

Organizing information for the statistical theory of liquid water

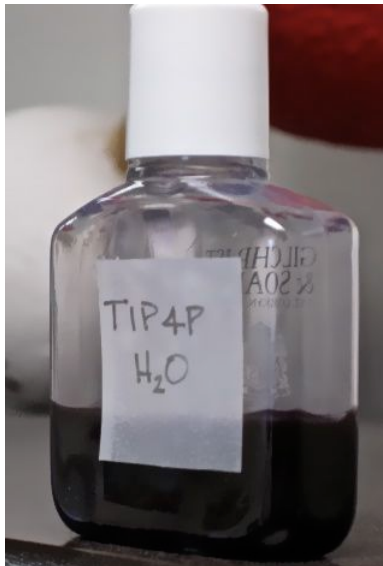
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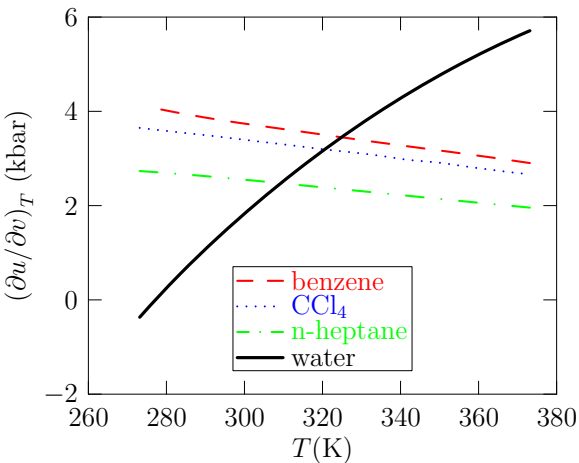
December 23, 2010



We do not have a molecular-scale stat-mech theory of liquid water.



Basic distinctions between water and simple liquids



For a van der Waals liquid

$$\left(\frac{\partial u}{\partial v}\right)_T = a \rho^2$$

is independent of T .

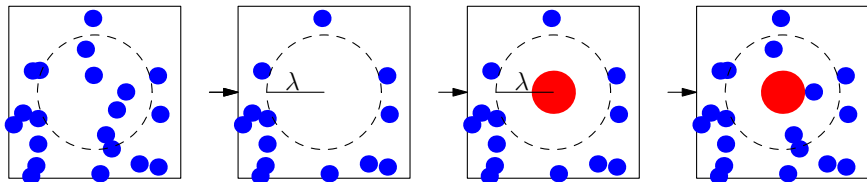
You have to start some place . . .

Model	Multiplicity
BNS/ST2	(4-6)
MCY	(3-4)
TIPXP	(5-10)
SPC	(5-10)
CFM/Polarization . . .	(3-5)
TTMX-R/F	(3-5)
AIMD (density functionals, pseudo-potentials . . .)	> 10
liquid water (<u>the real thing</u>)	<u>1</u>

- 1 What should we **require** of a theory of liquid water?
 - Stat-mech — water is not a van der Waals liquid.
 - Applicability to each physical force-field model but one explanation at the end.
- 2 What is it going to **cost**?
 - The theory will be essentially numerical.

Molecular quasi-chemical theory

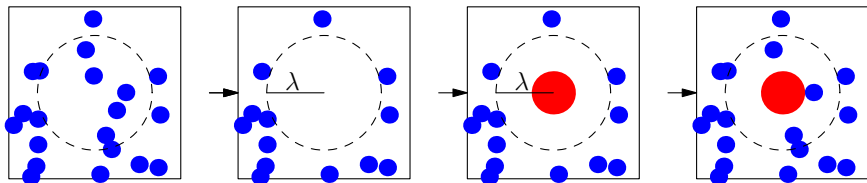
$$\beta\mu^{(\text{ex})} = -\ln p^{(0)}(n_\lambda = 0) + \ln \langle e^{\beta\varepsilon} | n_\lambda = 0 \rangle + \ln p(n_\lambda = 0)$$



Design goal: these contributions should be evaluated from physical data, *i.e.*, from simulation of the physical system.

network-liquid theorem

$$\beta\mu^{(\text{ex})} = -\ln p^{(0)}(n_\lambda = 0) + \ln \langle e^{\beta\epsilon} | n_\lambda = 0 \rangle + \ln p(n_\lambda = 0)$$

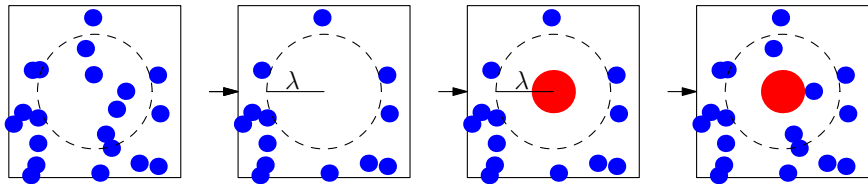


If the interactions vanish beyond λ -range (in the outer shell),
then

$$\beta\mu^{(\text{ex})} = -\ln p^{(0)}(n_\lambda = 0) + \ln p(n_\lambda = 0).$$

When interactions don't vanish in the outer shell:

$$\beta\mu^{(\text{ex})} = -\ln p^{(0)}(n_\lambda = 0) + \ln \langle e^{\beta\varepsilon} | n_\lambda = 0 \rangle + \ln p(n_\lambda = 0)$$

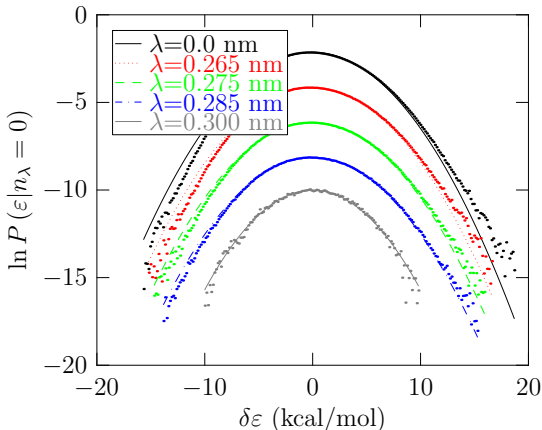


$$\ln \langle e^{\beta\varepsilon} | n_\lambda = 0 \rangle \approx \beta \langle \varepsilon | n_\lambda = 0 \rangle + \beta^2 \langle \delta\varepsilon^2 | n_\lambda = 0 \rangle / 2 ,$$

a **Gaussian (normal distribution) model**. This will be ok when $\lambda \sim \infty$ because then the outer-shell interactions are numerous and weakly correlated.

For liquid water, select the necessary ($n_\lambda = 0$) sub-ensemble

$T = 300\text{K}$,
 $\rho = 1 \text{ atm}$,
(TIP3P)



See:¹

¹J. K. Shah, D. Asthagiri, L. R. Pratt, M. E. Paulaitis, *J. Chem. Phys.* **127**, 144508 (2007): “Balancing Local Order and Long-Ranged Interactions in the Molecular Theory of Liquid Water”



What did you expect?

'Water Revisited'¹

(ST2)

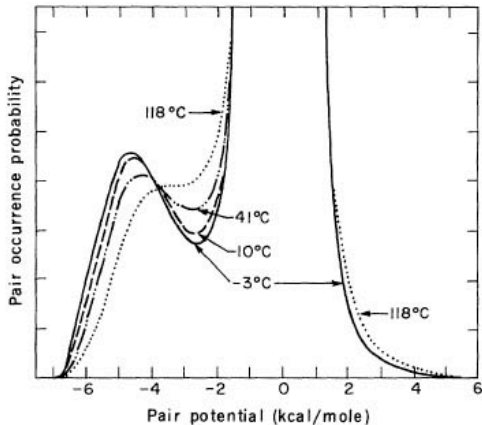


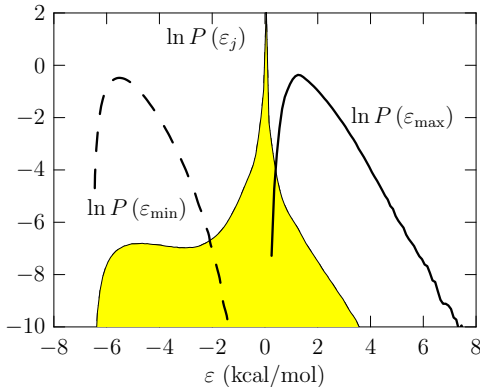
Fig. 4. Distribution function for effective pair interactions between molecules in liquid water (at 1 gram per cubic centimeter).

¹F. H. Stillinger *Science* **209**, 451-457 (1980)

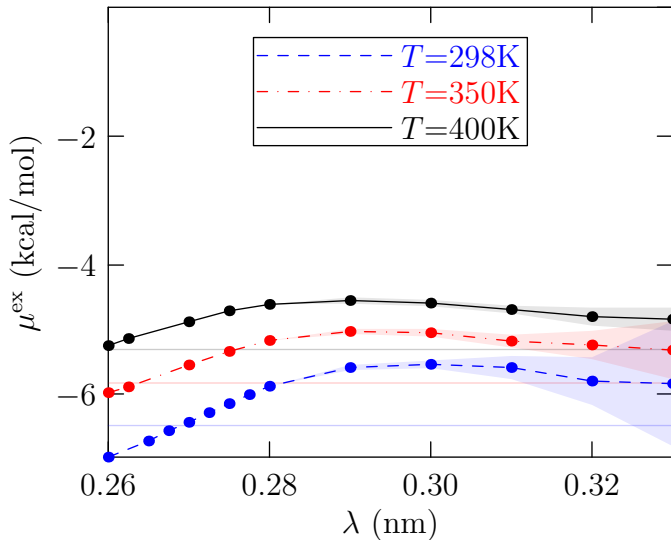
Explain!

- The 'Water Revisited' distribution is $P(\epsilon_j)$. As a distribution, it does not have a useful $N \rightarrow \infty$ limit.
- $P(\epsilon)$ is much simpler, does not have an obvious signature of an H-bond energy, is broad, but a Gaussian model is valid.

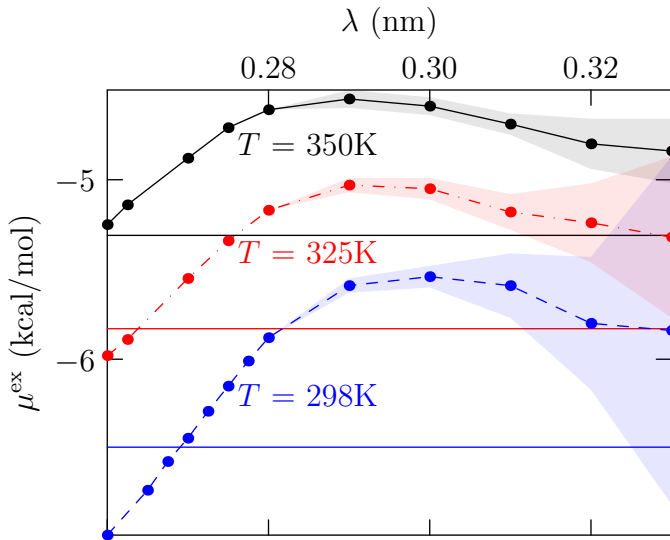
$$\epsilon = \sum_{j=1}^N \epsilon_j$$



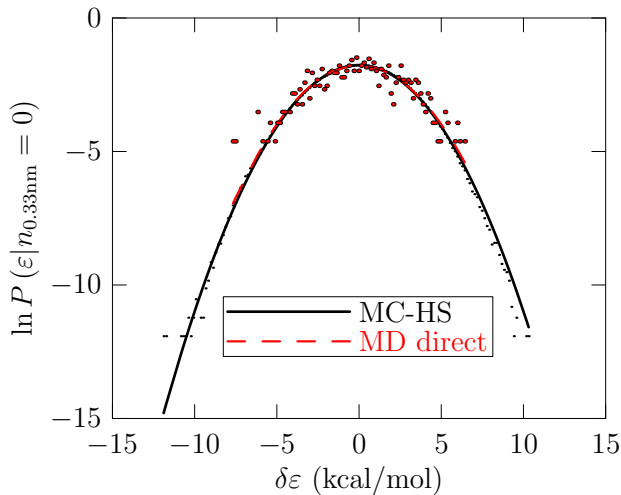
Free energy predictions as they depend on conditioning radius λ



Free energy predictions as they depend on conditioning radius λ

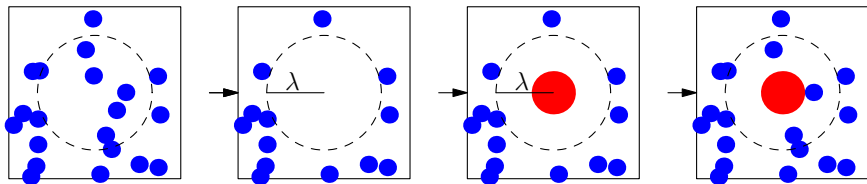


The strongly conditioned distributions $P(\varepsilon | n_\lambda = 0)$ are slightly *sub-Gaussian*:



The free energy comes solely from the outer-shell contribution if $\lambda \approx 0.33$ nm.

$$\beta\mu^{(\text{ex})} = -\ln p^{(0)}(n_\lambda = 0) + \ln \langle e^{\beta\varepsilon} | n_\lambda = 0 \rangle + \ln p(n_\lambda = 0)$$



- For that value the *network-liquid* contributions balance:

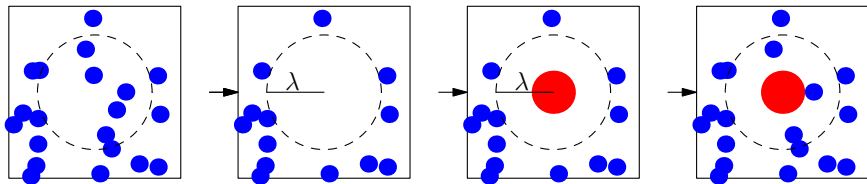
$$-\ln p_W^{(0)}(n_\lambda = 0) + \ln p_W(n_\lambda = 0) \approx 0.$$

- So, for the free energy

$$\mu_W^{(\text{ex})} \approx \langle \varepsilon | n_\lambda = 0 \rangle + \beta \langle \delta\varepsilon^2 | n_\lambda = 0 \rangle / 2.$$

Conclusion for network-liquid models:

$$\beta\mu^{(\text{ex})} = -\ln p^{(0)}(n_\lambda = 0) + \ln \langle e^{\beta\varepsilon} | n_\lambda = 0 \rangle + \ln p(n_\lambda = 0)$$

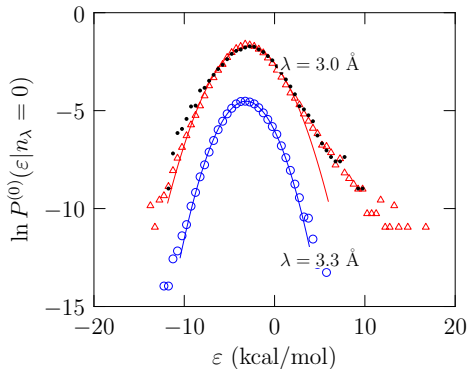


- If you get inner-shell occupancies $p_W(n_\lambda)$ right, and you get hydrophobic things $p_W^{(0)}(n_\lambda)$ right, **you do *not* get the free energy of liquid water right**. Making/breaking of discrete H-bonds is unsatisfactory as a sole explanation for the free energy of liquid water.

Explain!

- Interactions at outer-shell range are strong. Big, well-recognized contributions come from outer shells.
- The number of outer-shell partners of a water molecule is large enough that a Gaussian distribution of binding-energy distributions can be satisfactory.
- **The biggest difficulty** is that these binding energy distributions are very broad.

$$P^{(0)}(\varepsilon | n_\lambda = 0) = e^{\beta(\varepsilon - \mu^{(ex)})} P(\varepsilon | n_\lambda = 0)$$



V. Weber and D. Asthagiri, "Thermodynamics of water modeled using ab initio simulations," *J. Chem. Phys.* **133**, 141101(2010).

What have we learned that's new?

- Network-liquid theorem for the free energy of network-liquid models.
- For realistic models of liquid water:
 - 1 Network-liquid contributions to the free energy can be small (even zero).
 - 2 Binding energies distributions are Gaussian to a useful degree.
 - 3 Outer-shell contributions dominate the free energy.