DFT**	**Classical DFT**
Basic variable	$n(\mathbf{r})$	$\rho(\mathbf{r})$
Theorem	Hohenberg–Kohn (1964)	Evans (1979)
Variational object	$E[n]$	$\Omega[\rho]$
Classical mean-field	$E_H[n]$ (known)	mean-field Coulomb part of excess free energy $F_{\text{ex}}[\rho]$
External	$\int V_{\text{ext}} n \, d\mathbf{r}$	$\int V_{\text{ext}} \rho \, d\mathbf{r}$
Unknown correlations	$E_{\text{xc}}[\text{n}]$	nontrivial $F_{\text{ex}}[\rho]$

$$\boxed{E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int v_{\text{ext}} \, n \, d\mathbf{r}}$$

$$\boxed{\Omega[\rho] = F_{\text{id}}[\rho] + F_{\text{ex}}[\rho] + \int (V_{\text{ext}} - \mu)\rho \, d\mathbf{r}}$$

Reference Models for Excess Functional F_{ex}

Hard-Sphere Repulsion (Packing Effects)

- Based on Fundamental Measure Theory (FMT)
- Rosenfeld (1989) introduced weighted densities to capture excluded-volume effects.
- White Bear refinements (1997–2002) improved accuracy for freezing & mixtures.
- Captures oscillatory density layering near walls or solutes.
- **Analogy:** provides the “baseline correlation functional,” similar to LDA in quantum DFT.

References

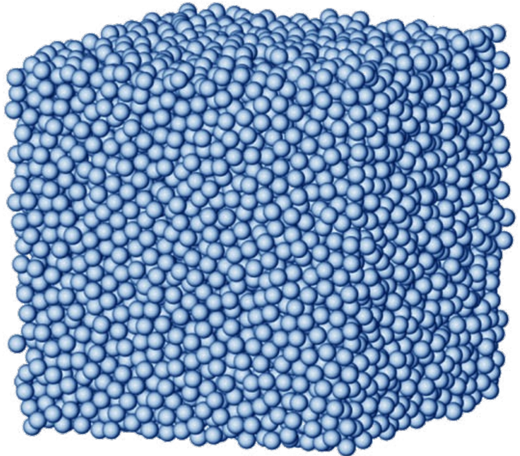
- Y. Rosenfeld, *Phys. Rev. Lett.* **63**, 980 (1989).
- R. Roth et al., *J. Phys.: Condens. Matter* **14**, 12063 (2002).
- H. Hansen-Goos & R. Roth, *J. Phys.: Condens. Matter* **18**, 8413 (2006).
- R. Roth, *J. Phys.: Condens. Matter* **22**, 063102 (2010).

Why “White Bear”? Not an acronym, just a nickname by Roth et al. (2002). The original Rosenfeld FMT predicted inaccurate freezing density, and inconsistent mixture thermodynamics.

“White Bear” functional (2002): Recast F_{ex} so bulk equation of state matches EOS for hard-spheres. It greatly improved the accuracy for freezing & mixtures.

“White Bear II” (Hansen-Goos & Roth, 2006) further refined for exact scaled-particle consistency.

- “Black bear” → original FMT with shortcomings.
- “White Bear” → corrected functional.



Baranau et al. Soft Matter 9, 3361 (2013)

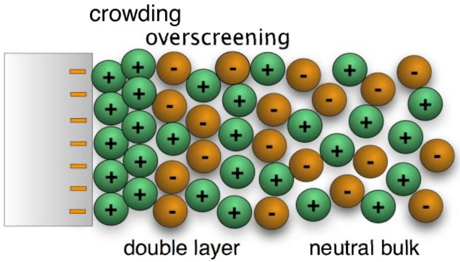
Dispersion and Electrostatic Interactions

Dispersion / Attractions

- Mean-field addition:
- $F_{\mathrm{att}}[\rho] = \frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}'\, \rho(\mathbf{r})\, U_{\mathrm{att}}(|\mathbf{r}-\mathbf{r}'|)\, \rho(\mathbf{r}')$ with attractive pair potential $U_{\mathrm{att}}(|\mathbf{r}-\mathbf{r}'|)$.
- Weighted-Density Approximations (WDA) uses uniform-fluid correlations as input.
- Applications: liquid–vapor coexistence, capillarity, freezing.

References

- A. R. Denton & N. W. Ashcroft, *Phys. Rev. A* **39**, 4701 (1989).
- R. Evans, *Mol. Phys.* **42**, 1169 (1981).



M. Bazant et al. PRL 106, 046102 (2011)

Electrostatics / Ionic Correlations

- Primitive model: charged hard spheres in dielectric.
- Excess free energy split into short-range (FMT) + Coulombic correlation (e.g., mean spherical approximation, MSA).
- Captures ionic layering and overscreening near charged electrodes.
- Important for electrolytes, ionic liquids, double-layer capacitance.

References

- J.-P. Hansen & I. R. McDonald, *Theory of Simple Liquids* (4th ed., 2013).
- R. Evans, “Density Functionals in the Theory of Nonuniform Fluids,” in Fundamentals of Inhomogeneous Fluids, ed. D. Henderson (Dekker, 1992).

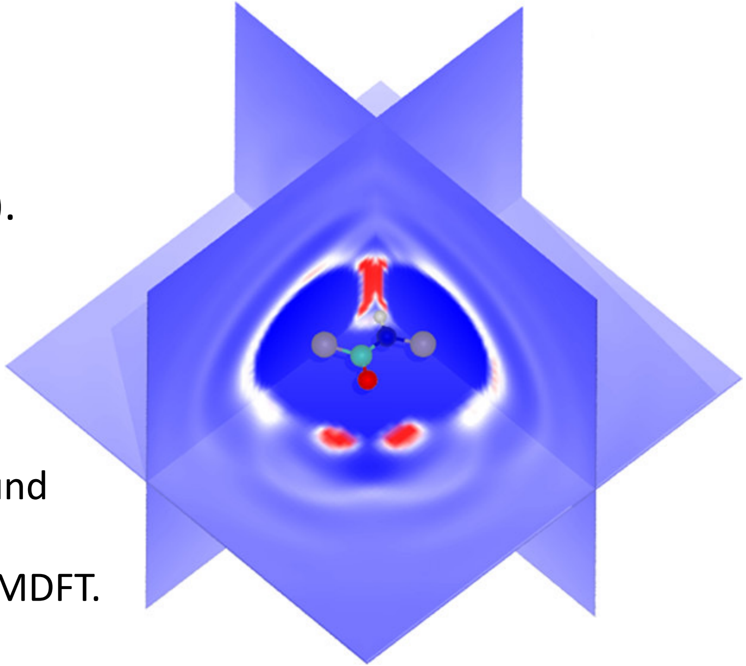
Molecular Fluids

Accounting for Orientation and Polarization)

- Molecular DFT (MDFT): Density extended to include orientation $\rho(r, \omega)$.
- Captures solvent polarization, hydrogen bonding, solvation structure.
- Efficient alternative to explicit solvent MD.
- Applications: solvation free energies, hydration shells, interfacial water.

References

- G. Jeanmairet et al., J. Phys. Chem. Lett. 4, 619 (2013).



3-D water density around
a N-methyl-acetamide
molecule obtained by MDFT.

Solvation Applications

Hydration Structure

- Ions (Na^+, Cl^-) in water: MDFT predicts radial distribution and free energy.
- Captures first solvation shell and dielectric screening.

Electrochemical Interfaces

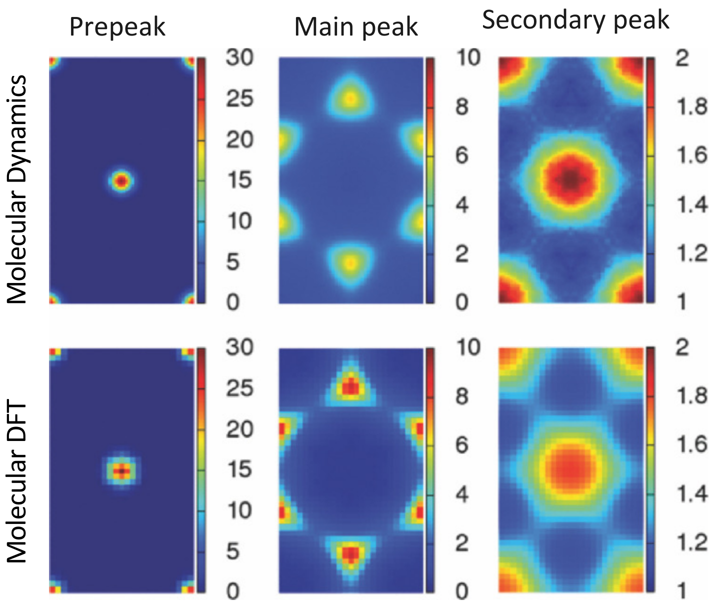
- Charged electrode + electrolyte: cDFT/MSA →double layer, overscreening, specific ion adsorption.

Porous Media / Adsorption

- Capillary condensation, wetting transitions.
- DFT predicts adsorption isotherms in porous carbons, MOFs.

References

- M. Levesque et al. *J. Chem. Phys*. 137, 224107 (2012)
- R. Evans, *Rep. Prog. Phys.* **67**, 1209 (2004).



Model solvent density of molecular solvent at clay interface [Levesque 2020].

Solvent Charge Density around Na^+ at Graphite Electrode

Setup

- Graphite electrode described by screened Poisson equation with Thomas–Fermi screening
- Na^+ ion fixed 5.1 Å above electrode, Solvent: SPC/E water.

Methods

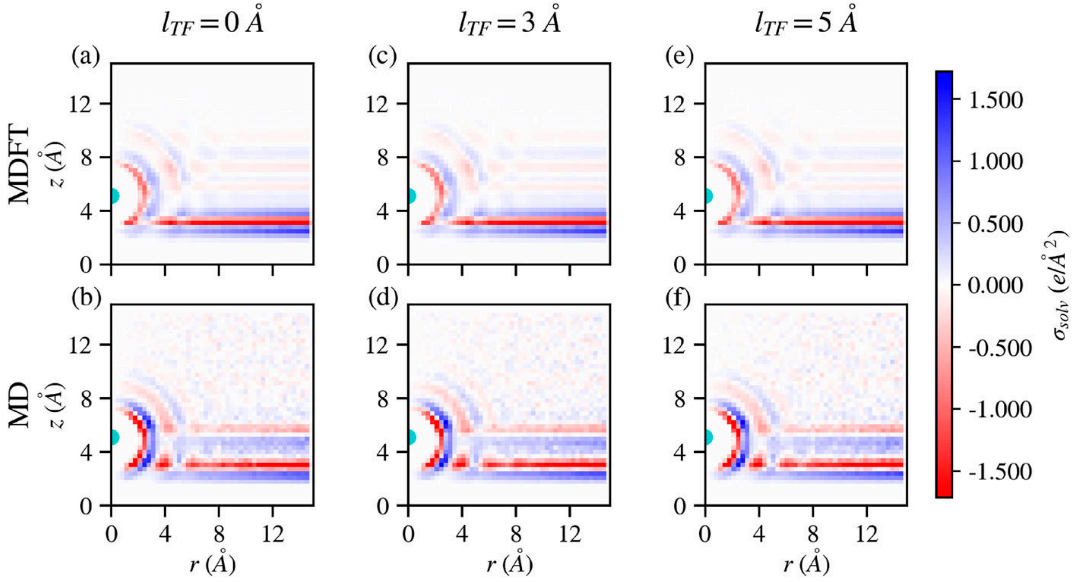
- Molecular Dynamics (8 ns, explicit water)
- Molecular DFT
  (implicit functional minimization)

Observable

- Average solvent charge density in cylindrical coordinates:

$$\rho_{\mathrm{solv}}(r,z) = \left\langle \sum_k q_k \; \delta(r_k - r)\, \delta(z_k - z) \right\rangle$$

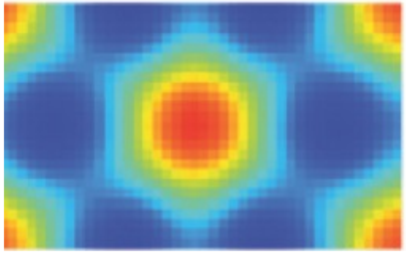
S. Nair, G. Jeanmairet, B. Rotenberg,
J. Chem. Phys. **163**, 014107 (2025).



Average charge density of water molecules in the (*r*, *z*) plane

From Implicit Solvation to Classical DFT

Concept: Reformulates equilibrium statistical mechanics in terms of density fields.

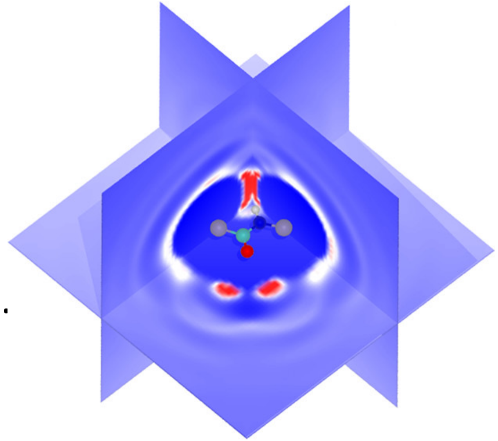


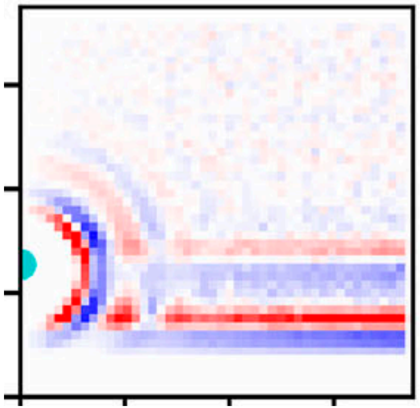
Theorems:

- Evans (1979): one-body density uniquely determines external potential.
- Variational principle: minimize $\Omega[\rho]$ for equilibrium.

Functional decomposition:

- $F_{\mathrm{id}}[\rho]$: ideal-gas entropy (exact).
- $F_{\mathrm{ex}}[\rho]$: interactions/correlations (approximated).
- $\mathrm{V}_{\mathrm{ext}}\ \rho$: system-specific external field.





Reference models for $F_{ex}[\rho]$:

- FMT (hard-sphere packing, White Bear refinements).
- Mean-field/WDA (dispersion).
- MSA hybrids (electrostatics).
- MDFT (orientation, water, solvation).

Applications:

- Hydration shells & solvation free energies.
- Electrochemical double layers, ion adsorption.
- Porous media: capillarity, adsorption isotherms.

cDFT sits between continuum solvation models (PCM) and explicit MD, combining efficiency with molecular-level accuracy.