
Fixing Nonlocality in the Primitive Model

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a PDT-like DFT

I'm presenting ongoing work centered around 3 recent manuscripts on arXiv. One of them (the proof of concept study) was published, and the rest should follow shortly I hope. As a warning, it did seem like I was opening a Pandora's box as the work was being done.

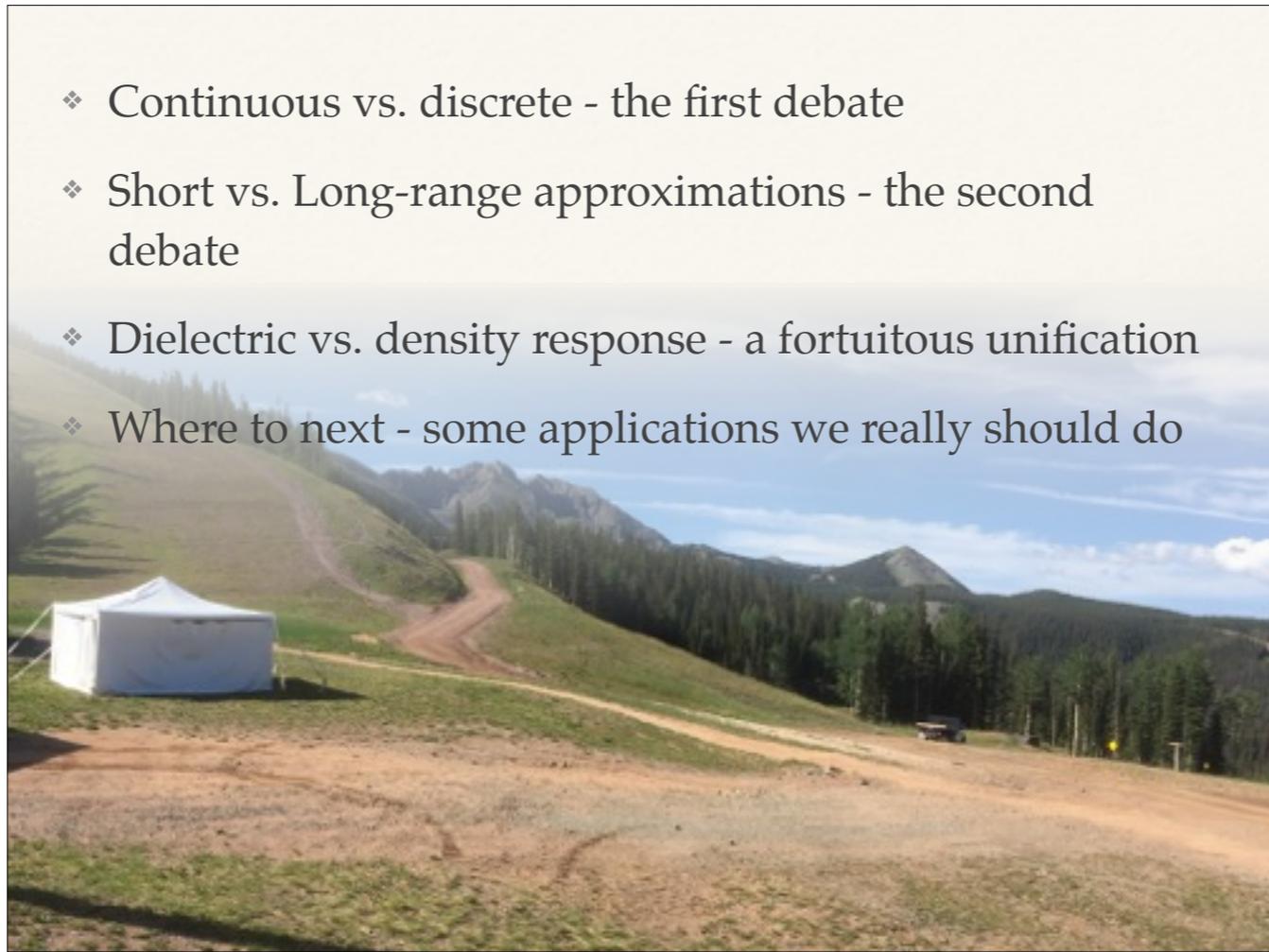
“ No doubt science cannot admit of compromises, and can only bring out the complete truth. Hence there must be controversy, and the strife may be, and sometimes must be, sharp. But must it even then be personal? Does it help science to attack the man as well as the statement? On the contrary, has not science the noble privilege of carrying on its controversies without personal quarrels?”

– *Rudolf Virchow*

In his collected writings of 1861, preface. Quoted in Proceedings of the Royal Society of London, Vol. 75, 300.

Our field is not without controversy. I've seen my share, and I think these should be discussed often, since they remind us to question our assumptions.

- ❖ Continuous vs. discrete - the first debate
- ❖ Short vs. Long-range approximations - the second debate
- ❖ Dielectric vs. density response - a fortuitous unification
- ❖ Where to next - some applications we really should do



I've phrased things here to constantly show two points of view on the same topic - two diverging paths if you will. Perhaps it will lead to a wider context and lead you along a more civilized path to my main idea than I was able to take.

Continuous vs. Discrete

The Pratt/Chandler Divide

- ❖ Use water $g(r)$ to get μ_α^{ex}
- ❖ But, is the correlation function or the distribution more important?

$$\mu_\alpha^{\text{ex}}(\mathcal{R}^n) \approx \bar{\mu}_\alpha^{\text{ex}}(\mathcal{R}^n) + \langle \Phi_\alpha | \mathcal{R}^n \rangle_r - \frac{\beta}{2} \langle \delta \Phi_\alpha^2 | \mathcal{R}^n \rangle_r. \quad (4.22)$$

The thermodynamic chemical potential is then obtained by averaging the Boltzmann factor of this conditional result using the *isolated solute* distribution function $s_\alpha^{(0)}(\mathcal{R}^n)$.

$$\beta \bar{\mu}_\alpha^{\text{ex}}(\mathcal{R}^n) = \ln \left[1 + \sum_{m \geq 1} \left(\frac{\hat{p}_\alpha(m | \mathcal{R}^n)}{\hat{p}_\alpha(0 | \mathcal{R}^n)} \prod_{k=1}^{k_{\text{max}}} e^{-\zeta_k m^k / k!} \right) \right]. \quad (4.32)$$

Beck, Paulaitis, Pratt, PDT Book, 2006

Next we define the functions $c_{Aw}(r)$ and $c_{AA}(r)$ through the following Ornstein–Zernike-like equations:

$$h_{Aw}(r) = c_{Aw}(r) + \rho_w \int d\mathbf{r}' c_{Aw}(|\mathbf{r} - \mathbf{r}'|) h_{wW}(r') \quad (2.26a)$$

and

$$h_{AA}(r) = c_{AA}(r) + \rho_w \int d\mathbf{r}' c_{Aw}(|\mathbf{r} - \mathbf{r}'|) h_{wA}(r'), \quad (2.26b)$$

where $h_{wW}(r) = g_{wW}^{(0)}(r) - 1$ is the radial pair correlation function for pure liquid water.

Pratt and Chandler, JCP 67, 1977.
 Pratt and Chandler, JCP 73, 1980.

$$\frac{\delta^2 \beta A}{\delta \langle \rho_{\alpha M}(\mathbf{r}) \rangle \delta \langle \rho_{\gamma M}(\mathbf{r}') \rangle} = \chi_{\alpha M \gamma M}^{-1}(\mathbf{r}, \mathbf{r}'). \quad (3.5)$$

According to its definition [the right-hand side of Eq. (2.6)], χ is symmetric positive definite for all real density fields. It follows that its inverse and therefore the second

C. Direct correlation functions

The direct correlation function, $\bar{c}_{\alpha M \gamma M}(\mathbf{r}, \mathbf{r}')$, is defined in terms of the functional inverse of the susceptibility

$$\chi_{\alpha M \gamma M}^{-1}(\mathbf{r}, \mathbf{r}') = \frac{1}{\langle \rho_{\alpha M}(\mathbf{r}) \rangle} \delta_{\alpha \gamma} \delta_{MM} \delta(\mathbf{r} - \mathbf{r}') - \bar{c}_{\alpha M \gamma M}(\mathbf{r}, \mathbf{r}'), \quad (2.11)$$

Chandler, McCoy, and Singer, JCP 85, 1986.

We all know the Pratt-Chandler theory as the genesis of some interesting hydrophobic literature. According to Pratt, that paper was proved wrong 6 months later, and revised to a 1980 paper which should be cited instead henceforth and forevermore. However, the 1980 paper was focused on 3-body correlations, while the 1977 paper used the direct correlation function to derive a density. The result we see now is that Pratt went on to carefully look at molecular number distributions and 1st solvation shell occupancy statistics. Chandler went the other way to develop a continuum solvent density functional theory that makes many approximations to keep things at the pair correlation level.

Eventually, both would be used to compute solvation free energies.

The Weeks/Pratt Divide

- ❖ SR reference fluid, LR and 'effective LR' fields.
- ❖ These are effective closures for integral equations - uniform density or LR structuring.

$$K_n(R) \approx \frac{\xi^n}{n!} \int_v d\mathbf{r}_1 \cdots \int_v d\mathbf{r}_n \exp \left[- \sum_{i=1}^n \beta \varphi_{SCF}(\mathbf{r}_i) \right]$$

$$\phi_{SCF} \rightarrow \rho_R - \sum_{i>j=1}^n \beta u(\mathbf{r}_{ij}) \equiv K_n^{(0)}(R; \beta \varphi_{SCF}). \quad (3)$$

$$\rho_R \rightarrow \phi_{SCF} \quad [\beta \varphi(\mathbf{r})_{SCF}]_{new} = [\beta \varphi(\mathbf{r})_{SCF}]_{old} + f \ln \left[\frac{\rho(\mathbf{r})}{\rho} \right], \quad (7)$$

Pratt and Ashbaugh, PRE 2003.

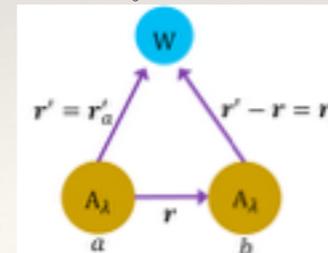
$$\phi_R \rightarrow \rho_{0,R} \quad \Delta \rho_{0,R}(\mathbf{r}_1) / \rho_{0,R1}(\mathbf{r}_1) = \int d\mathbf{r}_2 c_0(\mathbf{r}_1, \mathbf{r}_2; [\rho_{0,R1}]) \times \Delta \rho_{0,R}(\mathbf{r}_2). \quad (8)$$

$$\rho_{0,R}, \phi \rightarrow \phi_R \quad \phi_R(\mathbf{r}_1) - \phi(\mathbf{r}_1) \equiv \phi_s(\mathbf{r}_1) = \int d\mathbf{r}_2 [\rho_0(\mathbf{r}_2; [\phi_R]) - \rho_B] u_1(r_{12}). \quad (4)$$

Weeks, Katsov, Vollmayr, PRL 1998.

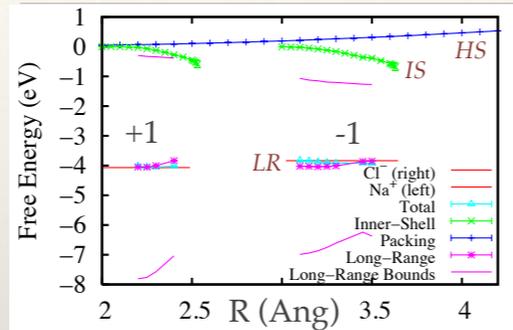
Gao et. al., JPCB 2018.

$$w_{AA} \approx u_{1,AA} + 2 \int dr' \delta \rho_{W|A}(r') u_{1,WA}(r' - r)$$

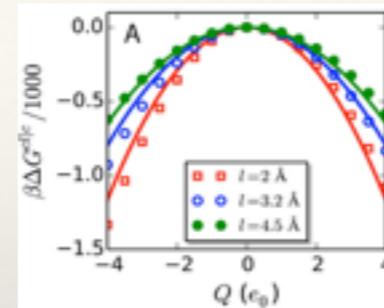


Fast-forward two decades to find a difference of opinion on how to deal with (continuous) long-range structure of discrete molecules. Weeks has presented a self-consistent field theory (LMF) that approximates the long-range intermolecular forces as continuous, and leaves the short-range ones as discrete. Pratt developed competing self-consistent field theory ideas. Recently, the two were happily reunited when considering an old application - the pair correlation between two hydrophobes. This means we can try and cross-fertilize LMF and quasi-chemical theory ideas.

Calculating All Contributions



Rogers, JCP 2008.



Remsing, JPCB 2016.

$0 \xrightarrow{HS} HS \xrightarrow{LR} HS+dispersion \xrightarrow{IS} LJ \xrightarrow{loc} LJ+erfc \xrightarrow{far} LJ + 1/r$

Table 2. Hydration Entropy Data^a

ion	$s_{en,loc}^{ex}$	$s_{en,far}^{ex}$	$s_{en,tot}^{ex}$	s_{IS}^{ex}	s_{HS}^{ex}	s_{LR}^{ex}	s_{dW}^{ex}	s_{tot}^{ex}	$s^{ex}(expt)$
F ⁻	-36.6(2.2)	-3.5(0.8)	-40.0(2.6)	5.4(0.1)	-14.2	-0.44(0.04)	-9.2	-49.2	-30.4
Cl ⁻	0.5(0.8)	-3.1(0.5)	-2.7(1.1)	10.8(0.3)	-22.0	-0.72(0.04)	-11.9	-14.6	-15.4
Br ⁻	3.9(0.8)	-2.2(0.3)	1.7(0.9)	12.2(0.4)	-22.9	-0.60(0.08)	-11.3	-9.6	-11.6
I ⁻	15.0(0.6)	-2.7(0.2)	12.4(0.7)	15.1(0.5)	-27.0	-0.76(0.17)	-12.7	-0.3	-7.3
I _{ig} ⁻	19.3(0.7)	-2.3(0.3)	17.0(0.8)	18.0(0.9)	-30.1	-0.86(0.16)	-13.0	4.0	
Na ⁺	-9.5(1.8)	-4.4(0.3)	-13.9(1.8)	6.6(0.1)	-12.2	-0.08(0.02)	-5.7	-19.6	-16.3
K ⁺	1.5(0.9)	-2.7(0.3)	-1.2(0.9)	9.1(0.2)	-16.9	-0.22(0.03)	-8.0	-9.1	-7.7

Matyushov, JCP 2004.

Beck, JPCB 2011.

In practical applications, we always end up calculating all the contributions to solvation free energies anyway. The top-left shows how a separation of solvation free energy for Na⁺ and Cl⁻ ions looks when you focus on discrete molecules (punching holes in the solvent) first. The top-right shows the first part of how it looks when you focus first on adding the strong, but smooth (continuous) electric field of a Gaussian-screened point charge.

These kind of join together when you look at the lower panel, where all possible steps I can think of are done. The application is really important, since it can pinpoint which free energy is most “ion-specific.” Note that both continuous and discrete approaches were also put together by Matyushov to study charge transfer and dipolar solvation.

Applications

Widom, JPC 1982.

- ❖ We have to be able to look at particle structures locally and density distributions in the long-range.
- ❖ Interfaces illustrate this nicely, and early on it was believed HS theories would work locally and mean-field for LR.
- ❖ Perturbation theories had success with local structures, but not LR (unless LR didn't change).

$$-\int_{r>\sigma} \phi_{\text{attr}}(r) [\rho(\mathbf{r} + \mathbf{r}') - \rho(\mathbf{r})] d\tau_{r'} = \mu[\rho(\mathbf{r}), T] - \mu_{\text{local}} \quad (22)$$

Here $\mu[\rho(\mathbf{r}), T] = kT \ln \lambda[\rho(\mathbf{r}), T]$ with $\lambda(\rho, T)$ given by (18),

This novel application of the potential-distribution theory illustrates its usefulness. Although, as we saw, it is the basis of important practical techniques in the theory of uniform fluids, it is probably in its applications to nonuniform fluids that its real power and versatility become apparent.

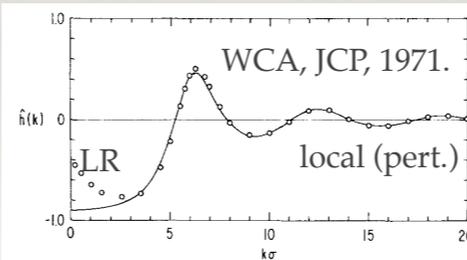


FIG. 3. Plot of $\hat{h}(k)$ for $\rho^*=0.5426$, $T^*=1.326$. The line represents Eq. (15'); the circles are the molecular dynamics results (Ref. 1).

Why debate about continuous vs. discrete? The answer is of course that good theories have to be mindful of the difference (and usually include both). An example par excellence is the structure factor, $S(k)$, for LJ fluids. Using a discrete-like 'hard-sphere' packing problem predicts the structure factor at large k (short distance). A continuous long-range correction is later added to the free energy.

SR vs. LR - The Second Debate

Actually, it has been realized for a long time, with the wave-vector analysis of $E_{xc}[n]$ by Langreth and Perdew [4], that the LDA describes accurately (but not exactly in general [5]) short wavelength density fluctuations, but is inadequate for long wavelength fluctuations. A dual analysis in real space of the exchange-correlation energy (see, e.g., Ref. [6]) leads to the same conclusion that the LDA is accurate at small interelectronic distances but fails at large distances. This observation led to the development of the first gradient corrected functionals [7–12] with the basic objective to cure the wrong long-range contribution to the exchange-correlation energy of the LDA.

Toulouse, Colonna and Savin, PRA 70, 2004.

This brings us to the 2nd debate. What is short-range (SR) and what is long-range (LR)? Which is “easier” and which is a “perturbation.”? This is an age-old question even for electronic density functional theory.

Virial vs. Compressibility

- ❖ Short-range repulsion provides good large-k structure.
- ❖ Organization at small k is included perturbatively.
- ❖ Virial route to computing pressure relies on good SR part. — usually preferred
- ❖ Compressibility route relies on small-k (hence LR). — usually neglected

Perry, Massey and Cummings, Fl. Phase Equ., 39, 1988.

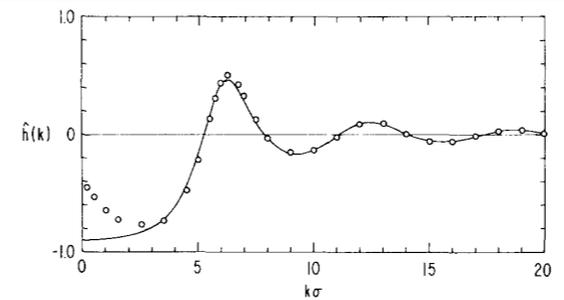
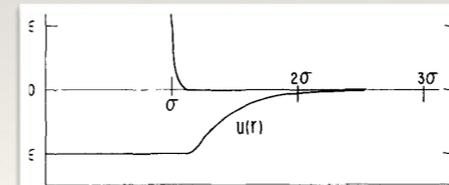


FIG. 3. Plot of $\hat{h}(k)$ for $\rho^*=0.5426$, $T^*=1.326$. The line represents Eq. (15'); the circles are the molecular dynamics results (Ref. 1).

Weeks, Chandler, Anderson JCP 54, 1971.



1. Separation of the Lennard-Jones potential, part containing all the repulsive forces, $u_0(r)$, and part containing all the attractive forces, $u(r)$.

The SR/LR question is loaded from the very beginning, since there are two well-known ways to go once you predict the structure factor of a fluid. The virial route relies on getting the large-k (small distance) structure factor right. The compressibility route, on the other hand, relies on the small-k (large distance) structure factor. As we have seen the WCA model has a correction that is an integral over the radial distribution function. Could there be a corresponding, 1-step, “truncate $g(r)$ ” correction to good predictions of the short-range structure factor?

MDFT / OZ Equation, $c(r \rightarrow \sigma)$

$$\beta \Delta A = \beta \Delta E + \Gamma^3 / 3\pi \quad (3.4)$$

finally the parameter Γ is determined by solving the algebraic equation³

$$2\Gamma = \alpha \left\{ \sum_{i=1}^n \rho_i \left[\left(z_i - \frac{\pi \sigma_i^2 P_n}{2\Delta} \right) / (1 + \Gamma \sigma_i) \right]^2 \right\}^{1/2} \quad (2.19)$$

the degree of this equation depends on the number of ions involved: for a binary salt it is of the 6th degree and has

Blum and Hoyer, JPC 81, 1977.

Lohe and Donohue, AIChE J. 43, 1997.

$$\hat{G}_{ZZ}(\mathbf{k}; \rho_N, T) = \rho_N k^2 / [\kappa_D^2 + k^2 + a^{-2} g_0(\kappa_D a, ka)],$$

$$\nabla_r^2 \tilde{\phi}_\sigma(\mathbf{r}; \mathbf{r}') = -(4\pi/D) [q_\sigma \delta(\mathbf{r} - \mathbf{r}') - q_0 \rho_Z(\mathbf{r})], \quad |\mathbf{r} - \mathbf{r}'| \leq a,$$

$$\nabla_r^2 \tilde{\phi}_\sigma(\mathbf{r}; \mathbf{r}') = \tilde{\kappa}_D^2(\mathbf{r}) \tilde{\phi}_\sigma(\mathbf{r}; \mathbf{r}'), \quad |\mathbf{r} - \mathbf{r}'| \geq a,$$

Lee and Fisher, EPL 39, 1997.

Ultrasoft Restricted Primitive Model

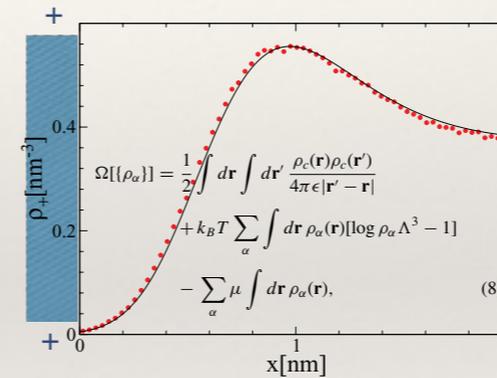


FIG. 8. The coion density profile for $R = 0.8$ nm obtained from the simulation (symbols) and the FSPB equation (solid line). The remaining parameters are as in Fig. 7.

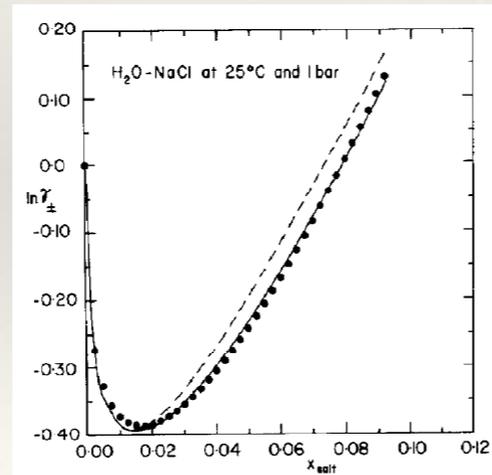
Frydel and Levin, JCP 138, 2013.

Nikoubashman et. al., JCP 137, 2012.

Here's an example - and the heart of this talk really. The "primitive model" of electrolytes is essentially a hard-sphere model for ions with a perturbative correction calculated in the usual virial way. On the opposite side, the URPM has no hard centers at all. It was shown to predict one of the most counterintuitive properties of strong electrolytes - counterion condensation near a charged wall. We haven't tested a perturbative correction for it, but Lee and Fisher have shown that zeroing out the ion density in a radius 'a' gives some nice results for phase diagrams.

- ❖ Working models compare well with experiment
- ❖ high-dens. corrections to μ^{ex}
- ❖ insulator / conductor phase trs.
- ❖ All are missing a systematic method for improvement
- ❖ All assume known, constant dielectric:

see also Debenedetti



Perry, Massey, Cummings Fl. Phase Equ. 39, 1988.

Maribo-Morgenson et. al., Ind. and Chem. Eng. Res., 51, 2012.

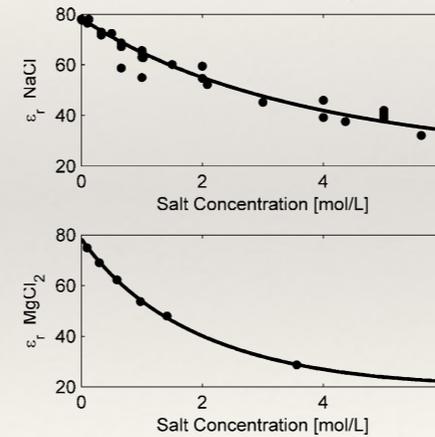
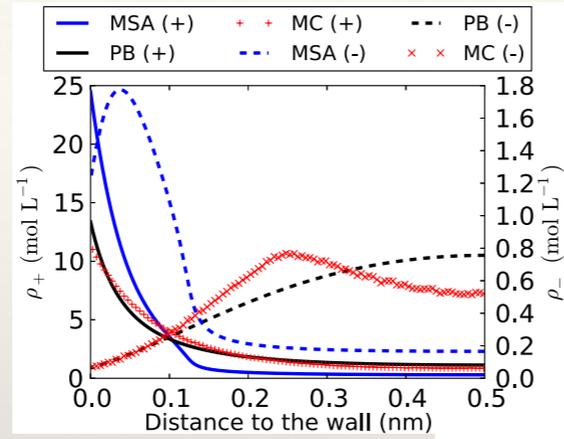


Figure 3. Effect of salt concentration on relative static permittivity of NaCl and MgCl_2 using eq 44. Experimental data indicated by the filled circle (●) is taken from the collections of Akhadov³⁶ and Barthel et al.³⁷

This is how you get phase diagram information from these models. You calculate free energies as functions of concentration and temperature. Traditionally, you re-scale radii until it matches experiment. Partial success here sets the bar high for new theories.

Joubaud, PRE 89, 2014.



$[2+] = [-2] = 0.5 \text{ mol/L}$
 $s = -2 \text{ C/m}^2$
 $d = 2.27 \text{ \AA}$
 $T^* = 0.08$

C. Caccamo / Physics Reports 274 (1996) 1-105

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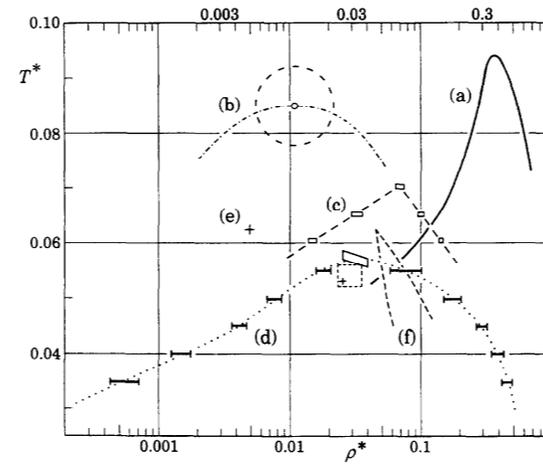
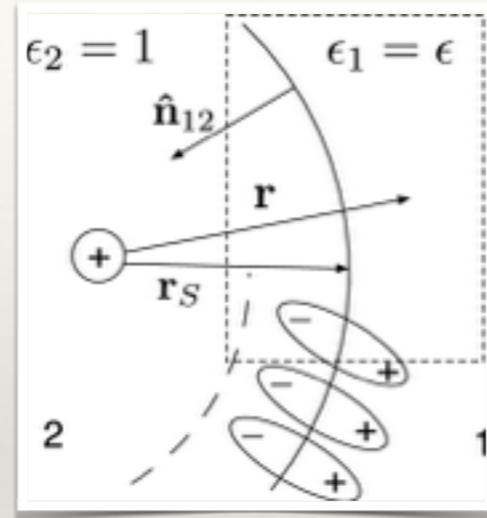


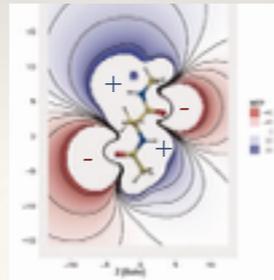
Fig. 31. Coexistence curves (and critical parameters) for the restricted primitive model. Computer simulation by: (a) Vorontsov-Veliamianov et al. (1970, 1976) (c) Valleau (1991); (d) Panagiotopoulos (1992). Theories: (b) Stell et al. (1976); (e) pure DH estimate Plot (f) (Friedman and Larsen, 1979). Curves connecting data points in case (c) and (d) are guides to the eye. The sloping box probably contains the critical point. The square box delimits the range of critical parameters according to some recent simulations, with the cross inside corresponding to the Orkoulas and Panagiotopoulos (1994) estimate (from Fisher, 1994; Fisher and Levin, 1996).

Nevertheless, Joubaud showed that simply adjusting radii does not actually resolve the issue, since neither the MSA (SR-first) nor the Poisson-Boltzmann (LR-first) theory can match Monte Carlo results for counterion condensation. They can, however, roughly pinpoint a low-density KT-phase transition for bulk electrolytes.

Dielectrics vs. Density Response



Matyushov, JCP 140, 2014.



Kramer, Gedeck, and Meuwly, JCC 33, 2012.

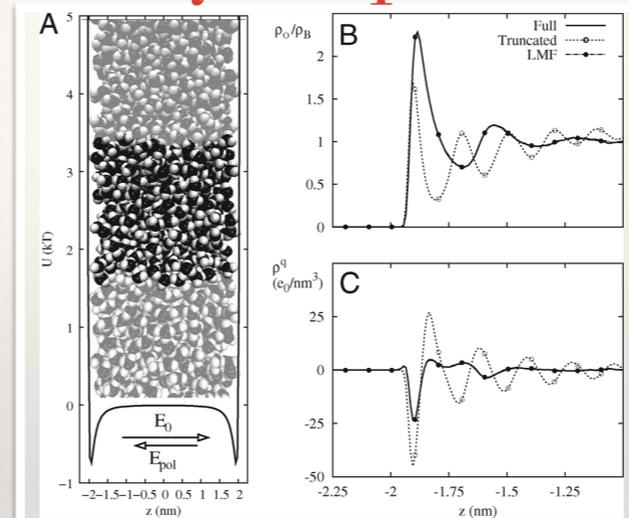
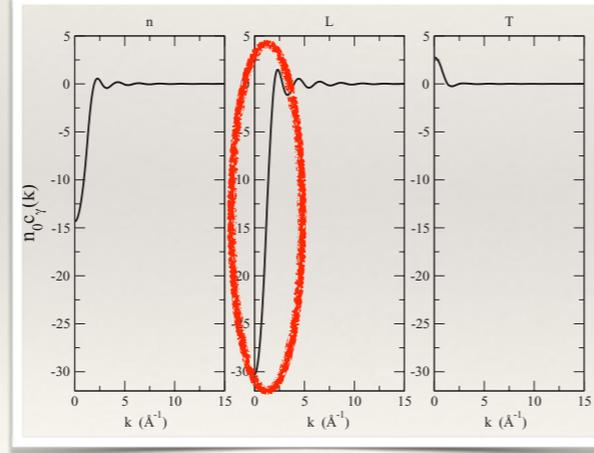
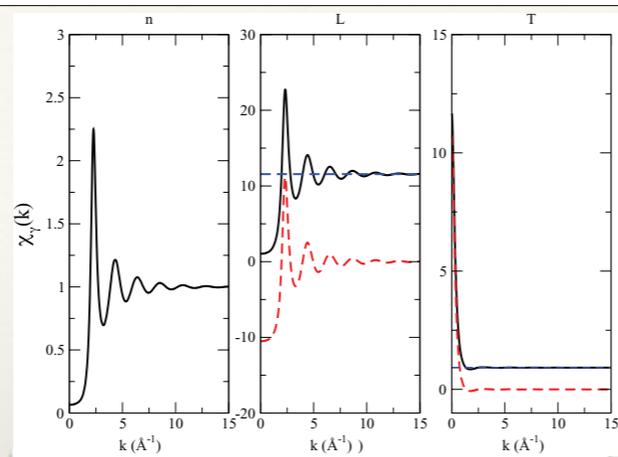


Fig. 2. Model hydrophobic wall confinement of SPC/E water with an applied field. GT water with $\sigma = 0.6$ nm fails whereas treatment with full LMF theory succeeds. (A) The simulation system and nearest images in the y direction confined by the Lennard-Jones wall potential. (B) The oxygen density profile relative to the bulk density. (C) The charge density profile. Density profiles are only shown for $z < -1.0$ nm for greater clarity of the atomic level behavior, though these densities are strictly asymmetric about the origin.

Rodgers and Weeks, PNAS 105, 2008.

That brings us to our third debate, which turns out not to be a real debate. On the left is an illustration of the classic problem of dielectric models - determining a dividing surface between vacuum and polarizable continuum. On the right is a direct calculation of water polarization response to an applied field. The fact that we can compute these response functions, and that they are response functions either way, kind of makes the point moot. Dielectric models are linear density response.



Jeanmairet, Levy, Levesque and Borgis,
J. Phys. Condens. Matt. 28, 2016.

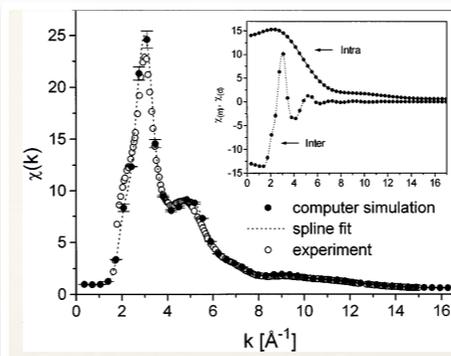


FIG. 3. Response function $\chi(k)$; symbols and lines are as in Fig. 2. The inset shows the intramolecular (χ_m) and intermolecular (χ_d) contributions. Solid line: analytical calculation of the intramolecular part via Eq. (2).

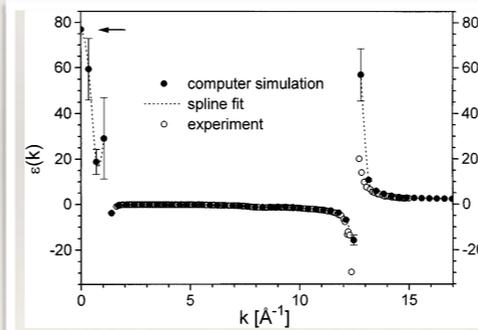


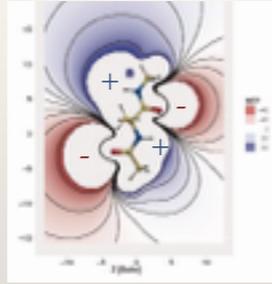
FIG. 2. CS data for $\epsilon(k)$ due to Eq. (5) together with the values determined from neutron diffraction data [12]. For $k = 0$ the value of the macroscopic dielectric constant, $\epsilon \approx 77$, is added (arrow) [17] obtained in a CS for the CF model of water [18] using the Kirkwood equation.

Bopp, Kornyshev and Sutmann, PRL 76, 1996.

This is hammered home by the dielectric response measurement of the dipole-dipole correlation function (top-right). The inter-molecular response curve matches very closely to the same calculation done later on the top-left (center panel). The top-right and bottom-right pictures show the same information, but the dielectric is just a poorly behaved function. The full set of density response functions (left sides) are nice, and can always be inverted (bottom-left). Finally, the circled peak gives us the clue we need to resolve continuous vs. discrete and SR vs. LR! In a continuum, there's no peak - it's a flat line. The peak width gives a physical, dividing size scale.

Where to next ?

$$\Psi_\alpha(r)$$



$$\frac{\rho_\alpha(r)}{\rho_\alpha^0} = e^{-\beta\mu_\alpha^{\text{ex}}(r)} = \langle e^{-\beta\Psi_\alpha(r)} \rangle \quad \text{Widom, JPC 86, 1982.}$$

$$\begin{aligned} \text{A)} \quad &= e^{-\beta\mu_{\text{ref}}^{\text{ex}}} \langle e^{-\beta\Psi_\alpha} \rangle_{\text{ref}} && \text{various authors} \\ &= \langle e^{-\beta\Psi_\alpha^{\text{SR}}} \rangle_0 \langle e^{-\beta\Psi_\alpha^{\text{LR}}} \rangle_{\text{SR}} \end{aligned}$$

$$\text{B)} \quad = \langle e^{-\beta\Psi_\alpha^{\text{LR}}} \rangle_0 \langle e^{-\beta\Psi_\alpha^{\text{SR}}} \rangle_{\text{LR}} \quad \text{Remsing \& Weeks, JPCB 120, 2016.}$$

Rogers, arXiv 1712.09427

To exploit this, let's build a rigorous expression for the solvation free energy by doing a SR, cavity step and a LR, perturbative step. That's option (A). Of course the other order of those two is option (B).

Paths Diverge Again

Toulouse, Colonna and Savin, PRA 70, 2004.

$$F[n] = F^\mu[n] + \bar{F}^\mu[n], \quad (2)$$

where $F^\mu[n]$ is the universal functional corresponding to the long-range interaction $\hat{V}_{ee}^\mu = \sum_{i<j} v_{ee}^\mu(r_{ij})$

$$F^\mu[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ee}^\mu | \Psi \rangle, \quad (3)$$

and $\bar{F}^\mu[n] = F[n] - F^\mu[n]$ is by definition the complement (short-range) part.

The exact ground-state energy of an electronic system in the external local nuclei-electron potential $v_{ne}(\mathbf{r})$ can be written using this short-range functional $\bar{F}^\mu[n]$ via application of the variational principle

$$\begin{aligned} E &= \min_n \left\{ F^\mu[n] + \bar{F}^\mu[n] + \int n(\mathbf{r}) v_{ne}(\mathbf{r}) d\mathbf{r} \right\} \\ &= \min_\Psi \left\{ \langle \Psi | \hat{T} + \hat{V}_{ee}^\mu | \Psi \rangle + \bar{F}^\mu[n_\Psi] + \int n_\Psi(\mathbf{r}) v_{ne}(\mathbf{r}) d\mathbf{r} \right\} \\ &= \langle \Psi^\mu | \hat{T} + \hat{V}_{ee}^\mu | \Psi^\mu \rangle + \bar{F}^\mu[n_{\Psi^\mu}] + \int n_{\Psi^\mu}(\mathbf{r}) v_{ne}(\mathbf{r}) d\mathbf{r}. \quad (4) \end{aligned}$$

Rodgers and Weeks, PNAS 105, 2008.

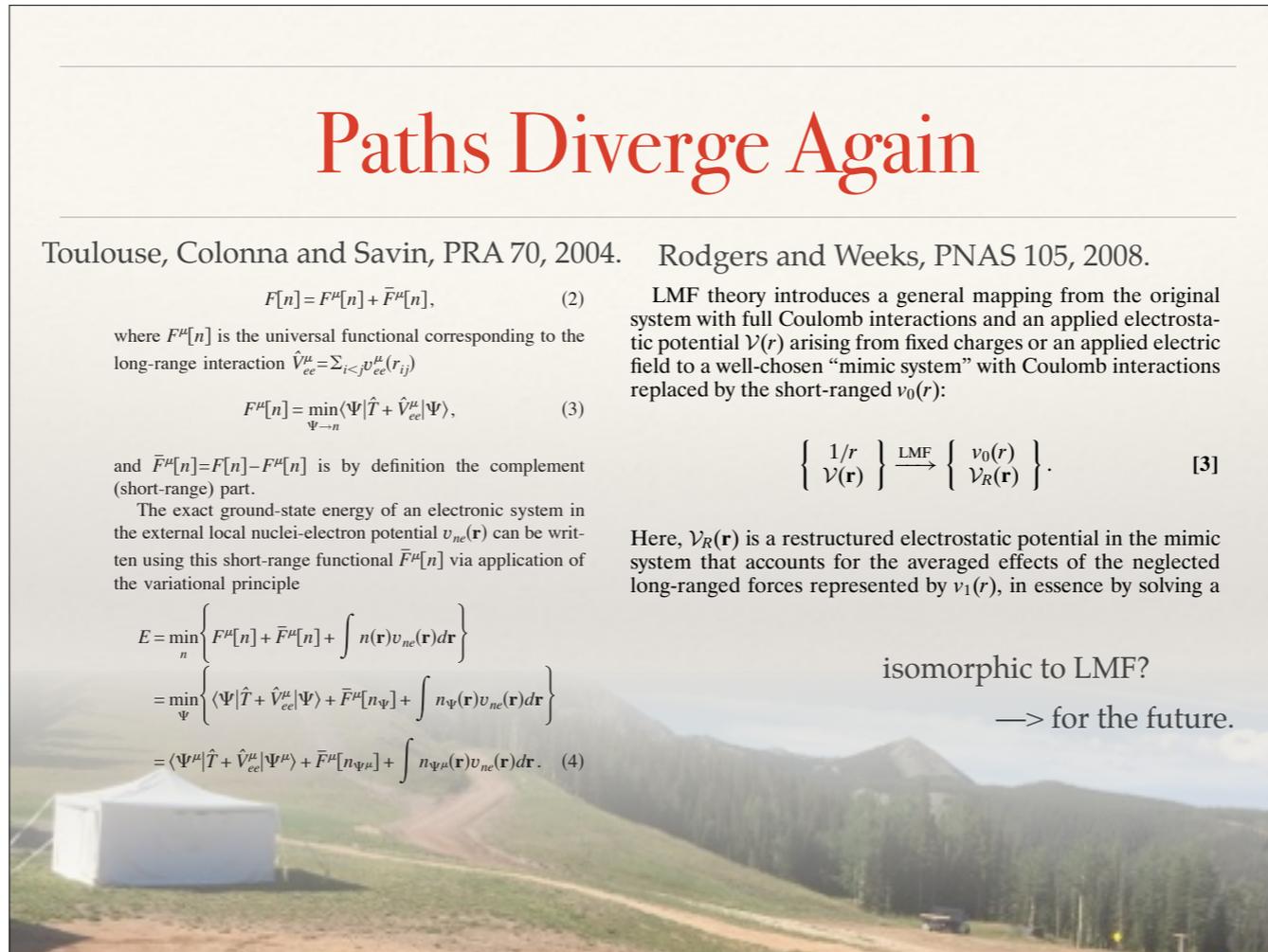
LMF theory introduces a general mapping from the original system with full Coulomb interactions and an applied electrostatic potential $\mathcal{V}(r)$ arising from fixed charges or an applied electric field to a well-chosen “mimic system” with Coulomb interactions replaced by the short-ranged $v_0(r)$:

$$\left\{ \begin{array}{l} 1/r \\ \mathcal{V}(\mathbf{r}) \end{array} \right\} \xrightarrow{\text{LMF}} \left\{ \begin{array}{l} v_0(r) \\ \mathcal{V}_R(\mathbf{r}) \end{array} \right\}. \quad [3]$$

Here, $\mathcal{V}_R(\mathbf{r})$ is a restructured electrostatic potential in the mimic system that accounts for the averaged effects of the neglected long-ranged forces represented by $v_1(r)$, in essence by solving a

isomorphic to LMF?

—> for the future.



But now, do we really want to treat the LR part first because it's easy and leave “everything else” for later? There turns out to be a strong connection between this way of thinking and the split-range electronic DFT and the LMF theory that I can't get into here.

But, we have an LR answer!

$$\mu_{\alpha}^{\text{ex}}(\mathcal{R}^n) \approx \tilde{\mu}_{\alpha}^{\text{ex}}(\mathcal{R}^n) + \langle \Phi_{\alpha} | \mathcal{R}^n \rangle_r - \frac{\beta}{2} \langle \delta \Phi_{\alpha}^2 | \mathcal{R}^n \rangle_r. \quad \text{PDT Book, Ch. 4}$$

$$\mu^{\text{ex}}[\Psi_{\alpha}] = \min_{\rho} \left\{ \int \rho(r) \Psi_{\alpha}(r) dr - T s^{\text{ex}}[\rho] \right\} \quad \text{new(ish)}$$

$$\approx \mu_{\text{ref}}^{\text{ex}} + \int \rho_{\text{ref}}^{(1)}(r) \Psi_{\alpha}^{\text{LR}}(r) - \frac{\beta}{2} \iint dr dr' \Psi_{\alpha}^{\text{LR}}(r) \rho_{\text{ref}}^{(2)}(r, r')^{-1} \Psi_{\alpha}^{\text{LR}}(r')$$

Solvation energy variance.

$$s^{\text{ex}}[\rho_{\alpha}]/k_B = \min_{\Psi} \left\{ \beta \int \rho_{\alpha}(r) \Psi(r) dr - \beta \mu^{\text{ex}}[\Psi] \right\}$$

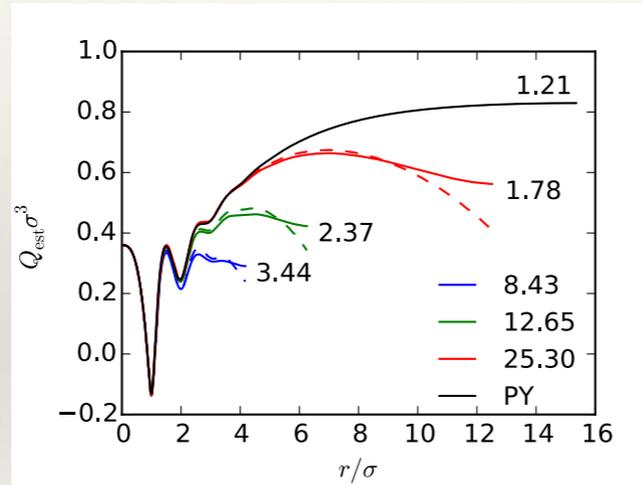
Legendre transform pair.

Rogers, arXiv 1712.09427

In any case, it doesn't really matter because even choosing path (A), the LR part is still a response of the solvent to a smooth, long-ranged potential. It's fairly well-known that the solvent response can be cast as an extremum principle. In QCT, we turn out to be minimizing an excess chemical potential or maximizing an excess entropy. Take your pick.

We can compute the LR answer.

Why we need Fourier-space.

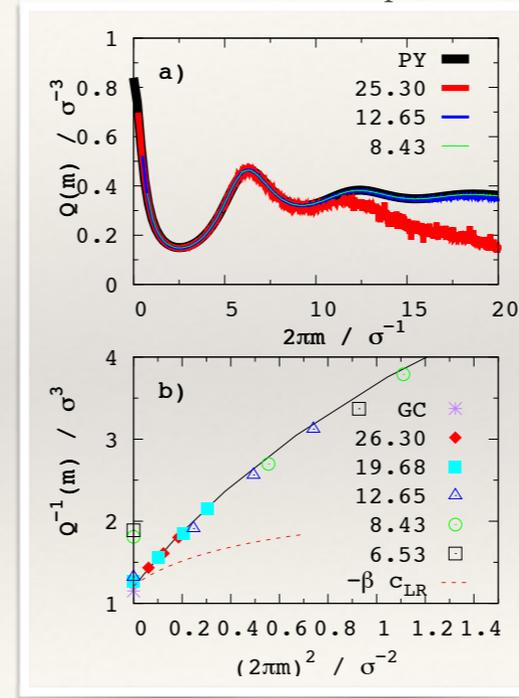


Rogers, JCP 2018.

❖ Short k behavior is fine!

Rogers, arXiv 1712.09427

Accum. in Fourier-space.



The problem with using DFT (finding the functional) has been overcome by several authors. Our paper above comes with a nice code and works at short-k, as seen by this proof-of-concept to compute LJ $S(k)$. That's important for an LR functional!

Modular Codes Please

<https://github.com/frobnitzem/EwaldCorrel>

```
s = sfac(L, [128,128,128], 4)
s.sfac(N, q, atoms) # compute structure factor
Q += s.S() * s.S().conjugate()

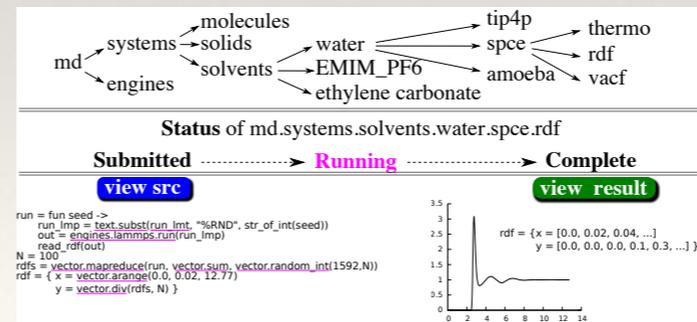
s.en() # also computes LR en, virial and force
s.de1(vir)
s.de2(N, q, atoms, dx)
```

$$L, \text{vir} \in \mathcal{M}_{3 \times 3}$$

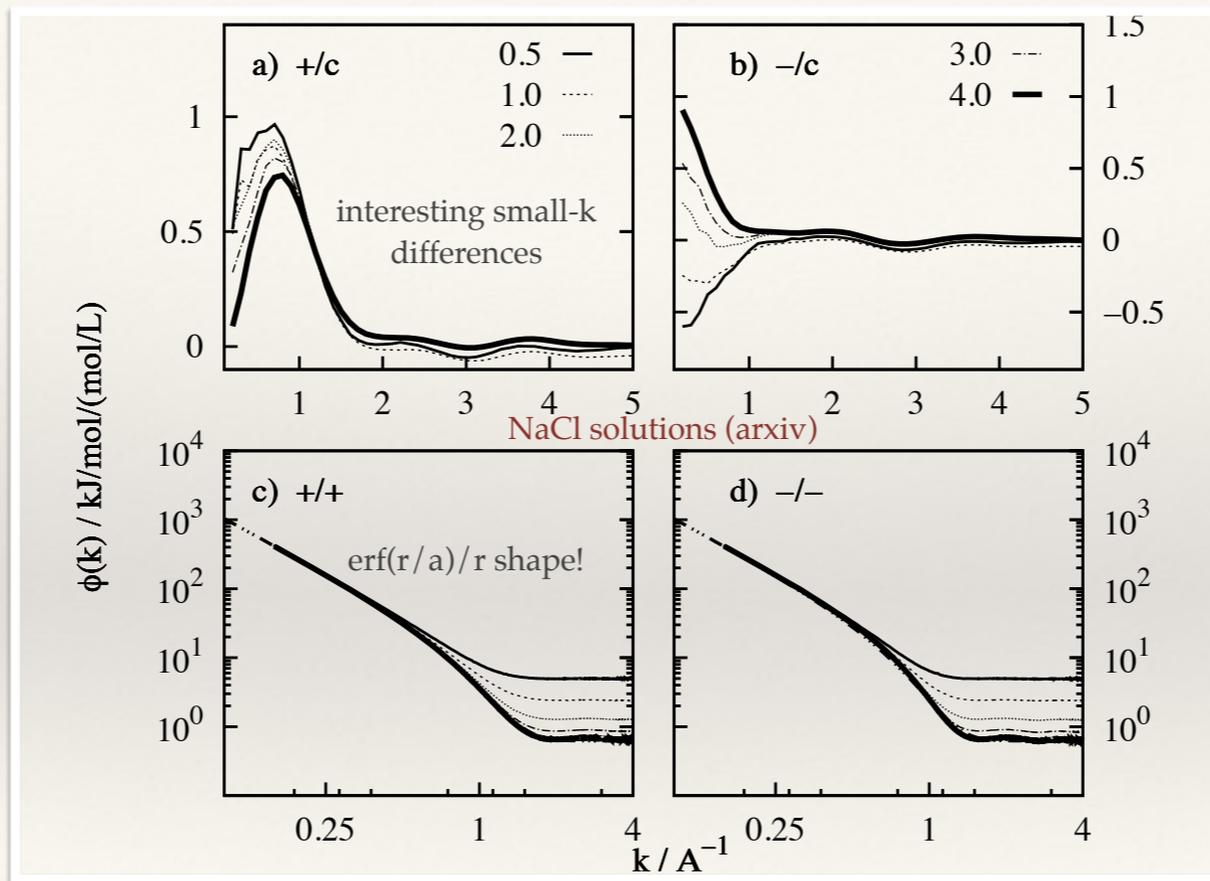
$$q \in \mathbb{R}^N$$

$$\text{atoms}, dx \in \mathbb{R}^{N \times 3}$$

parallelsience.com Named Reference = complete result



It is a modular code, and you can find it here.



Rogers, arXiv 1712.09427

When I apply this to ions, I find an amazingly good fit of the density functional to $\text{erf}(r/a)/r$ — the potential due to a screened charge. That comes from the simulation, I didn't force it to be an erf-shape. It seems nature has a range-separation in mind.

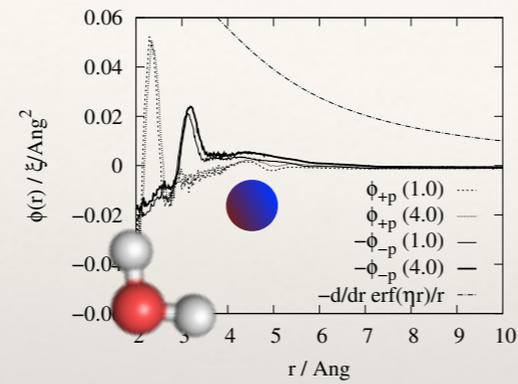


FIG. 5. Ion-dipole direct correlation functions for 1M and 4M salt concentrations, scaled by the Coulomb constant, $\xi = 1/4\pi\epsilon_0$. The long-range Coulomb expression given by the dashed-dotted line at the bottom was subtracted from each of the lines using $\eta_{+p} = 1/1.9\text{\AA}$ and $\eta_{-p} = 1/2.3\text{\AA}$. The only major feature that remains is a peak around the distance of the first maximum in $g(r)$ (Fig. 2).

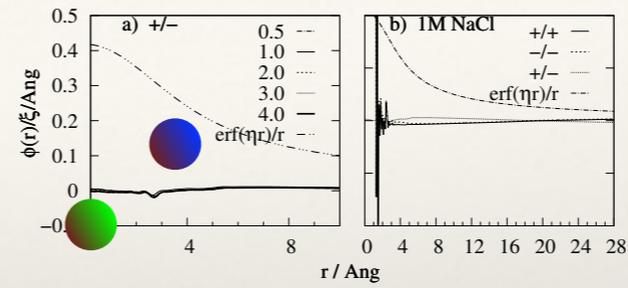
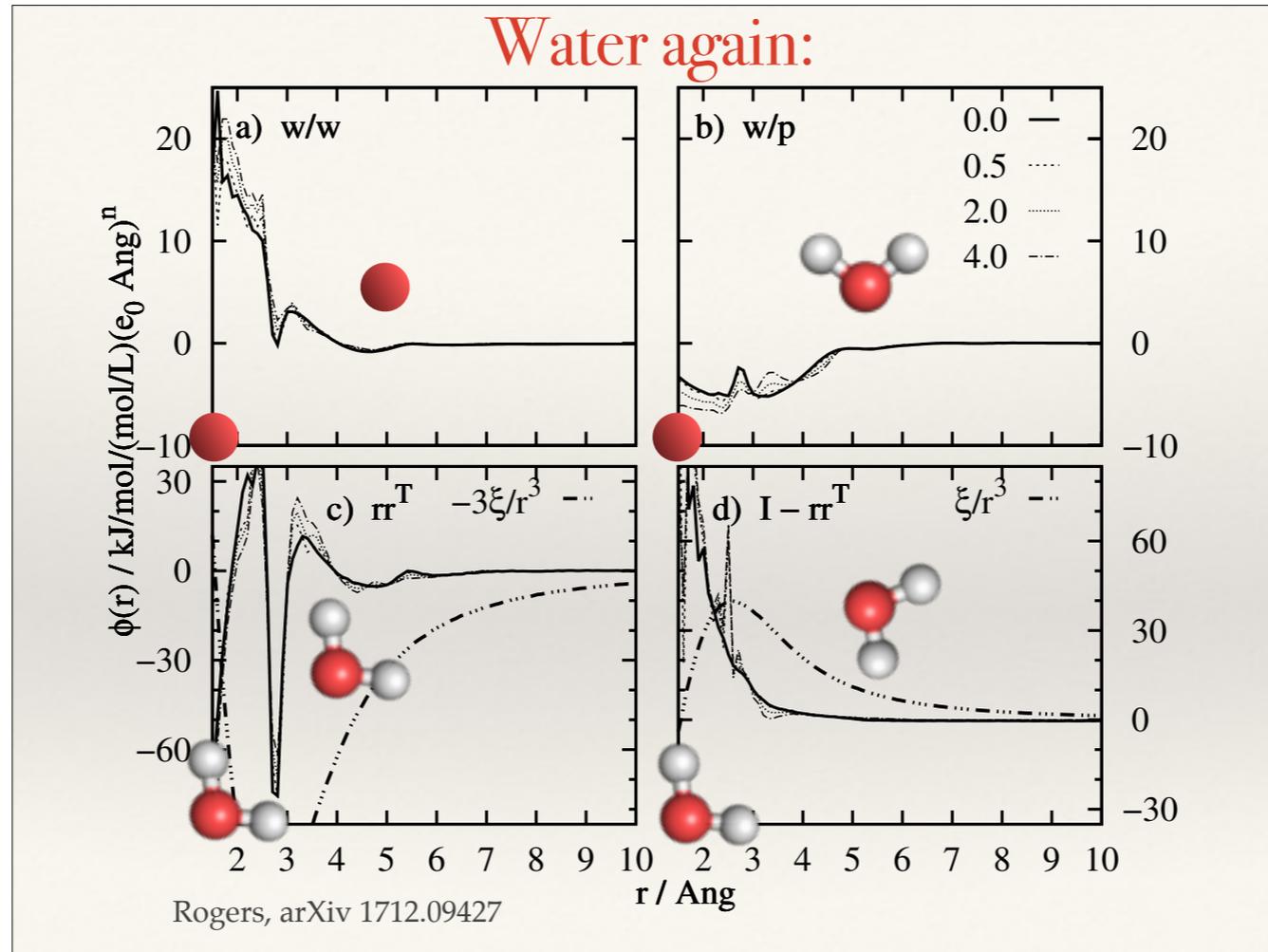


FIG. 7. Ion center of mass direct correlation functions scaled by the Coulomb constant, $\xi = 1/4\pi\epsilon_0$. Panel a shows concentration dependence of cation-anion interactions (using $\eta = 1/2.7\text{\AA}$), while panel b compares direct correlation functions between like and unlike ions. In every case, the curves are drawn after subtracting the screened Coulomb expression appropriate for each pair (dashed-dotted lines). The screening distances used for like ions were the same as in Fig. 6.

Rogers, arXiv 1712.09427

You can also look at the water-ion and ion-ion center to center density functionals.

Water again:



The water-water ones have been shown by other authors, but here I show they have minimal dependence on salt concentration up to 4M!

Analytical LR Results

- ❖ A range-separated theory for long-range interactions that's mostly correct.
- ❖ Packing terms are missing, and can be done first (as in PDT) or second (similar to a $y(r)$ -based theory).

$$\sigma_{\text{LR}}^2 = \sigma_{\text{LR,Born}}^2 + \sigma_{\text{LR,DH}}^2$$

$$f = \beta e^{-k^2/4\eta^2} / \epsilon_0 k^2$$

$$\beta^2 \sigma_{\text{LR,Born}}^2 = z_\alpha^2 \langle k, f^2(k) \chi^{-1} \circ k \rangle$$

$$= \frac{z_\alpha^2}{V} \sum_k f(k) - \bar{f}(k),$$

$$\begin{aligned} \beta^2 \sigma_{\text{LR,DH}}^2 &\rightarrow \frac{\beta z_\alpha^2}{(2\pi)^3 \epsilon_r \epsilon_0} \int_{0+}^{\infty} \frac{4\pi \kappa^2 e^{-k^2/2\eta^2}}{k^2 + \kappa^2 e^{-k^2/4\eta^2}} dk \\ &= \frac{\beta z_\alpha^2 \kappa}{4\pi^2 \epsilon_r \epsilon_0} \int_{-\infty}^{\infty} \frac{e^{-k^2 u^2}}{k^2 e^{k^2 u^2} + 1} dk. \end{aligned}$$

Rogers, arXiv 1712.09427

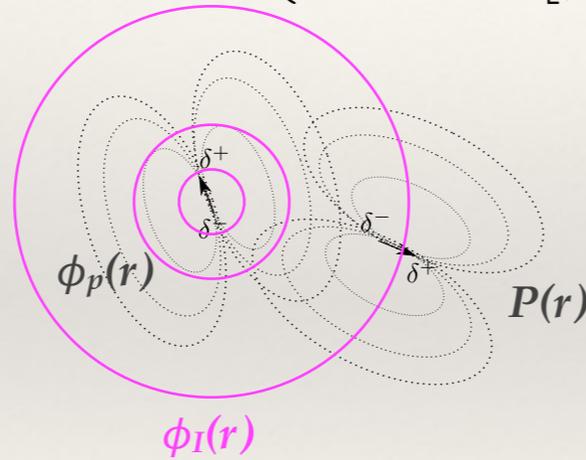
Trying out this range-separated theory, we find the LR energies are exactly what you'd expect - Born plus Debye-Huckel. I didn't plot them, but these functions actually provide a minimum in the activity curve.

Casimir Connection

$$-\log Z[\phi] = \inf_n \left\{ \mathcal{F}_n[\phi_I] + \inf_P \left[\int dr \frac{P^2}{2n\sigma^2} - \frac{1}{2} \langle P, \chi^{-1} * P + \phi_P \rangle \right] \right\}$$

self-energy

polarization energy



❖ What is the polarization contribution to μ^{ex} for a polarizable dipole?

Rogers, arXiv 1807.05963.

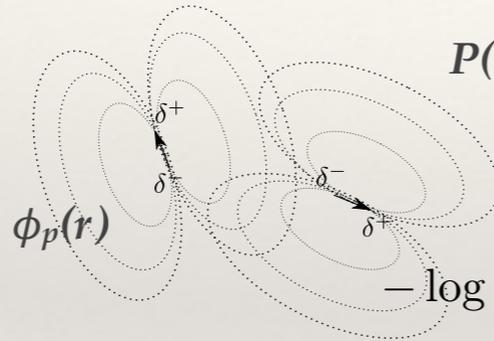
Even better, you can eliminate numerical errors by collecting correlations on a finite set of basis functions for any molecule and forgetting there ever was such a thing as an “OZ closure.” Using density and dipole-dipole correlations on a 4x4 matrix basis, you get a density functional with a radial part and a dipole response part.

Casimir Connection

$$-\frac{1}{2} \langle \phi_p, (I\delta(r, r') / \sigma^2 n(r) - \chi^{-1}(r, r'))^{-1} * \phi_p \rangle$$

$P(r)$ dielectric response

instantaneous solvent polarization energy



$$-\log \int Z[\phi_p] dP_0(\phi_p) = \frac{3}{2} \log \left(1 - \frac{\beta\sigma}{4\pi\epsilon_0} q[n] \right)$$

$$q[n] = \left\langle \frac{r_x}{r^3}, \sigma^2 n(r) \frac{r_x}{r^3} \right\rangle$$

Hamaker integral

$$+ \left\langle \frac{r_x}{r^3}, \sigma^4 n(r) \chi^{-1}(r, r') n(r') * \frac{r_x}{r^3} \right\rangle + \dots$$

Correlation correction

Rogers, arXiv 1807.05963.

The free energy for solvating a dipole is this integral here. Expanding in the polarizability (σ^2) gives a Hamaker integral between the newly inserted dipole and the solvent at first order. Second order is a correlation correction for solute-solvent-solvent double polarization.

Conclusions

- ❖ Range splitting is a recurring theme
 - ❖ (different approximations apply)
 - ❖ Avoiding origin singularities makes things better.
 - ❖ SR is best done in YBG-type ($g(r)$) theories, while LR is best done in OZ-type ($c(r)$) theories.
- ❖ Another is how do we make progress without losing the connection to molecular distributions like $P(n)$.
 - ❖ There are now several DFT routes for this.

Conclusions

- ❖ Can we finally supplant Pitzer?
 - ❖ Model $N_w(N_{ion}, P, V, T)$ recent Debenedetti JCP motivating this.
 - ❖ Need more analytic functional forms for $c(k)$ (MD data / ancient literature).
- ❖ More to come: mesoscale applications
 - ❖ These will clarify SR vs LR at interfaces.