From Particles to Fields:

How the cDFT and PF models can improve the fluid-solid description?

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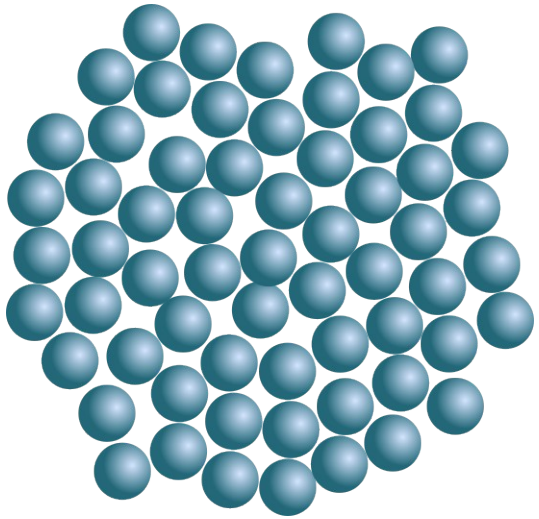
XII Equifase, Campinas-SP, October 24-27, 2022

Do You Have 10 Minutes to talk about Classical DFT?

A Bridge between Different Length Scales

MC, MD



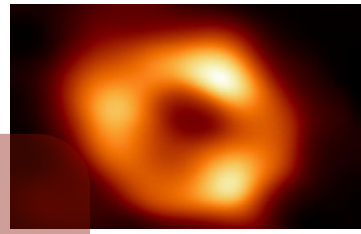
Individual particles

Approximation by a Free-energy functional

DFT

Density field

Multi-Scale Modelling



$\tau(s)$

10^3

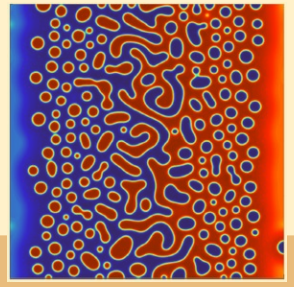
1

10^{-3}

10^{-6}

10^{-9}

10^{-12}



Macroscopic Models

Thermodynamics

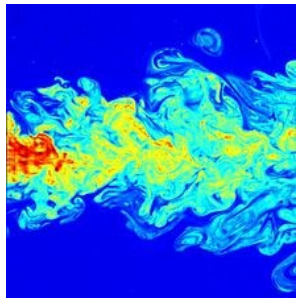
Hydrodynamics

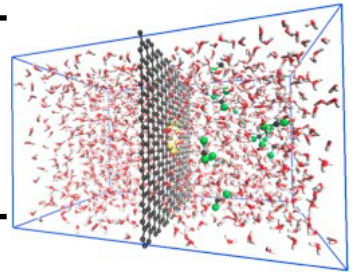
Continuum medium Models

Poisson Bolztmann,

DFT,

Phase Field





Mesoscopic Dynamics

Lattice Boltzmann,

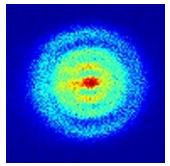
DPD

Molecular Dynamics

$$m\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2} = -\nabla V(\boldsymbol{r})$$

Quantum Mechanics

$$H\,|\psi\rangle = i\hbar\frac{\partial}{\partial t}\,|\psi\rangle$$



10^{-12} 10^{-9} 10^{-6} 10^{-3} 1 $l(m)$

Mind the Gap!

Classical Density Functional Theory

Grand Potential

$$\Omega(V,T,\mu) = F[\rho(\boldsymbol{r})] + \int_V \mathrm{d}\boldsymbol{r}\,[V_{\mathrm{ext}}(\boldsymbol{r}) - \mu]\,\rho(\boldsymbol{r})$$

External potential acts as a chemical potential

Free Energy Functional

$$F[\rho] = F_{\mathrm{id}}[\rho] + F_{\mathrm{exc}}[\rho]$$

Excess Functionals

FMT, MFA, WDA, MMFA, FMSA, ...

Particle-particle interaction

Equilibrium

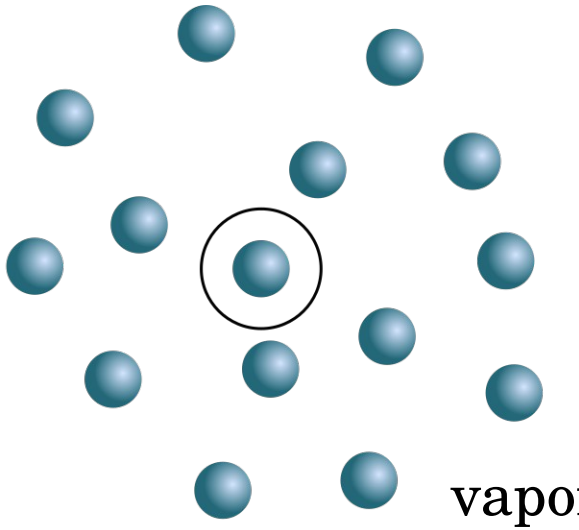
$$\Omega[\rho(\boldsymbol{r})] \geq \Omega[\rho(\boldsymbol{r})]_{\mathrm{eq.}}$$

Equilibrium Condition

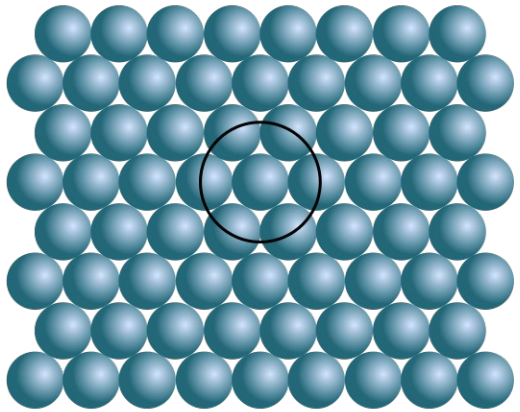
$$\left.\frac{\delta\Omega}{\delta\rho(\boldsymbol{r})}\right|_{V,\mu,T} = k_B T \ln\left(\Lambda^3\rho(\boldsymbol{r})\right) + \frac{\delta F_{\mathrm{exc}}[\rho]}{\delta\rho(\boldsymbol{r})} + V_{\mathrm{ext}}(\boldsymbol{r}) - \mu = 0$$

Wu, J., & Li, Z. Annual Review of Physical Chemistry, 58(1), 85-112. (2007)

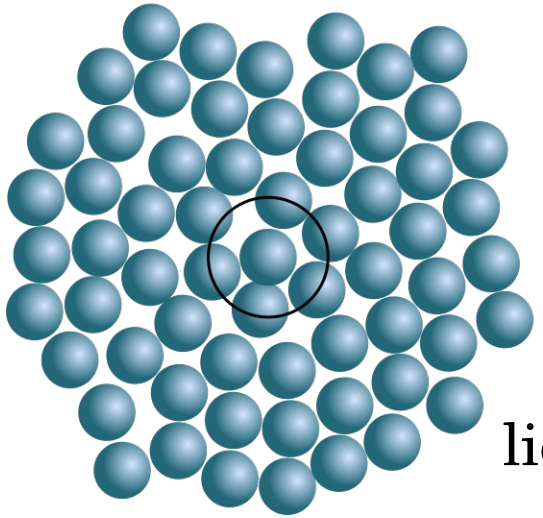
Lennard-Jones Fluids



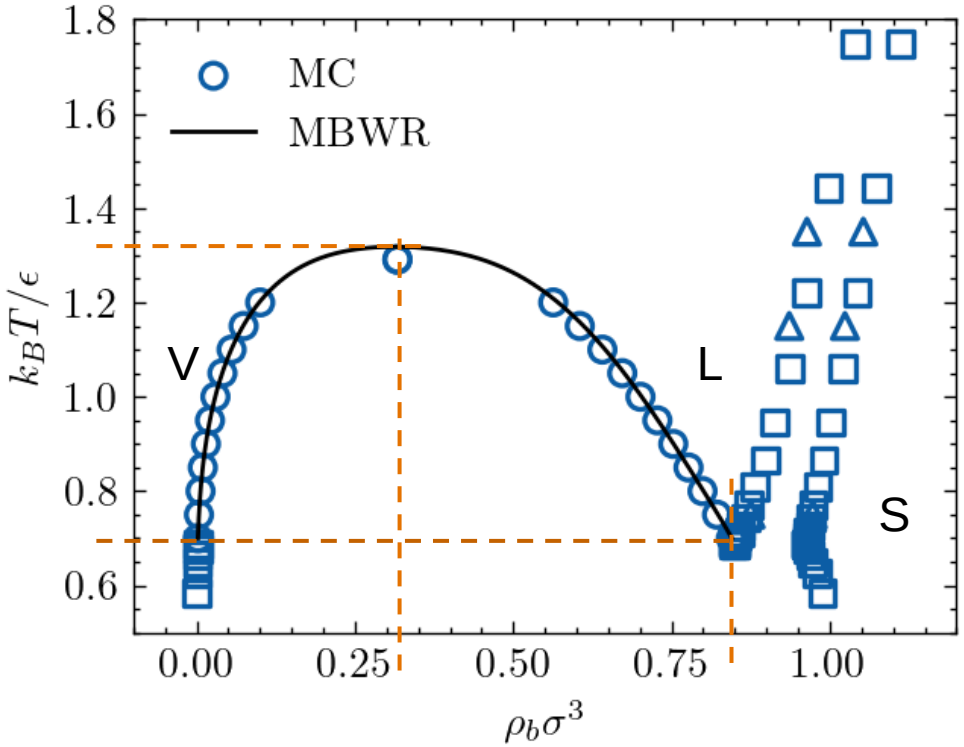
vapor



solid



liquid

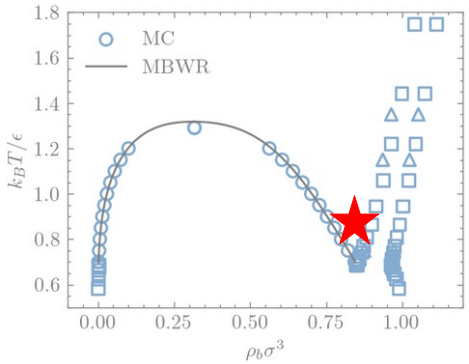


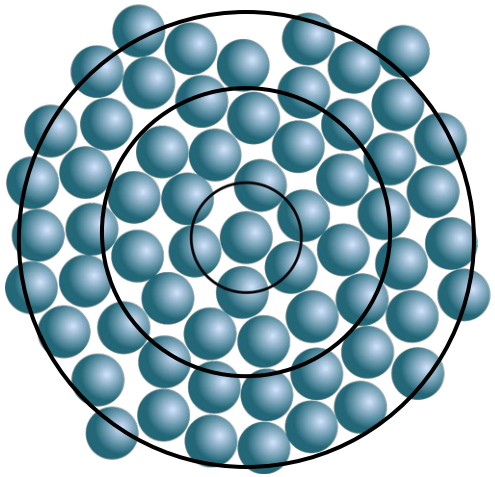
Lennard-Jones potential

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

Hansen, J.P. and McDonald, I.R., 2013. Theory of simple liquids: with applications to soft matter.
J. K. Johnson, J. A. Zollweg, and K. E. Gubbins, Molecular Physics 78, 591 (1993).

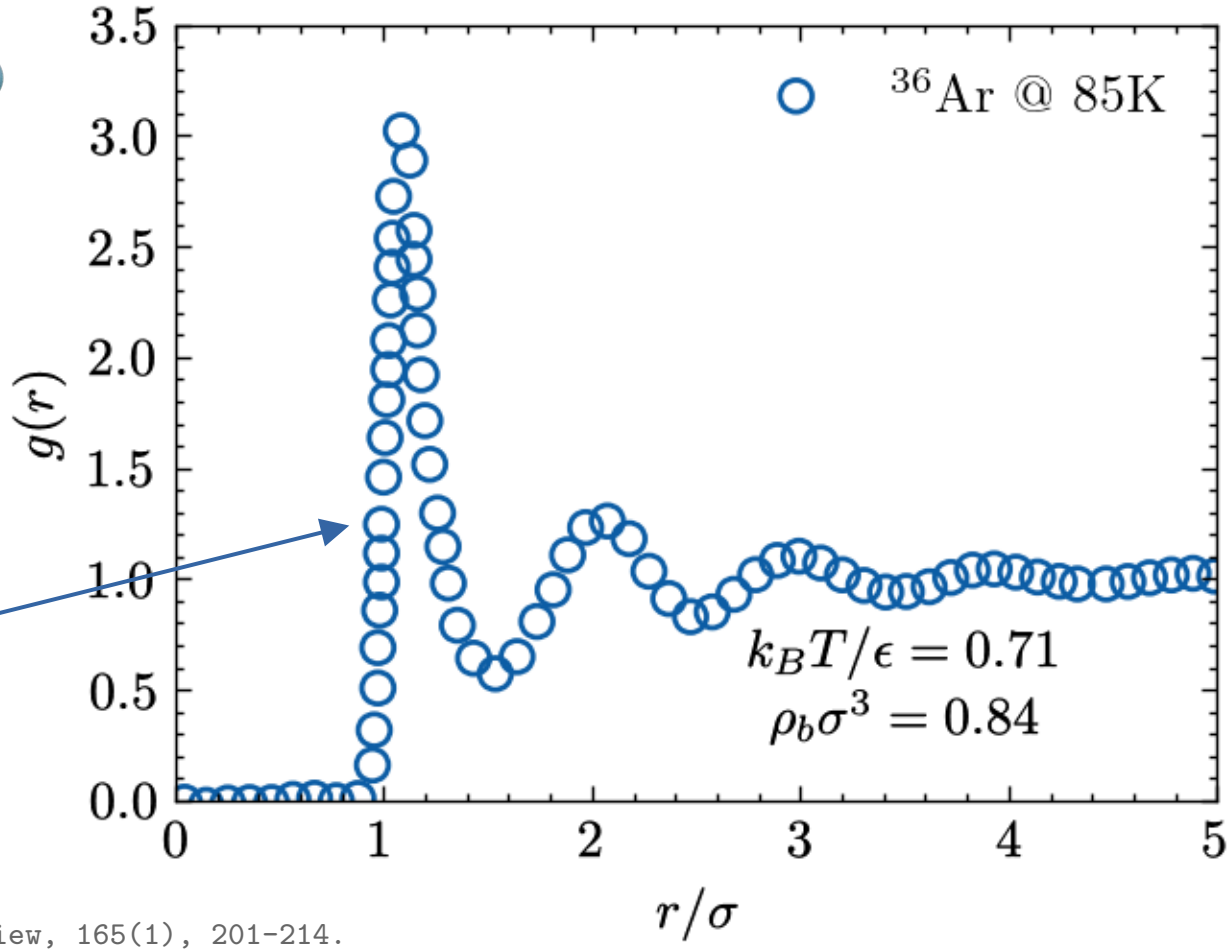
Radial Distribution Function





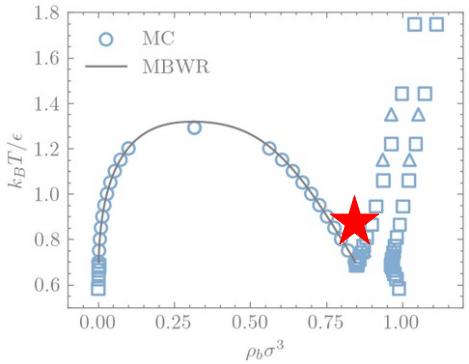
liquid

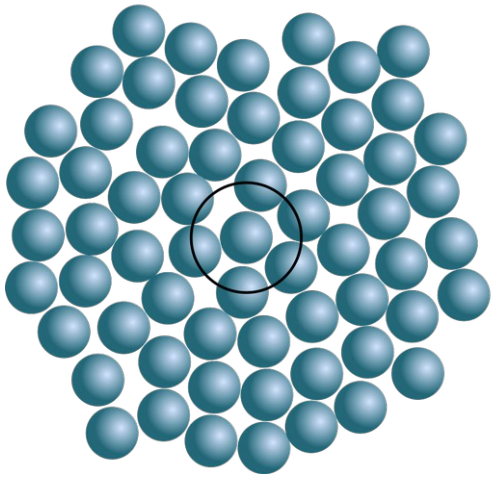
Data from X-Ray Experiment



Verlet, L. (1968). Physical Review, 165(1), 201-214.

Radial Distribution Function

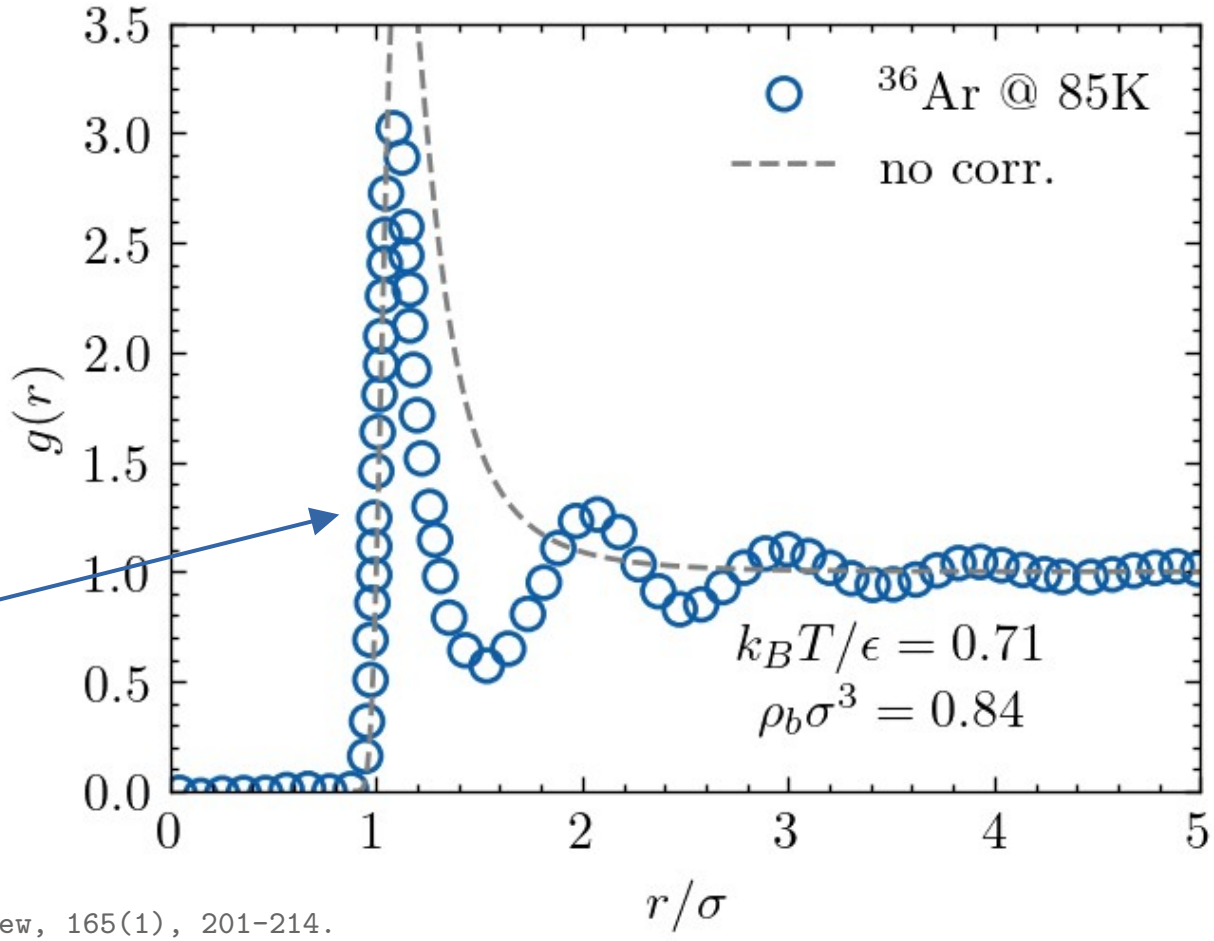




$$\rho(\boldsymbol{r}) = \rho_b e^{-\beta V_{\text{ext}}(\boldsymbol{r})}$$

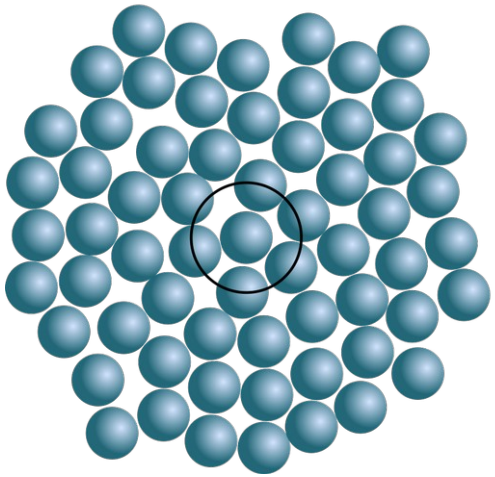
liquid

Data from X-Ray Experiment



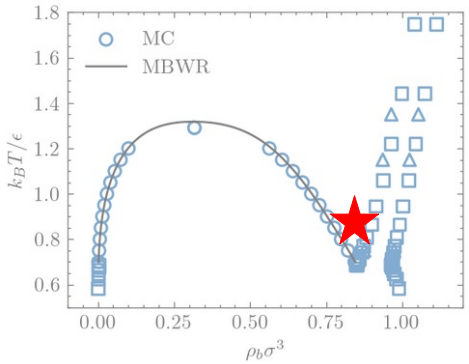
Verlet, L. (1968). Physical Review, 165(1), 201-214.

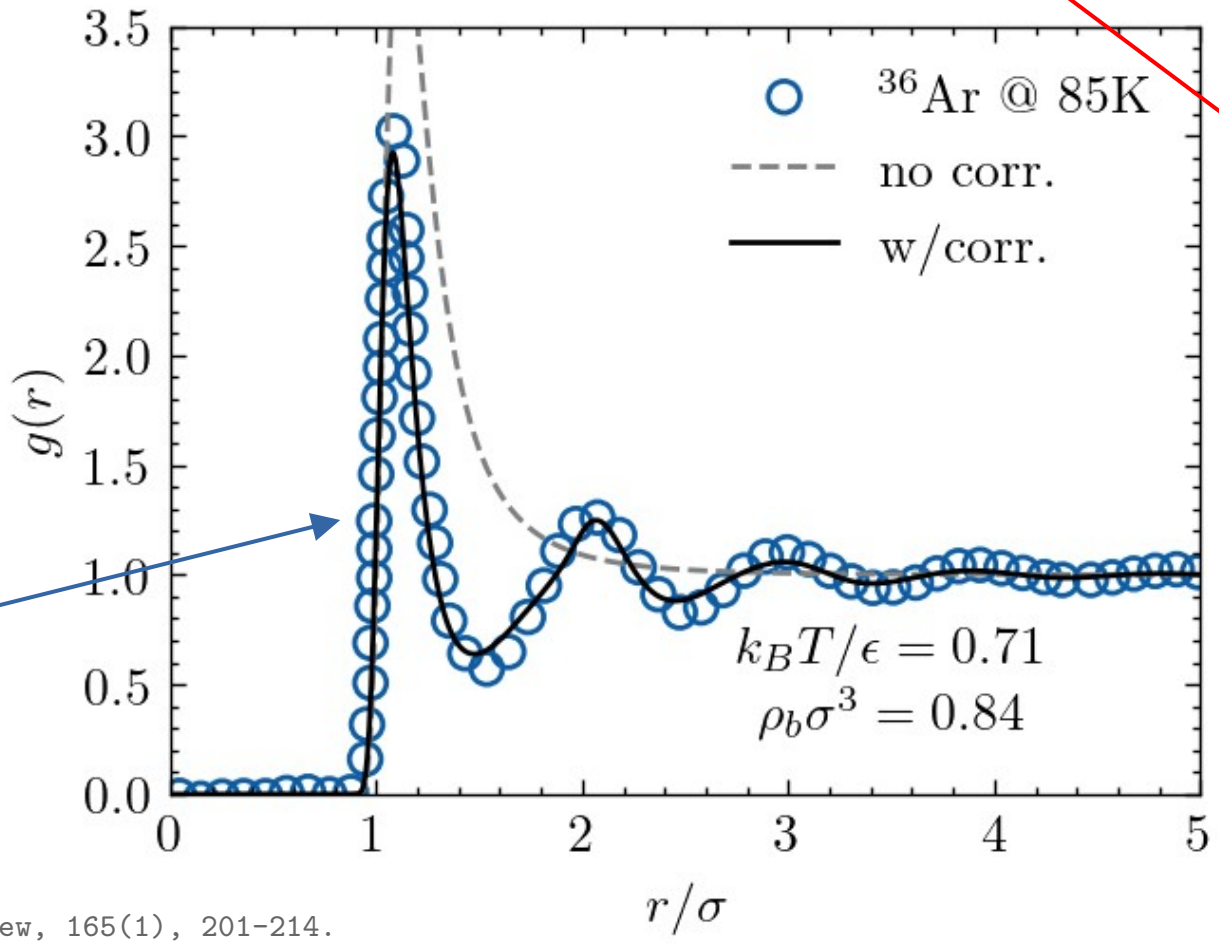
Radial Distribution Function



liquid

$$\rho(\boldsymbol{r}) = \rho_b e^{-\beta V_{\text{ext}}(\boldsymbol{r}) - \beta \frac{\delta F_{\text{exc}}[\rho]}{\delta \rho(\boldsymbol{r})} + \beta \mu_{\text{exc}}}$$





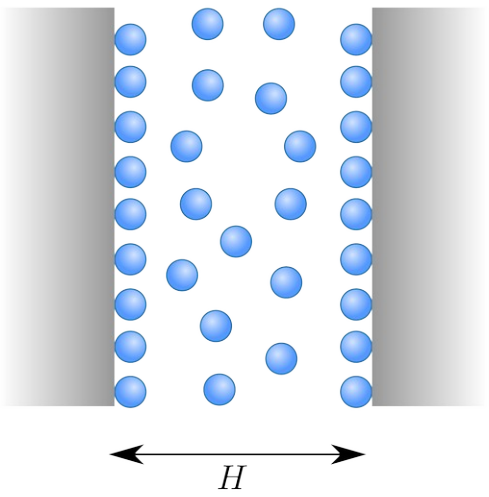
Data from X-Ray Experiment

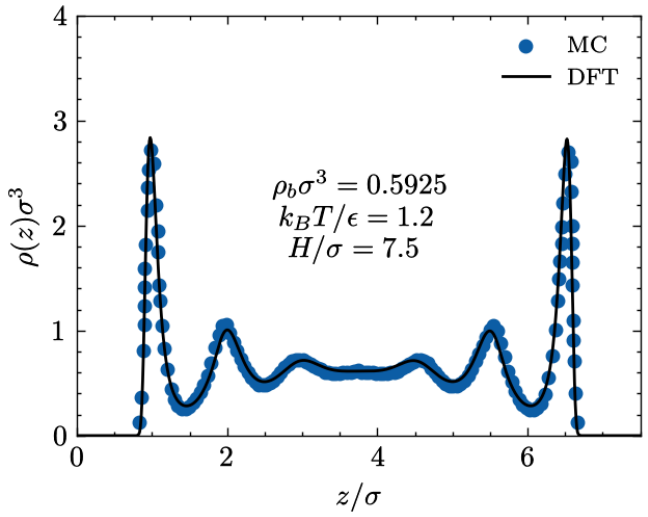
Density Correlations are very important!

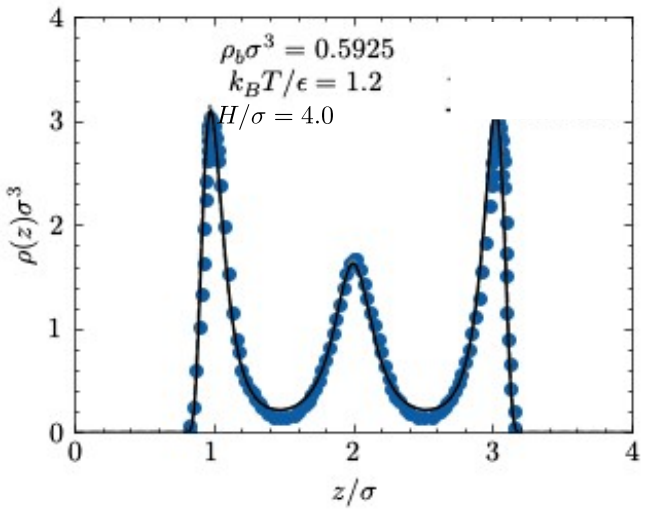
Non-local DFT

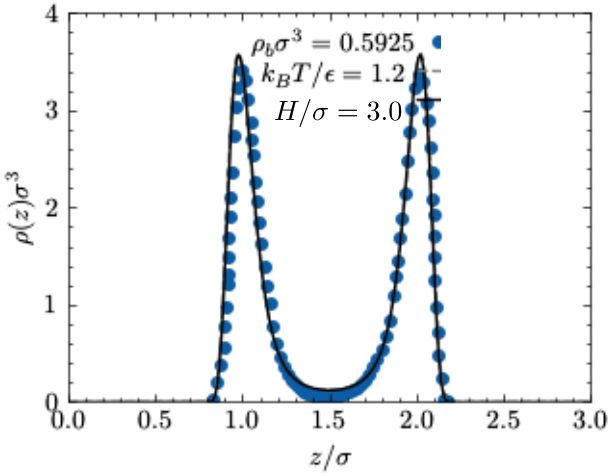
Verlet, L. (1968). Physical Review, 165(1), 201-214.

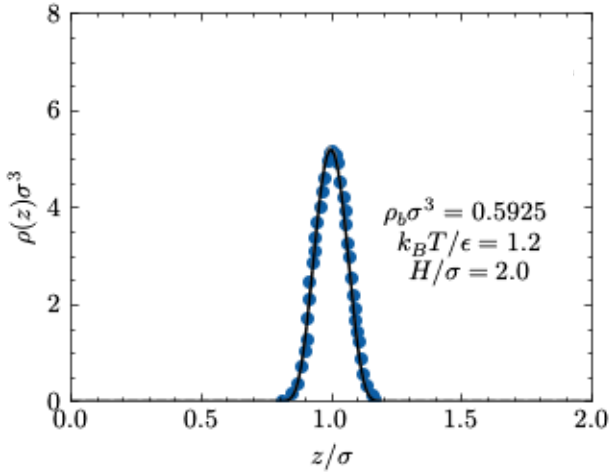
Fluid Inside a Slitlike Pore

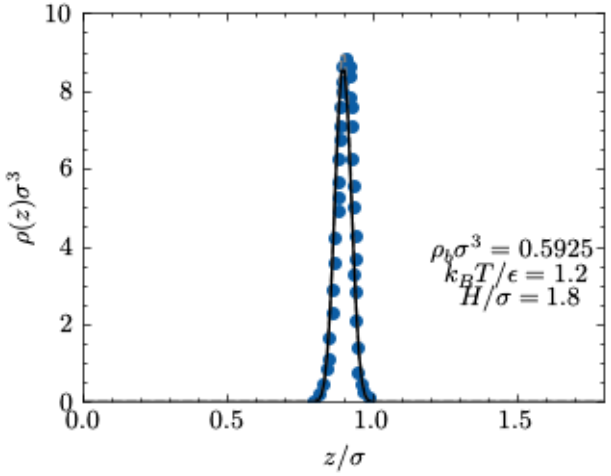






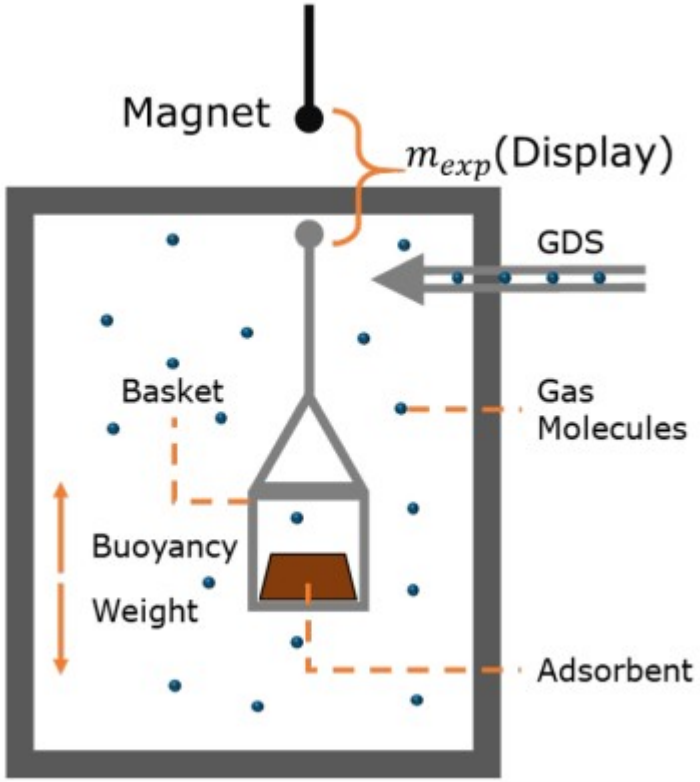


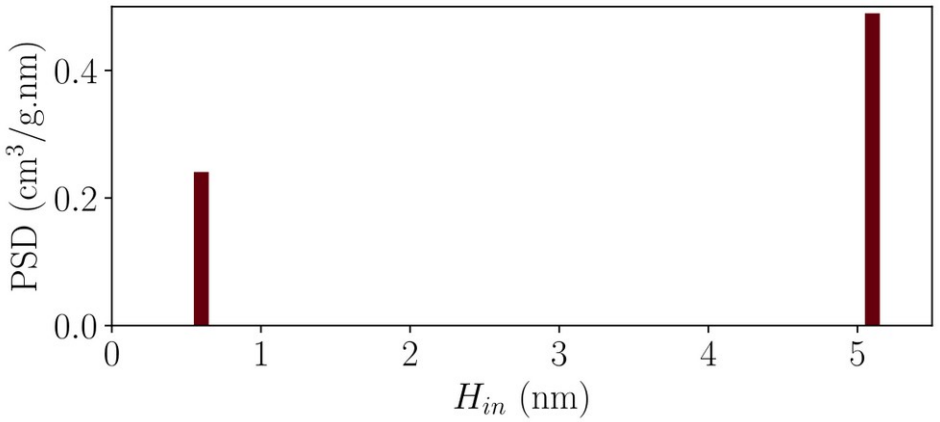


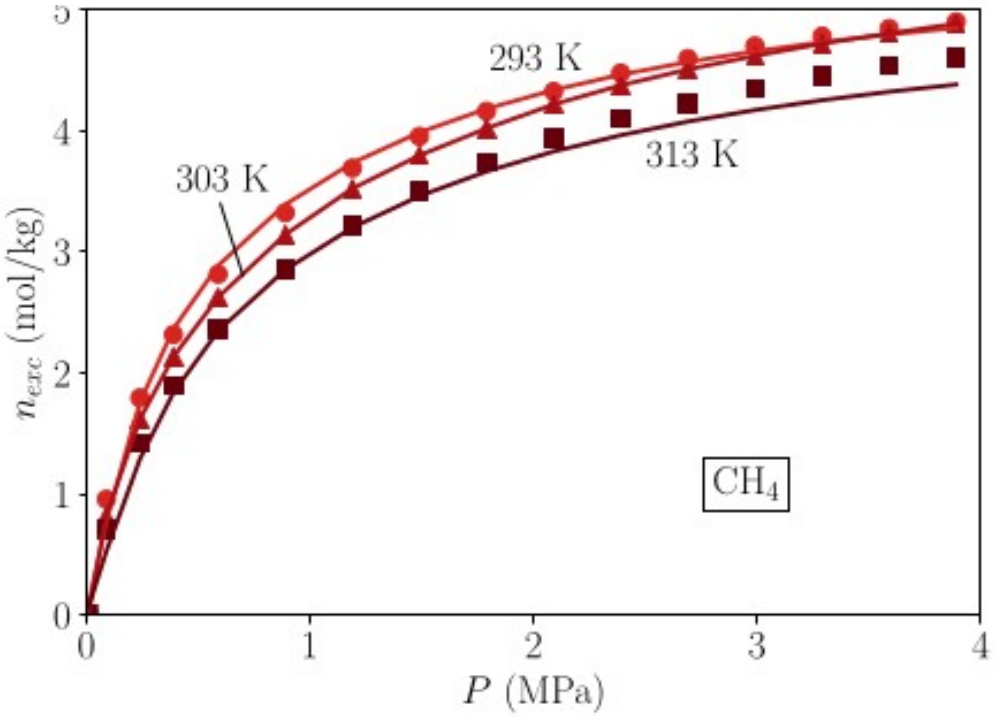


Snook, I. K., & van Megen, W. (1980). The Journal of Chemical Physics, 72(5), 2907-2913
Tang, Y., & Wu, J. (2004). Physical Review E, 70(1), 011201.

Adsorption in Activated carbon







PCP-SAFT

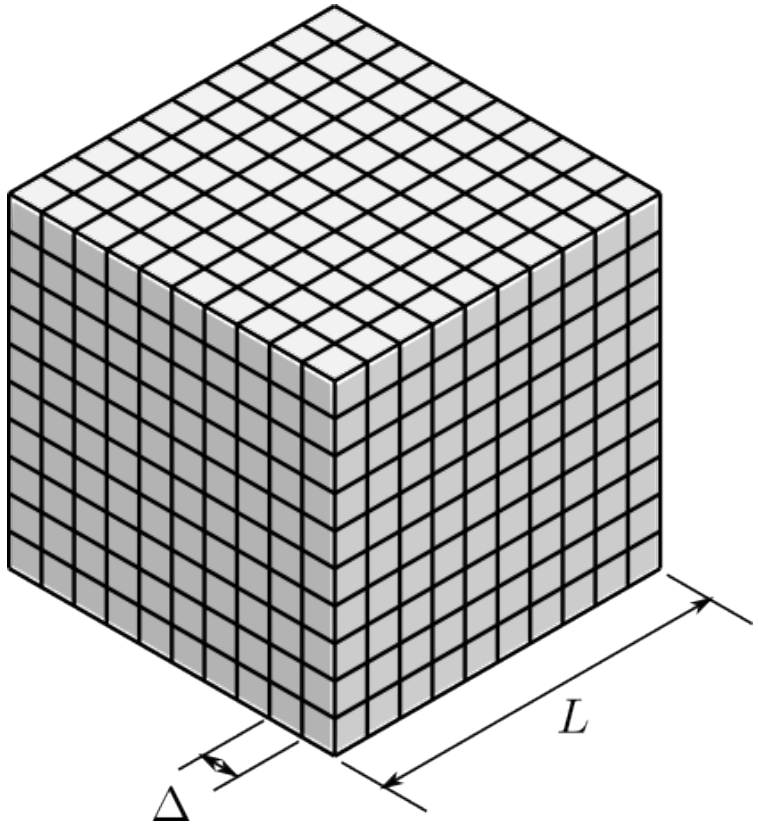
$$F_{\text{exc}} = F_{\text{hc}} + F_{\text{disp}} + F_{\text{qq}}$$

Sermoud, V. M., Barbosa, G. D., Soares, E. do A., et al (2022). Chemical Engineering Science, 247, 116905.

Can we go beyond symmetrical geometries?

DFT in 3D Geometries

$$\Omega[\{\rho_{\boldsymbol{R}}\}] = \sum_{\boldsymbol{R}} \left[k_B T \rho_{\boldsymbol{R}} (\ln(\rho_{\boldsymbol{R}} \sigma^3) - 1) + F^{\text{exc}}_{\boldsymbol{R}} + \rho_{\boldsymbol{R}} V^{\text{exc}}_{\boldsymbol{R}} - \mu \rho_{\boldsymbol{R}}\right] \Delta^3$$



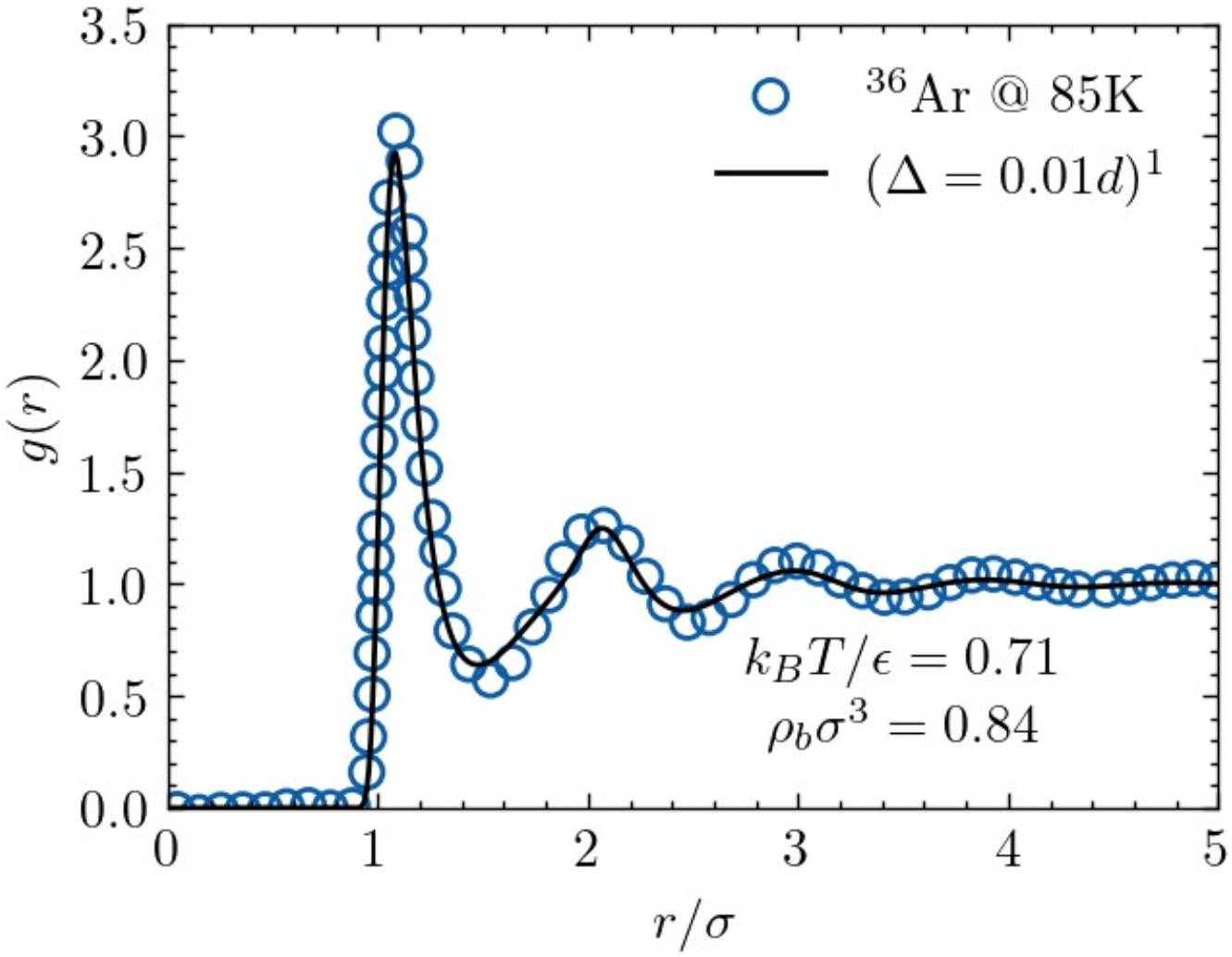
Convolution (FFT)

$$n(\boldsymbol{r}) = \int \rho(\boldsymbol{r}')\omega(\boldsymbol{r} - \boldsymbol{r}')\,\mathrm{d}\boldsymbol{r} \Longrightarrow \tilde{n}_{\boldsymbol{k}} = \tilde{\rho}_{\boldsymbol{k}} \tilde{\omega}_{\boldsymbol{k}}$$

Extremum condition (FIRE)

$$\left\| \frac{\partial \Omega}{\partial \rho_{\boldsymbol{R}}} \right\| < \epsilon_{\text{tol}}$$

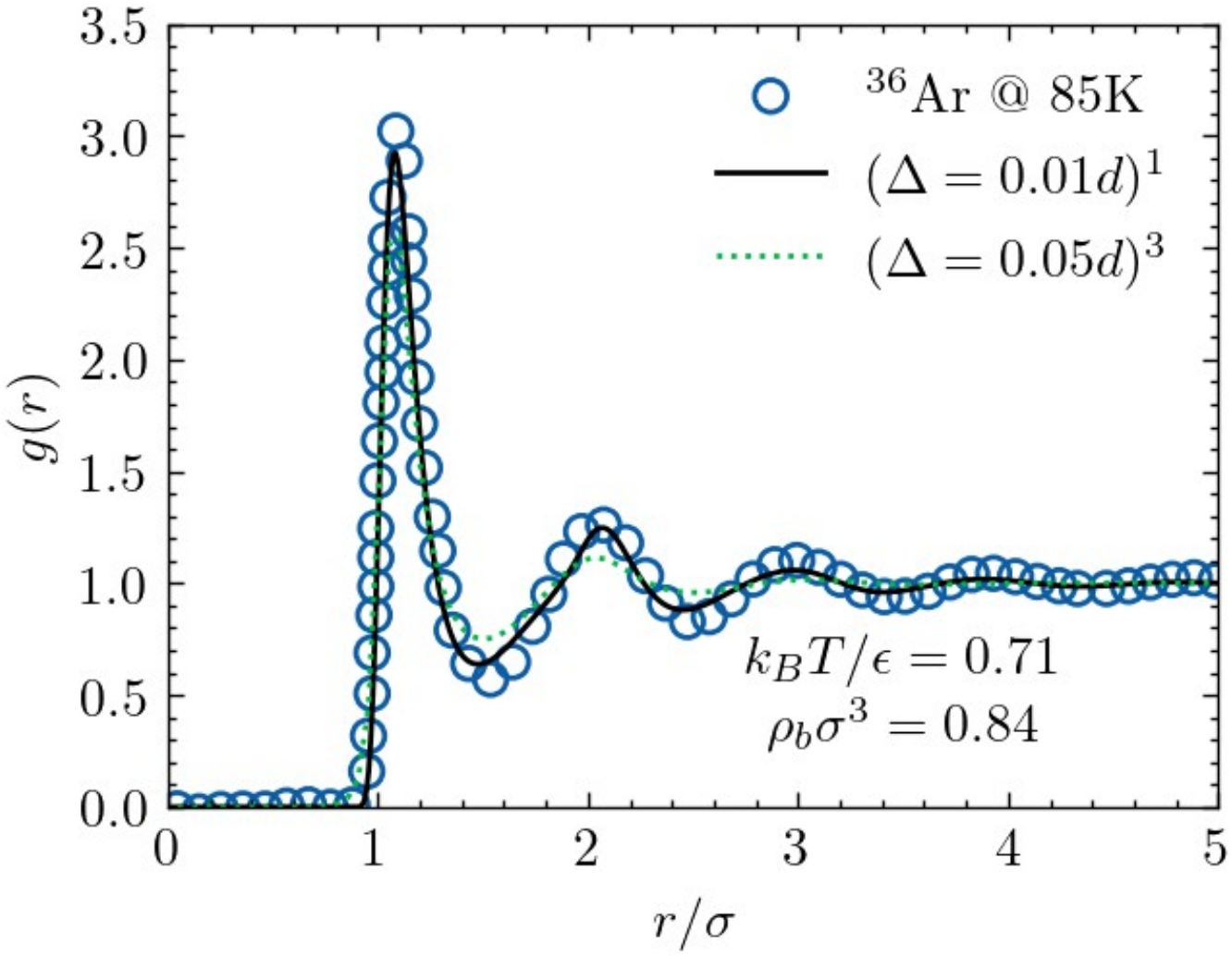
Gridsize vs. Time Consumption



Grid	Time(s)
0.01^1	8

Verlet, L. (1968). Physical Review, 165(1), 201-214.

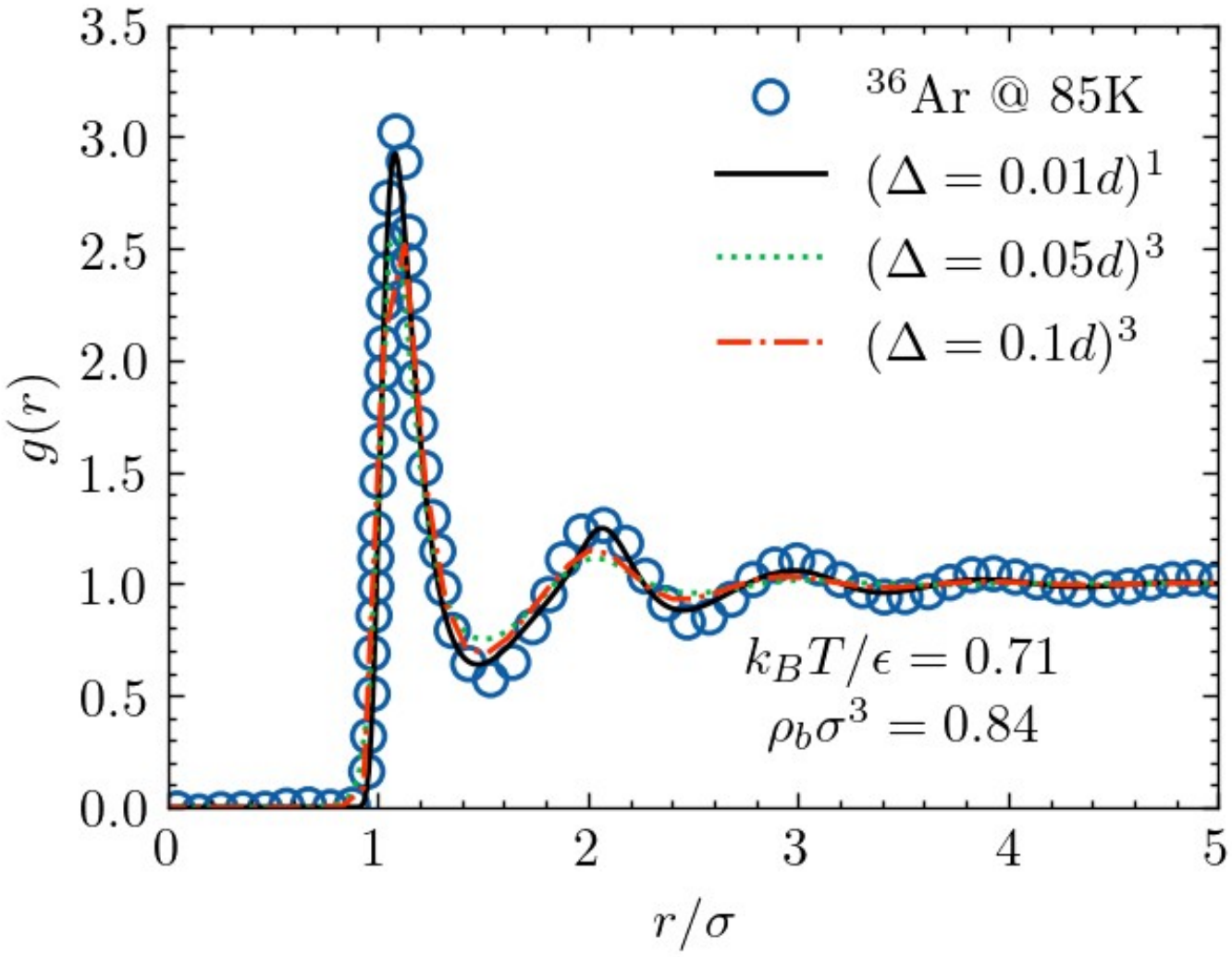
Gridsize vs. Time Consumption



Grid	Time(s)
0.01^1	8
0.05^3	545

Verlet, L. (1968). Physical Review, 165(1), 201-214.

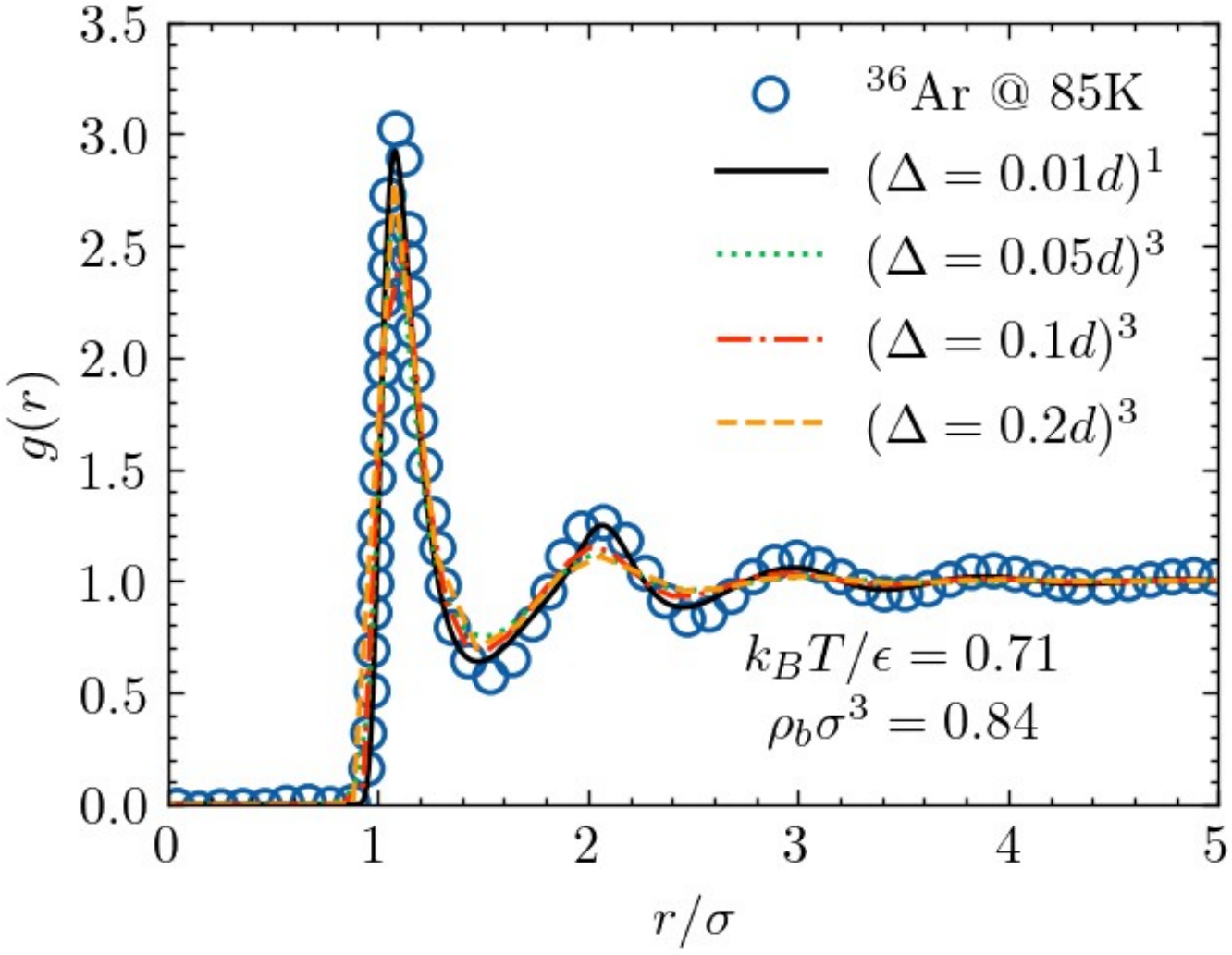
Gridsize vs. Time Consumption



Grid	Time(s)
0.01^1	8
0.05^3	545
0.1^3	177

Verlet, L. (1968). Physical Review, 165(1), 201-214.

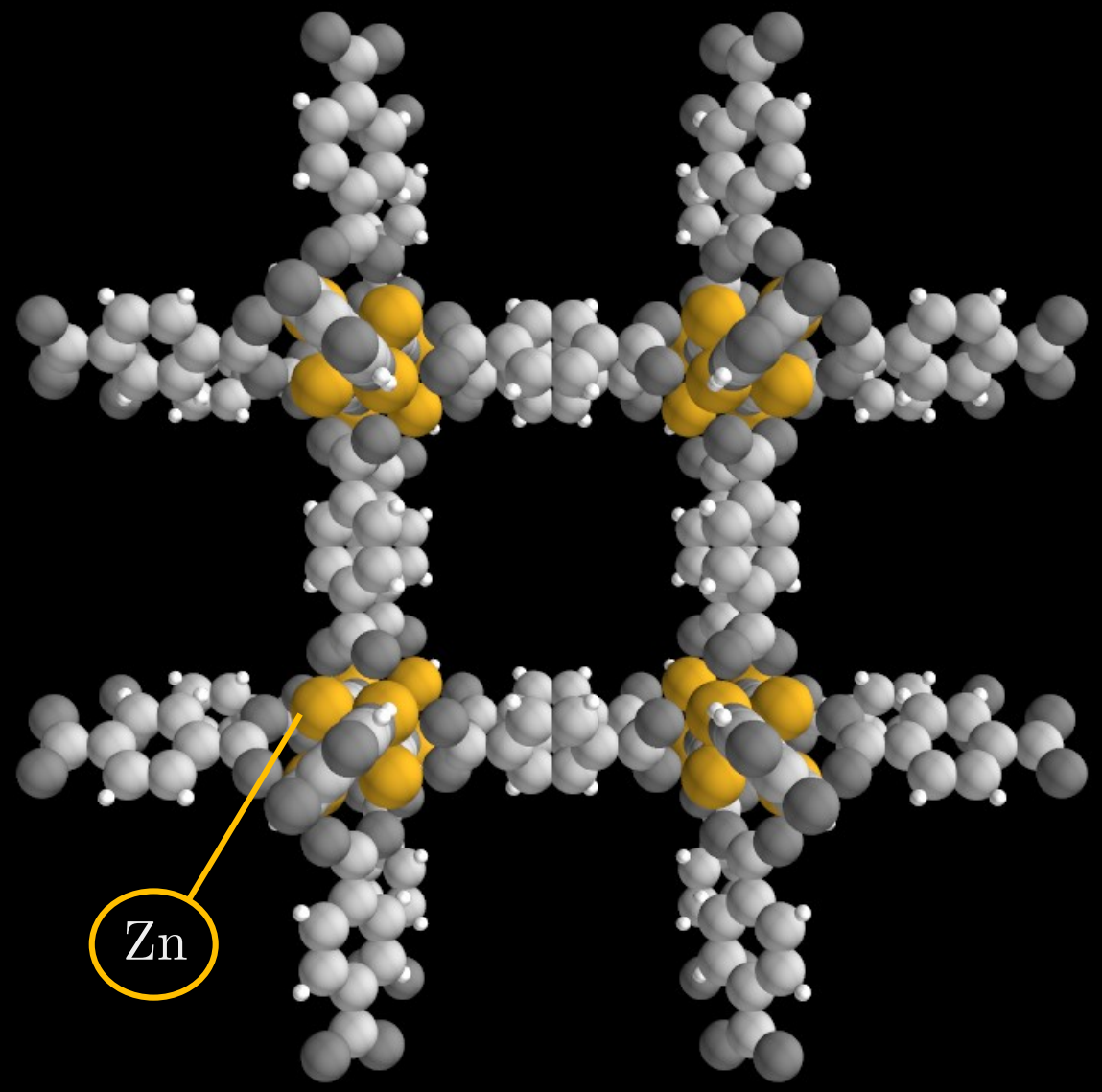
Gridsize vs. Time Consumption



Grid	Time(s)
0.01^1	8
0.05^3	545
0.1^3	177
0.2^3	27

Verlet, L. (1968). Physical Review, 165(1), 201-214.

Metal Organic Framework



MOF-5

DREIDING Force Field

H, C, O, Zn

External Potential

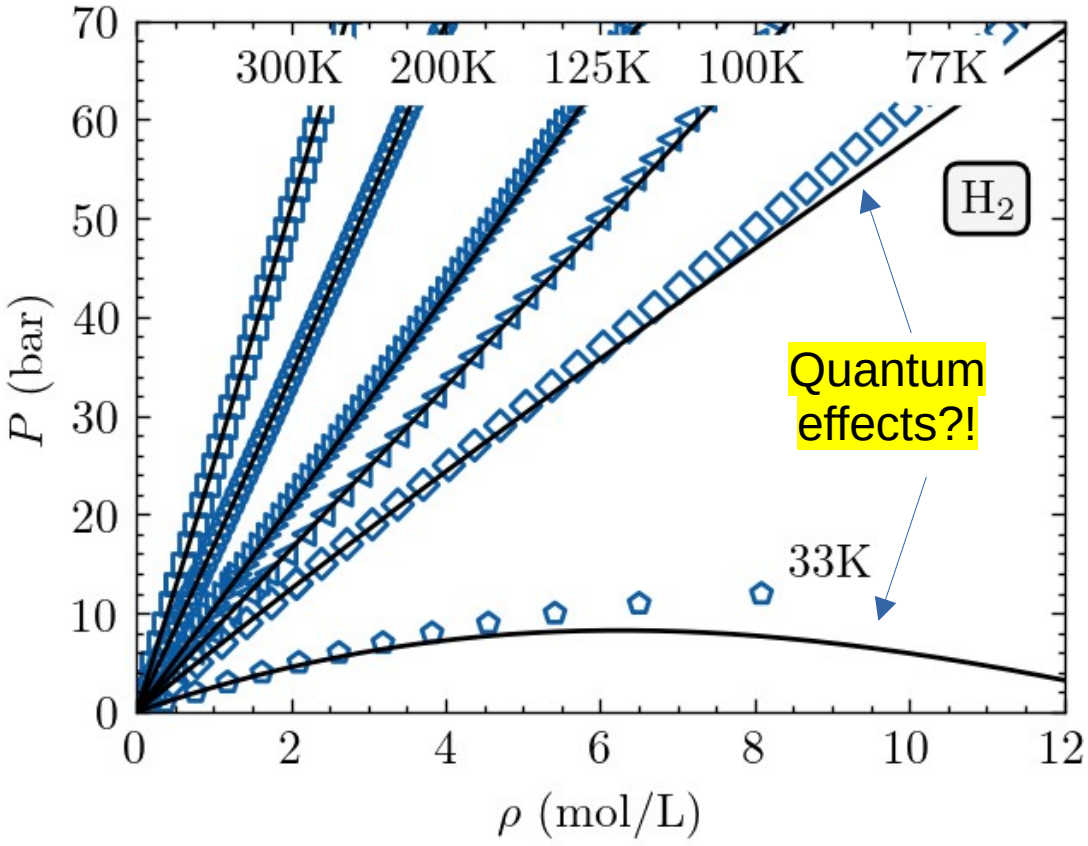
$$V^{\text{ext}}(\boldsymbol{r}) = \sum_{j \in \text{ solid}} u_j^{(\text{lj})}(|\boldsymbol{r} - \boldsymbol{r}_j|)$$

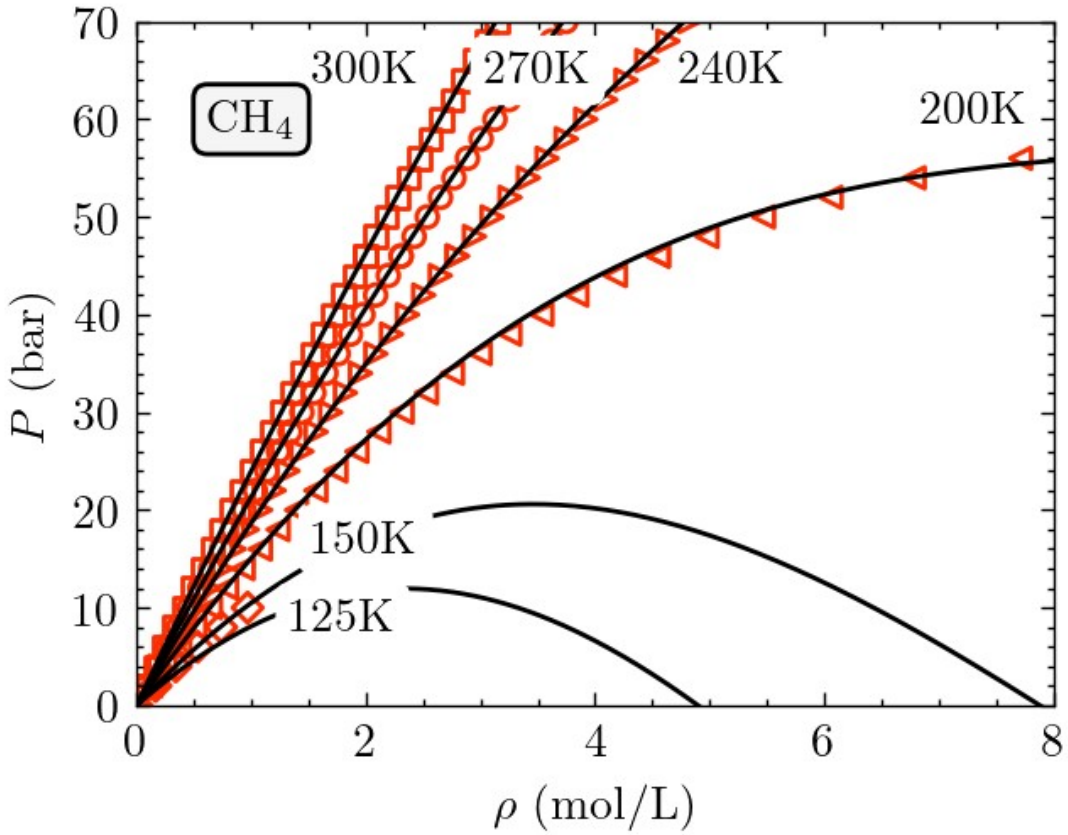
Lorentz-Berthelot mixing rules

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj})$$

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$$

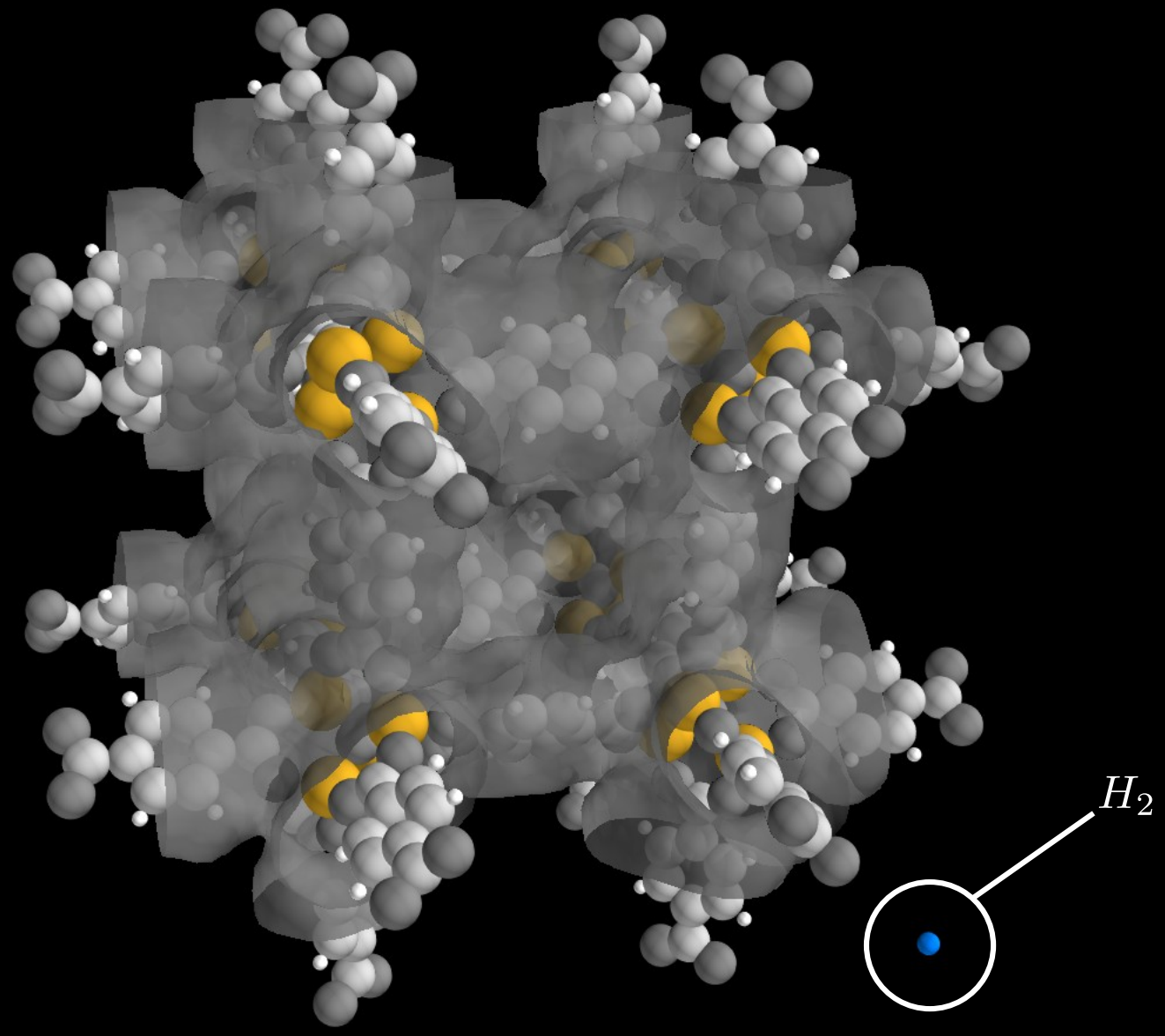
Equation of State – MBWR – LJ fluid





Leachman, J.W.; Jacobsen, R.T.; Penoncello, S.G.; Lemmon, E.W., J. Phys. Chem. Ref. Data, 2009, 38, 3, 721-748
Setzmann, U.; Wagner, W., J. Phys. Chem. Ref. Data, 1991, 20, 6, 1061-1155

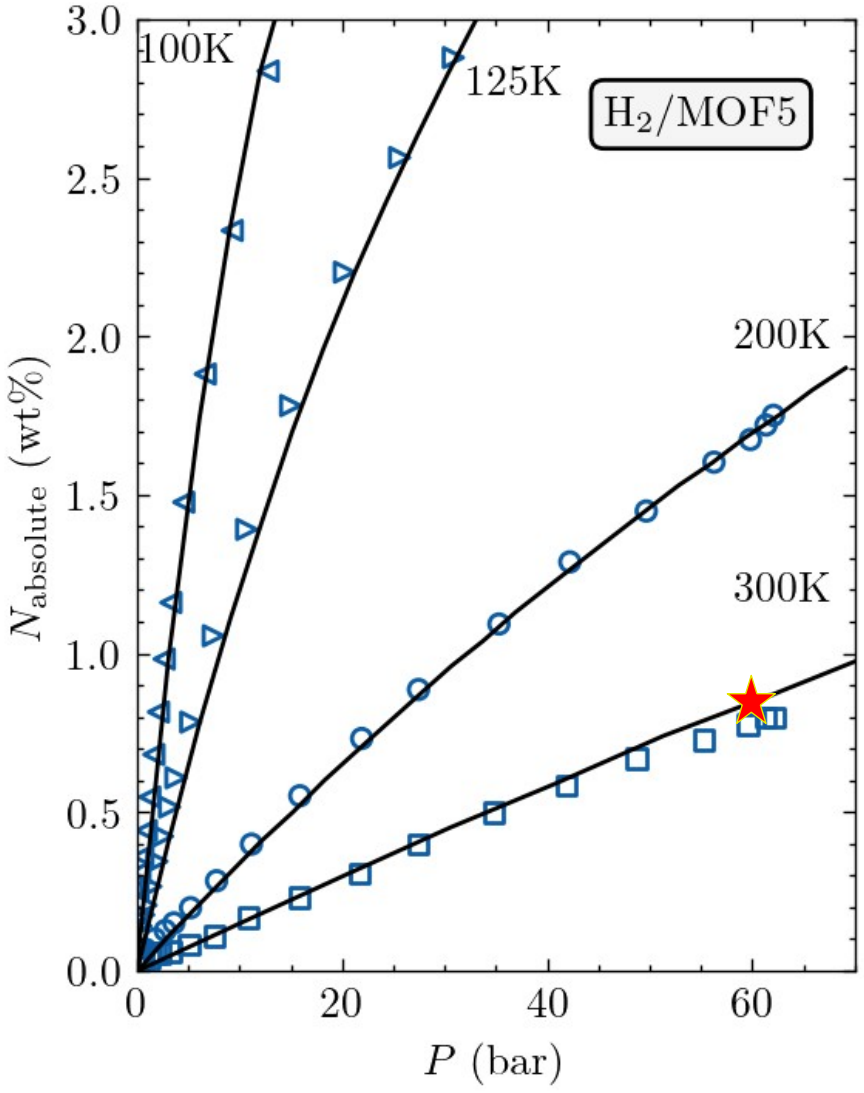
External Potential for H2

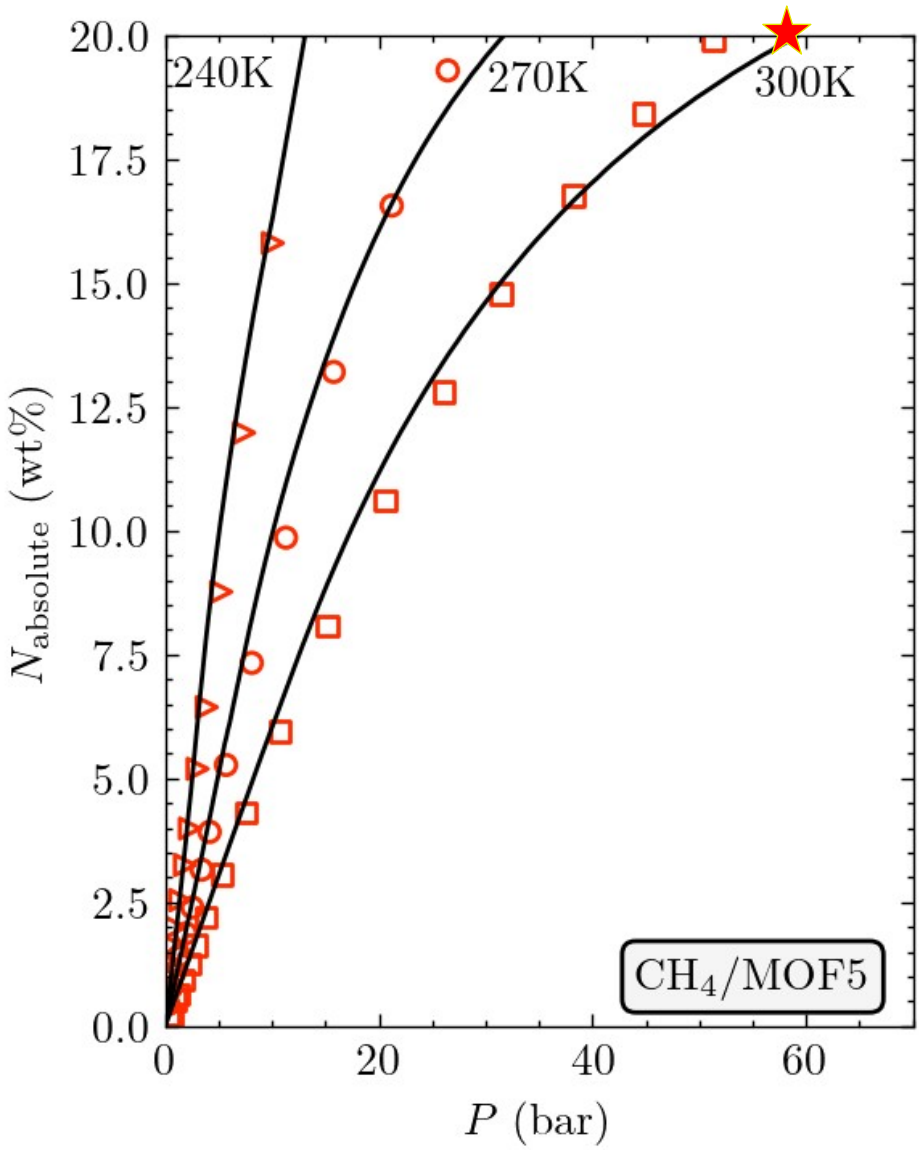


Adsorption Isotherms

No fitted parameter!

Exp.Data
DFT



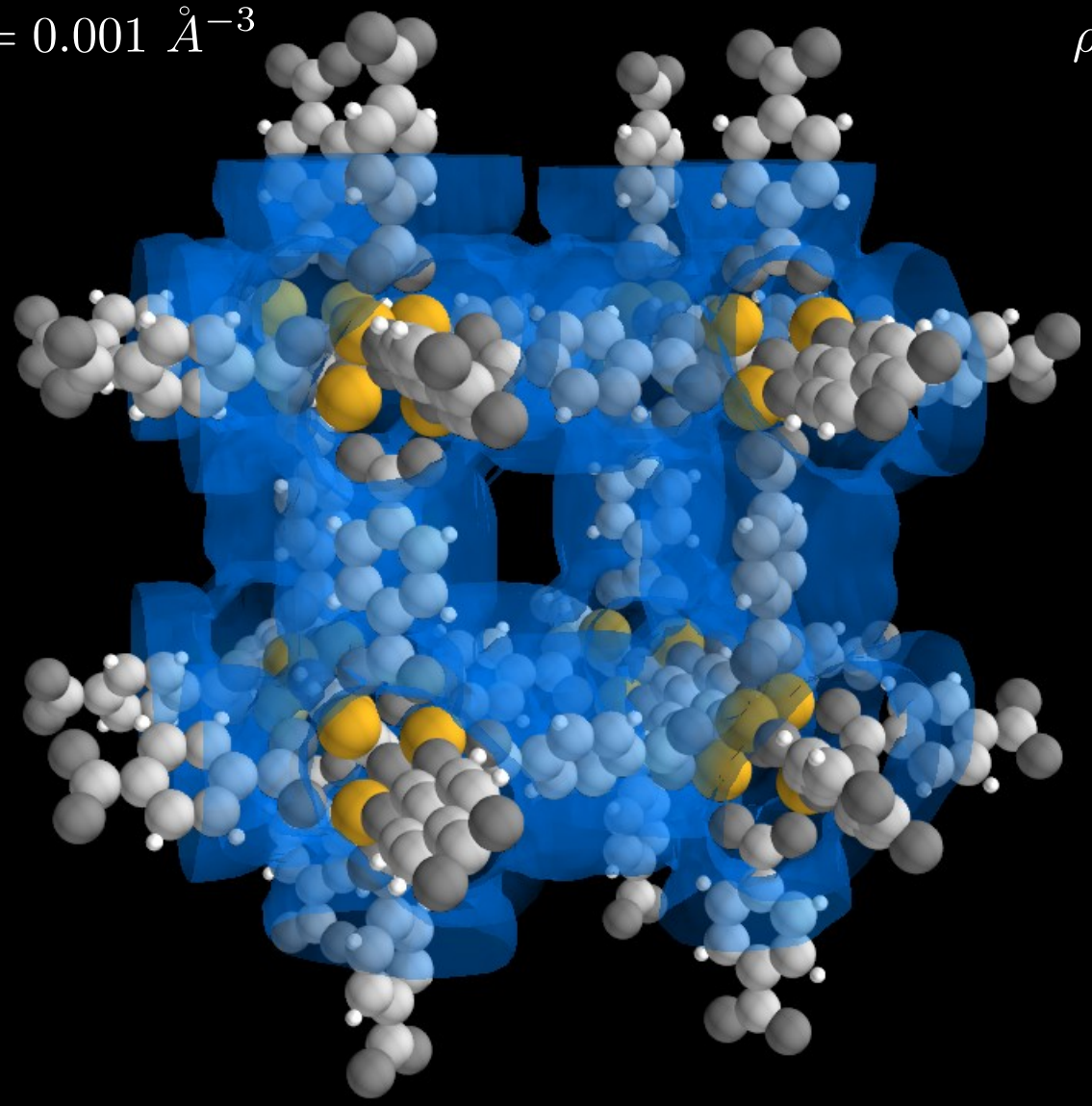


Zhou, W., Wu, H., Hartman, M. R., & Yildirim, T. (2007). The Journal of Physical Chemistry C, 111(44), 16131-16137.

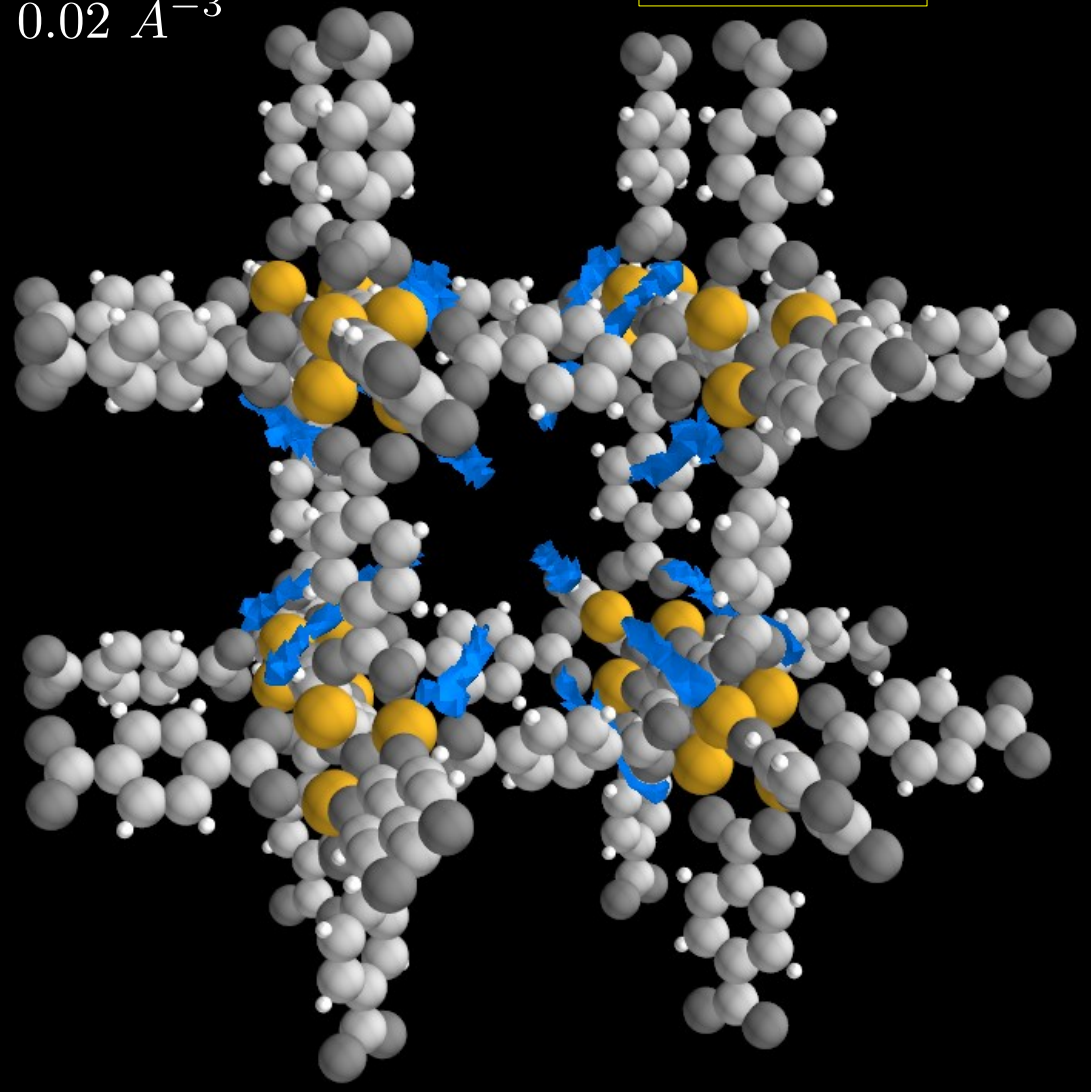
Isosurfaces of H_2 Local Density

$P = 60$ bar
$T = 300$ K

$\rho = 0.001\ \mathring{A}^{-3}$



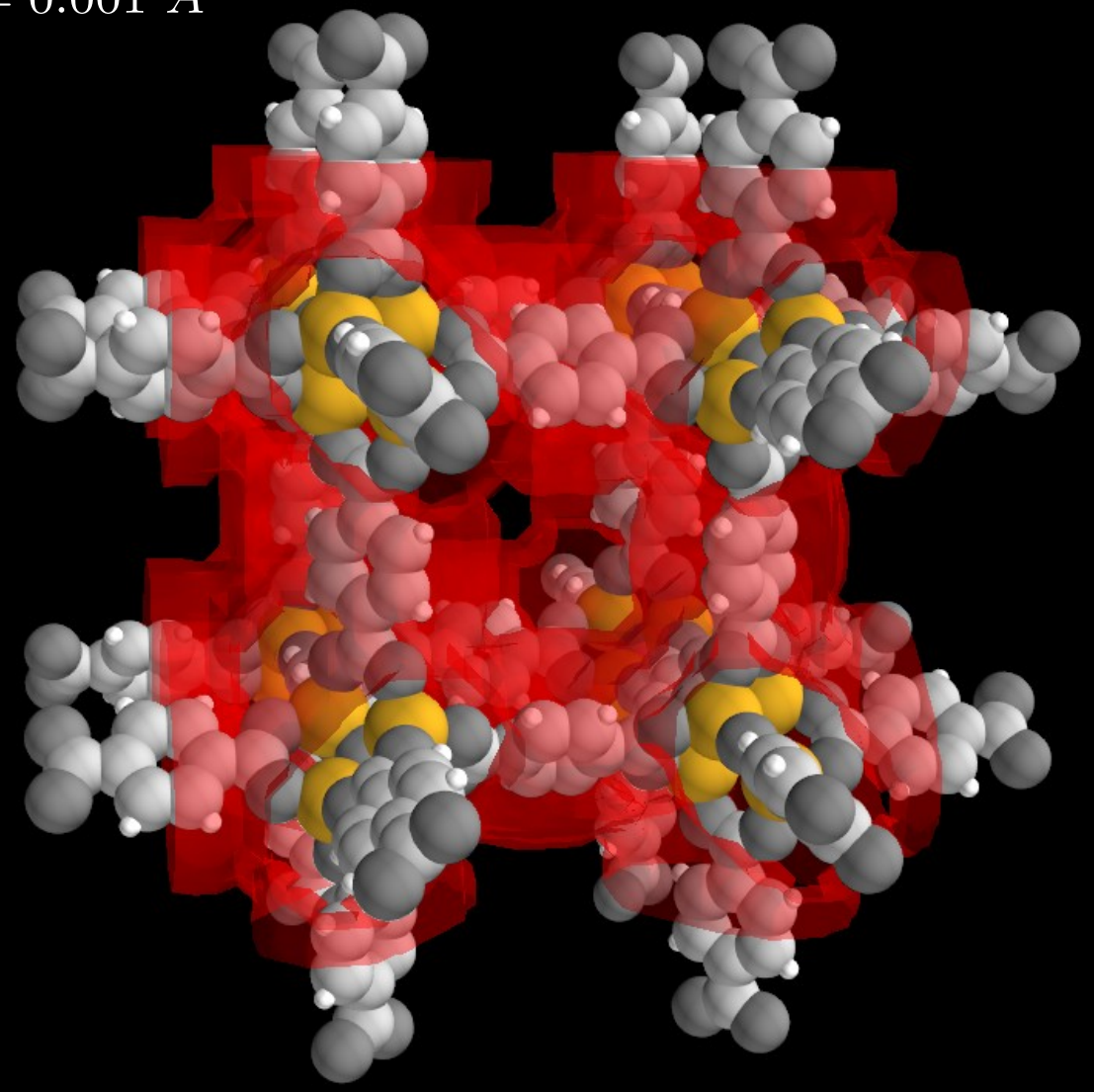
$\rho = 0.02\ \mathring{A}^{-3}$



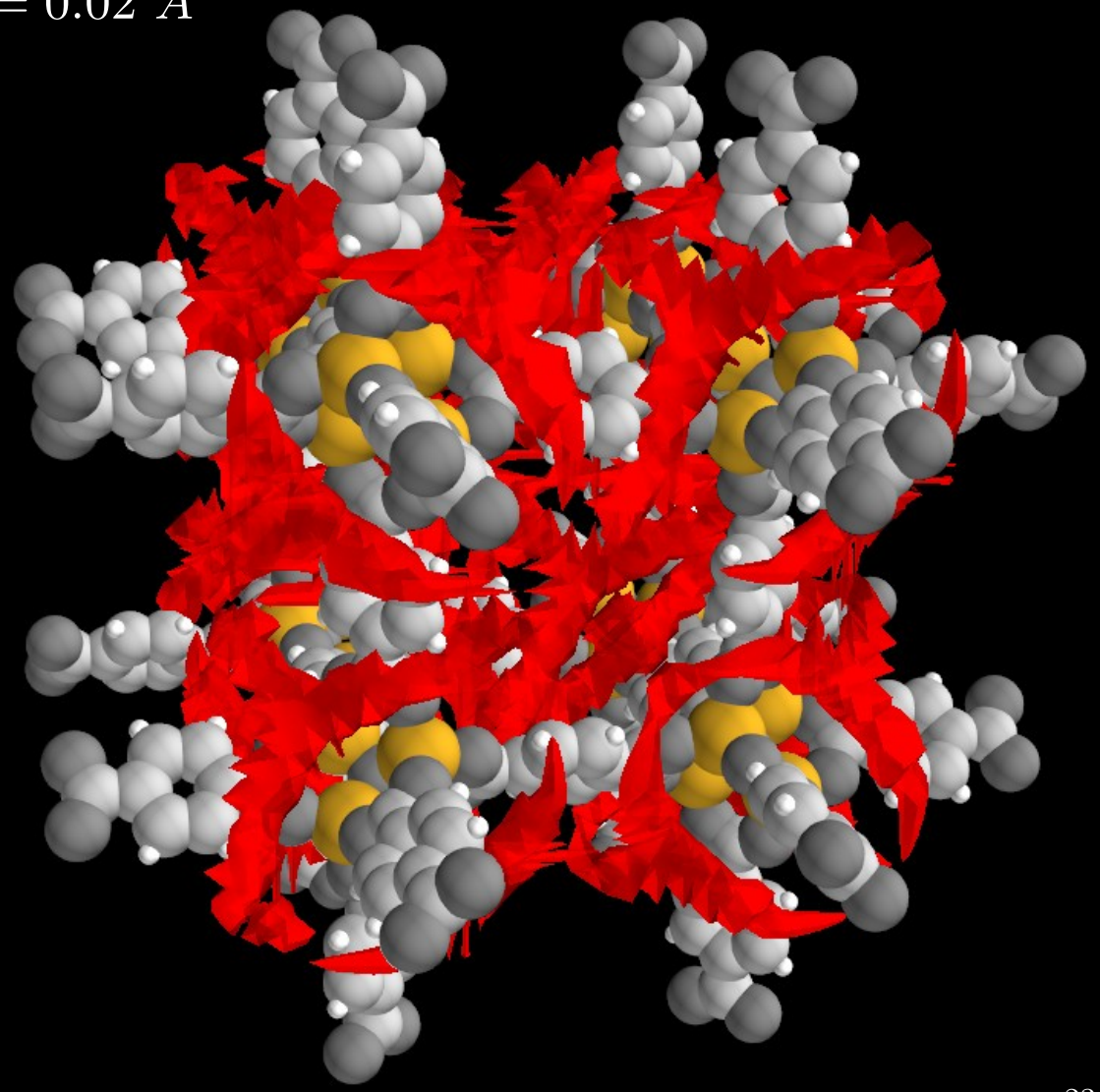
Isosurfaces of CH_4 Local Density

$P = 60$ bar
$T = 300$ K

$\rho = 0.001\ \mathring{A}^{-3}$



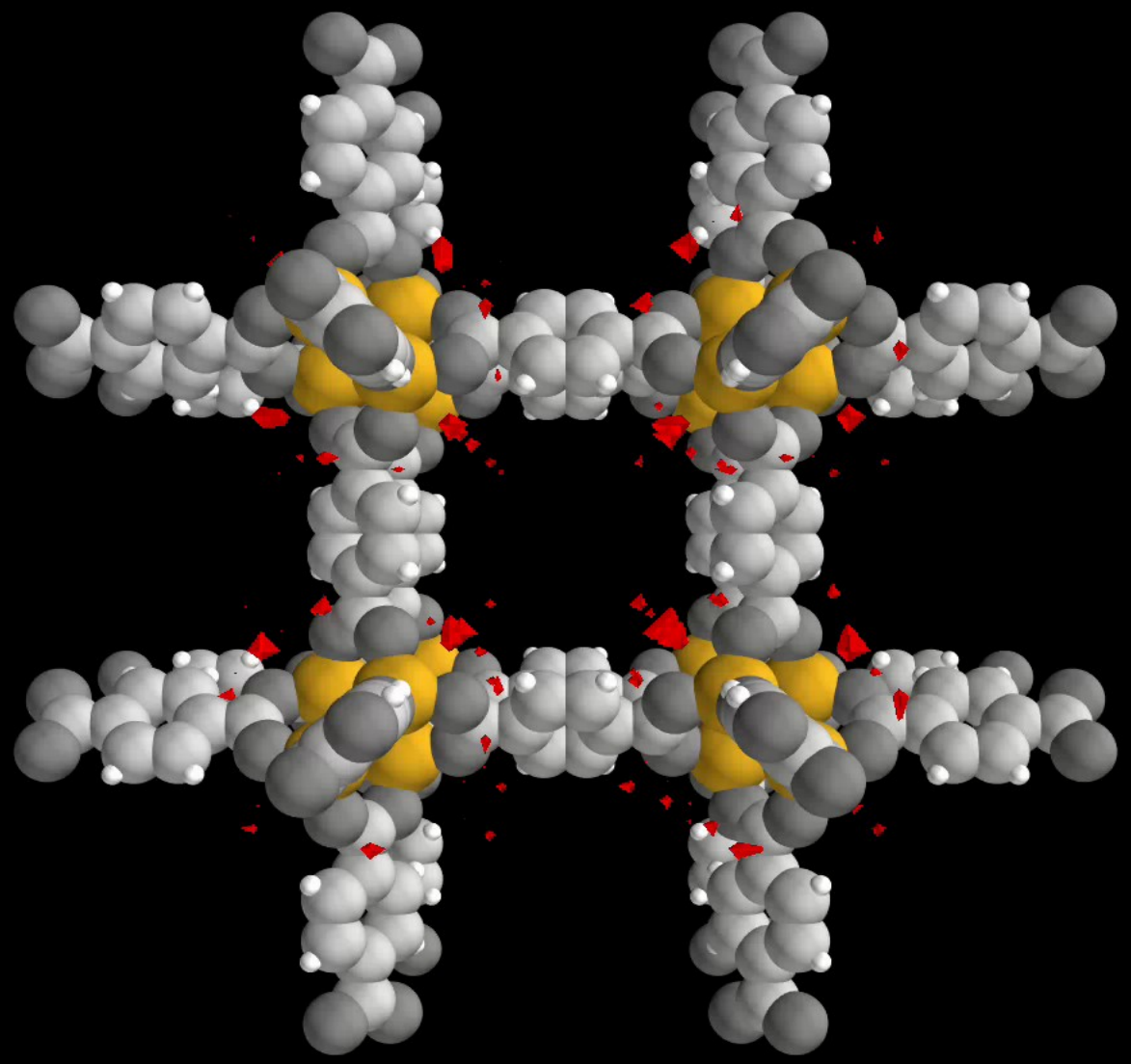
$\rho = 0.02\ \mathring{A}^{-3}$



Video

$P = 60$ bar
$T = 300$ K

$\rho = 0.08\ \mathring{A}^{-3}$

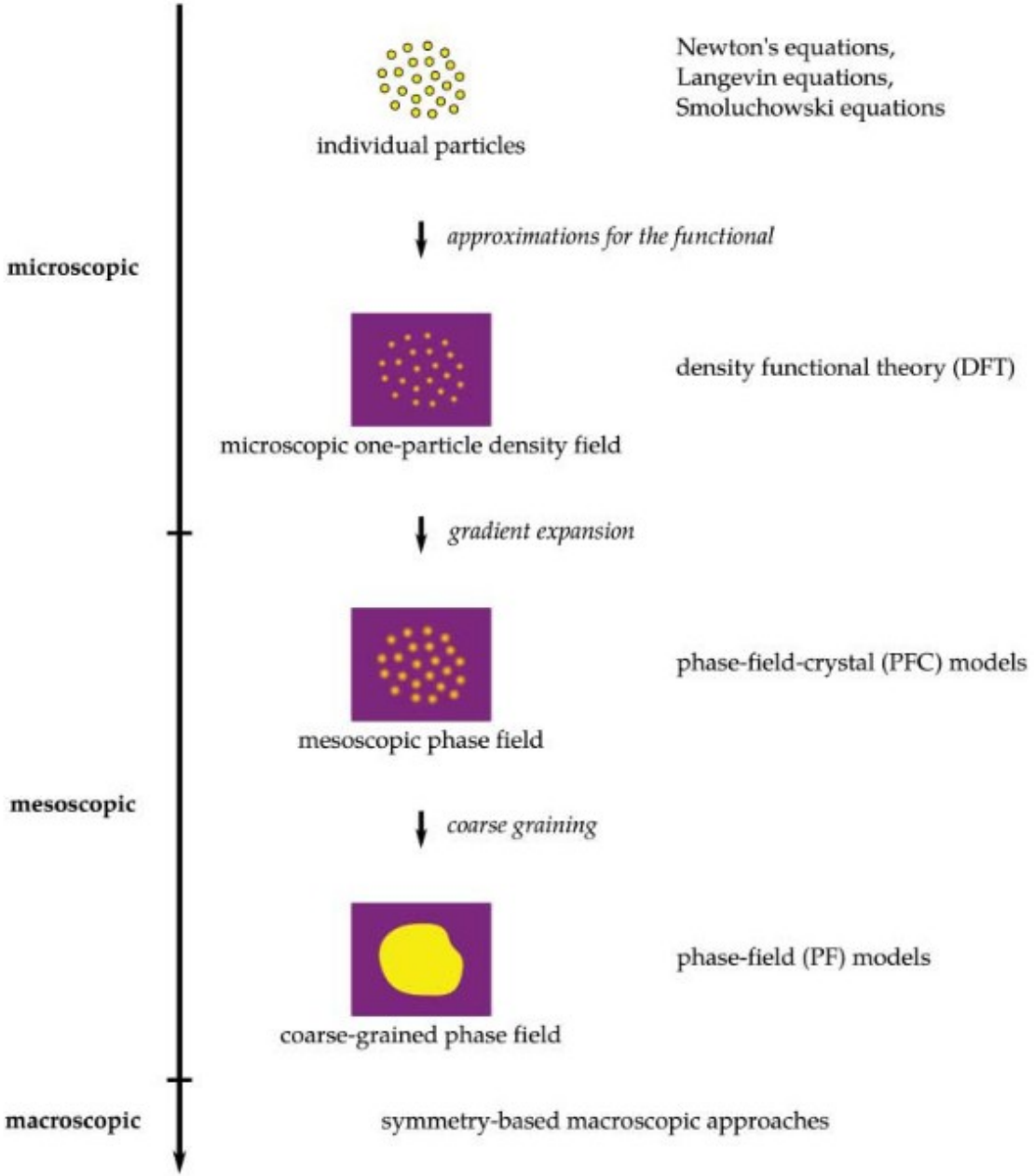


Conclusions and Perspectives

Conclusions

- The **size correlations are very important** to describe the high concentration systems;
- The **fluid-solid interaction can be described** by the DFT on the same level of MC/MD;
- There is a connection between **DFT and Phase-Field Models. (Possible Scale Integration)**

- **Future works:**
  - Extensions to associative interactions, chain-like systems.
  - Quantum DFT? Chemisorption
  - Machine-learning functionals



Acknowledgments

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Elvis Do Amaral Soares

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CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

CAPES

PETROBRAS