

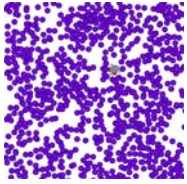
Simulations of Solubilities and Solvation Energies in Supercritical Fluids

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- accuracy of simulations & potentials
- effect of solvent heterogeneity
- effect of density augmentation





Solubility and Solvation Energy

- solubility of solids in room-temperature SCFs (e.g. naphthalene in CO₂)

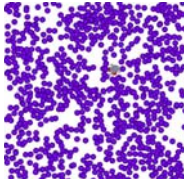
$$x_2(T, P) = A \exp\{-\Delta_{sol}G(T, P) / RT\}$$

solute mole fraction solvation free energy

$$A = \frac{P_2^{sat}(T)}{RT} \bar{V}_1(T, P)$$

vapor P of solid molar V of SCF

- the key quantity is the solvation free energy (excess chemical potential): the free energy associated with transfer of solute from gas to solution
- simulating solubilities \cong simulating $\Delta_{sol}G$



Simulating $\Delta_{sol}G$

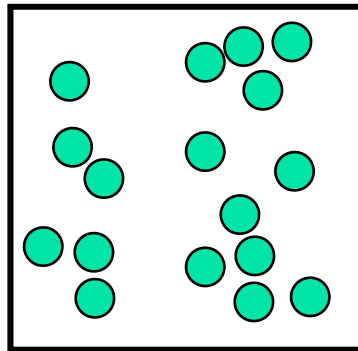
- the fundamental relationship

$$\Delta_{sol}G = -k_B T \ln \left\langle \exp\left(\underbrace{-V_{uv}}_{\text{solute-solvent interaction energy}} / k_B T \right) \right\rangle_0$$

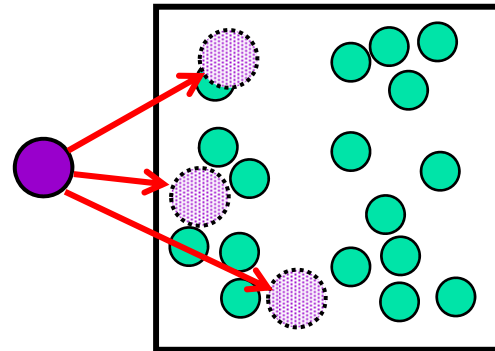
average over equilibrium solvent *in the absence of the solute*

- particle insertion approach:

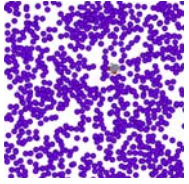
equilibrium solvent



test insertions



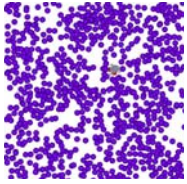
- method fails at high ρ , but excellent for SCFs



Simulation Methodology

- equilibrium configurations of neat SC solvents from NVT, NPT molecular dynamics (or Monte Carlo)
- 1000 solvent molecules
- ~200 configurations collected over runs of 2-5 ns
- attempt insertions at 10^4 - 10^5 locations and 10 solute orientations for each configuration

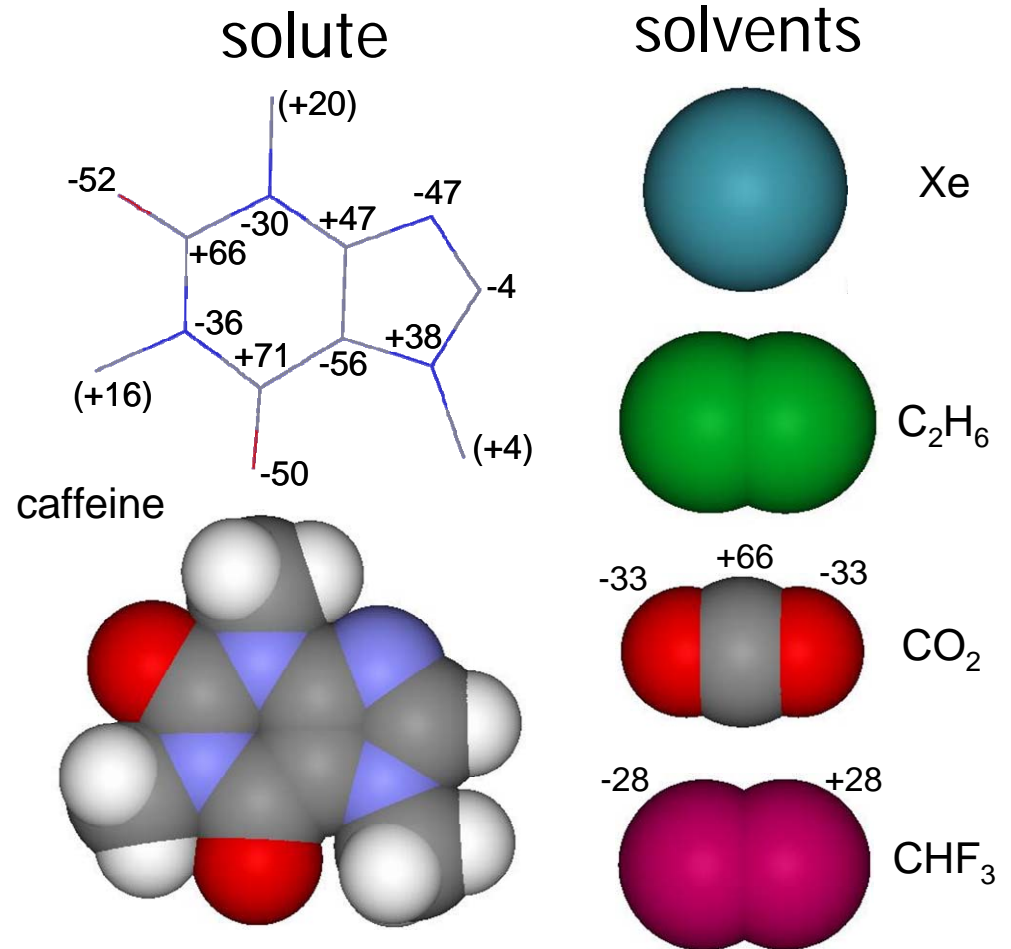
- solvents examined: Xe, C₂H₆, CO₂, CHF₃ (& HS)
- solvent conditions: $T - T_c = 5$ -20 K, $0.2 < \rho / \rho_c < 3$

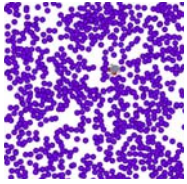


"Realistic" Interaction Models

site-site LJ+q form:
$$u_{ij} = \sum_{a \in i} \sum_{b \in j} 4\epsilon_{ab} \left\{ \left(\frac{\sigma_{ab}}{r_{ab}} \right)^{12} - \left(\frac{\sigma_{ab}}{r_{ab}} \right)^6 \right\} + \frac{1}{4\pi\epsilon_0} \frac{q_a q_b}{r_{ab}}$$

- solvents tuned for neat fluid properties
- solute geometries & charges from *ab initio* calculations
- LJ parameters from OPLS-AA force field





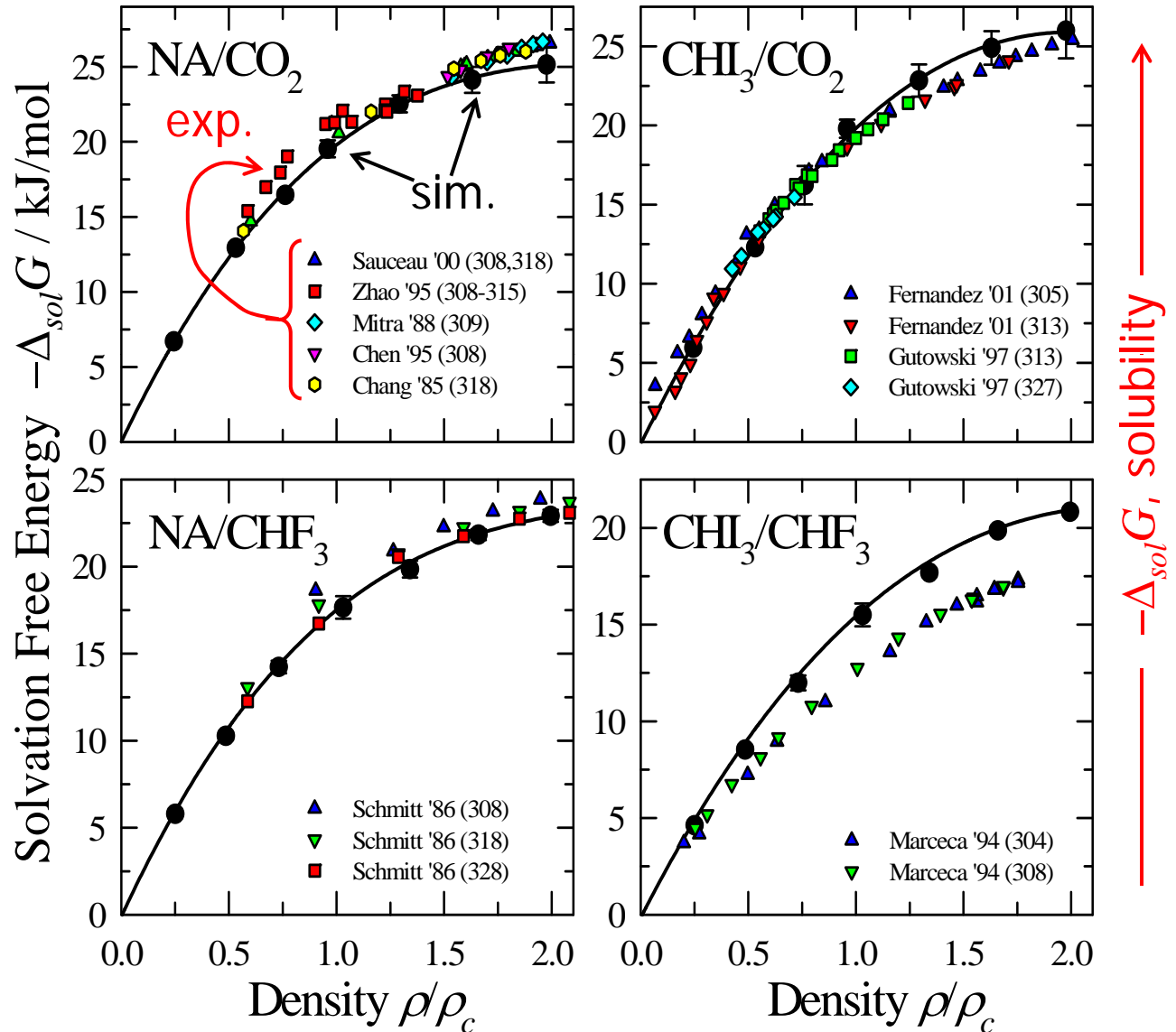
Density Dependent Data

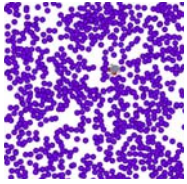
data set #1:

$0.5 < \rho/\rho_c < 2$; $T_c + 10K$

| Solute | Solvent |
|------------------|-------------------------------|
| I ₂ | Xe |
| I ₂ | CHF ₃ |
| CHI ₃ | Xe |
| CHI ₃ | C ₂ H ₆ |
| CHI ₃ | CO ₂ |
| CHI ₃ | CHF ₃ |
| naphthalene | C ₂ H ₆ |
| naphthalene | CO ₂ |
| naphthalene | CHF ₃ |
| anthracene | C ₂ H ₆ |
| anthracene | CO ₂ |
| anthracene | CHF ₃ |

note: $\uparrow -\Delta_{sol}G$





Comparison to Experiment (#1)

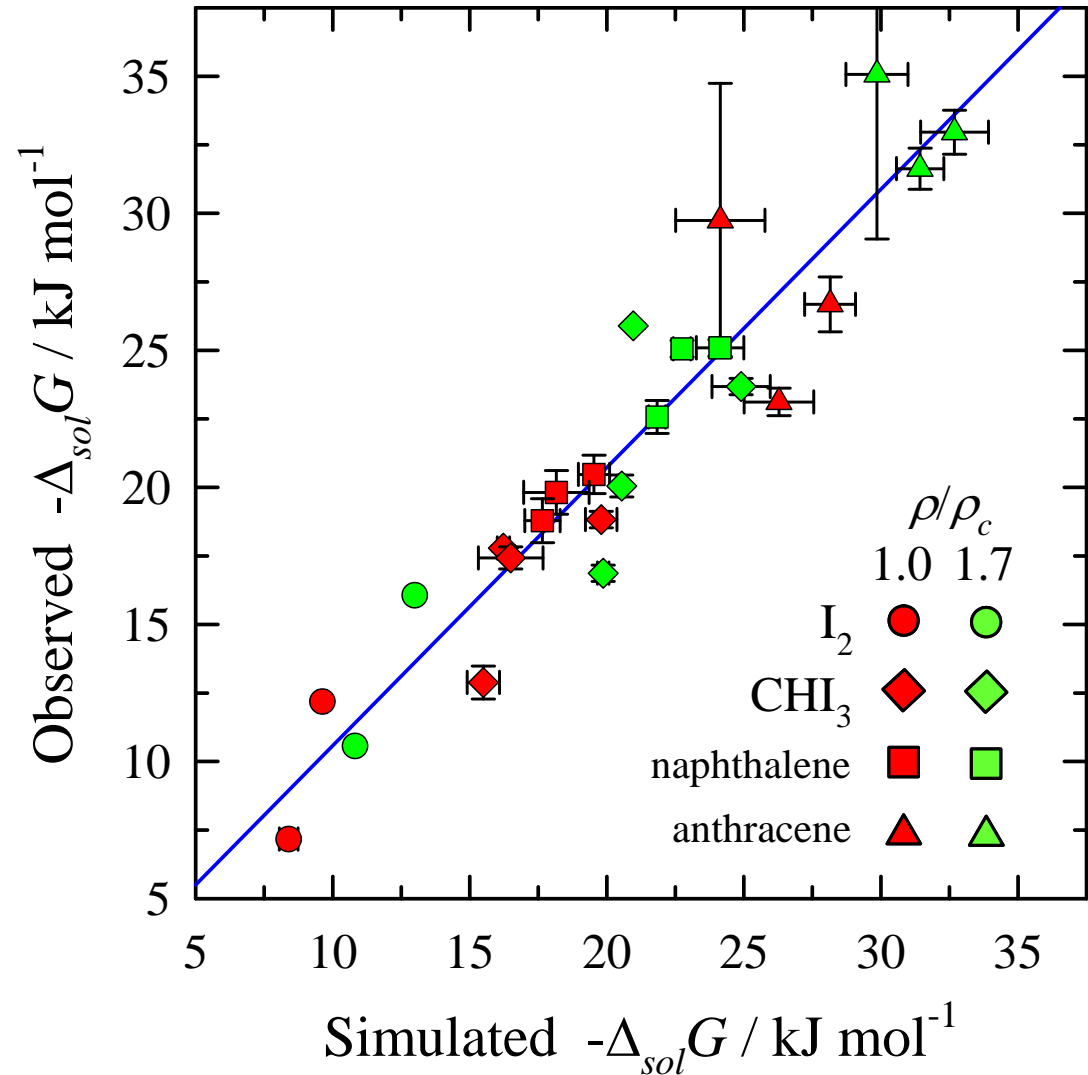
- 4 solutes
- 4 SC solvents
- 12 $u+v$ combinations
- 2 selected densities, $1.0\rho_c$ and $1.7\rho_c$

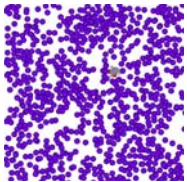
results:

$$\Delta G_{obs} = 1.01\Delta G_{sim} - .43$$

$$r^2 = 0.88$$

$$\text{MAD} = 1.9 \text{ kJ/mol (10\%)}$$

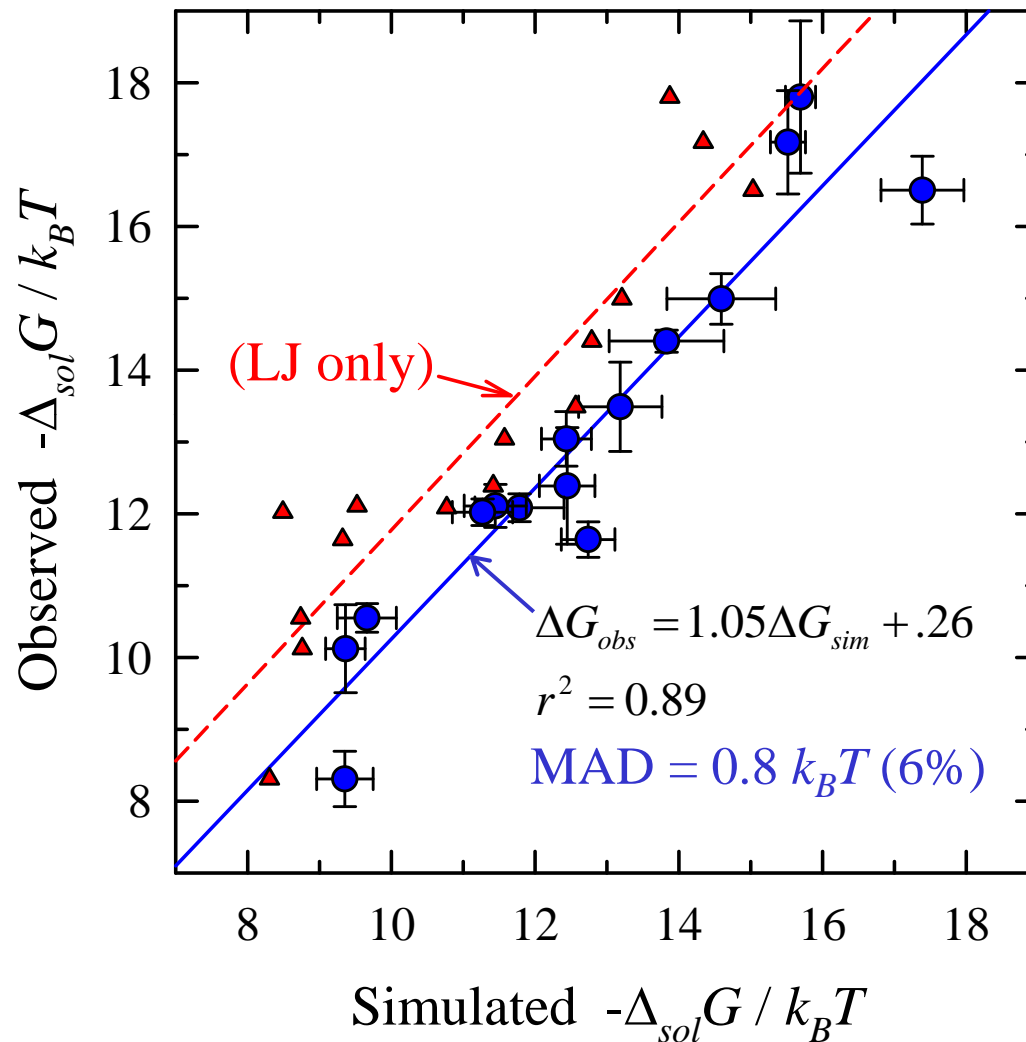
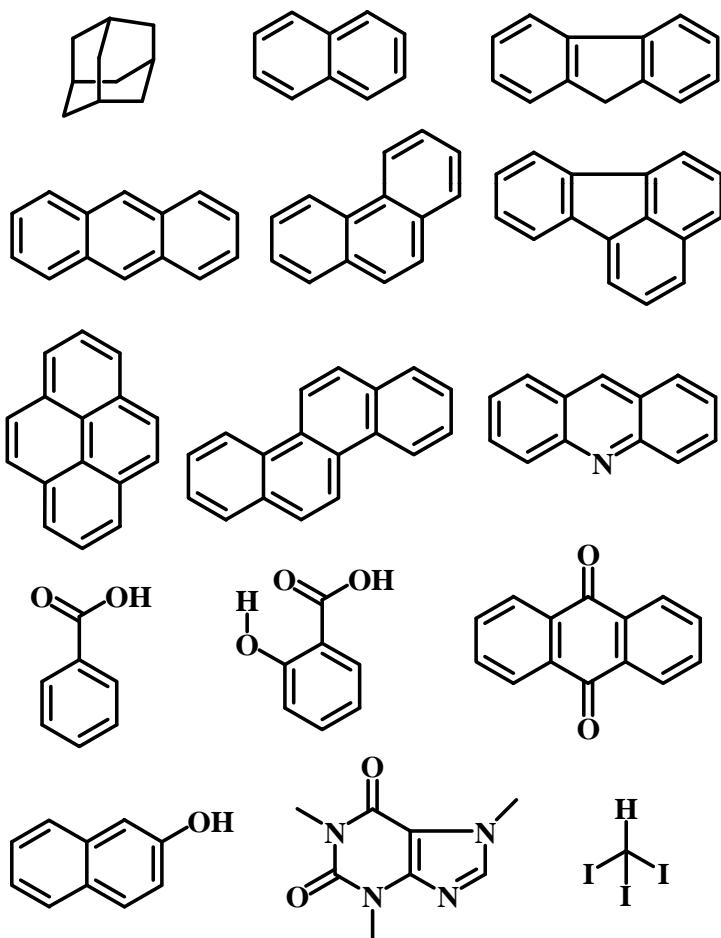




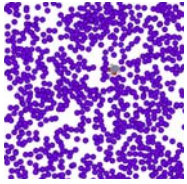
Comparison to Experiment (#2)

data set #2:

15 solutes in SC CO₂ (1.6ρ_c)
from E compilation of Teja & co.¹



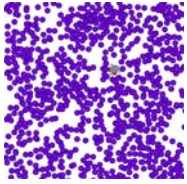
1. J. Mendez-Santiago & A. S. Teja, *Fluid Phase Equilibria* **158-160**, 501-510 (1999).



Summary of Sim-Expt Comps.

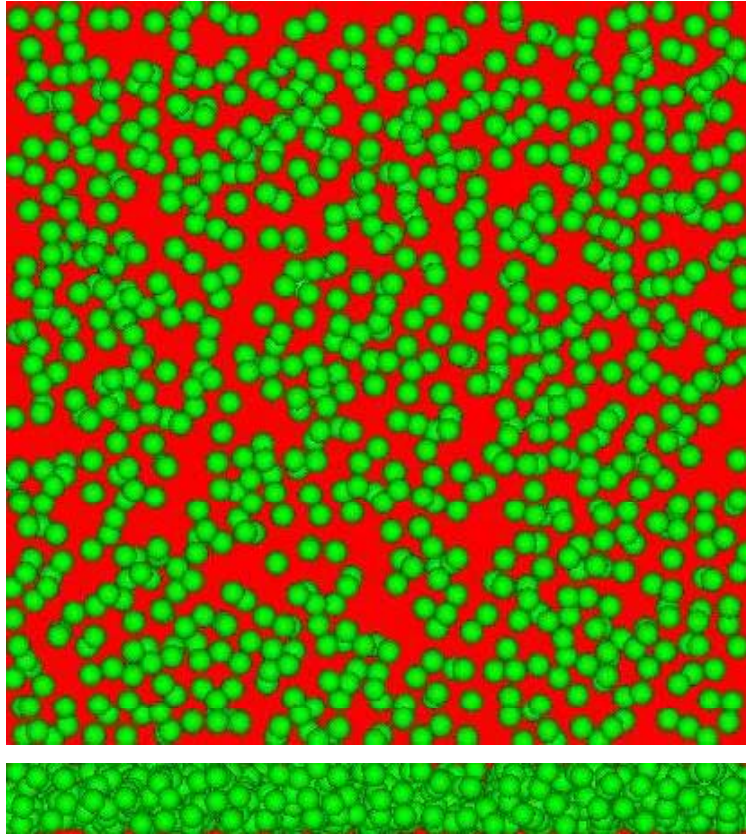
- ❑ simulations predict $\Delta_{sol}G$ to an accuracy of $\sim 2\text{kJ/mol}$ ($\sim 10\%$) without any adjustment of potentials (OPLS-AA) or empirical input
- ❑ but solubilities only accurate to within a factor of 2
- ❑ in CO_2 electrical interactions typically account for $\sim 15\%$ of $\Delta_{sol}G$ even for non-dipolar solutes
- ❑ (choice of combining rules matters)

- next use Xe and model solutes to examine effects of solvent density inhomogeneity and local density augmentation



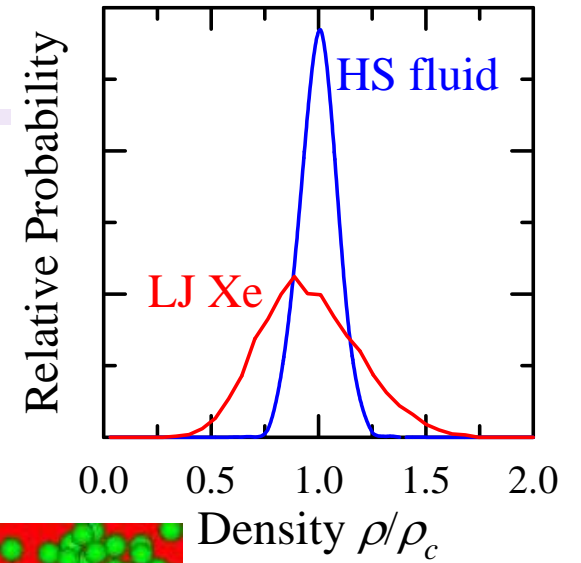
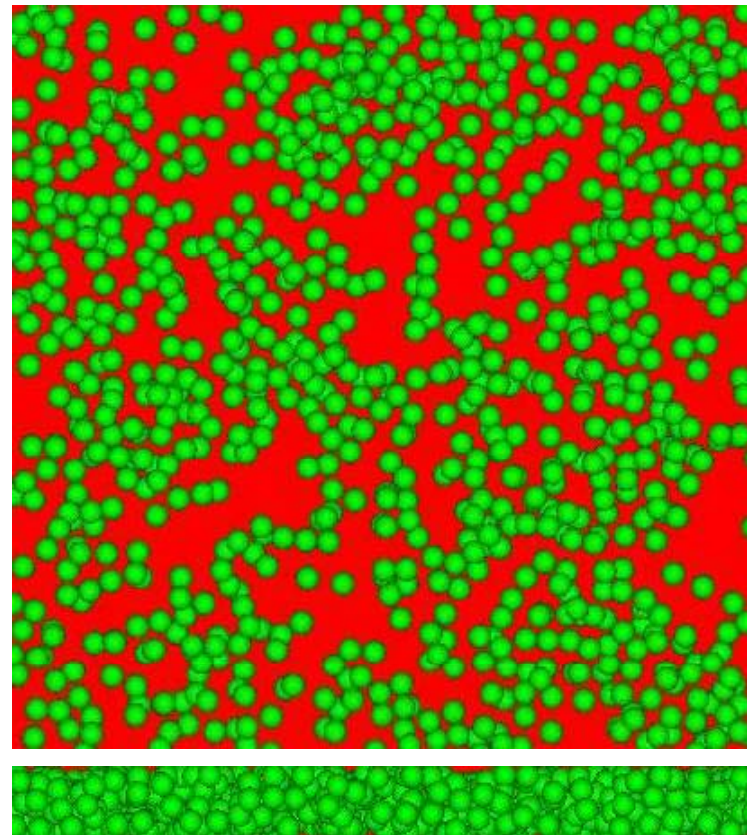
Solvent Heterogeneity

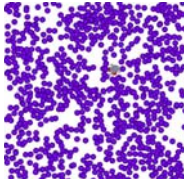
HS Fluid



"Xe" $T_c + 10K$, $\rho = \rho_c$

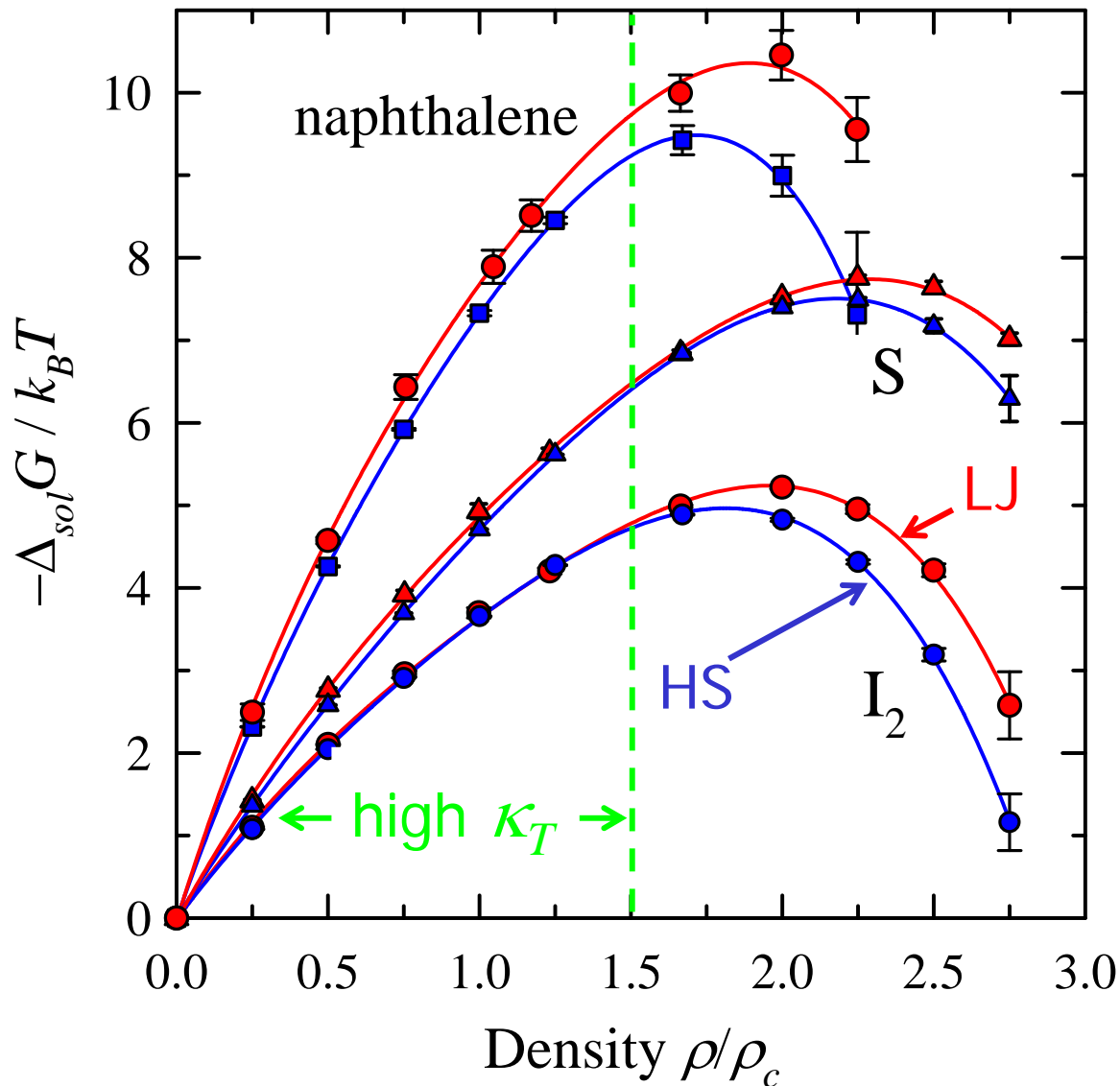
LJ Fluid





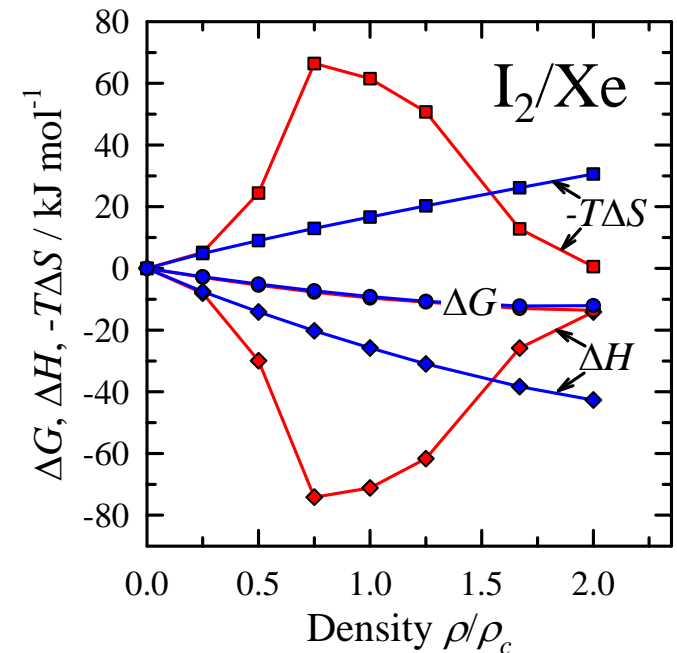
Effect on $\Delta_{sol}G$

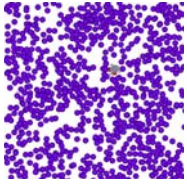
Three Solutes in "Xe" (300 K)



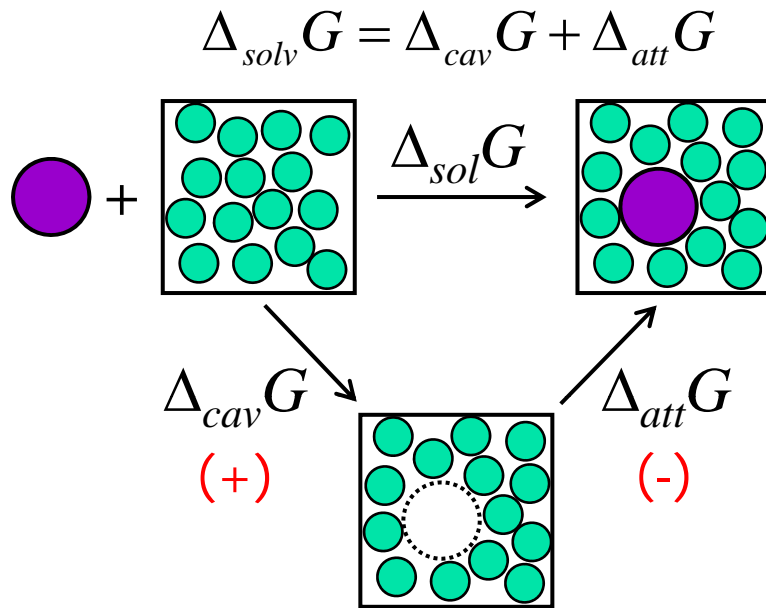
- density heterogeneity. large κ_T have little effect on solubility

- but derivative quantities $\Delta_{sol}H$, $\Delta_{sol}S$ are affected





Density Dependence, $\Delta_{cav}G$ & $\Delta_{att}G$



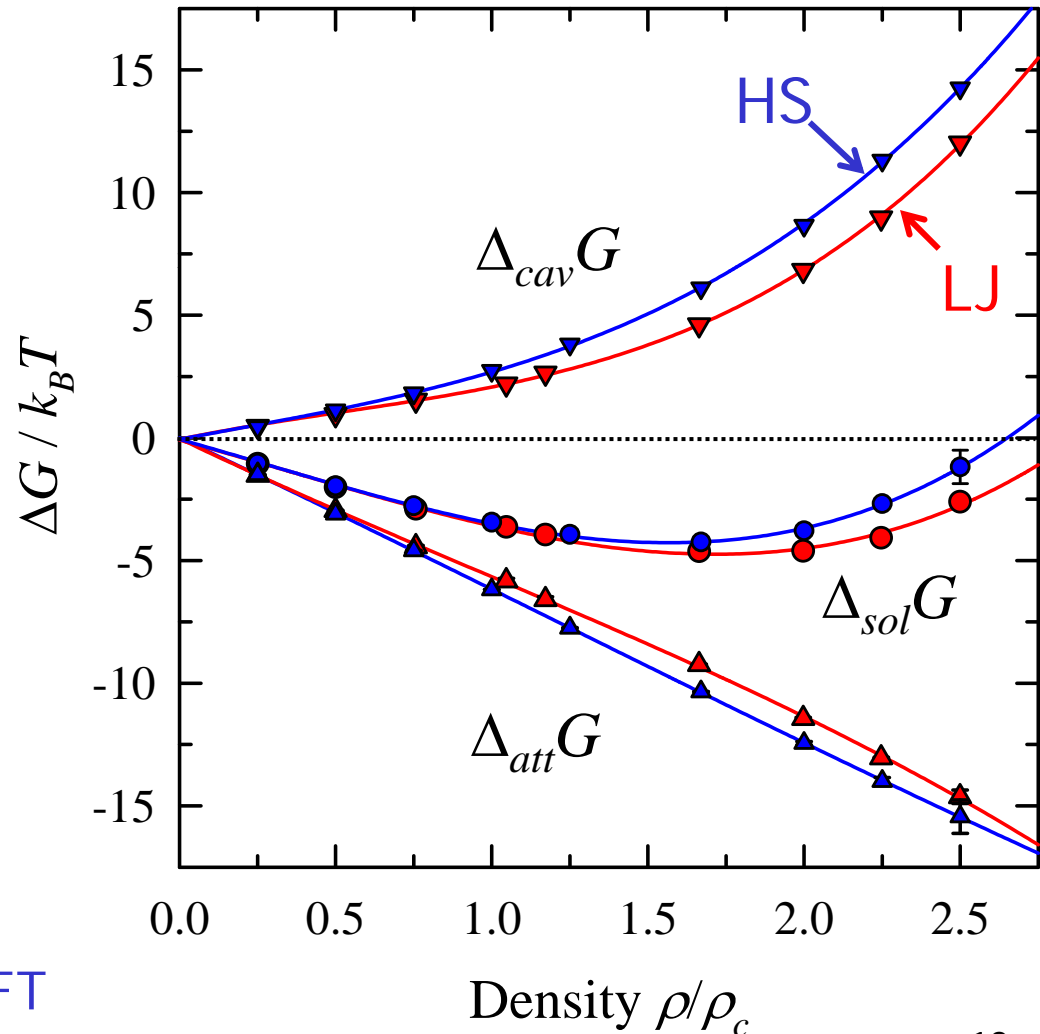
- $\Delta_{cav}G$ of spherical solutes from cavity size distributions

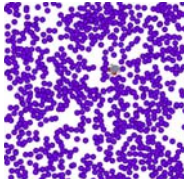
$$\Delta_{cav}G(R) = -k_B T \ln P(R)$$

$$P(R) = \int_R^{\infty} p_{\max}(r) dr$$

- for atomic solvents $\Delta_{cav}G$ reasonably predicted by SPT, HFT

Single-Site "Benzene" in Xe





$\Delta_{att}G$ of Single-Site Solutes

Representative Solutes

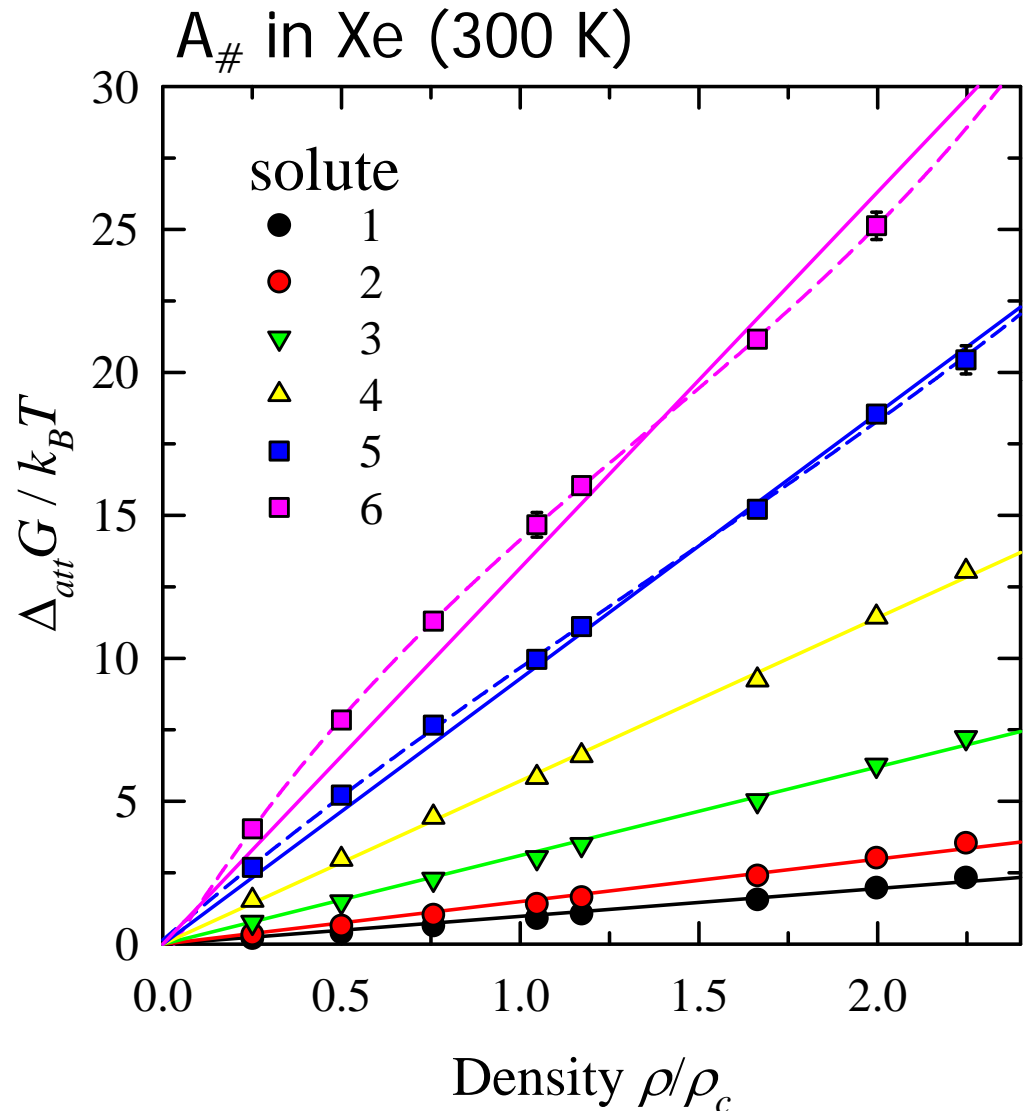
| # | solute | σ /Å | ϵ/k_B /K | obs. slope | est. slope |
|---|---------------|----------------|----------------------|---------------|---------------|
| 1 | “Ne” | 2.5 | 55 | 1.0 | 0.7 |
| 2 | “Ar” | 3.0 | 94 | 1.5 | 1.1 |
| 3 | “Xe” | 4.0 | 210 | 3.1 | 2.5 |
| 4 | “benzene” | 5.0 | 372 | 5.7 | 4.8 |
| 5 | “naphthalene” | 6.0 | 544 | 9.3 | 8.0 |
| 6 | “anthracene” | 7.0 | 646 | 13 | 12 |

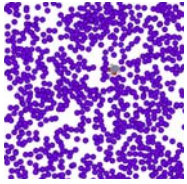
- for an unstructured fluid expect

$$\Delta_{att}G \cong U_{att} = -\frac{32\pi}{9} \epsilon_{uv} \sigma_{uv}^3 \rho$$

- $\Delta_{att}G$ & thus $\Delta_{sol}G$ predictable for atomic systems

- effect of density augmentation?





Free Energy vs. Interaction Energy

2 systems with explicit solutes:

#1: $\sigma_{uv} = \sigma_{vv}$, $\epsilon_{uv} = 2\epsilon_{vv}$ (313 K)

#2: $\sigma_{uv} = \sigma_{vv}$, $\epsilon_{uv} = 4\epsilon_{vv}$ (300 K)

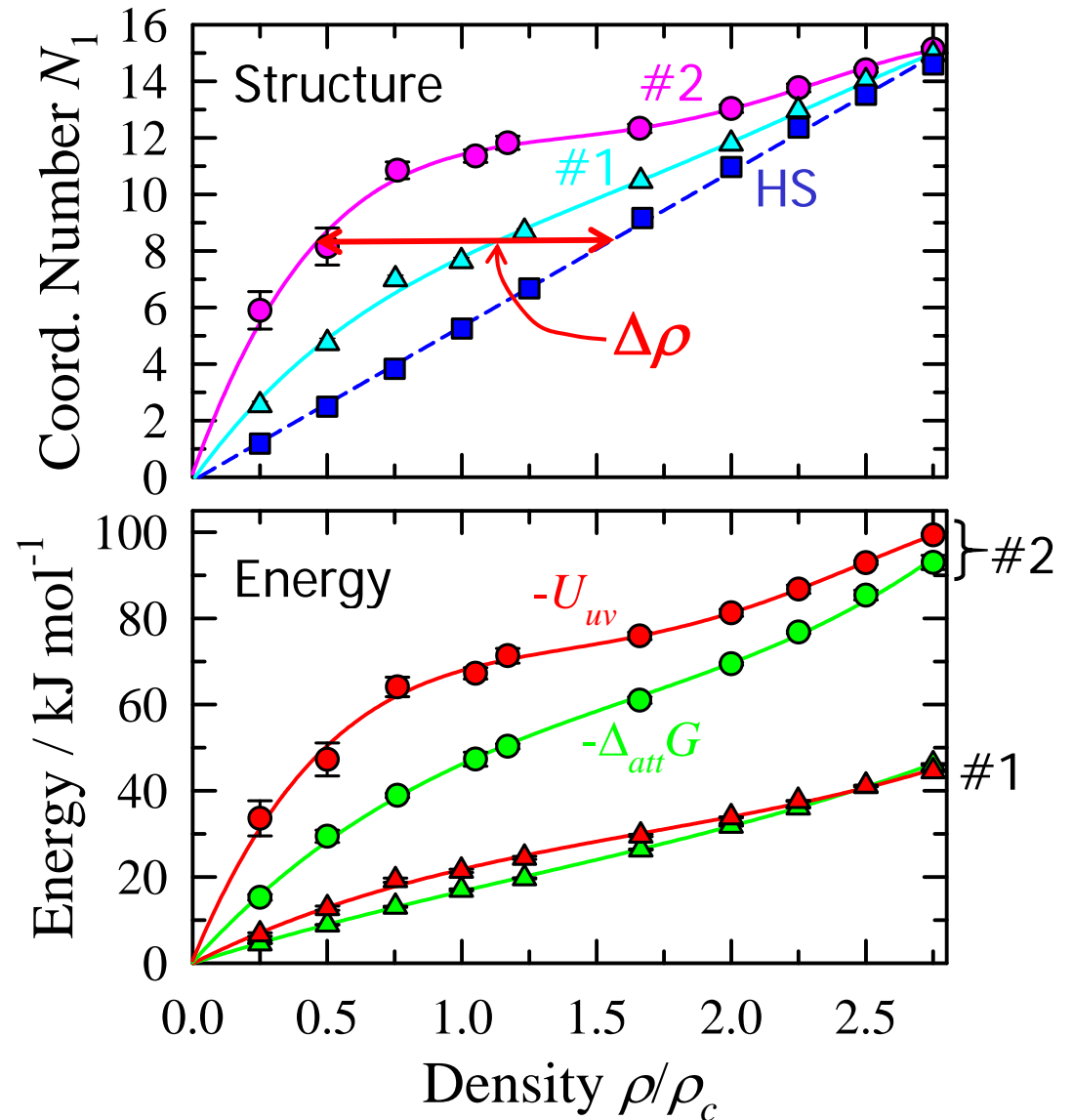
N_1 = coordination number

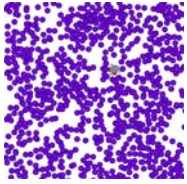
U_{uv} = solute-solvent interaction energy (electronic shifts)

$\Delta_{att}G$ = attractive component of solvation free energy

Effective Density Augmentation

| # | $\Delta\rho_{eff}/\rho_c$ | | |
|---|---------------------------|----------|-----------------|
| | N_1 | U_{uv} | $\Delta_{att}G$ |
| 1 | 0.4 | 0.4 | 0.06 |
| 2 | 0.9 | 0.8 | 0.35 |





Why is $\Delta_{att}G$ different from U_{uv} ?

$$U_{uv} = \langle V_{uv}(\vec{R}) \rangle_1 \quad \begin{array}{l} \text{average u-v} \\ \text{interaction energy} \end{array}$$

$$\Delta_{att}G \cong k_B T \ln \langle \exp(+V_{uv}(\vec{R})/k_B T) \rangle_1$$

avg. in presence of solute

interpretation as weighted averages:

$$e^{U_{uv}/k_B T} = \exp\left\{ \frac{1}{k_B T} \int P(V_{uv}) V_{uv} dV_{uv} \right\}$$

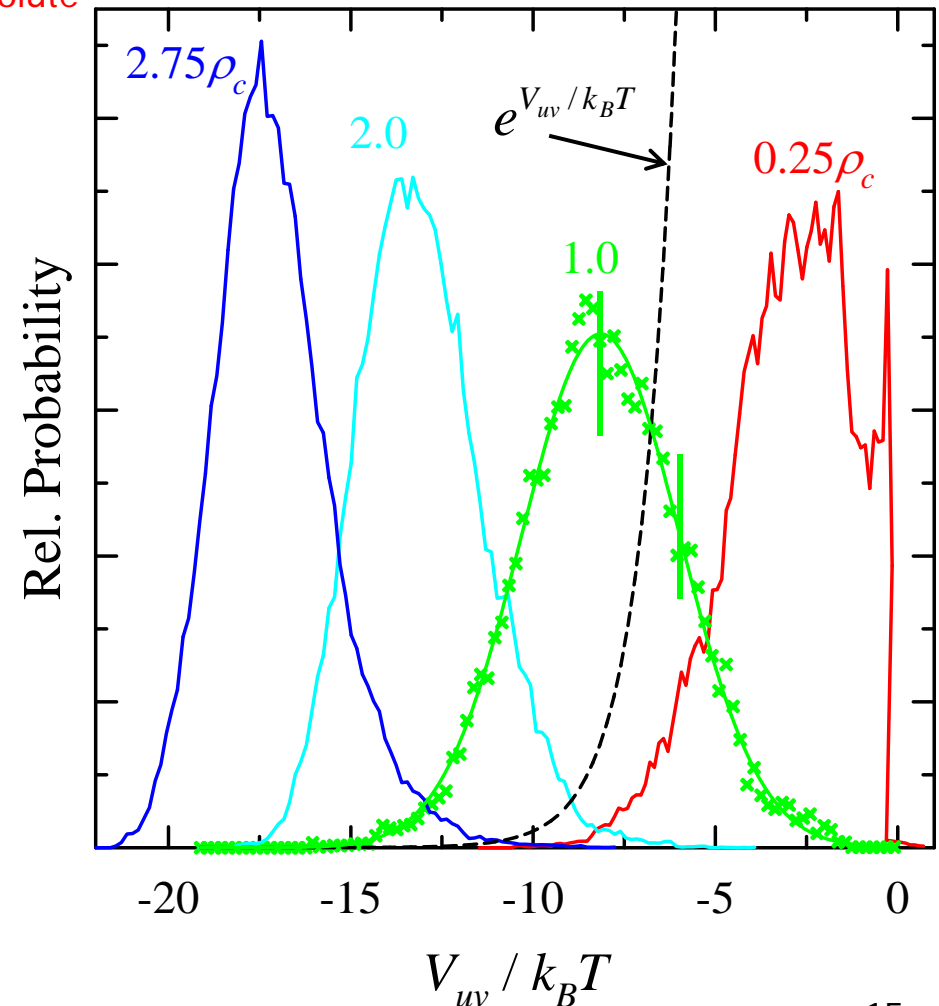
$$e^{\Delta_{att}G/k_B T} \cong \int P(V_{uv}) \exp(V_{uv}/k_B T) dV_{uv}$$

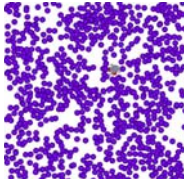
solvation free energy is biased toward large values of (less negative) of V_{uv}

$$\langle e^x \rangle \geq e^{\langle x \rangle} \quad \text{so} \quad \Delta_{att}G \geq U_{uv}$$

the difference increases with the width of the $P(V_{uv})$ distribution

Interaction Energy V_{uv}
Distributions (System #1)





Summary & Conclusions

- simulations using solvent potentials tuned for coexistence properties and all-atom solute representations with standard (OPLS) potential provide reasonable (10%) accuracy in prediction of solvation free energies and solubilities in SCFs
- solvation free energies are insensitive to the density fluctuations present in SC solvents (not true of enthalpies and entropies)
- solvation free energies depend much less on local density augmentation than do solute-solvent interaction energies (and spectral shifts)

