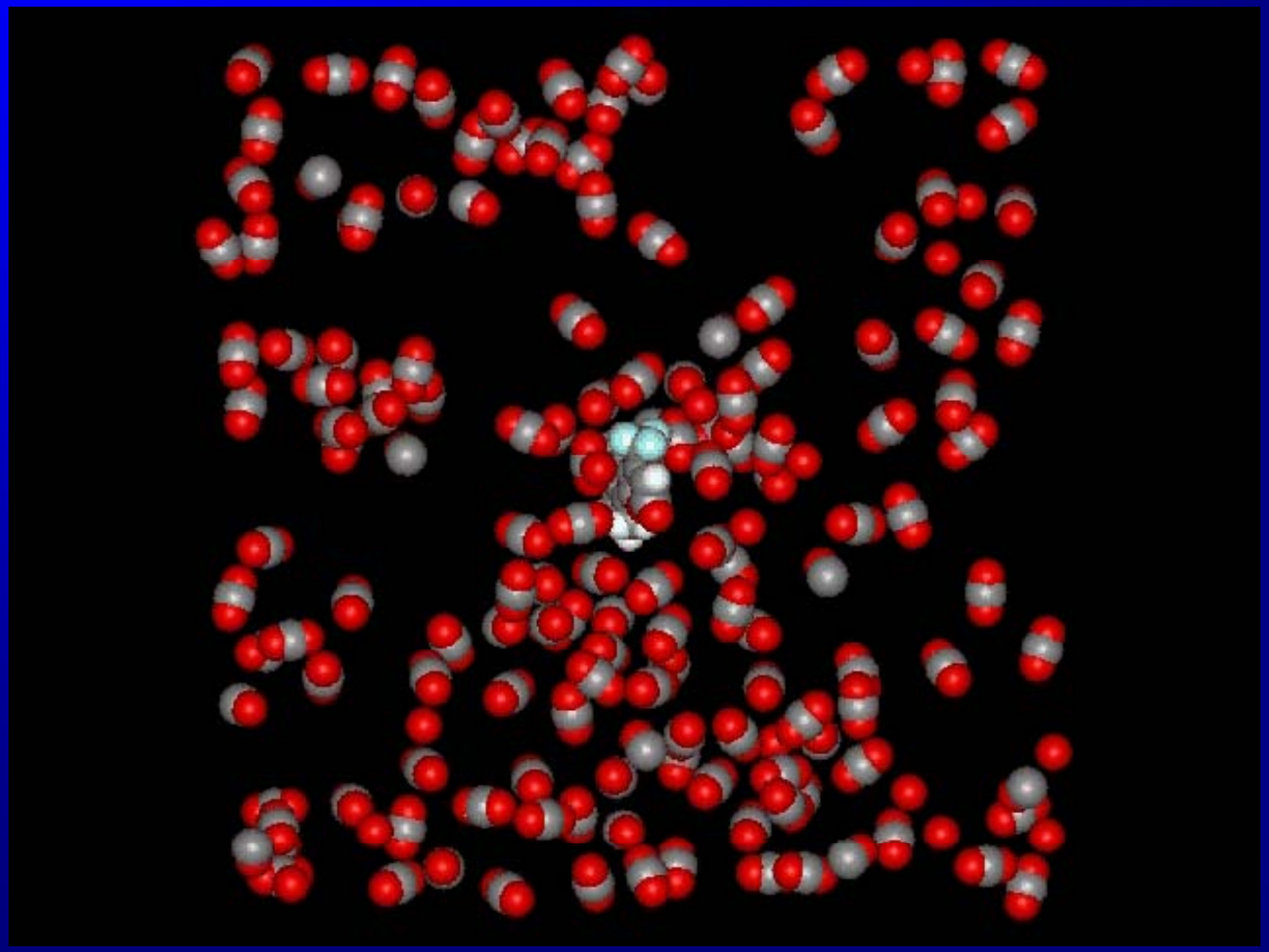
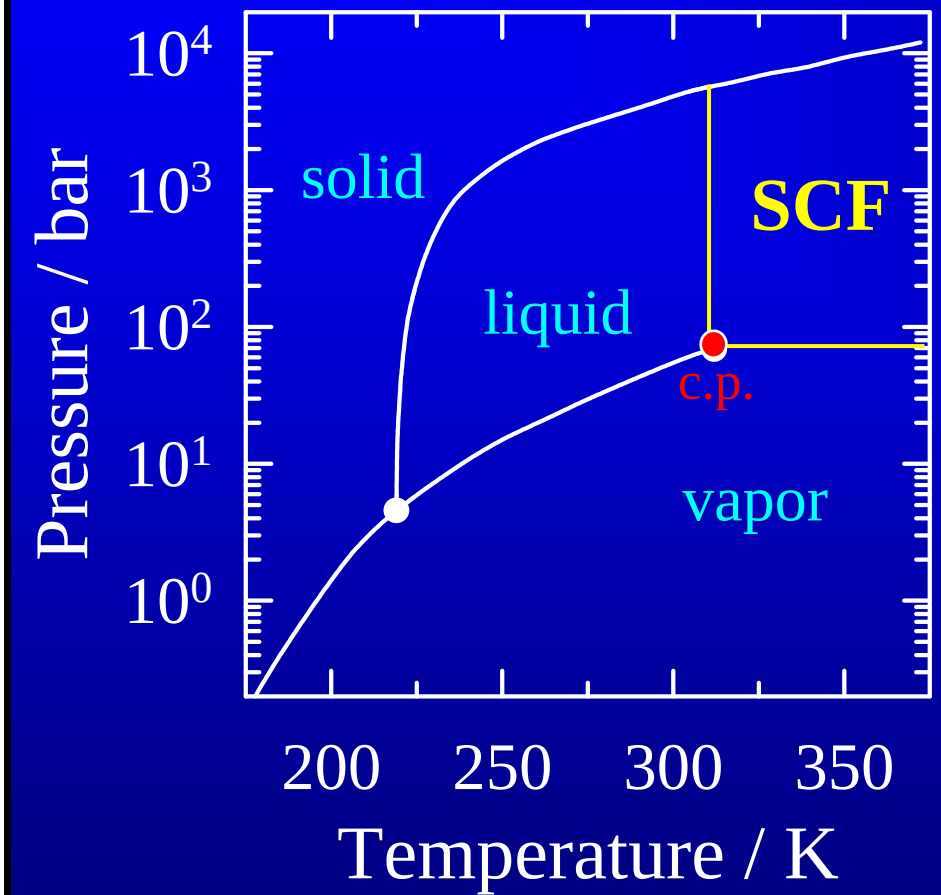
Solvation in Supercritical Fluids: Insights from Experiment & Simulation



University of Oregon 5/11/04

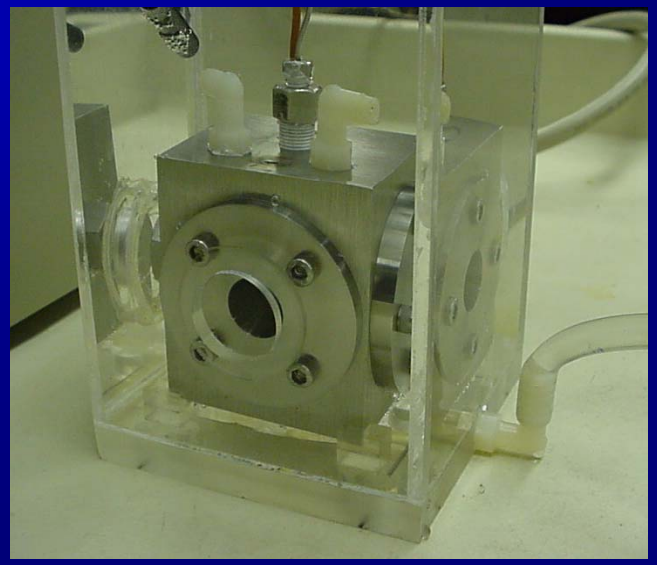
Supercritical Fluids

CO_2 Phase Diagram



Critical Properties of Select Fluids

Fluid	T_c/°C	P_c/bar	d_c/g cm^{-3}
C_2H_6	32	49	.21
CO_2	31	74	.47
CHF_3	26	48	.52
Ar	-122	49	.53
n-C_6H_{14}	234	30	.23
H_2O	374	221	.32



Adapted from P. G. Jessop & W. Leitner, *Chemical Synthesis using Supercritical Fluids* (Wiley, 1999).

SC Fluids as Solvents

Compared to Conventional Solvents:

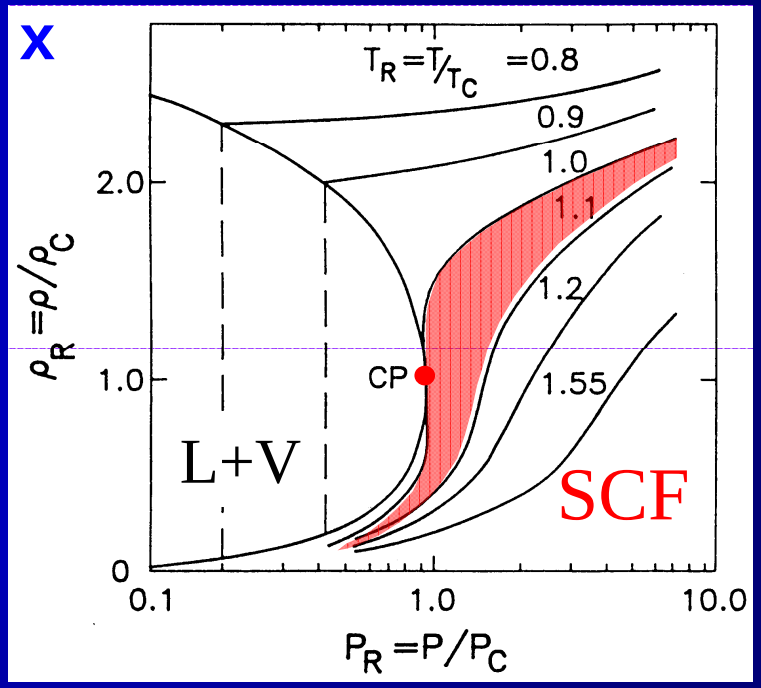
- molecules smaller, less attractive

+ pressure tunable

- lower polarity & solvent strength

+ lower viscosity, surface tension

Universal Phase Diagram



Some Typical Values (25-30°C)

Solvent	T/T_c	ρ/ρ_c	ε	δ	η
n-hexane	0.59	2.8	2	7	.3
THF	0.55	2.7	8	9	.5
acetonitrile	0.55	3.3	36	12	.3
C_2H_6	1.01	<2	<2	<7	<.1
CHF_3	1.01	<2	<8	<6	<.1

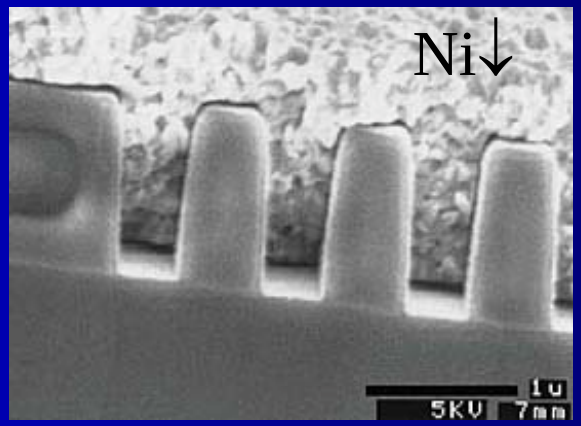
CO_2 – Solvent of the Future?

- environmentally benign
- "natural"
- inexpensive
- non-toxic, non-flammable

Practical Applications

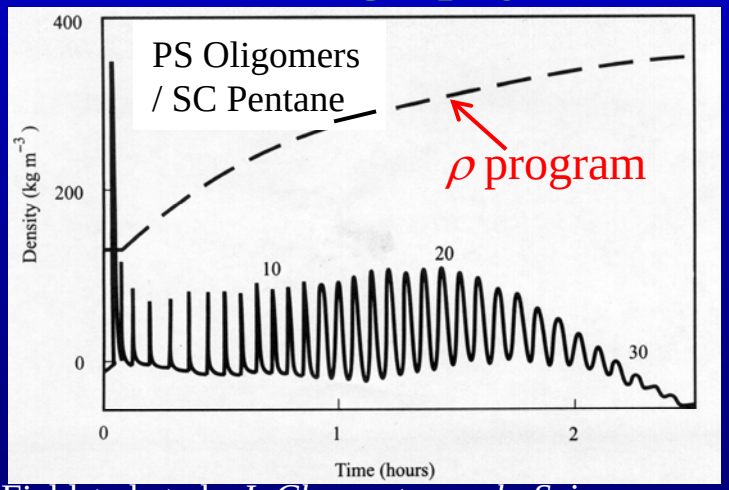
- pharmaceutical & food industries
- chromatography
- extraction & cleaning
- polymer synthesis, modification
- materials processing & fine particle production

"CFD" Fabrication



Blackburn & Watkins *C&ENews* (2001).

SC Chromatography

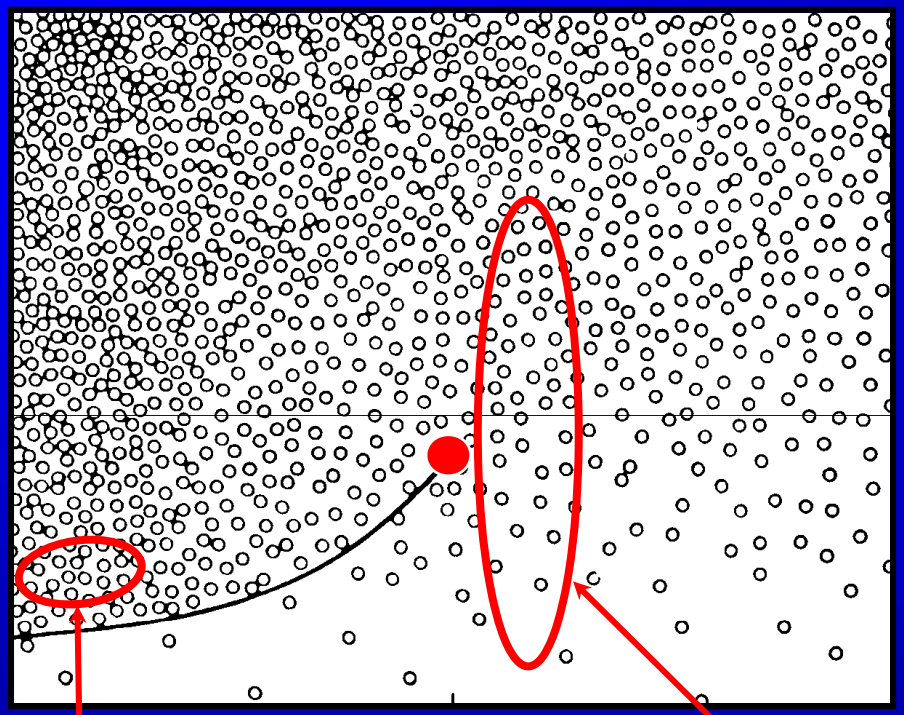


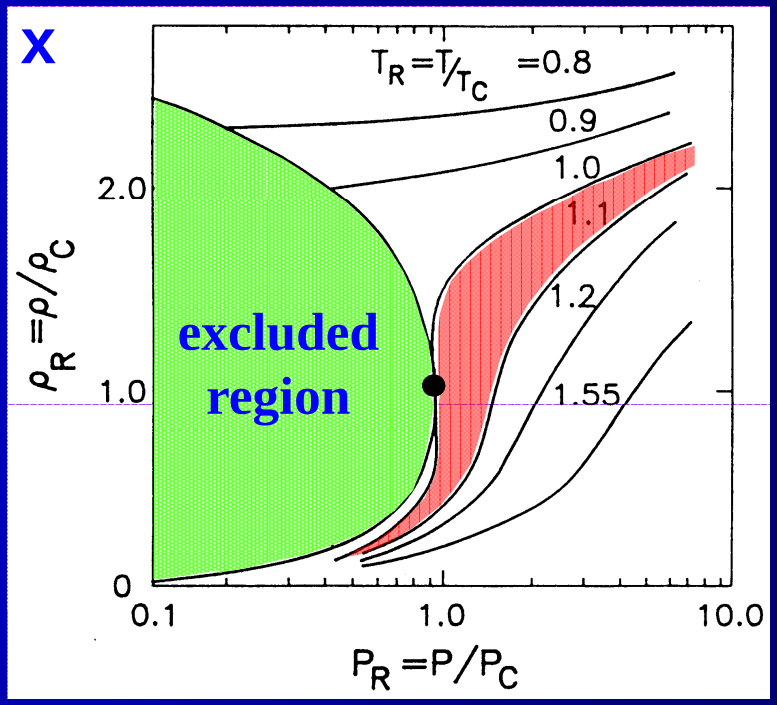
Fjeldsted et al., *J. Chromatograph. Sci.* **21**, 222 (1983).

Particle Formation

P. York, pdb Corp. (2001).

Fundamental Interest



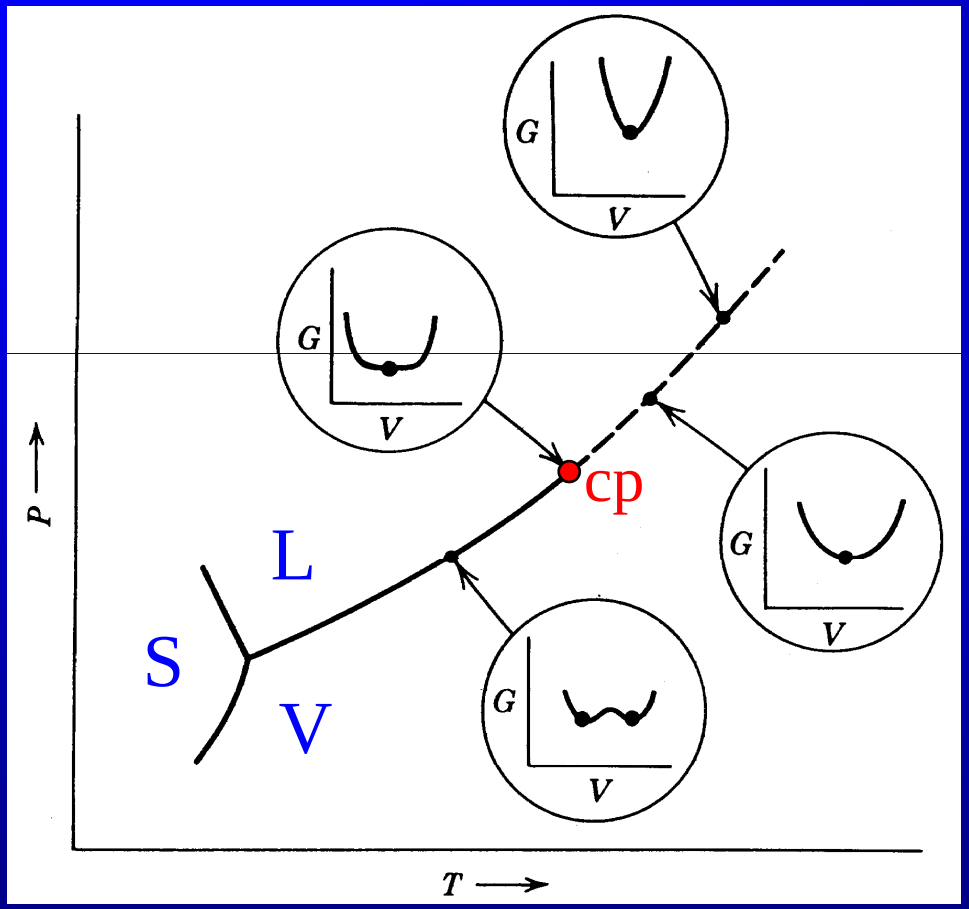


- nature of solvation in attractive regime?
- effects on chemical energetics, dynamics?

Figure adapted from: M. Buback, *Angew. Chem. Int. Ed. Engl.* **30**, 641 (1991).

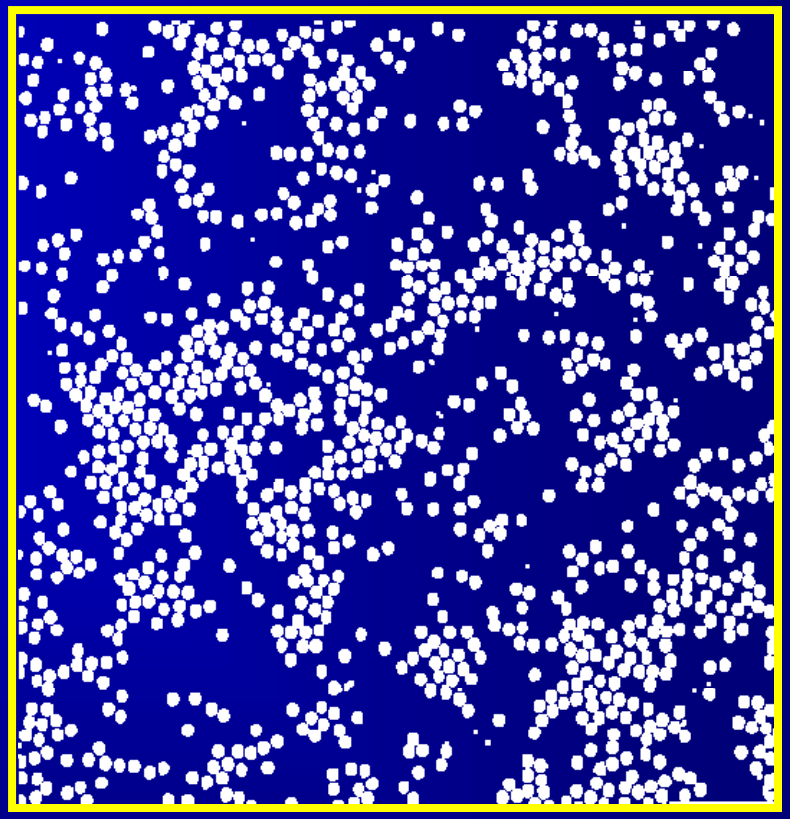
Special Nature of the Critical Point

Phase Ambivalence



from: H. B. Callen, *Thermodynamics* (Wiley, New York, 1985).

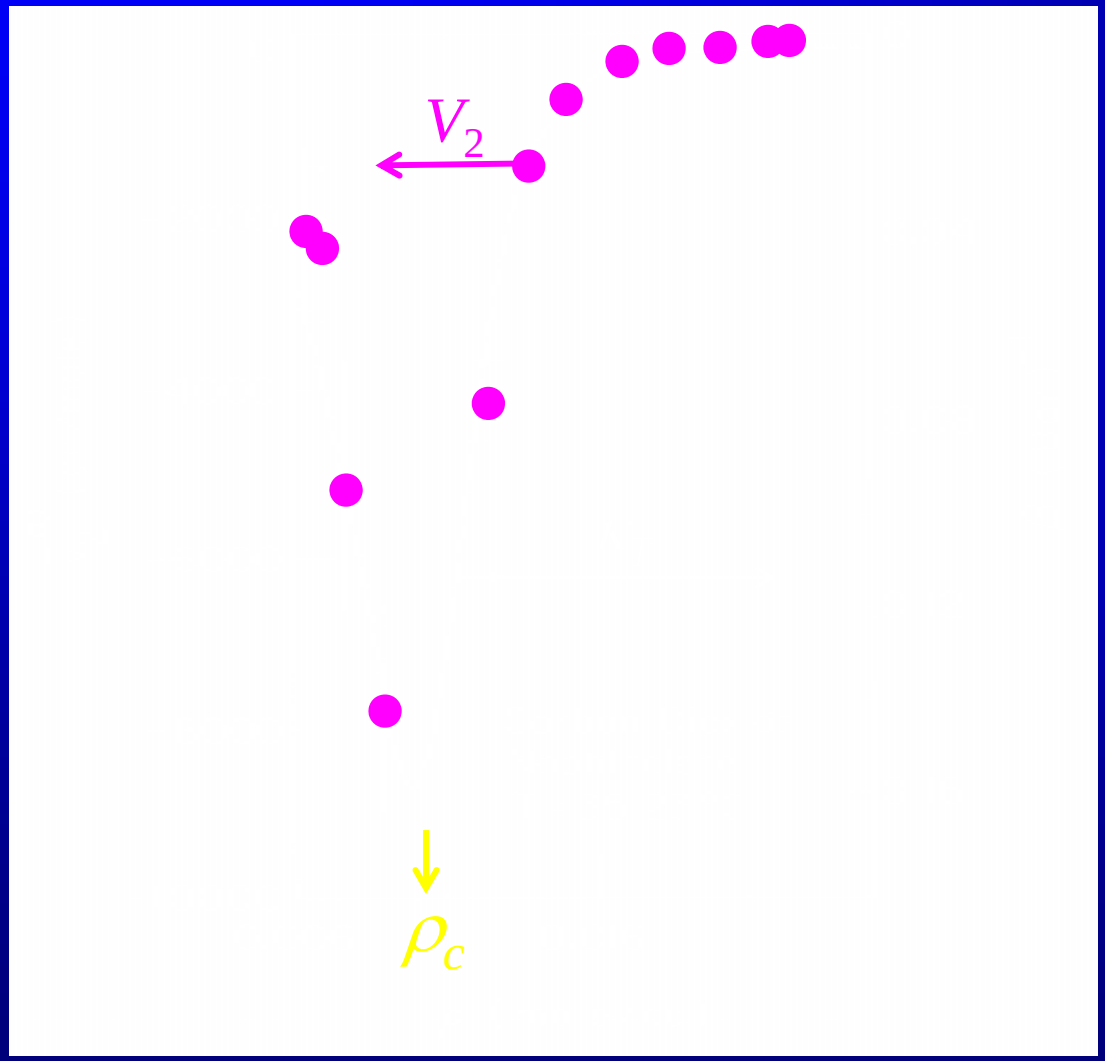
Density Fluctuations

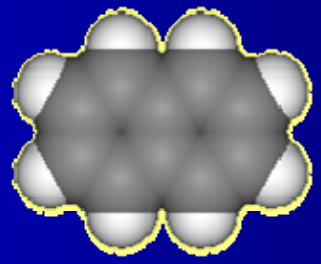


2d LJ simulations of Tucker & co., *J. Phys. Chem. B* **104**, 6258 (2000).

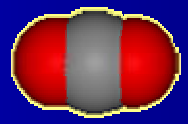
The Solvent's Perspective; Thermodynamics

Partial Molar Volumes near T_c: Naphthalene / sc-CO_2





74 cm^3 mol^{-1}

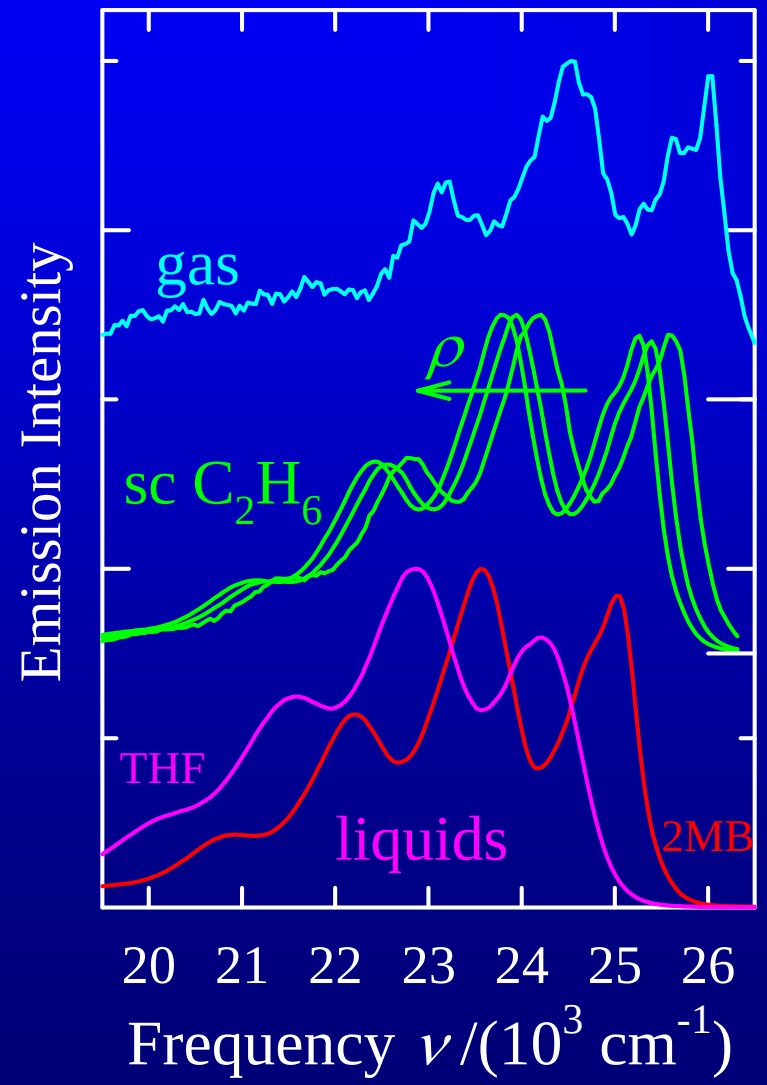


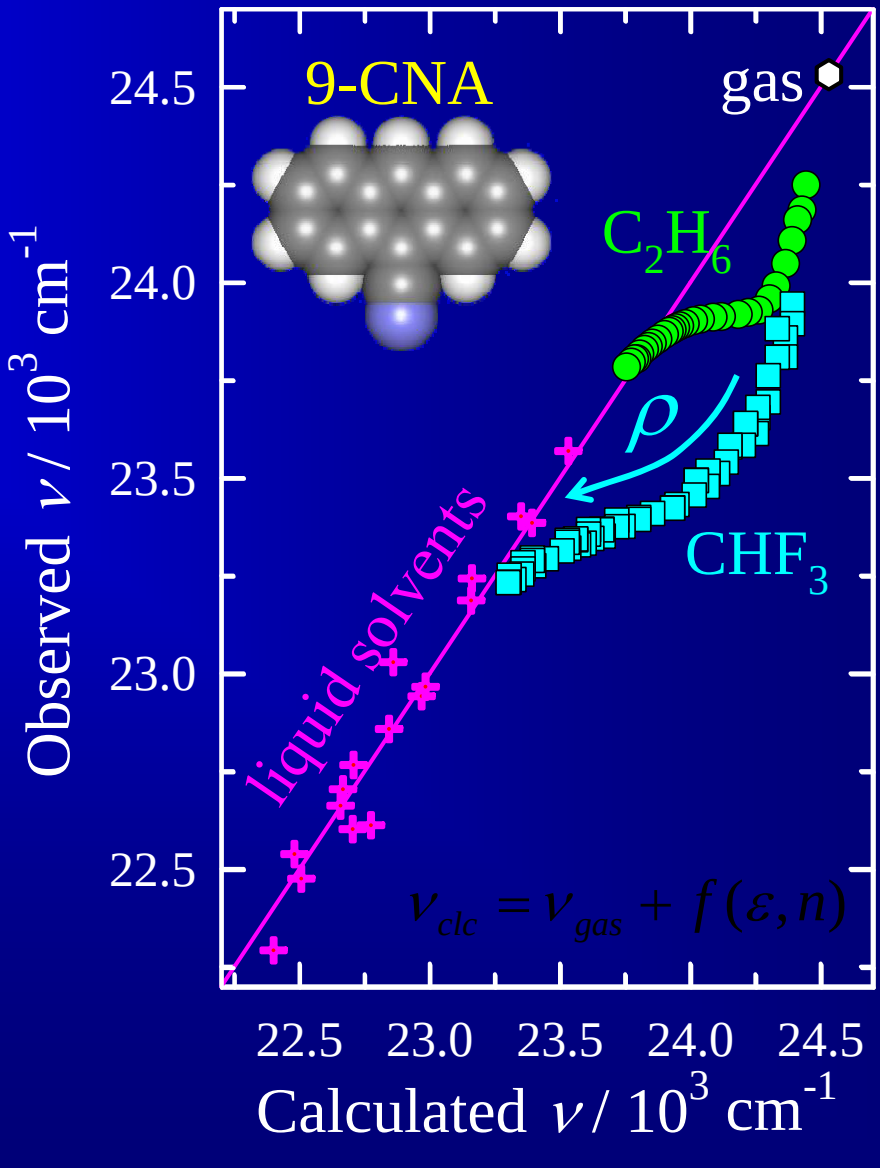
21 cm^3 mol^{-1}

C. A. Eckert, D. H. Ziger, K. P. Johnston, and S. Kim, *J. Phys. Chem.* **90**, 2738 (1986).

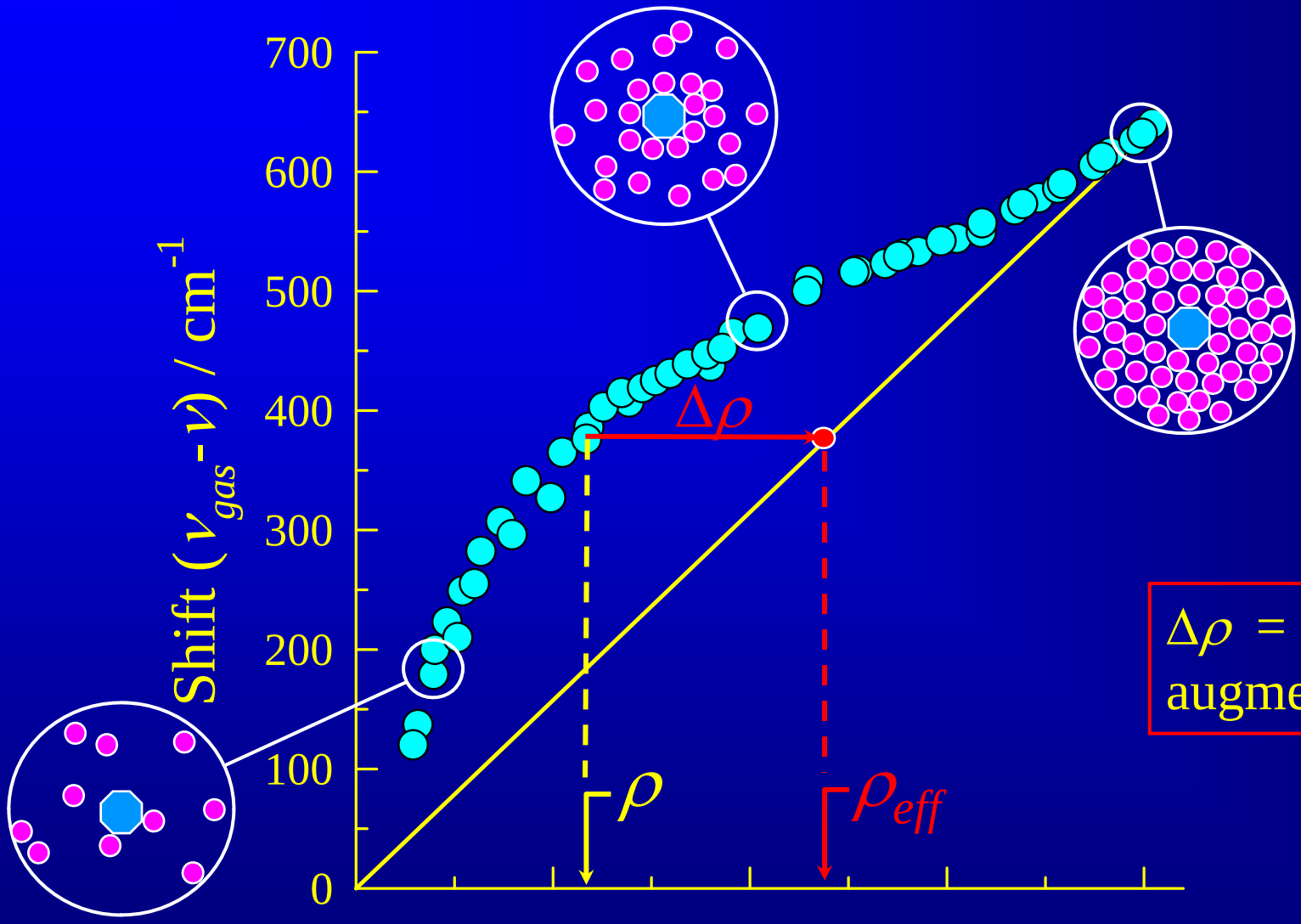
The Solute's Perspective; Spectroscopy

Emission Spectra, 9-CNA





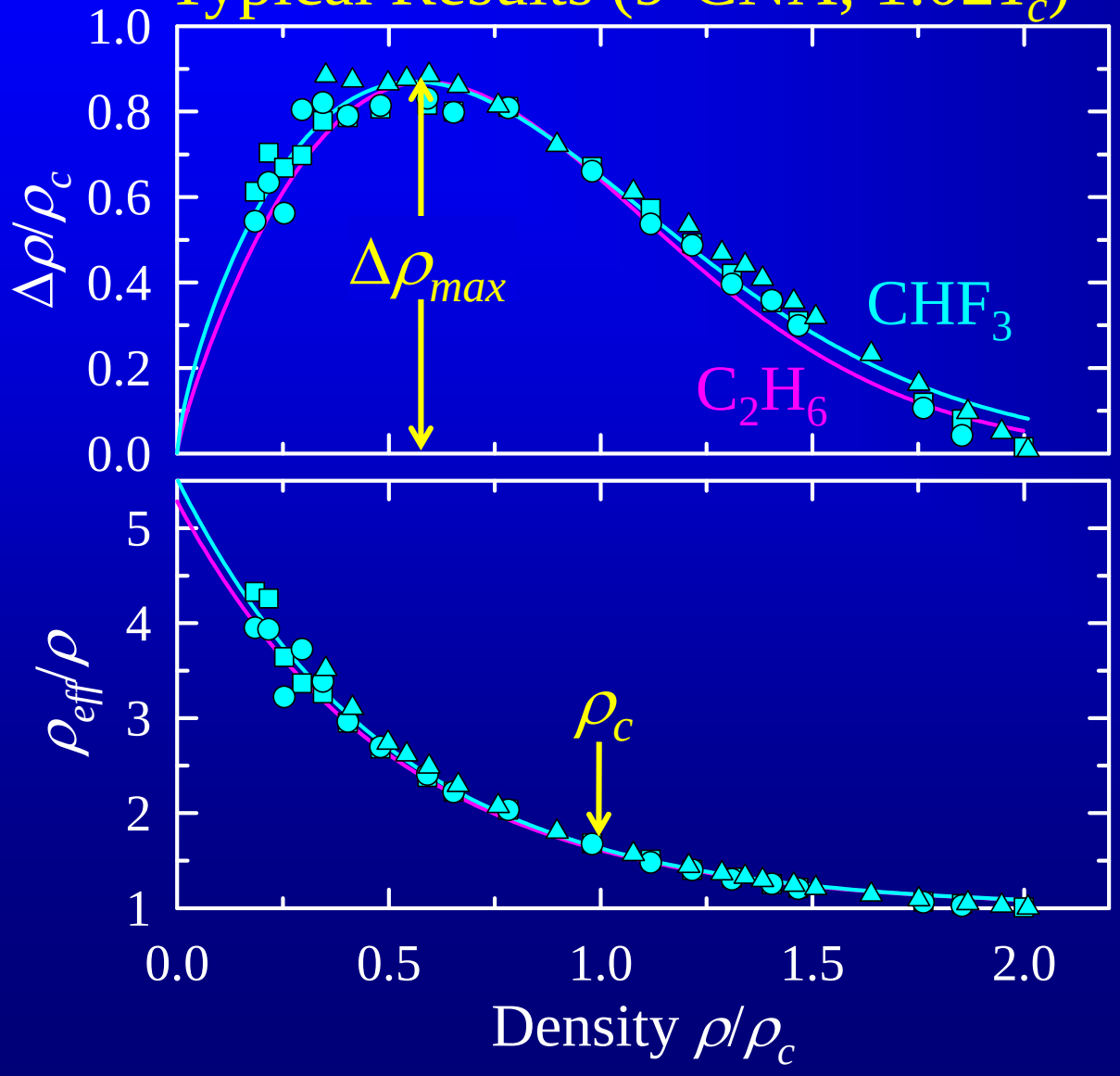
"Local Density Augmentation"



$\Delta\rho$ = "density augmentation"

Some Experimental Observations

Typical Results (9-CNA; 1.02T_c)



$\Delta\rho = \rho_{eff} - \rho$

"Augmentation"

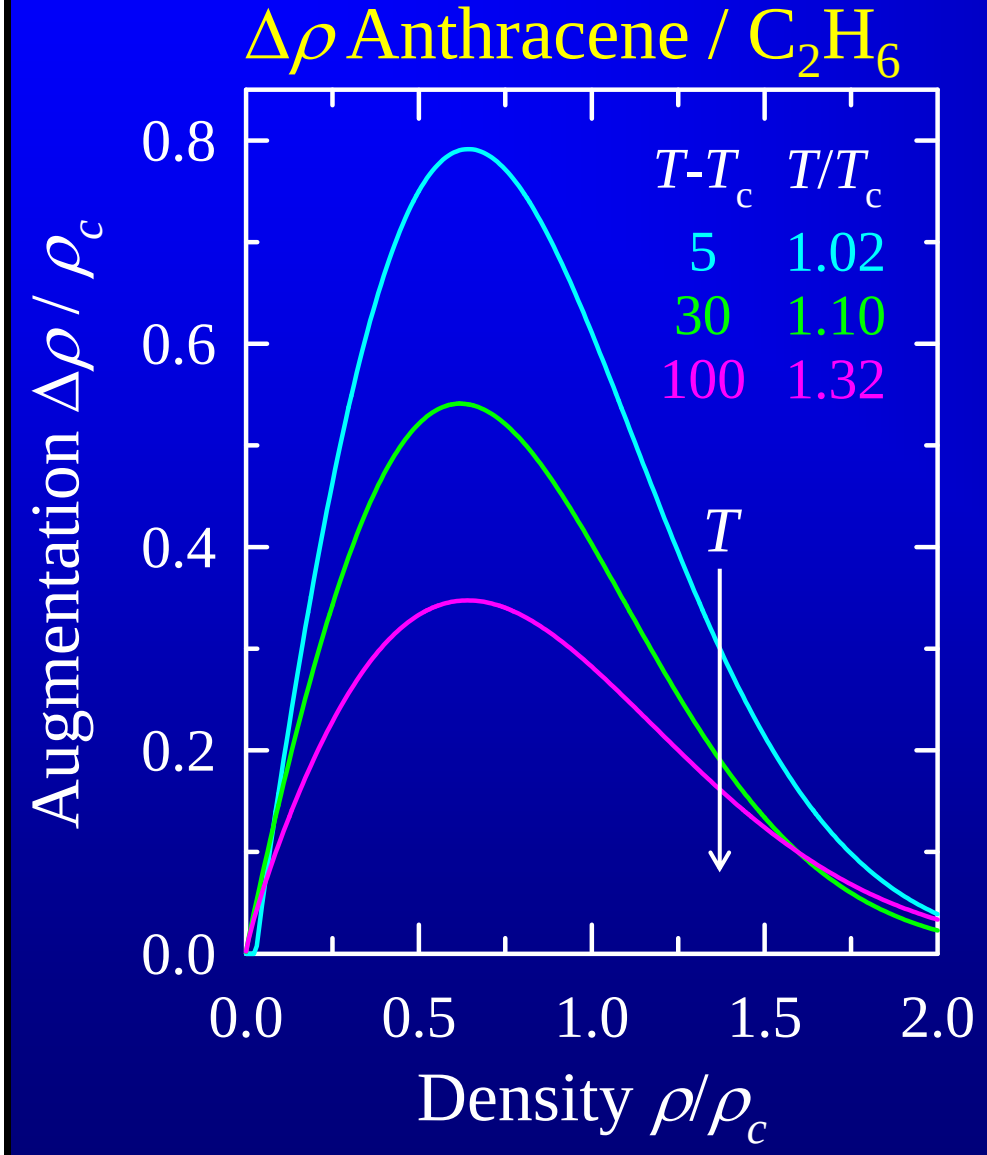
- $\Delta\rho_{max}$~0.5-1ρ_c
- many systems show similar $\Delta\rho$

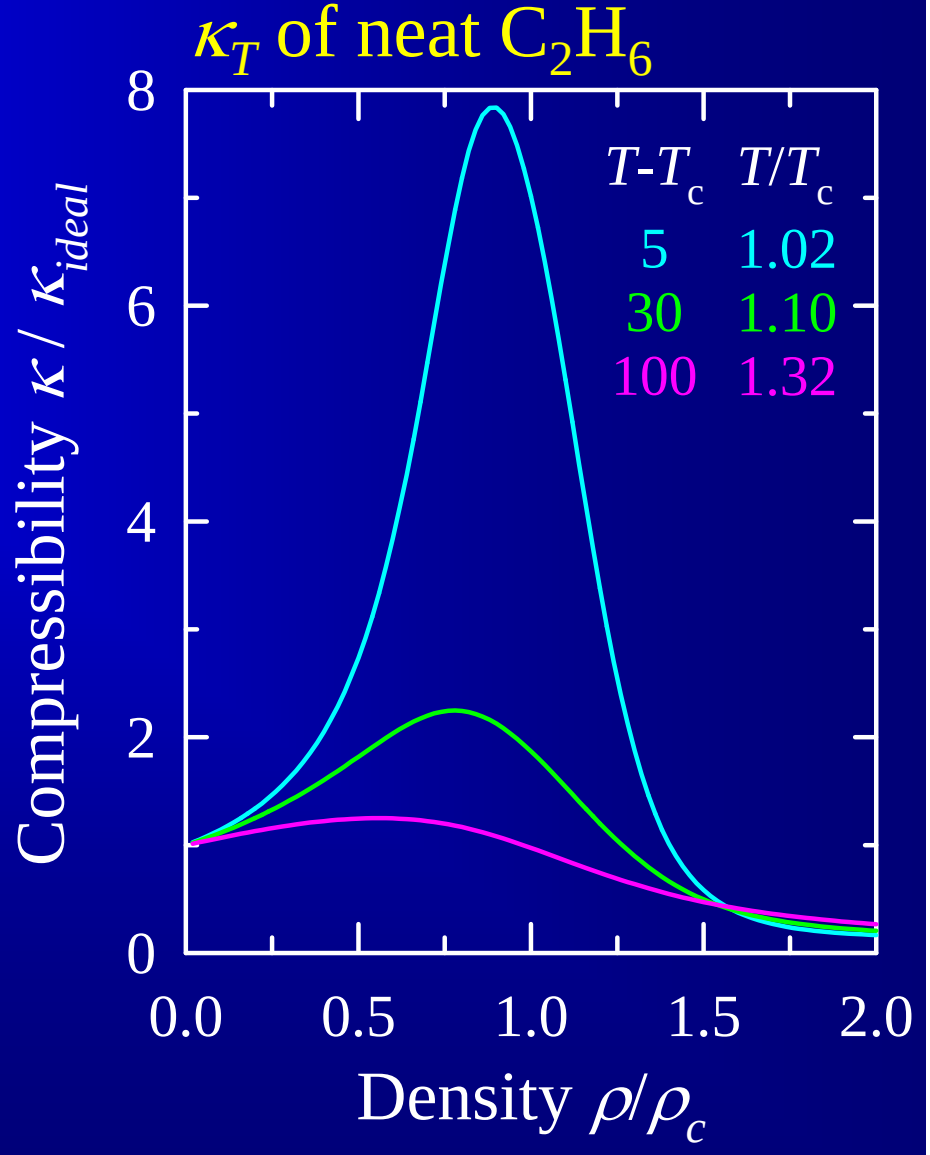
ρ_{eff}/ρ

"Enhancement"

- ρ_{eff}/ρ maximal (3-10) as $\rho \rightarrow 0$
- ρ_c unnoticed

Temperature Dependence

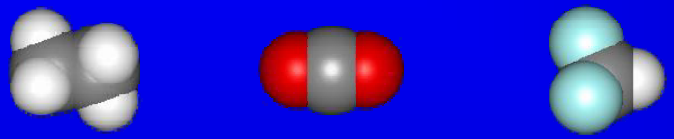




U-V Interaction Strength

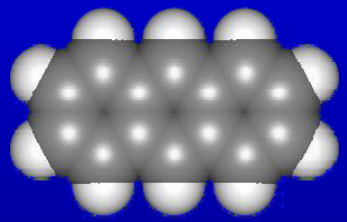
SC Solvents:

● C_2H_6 ■ CO_2 ◆ CHF_3

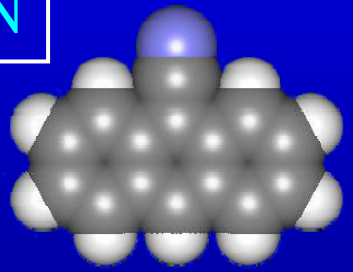


Solutes:

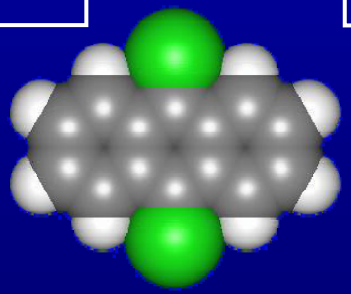
anthracene



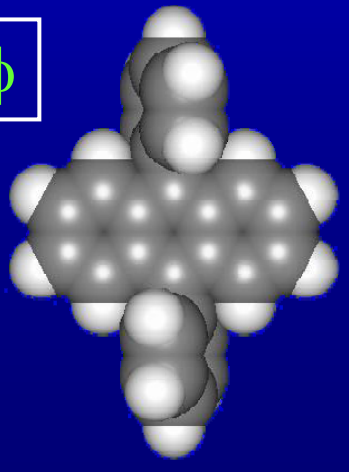
CN



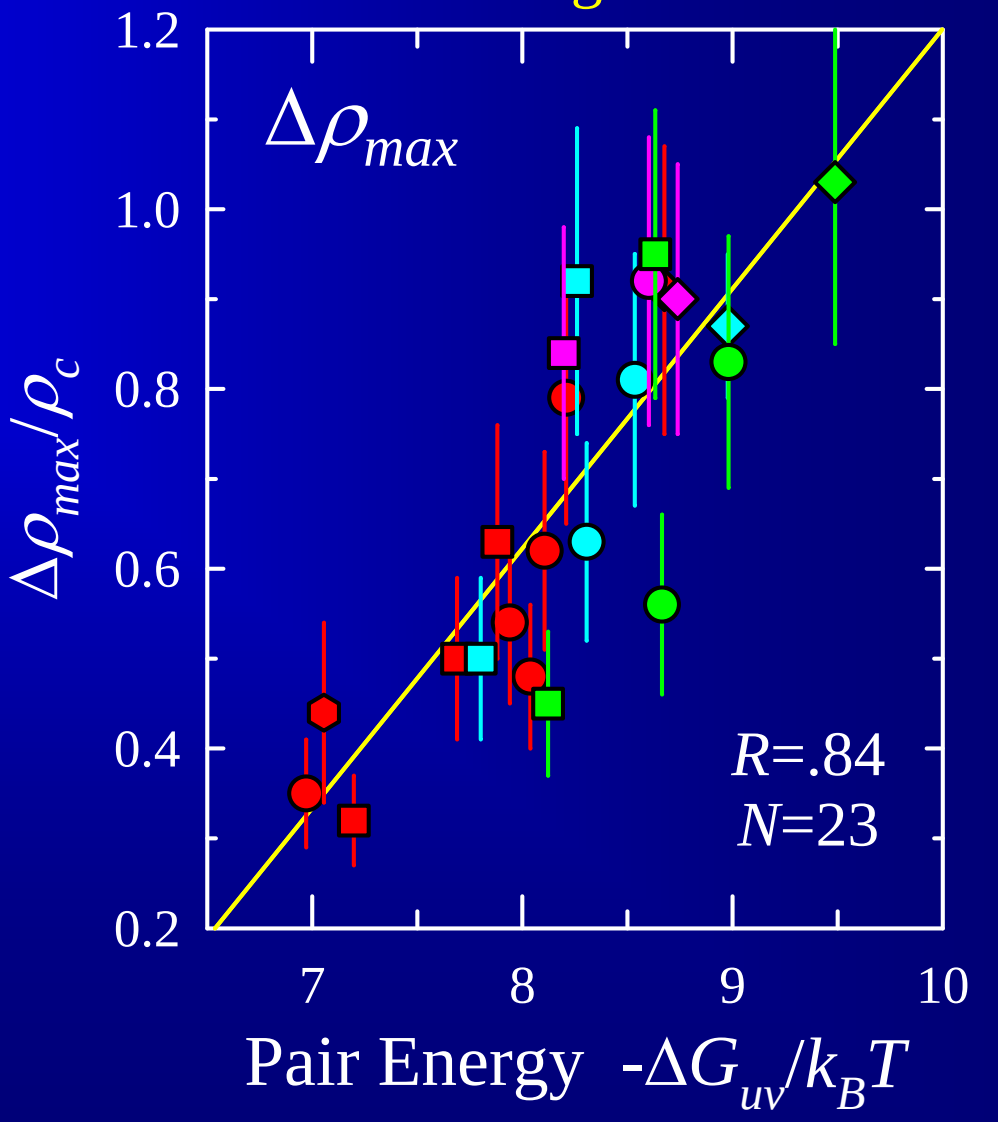
diCl



diϕ

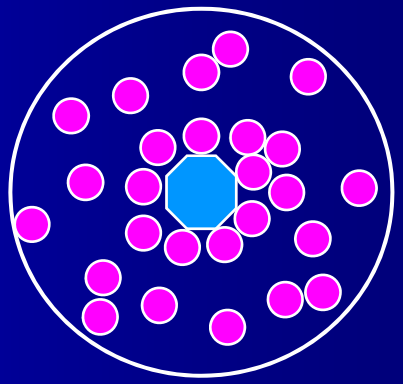


Maximum Augmentation



Experimental Summary

- solute may greatly perturb solvent; some solvation properties track divergent solvent behavior



- solute-centered observables report on local environment

- local density augmentation a large effect:

  ρ_{eff}/ρ = 2-3 near $\Delta\rho_{max}$

- $\Delta\rho$ not obviously tied to critical behavior; a direct function of solute-solvent interaction strength

Computer Simulations

Solvents:

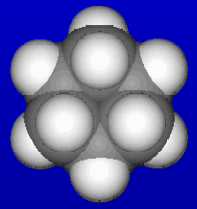
- Xe, C_2H_6, CO_2, CHF_3
- tuned to fit coexistence & other properties of real fluid

Solutes:

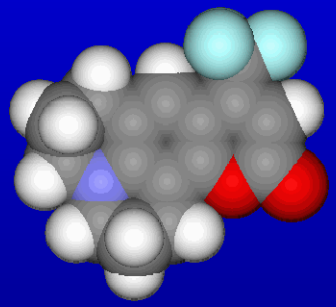
- *q* from *ab initio* calculations
- OPLS LJ parameters

Simulations:

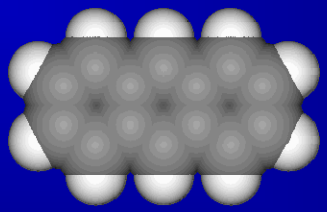
- classical MD, MC
- 1 solute, ~1000 solvents
- T_c+5-10 K, $0<\rho \leq 2\rho_c$
- *NVE*, *NVT*, *PVT*
- LJ + *q* site-site potentials

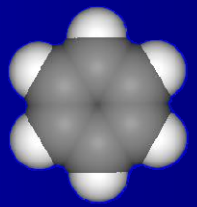


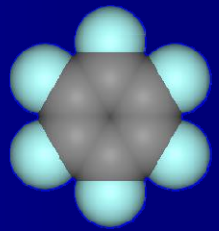
c-hexane



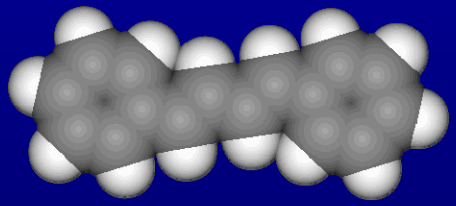
C153



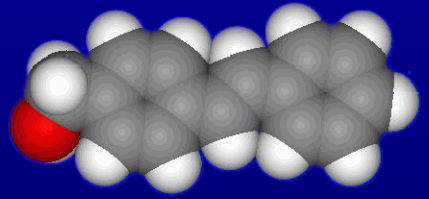




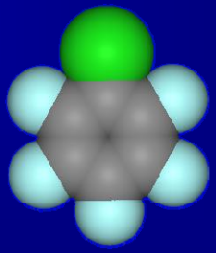
anthracene

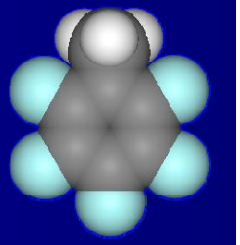


DPB



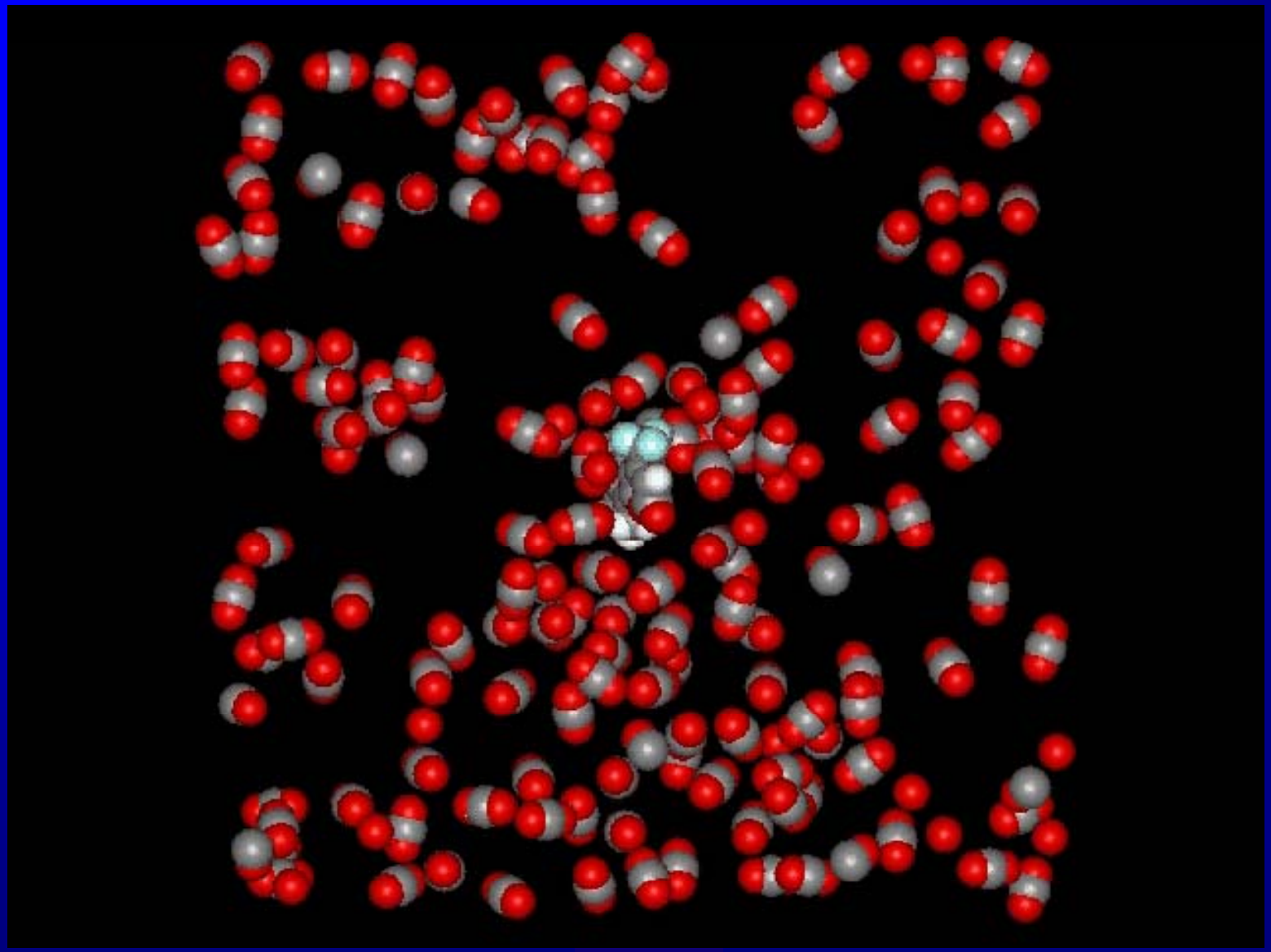
HMS





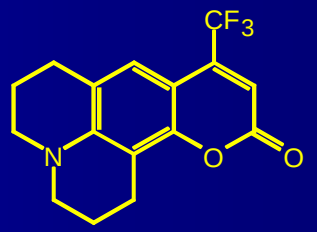
C_6H_6, C_6F_6, …

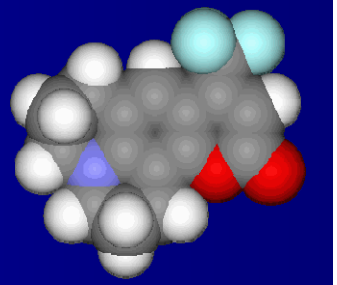
C153 / CO_2 T_c+5 K, 0.6ρ_c



60 Å

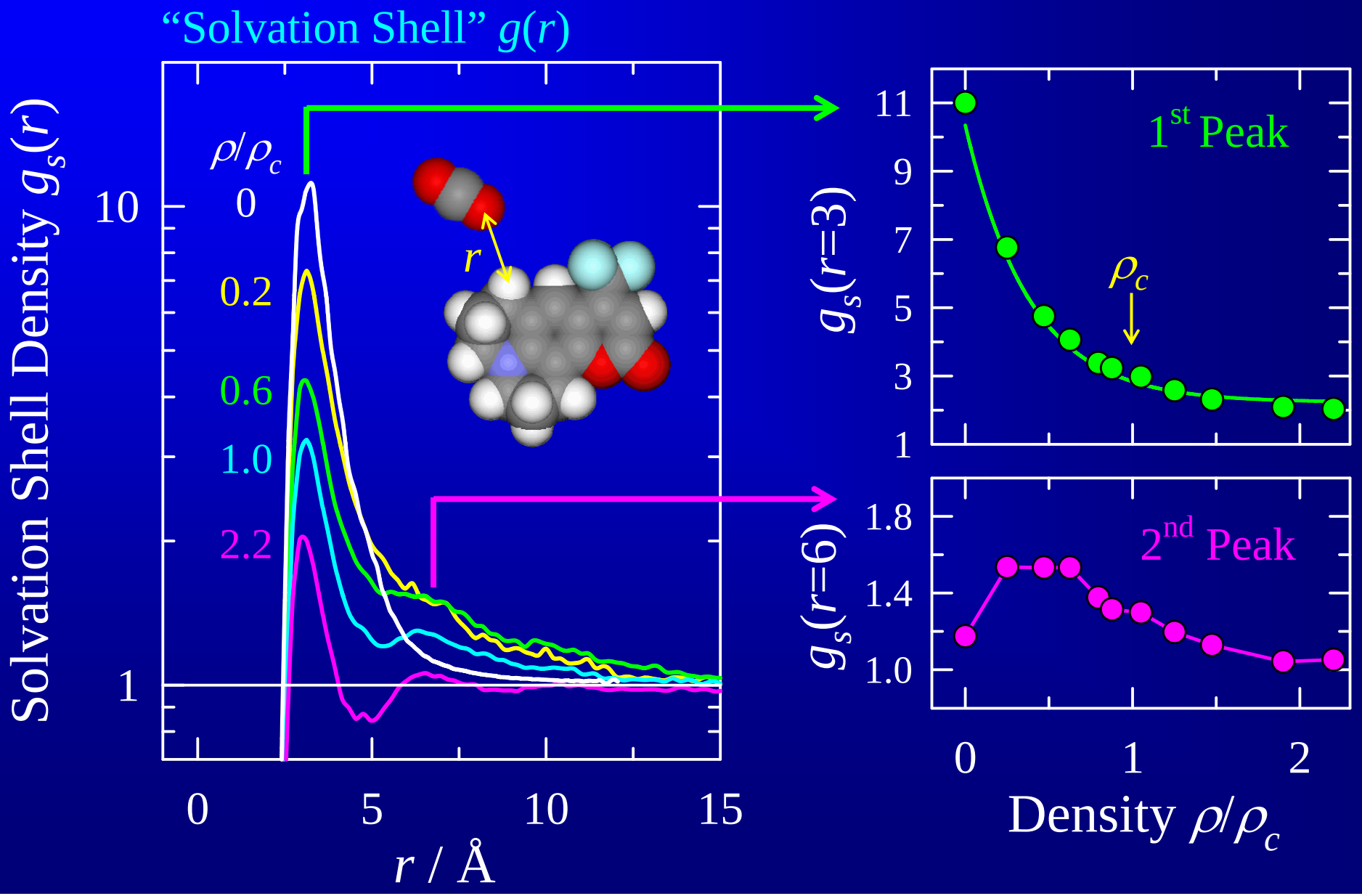
C153





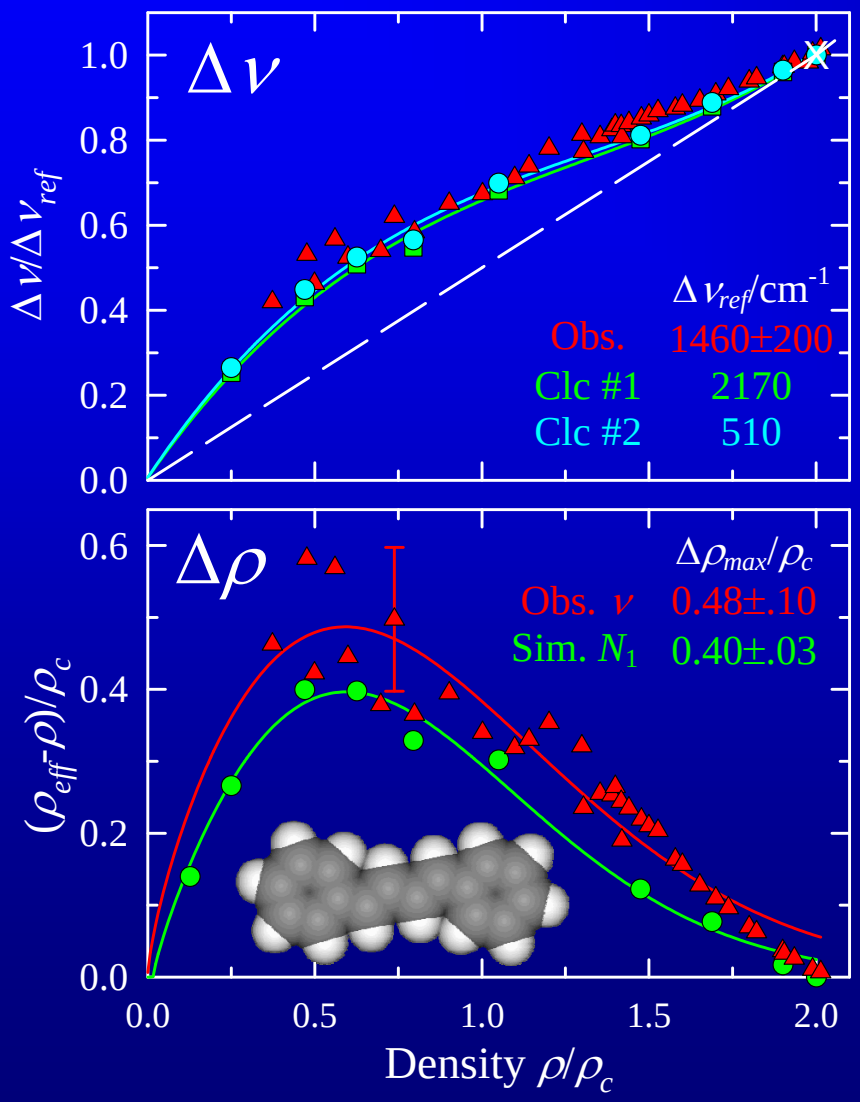
Δt = 40 ps
δt_f = .08 ps
~ .8 ps/s

Solvation Structure C153/CO_2 (T_c+5K)

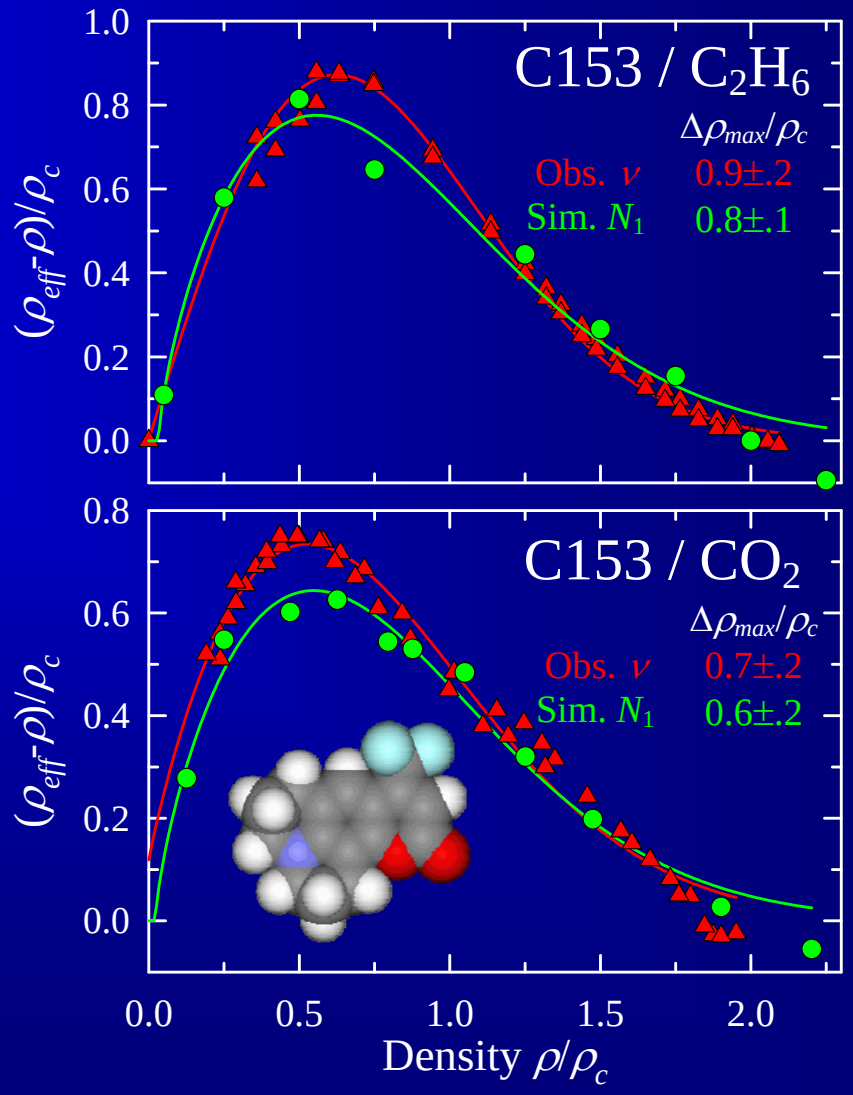


Comparisons to Experiment

DPB / CO_2



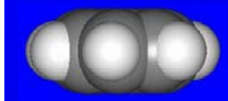
Coumarin 153 / C_2H_6 & CO_2

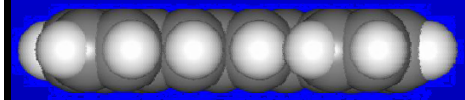


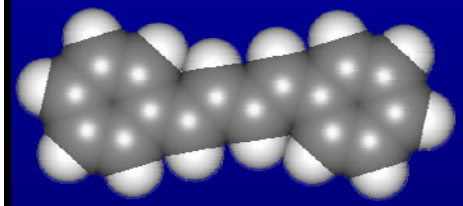
3d Solvation Structure - DPB/CO_2

$\rho(\vec{r}) / \rho(\infty)$

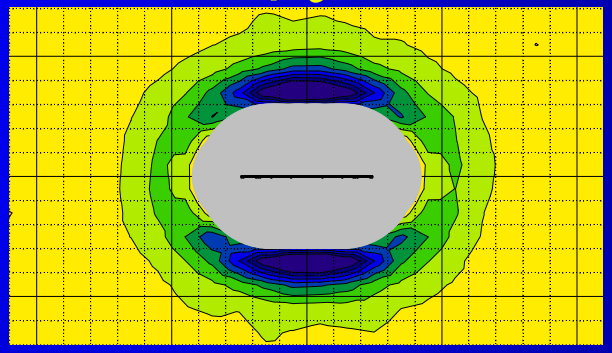
- 1.0 - 1.5
- 1.5 - 2.0
- 2.0 - 2.5
- 2.5 - 3.0
- 3.0 - 3.5
- 3.5 - 4.0
- 4.0 - 4.5
- 4.5 - 5.0
- > 5.0

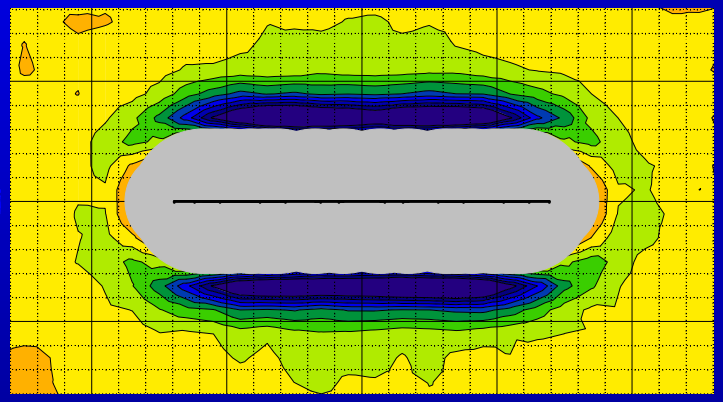


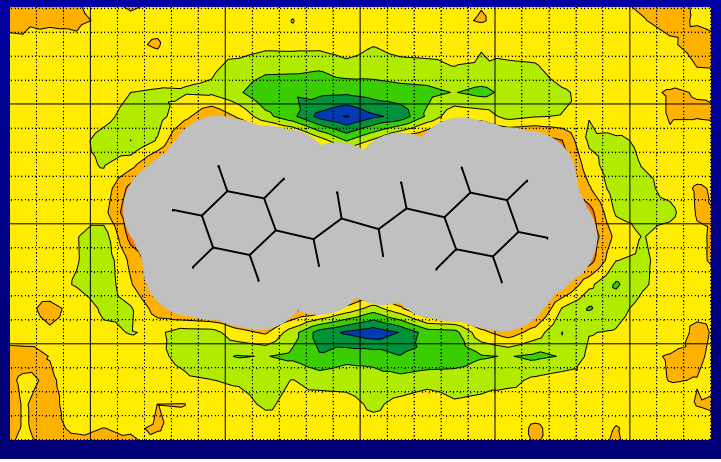




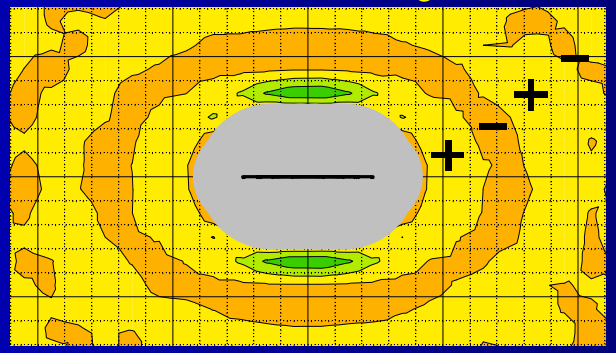
0.2 ρ_c

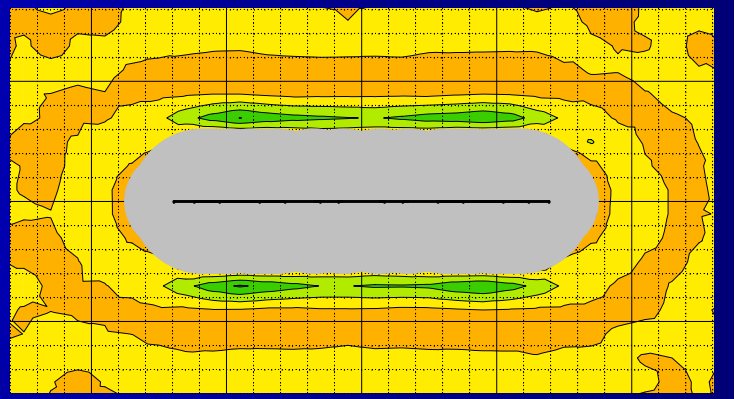


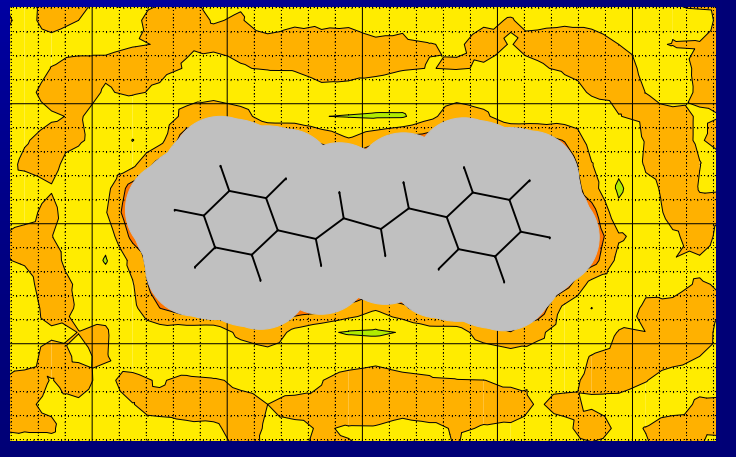




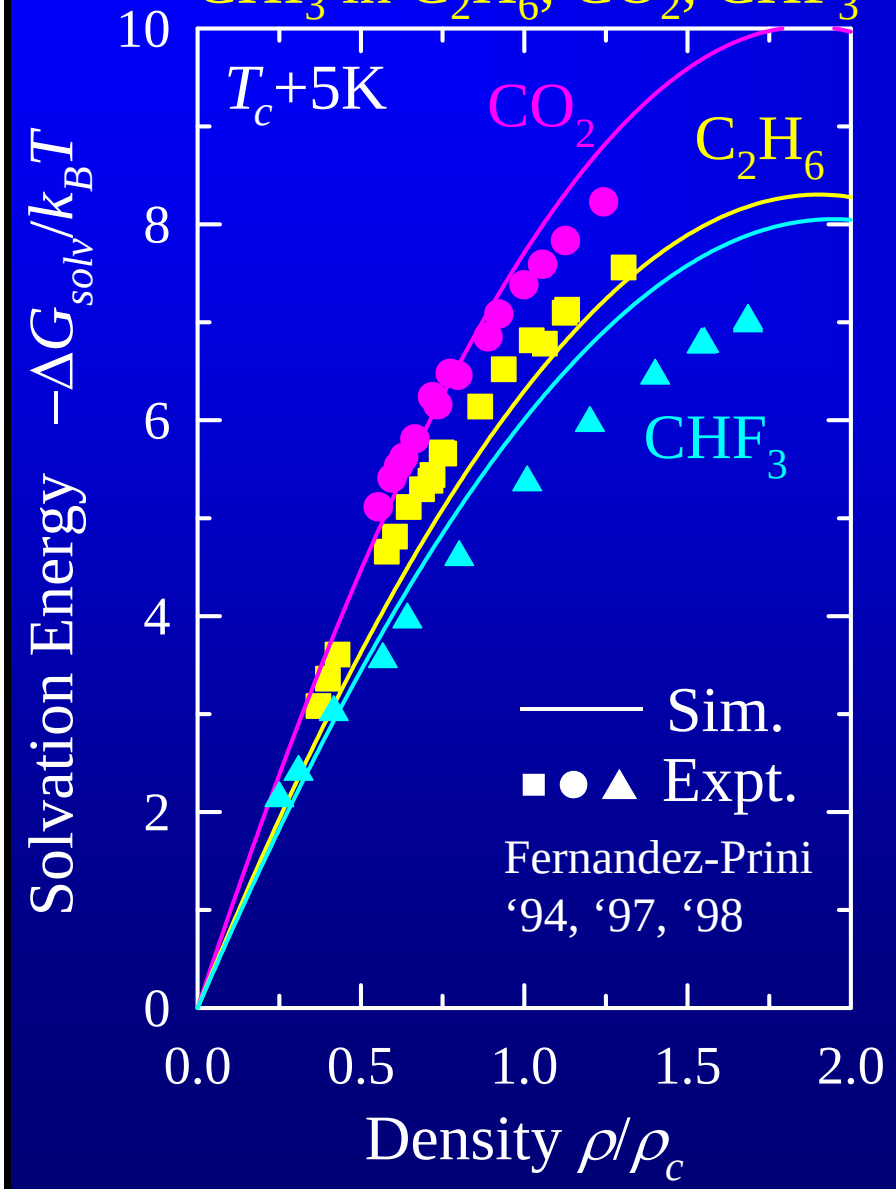
2.0 ρ_c

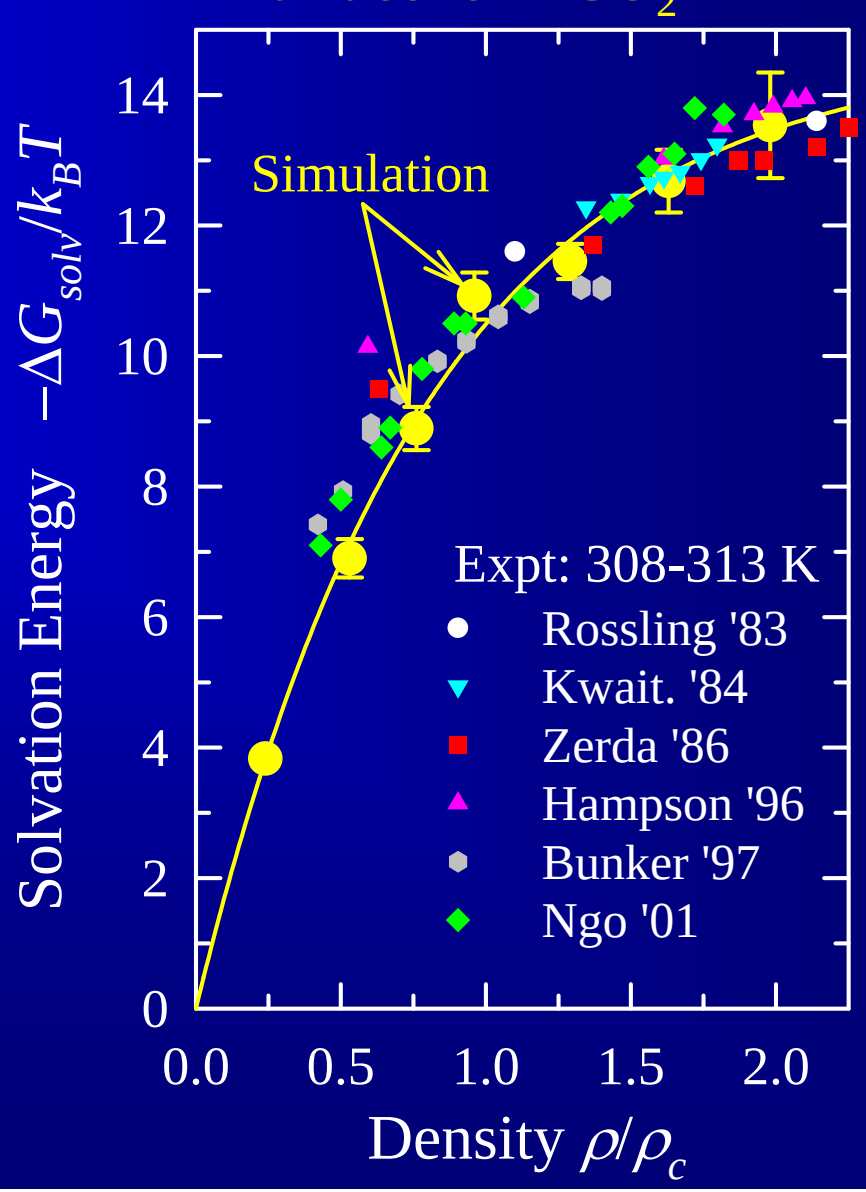






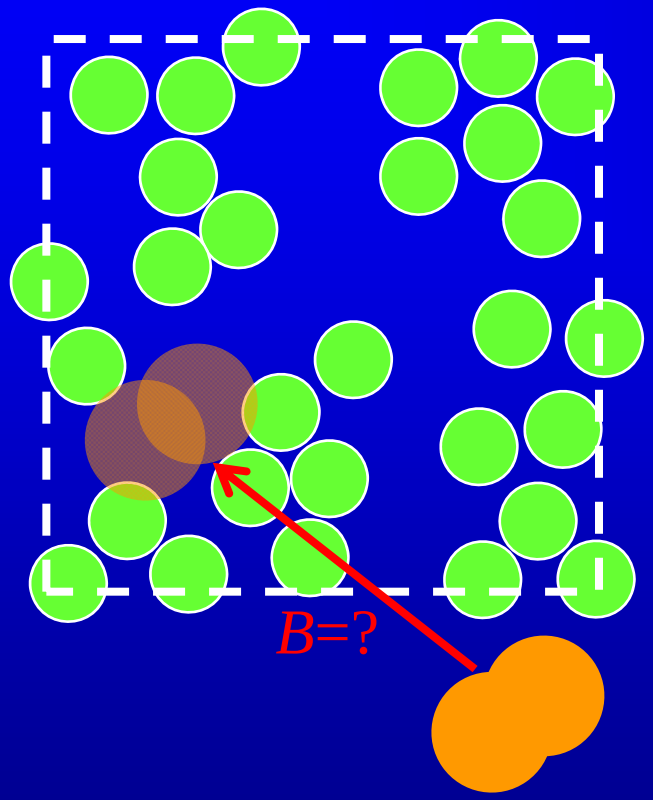
Effect on Solubilities? (ΔG_{solv})





$\Delta\rho$ None; Inhomogeneity Little

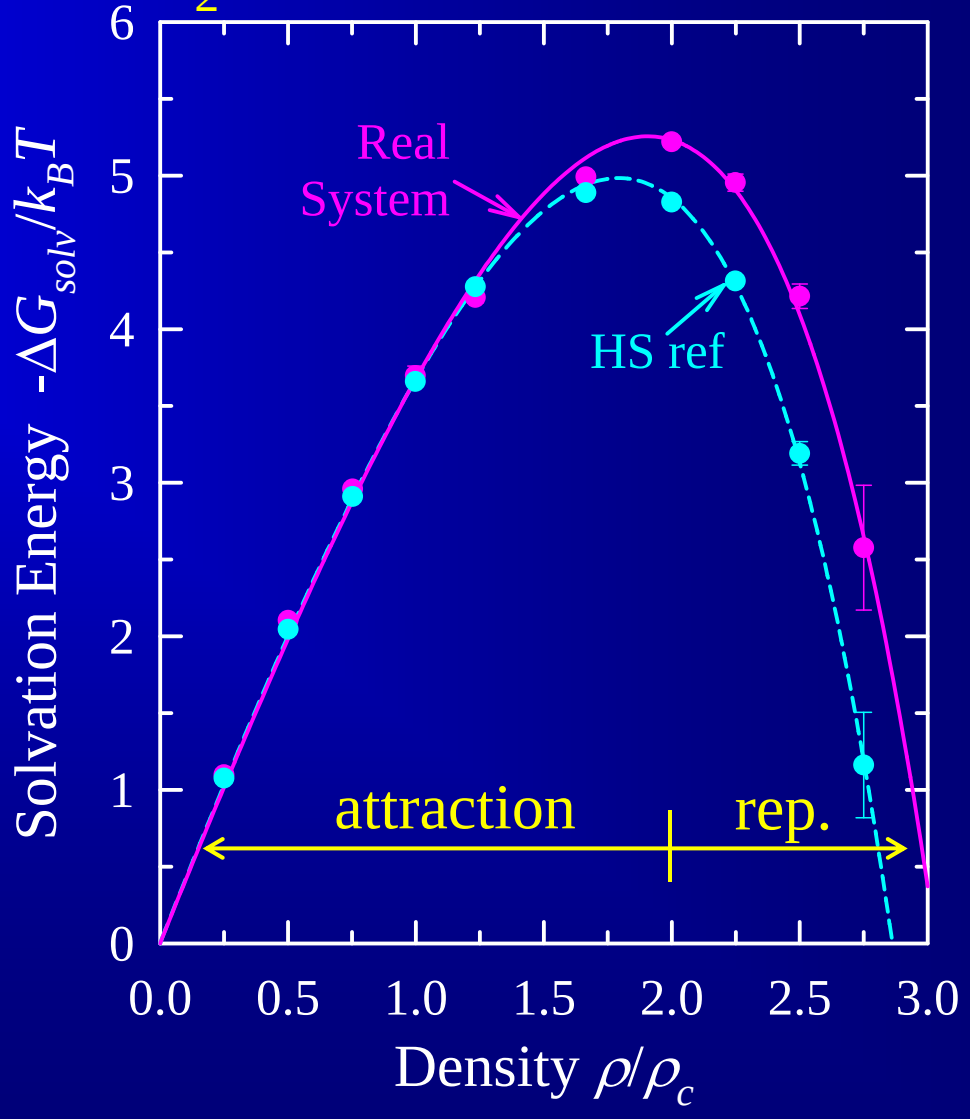
Test-Particle Insertion



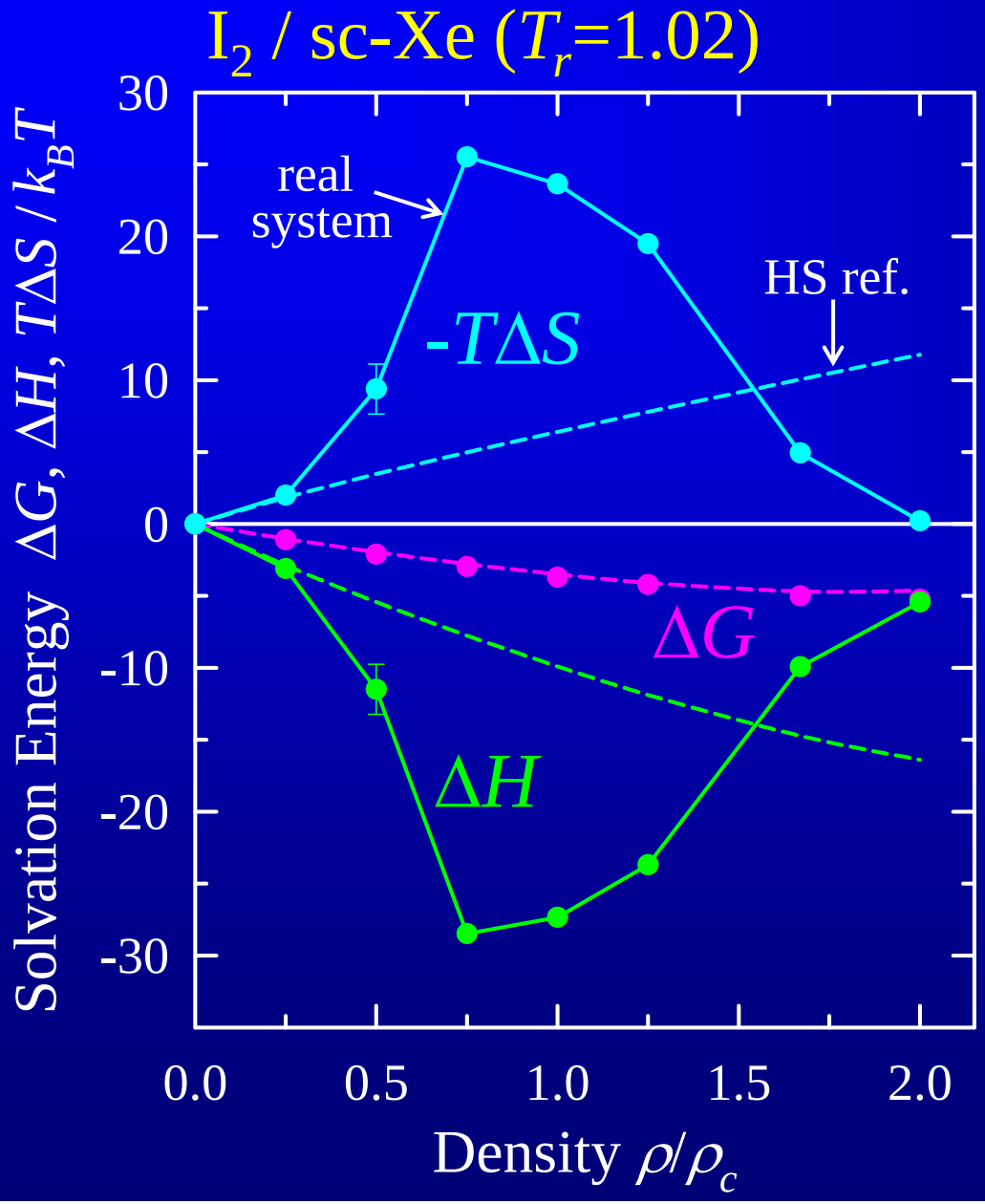
$$\frac{\Delta G_{solv}}{k_B T} = -\ln\left\langle e^{-B/k_B T}\right\rangle_0$$

(Widom, Ben-Naim)

I_2 / sc-Xe Simulations



Solvation Thermodynamics



$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S = -\left(\frac{\Delta G}{\partial T}\right)_P$$

- no $\Delta\rho$ effect on solubilities (!)
- ΔG insensitive to critical inhomogeneities
- ΔH and ΔS diverge due to critical fluctuations

Dynamical Effects?

Some Observations:

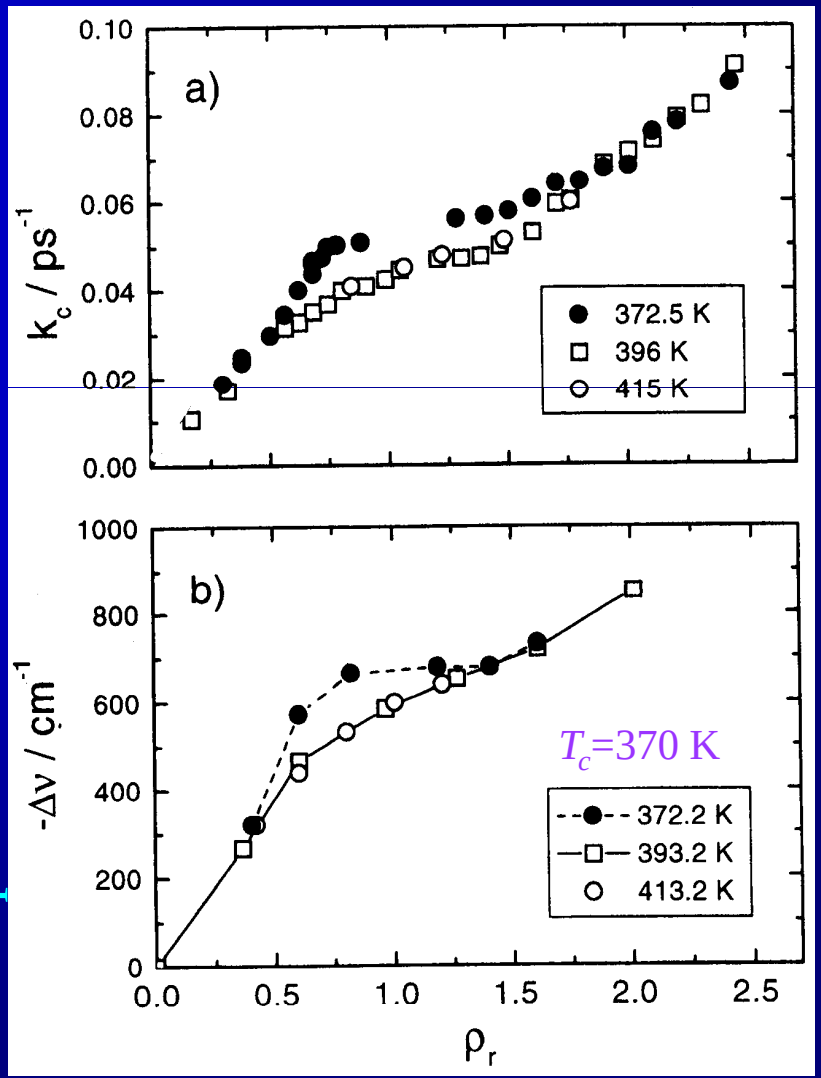
- Vibrational Relaxation
  - $W(CO)_6$ Fayer ‘00
  - azulene Schwarzer ‘97

  rates track $\Delta\rho$
- Translational Diffusion

  few measurements to low ρ; simulations show weak $\Delta\rho$ effect
- Rotational Motion
  - DPB, HMS Kauffman ‘95 (‘02)

  $\Delta\rho$ effect masked
- Raman Linewidths Neat sc-N_2
  - expt. (‘03) and simulations (Skinner ‘04) show weak critical “divergence”
- Solvation Dynamics, Chemical Reactions?

Azulene Vibrations / SC Propane

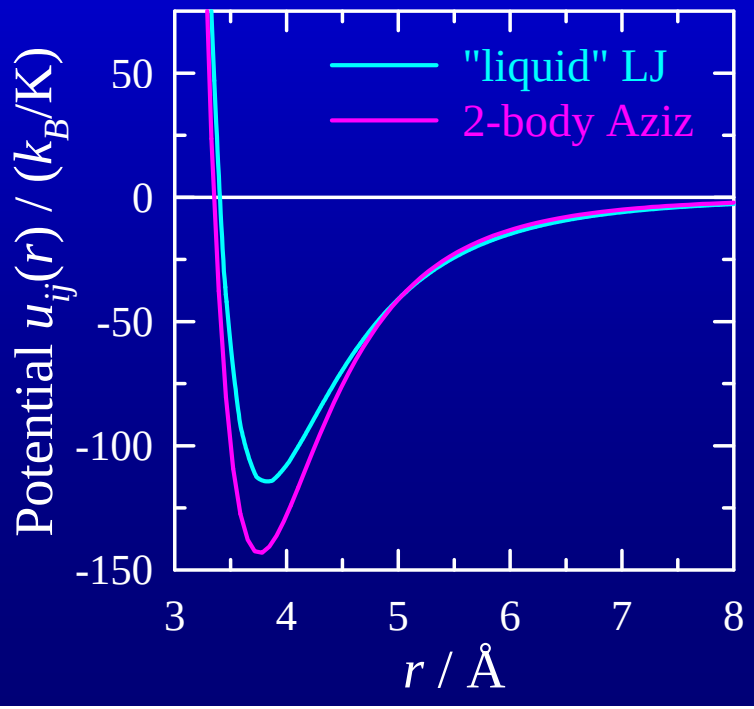


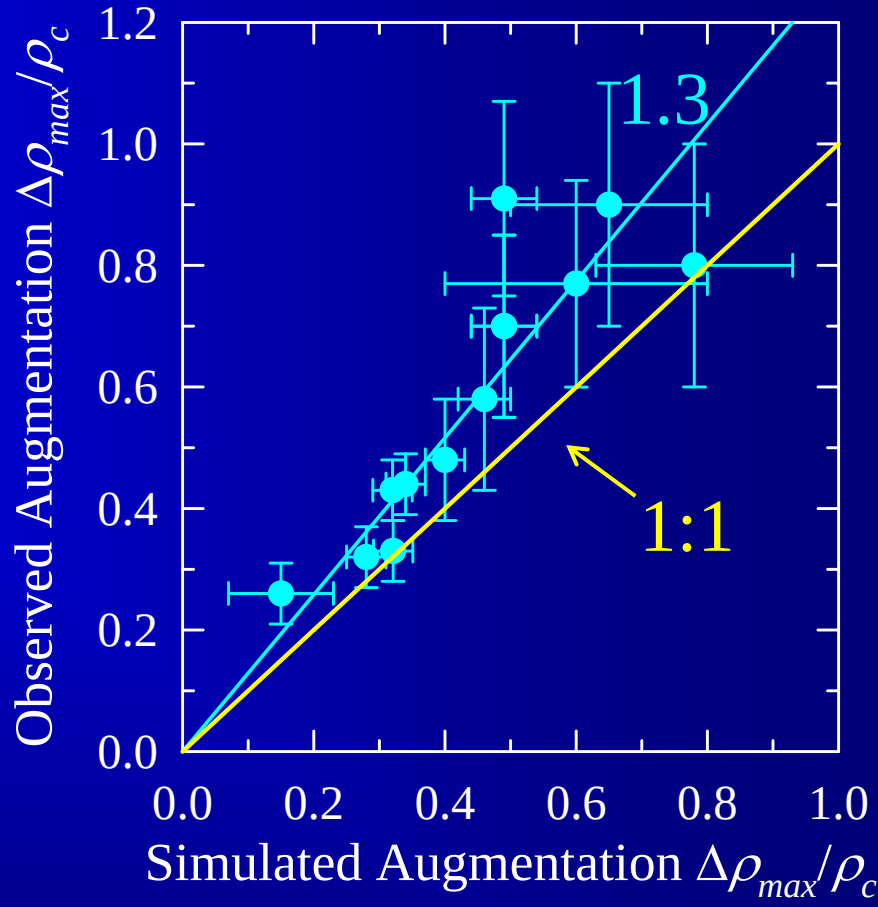
D. Schwarzer, J. Troe, & M. Zerezke, *J . Chem. Phys.* **107**, 8380 (1997).

A Lingering Discrepancy

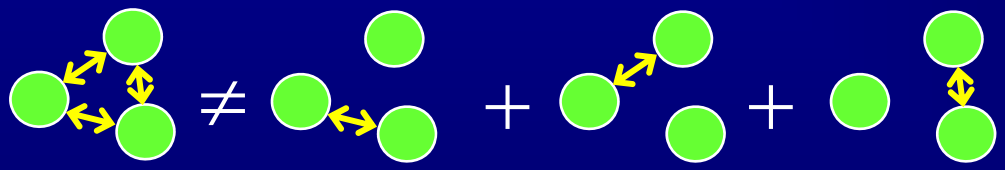
Realistic $\Delta\rho$ Comparisons

Solute	Solvent	Solute	Solvent
c-hexane	CO_2	DPB	CO_2
C_6F_6	CO_2	HMS	CO_2
C_6H_6	CO_2	anthracene	CO_2
CH_3-C_6F_5	CO_2	anthracene	CHF_3
Cl-C_6F_5	CO_2	anthracene	C_2H_6
C153	CO_2	C153	C_2H_6





Non-additivity:



Solvation in SCFs

- characterized by substantial “density augmentation”
- solute-solvent attraction is key for large solutes; role of “criticality” still unclear
- experiment and simulation (largely) agree; discrepancies reflect contribution of non-additive interactions

Summary & Conclusions

- SFs currently used in a variety of applications
  - analysis, extraction, cleaning
  - polymer synthesis & processing
  - particle/materials synthesis & processing
  - small molecule synthesis
- use is often environmentally motivated but SC solvents also superior in many applications
- fundamental studies still relatively young
  - basic features of solvation clear
  - frictional effects & impact on reactions require further study

Parting Shots

The Maroncelli Group

Zemin Su

Ranjit Biswas

Weiping Song

Nikhil Patel

Where We Work