# Classical density functional theory: Application to supercritical $CO_2$

Mohamed Houssein Mohamed, Francesca Ingrosso, Antoine Carof

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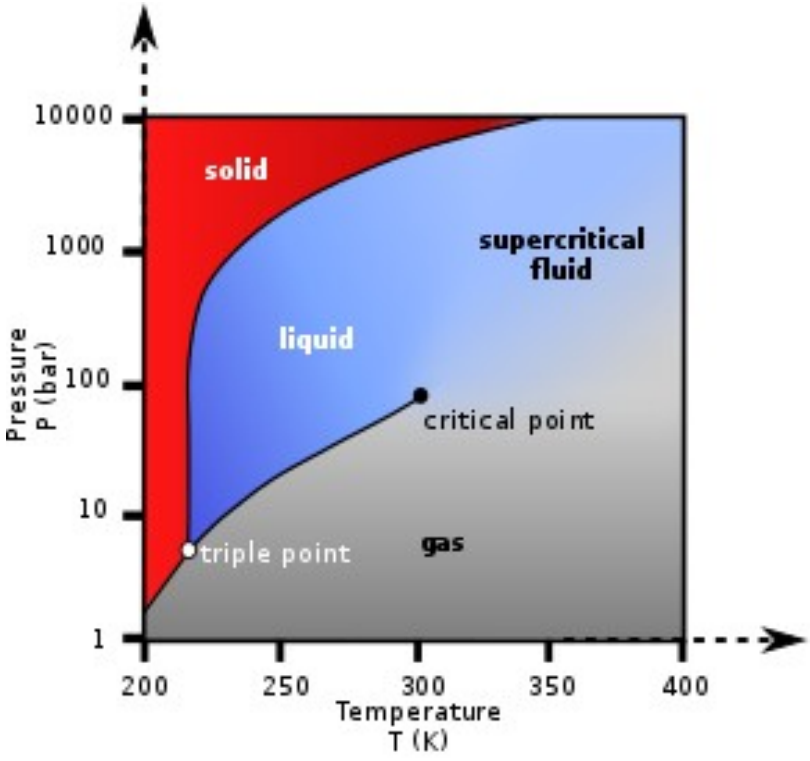
# Why supercritical $CO_2$ ?

**Supercritical Fluid (SCF)**: above the critical point!



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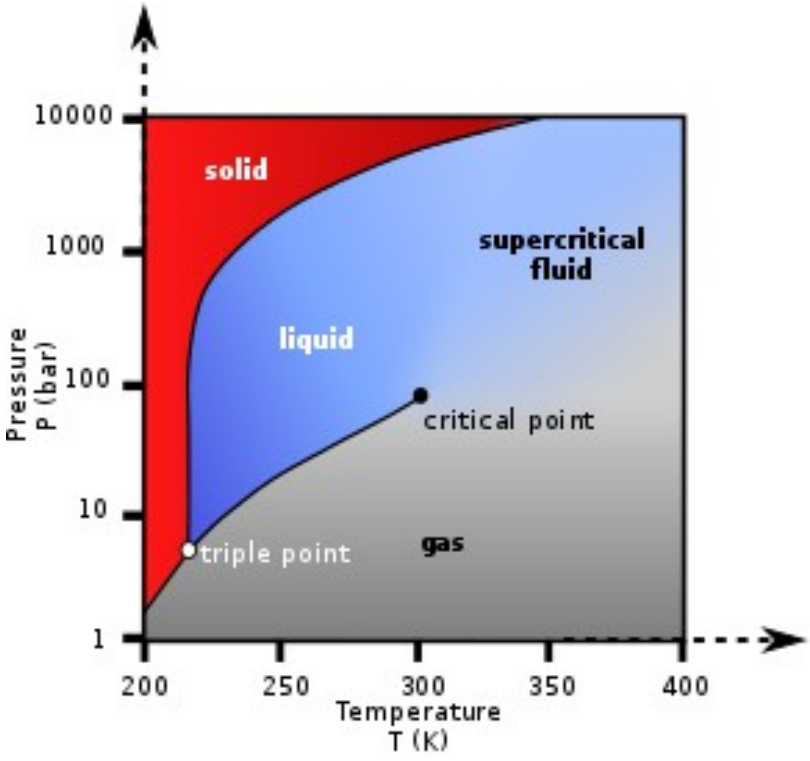

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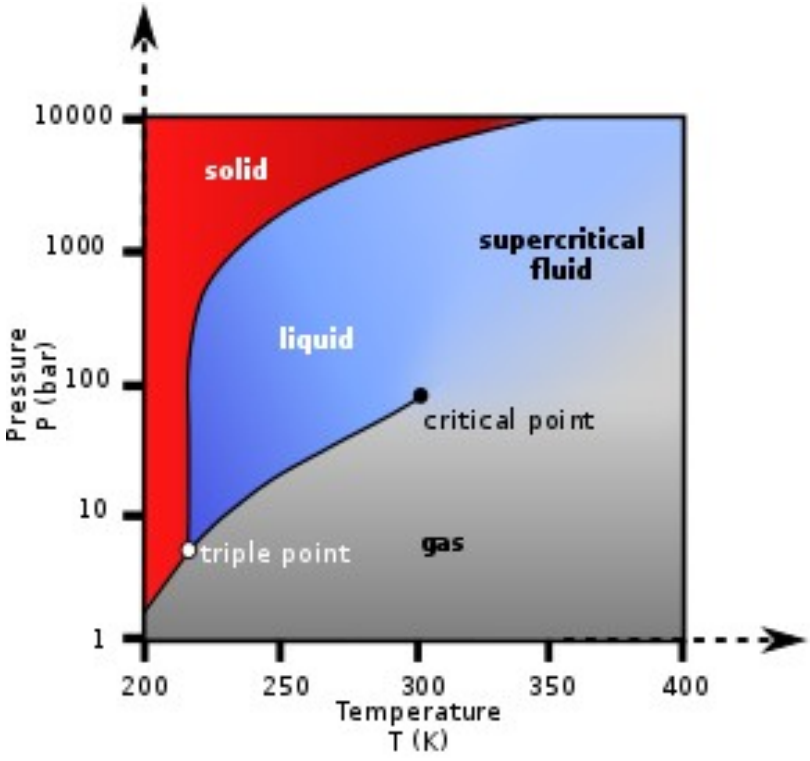

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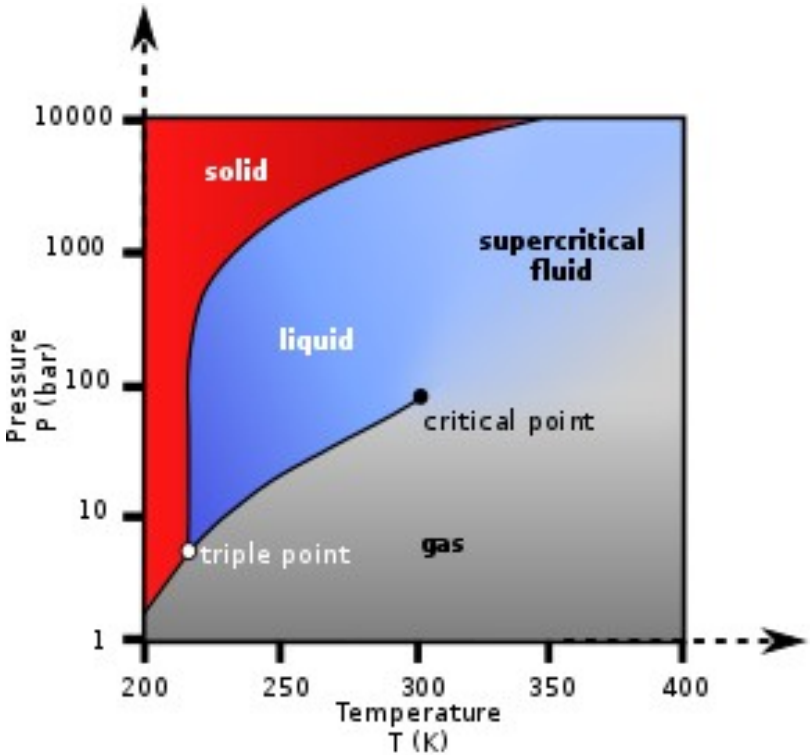


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**Application:** Decaffeination

**But not efficient….**

How to predict the solubility for a new molecule?

# How to calculate the solubility?

| | Simulation | Empiric |
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We need  a fast and accurate method

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cDFT works well for small & rigid molecule → Perfect for $CO_2$!

How to construct the free energy functional?

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$$\mathcal{F}[\rho] = \mathcal{F}_{\mathrm{id}}[\rho] + \mathcal{F}_{\mathrm{ext}}[\rho] + \mathcal{F}_{\mathrm{exc}}[\rho]$$

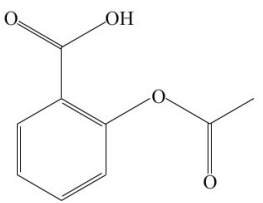
Ideal part (Entropy)

Solute-solvent interaction

Solvent-solvent interaction → Unknown

Litterature: $\mathcal{F}_{\mathrm{exc}}[\rho]$ = Hard sphere + Attrative potential

$CO_2$ and solute as a sphere




Objectives: cDFT with good accuracy + molecular description + evolution with P,T

# Construction of $\mathcal{F}_{\mathrm{exc}}[\rho]$

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quadratic term beyond the second order

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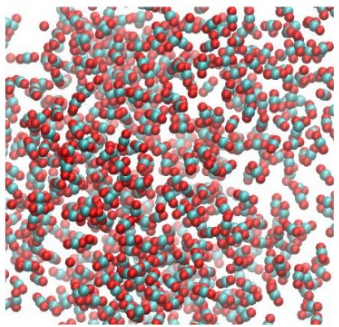
# Direct correlation function

MD simulations



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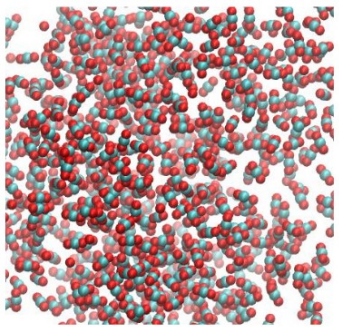
$T = 1.05\ T_c$

13500 $CO_2$

60 ns

# Direct correlation function

MD simulations → Pair correlation function



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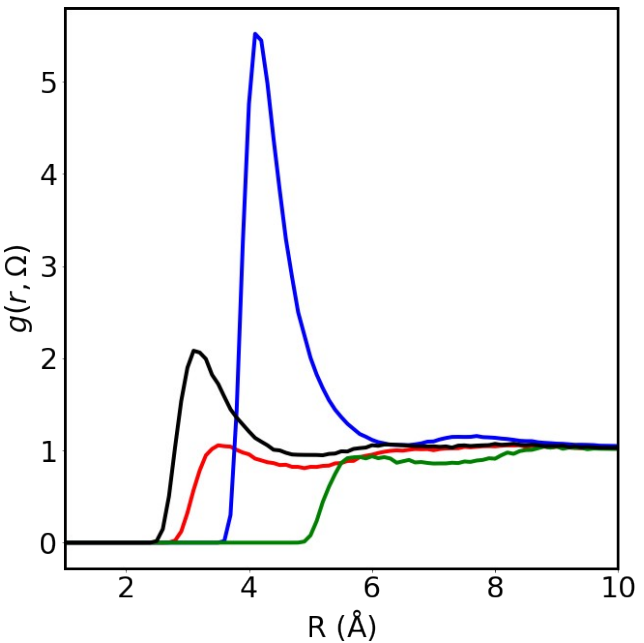


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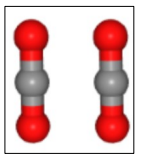

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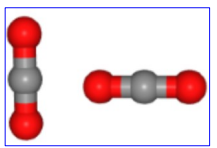

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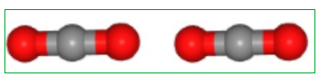

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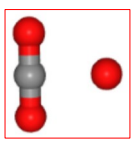
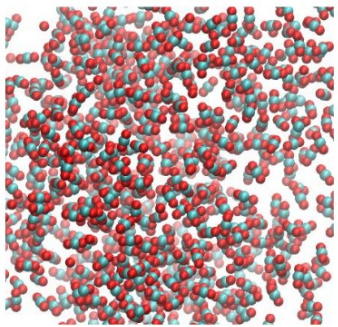


# Direct correlation function

$$c(12) = g(12) - 1 - \rho_0 \int (g(13) - 1)\, c(32)\, d3$$

MD simulations → Pair correlation function → Direct correlation function



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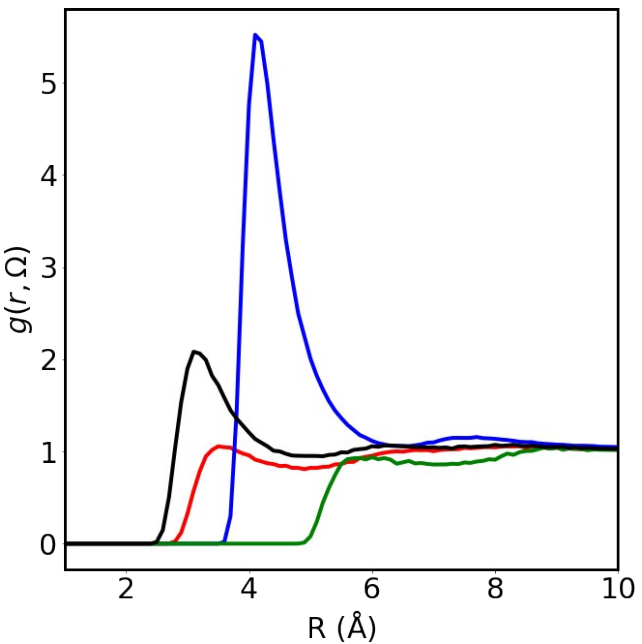
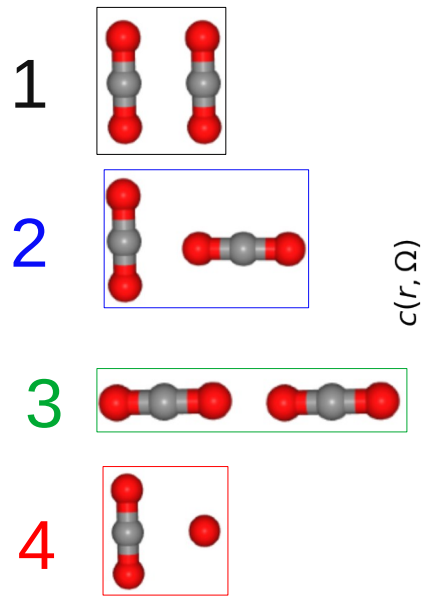
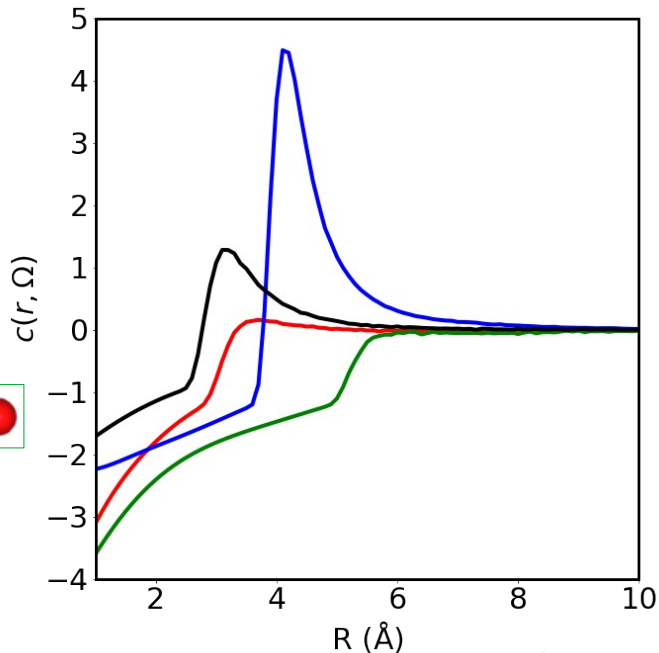
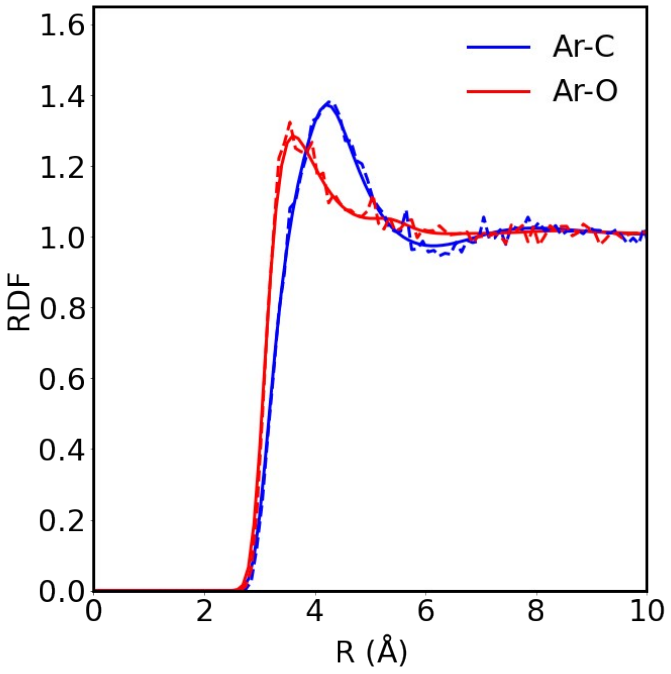


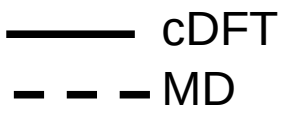



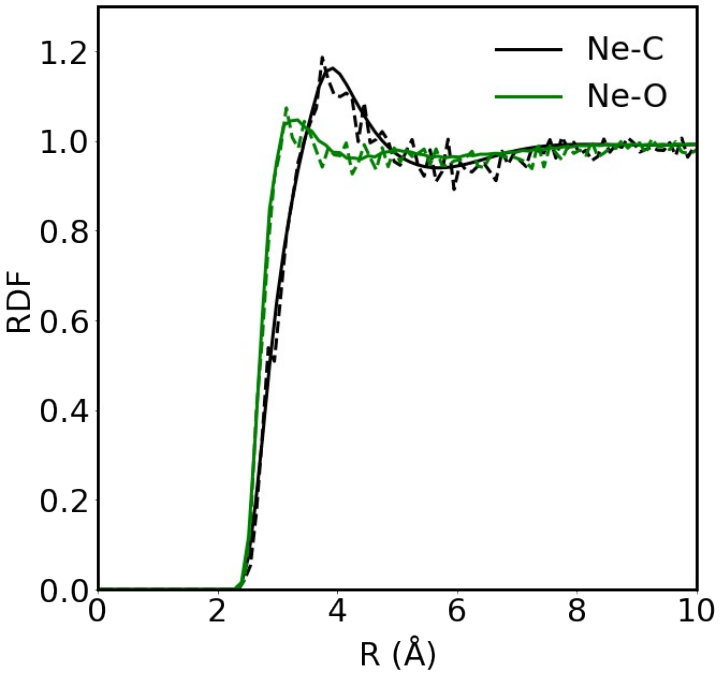



# Application of cDFT with spherical solute

We constructed our functional! $\mathcal{F}[\rho] = \mathcal{F}_{\mathrm{id}}[\rho] + \mathcal{F}_{\mathrm{ext}}[\rho] + \mathcal{F}_{\mathrm{exc}}[\rho]$



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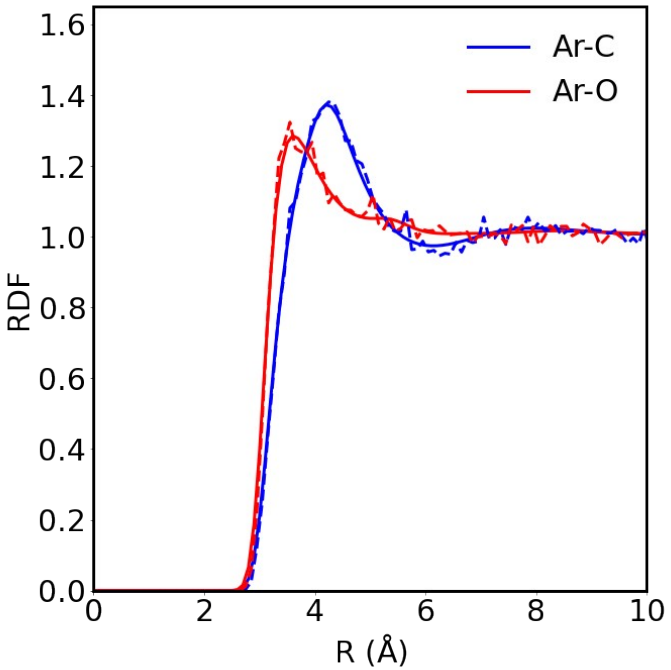
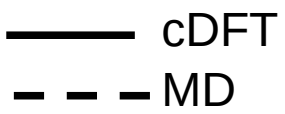
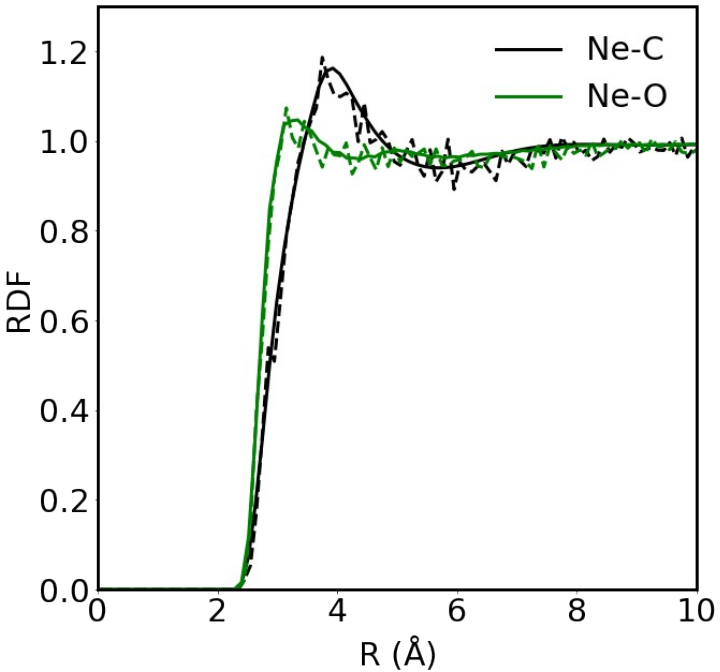


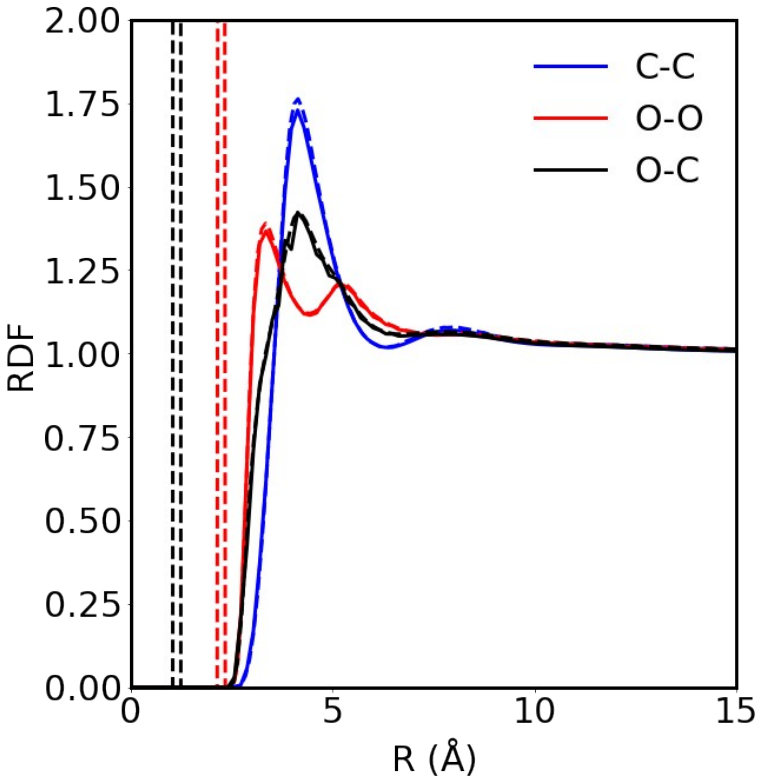



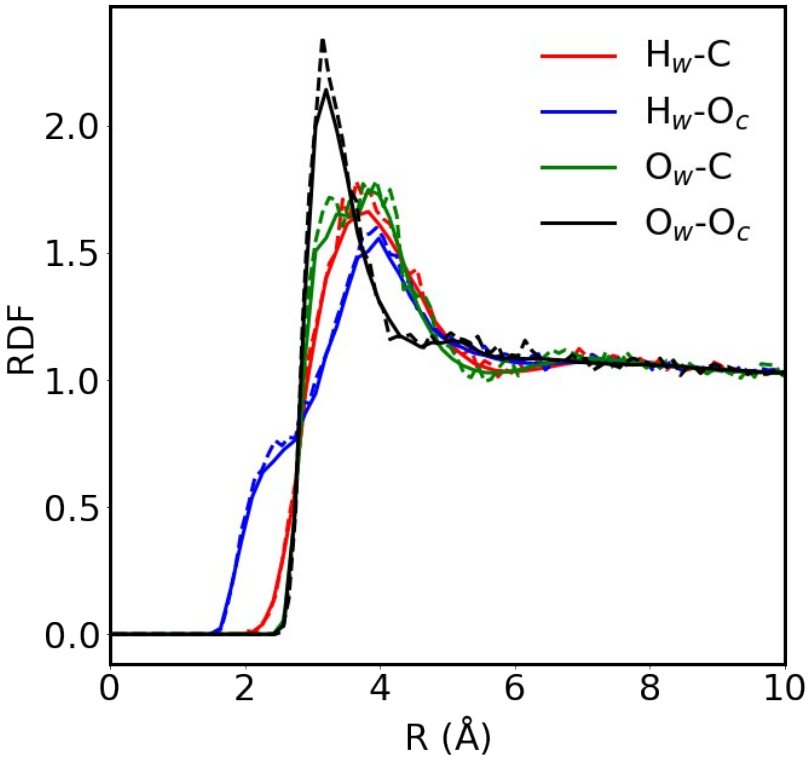




MD : 32 ns, 4000 $CO_2$, NVT (34h on 32 cores)  cDFT : 2 minutes on 1 core

cDFT is $10^5$ faster than MD!

# Application of cDFT with molecular solute



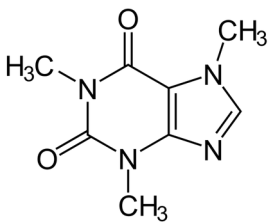



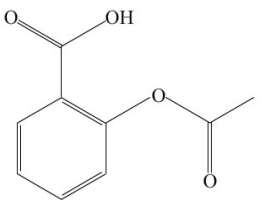
# Conclusion

Classical DFT gives excellent structure!

Look into solvation free energy

Study more complex solutes and test cDFT with MD

Caffeine 


Aspirin 


Find a method to generalise the calculation of direct correlation function for a given P and T

# The team

Francesca Ingrosso

Daniel Borgis

Antoine Carof

Luc Belloni

Gustave Szczepan

Maison de la Simulation

cea

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## Thank you!

Luc Belloni

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# MD simulations details

Canonical ensembe NVT at T = 1.05 $T_c$ N=13500 and $\rho = 0.8\ \rho_c$

Rigid $CO_2$ EPM2 Force field : 3 sites = LJ + charge

Near critical point : simulation of 62 ns

Trajectories were printed every 5 ps : 12000 configurations

Periodic boundary condition (PBC)