A coarse-grained Density Functional Theory for Adsorption

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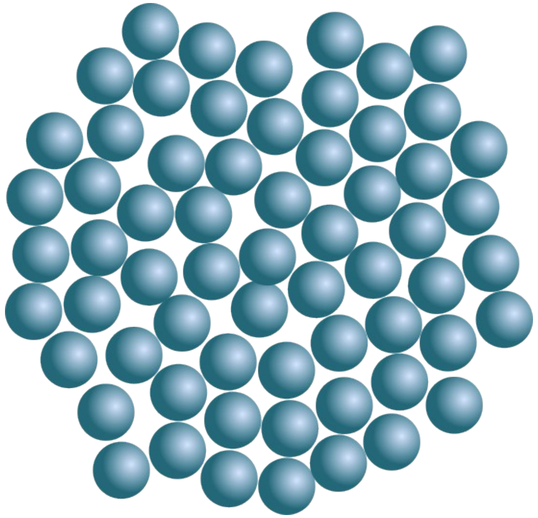
EBA 14, Brasília-DF, November 23-25, 2022

A Bridge between Different Length Scales

MC, MD



Individual particles

GROMACS, LAMMPS, CASSANDRA, RASPA

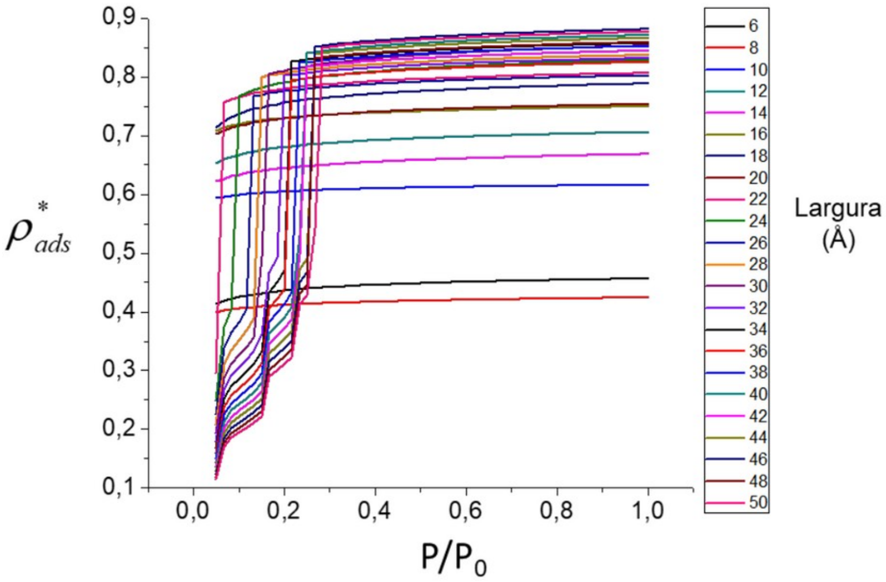
Approximation by a Free-energy functional

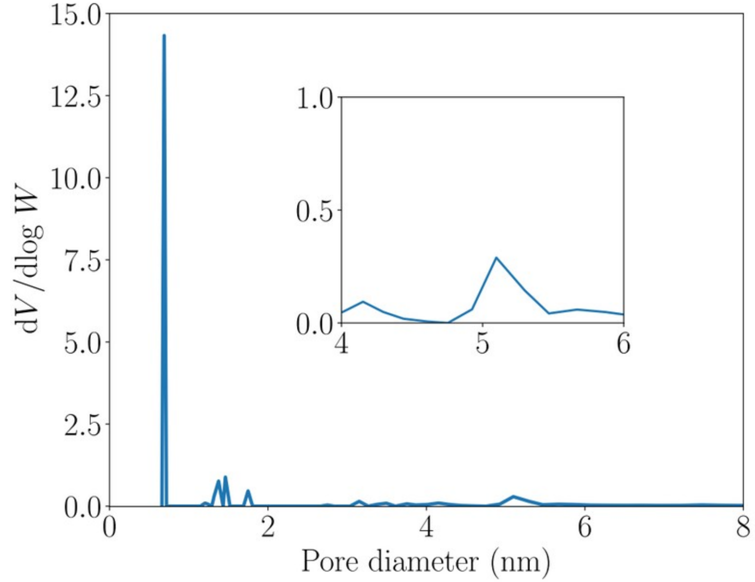
DFT

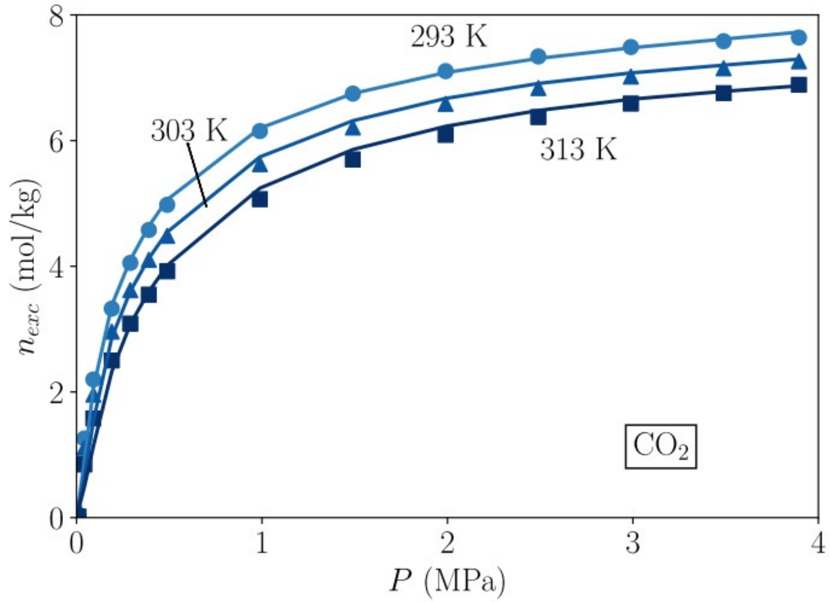
Density field

No-code available

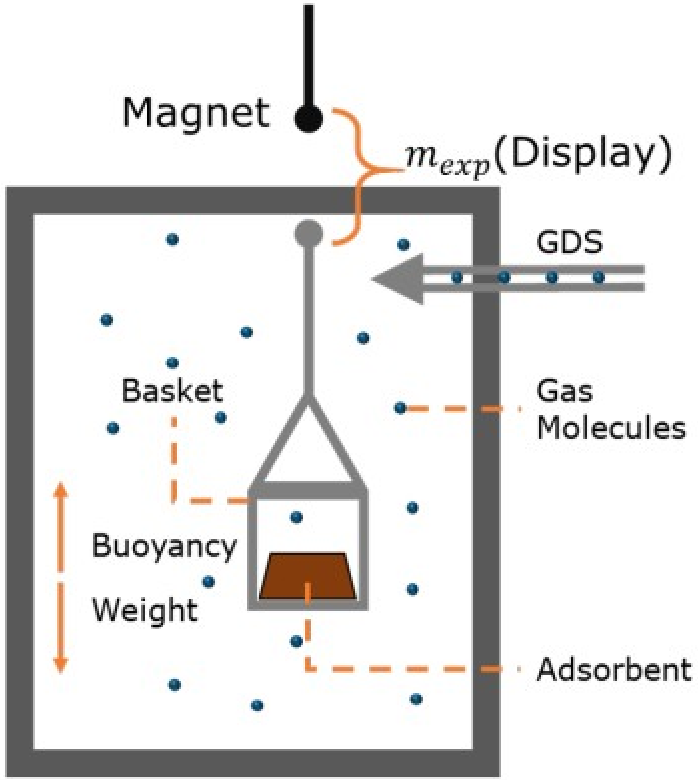
Main Problem



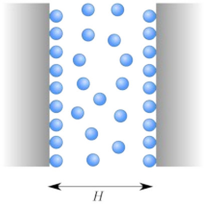


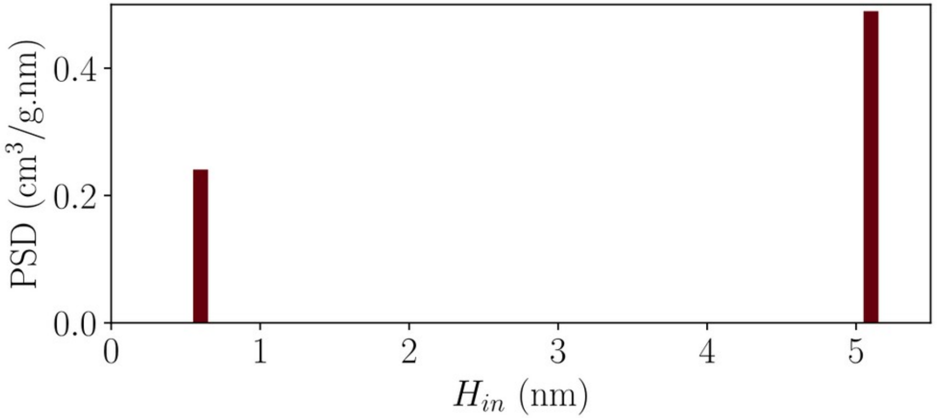


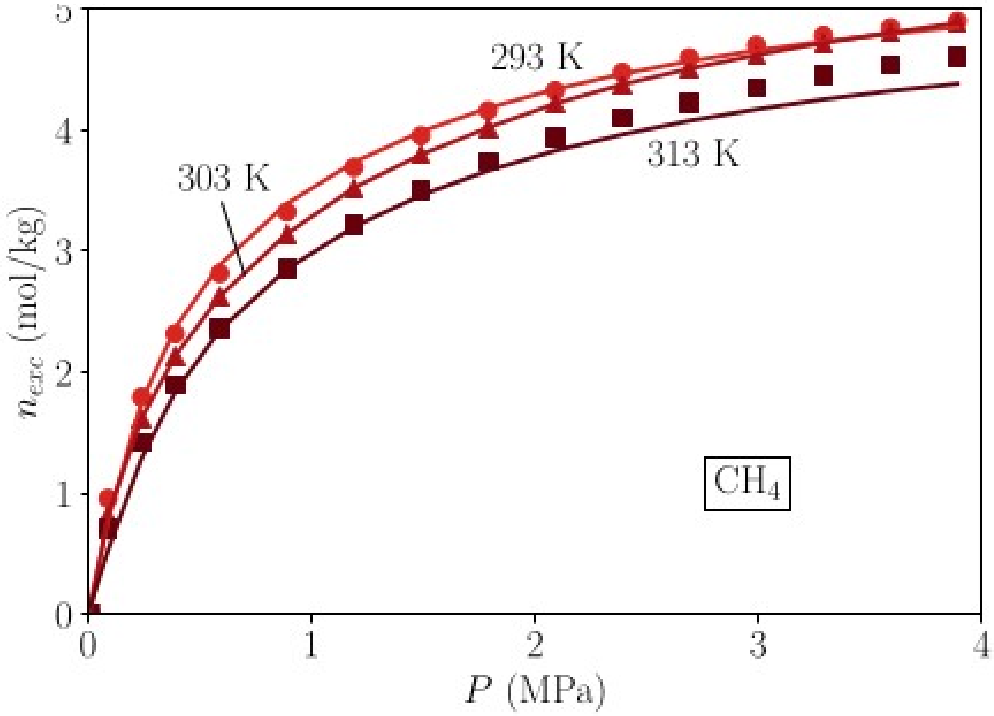
Adsorption in Activated carbon



PCP-SAFT

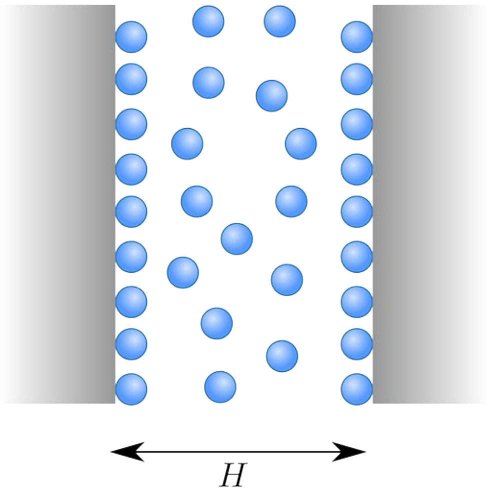


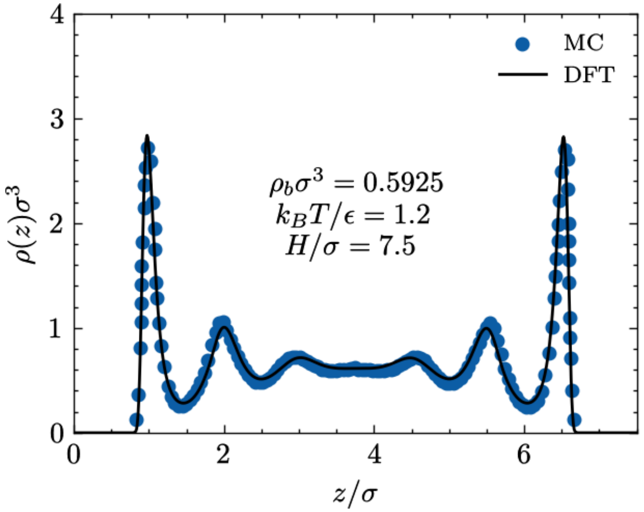


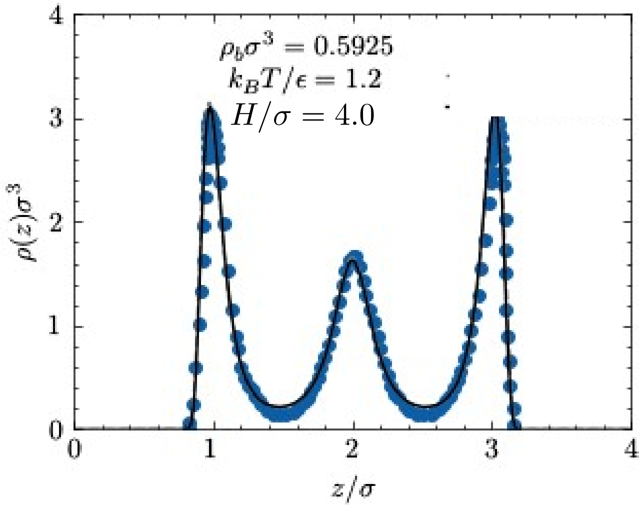


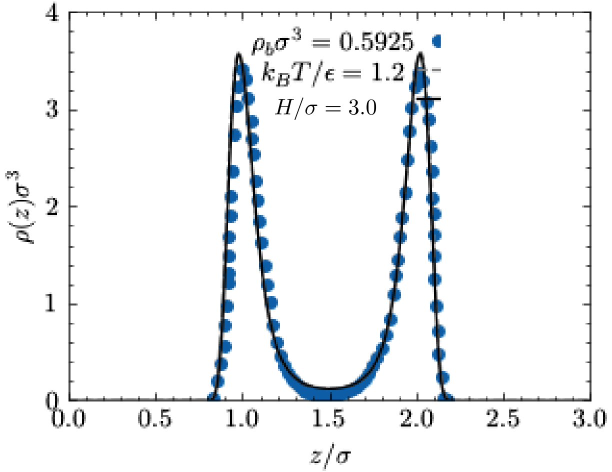
Sermoud, V. M., Barbosa, G. D., Soares, E. do A., et al (2022). Chemical Engineering Science, 247, 116905.

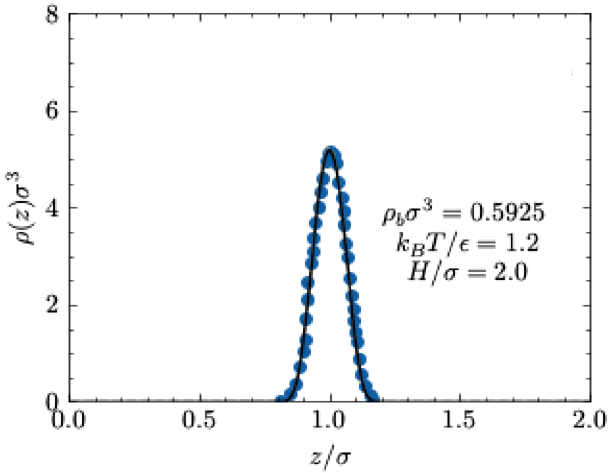
LJ Fluid Inside a Slitlike Carbon Pore

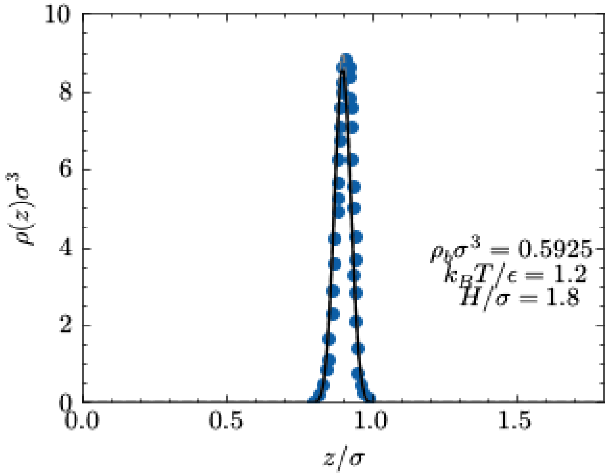










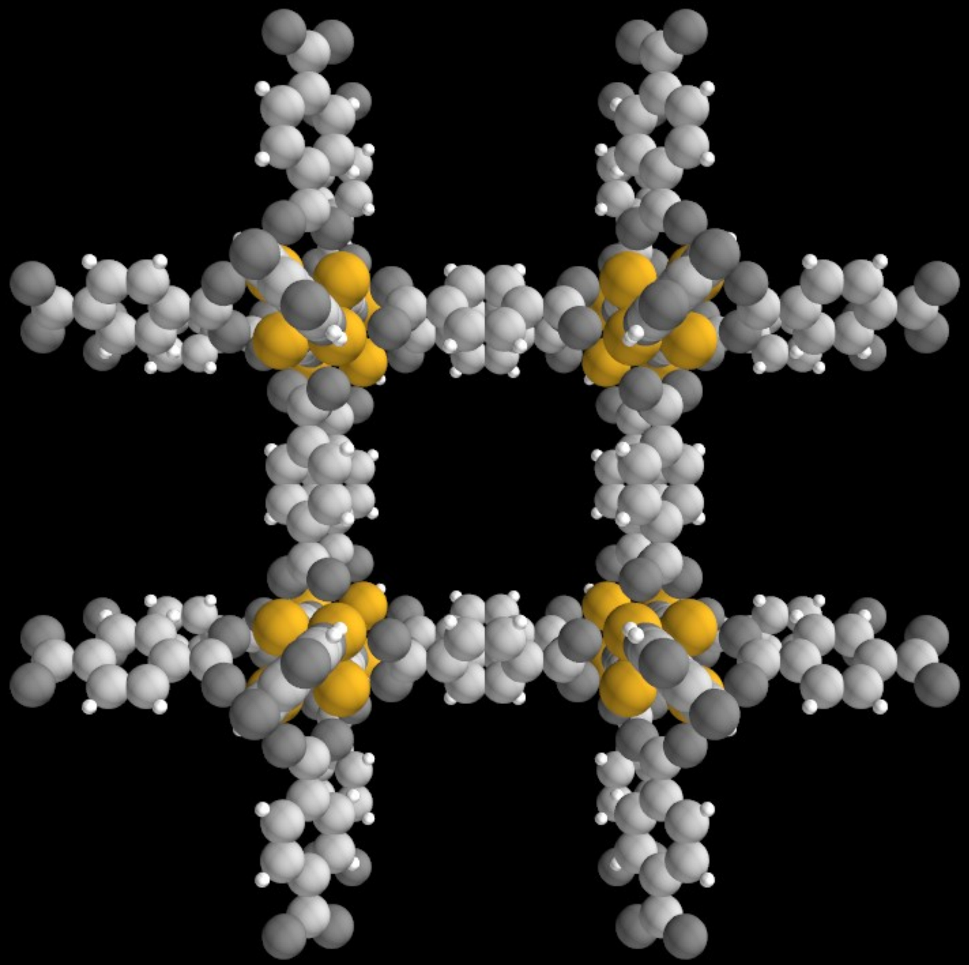


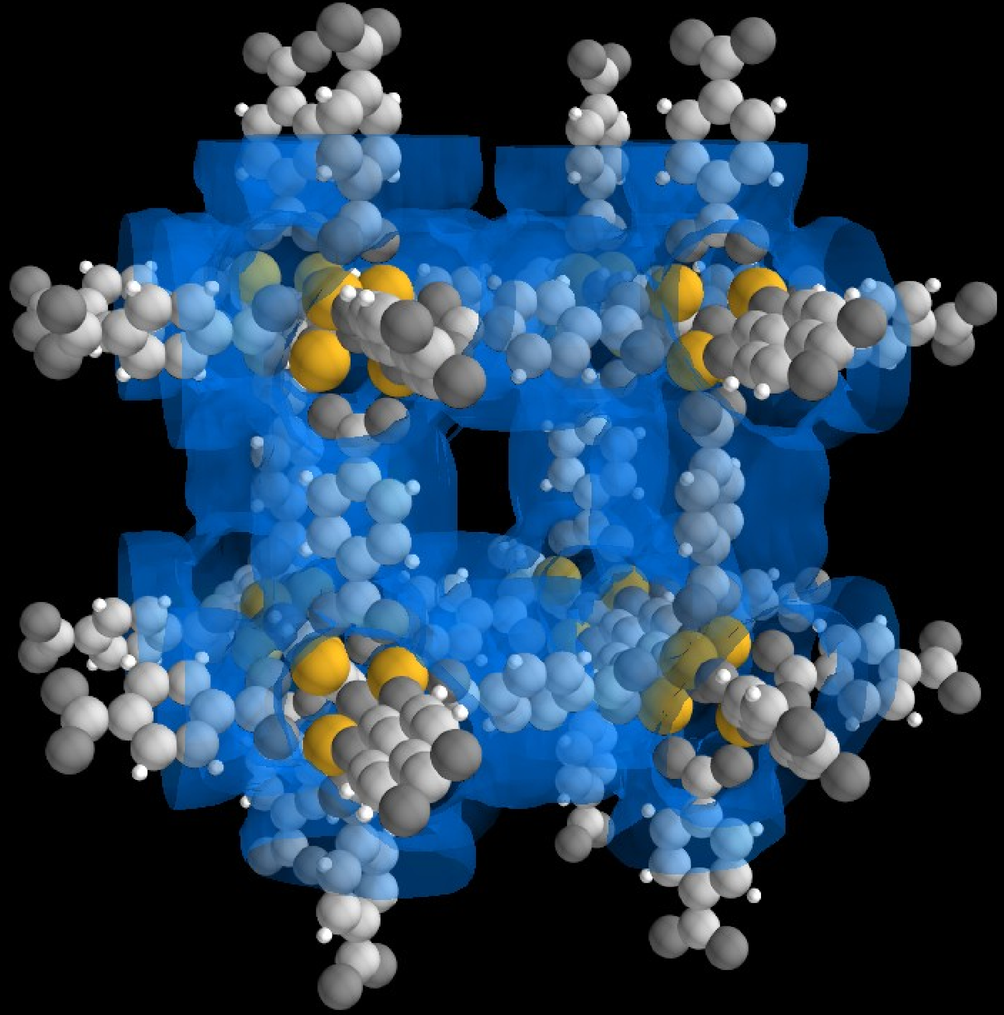
Snook, I. K., & van Megen, W. (1980). The Journal of Chemical Physics, 72(5), 2907-2913

H_2 Adsorption on MOF-5

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

$\rho = 0.001$ Å^{-3}





But Could we do something more simpler?

Classical Density Functional Theory

Grand Potential

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

External potential acts as a chemical potential

Free Energy Functional

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

Particle-particle interaction

Equilibrium

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

Equilibrium Condition

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

Adsorbed Quantity

$$N_{\text{ads}} = \int_V \mathrm{d}\boldsymbol{r}\,\rho(\boldsymbol{r})$$

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

WHAT CAN WE DO WITH CLASSICAL DFT?

Fluid Equation of State

vdW, GvdW, LJ,
PC-SAFT,...

Free-energy Functionals

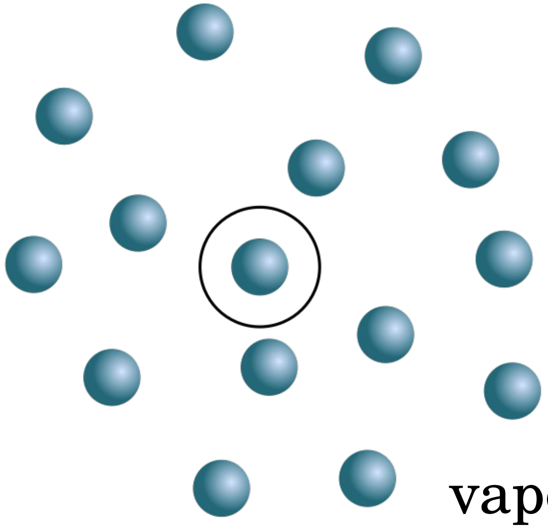
LDA,FMT, MFA, WDA,
MMFA, FMSA, ...

Confined fluid EOS

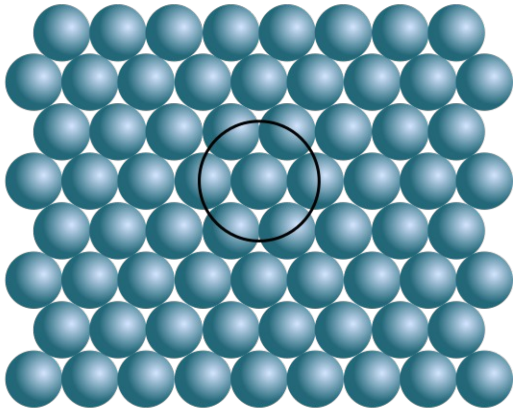
TRAVALONI, BARBOSA,...

Little approximations give Big reparametrization of the fluid-solid characteristics

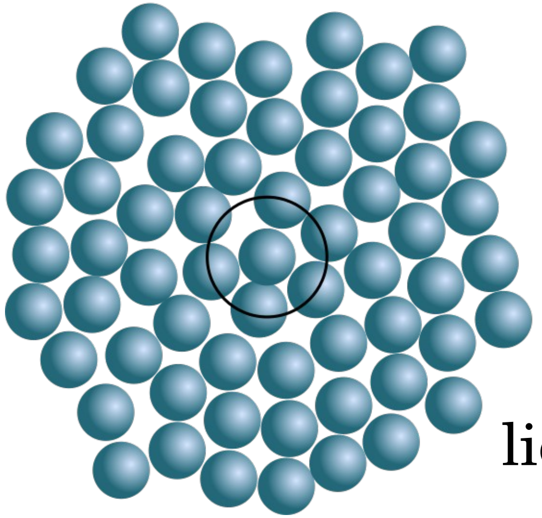
Lennard-Jones Fluids



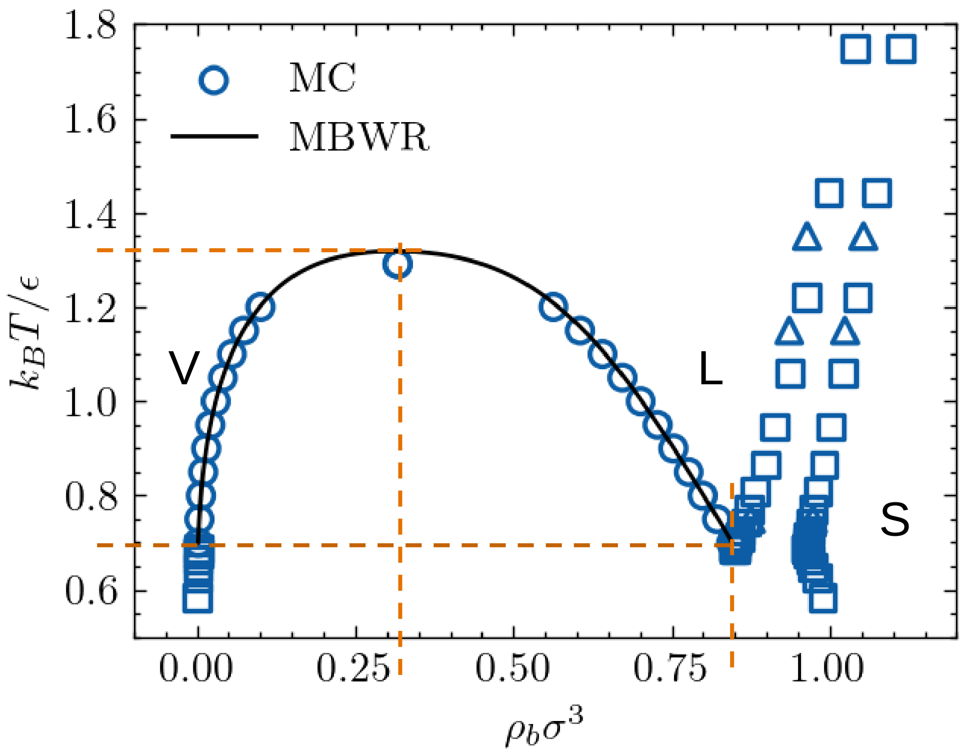
vapor



solid



liquid



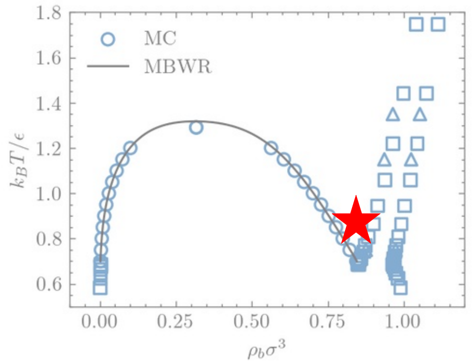
Lennard-Jones potential

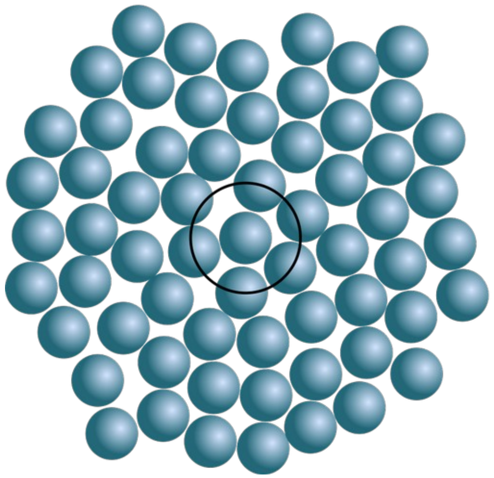
$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

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).

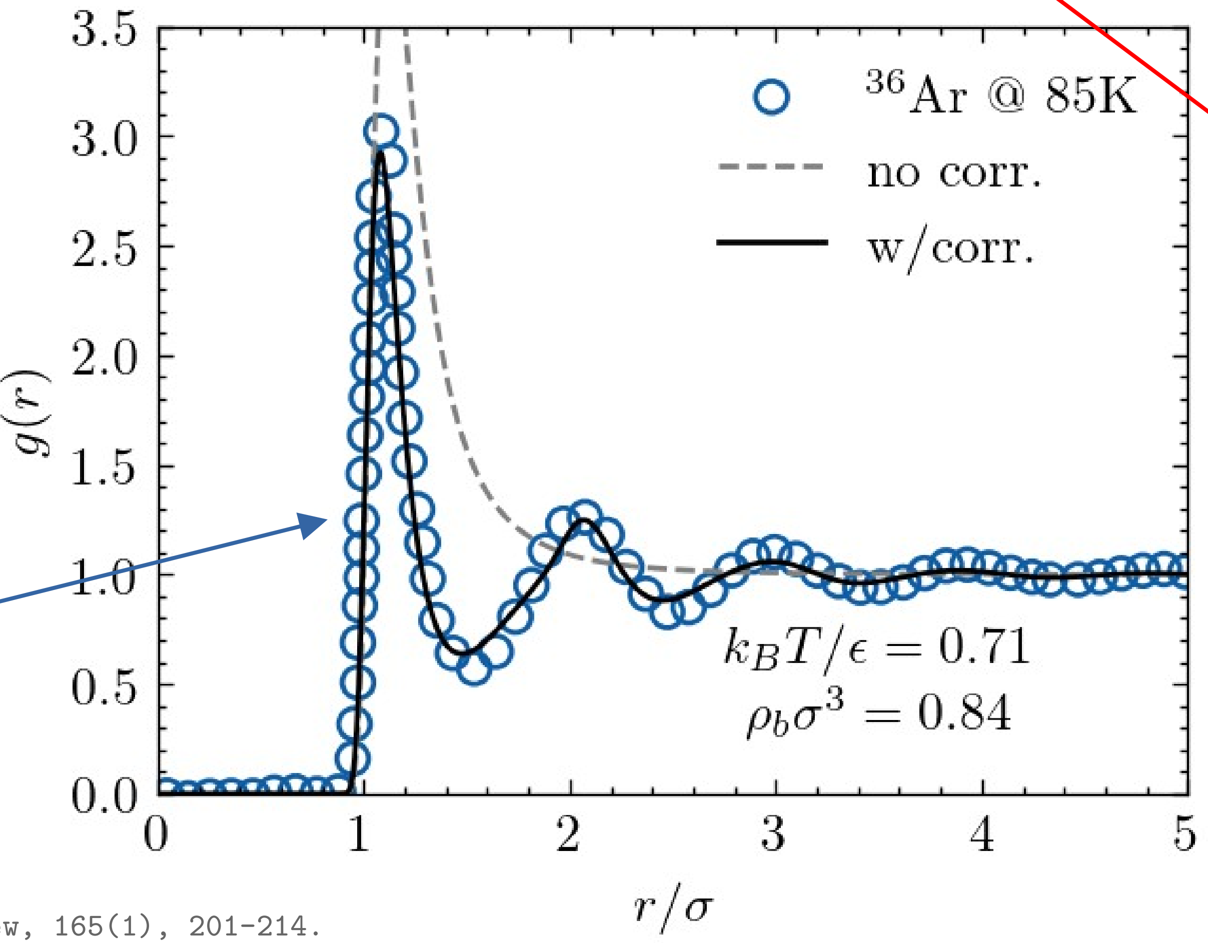
Radial Distribution Function

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





liquid



Data from X-Ray Experiment

Density Correlations are very important!

Non-local DFT

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

Gradient Expansion to describe Density Profiles

Gradient Expansion

Relative Density deviation

$$\rho(\boldsymbol{r}) = \rho_b(1 + \psi(\boldsymbol{r}))$$

Excess free-energy functional

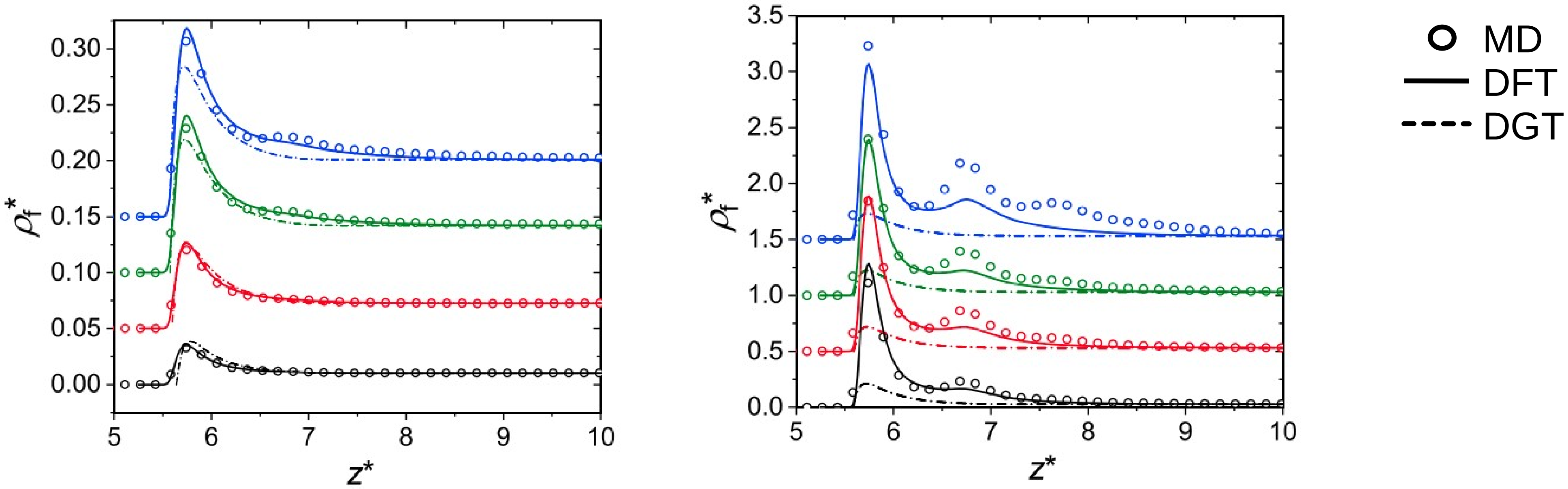
$$\tilde{c}^{(2)}(\boldsymbol{k}) = \tilde{c}_0^{(2)} + \tilde{c}_2^{(2)}\boldsymbol{k}^2 + \tilde{c}_4^{(2)}\boldsymbol{k}^4 + \cdots \longrightarrow c^{(2)}(\boldsymbol{r}) = c_0^{(2)} + c_2^{(2)}\nabla^2 + c_4^{(2)}\nabla^4 + \cdots$$

$$F_{\mathrm{exc}}[T,\rho] = F_{\mathrm{exc}}^{(0)} - \frac{\rho_0}{2}k_B T \int \mathrm{d}\boldsymbol{r}\left(B_1\psi^2 + B_2\psi\nabla^2\psi + B_3\psi\nabla^4\psi\right)$$

Emmerich et al. (2012). Advances in Physics, 61(6), 665-743.

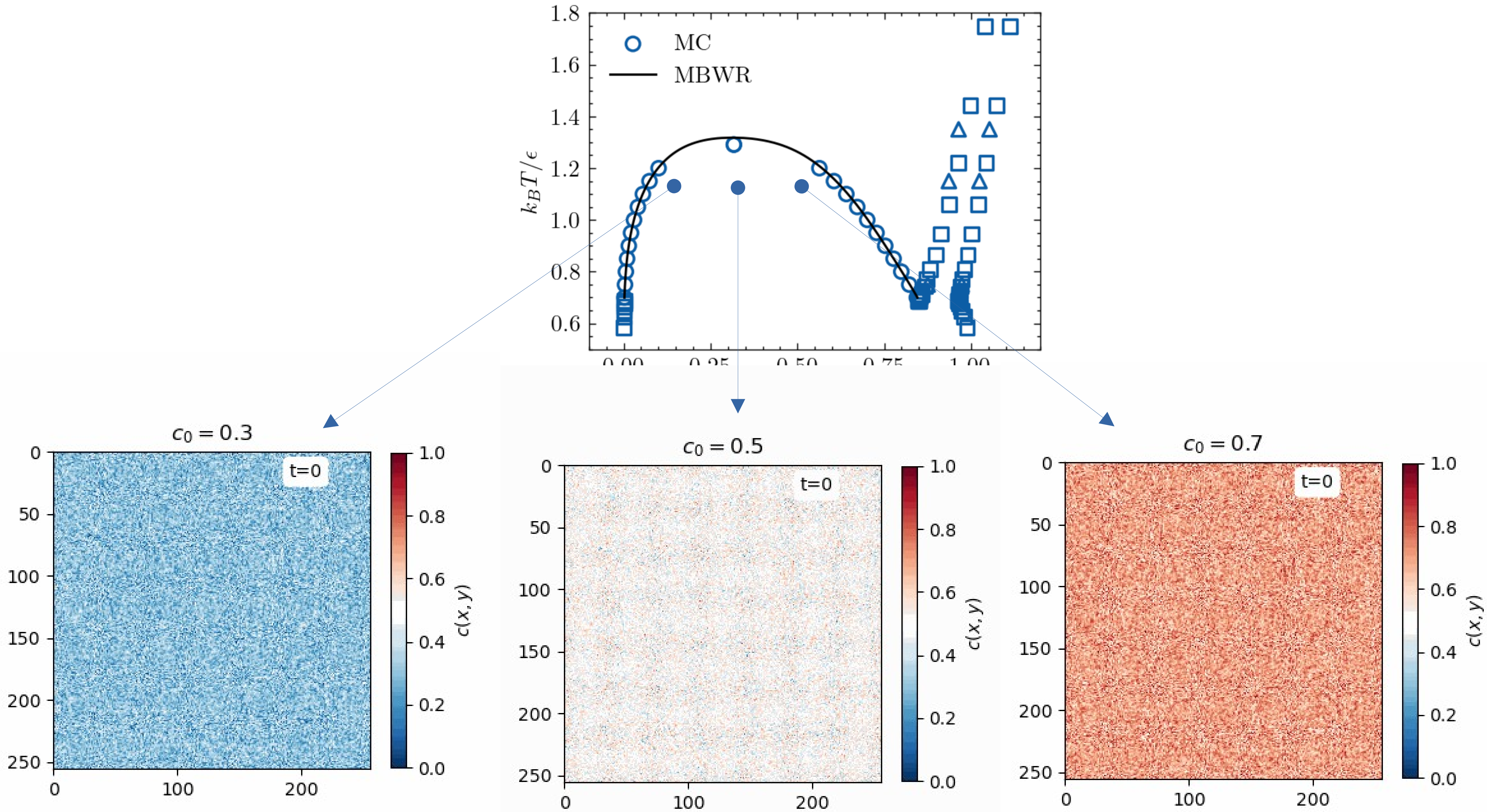
First Order Gradient Expansion = Density Gradient Theory

$$F_{\mathrm{exc}} = \int_V \mathrm{d}\boldsymbol{r} \left[f_{\mathrm{exc}}(\rho(\boldsymbol{r})) + B_2 (\nabla \rho(\boldsymbol{r}))^2 \right]$$



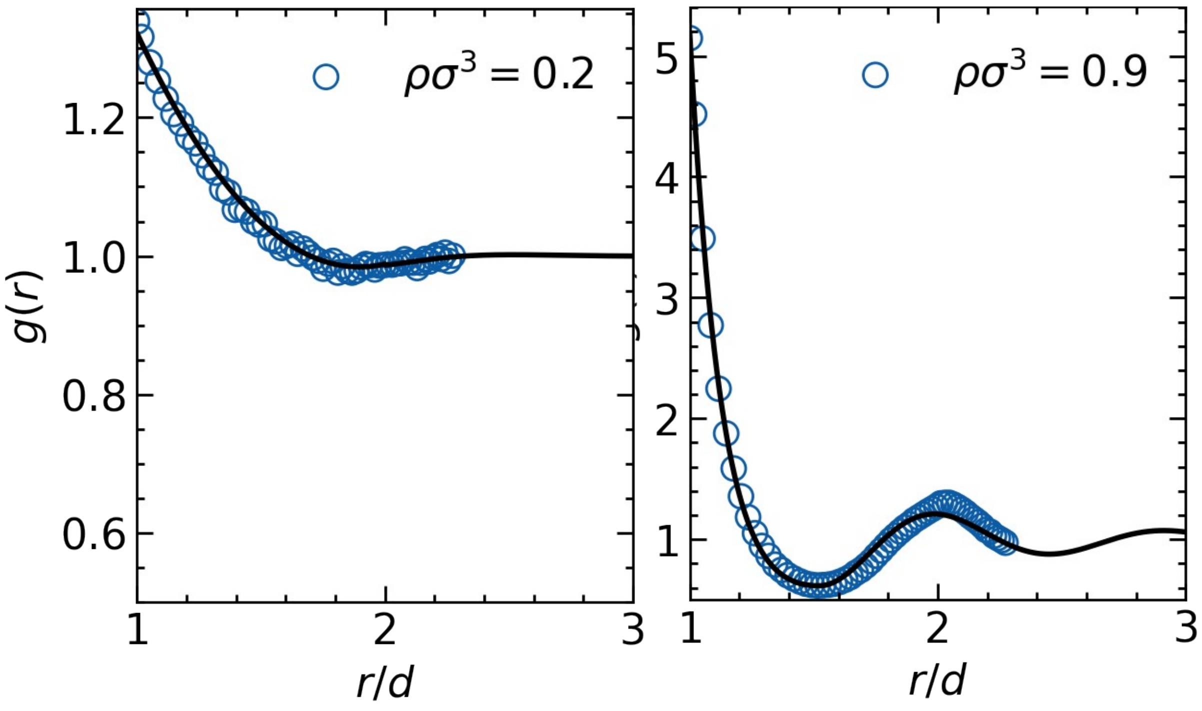
Liu, J., Heier, M., Chapman, W. G., & Langenbach, K. (2019).Journal of Chemical & Engineering Data, 65(3), 1222-1233.

Phase separation Dynamics



Second Order Gradient Expansion

$$F_{\mathrm{exc}} = \int_V \mathrm{d}\boldsymbol{r} \left[f_{\mathrm{exc}}(\rho(\boldsymbol{r})) + B_2(\nabla\rho(\boldsymbol{r}))^2 + B_4(\nabla^2\rho(\boldsymbol{r}))^4 \right]$$



The considered analytic representation of $g(r)$ is thus given by a superposition of the two functional forms given by Eqs. (11) and (13),

$$\begin{aligned} g(r) &= 0 \quad \text{for } r < \sigma \\ &= g^{\mathrm{dep}}(r) \quad \text{for } \sigma \leqslant r \leqslant r^\star \\ &= g^{\mathrm{str}}(r) \quad \text{for } r \geqslant r^\star. \end{aligned} \tag{14}$$

Here

$$g^{\mathrm{dep}}(r) = \frac{A}{r} e^{\mu[r-\sigma]} + \frac{B}{r} \cos(\beta[r-\sigma] + \gamma) e^{\alpha[r-\sigma]}, \tag{15}$$

and will be referred to as a *depletion* part of the RDF, and

$$g^{\mathrm{str}}(r) = 1 + \frac{C}{r} \cos(\omega r + \delta) e^{-\kappa r}, \tag{16}$$

Trokhymchuk, A., Nezbeda, I., Jirsák, J., & Henderson, D. (2005). The Journal of Chemical Physics, 123(2), 024501.

Density Profile Basis

$$F_{\text{exc}} = \int_V \mathrm{d}\boldsymbol{r} \left[f_{\text{exc}}(\rho(\boldsymbol{r})) + B_2(\nabla\rho(\boldsymbol{r}))^2 + B_4(\nabla^2\rho(\boldsymbol{r}))^4 \right]$$

$\Downarrow$

4^{th} order Ordinary Differential Equation

$\Downarrow$

$$\rho(z) = \rho_b + \sum_{n=1}^{4} c_n e^{-k_n z} \cos(\omega_n z + \phi_n)$$

Integral Quantities for Confined Fluids EOS

Adsorption Isotherms

Grand Potential

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

$$N_{\mathrm{ads}} = \int_V \mathrm{d}\boldsymbol{r}\,\rho(\boldsymbol{r})$$

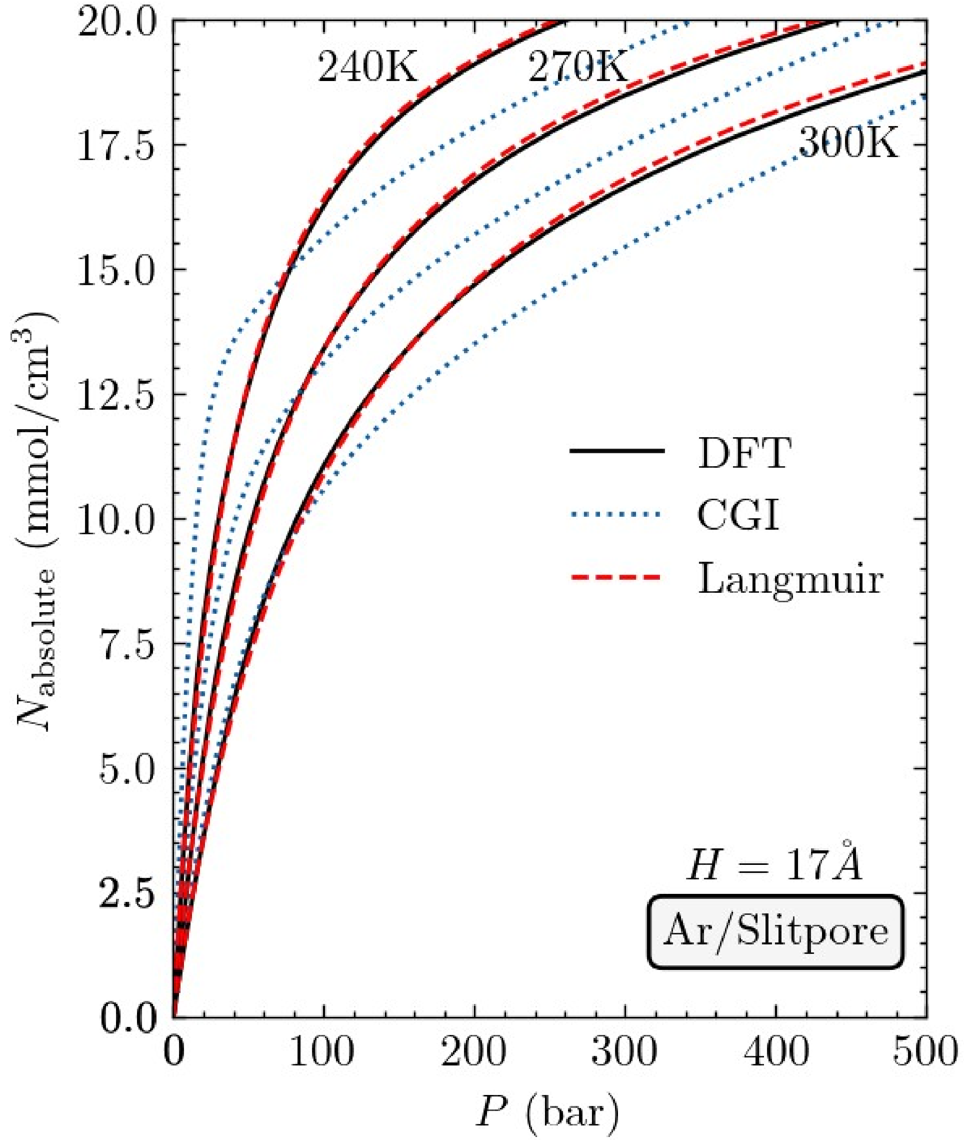
$$\langle X \rangle = \frac{1}{N_{\mathrm{ads}}} \int_V \mathrm{d}\boldsymbol{r}\,\rho(\boldsymbol{r}) X(\boldsymbol{r})$$

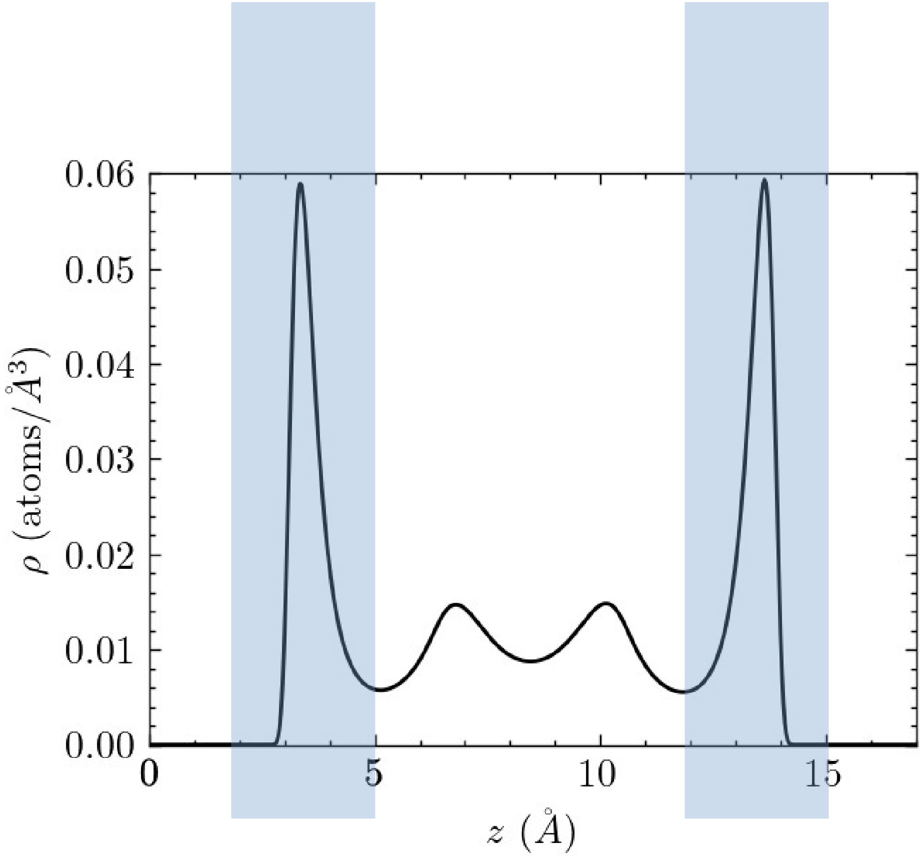
$$\frac{\langle F \rangle}{N_{\mathrm{ads}}} = \mu - \langle V_{\mathrm{ext}} \rangle + \omega \longrightarrow k_B T \ln(N_{\mathrm{ads}}) - k_B T \ln(N_* - N_{\mathrm{ads}}) = \mu - \langle V_{\mathrm{ext}} \rangle + \omega$$

Integral Langmuir-like Isotherm

$$\frac{N_{\mathrm{ads}}}{N_*} = \frac{e^{\beta\mu - \beta\langle V_{\mathrm{ext}} \rangle + \beta\omega}}{1 + e^{\beta\mu - \beta\langle V_{\mathrm{ext}} \rangle + \beta\omega}}$$

Adsorption Isotherms with Steele Potentuial



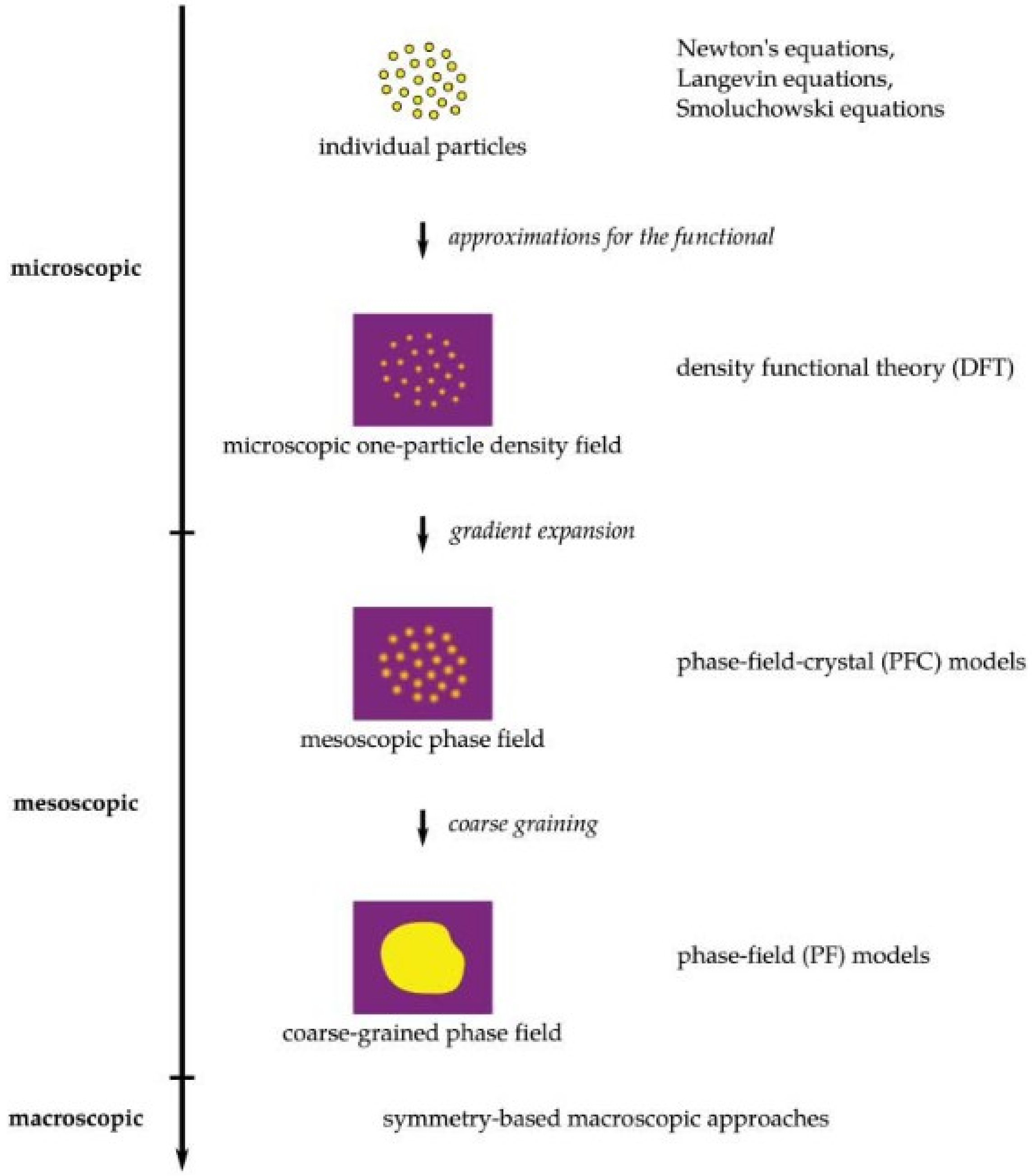


Conclusions and Perspectives

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);

- **Could we measure other quantities on confined fluids**?! (Profile vs. Isotherm)



Acknowledgments

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Back-Up Slides

Ornstein-Zernike Equation

$$h(r) = g(r) - 1 = c(r) + \rho \int c(|\boldsymbol{r} - \boldsymbol{r}'|)h(r')\,\mathrm{d}^3 r'$$

Relation with pair potential

Closure relations:

- **RPA** (**R**andom **P**hase **A**pproximation)**:** $c(r) = -\beta u(r)$
-
- **MSA** (**M**ean-**S**pherical **A**pproximation): $c(r) = \begin{cases} g(r)(1 - e^{-\beta u(r)}), r < \sigma \\ -\beta u(r), r > \sigma \end{cases}$
- **PY** (**P**ercus-**Y**evic): $c(r) = (1 - e^{-\beta u(r)})(h(r) + 1)$
- **HNC** (**H**yperne**t**ed-**C**hain) $c(r) = -\beta u(r) + h(r) - \ln(1 + h(r))$
- SCOZA, SMSA, HMSA, RY, ...

C. Caccamo, Integral Equation Theory Description of Phase Equilibriain Classical Fluids, Physics Report 274, 1-105 (1996).