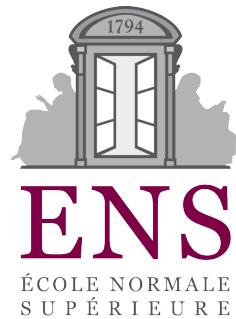


# Links between quantum and classical DFT and the problem of correlation in classical DFT

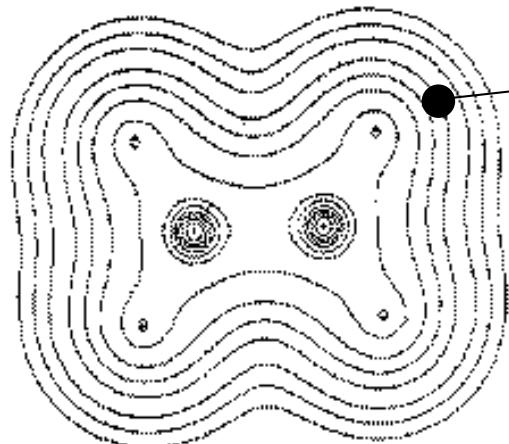
Daniel Borgis

Pôle de Physico-Chimie Théorique  
Ecole Normale Supérieure de Paris

GdR Corrélation, 27-29 Novembre 2013



## Electronic density functional theory (eDFT)



$$\rho(\mathbf{r}) = \text{electron density}$$

The ground state energy can be written as a functional of  $\rho(\mathbf{r})$

$$E[\rho] = T[\rho] + V_{ee}[\rho] + \underbrace{\int d\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r})}_{\text{Universal (but unknown !)}}$$

Functional minimization:  $\frac{\delta E[\rho]}{\delta \rho} = 0$  → 
$$\begin{cases} \rho_0(\mathbf{r}) \\ E[\rho_0(\mathbf{r})] \end{cases}$$

For the ground state

## Classical Density Functional Theory (cDFT)

**David Mermin**, *Thermal properties of the inhomogeneous electron gas*, Phys. Rev. 137 (1965).

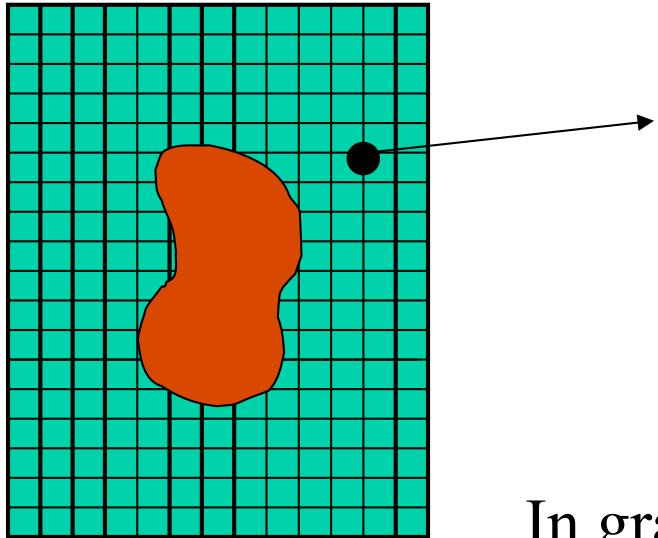
**R. Evans**, *The nature of the liquid-vapour interface and other topics in Statistical physics of non-uniform fluids*, Advances in Physics (1979).

**Y. Rosenfeld**, *Free-energy model for the inhomogeneous hard-sphere fluid mixture*, Phys. Rev. Lett. (1989).

And many others: J. Percus, JP Hansen, H. Löwen, ....

.....Mostly physicists !!

## Classical Density Functional Theory (cDFT)



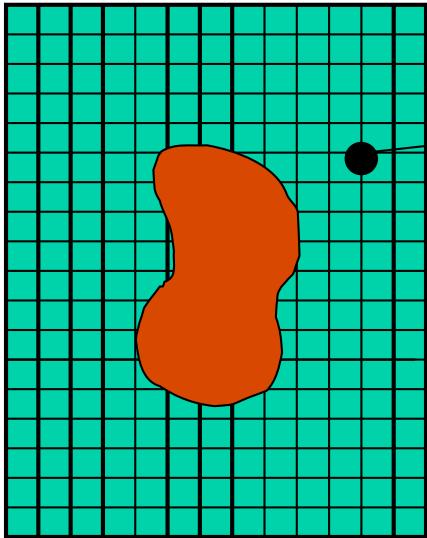
In grand canonical ensemble:

$$\Theta[\rho] = -T \underbrace{S[\rho]}_{\text{Intrinsic to a given solvent}} + F_{exc}[\rho] + \int d\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r}) - \mu_c N$$

Functional minimization:  $\frac{\delta\Theta[\rho]}{\delta\rho} = 0 \quad \rightarrow \quad \begin{array}{|c|} \hline \rho_0(\mathbf{r}) \\ \hline \Theta[\rho_0(\mathbf{r})] \\ \hline \end{array}$

Thermodynamic equilibrium

## Classical Density Functional Theory (cDFT)



$\rho(\mathbf{r})$ = solvent density

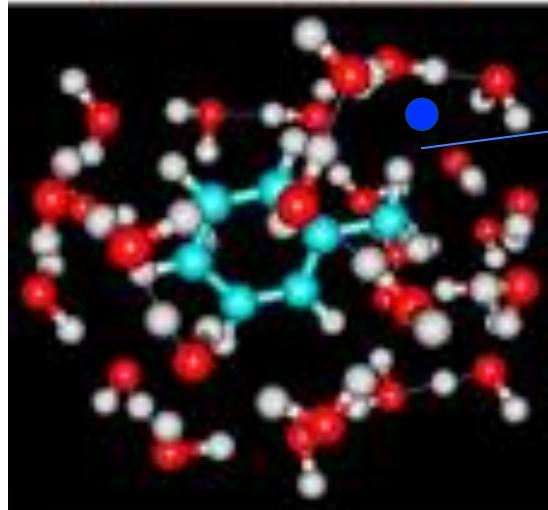
In grand canonical ensemble:

$$\Theta[\rho] = -T \underbrace{S[\rho]}_{\text{Intrinsic to a given solvent}} + F_{exc}[\rho] + \int d\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r}) - \mu_c N$$

Functional minimization:  $\frac{\delta\Theta[\rho]}{\delta\rho} = 0 \quad \rightarrow \quad \begin{array}{|c|} \hline \rho_0(\mathbf{r}) \\ \hline \Theta[\rho_0(\mathbf{r})] \\ \hline \end{array}$

Thermodynamic equilibrium

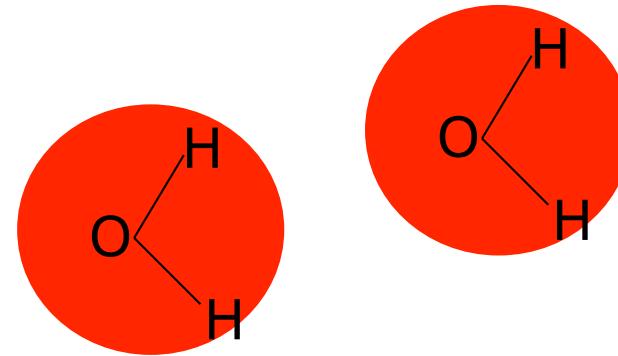
## Molecular Density Functional Theory (MDFT)



$$V_{ext}(\mathbf{r}_1, \Omega_1)$$

Basic ingredients: A MM force field

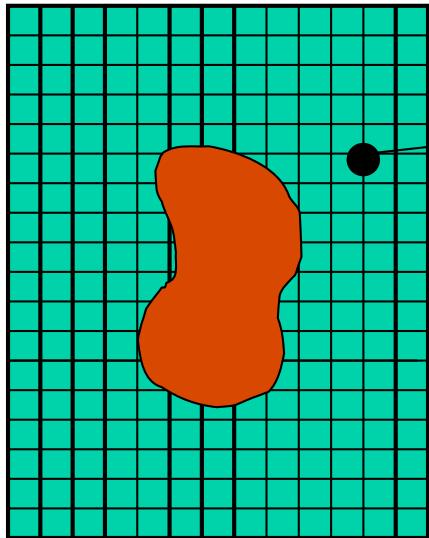
- Atomistic solvent model



$$u(r_{12}, \Omega_1, \Omega_2) = \sum_{i \in 1} \sum_{j \in 2} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{d_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{d_{ij}} \right)^6 \right] + \frac{q_i q_j}{d_{ij}}$$

- Atomistic (or quantum mechanical) solute creating at each point in space an external potential

# Molecular Density Functional Theory (MDFT)



$$V_{ext}(\mathbf{r}, \Omega)$$

Molecular picture

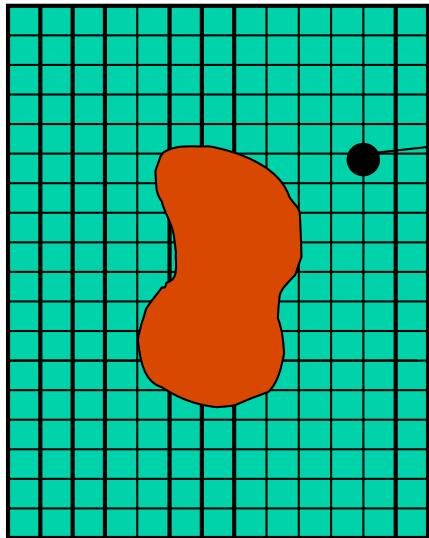
In grand canonical ensemble:

$$\Theta[\rho] = -T S[\rho] + \underbrace{F_{exc}[\rho]}_{\text{Intrinsic to a given solvent}} + \int d\mathbf{r} d\Omega V_{ext}(\mathbf{r}, \Omega) \rho(\mathbf{r}, \Omega) - \mu_c N$$

Functional minimization:  $\frac{\delta \Theta[\rho]}{\delta \rho} = 0 \rightarrow \begin{cases} \rho_0(\mathbf{r}, \Omega) \\ \Theta[\rho_0(\mathbf{r}, \Omega)] \end{cases}$

Thermodynamic equilibrium

## Molecular Density Functional Theory (MDFT)



$\rho(\mathbf{r}, \Omega)$  = position/orientation solvent density

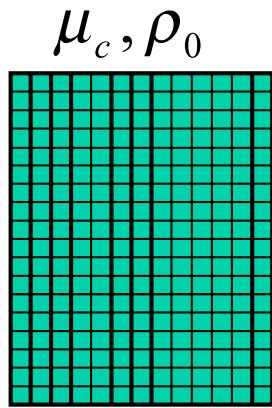
Molecular picture

In grand canonical ensemble:

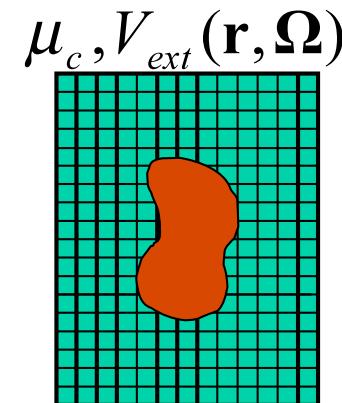
$$\Theta[\rho] = -T S[\rho] + \underbrace{F_{exc}[\rho]}_{\text{Intrinsic to a given solvent}} + \int d\mathbf{r} d\Omega V_{ext}(\mathbf{r}, \Omega) \rho(\mathbf{r}, \Omega) - \mu_c N$$

Functional minimization:  $\frac{\delta \Theta[\rho]}{\delta \rho} = 0 \rightarrow \begin{cases} \rho_0(\mathbf{r}, \Omega) \\ \Theta[\rho_0(\mathbf{r}, \Omega)] \end{cases}$

Thermodynamic equilibrium



$$\Theta[\rho_0]$$



$$\Theta[\rho(\mathbf{r}, \Omega)]$$

$$F[\rho] = \Theta[\rho] - \Theta[\rho_0]$$

$F_{\min}$  = Solvation free energy

But what is the functional ??

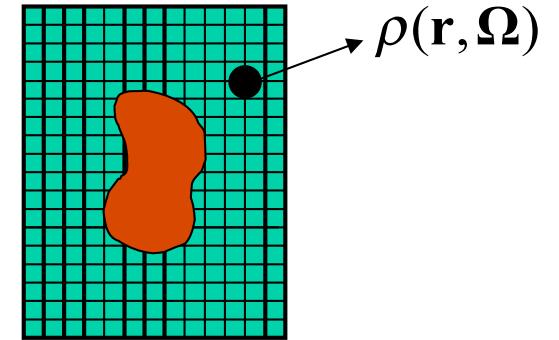
## The exact functional

$$F[\rho(\mathbf{x})] = F_{id}[\rho] + F_{exc}[\rho] + F_{ext}[\rho]$$

$$\mathbf{x} = (\mathbf{r}, \Omega)$$

$$F_{id}[\rho] = k_B T \int d\mathbf{x}_1 \left[ \rho(\mathbf{x}_1) \ln \left( \frac{\rho(\mathbf{x}_1)}{\rho_0} \right) - \rho(\mathbf{x}_1) + \rho_0 \right]$$

$$F_{ext}[\rho] = \int d\mathbf{x}_1 V_{ext}(\mathbf{x}_1) \rho(\mathbf{x}_1)$$

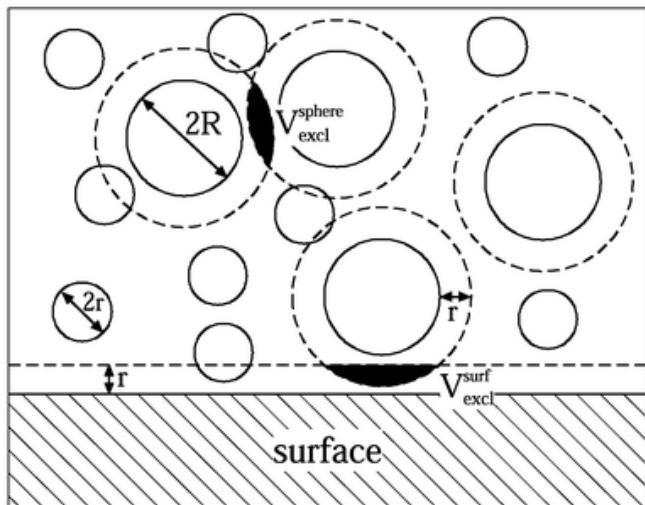


$$F_{exc}[\rho] = \frac{1}{2} \iint d\mathbf{x}_1 d\mathbf{x}_2 \Delta\rho(\mathbf{x}_1) u_{eff}(\mathbf{x}_1, \mathbf{x}_2; [\rho]) \Delta\rho(\mathbf{x}_2), \quad \Delta\rho(\mathbf{x}) = \rho(\mathbf{x}) - \rho_0$$

$u_{eff}(\mathbf{x}_1, \mathbf{x}_2; [\rho])$  = Effective solvent-solvent pair potential

$$u_{eff}(\mathbf{x}_1, \mathbf{x}_2; [\rho]) = u(\mathbf{x}_1, \mathbf{x}_2) + u_{cor}(\mathbf{x}_1, \mathbf{x}_2; [\rho])$$

# Fundamental Measure Theory for Hard-Sphere Mixtures



Y. ROSENFELD, *Phys. Rev. Lett.* **63**, 980 (1989).

E. KIERLIK and M. L. ROSINBERG, *Phys. Rev. A* **42**, 3382 (1990)

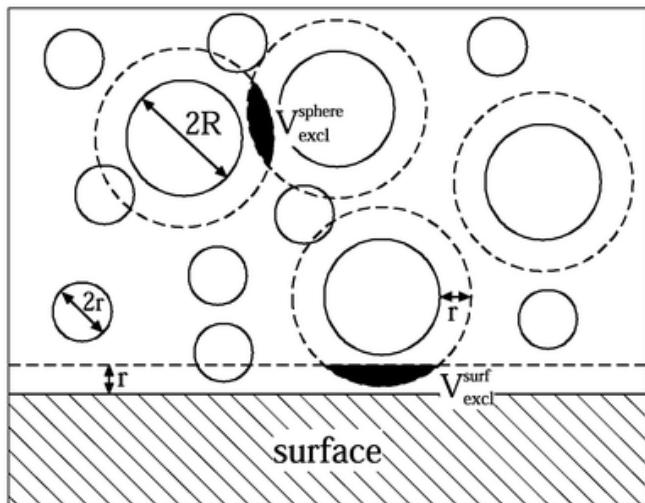
$$\Theta[\{\rho_i(\mathbf{r})\}] = \mathcal{F}[\{\rho_i(\mathbf{r})\}] + \Theta[\{\rho_i^0\}]$$

$$\begin{aligned}\mathcal{F}[\{\rho_i(\mathbf{r})\}] &= \mathcal{F}_{id}[\{\rho_i(\mathbf{r})\}] + \mathcal{F}_{ext}[\{\rho_i(\mathbf{r})\}] \\ &+ \mathcal{F}_{exc}[\{\rho_i(\mathbf{r})\}] - \mathcal{F}_{exc}[\{\rho_i^0\}] - \sum_i \mu_{exc}^i \int d\mathbf{r} (\rho_i(\mathbf{r}) - \rho_i^0)\end{aligned}$$

$$\mathcal{F}_{id}[\{\rho_i(\mathbf{r})\}] = k_B T \sum_i \int d\mathbf{r} \left[ \rho_i(\mathbf{r}) \ln \left( \frac{\rho_i(\mathbf{r})}{\rho_i^0} \right) - \rho_i(\mathbf{r}) + \rho_i^0 \right]$$

$$\mathcal{F}_{ext}[\{\rho_i(\mathbf{r})\}] = \sum_i \int d\mathbf{r} V_i(\mathbf{r}) \rho_i(\mathbf{r})$$

# Fundamental Measure Theory for Hard-Sphere Mixtures



E. KIERLIK and M. L. ROSINBERG, *Phys. Rev. A* **42**, 3382 (1990)

E. KIERLIK and M. L. ROSINBERG, *Phys. Rev. A* **44**, 5025 (1991)

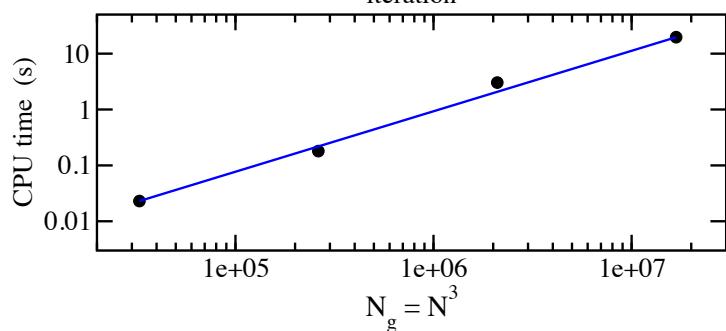
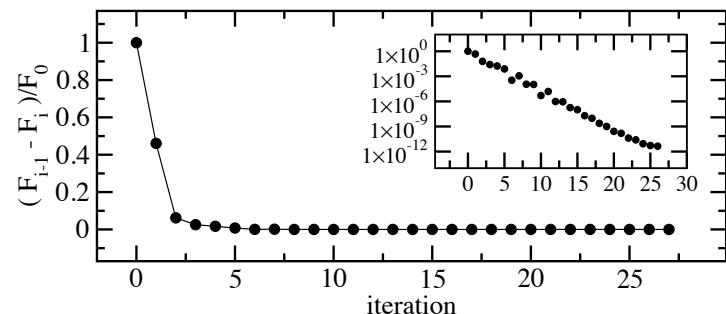
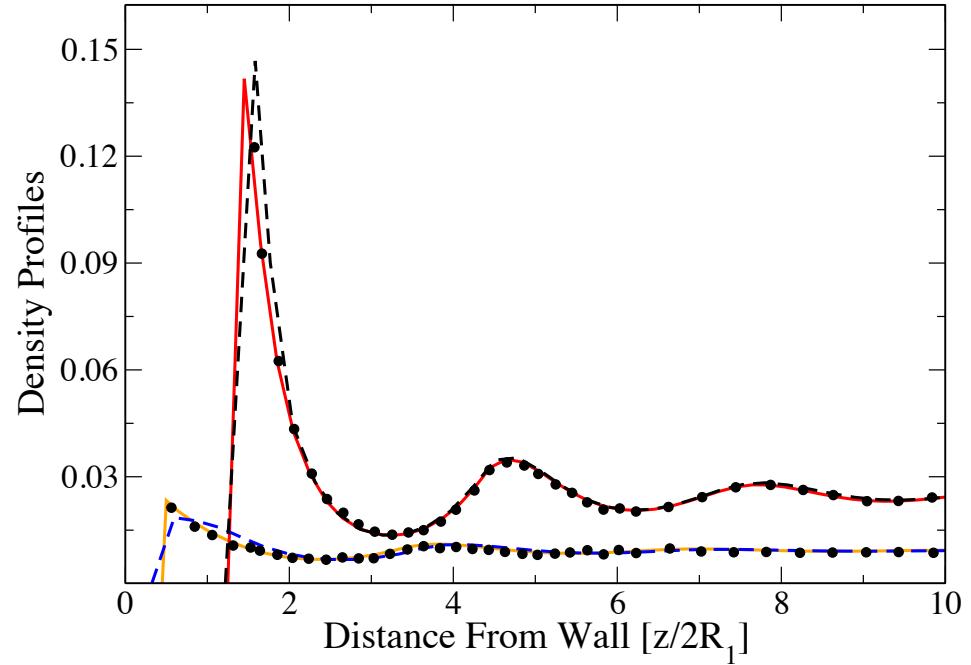
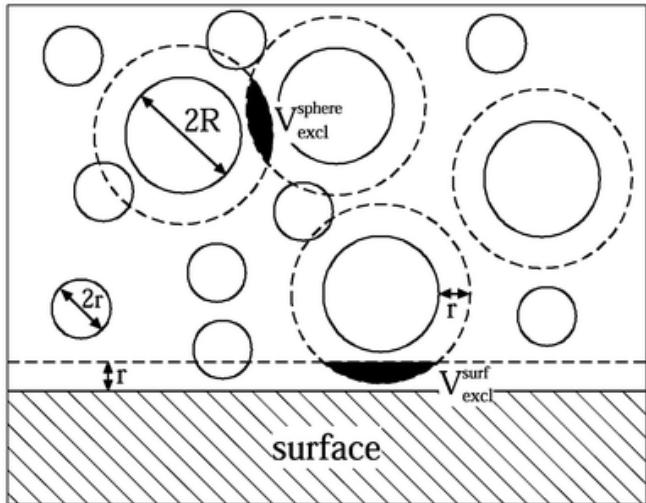
$$\mathcal{F}_{\text{exc}}[\{\rho_i(\mathbf{r})\}] = k_B T \int d\mathbf{r} \Phi(\{n_\alpha(\mathbf{r})\})$$

$$n_\alpha(\mathbf{r}) = \sum_i \int d\mathbf{r}' \rho_i(\mathbf{r}') \omega_\alpha^i(\mathbf{r} - \mathbf{r}') = \sum_i \rho_i(\mathbf{r}) * \omega_\alpha^i(\mathbf{r})$$

$$\begin{aligned} \omega_3^i(\mathbf{r}) &= \Theta(R_i - r) & \omega_1^i(\mathbf{r}) &= \frac{1}{8\pi} \delta'(R_i - r) \\ \omega_2^i(\mathbf{r}) &= \delta(R_i - r) & \omega_0^i(\mathbf{r}) &= \frac{1}{8\pi} \delta''(R_i - r) + \frac{1}{2\pi r} \delta'(R_i - r) \end{aligned}$$

$$\Phi^{\text{PY}}[n_\alpha] = -n_0 \ln(1 - n_3) + \frac{n_1 n_2}{1 - n_3} + \frac{1}{24\pi} \frac{n_2^3}{(1 - n_3)^2},$$

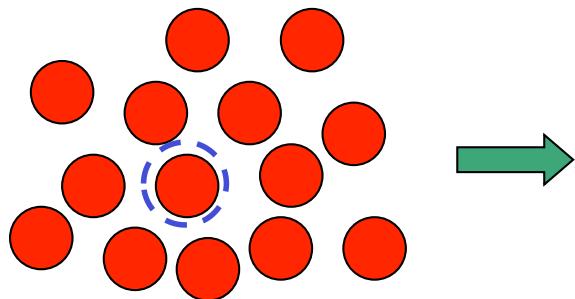
# Fundamental Measure Theory for Hard-Sphere Mixtures



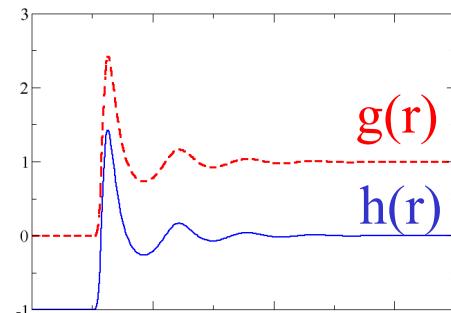
M. Levesque, R. Vuilleumier, and D. Borgis  
JCP **137**, 2012

## Basic theory of liquids: The Ornstein-Zernike equation

Pair potential  $u(r_{12})$



$$h(r_{12}) = g(r_{12}) - 1$$



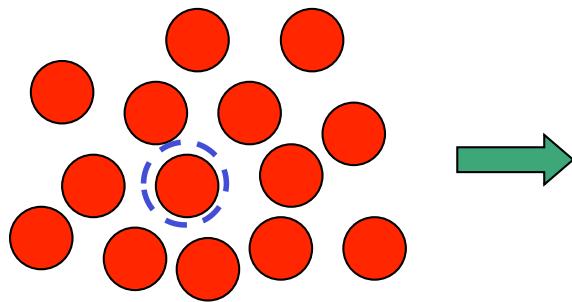
$$\frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} = g(\mathbf{r}_1, \mathbf{r}_2)$$

$$\frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} = \rho(\mathbf{r}_2)g(\mathbf{r}_1, \mathbf{r}_2)$$

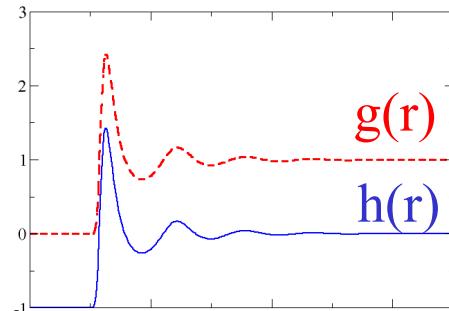
$$= \rho(\mathbf{r}_2) (1 + h(\mathbf{r}_1, \mathbf{r}_2))$$

## Basic theory of liquids: The Ornstein-Zernike equation

Pair potential  $u(r_{12})$



$$h(r_{12}) = g(r_{12}) - 1$$



$$\frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} = g(\mathbf{r}_1, \mathbf{r}_2)$$

$$\frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} = \rho(\mathbf{r}_2)g(\mathbf{r}_1, \mathbf{r}_2)$$

$$= \rho(\mathbf{r}_2) (1 + h(\mathbf{r}_1, \mathbf{r}_2))$$

$$\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{R}_i), \quad \Delta\hat{\rho}(\mathbf{r}) = \hat{\rho}(\mathbf{r}) - \rho_0$$

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = \langle \Delta\hat{\rho}(\mathbf{r}_1) \Delta\hat{\rho}(\mathbf{r}_2) \rangle = \rho_0 \delta(\mathbf{r}_1 - \mathbf{r}_2) + \rho_0^2 h(\mathbf{r}_1, \mathbf{r}_2)$$

$$\chi^{-1}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\rho_0} \delta(\mathbf{r}_1 - \mathbf{r}_2) - c(\mathbf{r}_1, \mathbf{r}_2)$$

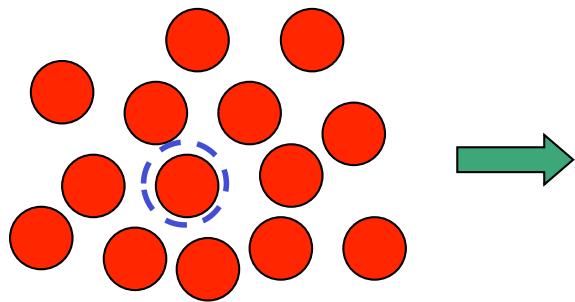
$$\int d\mathbf{r}_3 \chi(\mathbf{r}_1, \mathbf{r}_3) \chi^{-1}(\mathbf{r}_3, \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2)$$

Ornstein-Zernike:

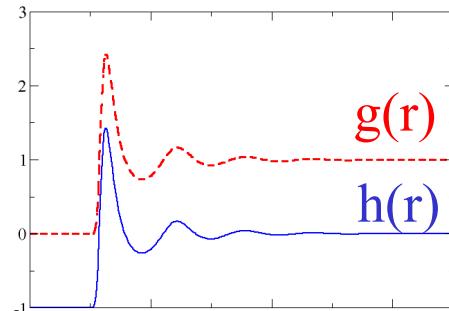
$$h(\mathbf{r}_1, \mathbf{r}_2) - c(\mathbf{r}_1, \mathbf{r}_2) = \int d\mathbf{r}_3 c(\mathbf{r}_1, \mathbf{r}_3) \rho(\mathbf{r}_3) h(\mathbf{r}_3, \mathbf{r}_2)$$

## Basic theory of liquids: The Ornstein-Zernike equation

Pair potential  $u(r_{12})$



$$h(r_{12}) = g(r_{12}) - 1$$



$$\frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} = g(\mathbf{r}_1, \mathbf{r}_2)$$

$$\frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} = \rho(\mathbf{r}_2)g(\mathbf{r}_1, \mathbf{r}_2)$$

$$= \rho(\mathbf{r}_2) (1 + h(\mathbf{r}_1, \mathbf{r}_2))$$

$$\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{R}_i), \quad \Delta\hat{\rho}(\mathbf{r}) = \hat{\rho}(\mathbf{r}) - \rho_0$$

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = \langle \Delta\hat{\rho}(\mathbf{r}_1) \Delta\hat{\rho}(\mathbf{r}_2) \rangle = \rho_0 \delta(\mathbf{r}_1 - \mathbf{r}_2) + \rho_0^2 h(r_{12})$$

$$\chi^{-1}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\rho_0} \delta(\mathbf{r}_1 - \mathbf{r}_2) - c(r_{12})$$

$$\int d\mathbf{r}_3 \chi(\mathbf{r}_1, \mathbf{r}_3) \chi^{-1}(\mathbf{r}_3, \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2)$$

Ornstein-Zernike:

$$h(r_{12}) - c(r_{12}) = \rho_0 \int d\mathbf{r}_3 c(r_{13}) h(r_{32})$$

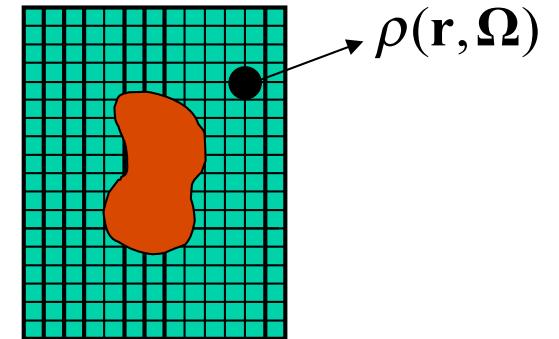
## The exact functional

$$F[\rho(\mathbf{x})] = F_{id}[\rho] + F_{exc}[\rho] + F_{ext}[\rho]$$

$$\mathbf{x} = (\mathbf{r}, \Omega)$$

$$F_{id}[\rho] = k_B T \int d\mathbf{x}_1 \left[ \rho(\mathbf{x}_1) \ln \left( \frac{\rho(\mathbf{x}_1)}{\rho_0} \right) - \rho(\mathbf{x}_1) + \rho_0 \right]$$

$$F_{ext}[\rho] = \int d\mathbf{x}_1 V_{ext}(\mathbf{x}_1) \rho(\mathbf{x}_1)$$



$$F_{exc}[\rho] = \frac{1}{2} \iint d\mathbf{x}_1 d\mathbf{x}_2 \Delta\rho(\mathbf{x}_1) u_{eff}(\mathbf{x}_1, \mathbf{x}_2; [\rho]) \Delta\rho(\mathbf{x}_2), \quad \Delta\rho(\mathbf{x}) = \rho(\mathbf{x}) - \rho_0$$

$u_{eff}(\mathbf{x}_1, \mathbf{x}_2; [\rho])$  = Effective solvent-solvent pair potential

$$u_{eff}(\mathbf{x}_1, \mathbf{x}_2; [\rho]) = u(\mathbf{x}_1, \mathbf{x}_2) + u_{cor}(\mathbf{x}_1, \mathbf{x}_2; [\rho])$$

## MEAN-FIELD APPROXIMATION

$$u_{eff}(\mathbf{r}_1, \mathbf{r}_2; [\rho]) = u(r_{12})$$

### Adiabatic connection methods

With respect to pair potential:

$$u_\alpha(r_{12}) = \alpha u(r_{12})$$

$$u_{eff}(\mathbf{r}_1, \mathbf{r}_2; [\rho]) = \int_0^1 d\alpha \ h_\alpha(\mathbf{r}_1, \mathbf{r}_2; u_\alpha) u(r_{12})$$

Same as in electronic  
DFT

With respect to density:

$$\rho_\alpha(\mathbf{x}) = \rho_0 + \alpha \Delta\rho(\mathbf{x})$$

$$\frac{1}{2} u_{eff}(\mathbf{r}_1, \mathbf{r}_2; [\rho]) = k_B T \int_0^1 d\alpha (\alpha - 1) c_\alpha(\mathbf{r}_1, \mathbf{r}_2; [\rho_\alpha])$$

- **MEAN-FIELD APPROXIMATION:**

$$u_{eff}(\mathbf{r}_1, \mathbf{r}_2; [\rho]) = u(r_{12})$$

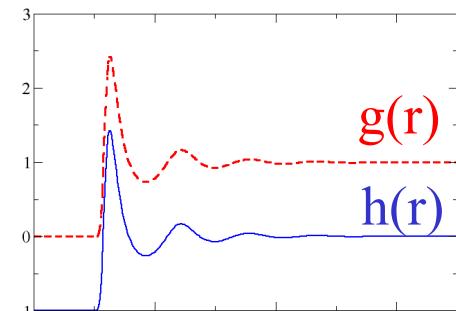
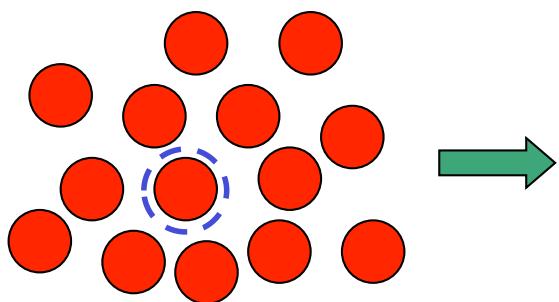
$$u_{cor}(\mathbf{r}_1, \mathbf{r}_2; [\rho]) = 0$$

- **HOMOGENEOUS REFERENCE FLUID APPROXIMATION**

$$u_{eff}(\mathbf{r}_1, \mathbf{r}_2; [\rho]) = -k_B T c(\mathbf{r}_1, \mathbf{r}_2; \rho_0) = -k_B T c(r_{12})$$

$c(\mathbf{r}_{12})$  is the direct correlation function of the homogeneous fluid connected to the pair correlation function  $h(\mathbf{r}_{12})$  through the **Ornstein-Zernike relation**

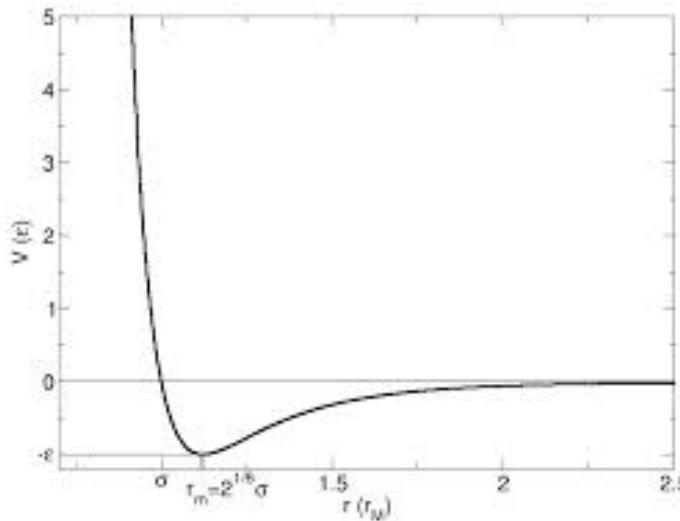
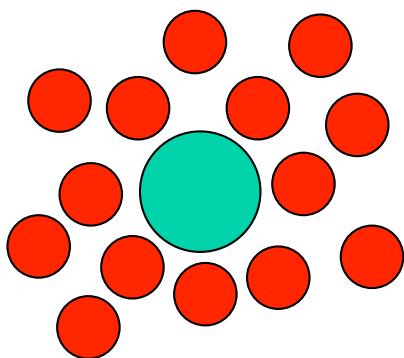
$$h(r_{12}) - c(r_{12}) = \rho_0 \int d\mathbf{r}_3 c(r_{13}) h(r_{32})$$



$$h = g - 1$$

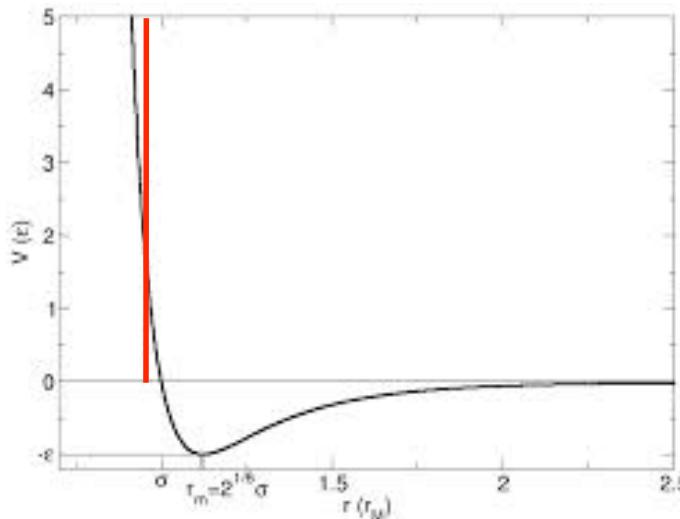
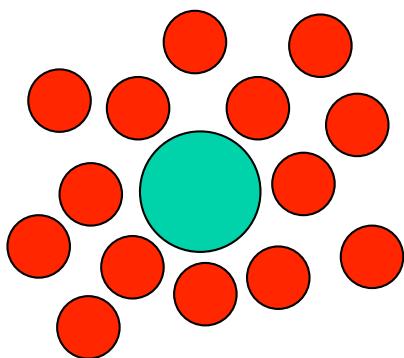
## Lennard-Jones fluid: HRF approximation

$$\begin{aligned}\mathcal{F}[\rho(\mathbf{r})] &= k_B T \int d\mathbf{r} \left[ \rho(\mathbf{r}) \ln \left( \frac{\rho(\mathbf{r})}{\rho_0} \right) - \rho(\mathbf{r}) + \rho_0 \right] + \int d\mathbf{r} V(\mathbf{r}) \rho(\mathbf{r}) \\ &- \frac{k_B T}{2} \int d\mathbf{r} d\mathbf{r}' \Delta\rho(\mathbf{r}) \Delta\rho(\mathbf{r}') c_S(|\mathbf{r} - \mathbf{r}'|; \rho_0)\end{aligned}$$



## Lennard-Jones fluid: HRF approximation

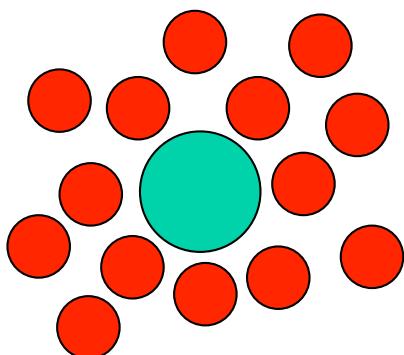
$$\begin{aligned}\mathcal{F}[\rho(\mathbf{r})] &= k_B T \int d\mathbf{r} \left[ \rho(\mathbf{r}) \ln \left( \frac{\rho(\mathbf{r})}{\rho_0} \right) - \rho(\mathbf{r}) + \rho_0 \right] + \int d\mathbf{r} V(\mathbf{r}) \rho(\mathbf{r}) \\ &- \frac{k_B T}{2} \int d\mathbf{r} d\mathbf{r}' \Delta\rho(\mathbf{r}) \Delta\rho(\mathbf{r}') c_S(|\mathbf{r} - \mathbf{r}'|; \rho_0)\end{aligned}$$

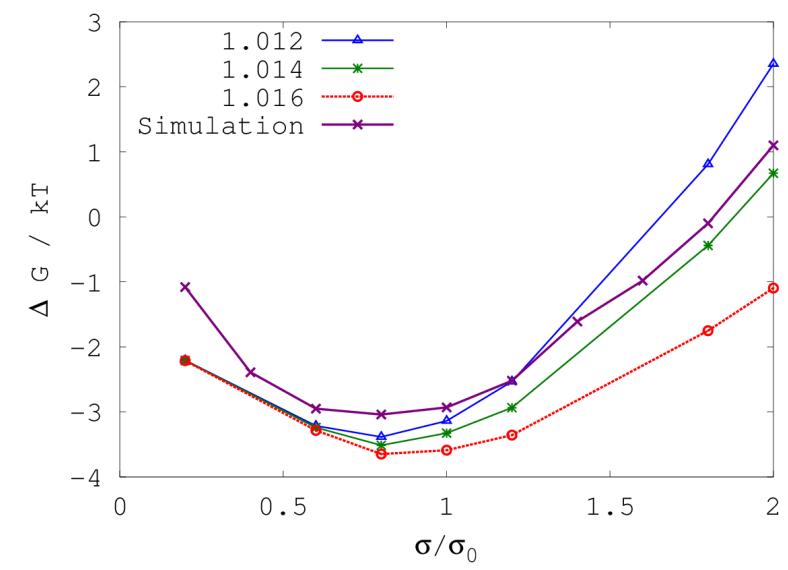
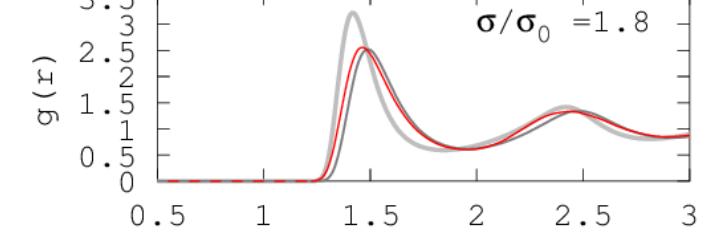
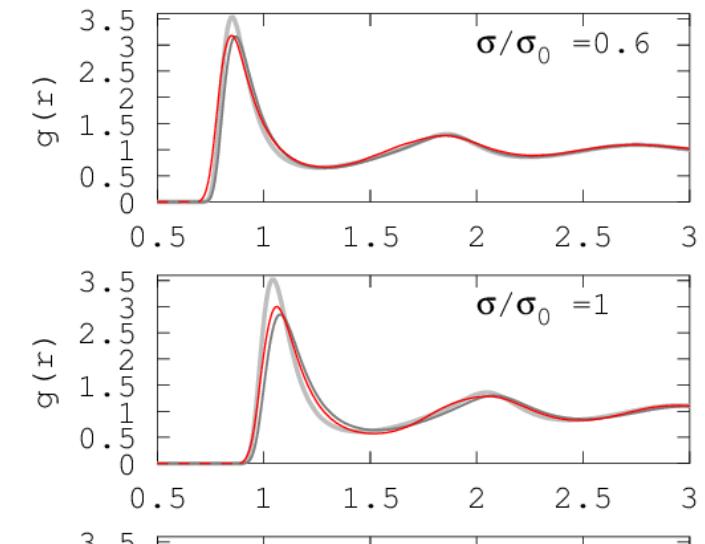
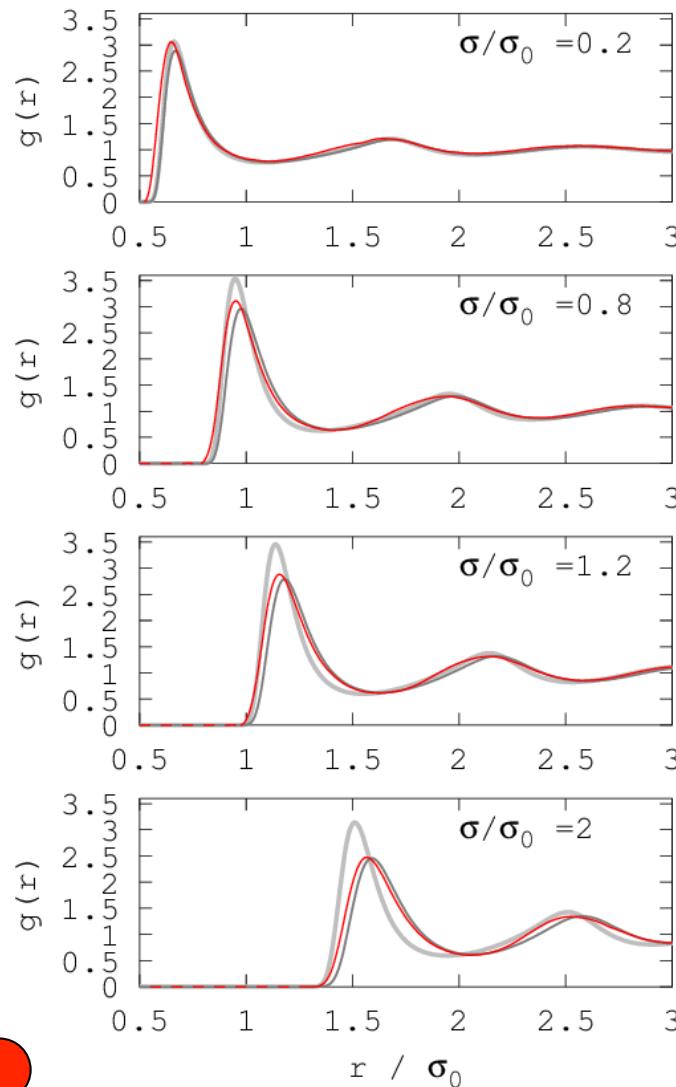
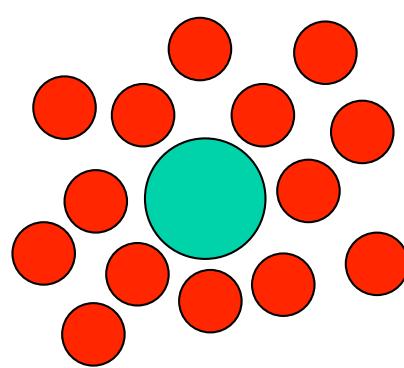


## Lennard-Jones fluid: HRF + HS bridge approximation

$$\begin{aligned}\mathcal{F}[\rho(\mathbf{r})] &= k_B T \int d\mathbf{r} \left[ \rho(\mathbf{r}) \ln \left( \frac{\rho(\mathbf{r})}{\rho_0} \right) - \rho(\mathbf{r}) + \rho_0 \right] + \int d\mathbf{r} V(\mathbf{r}) \rho(\mathbf{r}) \\ &- \frac{k_B T}{2} \int d\mathbf{r} d\mathbf{r}' \Delta\rho(\mathbf{r}) \Delta\rho(\mathbf{r}') c_S(|\mathbf{r} - \mathbf{r}'|; \rho_0) + \boxed{\mathcal{F}_B[\rho(\mathbf{r})]}\end{aligned}$$

$$\begin{aligned}\mathcal{F}_B[\rho(\mathbf{r})] &= \mathcal{F}_{exc}^{HS}[\rho(\mathbf{r})] - \mathcal{F}_{exc}^{HS}[\rho_0] - \mu_{exc}^{HS} \int d\mathbf{r} \Delta\rho(\mathbf{r}) \\ &+ \frac{k_B T}{2} \int d\mathbf{r} d\mathbf{r}' \Delta\rho(\mathbf{r}) \Delta\rho(\mathbf{r}') c_S^{HS}(|\mathbf{r} - \mathbf{r}'|; \rho_0) \\ &\text{All orders } \Delta\rho^n, n \geq 3\end{aligned}$$

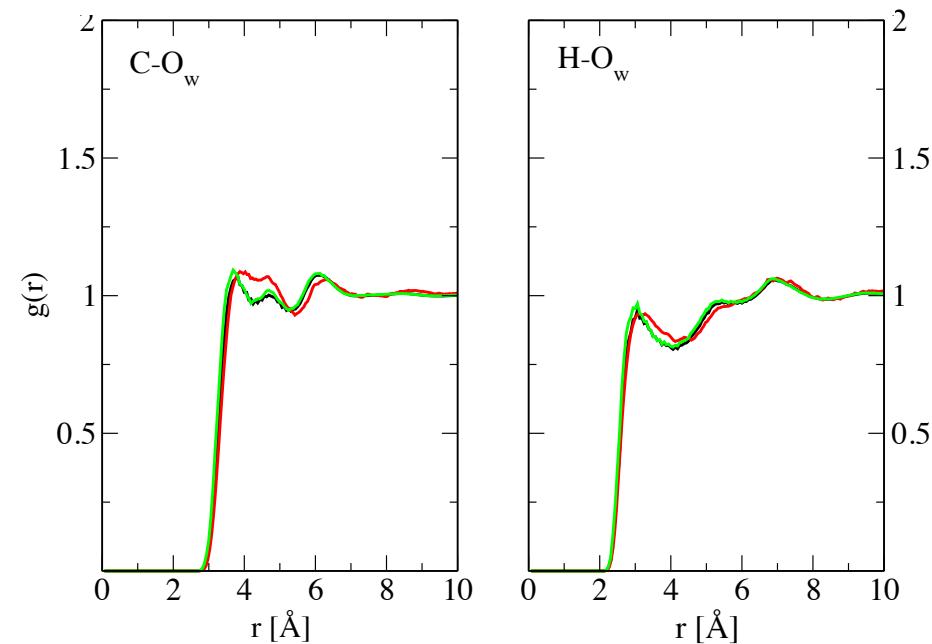
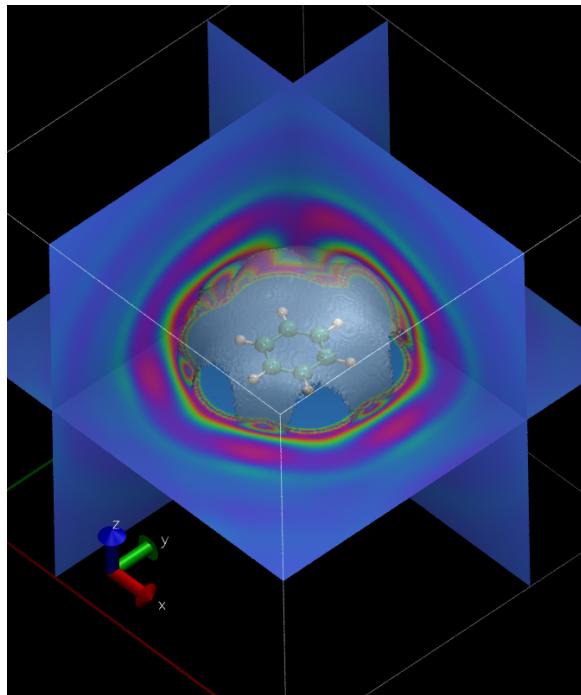




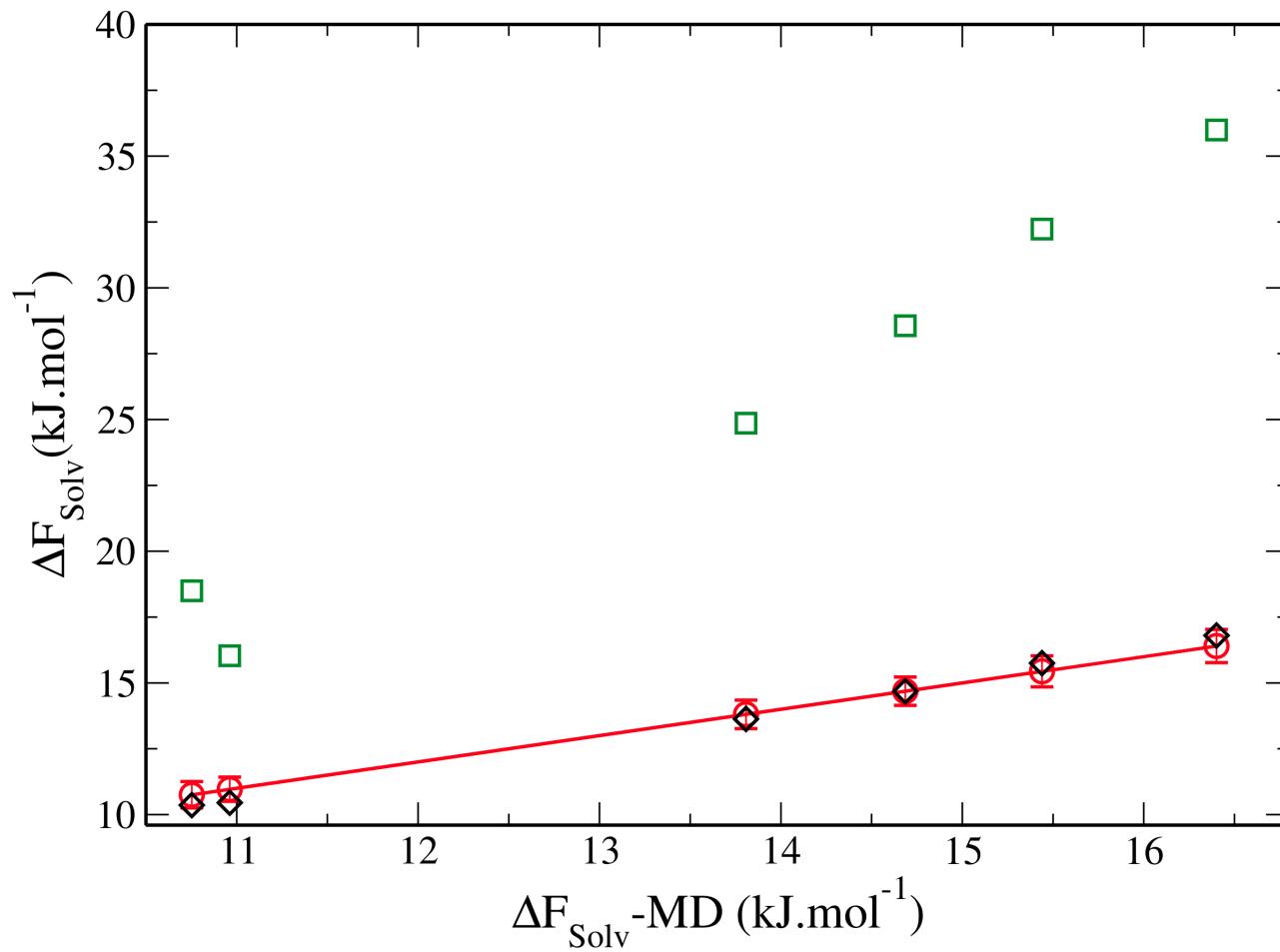
## Hard-sphere reference functional: Water

$$\begin{aligned}\mathcal{F}[\rho(\mathbf{r})] &= k_B T \int d\mathbf{r} \left[ \rho(\mathbf{r}) \ln \left( \frac{\rho(\mathbf{r})}{\rho_0} \right) - \rho(\mathbf{r}) + \rho_0 \right] + \int d\mathbf{r} V(\mathbf{r}) \rho(\mathbf{r}) \\ &\quad - \frac{k_B T}{2} \int d\mathbf{r} d\mathbf{r}' \Delta\rho(\mathbf{r}) \Delta\rho(\mathbf{r}') c_S(|\mathbf{r} - \mathbf{r}'|; \rho_0) + \mathcal{F}_B[\rho(\mathbf{r})]\end{aligned}$$

$$\begin{aligned}\mathcal{F}_B[\rho(\mathbf{r})] &= \mathcal{F}_{exc}^{HS}[\rho(\mathbf{r})] - \mathcal{F}_{exc}^{HS}[\rho_0] - \mu_{exc}^{HS} \int d\mathbf{r} \Delta\rho(\mathbf{r}) \\ &\quad + \frac{k_B T}{2} \int d\mathbf{r} d\mathbf{r}' \Delta\rho(\mathbf{r}) \Delta\rho(\mathbf{r}') c_S^{HS}(|\mathbf{r} - \mathbf{r}'|; \rho_0)\end{aligned}$$

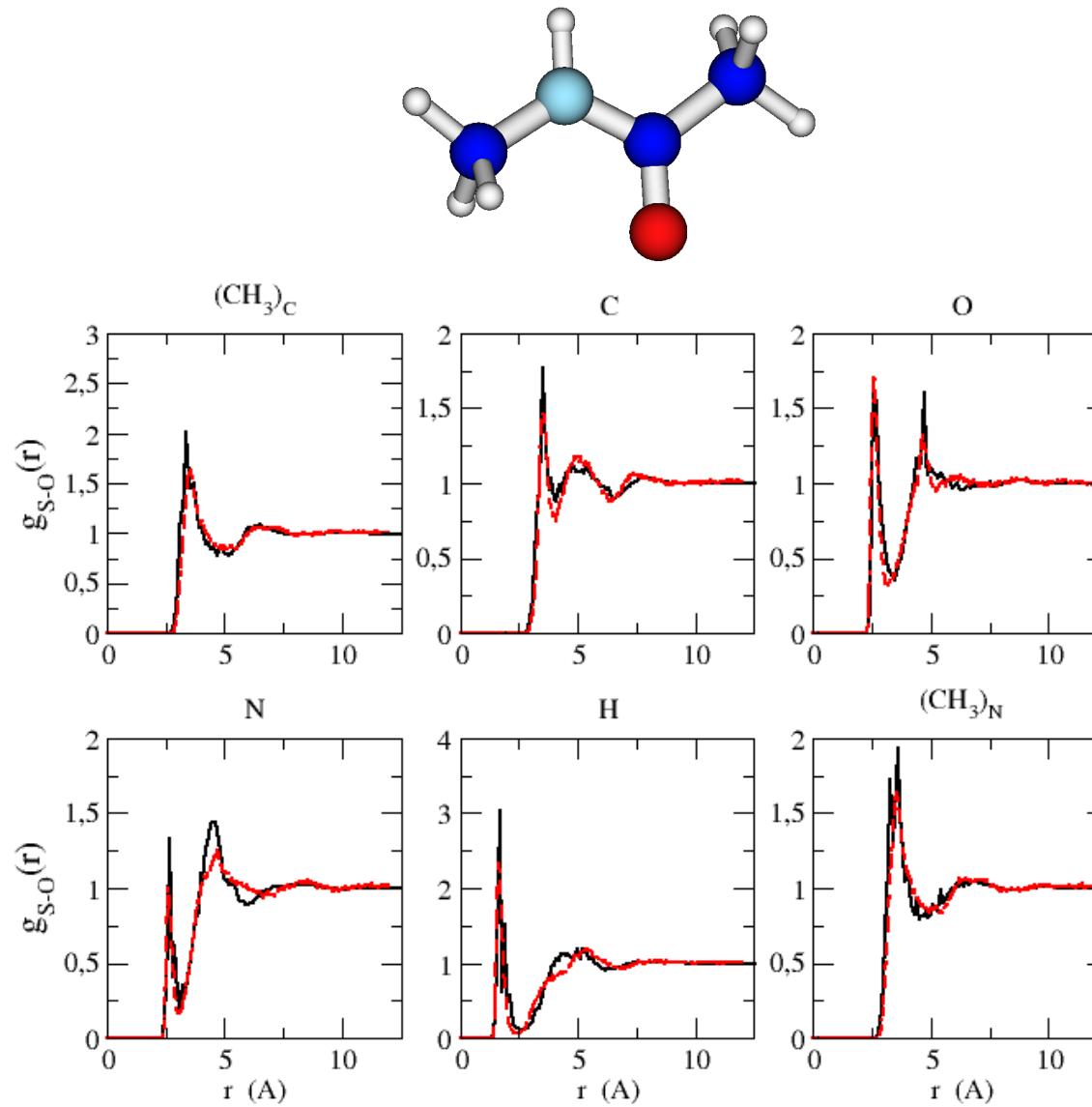


## Solvation in SPC water: Alkanes



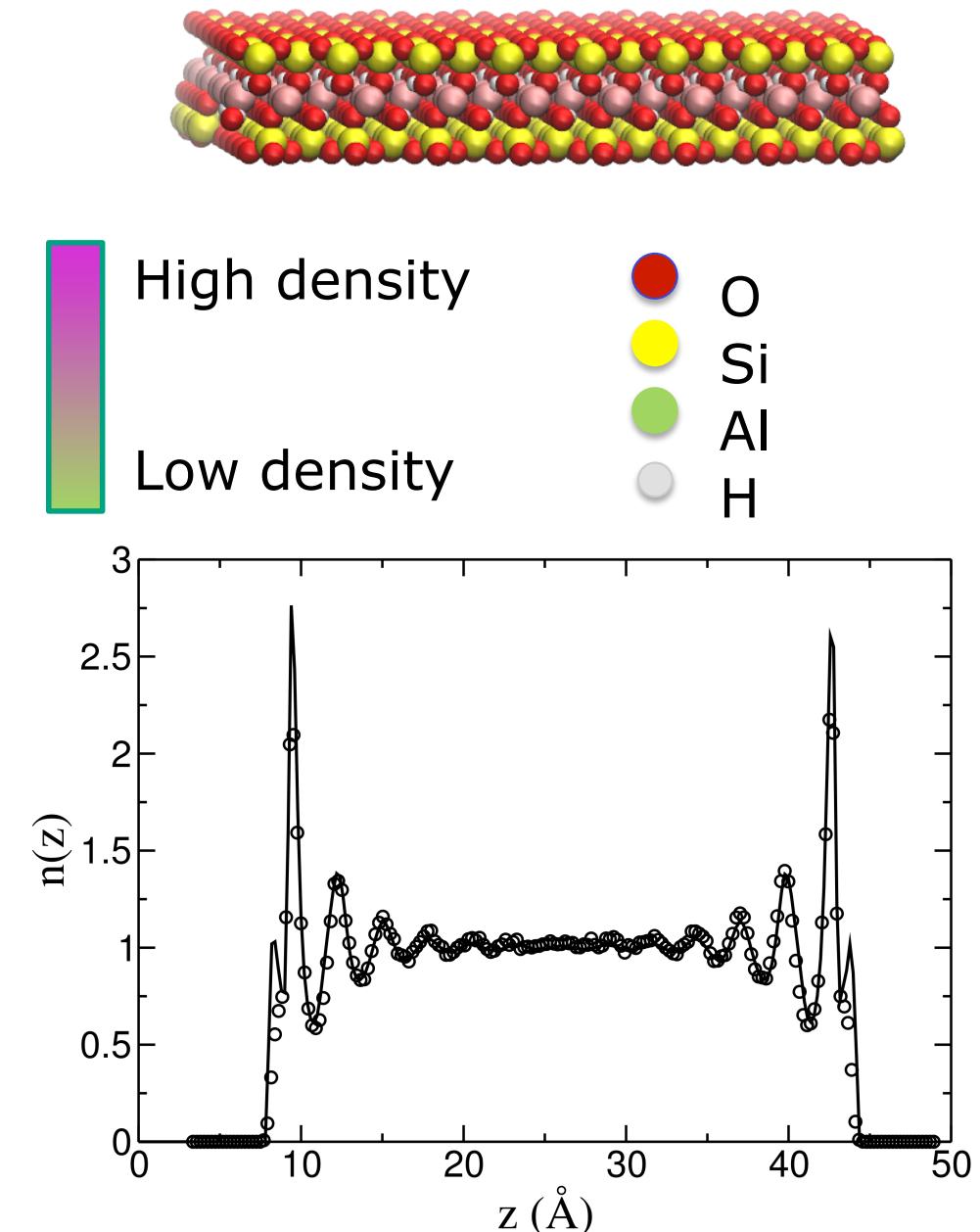
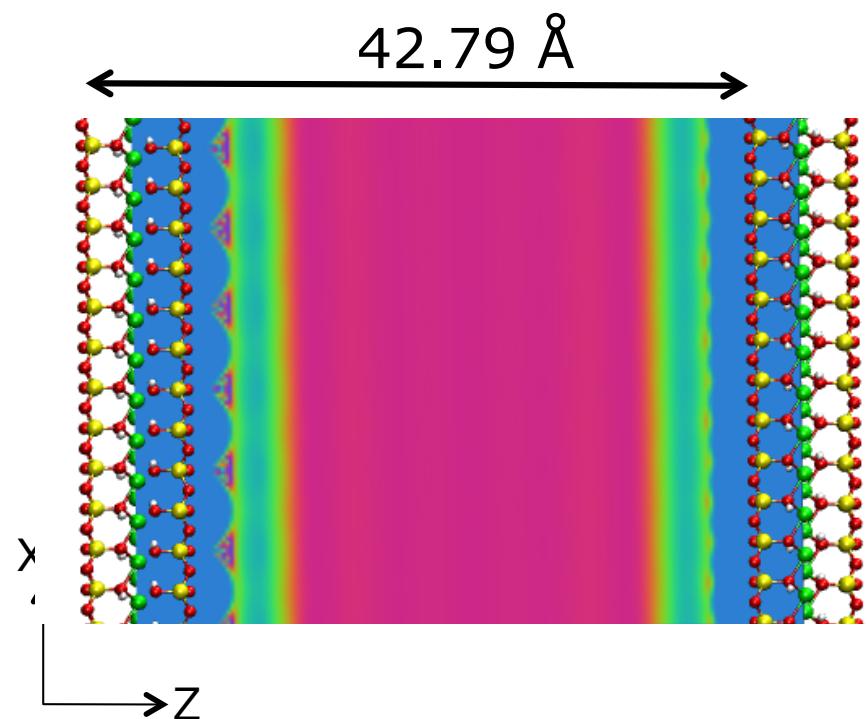
M. Levesque et al, J. Chem. Phys. **137**, 034115, 2012

# Solvation in SPCE water



— MD (20 h)  
— MDFT (< 1 mn)

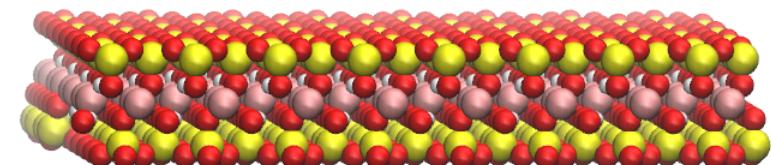
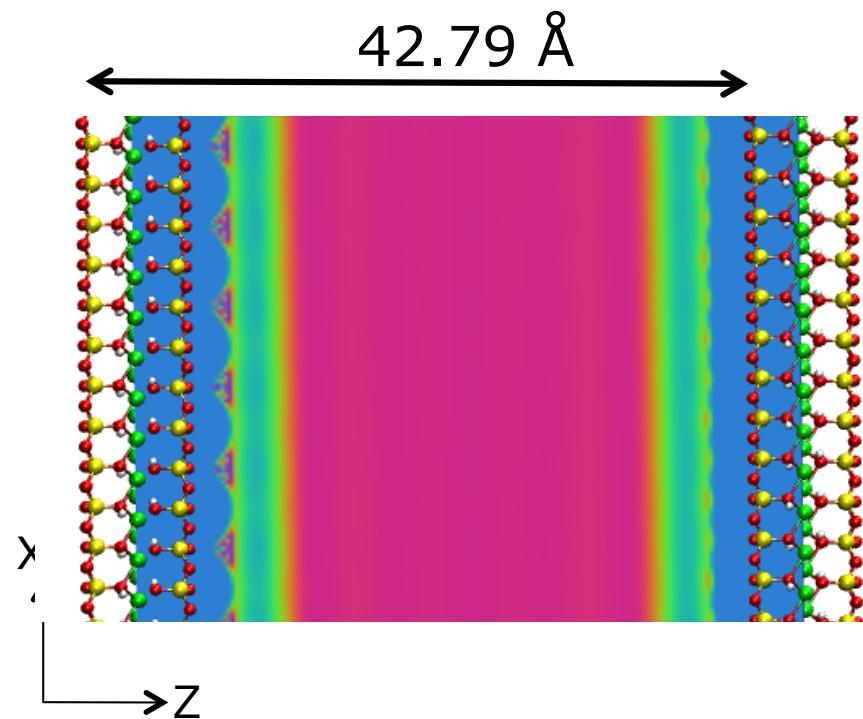
## Application to solvation of **pyrophyllite** (model neutral clay)



Collaboration with V. Marry  
and B. Rotenberg (UPMC, Paris)

M. Levesque et al, J. Chem. Phys. **137**,  
224107, 2012

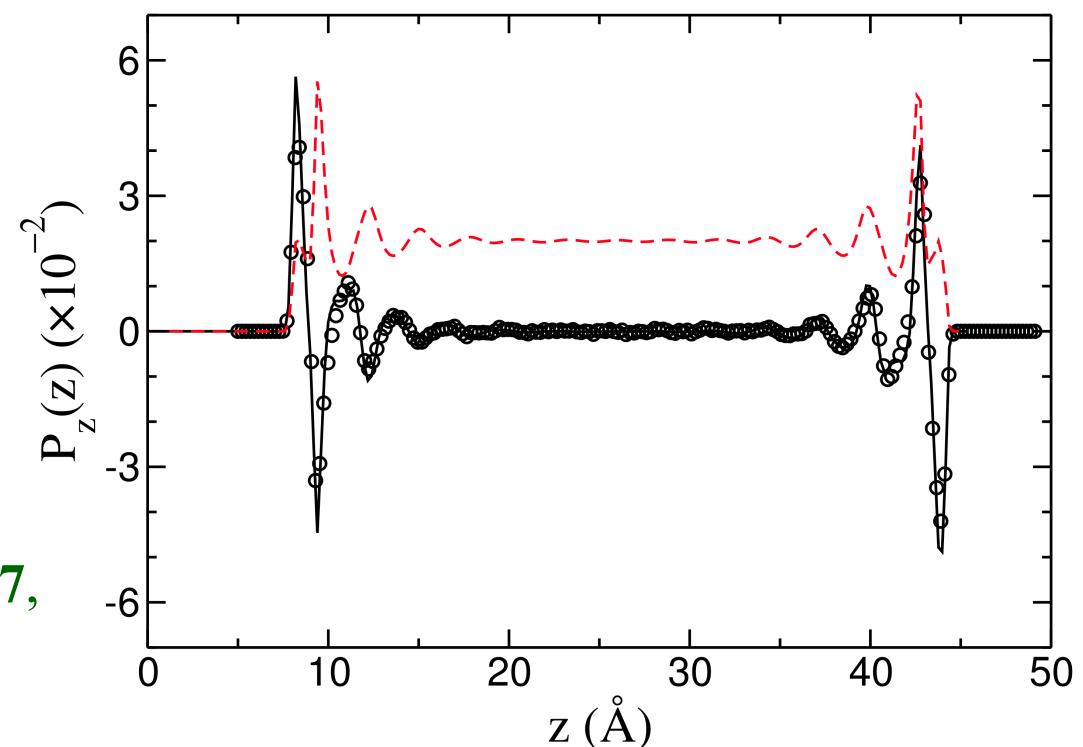
## Application to solvation of **pyrophyllite** (model neutral clay)



High density

Low density

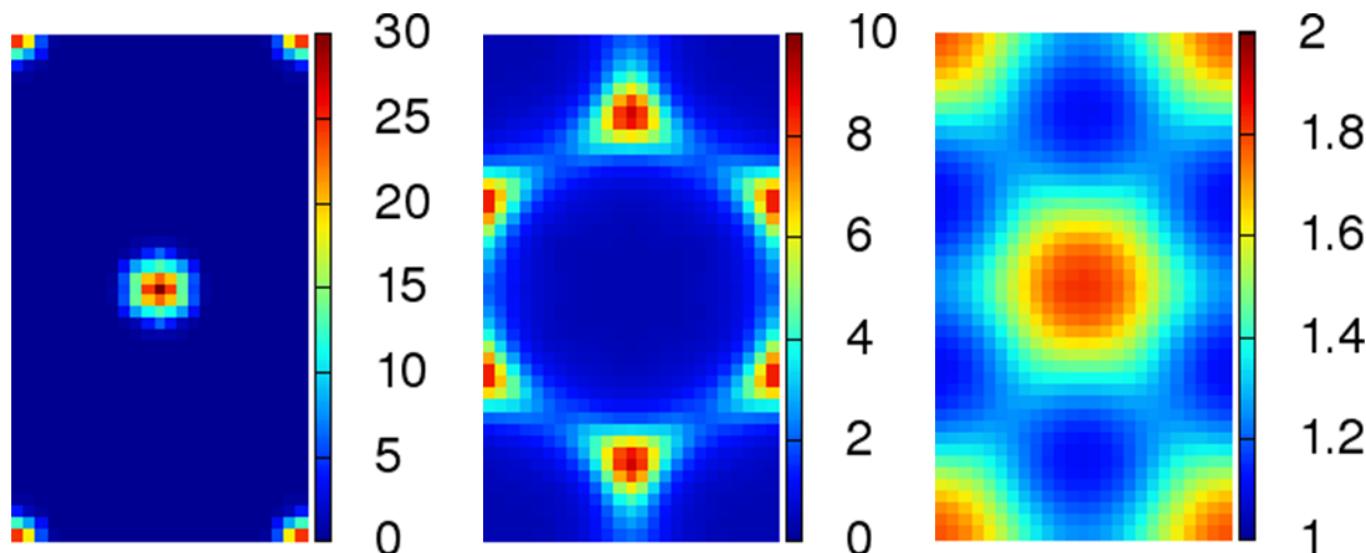
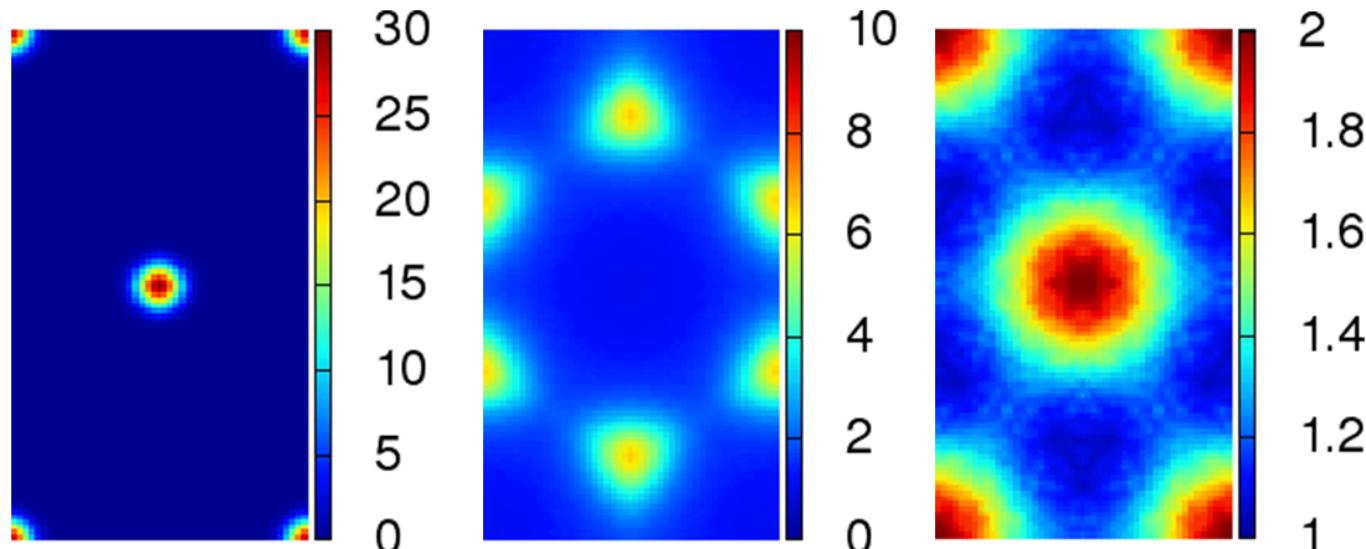
- O
- Si
- Al
- H



Collaboration with V. Marry  
and B. Rotenberg (UPMC, Paris)

M. Levesque et al, J. Chem. Phys. **137**,  
224107, 2012

## Application to solvation of **pyrophyllite**



## Conclusions

- In analogy to electronic DFT, one can compute solvation free energies, reorganization energies .... and microscopic solvation profiles using classical cDFT (MDFT)
- The functional can be minimized using 3D-grids for positions and angular grids for orientations.
- Good representation of correlations for simple (polar) liquids.  
Much harder for associated liquids such as water
- BEYOND:
  - Water and ionic solutions
  - Solvent mixtures, ....
  - eDFT/MDFT mixing

R. Ramirez et al, Phys. Rev E **66**, 2002  
J. Phys. Chem. B **114**, 2005  
Chem. Phys. **319**, 2005  
L. Gendre et al, Chem. Phys. Lett. **474**, 2009  
S. Zhao et al, J. Chem. Phys. **134**, 2011  
D. Borgis et al, J. Phys. Chem B **116**, 2012  
M. Levesque et al, J. Chem. Phys. **137**, 2012  
G. Jeanmairet et al, J. Phys. Chem. Lett. **2013**  
G. Jeanmairet et al, J. Chem. Phys. **2013**