# *How to use standard electronic structure tools for the theory of liquids:* Quasi-Chemical Theories of Associated Liquids
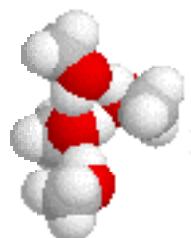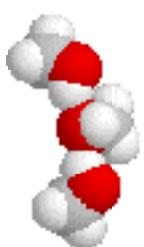
**R. L. Martin, P. J. Hay, L. R. Pratt, and R. A. LaViolette**

URL - http://www.t12.lanl.gov/~www/projects/
solvents.html

Dielectric Models -> Molecular Theory

- **Dielectric Models and Electrostatic Interactions in Solution,** "Molecular Theories and Simulation of Ions and Polar Molecules in Water," G. Hummer, L. R. Pratt, and A. E. Garcia, J. Phys. Chem. A **102**, 7887 (1998)**.**

- **"Hydrolysis of Ferric Ion in Water and Conformational Equilibrium,"** R. L. Martin, P. J. Hay, and L. R. Pratt, J. Phys. Chem. A **102**, 3565 (1998).

- **"Quasi-chemical Theories of Associated Liquids,"** L. R. Pratt and R. A. LaViolette, Molec. Phys. **94**, 909 (1998).

- **Example: liquid methanol** (work in progress, with R. A. LaViolette)
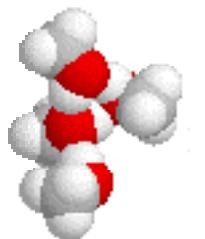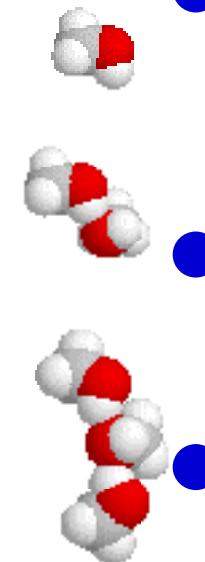
Dielectric Model

- **premier example of an "implicit water model"**

$$\nabla \bullet \boldsymbol{\varepsilon}(\mathbf{r})\nabla\Phi(\mathbf{r}) = -4\pi\boldsymbol{\rho}(\mathbf{r})$$

LA-UR-99-911
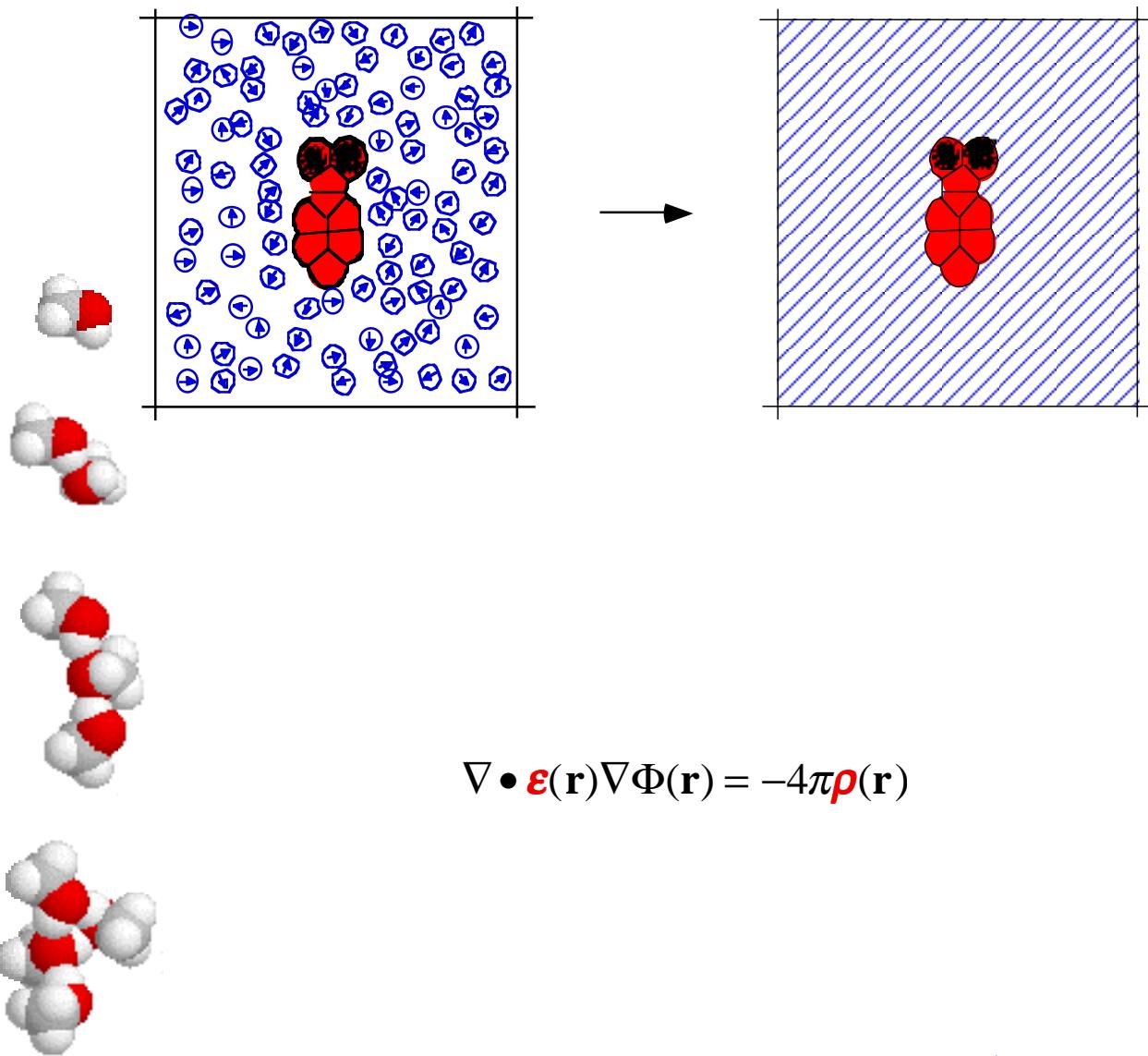
Dielectric Model

- **pro:**
  - physical - can be derived from a Hamiltonian (in more than one way!)
  - practical - reasonably treats huge effects that can't be ignored
  - chemical - can simultaneously include reasonable chemistry
  - empirical - parameterizations (radii) are not unreasonable

- **con:**
  - careful, molecular scale validation of the stat-mech is <u>MIXED!!!</u>
  - sometimes 100% empirical - parameters (radii) must be reconsidered for EVERY new result; parameters depend on (T,p,x); results are sensitive to parameters; any physical result (correct or not) can be reproduced
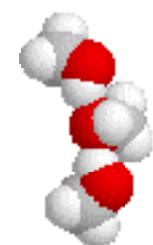
- **"Everything should be made as simple as possible, but no simpler." A. Einstein**
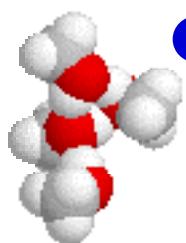
How to test?

- **Dielectric models are simplified ...**
  - second order perturbation theory,
  - or (equivalently) linear response,
 - or (equivalently) gaussian fluctuation of electrostatic potentials.

- **For a spherical ion**
  - Born model

$$\Delta\mu = -\frac{q^2}{2R}\left(\frac{\varepsilon - 1}{\varepsilon}\right)$$

 - second order perturbation theory
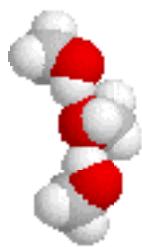
$$\Delta\mu = \Delta\mu_0 + q\langle\Phi\rangle_0 - \frac{\beta q^2}{2}\langle\delta\Phi^2\rangle_0$$

- **Test those approaches and avoid the issue of empirical adjustment of radii.**
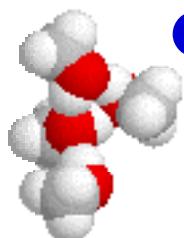
Specific examples
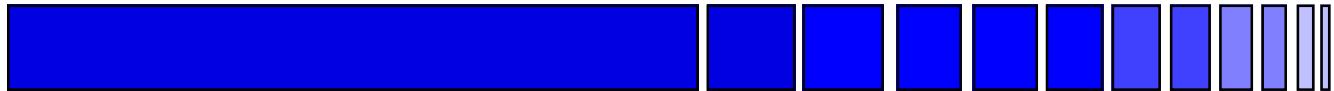
- **charging of spherical ions: linear response?**

  – "Free energy of ionic hydration," Hummer, Pratt, & Garcia, *J. Phys. Chem.* **100**, 1206 (1996).
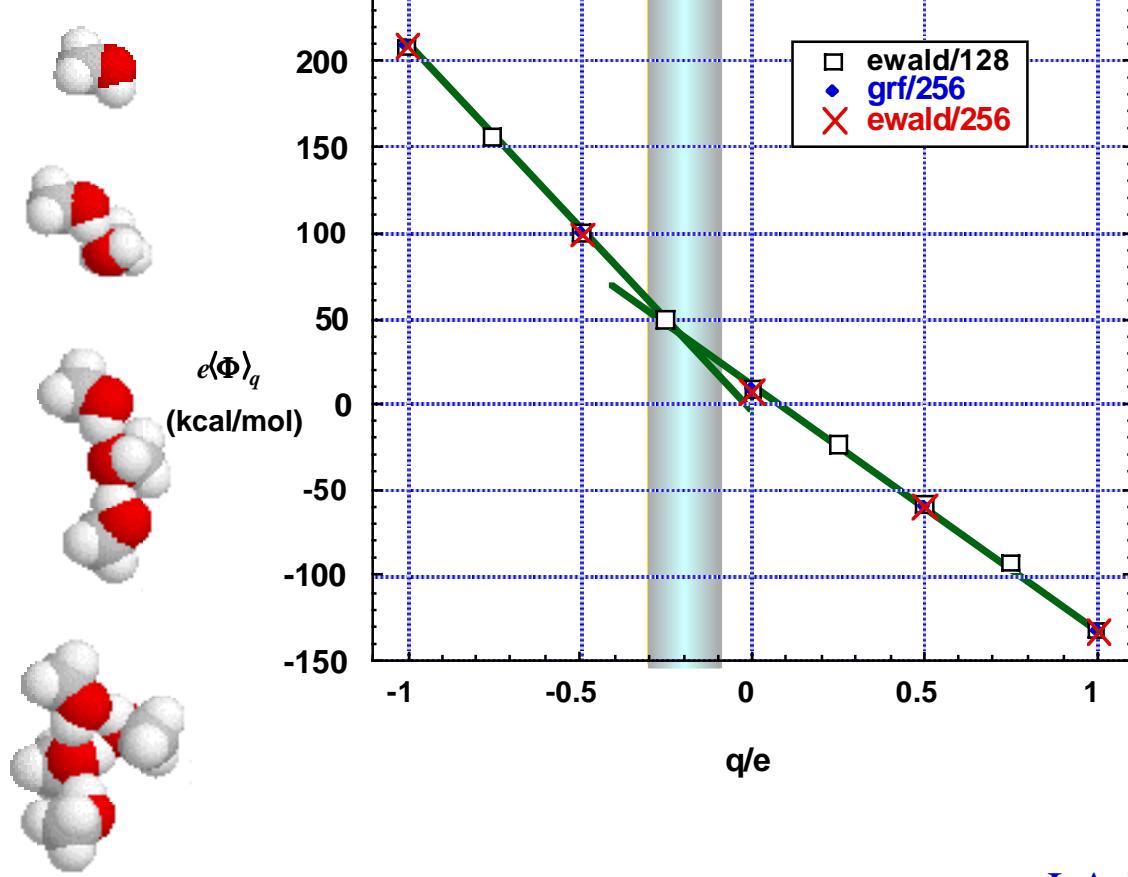
Specific examples

- **water in water: parabolic free energies?**
  - SPC model water, Rick & Berne (1994) + "Hydration free energy of water," Hummer, Pratt, & Garcia *J. Phys. Chem.* **99**, 14188 (1995), accurate agreement
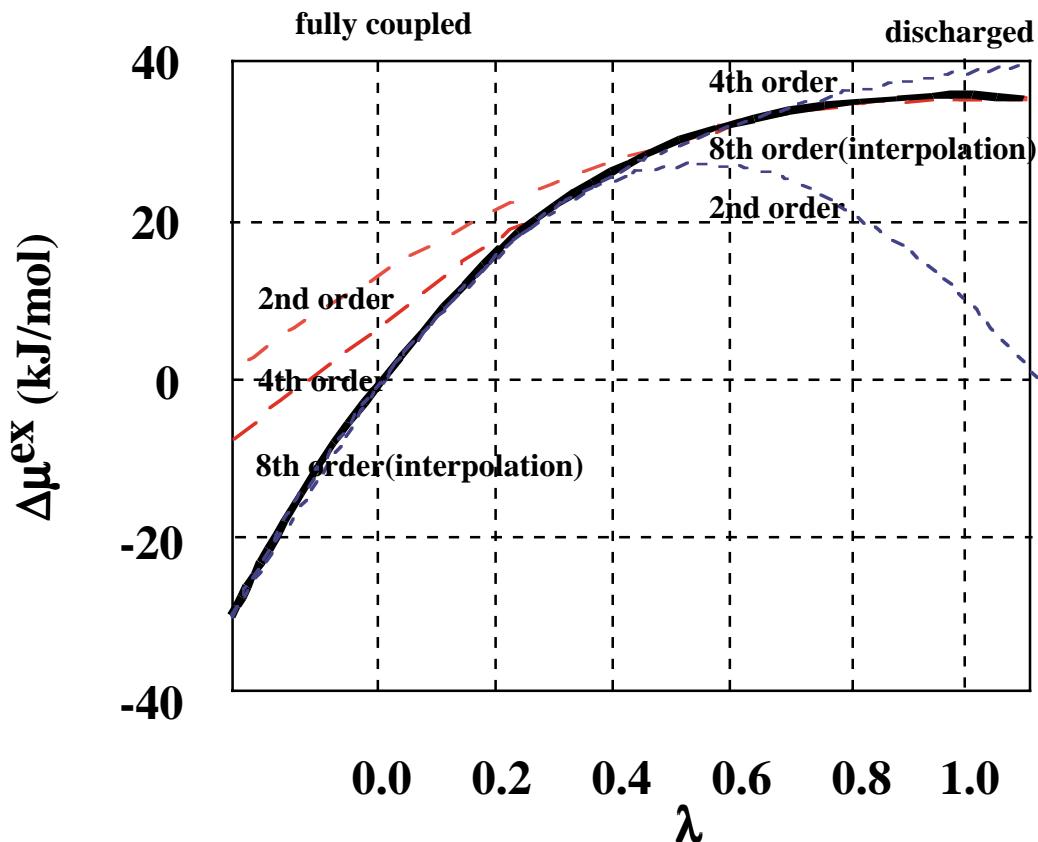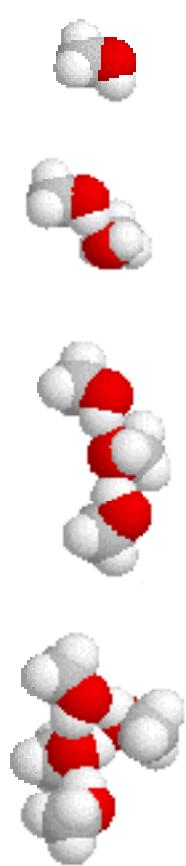
Physical conclusions from simulations

- **Dielectric models of hydration fail on a molecular scale when proton (H) structures near the solute lead to non-gaussian fluctuations of electrostatic potentials.**

 - Easiest examples to get "right" are classic cations, *e.g.* Na^+.

  - Neutral, polar, H-bonding molecules, *e.g.* H_2O or imidazole are more difficult cases for dielectric models when tested on a molecular scale. However, hydration free energies are smaller than for ions.

  - Negative ions are a problem and the hydration free energies are again large. Here chemistry will be more important also, *e.g.* HCO_3^-.
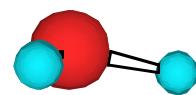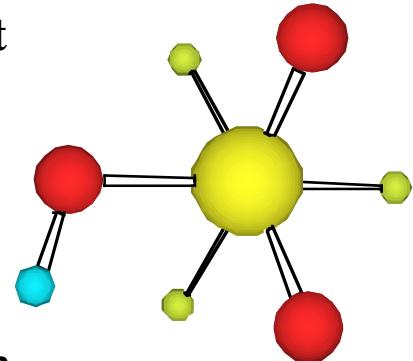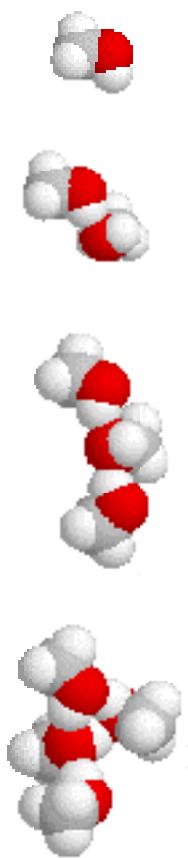
Fix it

- **Conformational substates**
  - **Gaussian model for each substate.** "Multistate gaussian model for electrostatic solvation free energies," Hummer, Pratt, & Garcia, *J. Am. Chem. Soc.* **119**, 8523 (1997)
  - **Not "dielectric saturation and electrostriction;" incrementally higher perturbation theory not that helpful - kinks!**
  - **Substates are categorized by numbers of close H-bonds to solute.**

$$\beta \Delta \mu(\lambda) = -\ln \sum_n w_n e^{-\beta \lambda m_n + (\beta \lambda \sigma_n)^2 / 2}$$
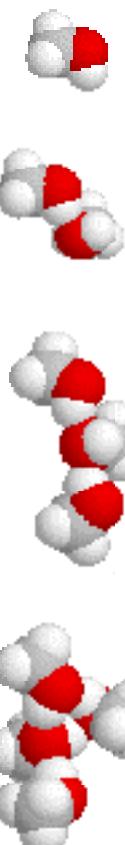
- **water: w_n, $1 \leq n \leq 6$, $\langle n \rangle = 3.64$, remaining max{error} about 5%.**

- **negative ions, *e.g.*, Cl^-, still a problem.**

Quasi-chemical
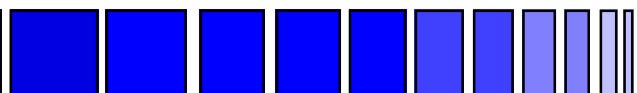
- **yet need a way to start with non-simulation theory, include chemistry and calculate**

- **Chemistry - it'll surprise you.**

2.913Å

3.447Å 2.108Å
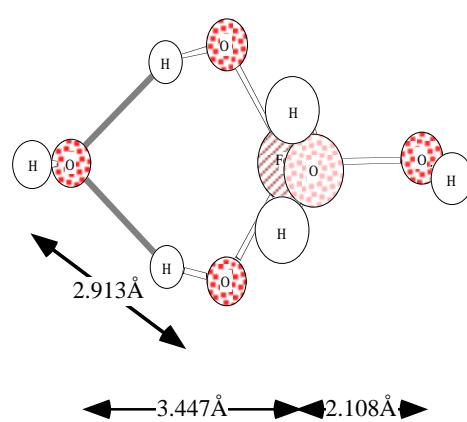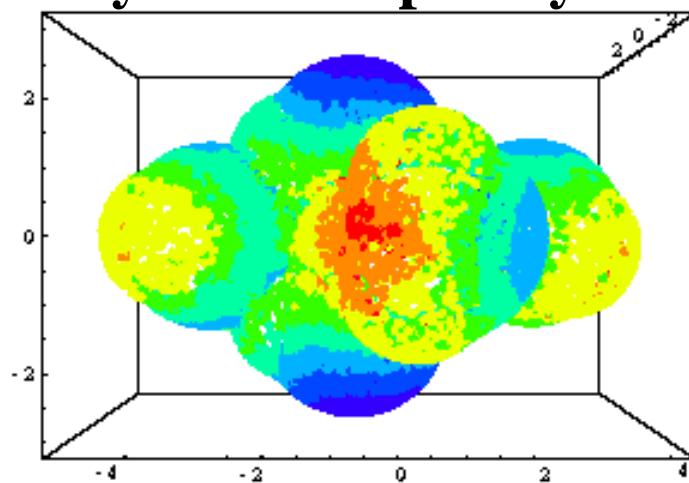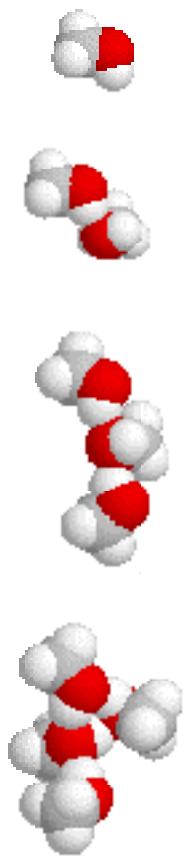
Specific example
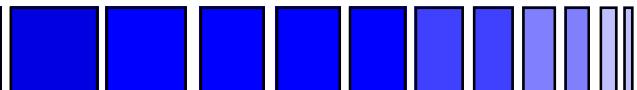
- **Absolute hydration free energy of the Fe^{3+} (*aq*) ion**
  - **experiment: {-1019, -1039}kcal/mol**
  - **calculation: -1020 kcal/mol** ["Hydrolysis of ferric ion in water and conformational equilibrium," Martin, Hay, & Pratt, *J. Phys. Chem. A* **102**, 3565(1998)]

$$Fe^{3+} + 6\ H_2O \quad \xrightleftharpoons{K_6} \quad Fe(H_2O)_6^{3+}$$

$$\boxed{X} \qquad 6\ \mu_{ligand}("p=1354\ atm")\ \Delta\mu_{complex}$$

$$\Delta\mu_{Fe^{3+}} = -RT\ln K_6 + \Delta\mu_{complex} - 6\mu_{ligand}$$

$$= -RT\ln\left[K_6\left(\frac{\rho_{ligand}RT}{1atm}\right)^6 \right]$$

$$+ \Delta\mu_{complex} - 6\Delta\mu_{ligand}$$

-629kcal/mol

-391 kcal/mol
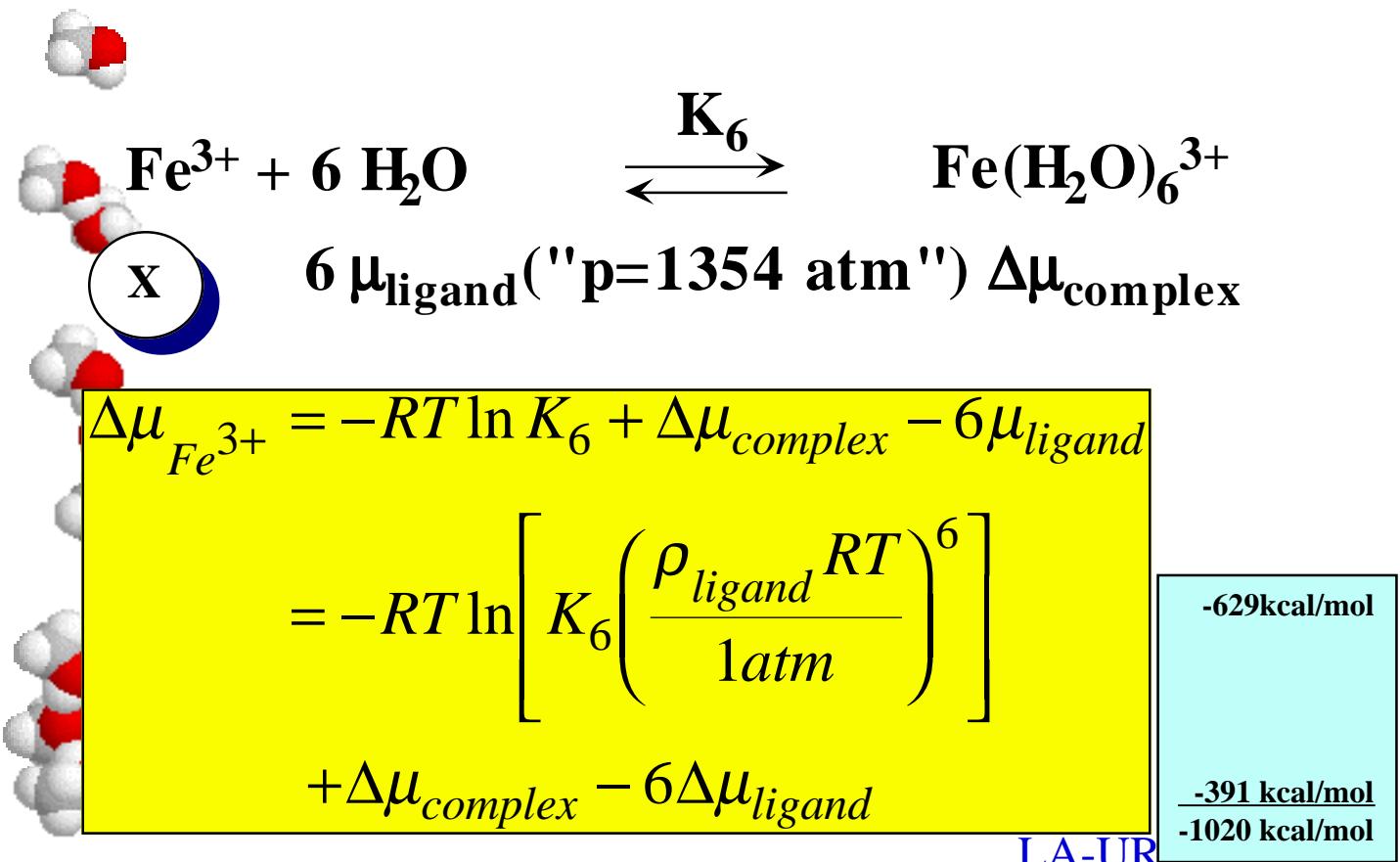
-1020 kcal/mol
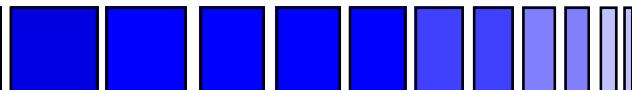
Hydrolysis

- **first hydrolysis (isodesmic format)**
  - calculated free energy change +2 kcal/mol (3 kcal/mol experiment) ... <u>up</u>hill.
  - the gas phase reaction is <u>down</u>hill about 148 kcal/mol., the liquid effects favor the reactants by about 150 kcal/mol.

$$Fe(H_2O)_6^{3+} + H_2O \leftrightarrow Fe(H_2O)_5(OH)^{2+} + H_3O^+$$
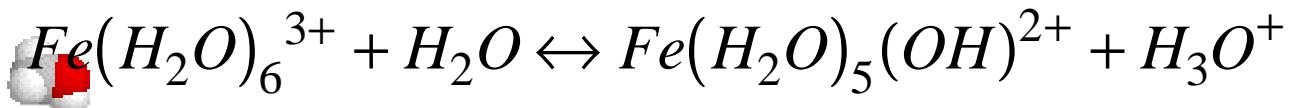
- **second hydrolysis**
  - several isomers (pictures next!), outer-sphere complex has a low energy
  - calculated free energy 16-18 kcal/mol (experiment: 5 kcal/mol)
  - conformational entropy?

$$Fe(H_2O)_5(OH)^{2+} + H_2O \leftrightarrow Fe(H_2O)_4(OH)_2^+ + H_3O^+$$

LA-UR-99-911
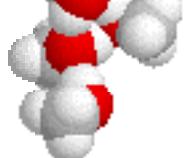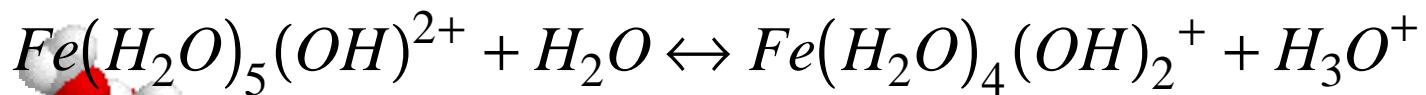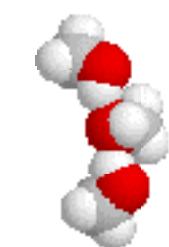
isomeric structures for
Fe(H₂O)₄(OH)₂⁺
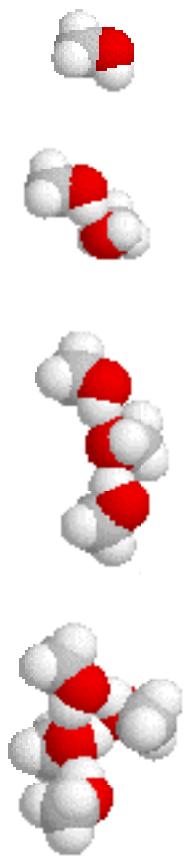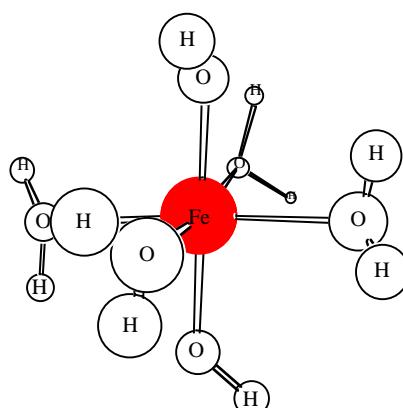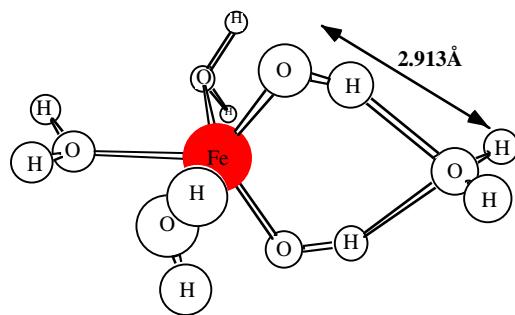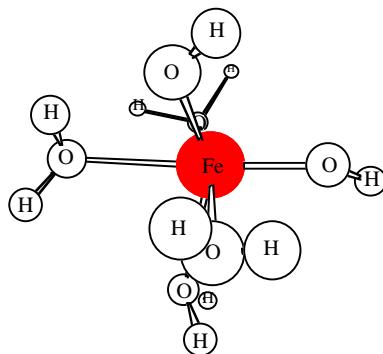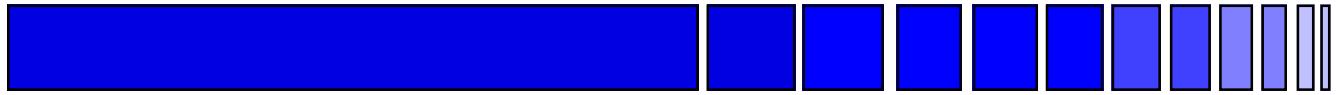
clustering...
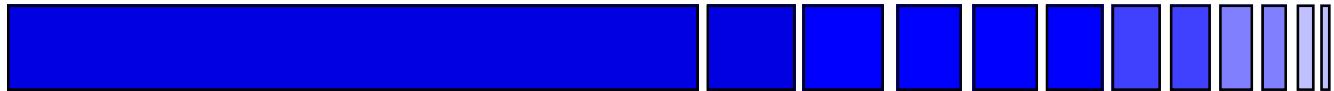
● **local (not spanning) clusters**
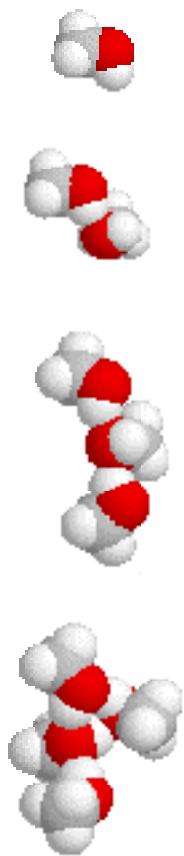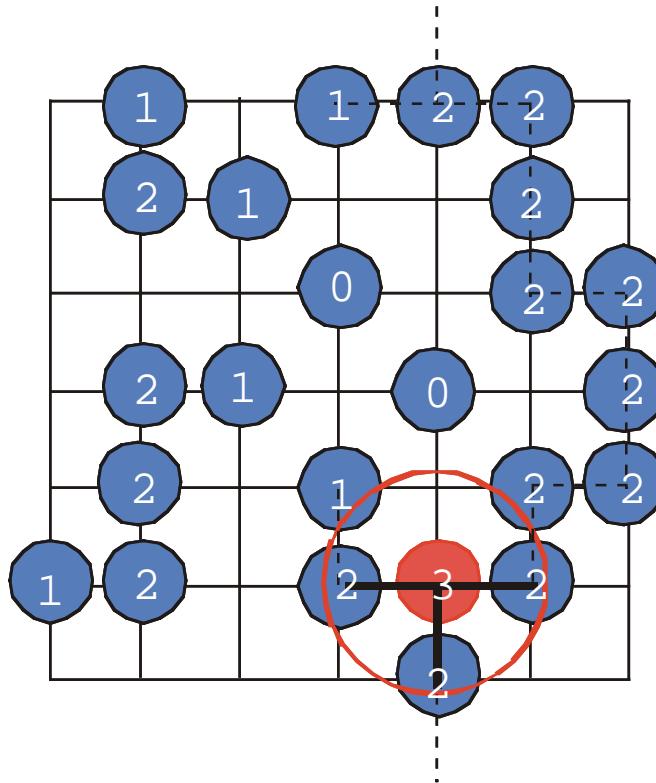
– "One of the principal objects of theoretical research in my department of knowledge is to find the point of view from which the subject appears in its greatest simplicity." J. W. Gibbs

Quasi-chemical formulation

$$X^{z-} + W \overset{K_1}{\longleftrightarrow} XW^{z-}$$

$$XW^{z-} + W \overset{K_2/K_1}{\longleftrightarrow} XW_2{}^{z-}$$

$$XW_2{}^{z-} + W \overset{K_3/K_2}{\longleftrightarrow} XW_3{}^{z-}$$

$$\vdots$$

$$XW_{n-1}{}^{z-} + W \overset{K_n/K_{n-1}}{\longleftrightarrow} XW_n{}^{z-}$$
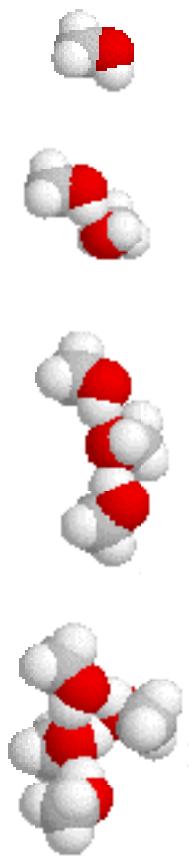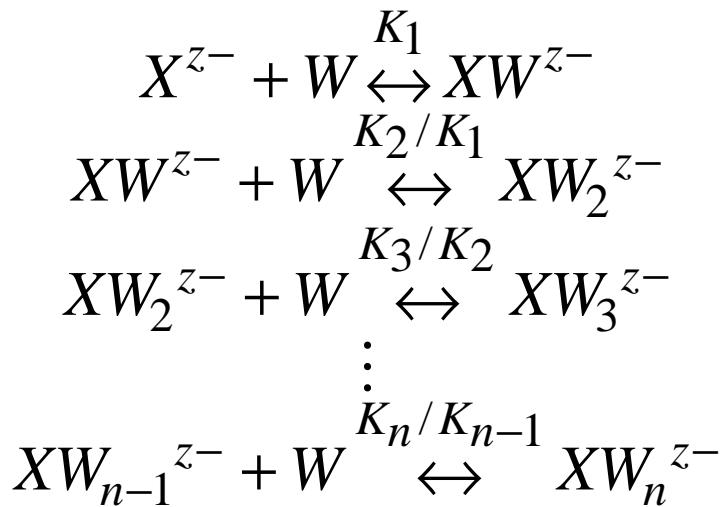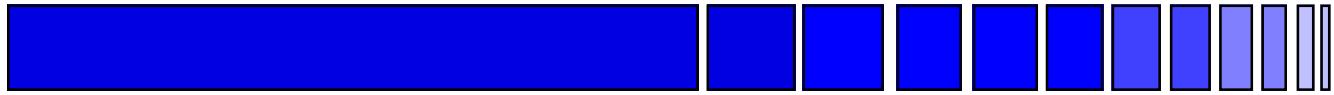
$$\mu_{X^{z-}} = RT \ln\left[\frac{\rho_{X^{z-}}}{(q_{X^{z-}}/V)}\right]$$

$$-RT \ln p_0$$

$$-RT \ln\left[\sum_{n=0} \tilde{K}_n \rho_W{}^n\right]$$

ideal,

packing,
chemistry ,
electrostatics,
entropy.

– p_0=probability of an open cavity for the cluster volume, *e.g.* (1-ρv).

extended (macromolecules)?
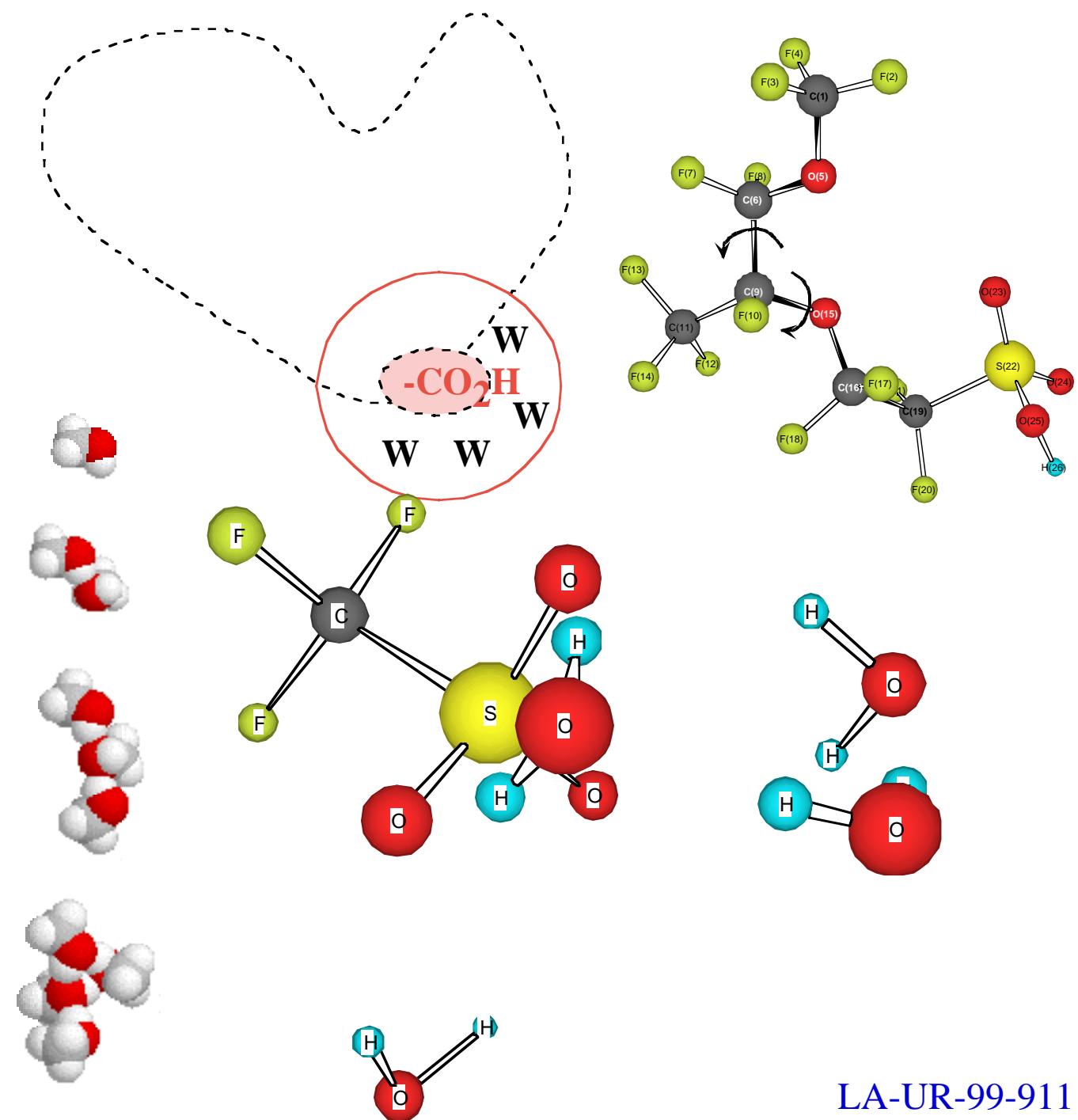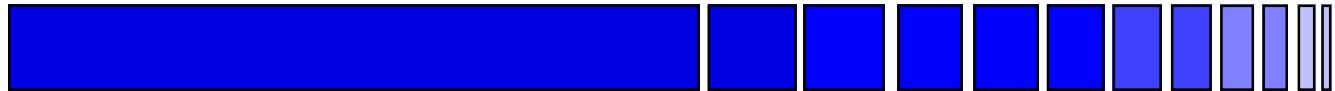
LA-UR-99-911

History ...

"COOPERATIVE PHENOMENA"

Guggenheim, Proc. Roy. Soc. London A
148, 304 (1935)

Bethe, Proc. Roy. Soc. London A
150, 552 (1935)

"QUASI-CHEMICAL"

Kikuchi, Phys. Rev. 81, 988 (1951)

"CLUSTER VARIATIONAL"

Durov, Zh. Fiz. Khi 67, 290 (1993)
"Quasichemi Models of L: Nonelectrolytes"

"CONDENSATION, NUCLEATION,
CLUSTERING"

Frenkel, J. Chem. Phys. 7, 200 (1939)
Band, Proc. J. Chem. Phys. 7, 324, 927 (1939)
Hill, J. Chem. Phys. 23, 617 (1955)

"PHYSICAL CLUSTERS"

Stillinger, J. Chem. Phys. 38, 1486 (1963)
Fisher, Physics (NY) 3, 255 (1967)

"DROPLET MODEL "

Heidemann and Prausnitz, Proc. Natl. Acad. Sci. USA. 73, 1773 (1976)
Pratt and Chandler, J. Chem. Phys. 66, 147 (1977)

"MOLECULAR LIQUIDS "

LaViolette and Pratt, Phys. Rev. A8, 2482 (1983)
Ludwig, Weinhold, Farrar, J. Chem. Phys. 107, 499 (1997)

"QUANTUM CHEMICAL EQUILIBRIUM "

Pratt and LaViolette, Molec. Phys. 94, 909 (1998)

"QUASI-CHEMICAL "

LA-UR-99-911
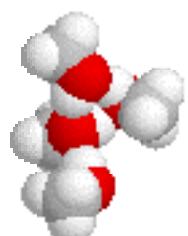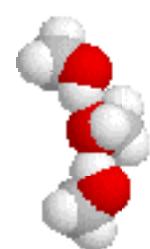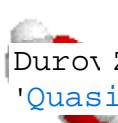
liquid methanol.01
(work in progress)

3.55Å

2.95Å
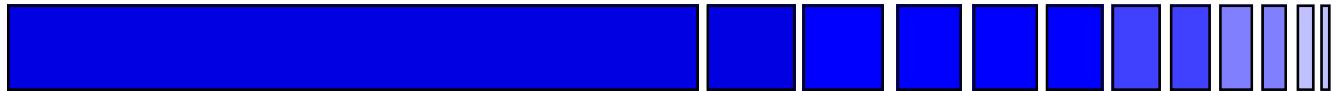
(G94, all results b3lyp/6-31g**)

$g_{oo}(r)$

$N(r)$

4

3

2

1

1   2   3   4   5

r(Å)
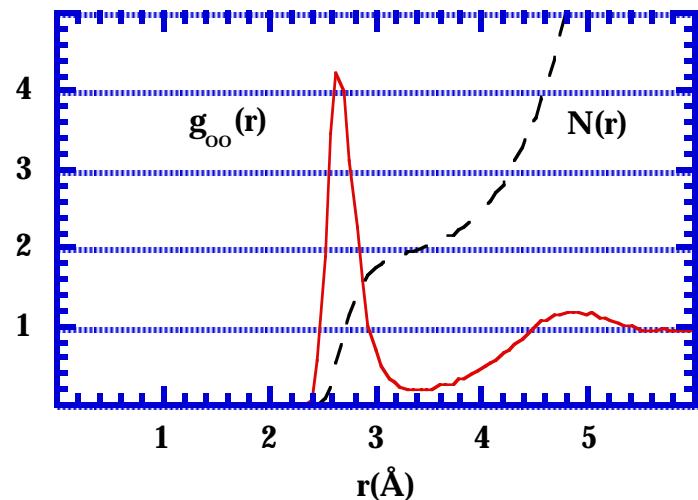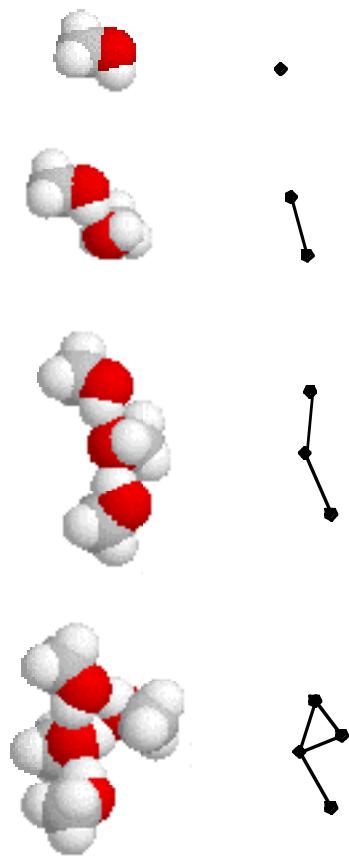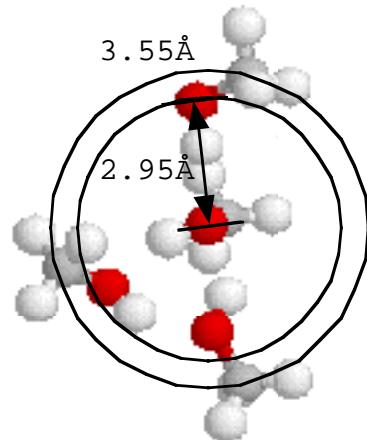
liquid methanol.02 (work in progress)

- **World's simplest model: this is amazing!**
  - Parameters: "mere" transcription from G94 output (except for primitive packing theory).
  - Critical density is about right, critical temperature is about 25% low.

μ/R (K)

T=512K
420K
400K
380K
360K

ρ (Å^3)

$$\mu/R = T\log(37216.2\rho)$$
$$-T\log\left((1-113.097\rho)\left(1+0.026407e^{2823/T}\rho\left(1+0.039077e^{2229/T}\rho\left(1+0.000131383e^{7675/T}\rho\right)\right)\right)\right)$$
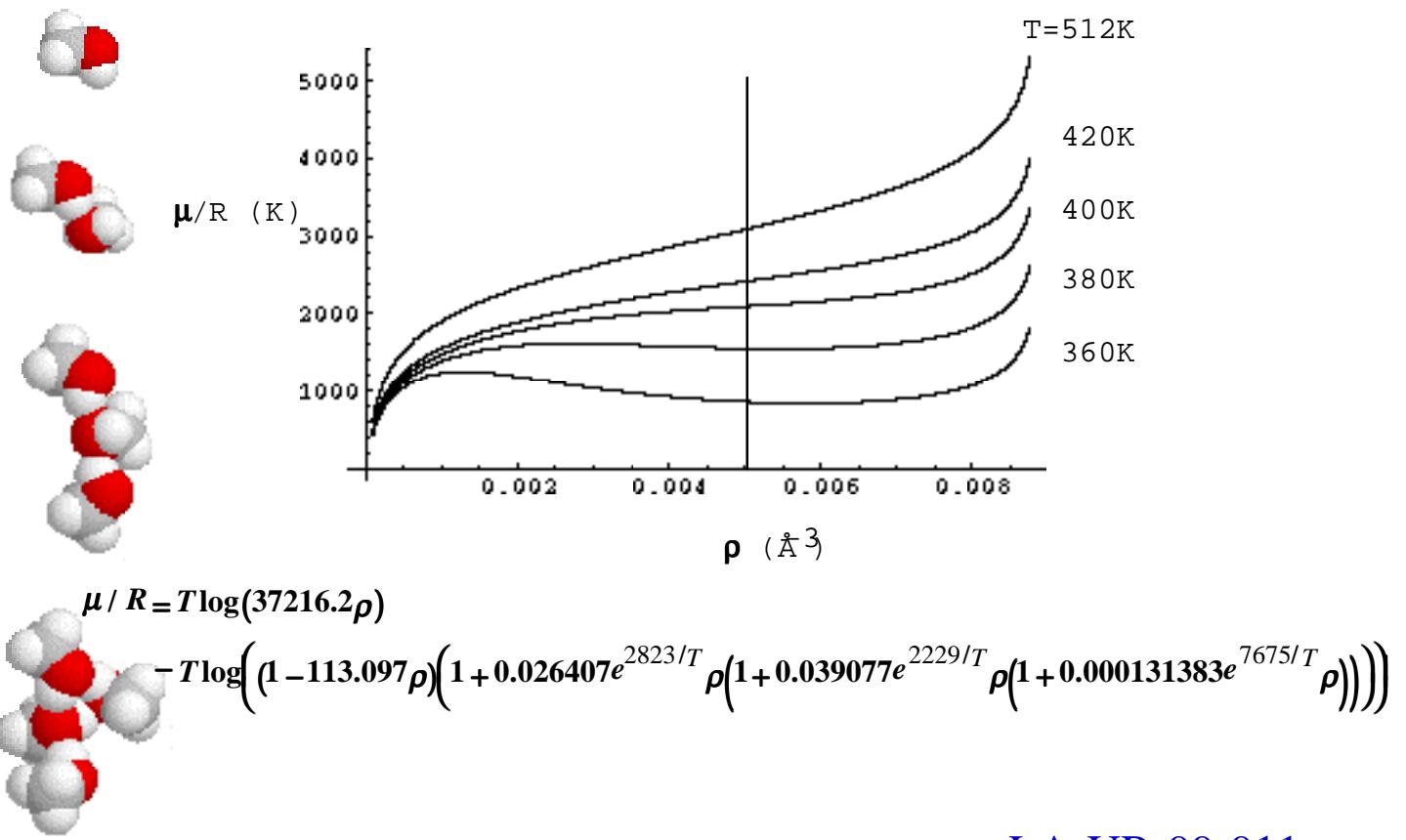
liquid methanol.03 (work in progress)

- **Slightly Engineered (for now): add van der Waals for extra-cluster contributions**

  – **Important**: Clusters only are **not** the whole story

  – Experimental critical point matched with vdW *a* and *b*.

$$\mu/R = T\left[\frac{1}{1-b\rho} - \log(1-b\rho) - 2a\rho/T\right] + T\log(37216.2\,\rho)$$

$$- T\log\left(1 + 539269\,e^{2823/T}\left(\frac{\rho}{T^3}\right)\left(1 + 796389\,e^{2229/T}\left(\frac{\rho}{T^3}\right)\left(1 + 2677\,e^{7675/T}\left(\frac{\rho}{T^3}\right)\right)\right)\right)$$
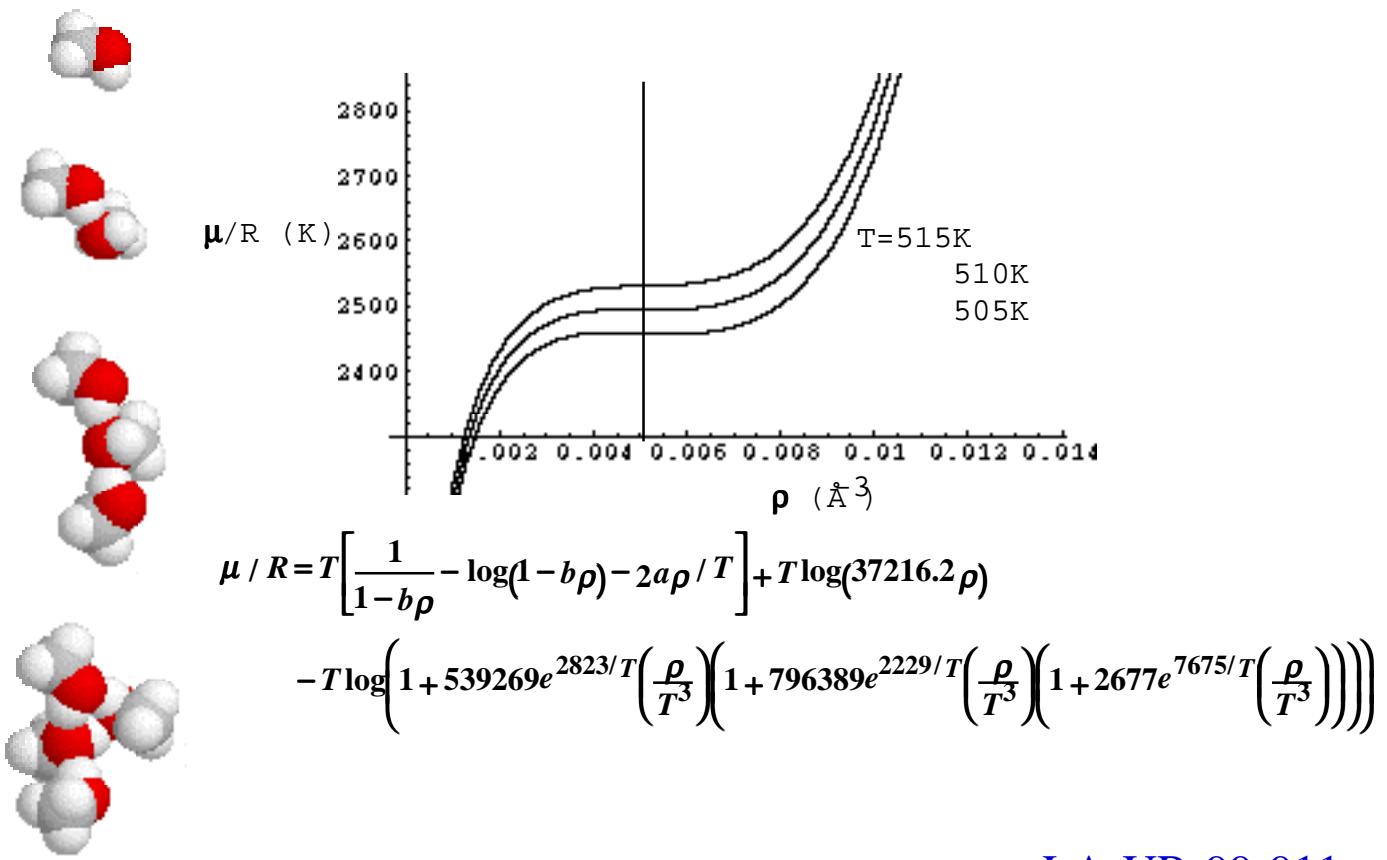
liquid methanol.04
(work in progress)

- **vdW parameters found are consistent with the quasi-chemical picture**

  - $\rho_c a = 1.14$ kcal/mol. *$2\rho a$* is the interaction potential energy of a methanol molecule with *all neighbors outside* the cluster. And this parameter value is less than typical hydrogen bonding energies. Therefore, the quasi-chemical theory appears to be properly and accurately isolating strong "chemical" interactions and leaving relatively weak interactions for perturbative stat-mech.

  - $\rho_c b = 0.334$ <=> cluster radius 3.15Å. This is consistent with the structuring seen from MD simulations. Tetramer structures are not crucial.
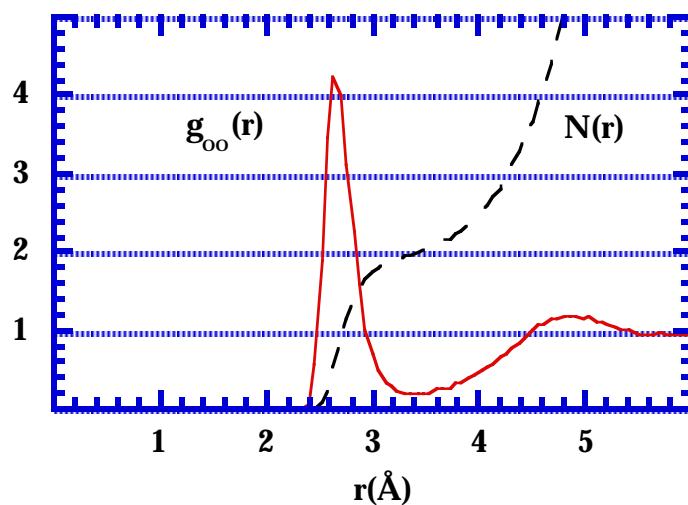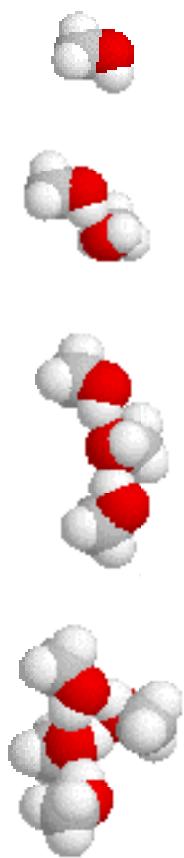
Conclusions
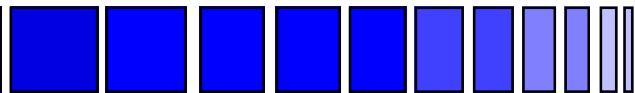
- **Dielectric models for hydration breakdown first because of near neighbor protons that lead to non-gaussian fluctuations of electrostatic potentials.**

- **Quasi-chemical approaches treat inner shells specially, permit an organized application of electronic structure calculations, should also fix problems with negative ions. This is real stat-mech.**

- **The quasi-chemical picture is clearly a "basic truth" of liquid methanol, but more work will be required to finish the stat-mech in this case.**