Taming Coulomb interactions in models for ions and water

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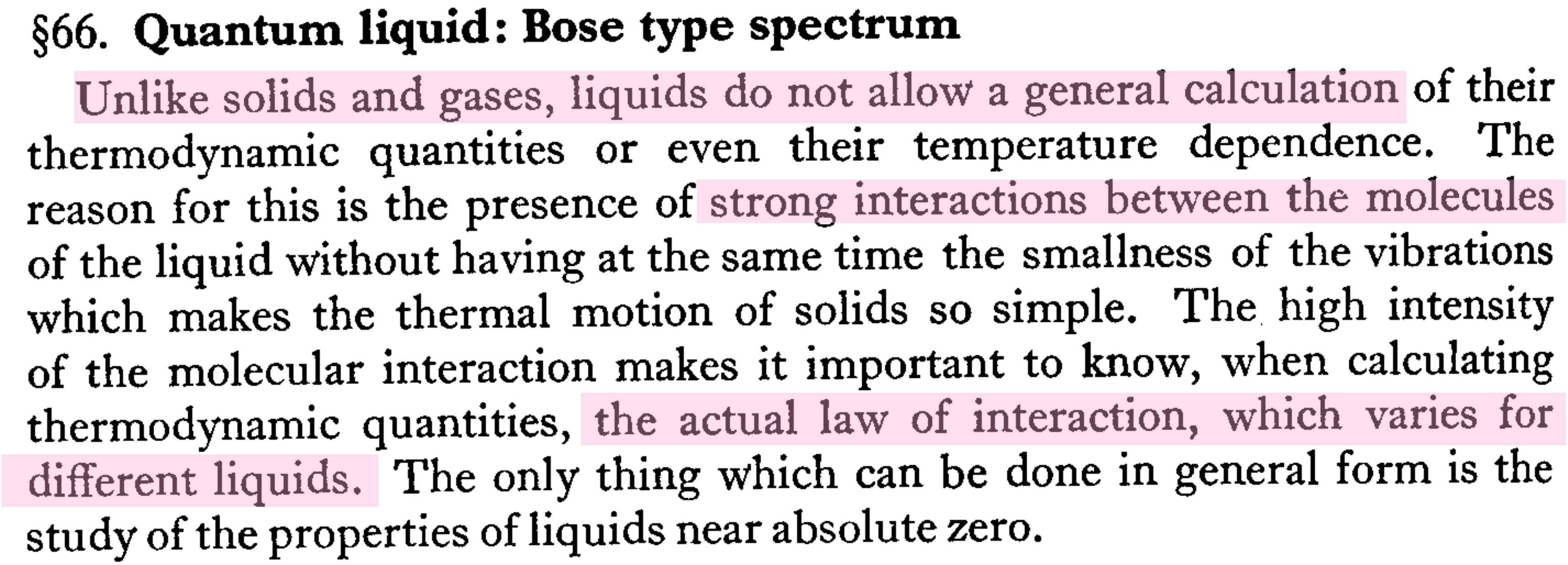
Should physicists study liquids at all?

Landau and Lifshitz (1958): Too messy; few general principles



§66. Quantum liquid: Bose type spectrum

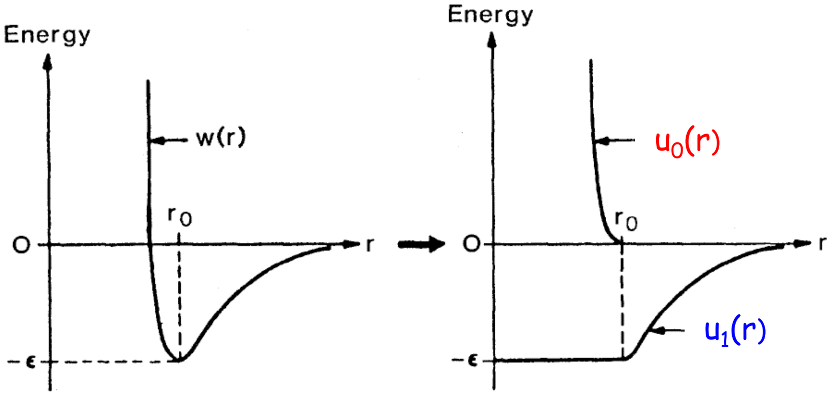
Unlike solids and gases, liquids do not allow a general calculation of their thermodynamic quantities or even their temperature dependence. The reason for this is the presence of strong interactions between the molecules of the liquid without having at the same time the smallness of the vibrations which makes the thermal motion of solids so simple. The high intensity of the molecular interaction makes it important to know, when calculating thermodynamic quantities, the actual law of interaction, which varies for different liquids. The only thing which can be done in general form is the study of the properties of liquids near absolute zero.

Some truth in this even today, but …

- Liquids are an important part of condensed matter
- Hard to get more basic than Coulomb interactions!
- Computers may help with the mess
- Important biophysical problems involve simple Coulomb interactions
  -- e.g. ions in ion channels, dipoles and H-bonds in water, …

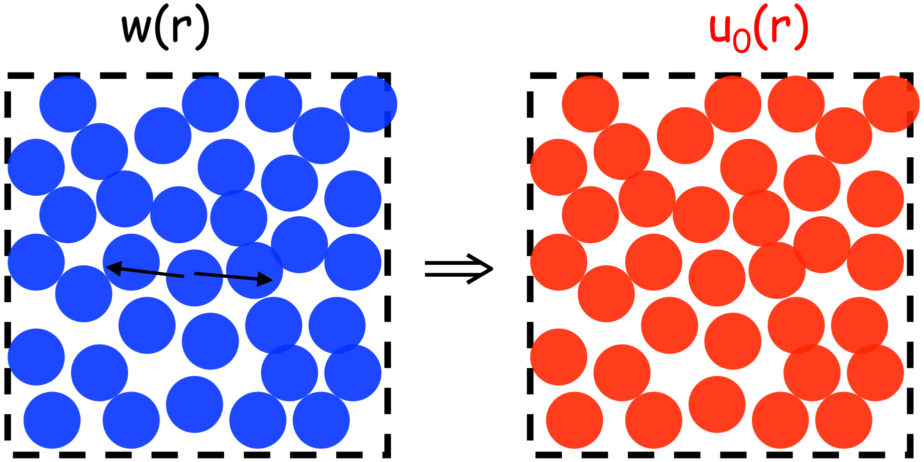
Idea: study the mess in minimal short-ranged models

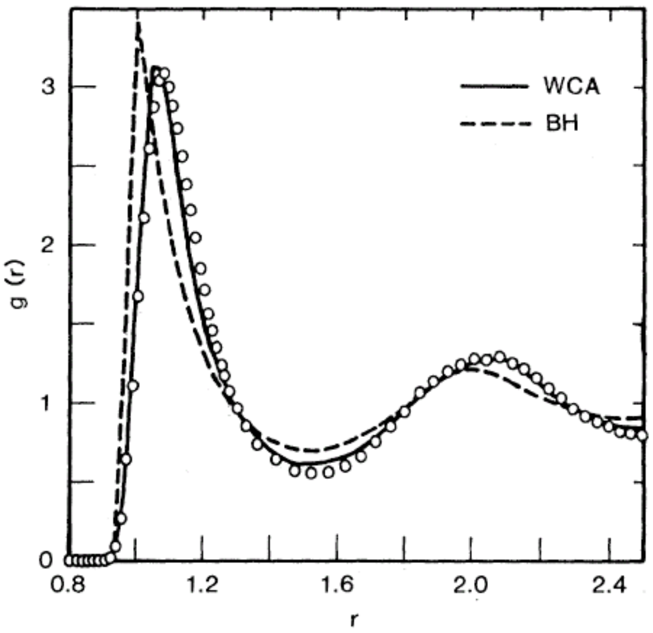
$w(r) = u_0(r) + u_1(r)$



Map from long to short in uniform LJ system

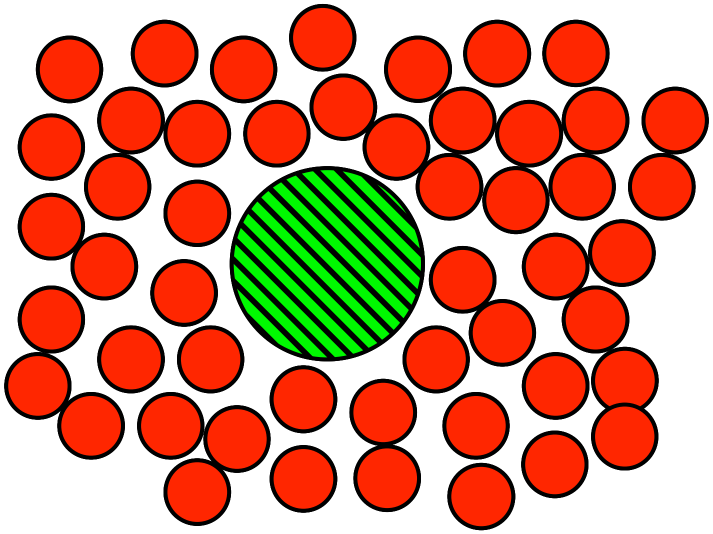
Attractive forces cancel



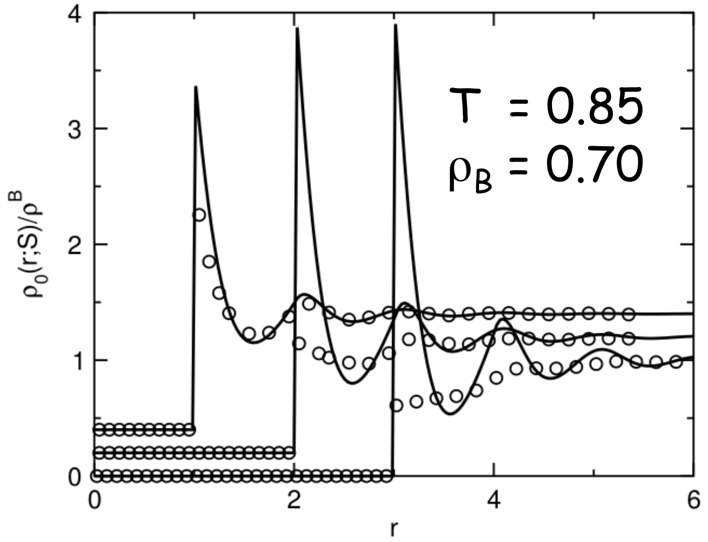


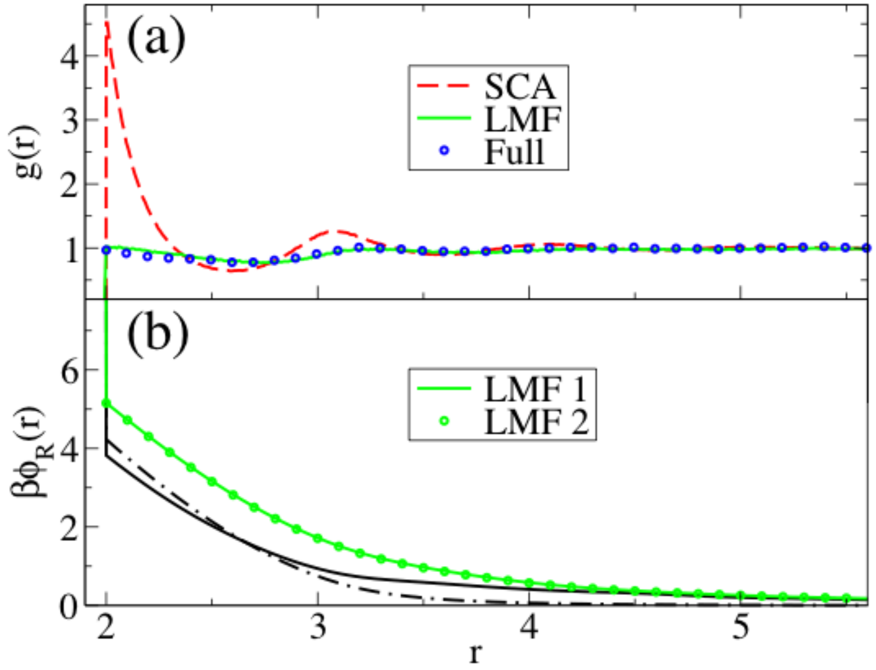
- Need slowly-varying u_1 for good cancellation
- Separate theory or simulation needed for messy reference system structure where $g_0(r) \approx g_{LJ}(r)$.
- Picture gives new physical insights. E.g., shows why van der Waals equation works so well
- Reference system not so messy after all: hard sphere model

Truncated models need effective field in nonuniform systems



Drying of HS solute in LJ fluid





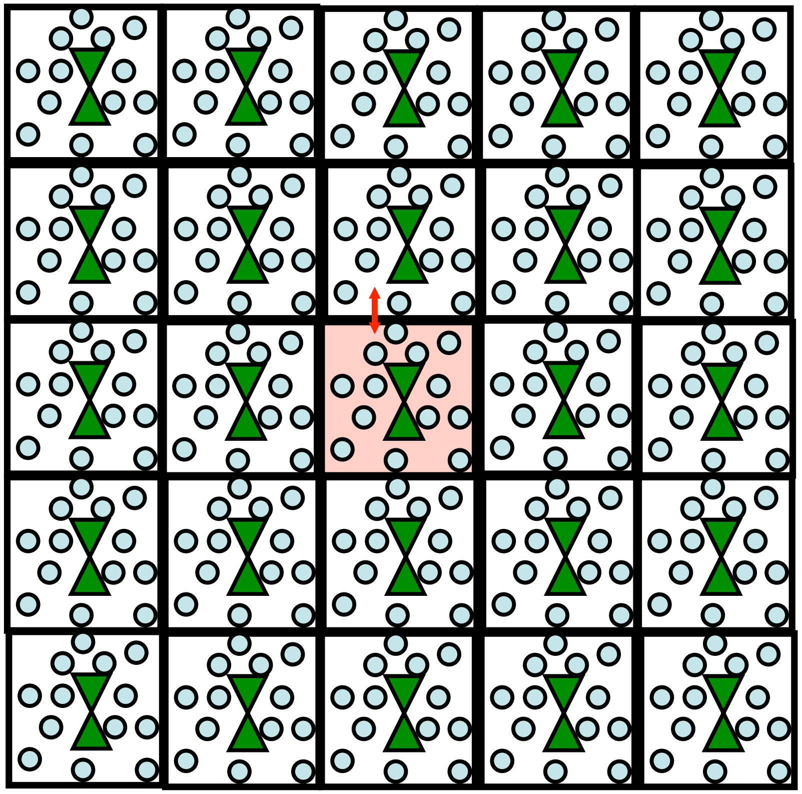
$$w(r) = u_0(r) + u_1(r)$$

$$\overset{\textit{Full}}{\begin{Bmatrix} w(r) \\ \phi(\mathbf{r}) \end{Bmatrix}} \xrightarrow{LMF} \overset{\textit{Mimic}}{\begin{Bmatrix} u_0(r) \\ \phi_R(\mathbf{r}) \end{Bmatrix}}$$

LMF theory provides an equation for ϕ_R and the requirements on u_0 for a *mimic* system.

$$\rho(\mathbf{r};[\phi]) = \rho_R(\mathbf{r};[\phi_R])$$

Simulations use periodic boundary conditions



- Short-ranged interaction $w_{LJ}(r)$ cut off at $r_C < L/2$; minimum image OK
- Boundary correction $\propto$ log L; not L^2

$$4\pi\int_{r_c}^{\infty} r^2 w_{LJ}(r)dr \ \text{small}$$

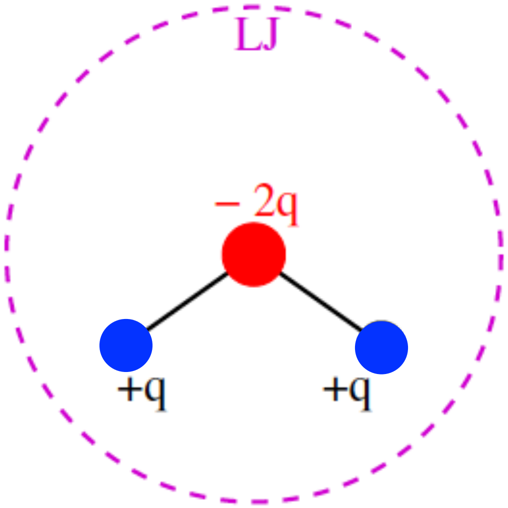
- Must sum images of images … for Coulomb interaction $w_c(r) = 1/r$

$$4\pi\int_{r_c}^{\infty} r^2 w_C(r)dr \ \text{infinite}$$

- All images included in Ewald or Lekner sums, but costly and complicated; periodicity of solutes can cause artifacts
- Black-box treatment of distant images prevents simple physical picture
- Simplest idea: Truncate Coulomb interactions and hope for the best!
  Cf. Ion reaction field methods (Hummer), Wolf truncations,
  Force-matching truncations (Voth)

Classical water models use point charges to describe both short-ranged H-bonds and long-ranged dipolar forces

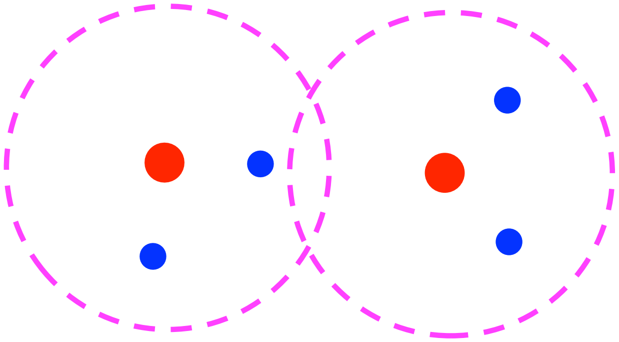
Extended Simple Point Charge (SPC/E) Model



σ_{LJ}= 3.166 A
q_H =+0.424
l_{OH}=1 A

Long range of Coulomb forces causes problems

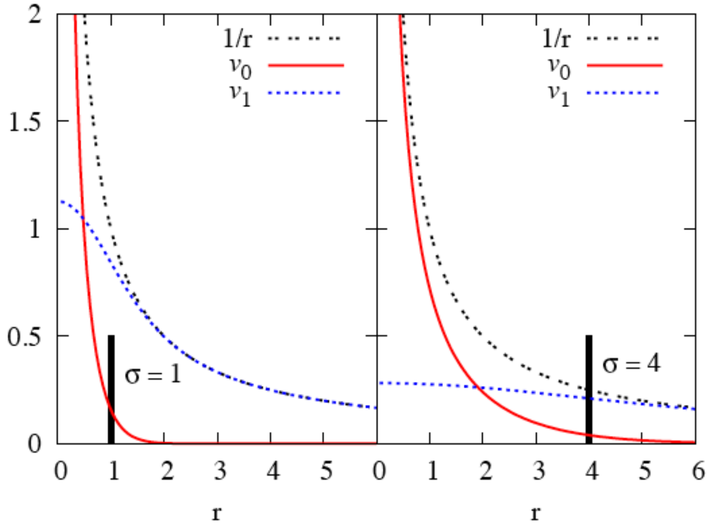
H-bonds in SPC/E water result from frustrated ion pairing



Properly truncated Coulomb interactions can describe local H-bonds well but not long-ranged dipolar forces

Max g_{OO} =2.75A

Truncation of Coulomb potential using Gaussian charge distribution

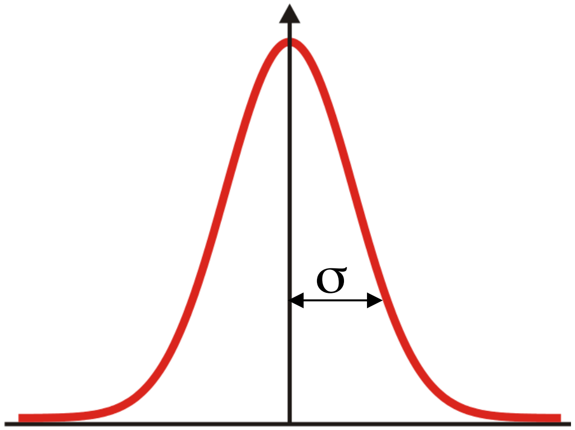


$1/r = v_0(r) + v_1(r)$

$v_1(r)$ is electrostatic potential from Gaussian charge distribution with width σ

$$v_1(r) \equiv \frac{1}{\pi^{3/2}\sigma^3}\int e^{-r'^2/\sigma^2}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' = \frac{\mathrm{erf}(r/\sigma)}{r}$$

Convolution with Gaussian: $v_1 = \rho_G * 1/r$

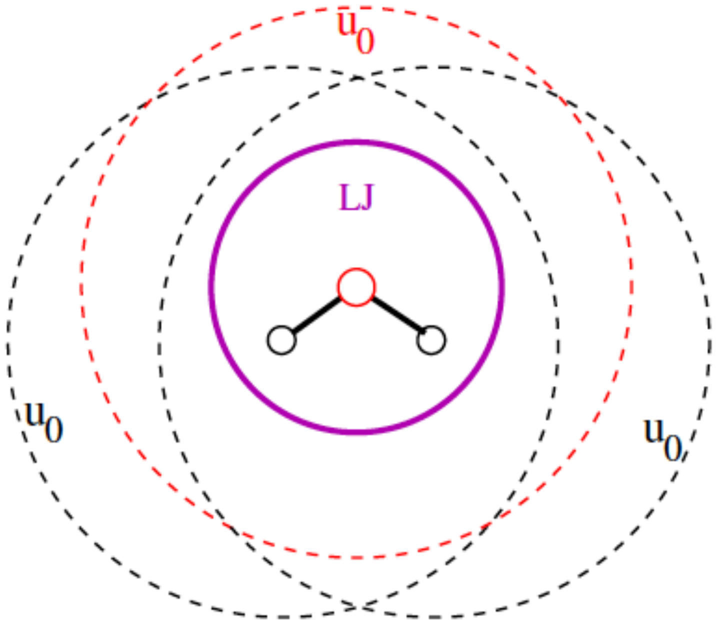


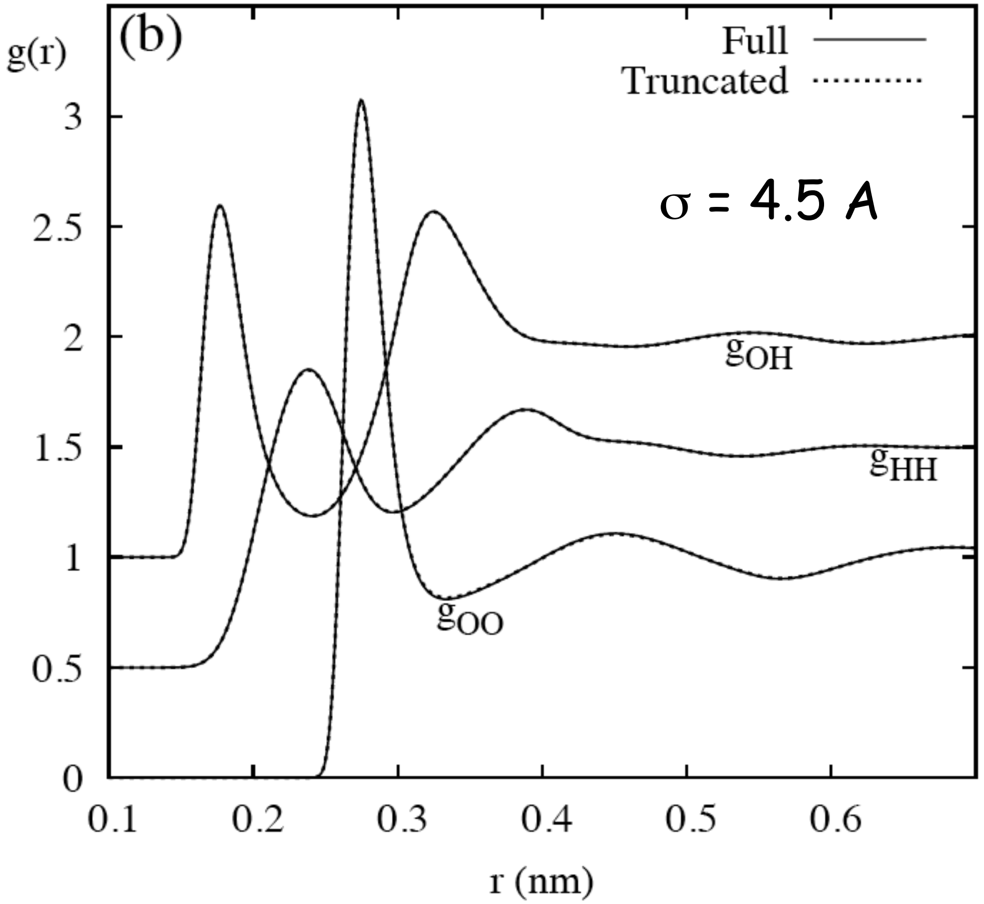
$$\rho_G(\mathbf{r}) = \frac{1}{\pi^{3/2}\sigma^3}\exp\left(-\frac{r^2}{\sigma^2}\right)$$

- Truncated "short" models replace $1/r$ by $v_0(r)$
- Screened Coulomb core potential $v_0(r) = 1/r - v_1(r)$ combines with other strong core interactions.
- Force from $v_0(r)$ approaches bare Coulomb force for $r < \sigma$

Choosing $\sigma > \sigma_{min} \approx$ nearest neighbor spacing in short water will capture local ion pairing, hydrogen bonding etc!

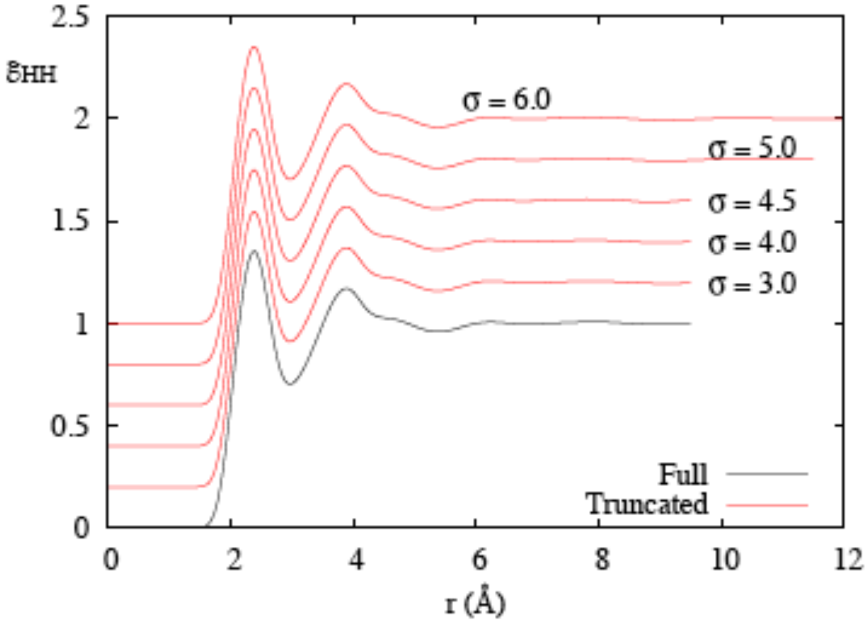
Simulations of bulk short water use $v_0(r)$ only:
Assumes complete cancellation of long-ranged forces



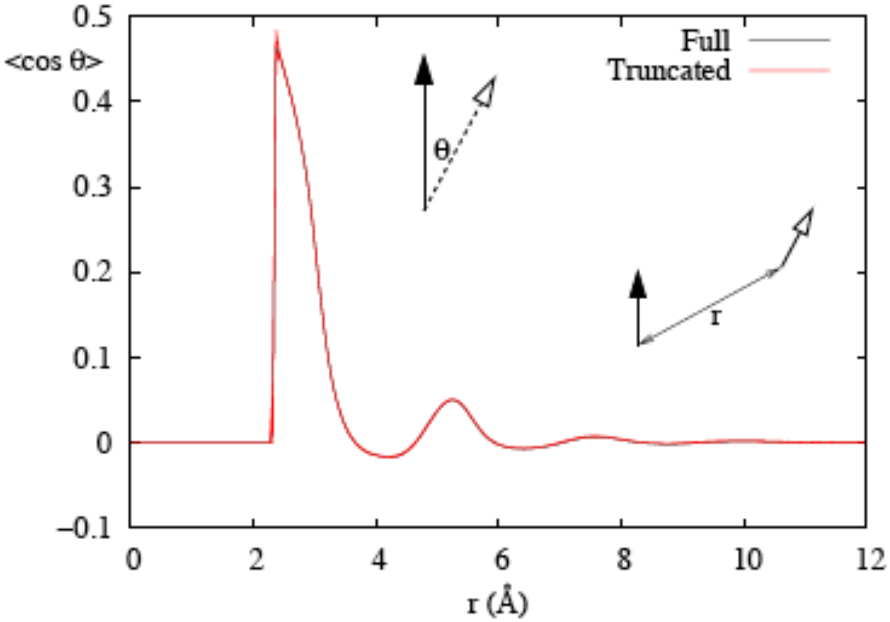


Short water gives very good description of local H-bond network while ignoring all effects of long-ranged dipolar interactions:
Ideal local model to test classical network picture

Very good description of dipole angle correlations in bulk water as well!



(c) g_{HH}

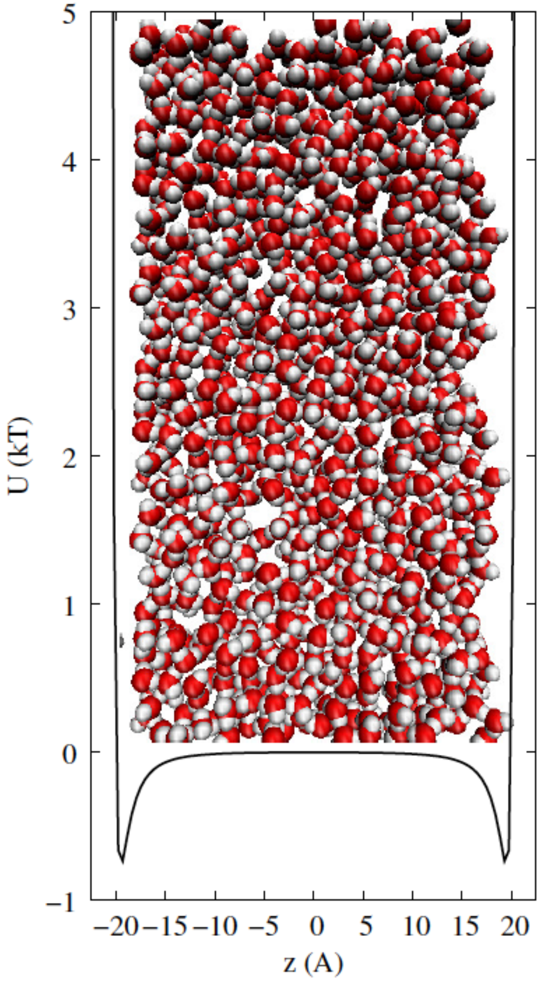


(d) Dipole-Dipole Correlations

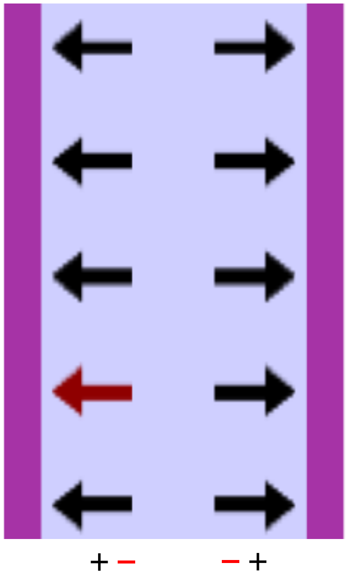
What about nonuniform systems where forces don't cancel?

Water and short water models near hydrophobic walls

SPC/E water (with 2D Ewald) and short water confined between hydrophobic walls; LJ 9-3 potential

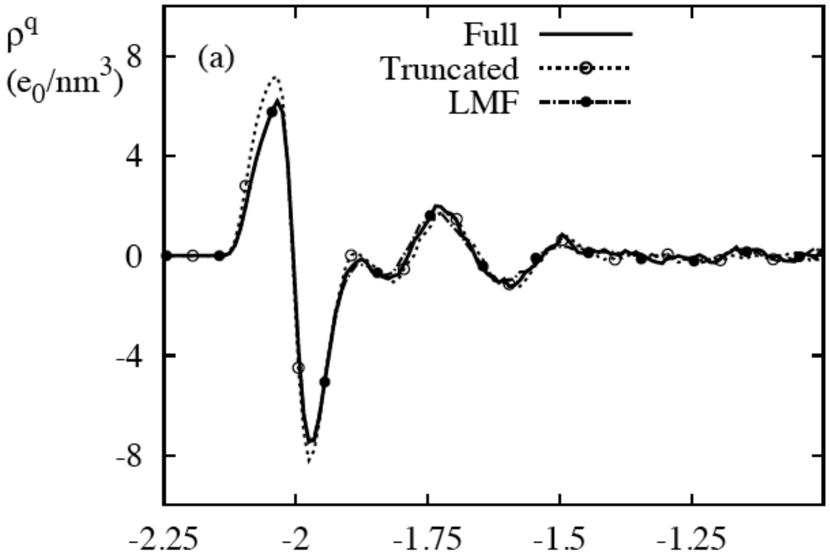


Lee, McCammon, and Rossky,
J. Chem. Phys. **80**, 4448 (1984)



Local H-bond structure near wall (1 broken H-bond) generates dipole layer

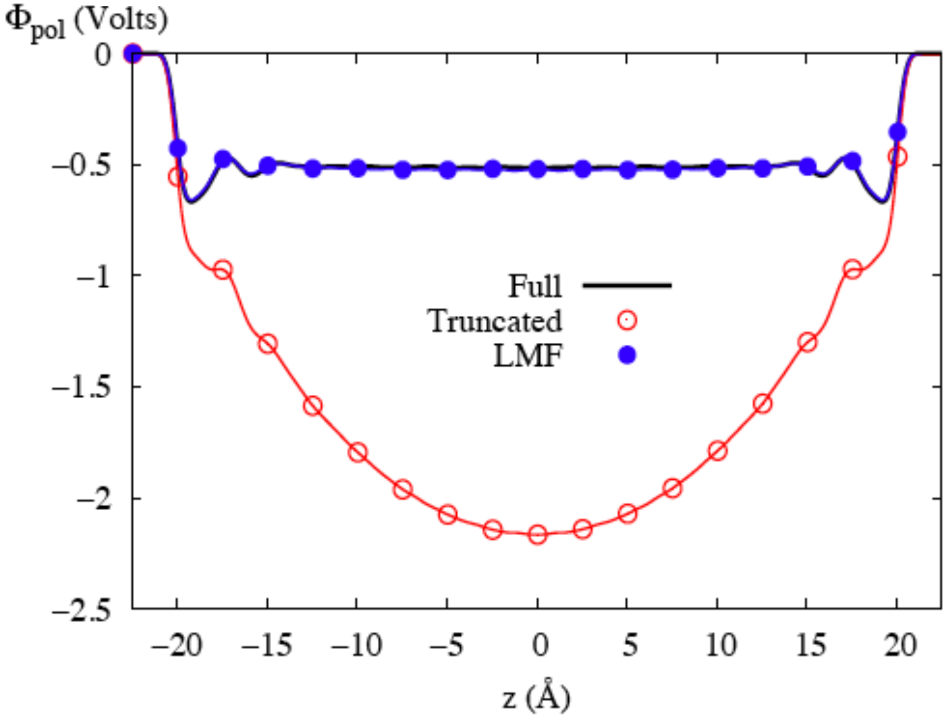
Local structure should be well captured by short water

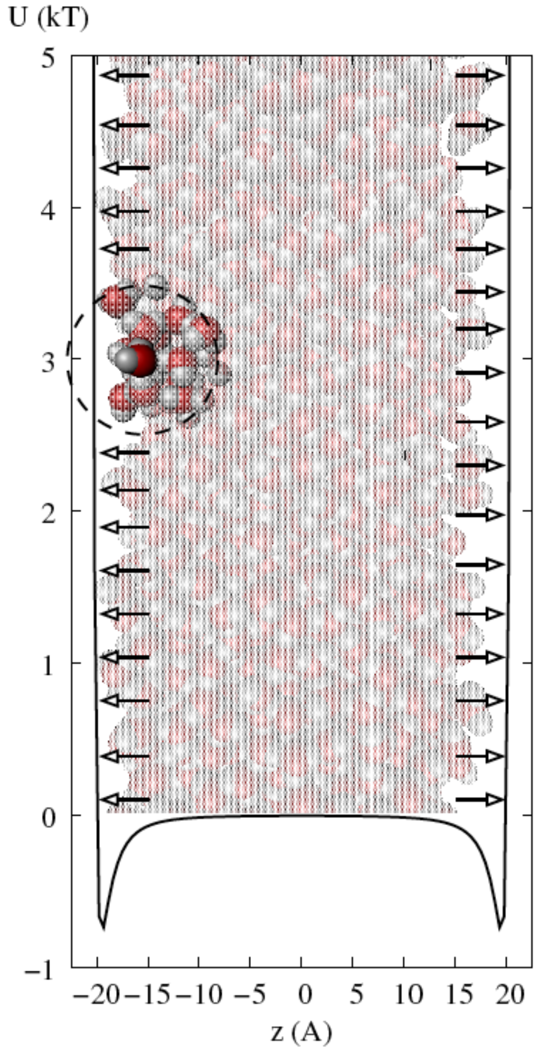


$$\rho^{(q)}(z) = q_O \cdot \rho_O(z) + q_H \cdot \rho_H(z)$$

Competition between local H-bond structure and long-ranged dipolar forces important for electrostatic properties

$$\phi_{pol}(z) = -\frac{e_0^2}{\varepsilon_0}\int_{-\infty}^{z} dz' \int_{-\infty}^{z'} dz'' \rho^{(q)}(z'')$$



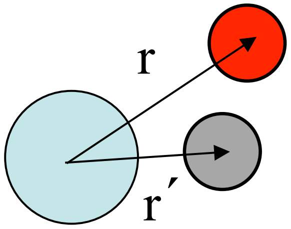


- Short system accounts only for local H-bonds
- Neglects competing long-ranged effects of dipole layers out to ∞ in x- and y-directions
- This is precisely what an effective LMF can capture!

LMF affects long-wavelength orientations of H-bond network

LMF theory determines ϕ_R from density-weighted mean-field average over slowly-varying u_1

Controlled use of mean field ideas by proper choice of u_1



$$\boxed{\phi_{\mathrm{R}}(\mathbf{r}) = \phi_0(\mathbf{r}) + \int d\mathbf{r}' \left\langle \rho(\mathbf{r}', \overline{\mathbf{R}}) \right\rangle_{\phi_{\mathrm{R}}} u_1\left(|\mathbf{r} - \mathbf{r}'|\right) + C}$$

Integrate YBG hierarchy
Need slowly-varying u_1

$$\rho_{\mathrm{R}}(\mathbf{r}; [\phi_{\mathrm{R}}]) \equiv \left\langle \rho(\mathbf{r}, \overline{\mathbf{R}}) \right\rangle_{\phi_{\mathrm{R}}}$$

Equilibrium density induced by ϕ_R is normalized ensemble average of microscopic configurational density

Microscopic density $$\rho(\mathbf{r}, \overline{\mathbf{R}}) \equiv \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$$

configuration $$\overline{\mathbf{R}} \equiv \{\mathbf{r}_i\}$$

Theory for Coulomb interactions needs only single LMF equation involving total charge density for restructured electrostatic potential

$$\mathcal{V}_R(\mathbf{r}) \equiv \mathcal{V}(\mathbf{r}) + \frac{1}{\epsilon}\int d\mathbf{r}'\, \rho_R^q(\mathbf{r}') \cdot v_1(|\mathbf{r}-\mathbf{r}'|)$$

convolution of full charge density and Gaussian-smoothed Coulomb potential $v_1 = \rho_G * 1/r$

$$\mathcal{V}_R(\mathbf{r}) = \mathcal{V}(\mathbf{r}) + \frac{1}{\epsilon}\int d\mathbf{r}''\, \rho_R^{q\sigma}(\mathbf{r}'') \cdot \frac{1}{|\mathbf{r}-\mathbf{r}''|}$$

convolution of full Coulomb potential and Gaussian-smoothed charge density

LMF restructured potential satisfies Poisson's equation
but with a Gaussian-smoothed charge density!

LMF theory and classical electrostatics:
why does it work so well?

- Classical electrostatics smoothes the total charge density over molecular scale fluctuations in deriving basic equations for polarization field P and other dielectric properties

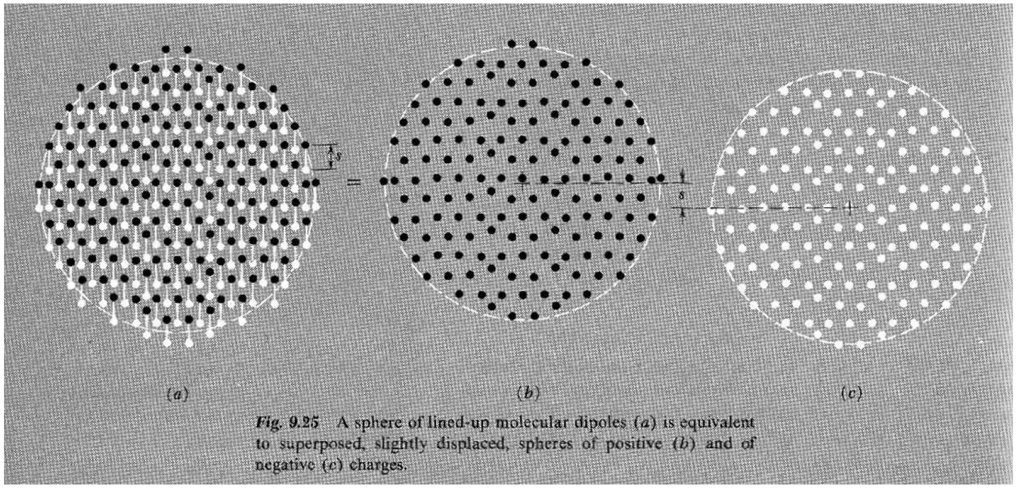
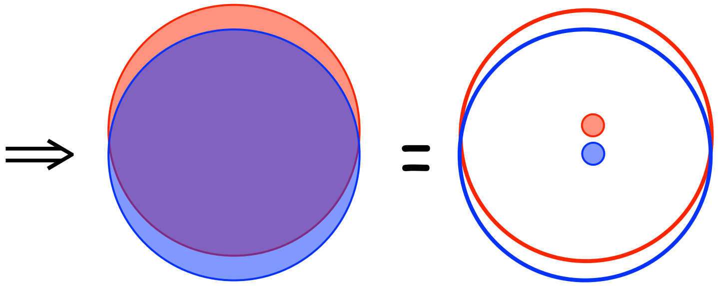


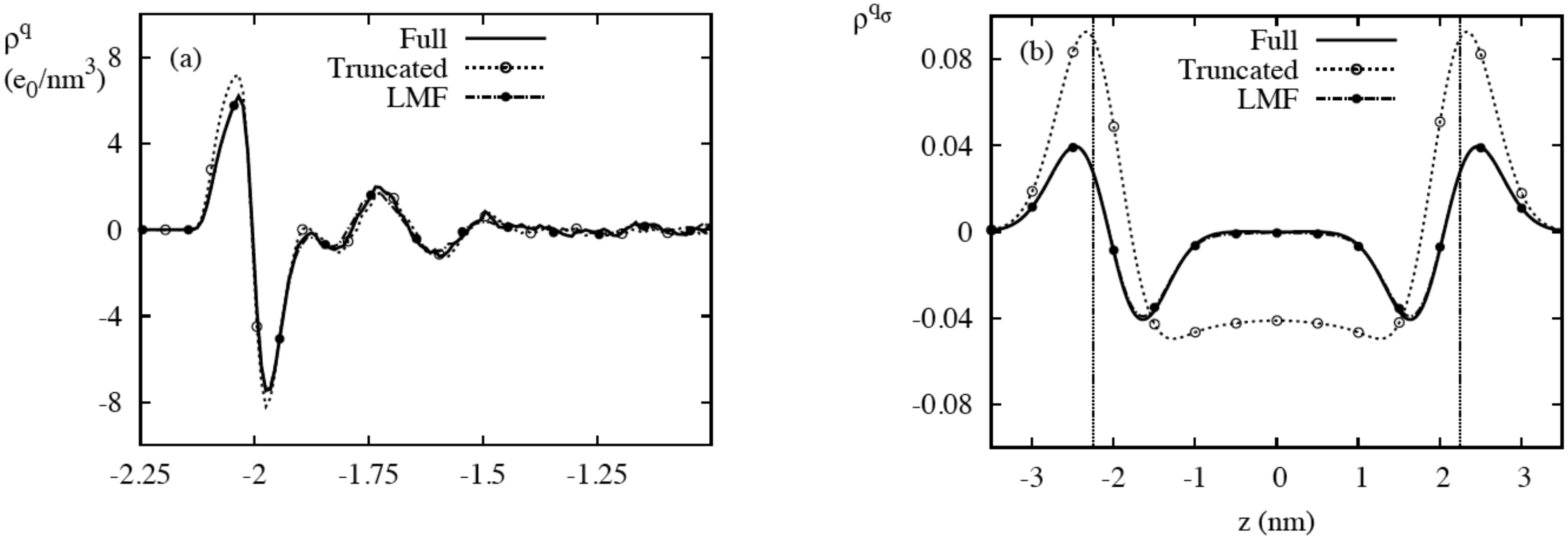
Fig. 9.25 A sphere of lined-up molecular dipoles (*a*) is equivalent to superposed, slightly displaced, spheres of positive (*b*) and of negative (*c*) charges.

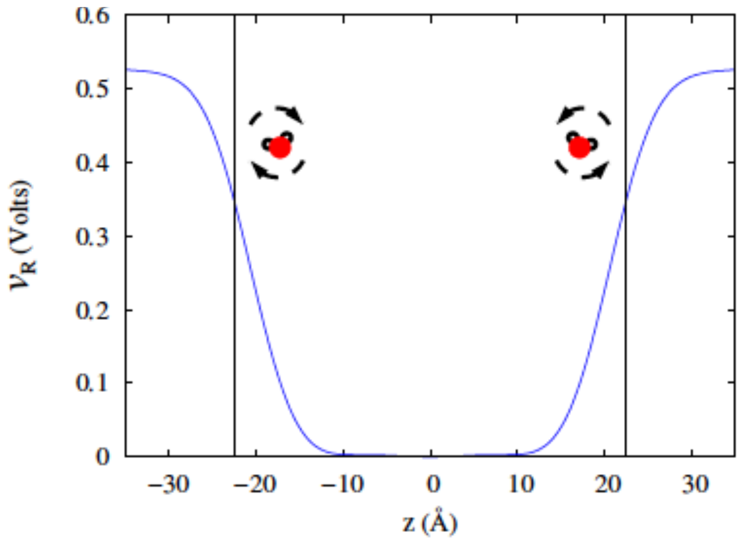


Purcell: Electricity
And Magnetism 1963

- LMF theory provides a general conceptual framework that shows how to carry out such smoothing in general environments and using realistic molecular models.
- σ may be a fundamental length scale in molecular electrostatics

Gaussian-smoothing of charge density cancels out simulation noise and atomic scale fluctuations to reveal underlying long-ranged electrostatics

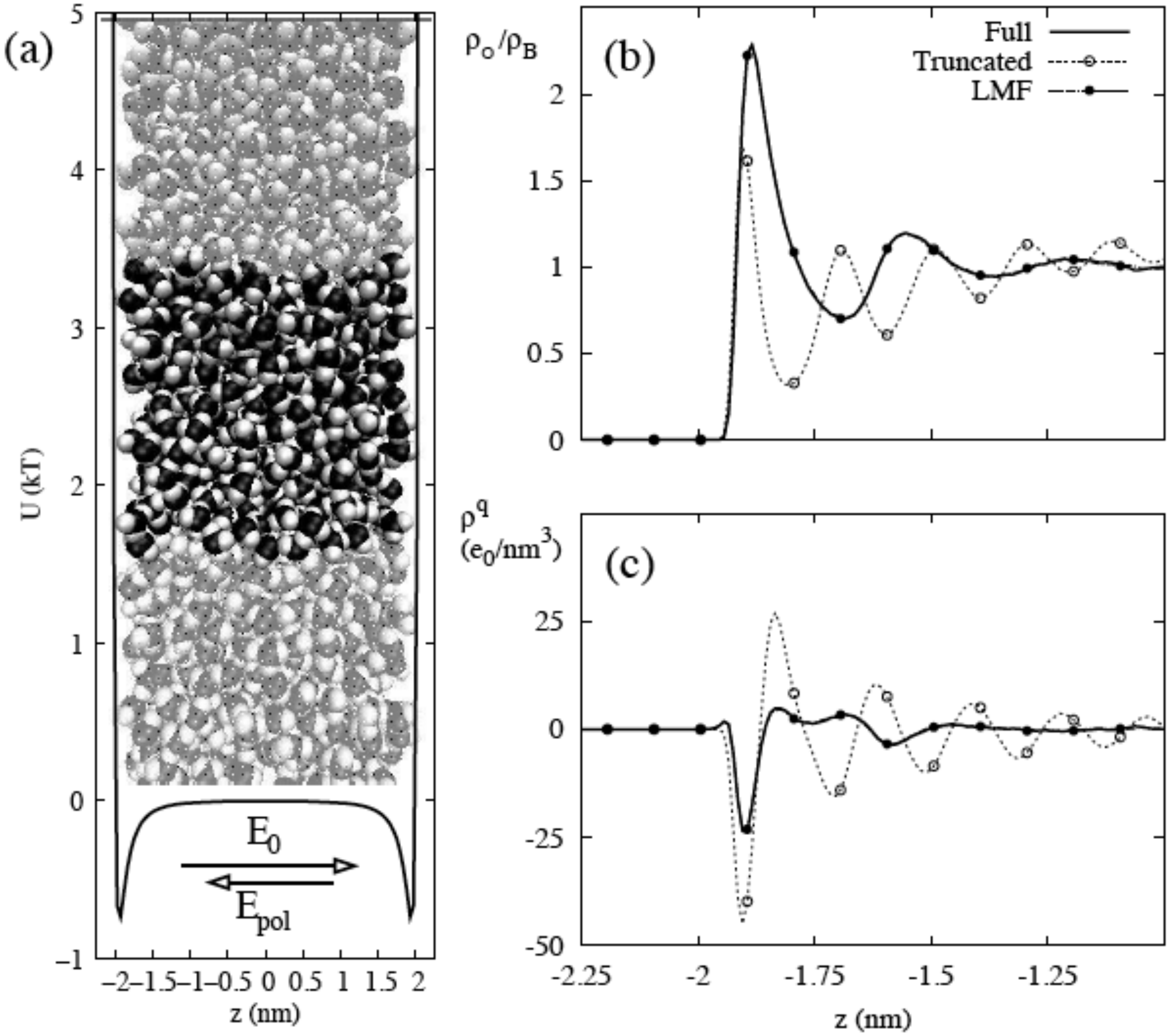




A self-consistent V_R applies a smooth reorienting torque on water molecules mimicking the action of a dipole layer

Smooth form should permit efficient solutions of LMF equation

LMF theory also corrects very poor results for short water in applied electric field



E=10V/nm

Message thus far:

Basic tradeoff: LMF theory can get very accurate results using truncated interactions in nonuniform environments, but must determine self-consistent effective field.

Systematic derivation shows LMF theory is very accurate provided that:

i) Perturbation u_1 is very slowly varying
ii) The density response to the effective field is accurately determined

We show that i) also allows us to find a very efficient way to satisfy ii) as well and thus accurately solve LMF equation. New solution method should yield linear scaling and remove artifacts from simple truncations.

Z. Hu and J.D. Weeks, Phys. Rev. Lett. **105**, 140602 (2010).

Iterative solution of self-consistent LMF equation

$$\boxed{\phi_{\mathrm{R}}(\mathbf{r}) = \phi_0(\mathbf{r}) + \int d\mathbf{r}'\,\rho_{\mathrm{R}}(\mathbf{r}';[\phi_{\mathrm{R}}])\,u_1(|\mathbf{r}-\mathbf{r}'|) + C}$$

LJ

$$\boxed{\mathcal{V}_{\mathrm{R}}(\mathbf{r}) = \mathcal{V}_0(\mathbf{r}) + \int d\mathbf{r}'\,\rho^{q}_{\mathrm{R,tot}}(\mathbf{r}';[\mathcal{V}_{\mathrm{R}}])\,v_1(|\mathbf{r}-\mathbf{r}'|) + C}$$

Water,
Ions, …

Iterate using simulations to determine density response to effective field

Density response often complicated
Usually need computer simulations

$$\begin{tikzcd}
\rho(\mathbf{r}) \arrow[d, bend left, "\mathrm{LMF}"] \\
\phi_R(\mathbf{r}) \arrow[u, bend left, "\mathrm{MD}"]
\end{tikzcd}$$

Field is smooth and slowly varying. Often easy to estimate qualitatively

Problem: each iteration with a new estimate for the effective field requires a new simulation

Solution: start with good initial guess $\tilde{\phi}_0$: "trial system"

Remaining change in field $\tilde{\phi}_{R1} \equiv \phi_R - \tilde{\phi}_0$ is likely small

Use linear response theory to compute change in density

Non-Boltzmann sampling method for nonuniform density

Total perturbation energy in configuration $\bar{\mathbf{R}}$: $\tilde{\Phi}_{R1}(\bar{\mathbf{R}}) \equiv \sum_{i=1}^{N} \tilde{\phi}_{R1}(\mathbf{r}_i)$

$$\langle \rho(\mathbf{r}, \overline{\mathbf{R}}) \rangle_{\phi_{\mathrm{R}}} = \frac{\int d\overline{\mathbf{R}} \rho(\mathbf{r}, \overline{\mathbf{R}}) e^{-\beta[U_0(\overline{\mathbf{R}}) + \tilde{\Phi}_0(\overline{\mathbf{R}}) + \tilde{\Phi}_{R1}(\overline{\mathbf{R}})]}}{\int d\overline{\mathbf{R}} e^{-\beta[U_0(\overline{\mathbf{R}}) + \tilde{\Phi}_0(\overline{\mathbf{R}}) + \tilde{\Phi}_{R1}(\overline{\mathbf{R}})]}} = \frac{\left\langle \rho(\mathbf{r}, \overline{\mathbf{R}}) e^{-\beta \tilde{\Phi}_{R1}(\overline{\mathbf{R}})} \right\rangle_{\tilde{\phi}_0}}{\left\langle e^{-\beta \tilde{\Phi}_{R1}(\overline{\mathbf{R}})} \right\rangle_{\tilde{\phi}_0}}.$$

Exponential reweighing of bin histograms used to determine density

Need saved configurations only of a single simulation of trial system!

Usually need tricks like umbrella sampling to evaluate averages over exponentials. But $\tilde{\Phi}_{\mathrm{R}1}(\overline{\mathbf{R}})$s slowly varying over most configurations by required choice of smooth perturbation u_1 so direct average often OK.

Same feature ensuring accuracy of basic LMF theory also permits simple and accurate solutions of self-consistency condition!

EXP and CLR equations for density perturbations

$$\left\langle \rho(\mathbf{r},\overline{\mathbf{R}}) \right\rangle_{\phi_{\mathrm{R}}} = \frac{\left\langle \rho(\mathbf{r},\overline{\mathbf{R}}) e^{-\beta \tilde{\Phi}_{\mathrm{R}1}(\overline{\mathbf{R}})} \right\rangle_{\tilde{\phi}_0}}{\left\langle e^{-\beta \tilde{\Phi}_{\mathrm{R}1}(\overline{\mathbf{R}})} \right\rangle_{\tilde{\phi}_0}}$$

EXP

Linearize:

$$\left\langle \rho(\mathbf{r},\overline{\mathbf{R}}) \right\rangle_{\phi_{\mathrm{R}}} \simeq \left\langle \rho(\mathbf{r},\overline{\mathbf{R}}) \right\rangle_{\tilde{\phi}_0} - \beta \left\langle \delta\rho(\mathbf{r},\overline{\mathbf{R}}) \delta\tilde{\Phi}_{R1}(\overline{\mathbf{R}}) \right\rangle_{\tilde{\phi}_0}$$

CLR

Use in LMF equation and iterate to self-consistency:

$$\phi_{\mathrm{R}}(\mathbf{r}) = \phi_0(\mathbf{r}) + \int d\mathbf{r}' \left\langle \rho(\mathbf{r}',\overline{\mathbf{R}}) \right\rangle_{\phi_{\mathrm{R}}} u_1\left(|\mathbf{r}-\mathbf{r}'|\right) + C.$$

LMF

- In linear regime with good trial $\tilde{\phi}_0$ get same answer from EXP and CLR
- Use this as objective test for accurate solution of LMF equation
- In practice CLR is most useful with bad initial guess

Conclusions

- SPC/E water, ions, and LJ can be very accurately described by short-ranged mimic system in effective external field
- Effective field accounts for mean field average of special long-ranged slowly varying component of Coulomb interactions
- Effective field satisfies Poisson's equation with Gaussian-smoothed charge density
- Effective field corrects major errors in electrostatic properties of nonuniform systems from simple truncations of long-ranged forces.
- No Ewald sums etc. needed in mimic simulations
- LMF method adapted to open-source DL-Poly MD code and in-house Langevin MD polymer simulation code; new efficient solution method
- Further work on ions, water near hydrophobic and superhydrophobic surfaces, dipolar fluids near silica surfaces, charged polymers, etc.
- LMF theory provides a unified conceptual framework for wide class of nonuniform fluids: ions, LJ fluids, polymer and water models,...