UFRJ

Applied Thermodynamics and Molecular Simulation

ATOMS

Termodinâmica Aplicada e Simulação Molecular

From micro to macro:
Applied Theory of Liquids and Colloids

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ATOMS Group

Applied Thermodynamics and Molecular Simulation

ATOMS

Termodinâmica Aplicada e Simulação Molecular

Prof. Frederico W. Tavares

Prof. Amaro Gomes Barreto Jr.

Prof. Papa M. Ndiaye

Prof. Carla L. Manske Camargo

4 professors
10 postdocs
~32 PhD students
~13 MsC students
~20 ICs students

http://atoms.peq.coppe.ufrj.br/

Facilities

Applied Thermodynamics and Molecular Simulation
ATOMS
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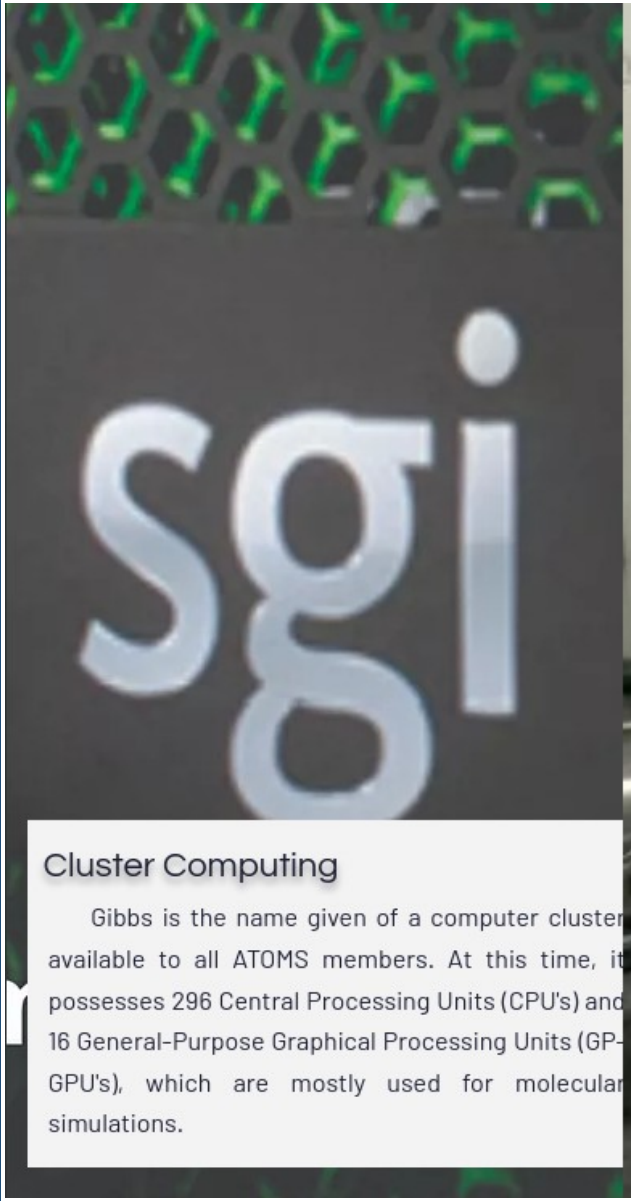


Cluster Computing

Gibbs is the name given of a computer cluster available to all ATOMS members. At this time, it possesses 296 Central Processing Units (CPU's) and 16 General-Purpose Graphical Processing Units (GP-GPU's), which are mostly used for molecular simulations.

HPF

The High Pressure Fluid equilibrium cell. It is used to observe phase transitions at pressure conditions up to 1000 bar.

SMB

The Simulated Moving Bed pilot plant. It is used to separation of enantiomers using adsorption technology.

Crystallization analyzer

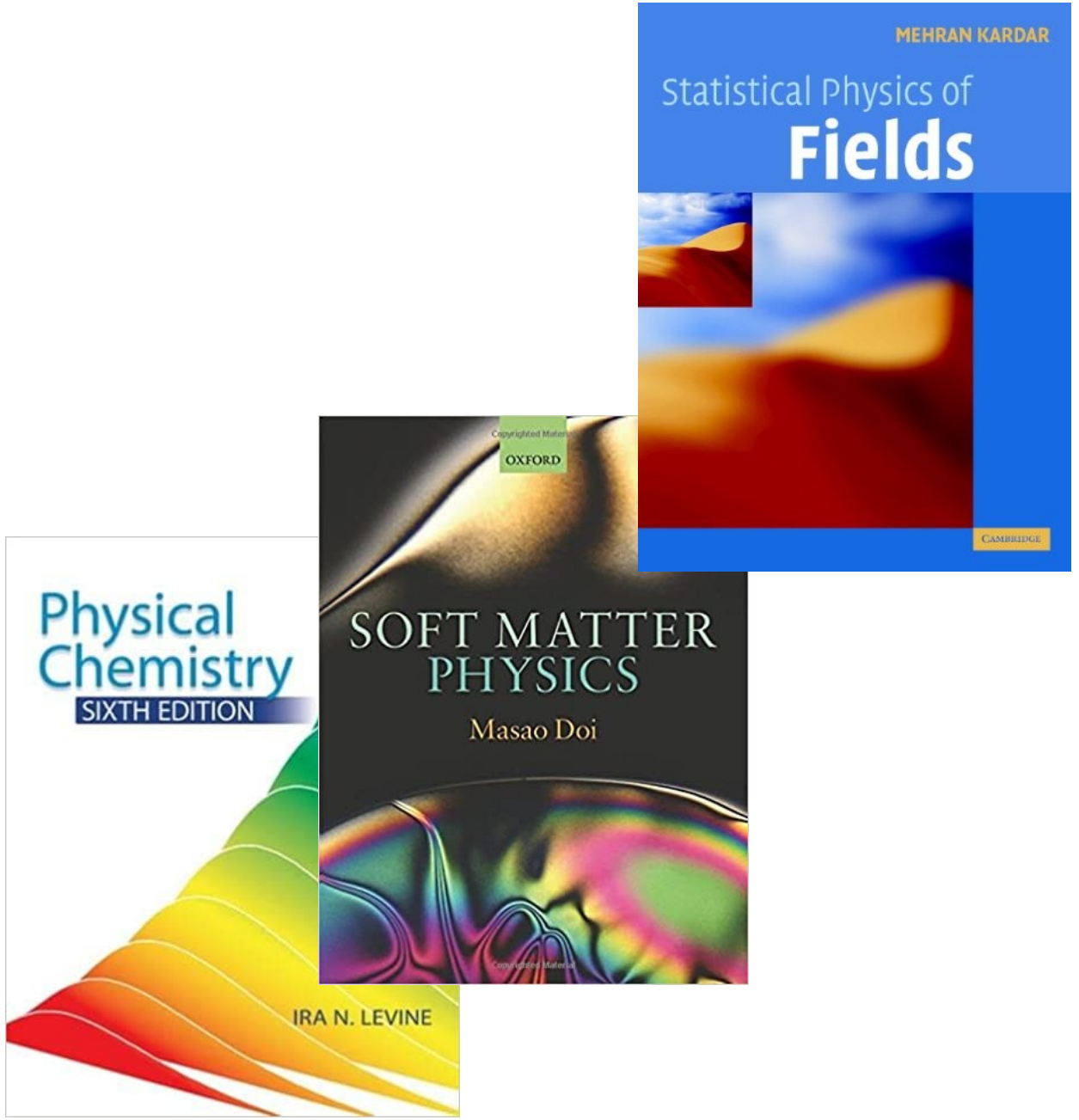
The Crystallization analyzer. It is used to observe particle size distribution in crystallization processes.

Research Areas

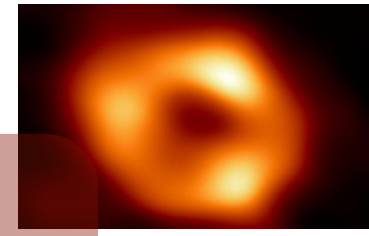
- **Thermodynamics and Structure of Confined Fluids**
- Thermodynamics and Kinetics of Gas Hydrates
- Organic and **Inorganic Precipitation and Deposition**
- **Structure-Property Relations of Complex Materials**
- Lattice Boltzmann Methods for Fluids in Porous Materials

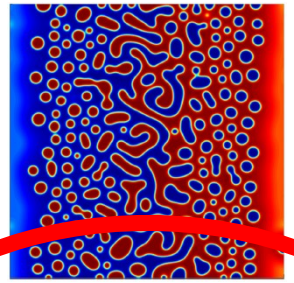
My Research Areas

- Thermodynamics
- Statistical Mechanics
- Transport Processes
- Gases, Liquids and Solids
- Electrochemical Systems
- Soft Matter Physics
- Statistical Theory of Fields



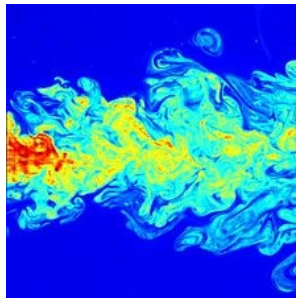
Multi-Scale Modelling





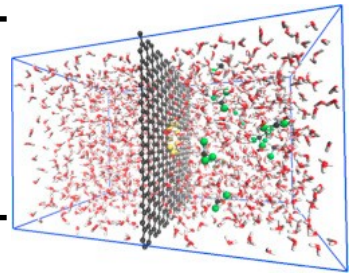
Macroscopic Models

Thermodynamics
Hydrodynamics



Continuum medium Models

Poisson Bolztmann,
DFT,
Phase Field



Mesoscopic Dynamics

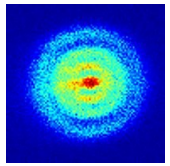
Lattice Boltzmann,
DPD

Molecular Dynamics

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

Quantum Mechanics

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



$\tau(s)$

10^{3}

1

10^{-3}

10^{-6}

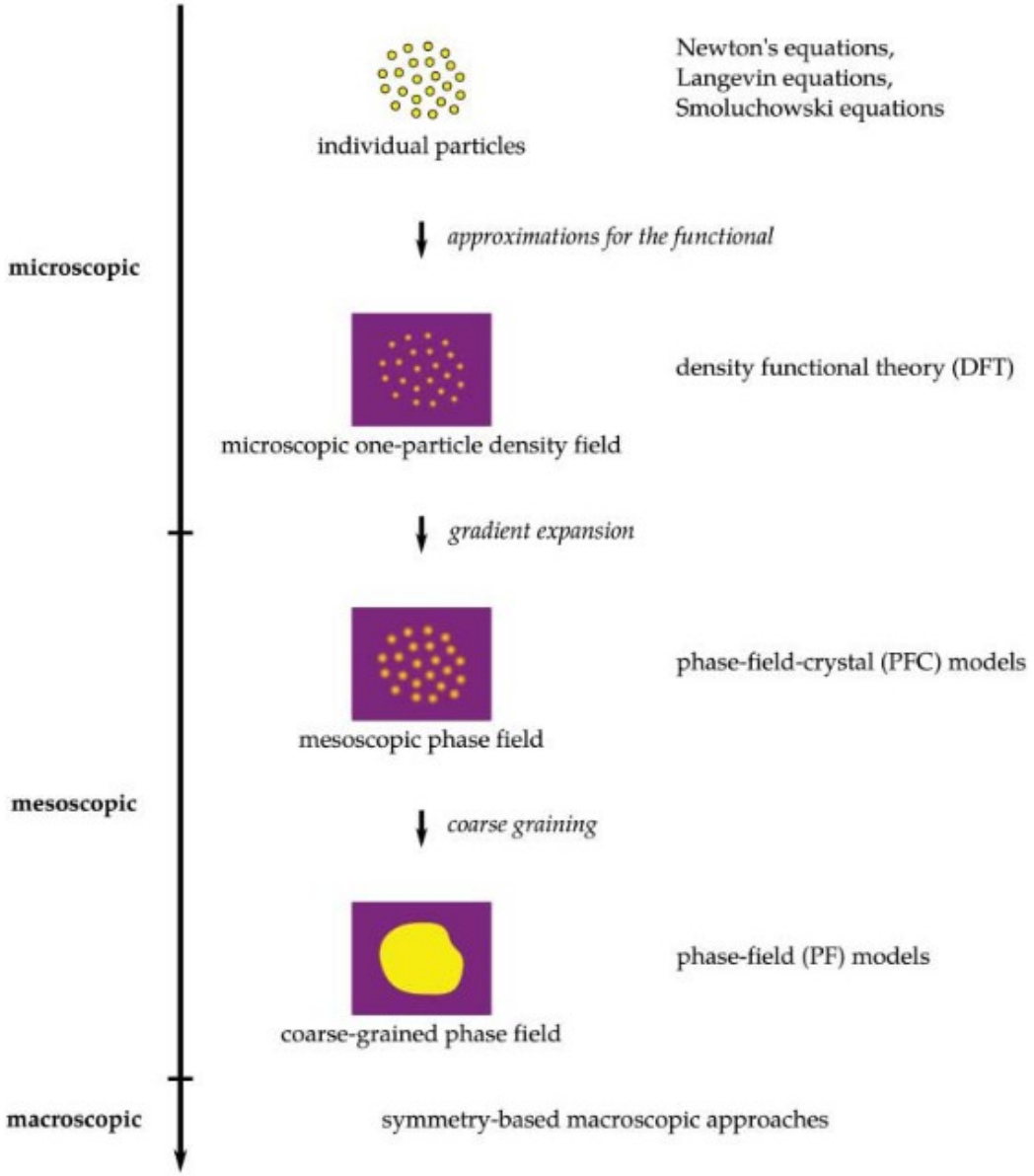
10^{-9}

10^{-12}

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

"More is different"
(Anderson, Paul)

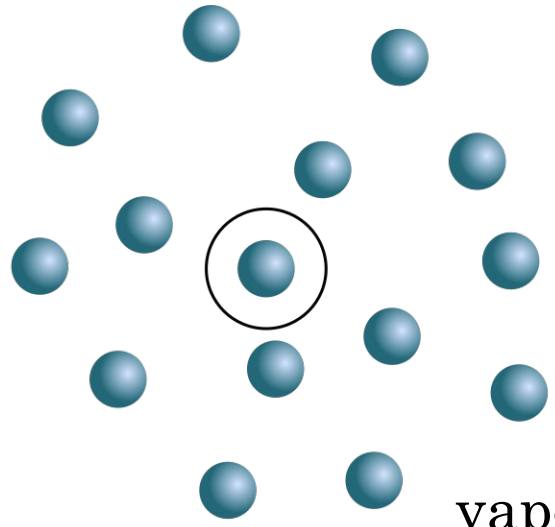
Classical DFT as Bridge between Length Scales



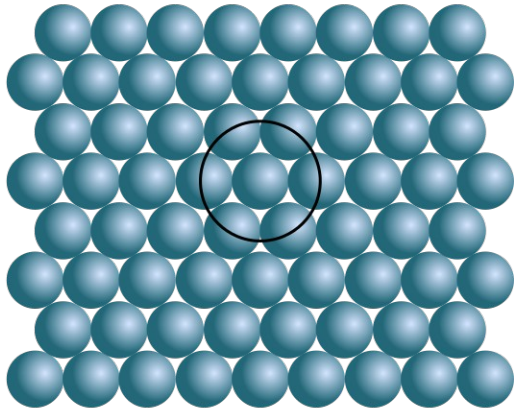
Emmerich et al. - Advances in Physics, 61(6), 665-743 (2012)

Density Functional Theory

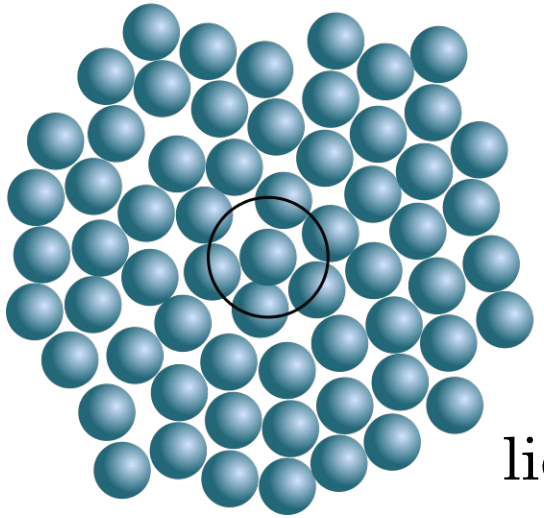
Theory of Liquids



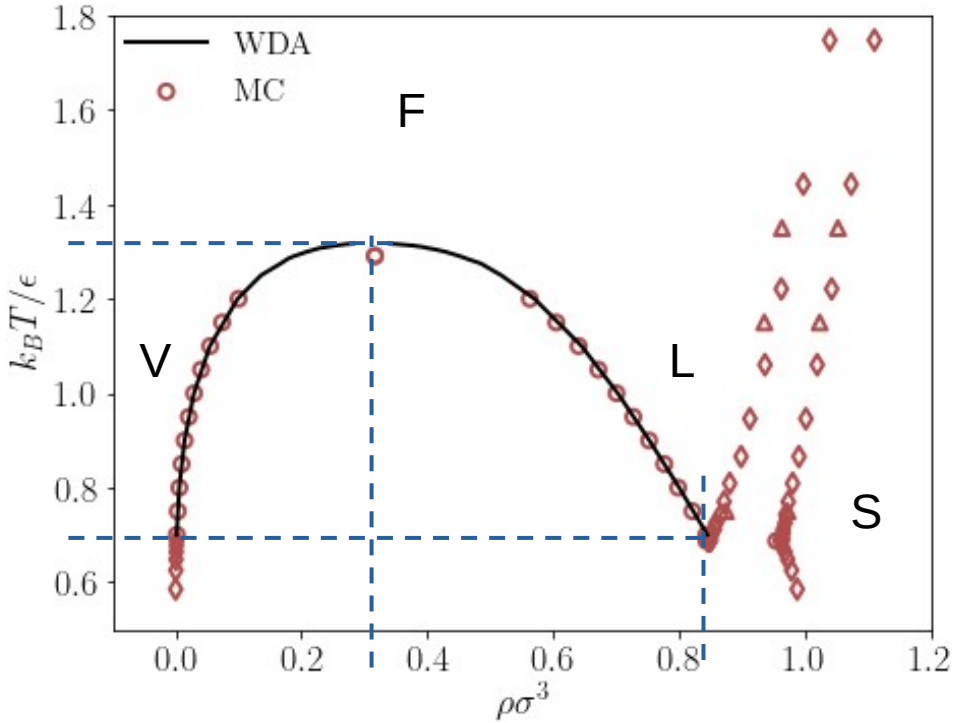
vapor



solid



liquid

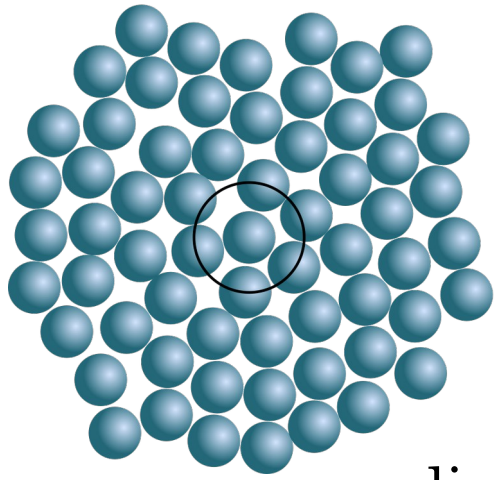


Lennard-Jones fluid

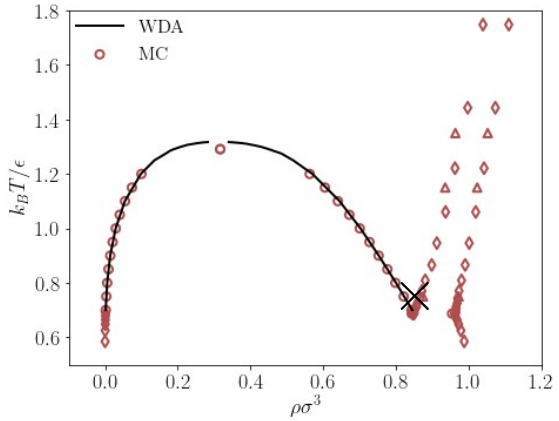
$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Hansen, J.P. and McDonald, I.R., 2013. Theory of simple liquids: with applications to soft matter. Academic press.

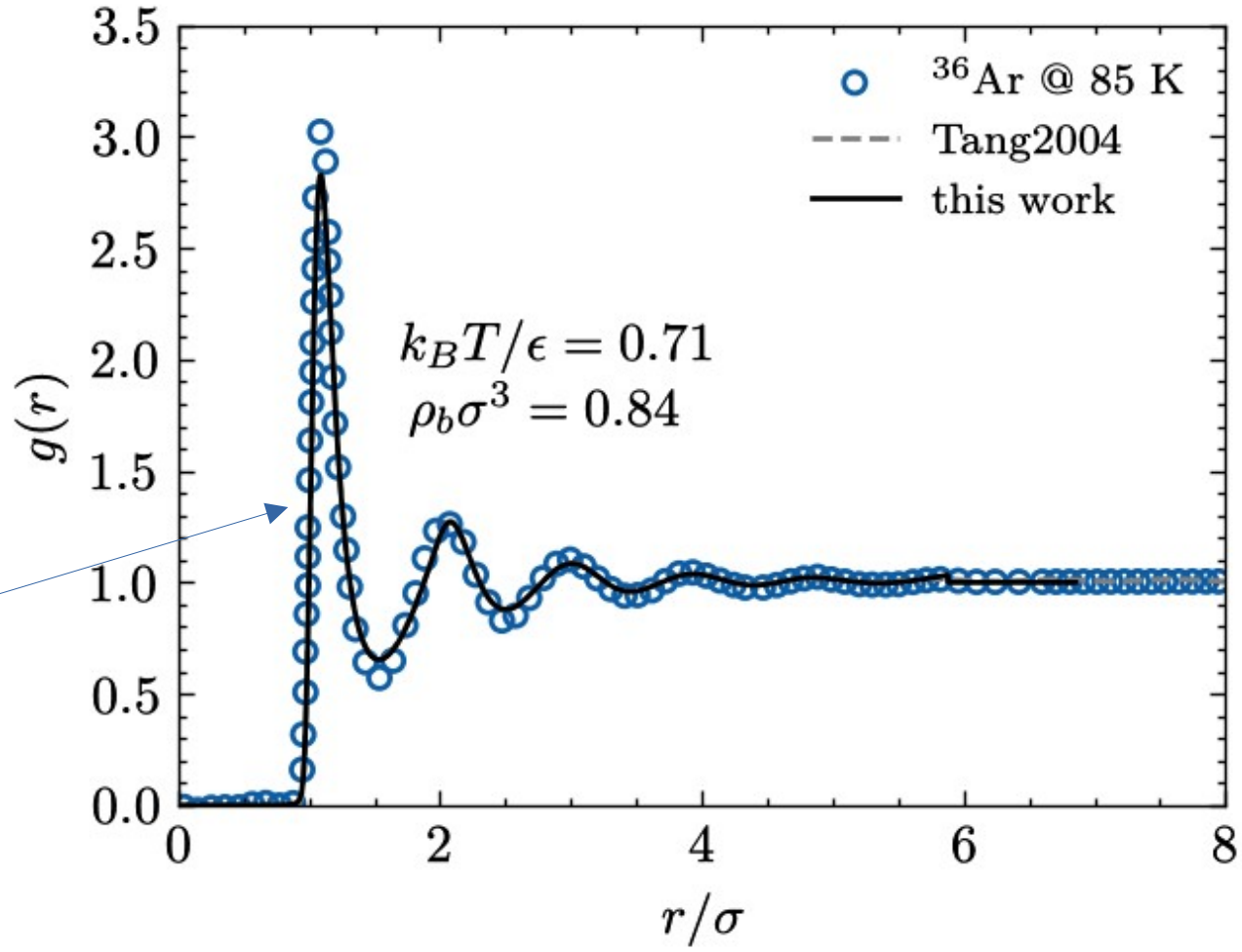
Radial Distribution Function



liquid



Data from X-Ray Experiment



Verlet, L. (1968). Physical Review, 165(

Statistical Theory of Liquids

Partition Functions

$$Q(N,T,V) = \frac{1}{N!}\frac{Z_N}{\Lambda^{3N}}$$

$$Z_N = \int \cdots \int e^{-\beta U_N(\boldsymbol{r}^N)}\, \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_N$$

Helmholtz Free-energy

$$F = -k_B T \ln Q$$

$$\Xi(V,T,\mu) = \sum_{N=0}^{\infty} Q(N,T,V) e^{\beta\mu N}$$

Grand Canonical Potential

$$\Omega = -k_B T \ln \Xi = F - \mu N$$

Density Distributions

$$\rho(\boldsymbol{r}) = \frac{N}{Z_N} \int \cdots \int e^{-\beta U_N(\boldsymbol{r}^N)}\, \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_{N-1} = \rho$$

$$\rho^{(2)}(\boldsymbol{r},\boldsymbol{r}') = \frac{N(N-1)}{Z_N} \int \cdots \int e^{-\beta U_N(\boldsymbol{r}^N)}\, \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_{N-2} = \rho^2 g(r)$$

Virial/Cluster Expansion, Integral Equations Theory, Perturbation Theory

McQuarrie, D.A., 2000. Statistical mechanics. Sterling Publishing Company.

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

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

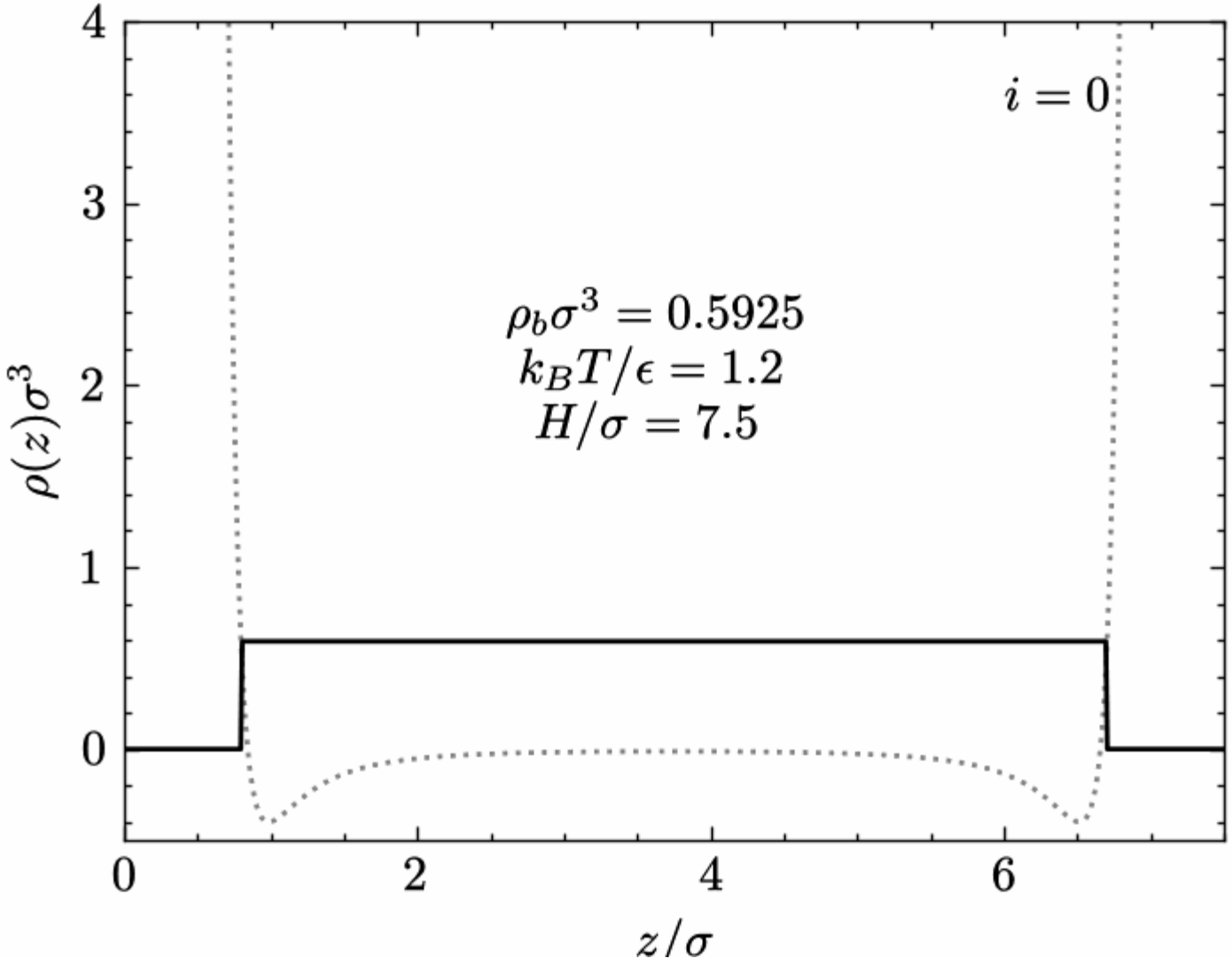
$$F_{\mathrm{id}}[T,\rho] = k_B T \int \mathrm{d}\boldsymbol{r}\,\rho(\boldsymbol{r})[\ln\left(\Lambda^3\rho(\boldsymbol{r})\right) - 1]$$

Equilibrium Condition

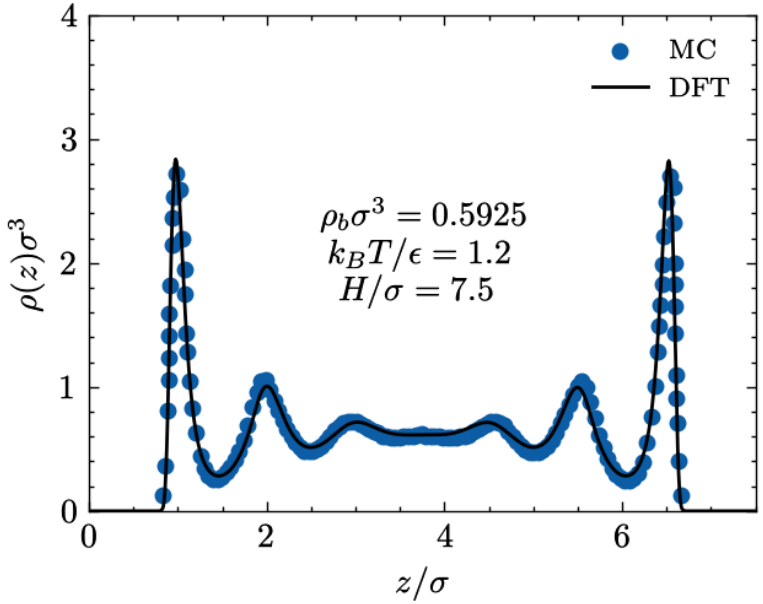
$$\left.\frac{\delta\Omega}{\delta\rho(\boldsymbol{r})}\right|_{V,\mu,T} = k_B T \ln\left(\Lambda^3\rho(\boldsymbol{r})\right) + \frac{\delta F_{\mathrm{exc}}}{\delta\rho(\boldsymbol{r})} + V_{\mathrm{ext}}(\boldsymbol{r}) - \mu = 0$$

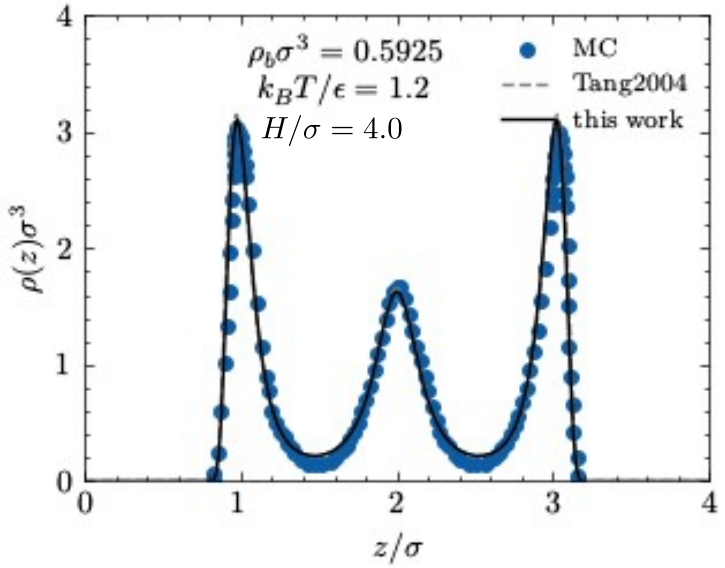
Wu, J., & Li, Z. Annual Review of Physical Chemistry, 58(1), 85-112. (2007)

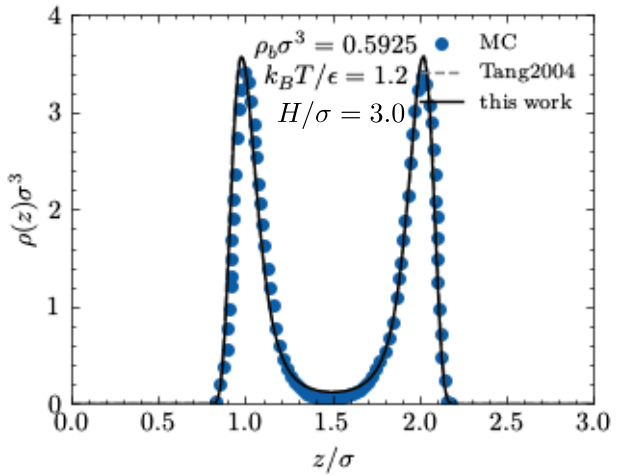
Fluid under external potential

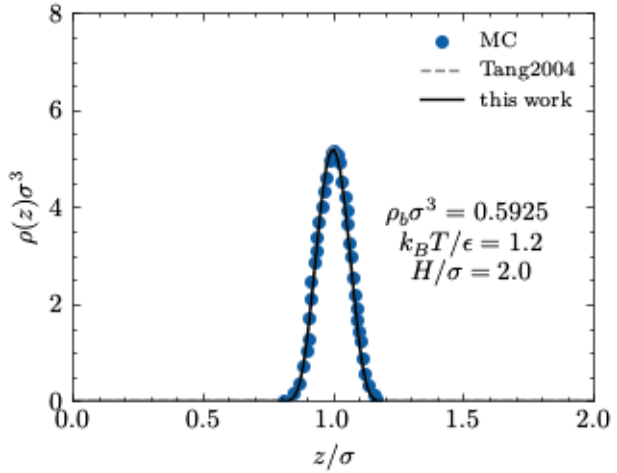


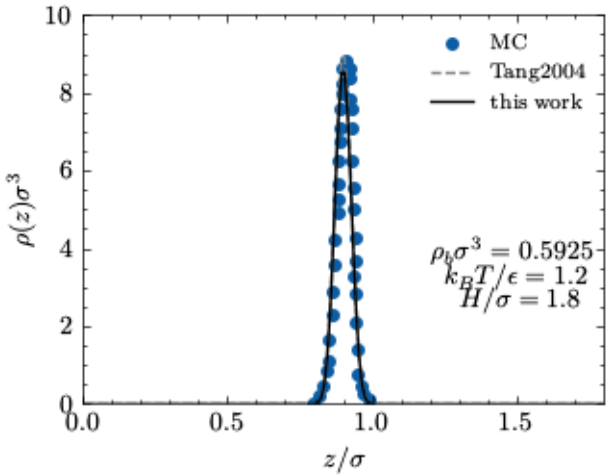
Fluid under external potential











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.

Excess free-energy

$$F_{\text{exc}}[\rho(\boldsymbol{r})] = F_{\text{hs}}[\rho(\boldsymbol{r})] + F_{\text{att}}[\rho(\boldsymbol{r})]$$

Accounts for the size and interaction effects

1- Perturbation Theories

$$F_{\text{att}}[T,\rho] = \frac{1}{2}\int_0^1 \mathrm{d}\lambda \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}'\, \rho(\boldsymbol{r})\rho(\boldsymbol{r}')u(|\boldsymbol{r}-\boldsymbol{r}'|)g(|\boldsymbol{r}-\boldsymbol{r}'|;\rho,T,\lambda)$$

2- Taylor's expansion

$$F_{\text{att}}[T,\rho] = F_{\text{att}}(\rho_{\text{ref}}) - \int \mathrm{d}\boldsymbol{r}\, c^{(1)}(\boldsymbol{r})[\rho(\boldsymbol{r}) - \rho_{\text{ref}}]$$
$$-\frac{1}{2}\int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}'\, [\rho(\boldsymbol{r}) - \rho_{\text{ref}}]c^{(2)}(\boldsymbol{r}-\boldsymbol{r}')[\rho(\boldsymbol{r}') - \rho_{\text{ref}}]$$

$$\lim_{\rho\to 0} c^{(2)}(\boldsymbol{r}-\boldsymbol{r}') = -\beta u(\boldsymbol{r}-\boldsymbol{r}')$$

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

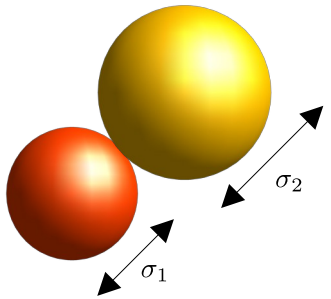
The Hard-Spheres Free-Energy

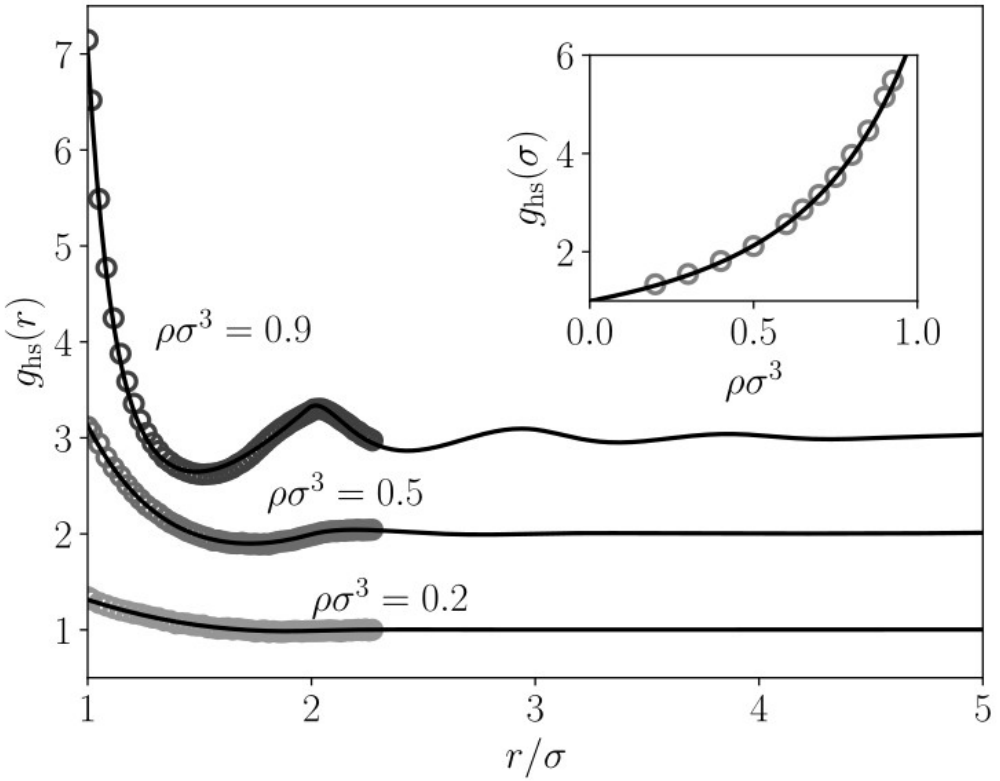
Fundamental Measure Theory

$$\beta F_{\rm hs}[\rho(\boldsymbol{r})] = \int \mathrm{d}\boldsymbol{r}\left\{f_1(n_3)n_0 + f_2(n_3)(n_1n_2 - \boldsymbol{n}_{v1}\cdot\boldsymbol{n}_{v2}) + f_3(n_3)(n_2^3 - 3n_2\boldsymbol{n}_{v2}\cdot\boldsymbol{n}_{v2})\right\}$$

Weigthed densities

$$n_\alpha(\boldsymbol{r}) \equiv \int \mathrm{d}\boldsymbol{r}'\,\rho_i(\boldsymbol{r}')\omega_\alpha^{(i)}(\boldsymbol{r}-\boldsymbol{r}')$$





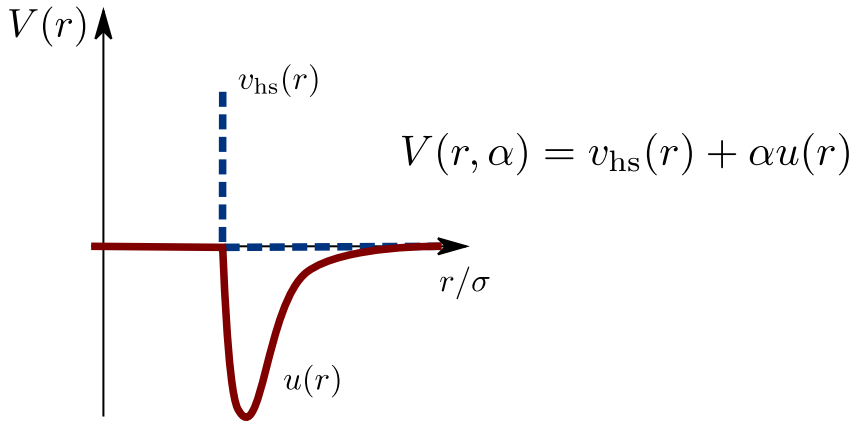
Weight functions

$$\omega_3(\boldsymbol{r}) = \Theta(\sigma/2 - |\boldsymbol{r}|),$$
$$\omega_2(\boldsymbol{r}) = |\boldsymbol{\nabla}\Theta(\sigma/2 - |\boldsymbol{r}|)| = \delta(\sigma/2 - |\boldsymbol{r}|),$$
$$\boldsymbol{\omega}_{v2}(\boldsymbol{r}) = \boldsymbol{\nabla}\Theta(\sigma/2 - |\boldsymbol{r}|) = \frac{\boldsymbol{r}}{r}\delta(\sigma/2 - |\boldsymbol{r}|),$$

com $\omega^{(0)}(\boldsymbol{r}) = \omega^{(2)}(\boldsymbol{r})/\pi\sigma^2, \omega^{(1)}(\boldsymbol{r}) = \omega^{(2)}(\boldsymbol{r})/2\pi\sigma$ e $\boldsymbol{\omega}^{(v1)}(\boldsymbol{r}) = \boldsymbol{\omega}^{(v2)}(\boldsymbol{r})/2\pi\sigma$.

Y. Rosenfeld, Phys. Rev. Lett., vol. 63, no. 9, pp. 980-983, Aug. 1989
Roth, R. (2010). Journal of Physics: Condensed Matter, 22(6), 063102.

Perturbation Theories



$$V(r,\alpha) = v_{\rm hs}(r) + \alpha u(r)$$

$$\frac{F_{\rm pert}}{N} = 2\pi\rho \int_0^\infty {\rm d}r\, r^2 u(r) \int_0^1 {\rm d}\alpha\, g(r;\rho,T,\alpha)$$

Taylor's expansion in the coupling parameter

$$\int_0^1 {\rm d}\alpha\, g(r;\rho,T,\alpha) = \sum_{n=1}^{\infty} \frac{1}{(n-1)!} \int_0^1 \alpha^{n-1} \left.\frac{\partial^{n-1} g(r;\rho,T,\alpha)}{\partial \alpha^{n-1}}\right|_{\alpha=0} {\rm d}\alpha$$

Coupling Parameter Expansion PT

$$\frac{F^{(1)}_{\rm SCPT}}{N} = 2\pi\rho \int_0^\infty {\rm d}r\, r^2 u(r) g_{\rm hs}(r;\rho)$$

$$\frac{F^{(2)}_{\rm SCPT}}{N} = \pi\rho \int_0^\infty {\rm d}r\, r^2 u(r) \left.\frac{\partial g(r;\rho,T,\alpha)}{\partial \alpha}\right|_{\alpha=0}$$

Barker-Henderson PT

$$\frac{F^{(1)}_{\rm BH}}{N} = 2\pi\rho \int_0^\infty {\rm d}r\, r^2 u(r) g_{\rm hs}(r;\rho)$$

$$\frac{F^{(2)}_{\rm BH}}{N} = -\pi\beta\rho\kappa_{\rm hs}(\rho) \frac{\partial}{\partial\rho}\left[\rho \int_0^\infty {\rm d}r\, r^2 [u(r)]^2 g_{\rm hs}(r;\rho)\right]$$

S. Zhou, Physical Review E 74, 031119 (2006).
S. Zhou, The Journal of Chemical Physics 125, 144518 (2006).
J. A. Barker and D. Henderson, The Journal of Chemical Physics 47, 2856-2861 (1967).
J. A. Barker and D. Henderson, The Journal of Chemical Physics 47, 4714-4721 (1967).

Self-consistent Perturbation Theory from DFT

Pair Potential

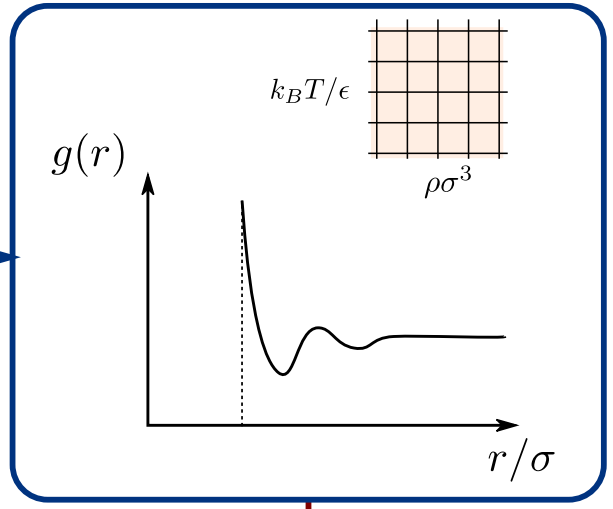
$$V(r) = v_{\mathrm{hs}}(r) + u(r)$$

$$g(\boldsymbol{r}) = e^{-\beta V(\boldsymbol{r})} e^{-\beta[\frac{\delta F_{\mathrm{exc}}}{\delta \rho(\boldsymbol{r})} - \mu_{\mathrm{exc}}]}$$

First Order DFT

$$F_{\mathrm{exc}}[\rho] = F_{\mathrm{hs}}[\rho] + F_{(1)}[\rho]$$

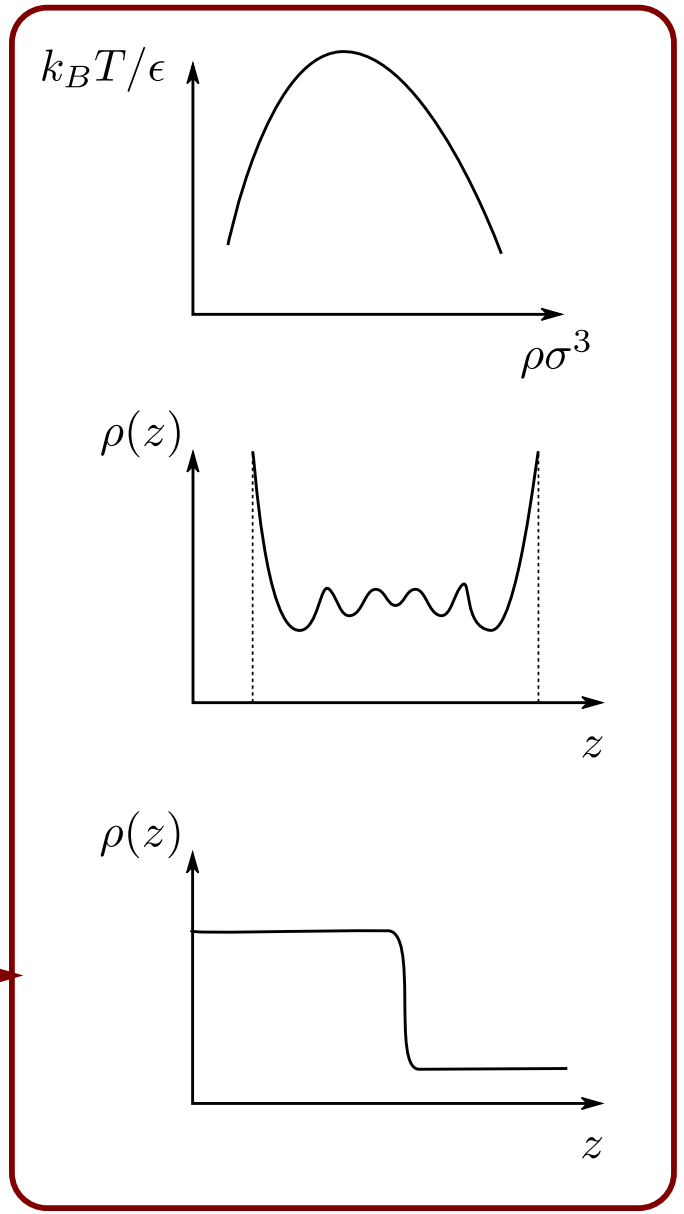
$$\frac{F_{(1)}}{N} = 2\pi\rho \int_0^\infty \mathrm{d}r\, r^2 u(r) g_{\mathrm{hs}}(r;\rho)$$



$$\frac{F_{(2)}}{N} = \pi\rho \int_0^\infty \mathrm{d}r\, r^2 u(r) \left.\frac{\partial g(r;\rho,T,\alpha)}{\partial \alpha}\right|_{\alpha=0}$$

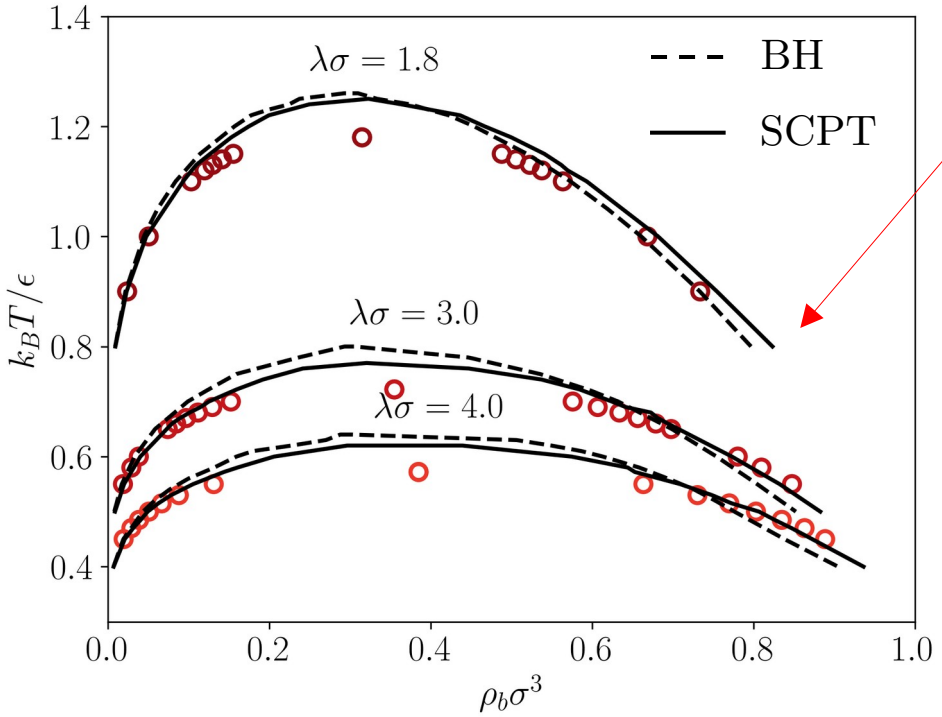
Second Order DFT

$$F_{\mathrm{exc}}[\rho] = F_{\mathrm{hs}}[\rho] + F_{(1)}[\rho] + F_{(2)}[\rho]$$

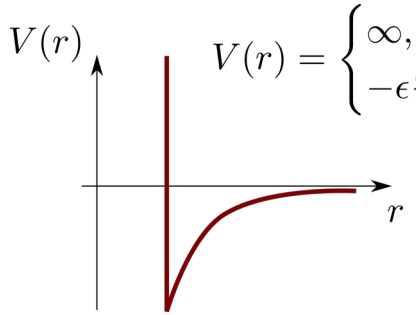


Soares, E., Barreto, A., & Tavares, F. (2021). Fluid Phase Equilibria, 542-543, 113095.

Phase Diagrams of Fluids

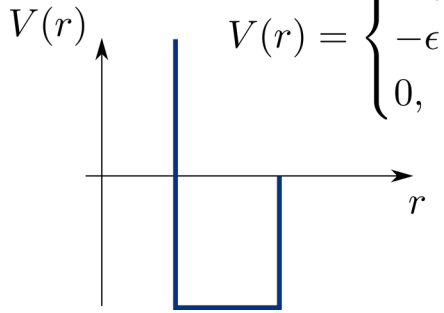


Yukawa fluid

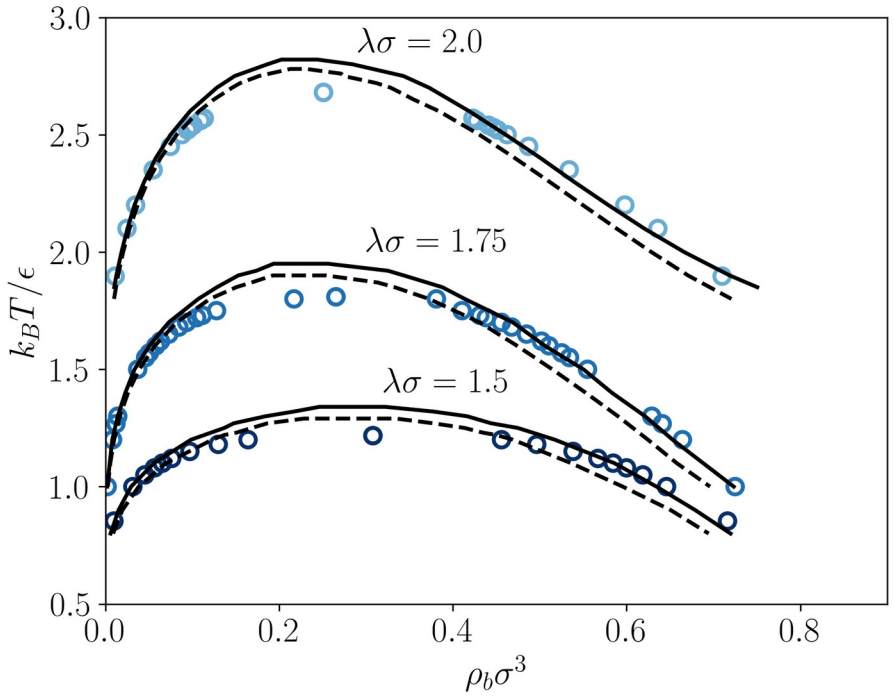


$$V(r) = \begin{cases} \infty, & r \leq \sigma \\ -\epsilon \frac{e^{-\lambda(r-\sigma)}}{r}, & r > \sigma \end{cases}$$

Square-well fluid



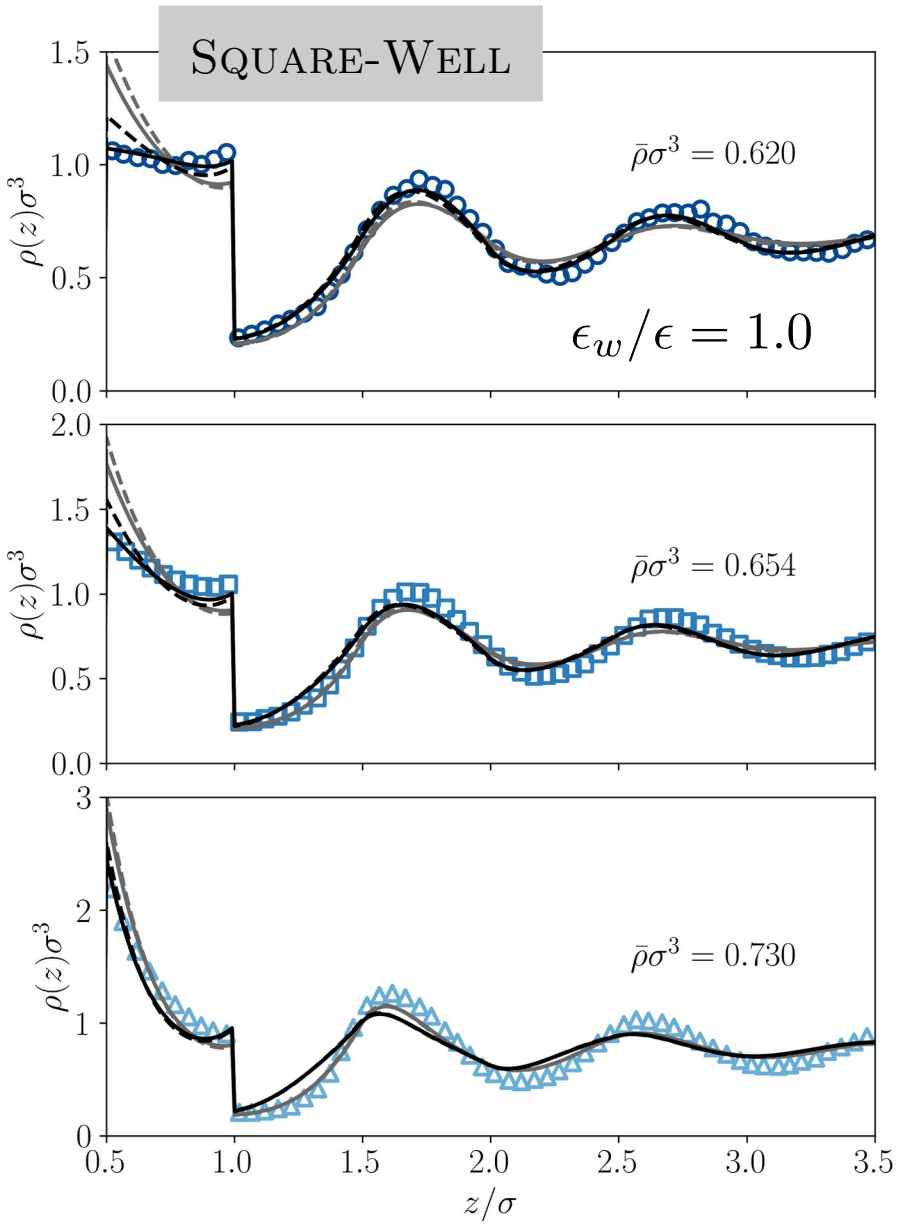
$$V(r) = \begin{cases} \infty, & r \leq \sigma \\ -\epsilon & \sigma < r \leq \lambda\sigma \\ 0, & r > \lambda\sigma \end{cases}$$

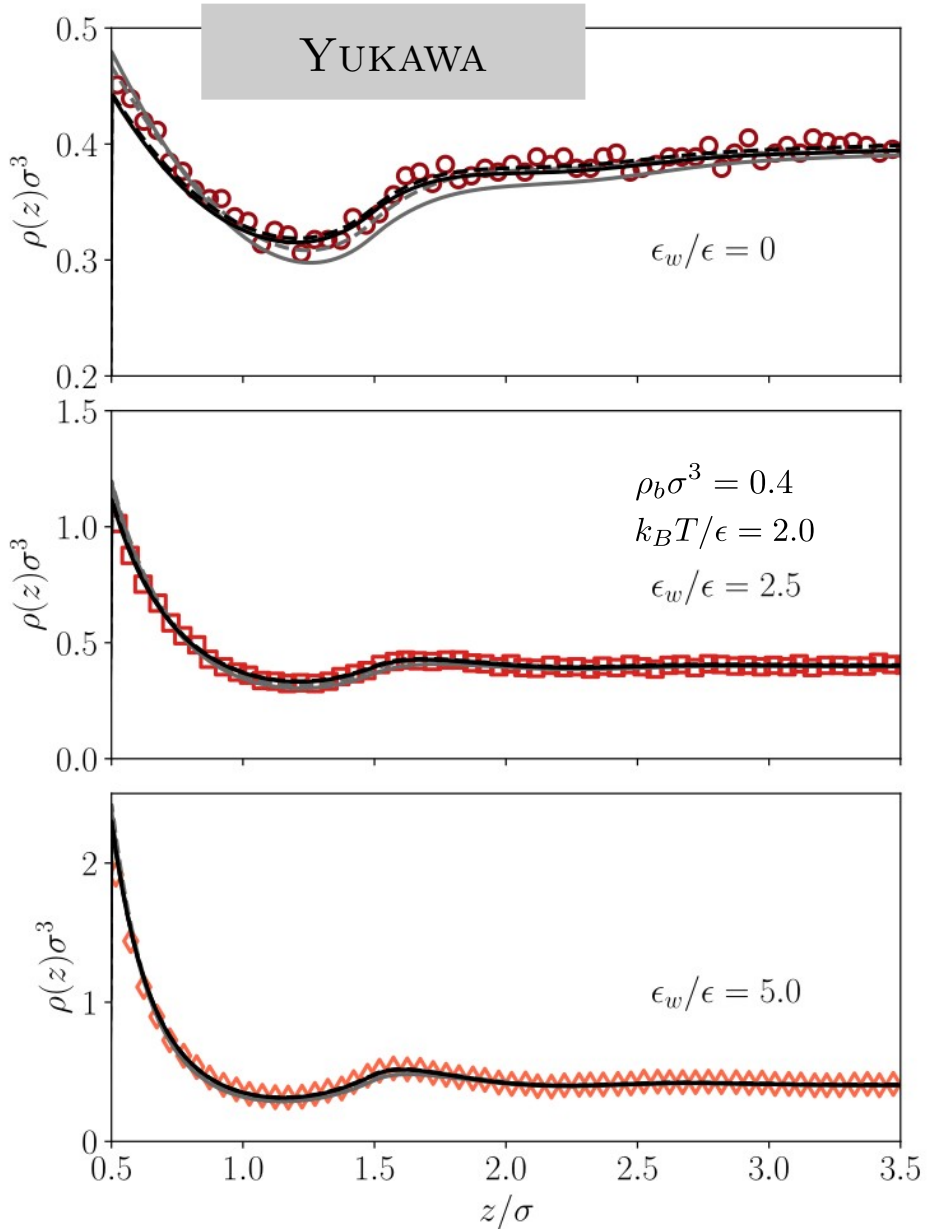


Soares, E., Barreto, A., & Tavares, F. (2021). Fluid Phase Equilibria, 542-543, 113095.

Fluid Near a Wall

$$\rho(\boldsymbol{r}) = \rho_{(b)} \exp\left[-\beta V_{\text{ext}}(\boldsymbol{r}) + c^{(1)}_{exc}(\boldsymbol{r}) + \beta\mu_{exc}\right]$$

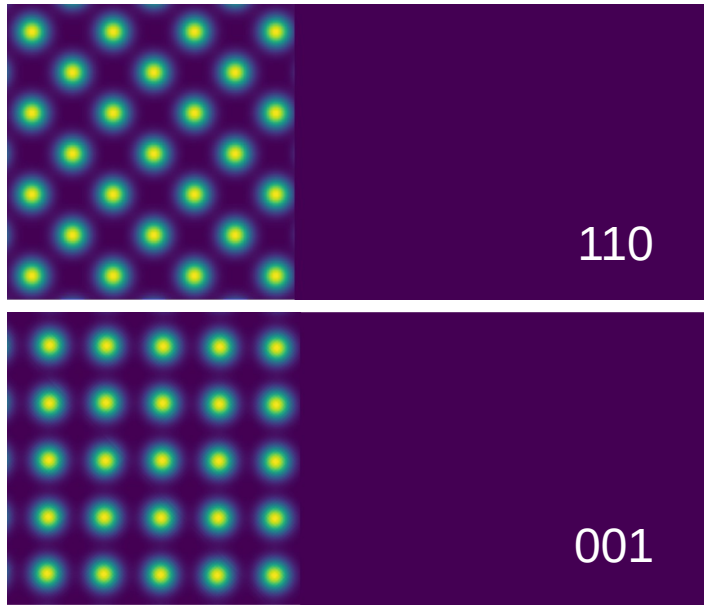




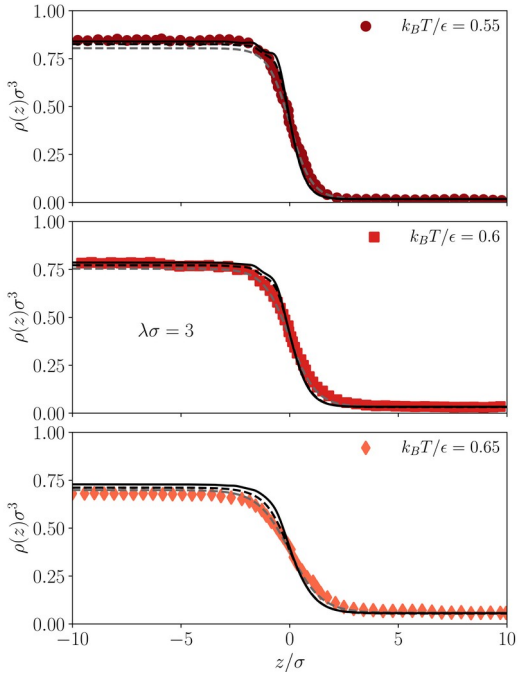
Interfacial Energy

$$\gamma = \frac{\Omega[\rho] - \Omega_b}{A}$$

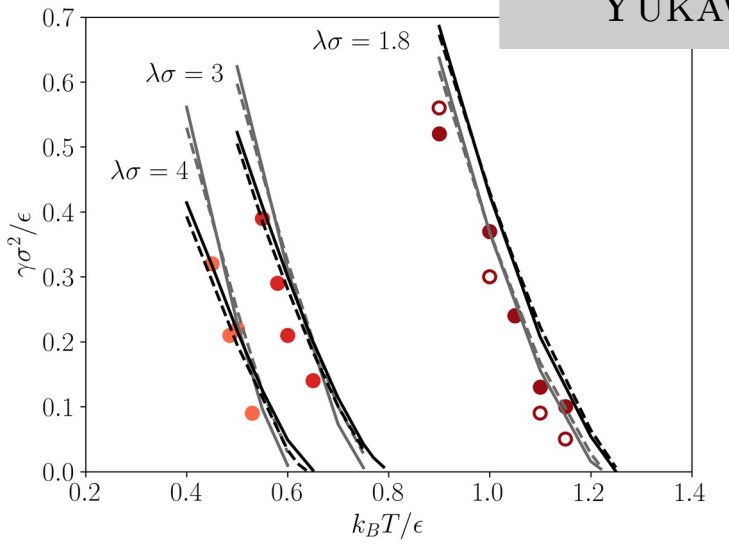
Solid-fluid interface

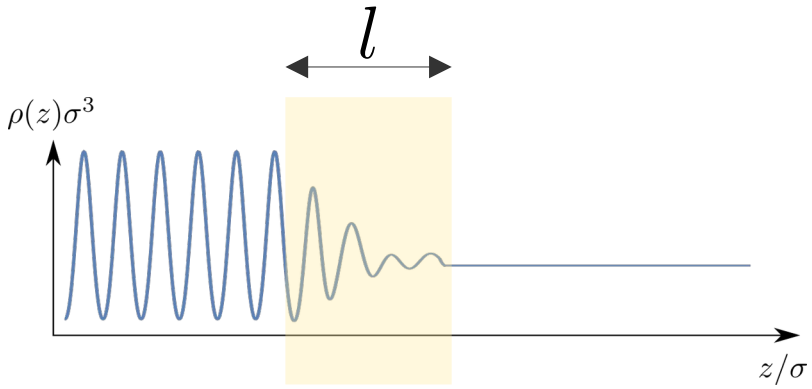


Vapor-liquid interface



Yukawa



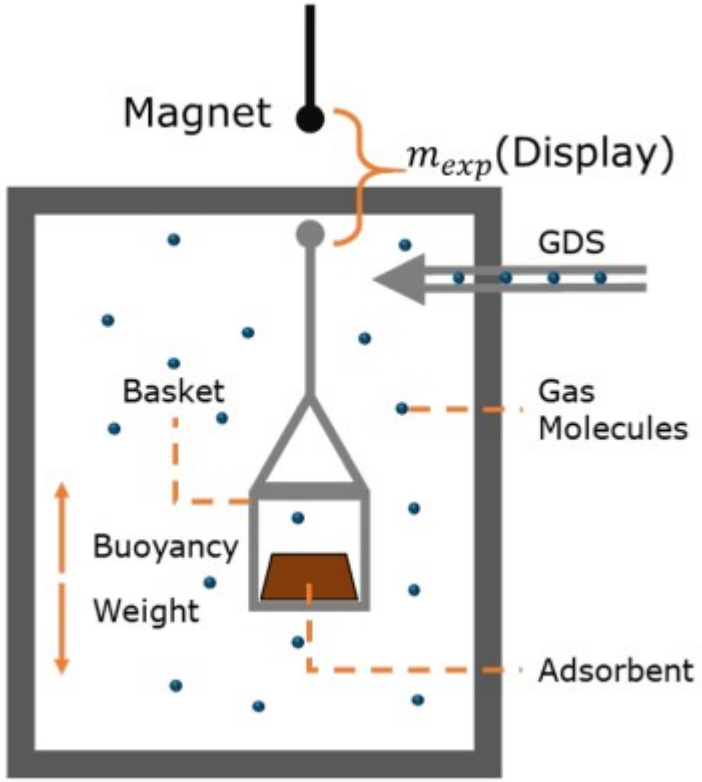


Interface width

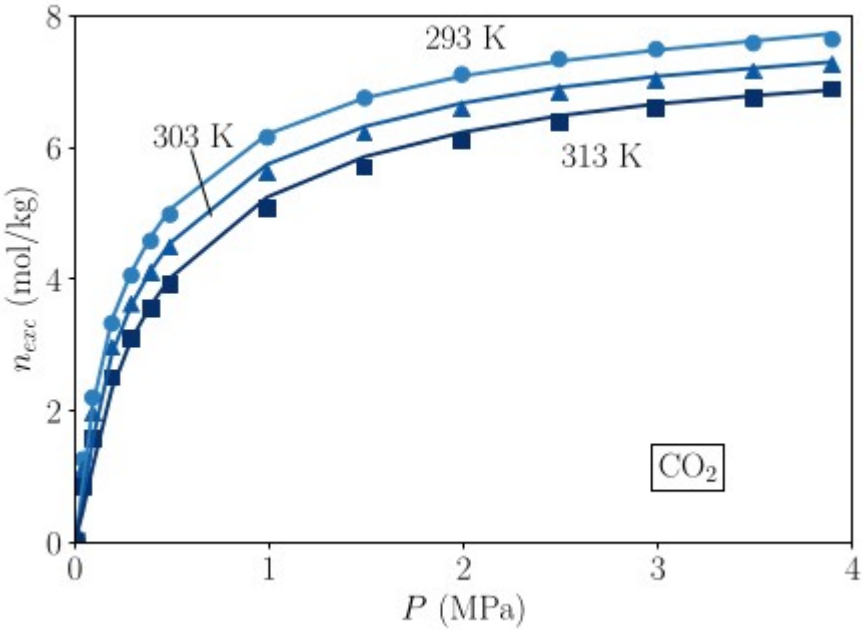
Soares, E., Barreto, A., & Tavares, F. (2021). Fluid Phase Equilibria, 542-543, 113095.

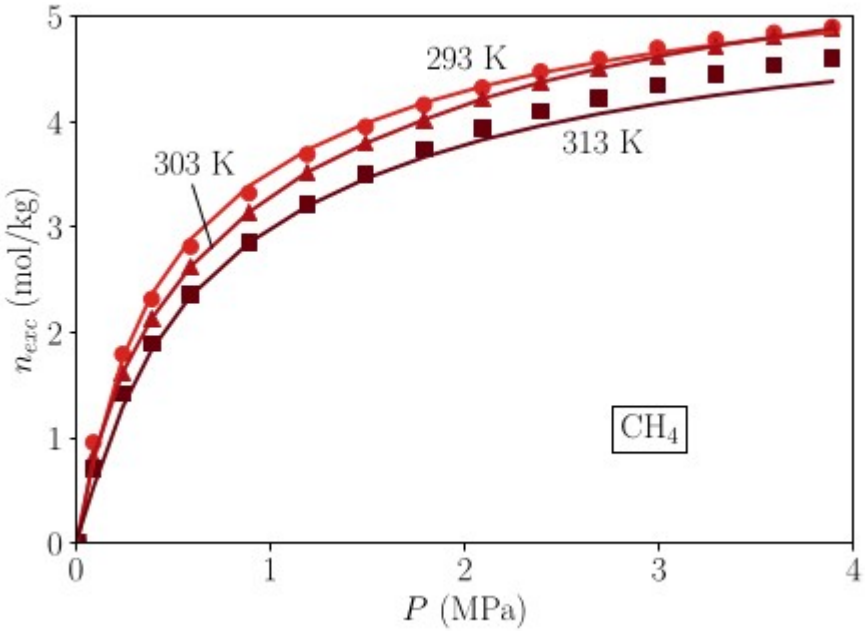
Adsorption

Adsorption in Activated carbon

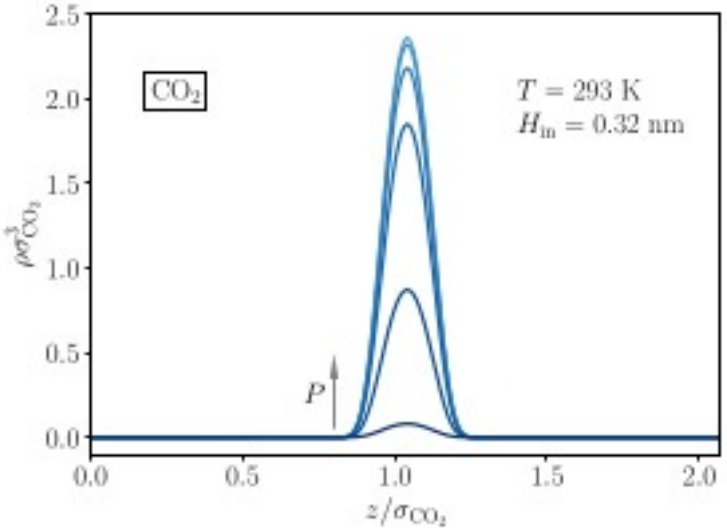


$$F^{exc} = F^{hs} + F^{hc} + F^{disp} + F^{qq}$$

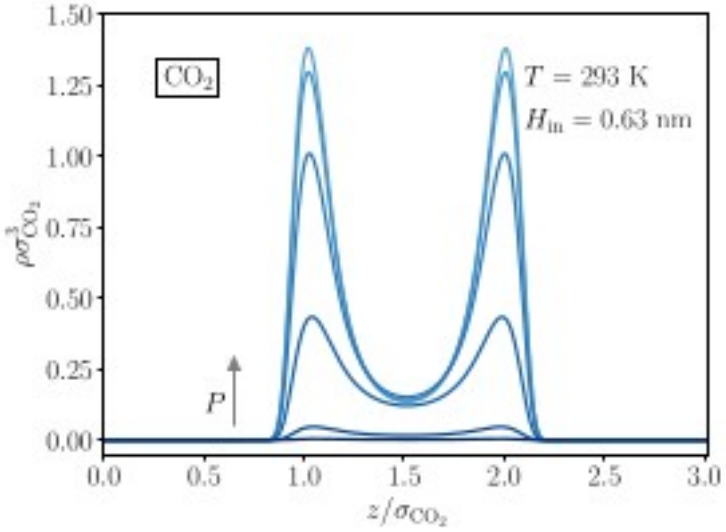




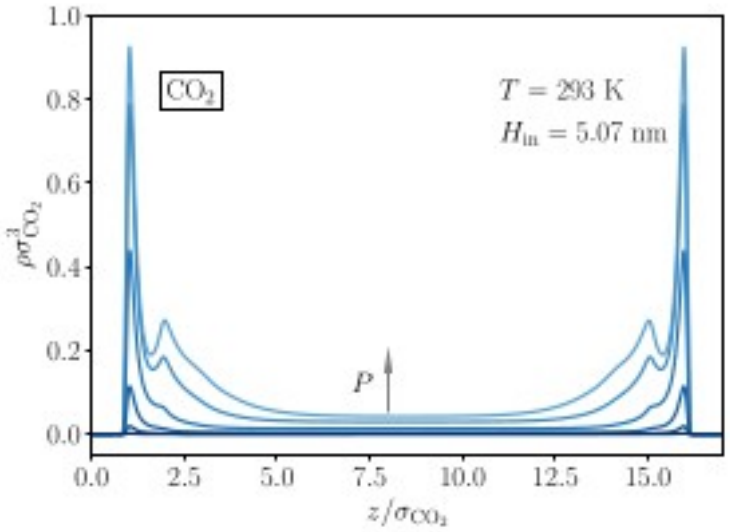
Sermoud, V. M., Barbosa, G. D., Soares, E. do A., et al (2022). Chemical Engineering Science, 247, 116905.



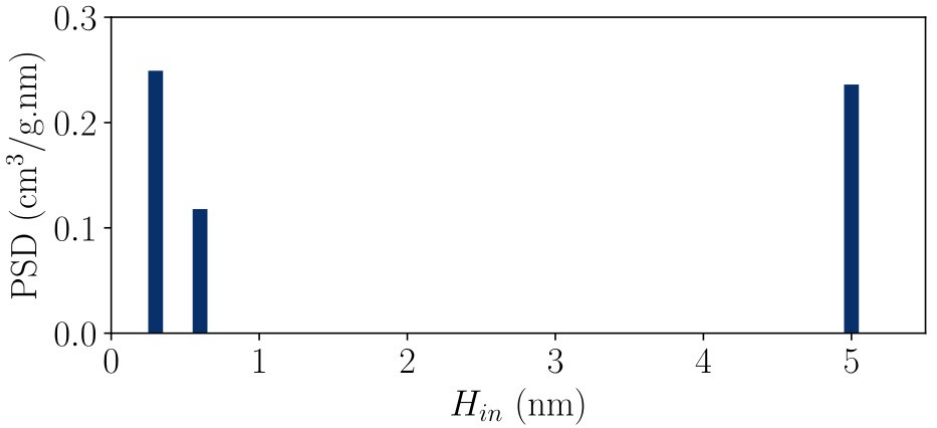
(a)



(b)

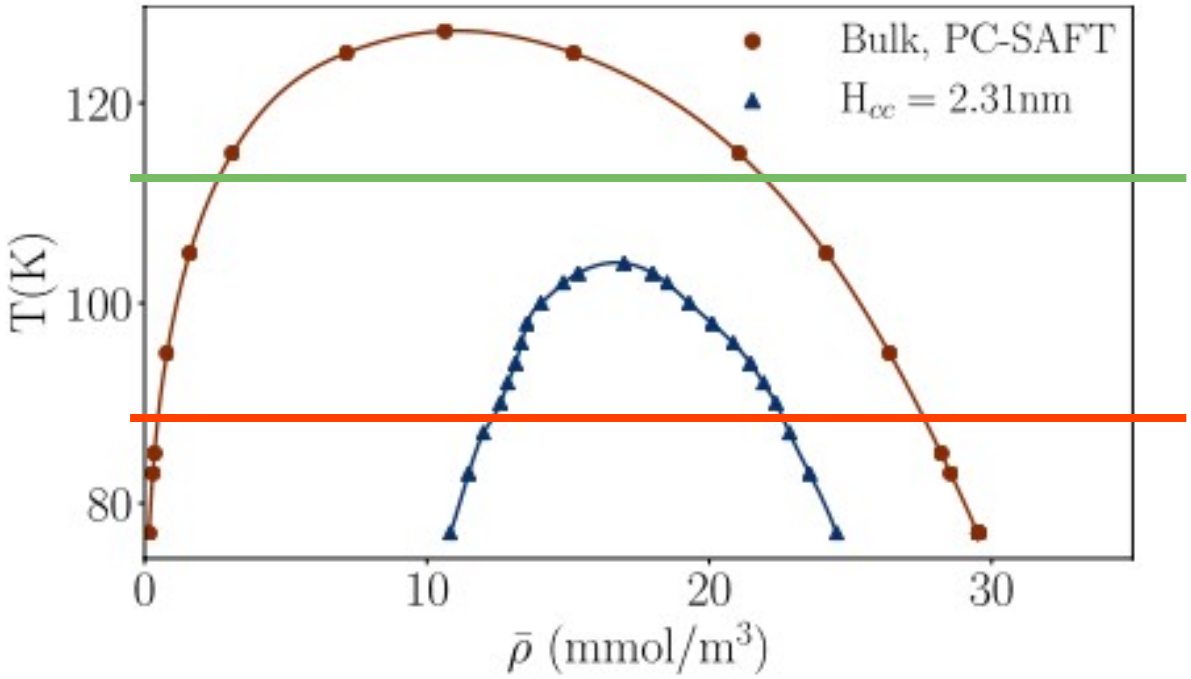


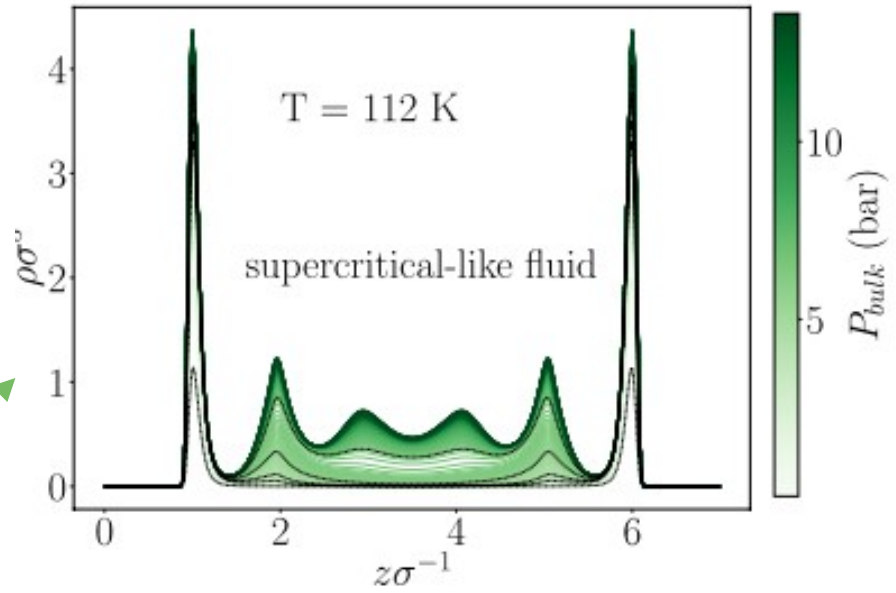
(c)

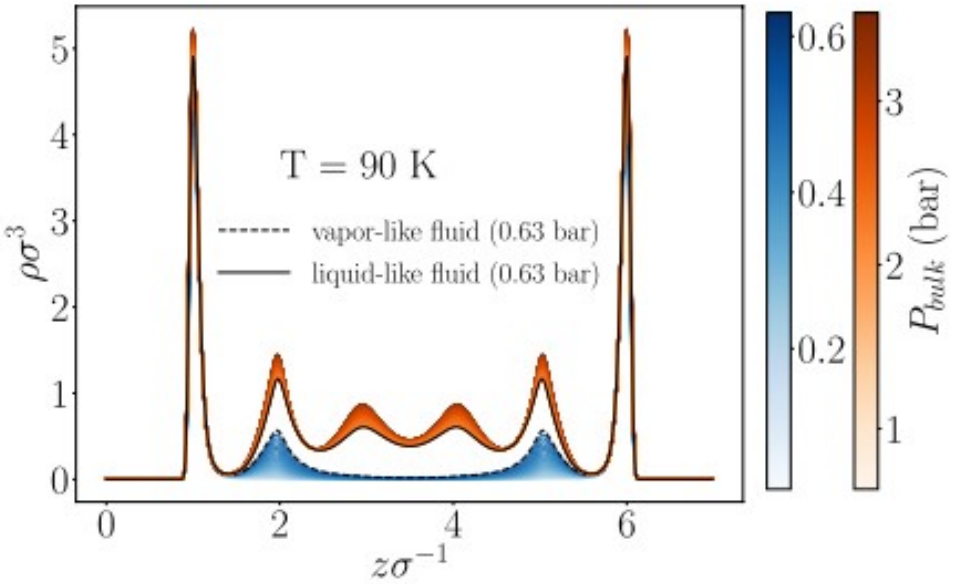


Sermoud, V. M., Barbosa, G. D., Soares, E. do A., et al (2022). Chemical Engineering Science, 247, 116905.

Confined Fluid

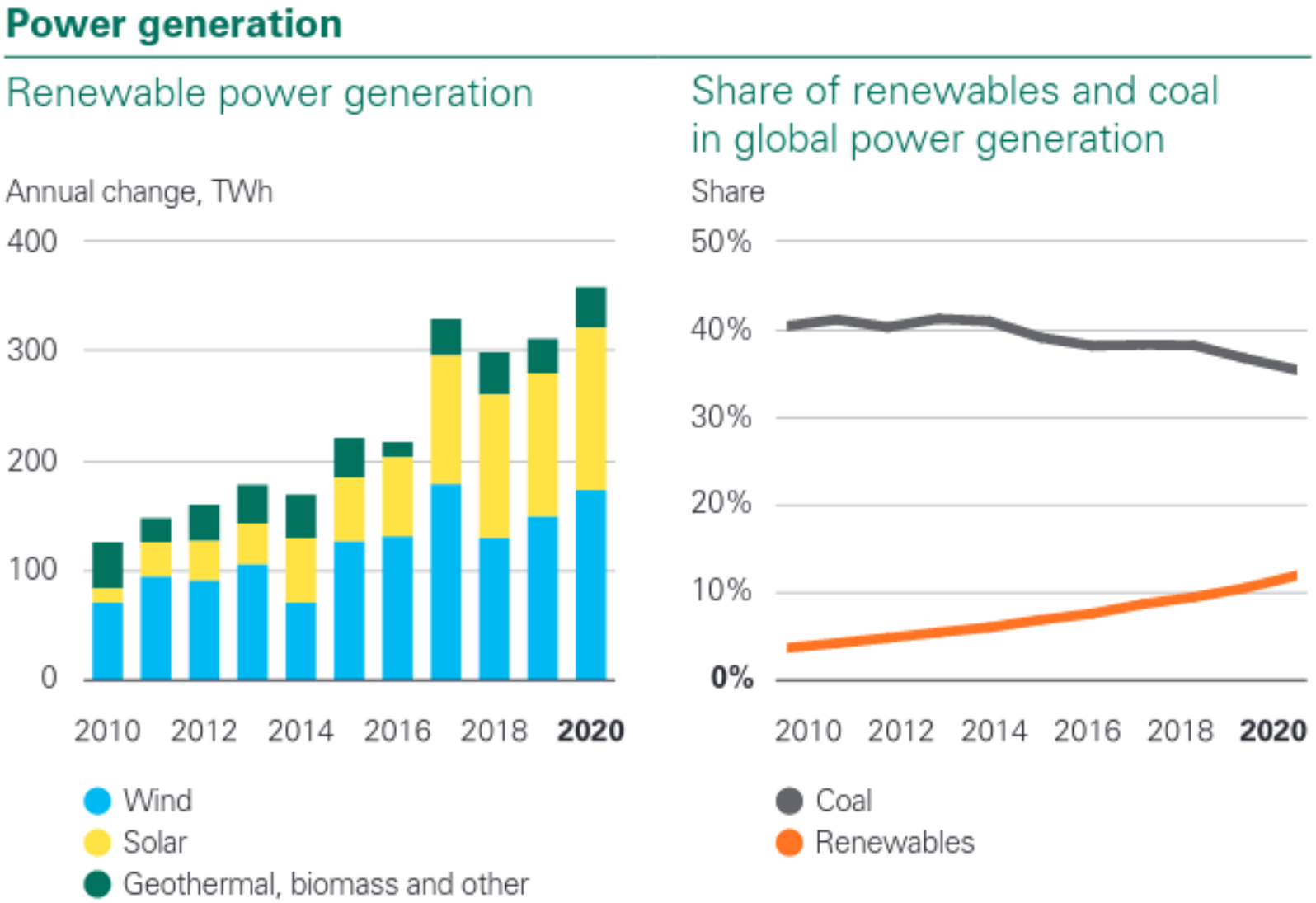






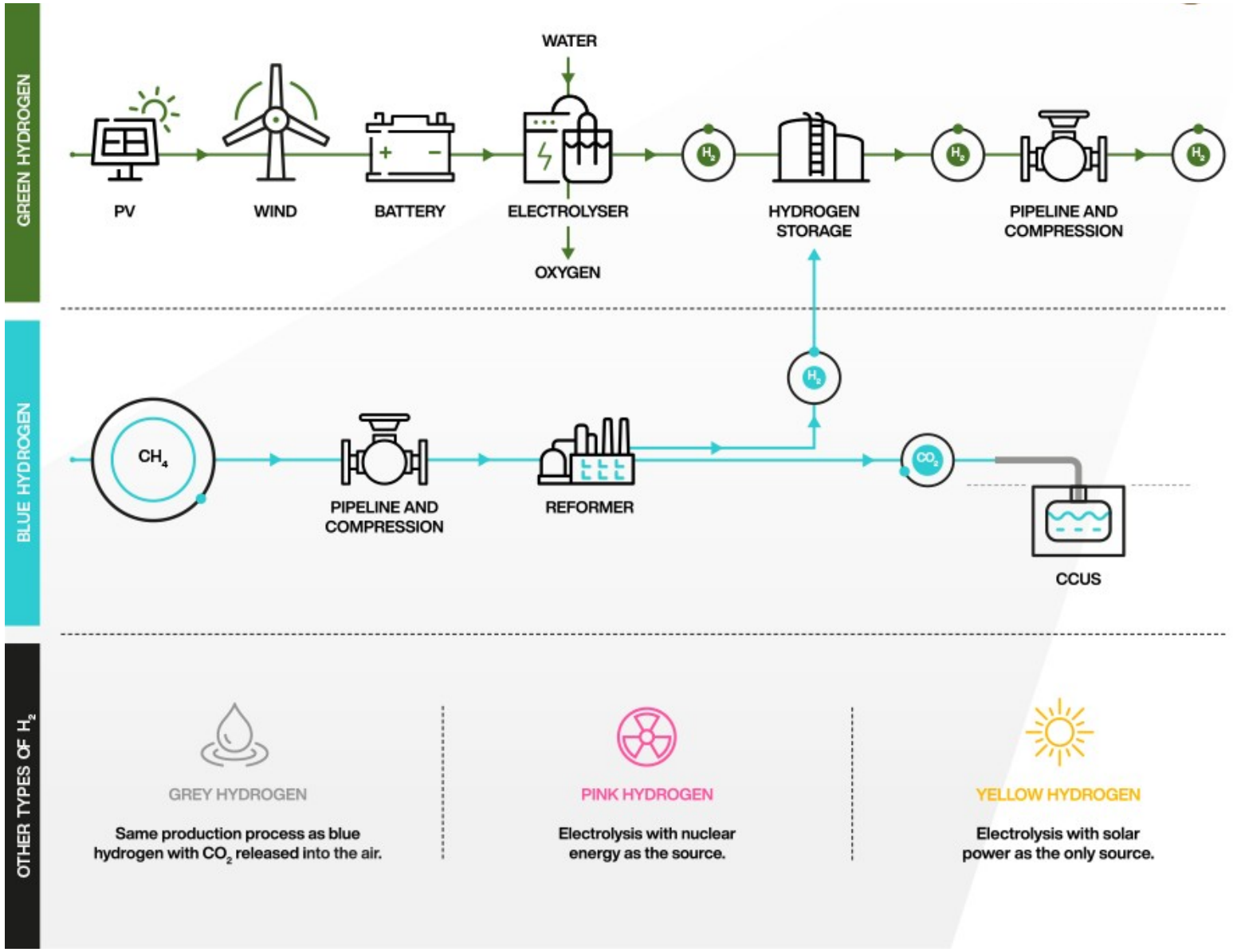
Sermoud, V. M., Barbosa, G. D., Soares, E. A.,et al (2021). Adsorption, 27(7), 1023-1034.

Green Energies



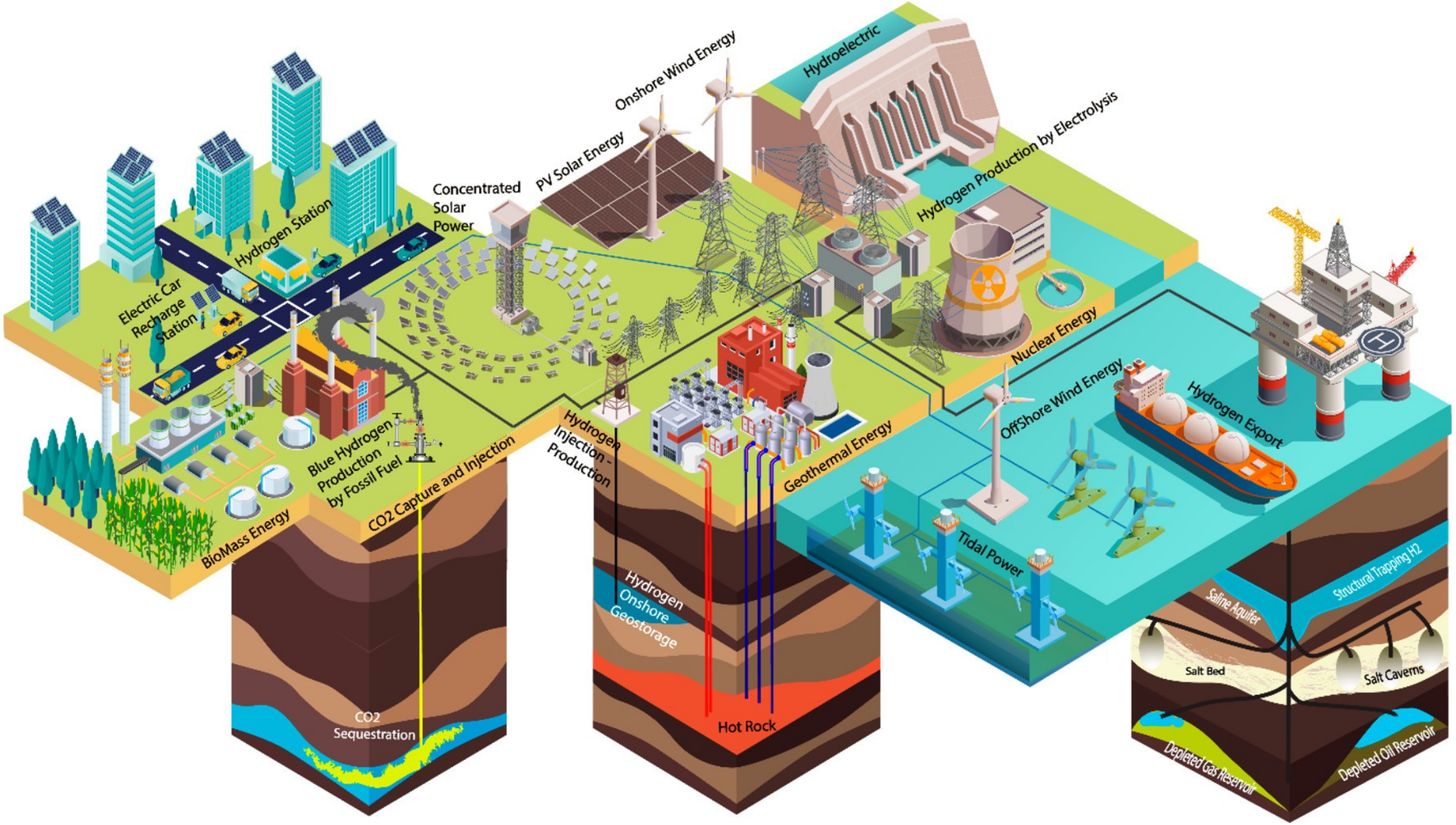
BP. Statistical Review of World Energy, 70th ed.; 2021

Different Colours of Hydrogen



https://www.petrofac.com/media/stories-and-opinion/the-difference-between-green-hydrogen-and-blue-hydrogen/

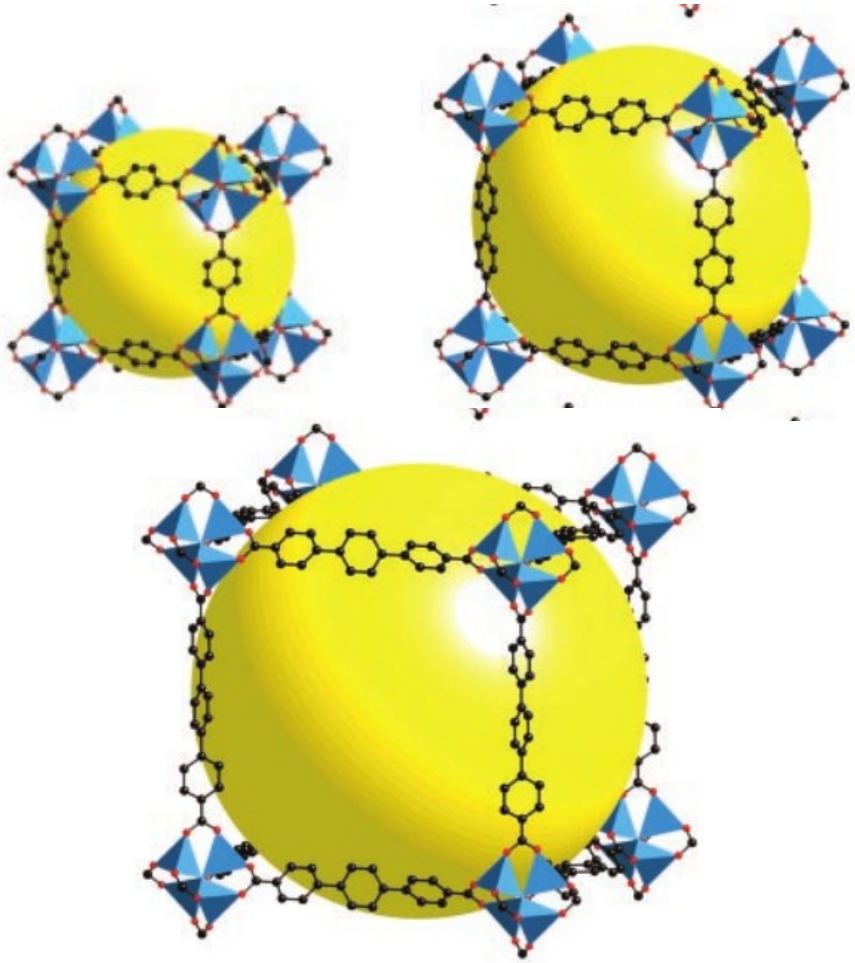
Hydrogen Storage and CO2 Capture

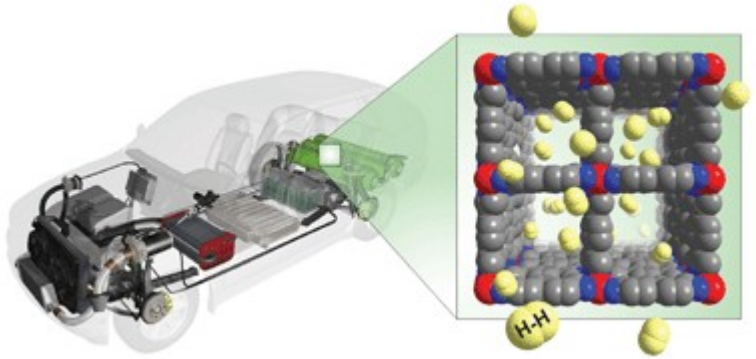


Aftab, A. Hassanpouryouzband, Q. Xie, L. L. Machuca, and M. Sarmadivaleh, Ind. Eng. Chem. Res., vol. 61, no. 9, pp. 3233-3253, Mar. 2022

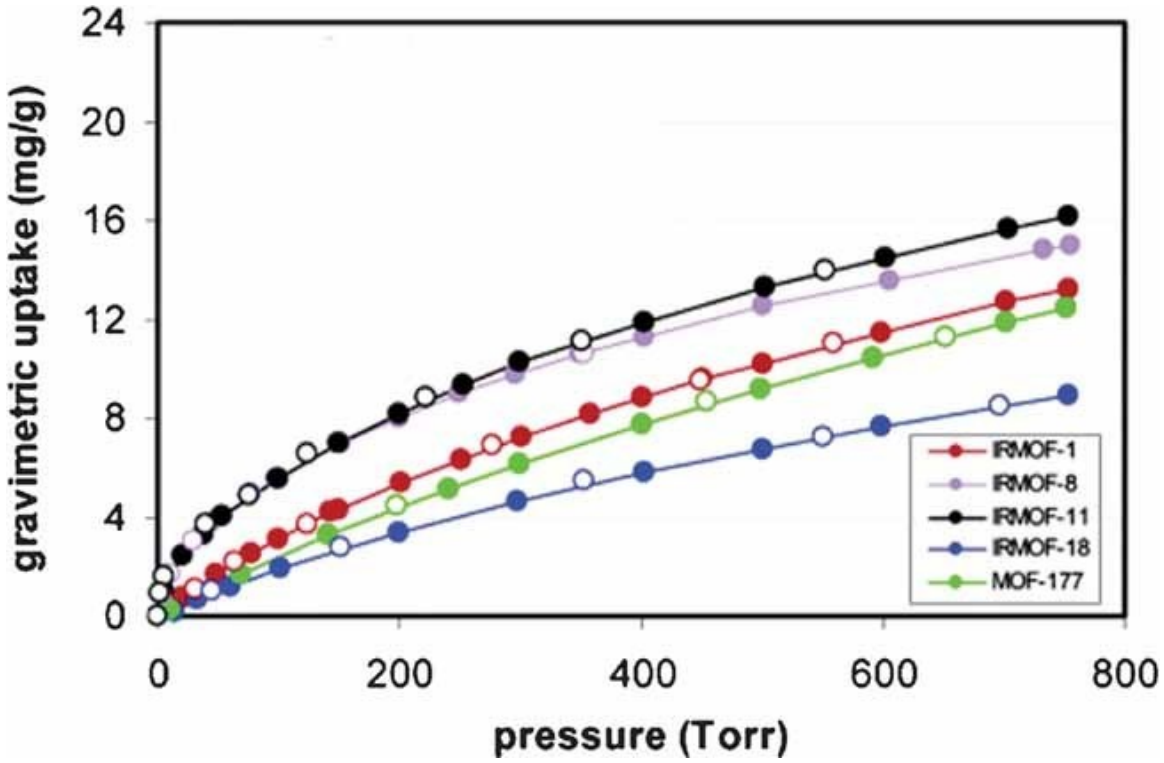
Hindenburg explosion - Lakehurst, USA - March 6, 1937

Metal Organic Framework - MOF



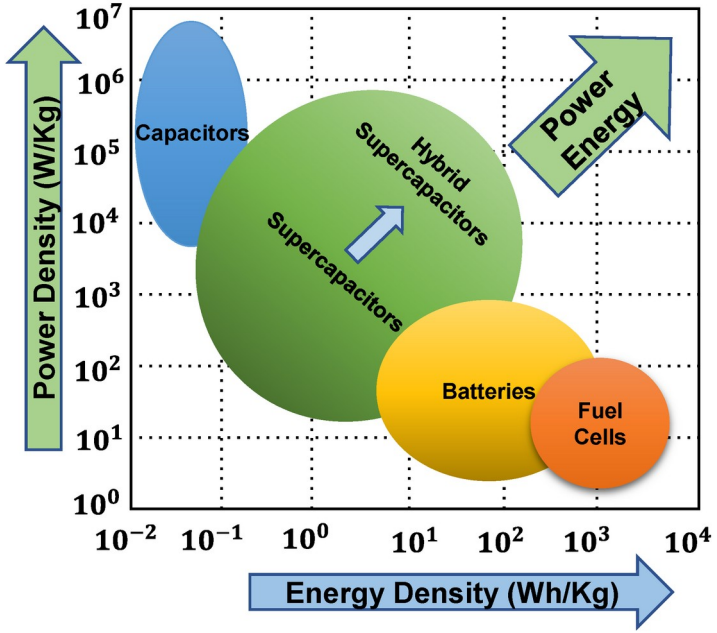


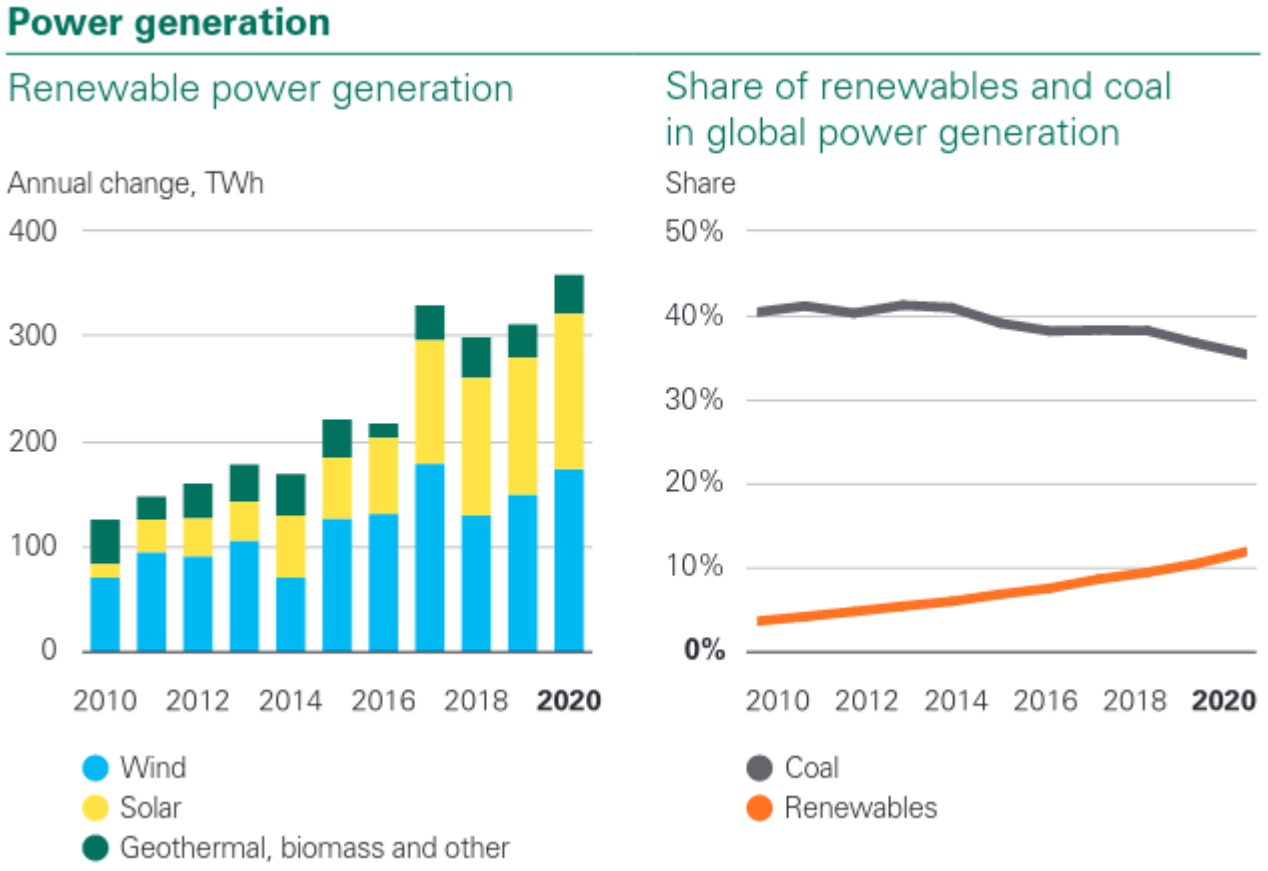
Knudsen effect



Rosi, Nathaniel L. et al. 2003. Science 300 (5622): 1127-29.
Hu, Y.H. and Zhang, L., 2010. Advanced Materials, 22(20), pp.E117-E130.

Batteries and Capacitors





Wayu, Mulugeta. (2021). Solids (2) 232-248.
BP. Statistical Review of World Energy, 70th ed.; 2021

Electrolyte Solutions

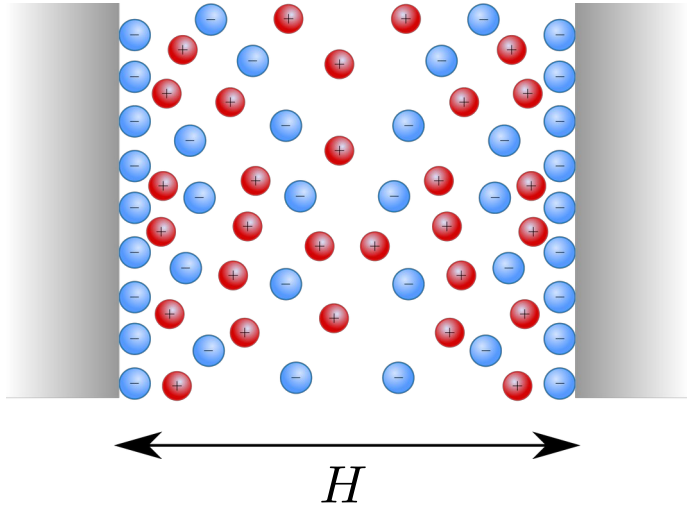
Classical Density Functional Theory *(DFT)*

Grand Potential functional

$$\Omega[\{\rho_k(\boldsymbol{r})\},\psi(\boldsymbol{r})] = F_{\text{id}} + F_{\text{exc}} + F_{\text{coul}} + \sum_i \int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}\,\left(V_i^{\text{ext}}(\boldsymbol{r}) - \mu_i\right)\rho_i(\boldsymbol{r}) + \int_{\partial\mathcal{V}} \mathrm{d}\boldsymbol{r}\,\sigma(\boldsymbol{r})\psi(\boldsymbol{r})$$

Coulomb's free-energy

$$F_{\text{coul}}[\{\rho_i(\boldsymbol{r})\},\psi(\boldsymbol{r})] = -\int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}\left\{\frac{\epsilon_0\epsilon_r}{2}|\boldsymbol{\nabla}\psi(\boldsymbol{r})|^2 - \sum_i Z_i e\rho_i(\boldsymbol{r})\psi(\boldsymbol{r})\right\}$$



Evans, R. et al (2016). Journal of Physics: Condensed Matter, 28(24), 240401.
Wu, J., & Li, Z. Annual Review of Physical Chemistry, 58(1), 85-112. (2007)

Classical Density Functional Theory *(DFT)*

Density Profiles

$$\left.\frac{\delta\Omega}{\delta\rho_i(\boldsymbol{r})}\right|_{V,\psi,\mu,T} = k_B T \ln\left(\Lambda_i^3 \rho_i(\boldsymbol{r})\right) + Z_i e\psi(\boldsymbol{r}) + \frac{\delta F_{\text{exc}}}{\delta\rho_i(\boldsymbol{r})} + V_i^{\text{ext}}(\boldsymbol{r}) - \mu_i = 0$$

$$\rho_i(\boldsymbol{r}) = \rho_i^{(b)} \exp\left[-\beta Z_i e\psi(\boldsymbol{r}) + c_i^{(1),\text{exc}}(\boldsymbol{r}) + \beta V_i^{\text{ext}}(\boldsymbol{r}) + \beta\mu_i^{\text{exc}}\right]$$

Poisson's Equation

$$\left.\frac{\delta\Omega}{\delta\psi(\boldsymbol{r})}\right|_{V,\rho_i,\mu,T} = \epsilon_0\epsilon_r\nabla^2\psi(\boldsymbol{r}) + \sum_i Z_i e\rho_i(\boldsymbol{r}) = 0$$

$$\left.\frac{\delta\Omega}{\delta\psi(\boldsymbol{r})}\right|_{\partial V,\rho_i,\mu,T} = -\frac{\epsilon_0\epsilon_r}{2}\hat{\mathbf{n}}(\boldsymbol{r})\cdot\boldsymbol{\nabla}\psi(\boldsymbol{r})\Big|_{\partial V} + \sigma(\boldsymbol{r}) = 0$$

Excess Free-energy functional

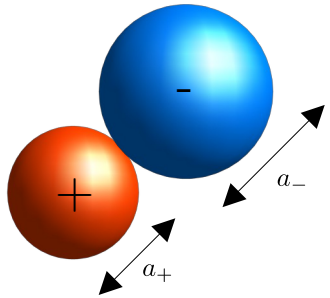
Accounts for the size and electrostatic correlations effects

$$F_{\text{exc}}[\rho(\boldsymbol{r})] = F_{\text{hs}}[\rho(\boldsymbol{r})] + F_{\text{ec}}[\rho(\boldsymbol{r})]$$

$$\mu_{\text{exc}} = \mu_{\text{hs}} + \mu_{\text{ec}}$$

Hard-Sphere Functional

$$\beta F_{\text{hs}}[\rho(\boldsymbol{r})] = \int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}\, \Phi_{\text{FMT}}(\{n^{(\alpha)}(\boldsymbol{r})\})$$



BFD functional

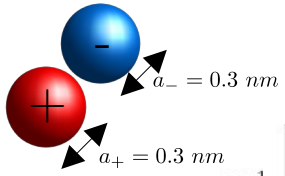
$$\begin{aligned}\beta F_{\text{ec}}[\rho(\boldsymbol{r})] = &\int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}\, \Phi_{\text{MSA}}(\{\rho_i^{(b)}\}) \\ &- \sum_i \int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}\, \frac{\partial \Phi_{\text{MSA}}(\{\rho_i^{(b)}\})}{\partial \rho_i^{(b)}} \Delta\rho_i(\boldsymbol{r}) \\ &- \frac{1}{2}\sum_{i,j} \int_{\mathcal{V}} \mathrm{d}\boldsymbol{r} \int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}'\, \Delta\rho_i(\boldsymbol{r}) \Delta c_{ij}^{(2),\text{MSA}}(|\boldsymbol{r}-\boldsymbol{r}'|) \Delta\rho_j(\boldsymbol{r}')\end{aligned}$$

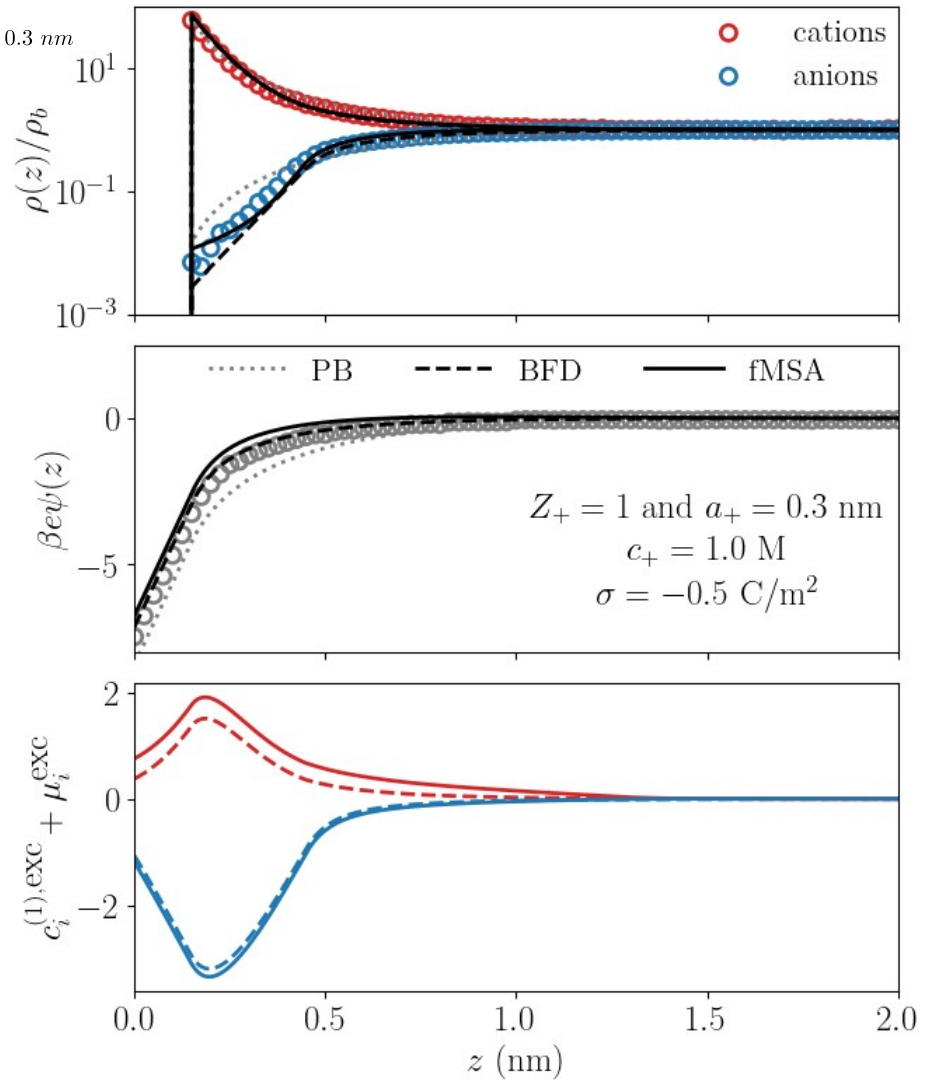
FMSA functional

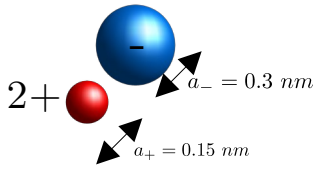
$$\begin{aligned}\beta F_{\text{ec}}[\rho(\boldsymbol{r})] = &\int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}\, \Phi_{\text{MSA}}(\{q_i^{(0)}(\boldsymbol{r})\}) \\ &- \frac{1}{2}\sum_{i,j} \int_{\mathcal{V}} \mathrm{d}\boldsymbol{r} \int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}'\, \rho_i(\boldsymbol{r}) \Delta c_{ij}^{(2),\text{MSA}}(|\boldsymbol{r}-\boldsymbol{r}'|) \rho_j(\boldsymbol{r}')\end{aligned}$$

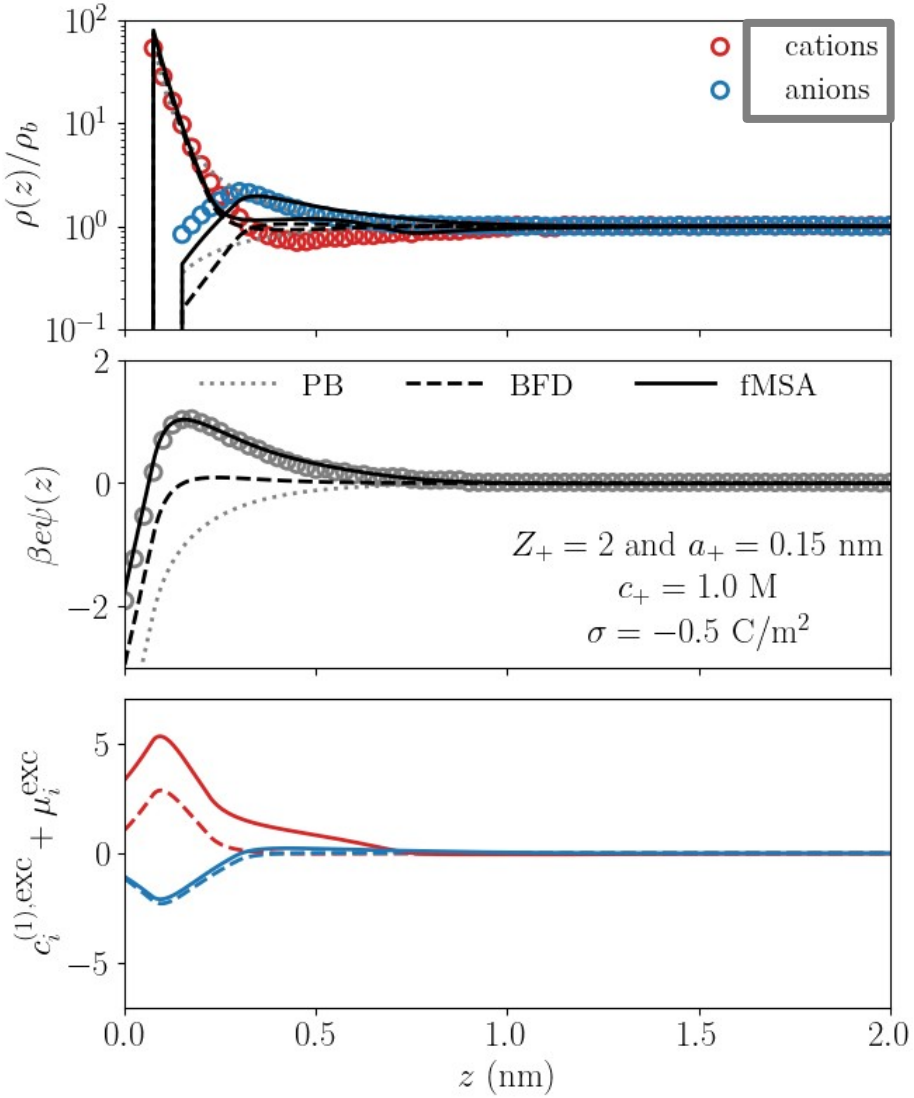
Waisman, E., & Lebowitz, J. L. (1972).The Journal of Chemical Physics, 56(6), 3086-3093.
Levin, Y. (2002). Reports on Progress in Physics, 65(11), 1577-1632.
Roth, R., & Gillespie, D. (2016). Journal of Physics Condensed Matter, 28(24), 244006.

Density Profiles





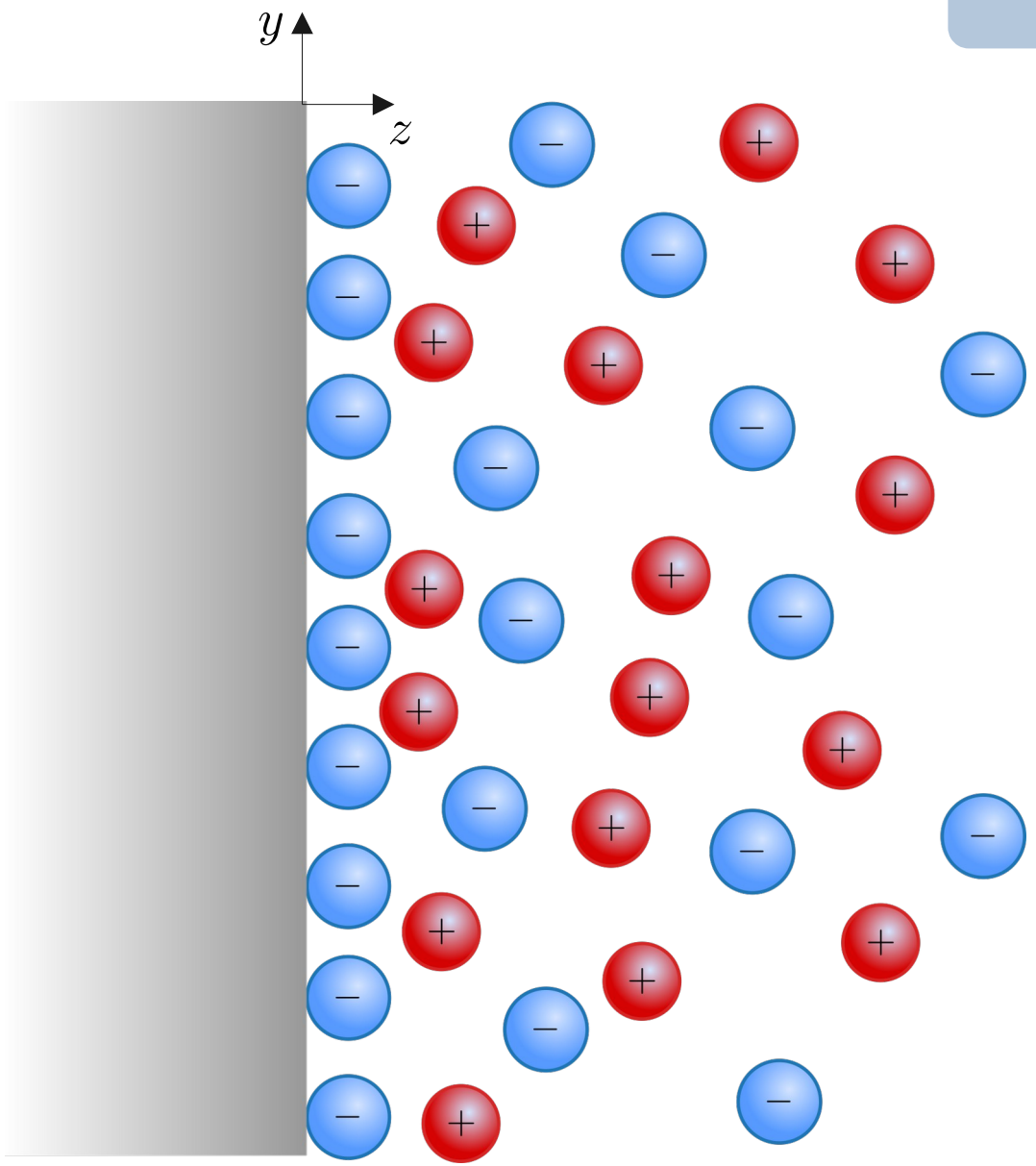


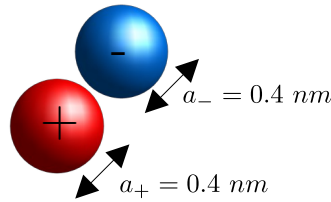


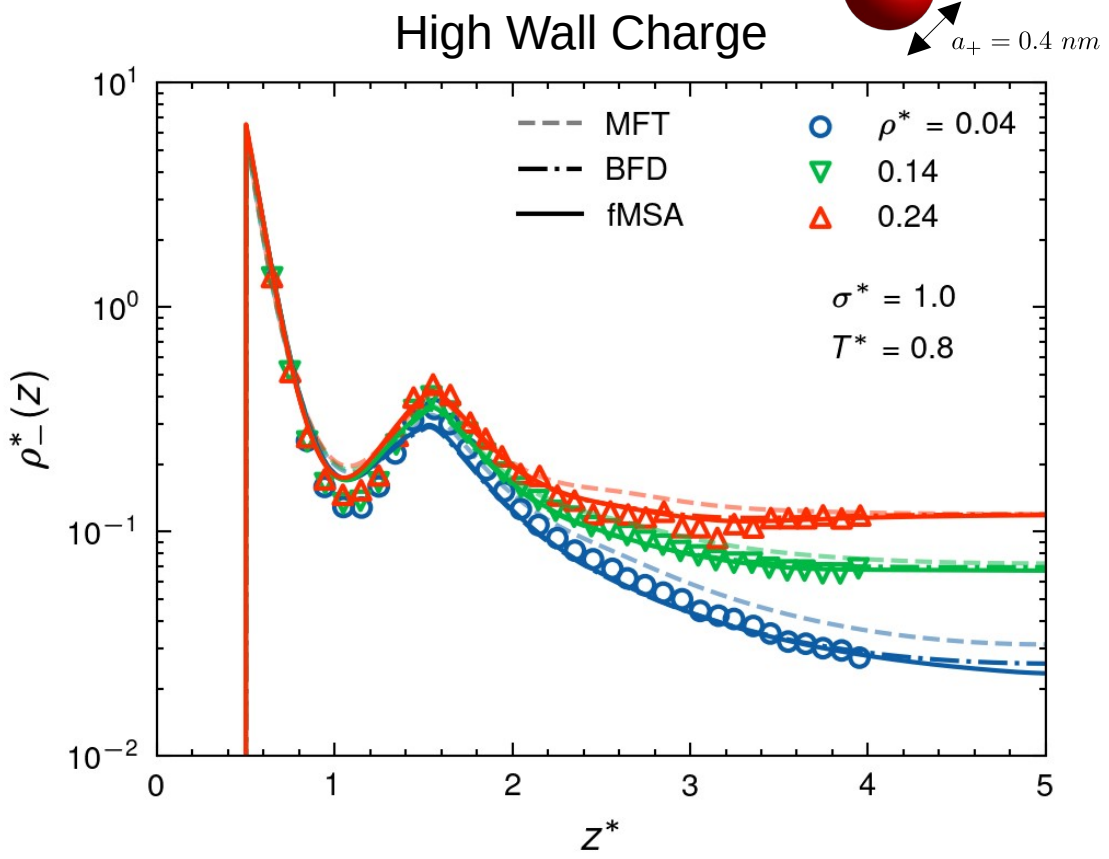
Voukadinova, Valiskó, and Gillespie. 2018. Physical Review E 98 (1): 012116.

Profiles near a Wall

$$\rho_i(\boldsymbol{r}) = \rho_i^{(b)} \exp\left[-\beta Z_i e\psi(\boldsymbol{r}) + c_i^{(1),exc}(\boldsymbol{r}) + \beta\mu_i^{exc}\right]$$

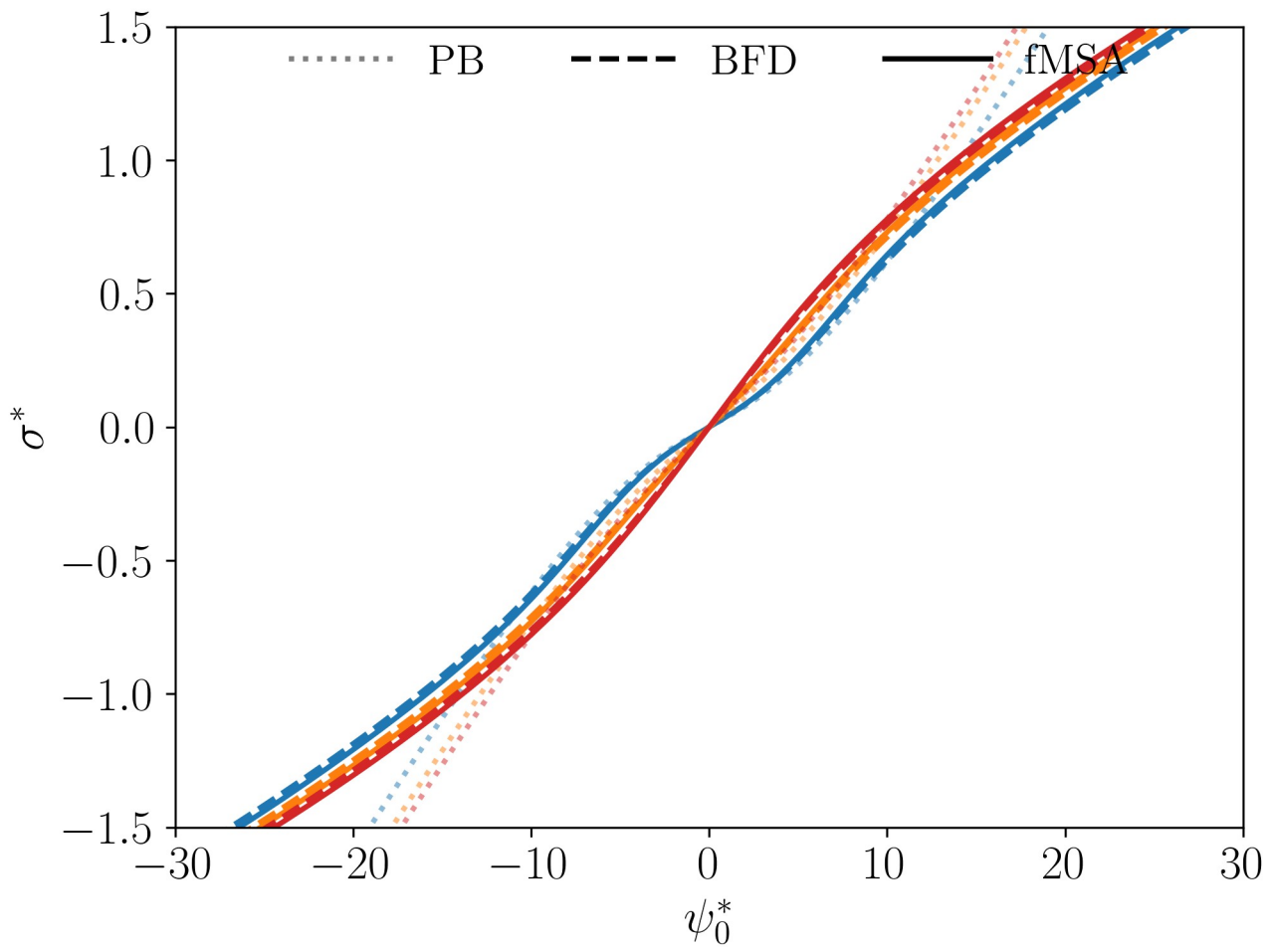






Lamperski, Stanisław, and Douglas Henderson. 2011. Molecular Simulation 37 (4): 264-68.

Surface Charge



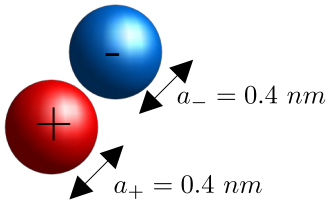
Global charge electroneutrality

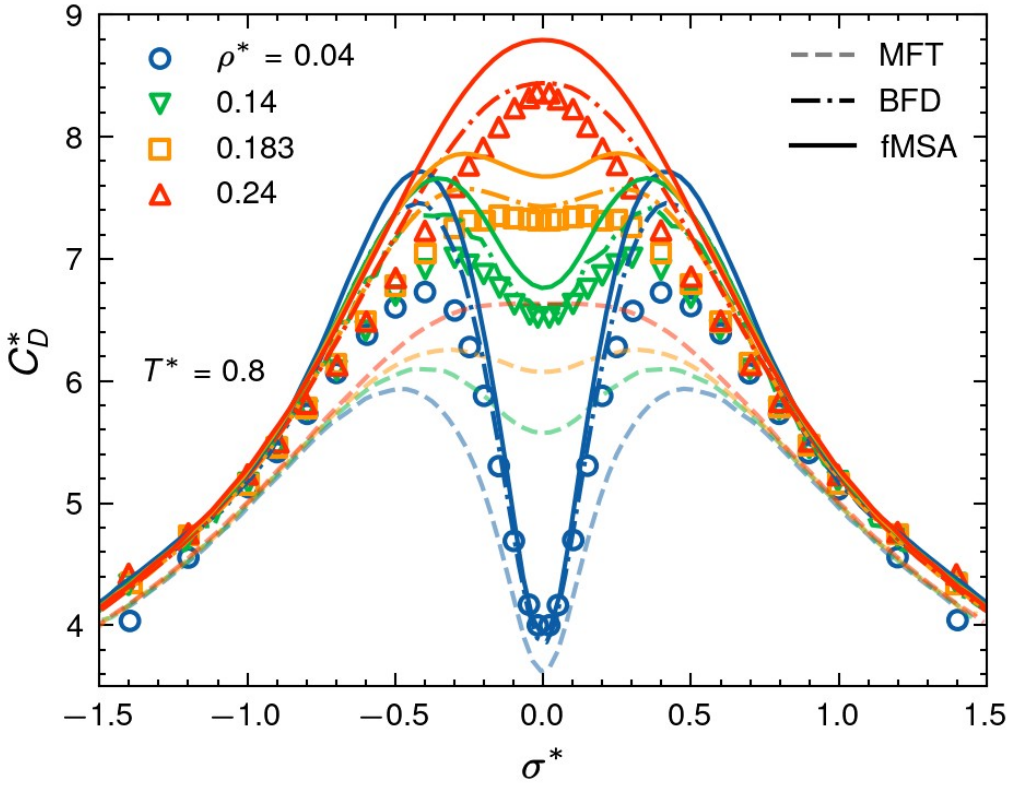
$$\sigma + \int_0^\infty \sum_i Z_i e \rho_i(z)\, \mathrm{d}z = 0$$

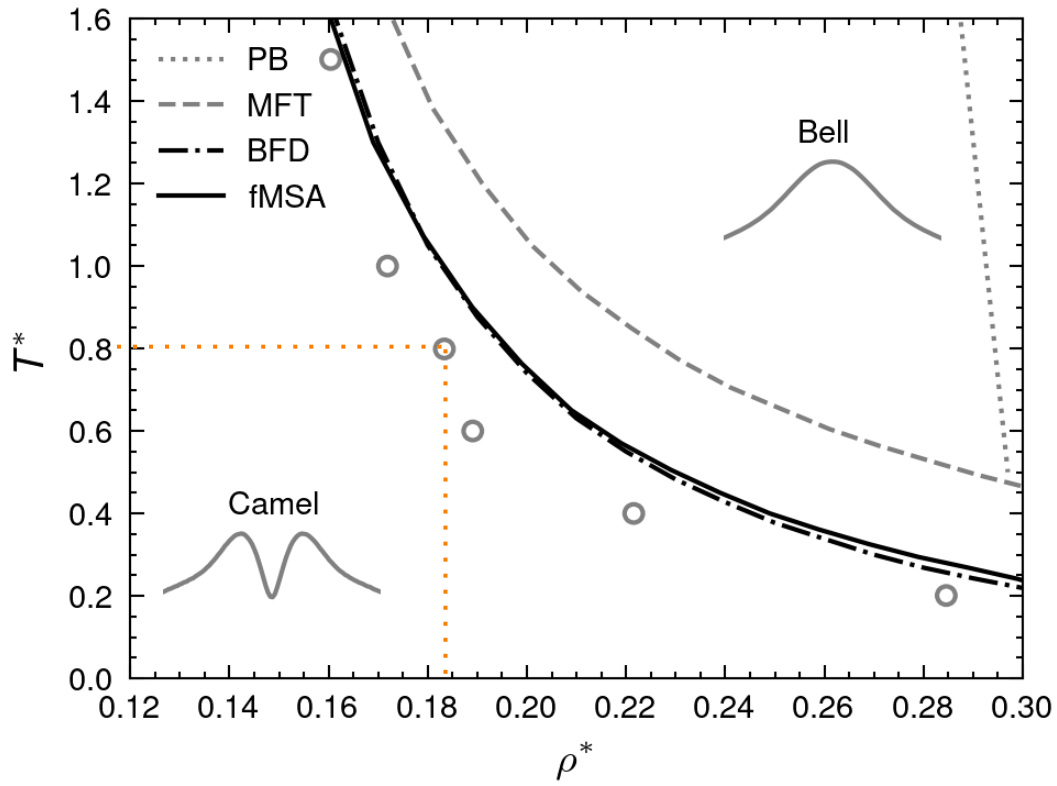
Differential Capacitance

$$C_D = \frac{\partial \sigma}{\partial \psi_0}$$

Bell-to-camel transition







Open symbols: MC data

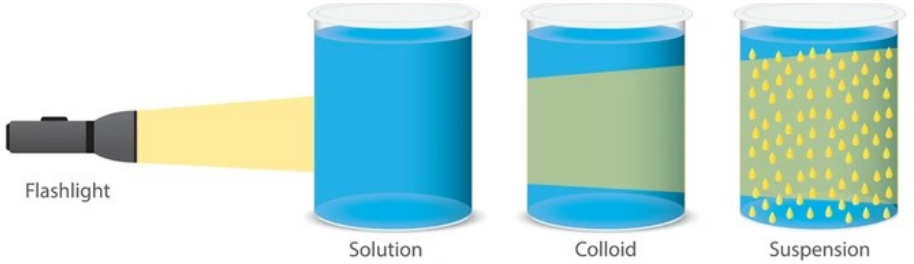
Lamperski, Stanisław, and Douglas Henderson. 2011. Molecular Simulation 37 (4): 264-68.

Colloidal Systems

Colloidal systems

Disperse phase (solute) in continuous medium (solvent).

Size between 0.1 nm and 100 nm.



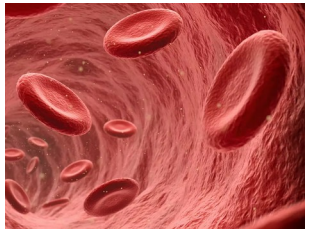
Tyndall Effect

Fog Smoke

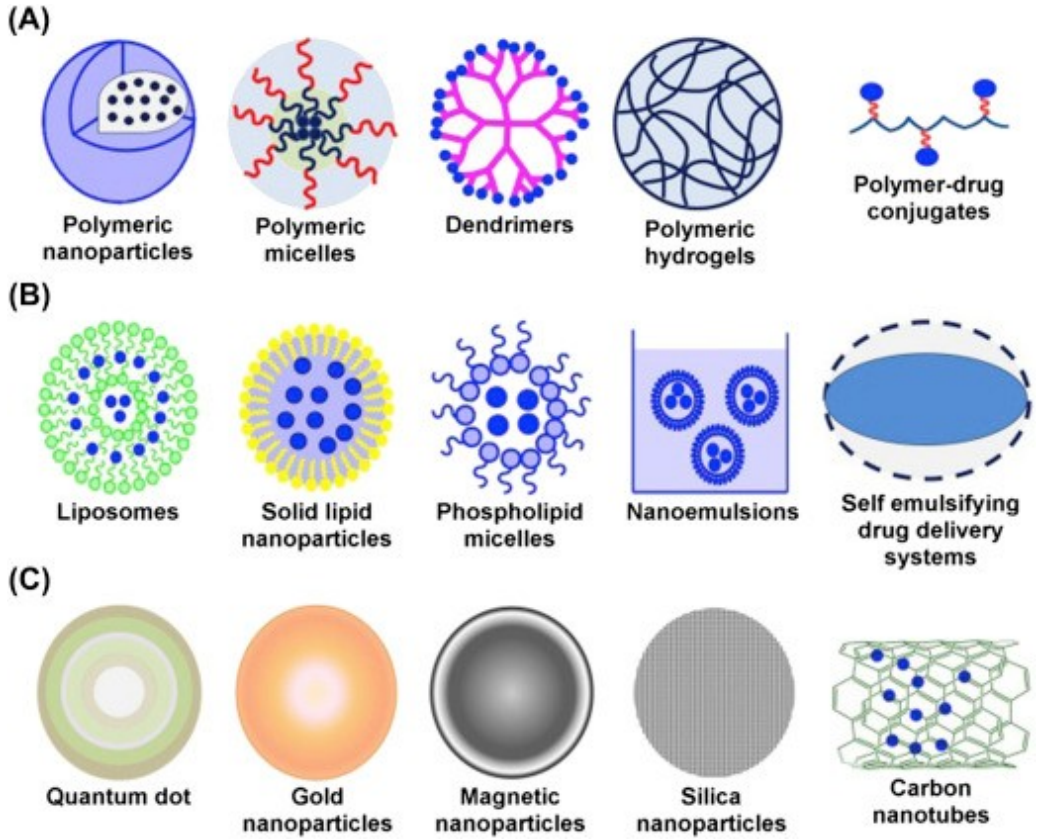
Milk

Paint

Aerogel

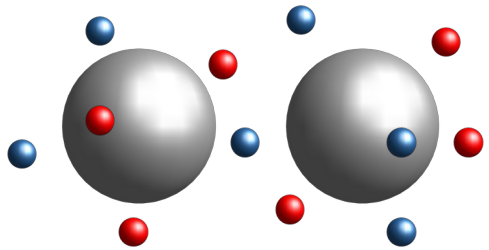


Blood



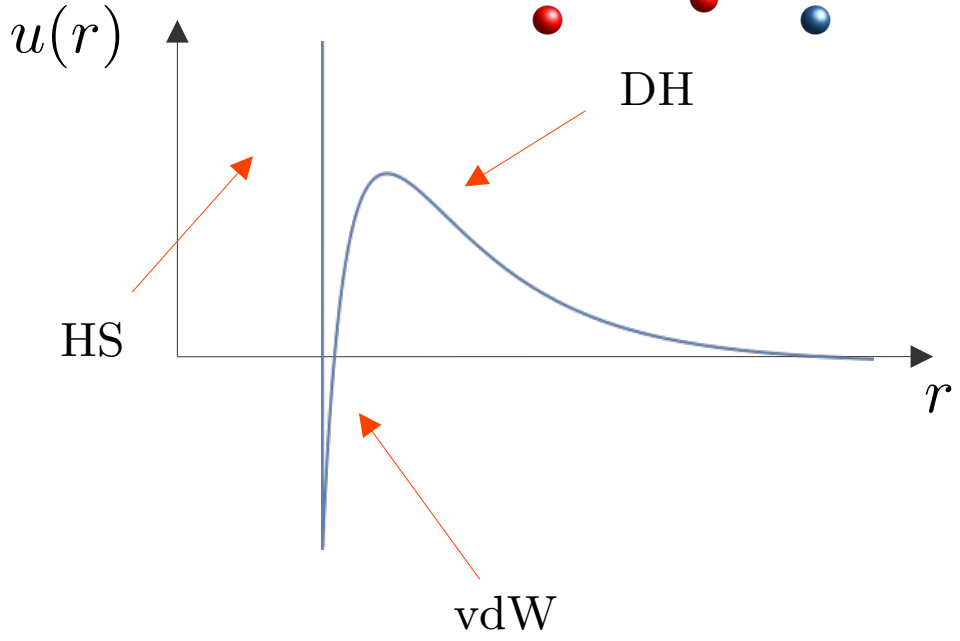
Lamperski, Stanisław, and Douglas Henderson. 2011. Molecular Simulation 37 (4): 264-68.
Goyal, Amit K., et al. Elsevier, 2019. 15-33

DLVO Theory of Colloidal Particles



Hard-sphere repulsion

$$u_{\mathrm{hs}}(r) = \begin{cases} \infty, & \text{for} \quad r < \sigma, \\ 0, & \text{for} \quad r \geq \sigma, \end{cases}$$



Electrostatic potential (Debye-Huckel)

$$u_{\mathrm{dh}}(r) = \frac{(Ze)^2}{4\pi\epsilon_0\epsilon_r(1+\frac{1}{2}\kappa\sigma)^2}\frac{\exp[-\kappa(r-\sigma)]}{r}$$

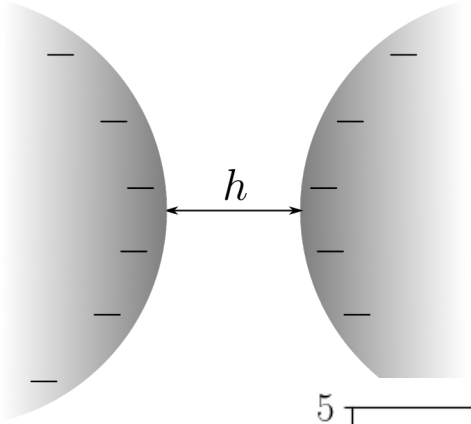
$$u(r) = u_{\mathrm{hs}}(r) + u_{\mathrm{dh}}(r) + u_{\mathrm{vdW}}(r)$$

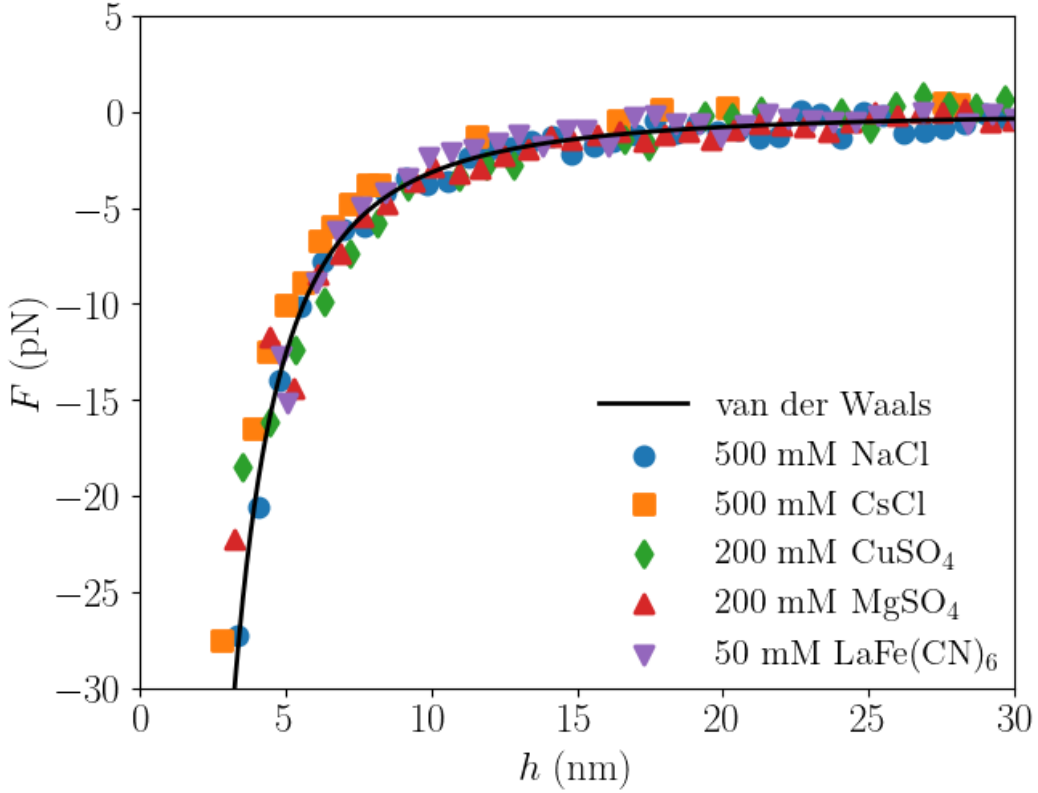
Attractive potential (Hamaker)

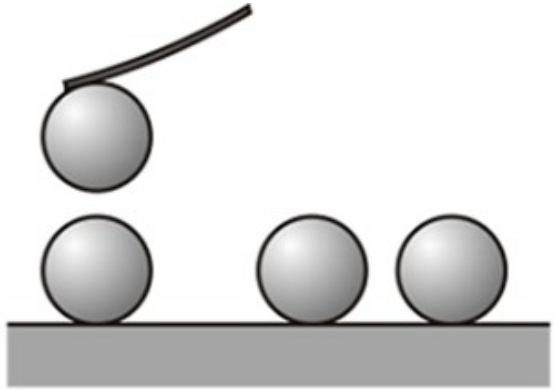
$$u_{\mathrm{vdW}}(r) = -\frac{A_H}{12}\left[\frac{\sigma^2}{r^2-\sigma^2} + \frac{\sigma^2}{r^2} + 2\ln\left(1-\frac{\sigma^2}{r^2}\right)\right]$$

E. J. W. Verweyand J. TH. G. Overbeek, Theory of the Stability of Lyophobic Colloids, Elsevier, Amsterdam, (1948)

Attractive force







AFM Measurements

$$F_{\mathrm{vdW}}(h) = -\frac{A_H R}{12}\frac{1}{h^2}$$

$$A_H = (1.7 \pm 0.1) \times 10^{-21}\ \mathrm{J}$$

Smith, A. M., Maroni, P., Trefalt, G., & Borkovec, M. (2019). The Journal of Physical Chemistry B, 123(7), 1733-1740.

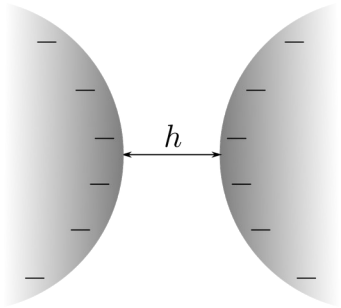
Repulsive force – Poisson Boltzmann

PB-ψ

$$\left.\frac{\delta\Omega}{\delta\psi(\boldsymbol{r})}\right|_{\partial V} = \psi(\boldsymbol{r}) - \psi_0 = 0$$

PB-σ

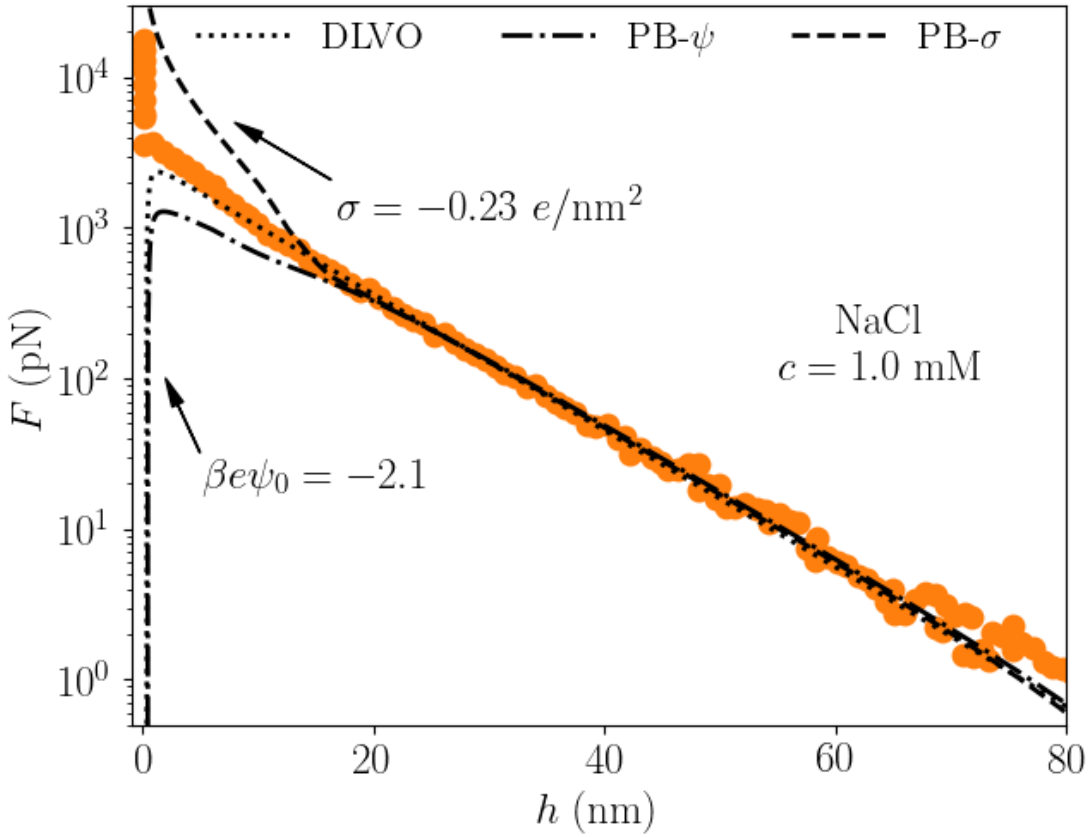
$$\left.\frac{\delta\Omega}{\delta\psi(\boldsymbol{r})}\right|_{\partial V} = -\epsilon_0\epsilon_r\hat{\mathbf{n}}\cdot\boldsymbol{\nabla}\psi(\boldsymbol{r}) - \sigma = 0$$



Derjarguin Approx.

$$W_{\text{ele}} = \int_h^\infty \Pi(h')\,\mathrm{d}h'$$

$$F_{\text{ele}} = 2\pi R_{\text{eff}} W_{\text{ele}}$$



Smith, A. M., Maroni, P., Trefalt, G., & Borkovec, M. (2019). The Journal of Physical Chemistry B, 123(7), 1733-1740.

Charge regulation model

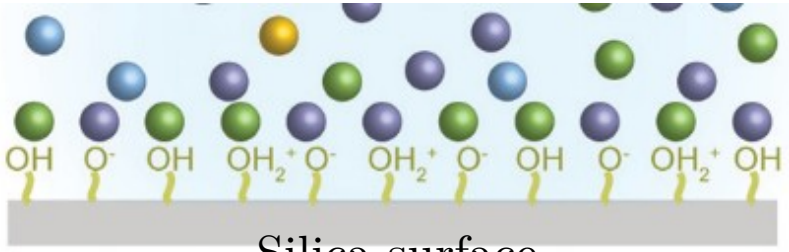
$$-\mathrm{SiOH} \leftrightarrow -\mathrm{SiO}^- + \mathrm{H}^+$$
$$-\mathrm{SiOH} + \mathrm{H}^+ \leftrightarrow -\mathrm{SiOH}_2^+$$

$$n_{\mathrm{H}^+} = 10^{-\mathrm{pH}} e^{-\beta e \psi_0}$$

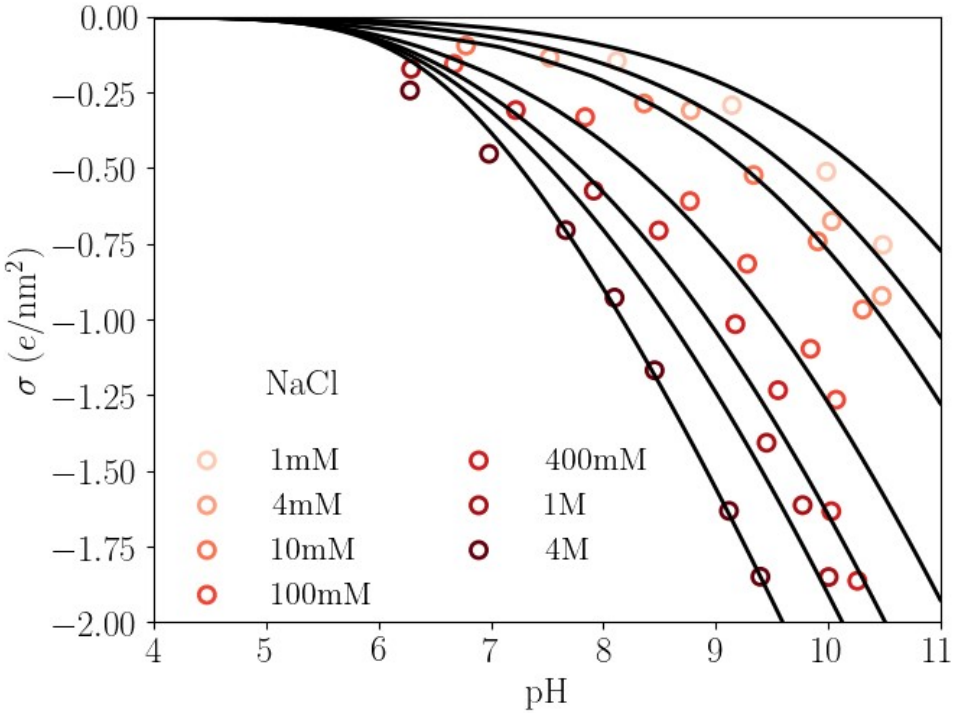
$$\sigma = -e n_{\mathrm{sites}} \frac{K_A - K_B (n_{\mathrm{H}^+}^{(s)})^2}{K_A + (n_{\mathrm{H}^+}^{(s)}) + K_B (n_{\mathrm{H}^+}^{(s)})^2}$$

$$\mathrm{p}K_A = -\log(K_A) = 7.6$$
$$\mathrm{p}K_B = -\log(K_B) = 1.9$$

$$n_{\mathrm{sites}} = 4.6\ \mathrm{nm}^{-2}$$

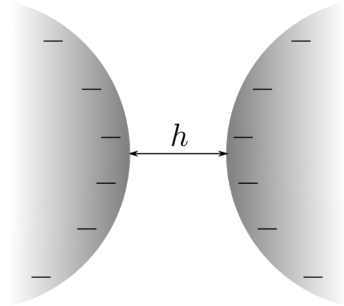


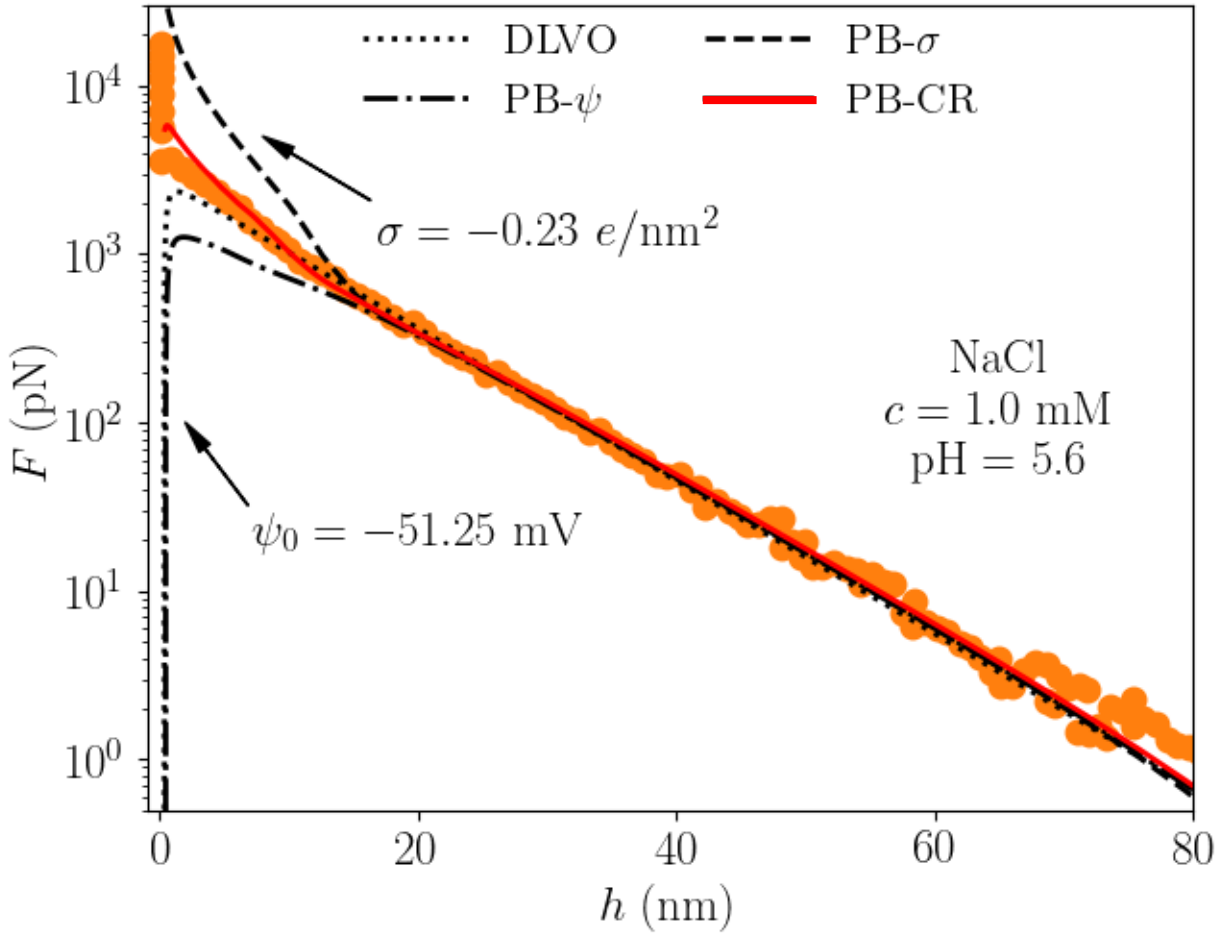
Silica surface



G.H. Bolt, The Journal of Physical Chemistry 61, 1166-1169 (1957).
T. Hiemstra, J. De Wit, and W. Van Riemsdijk, Journal of Colloid and Interface Science 133, 105-117 (1989).

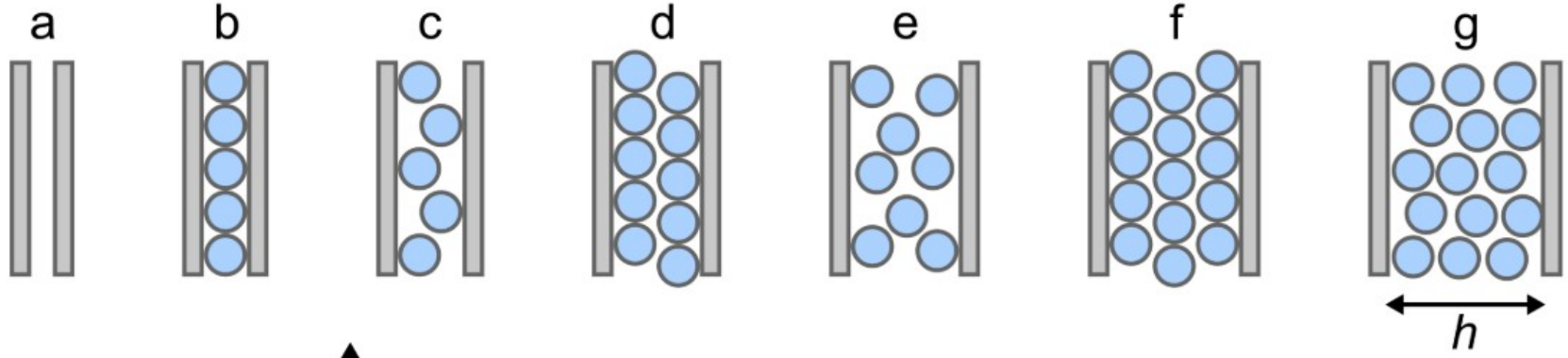
Repulsive force

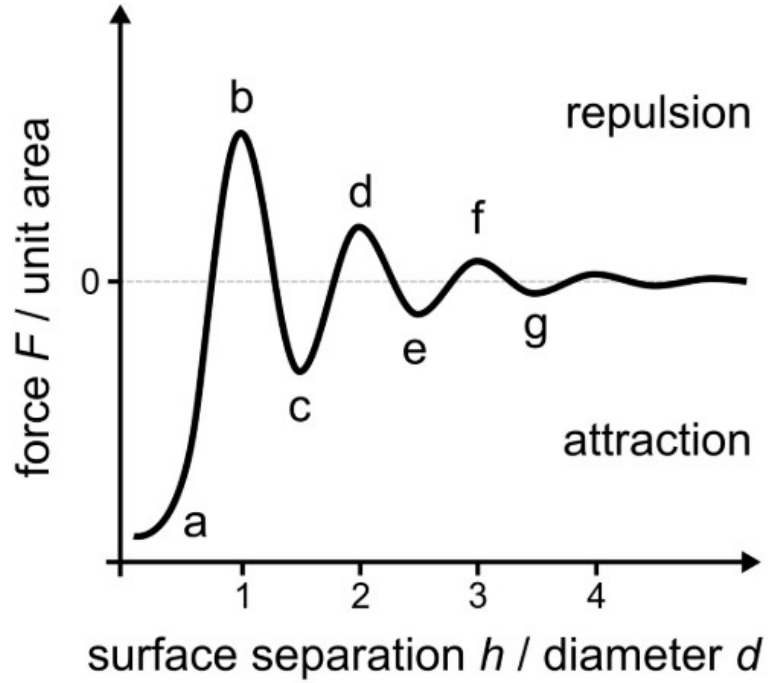


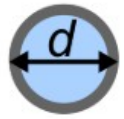


Smith, A. M., Maroni, P., Trefalt, G., & Borkovec, M. (2019). The Journal of Physical Chemistry B, 123(7), 1733-1740.

Repulsive force - Correlation





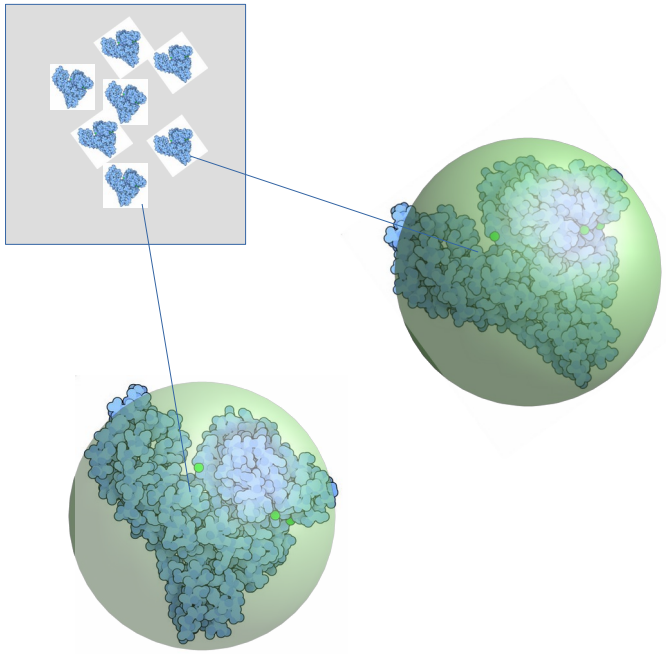


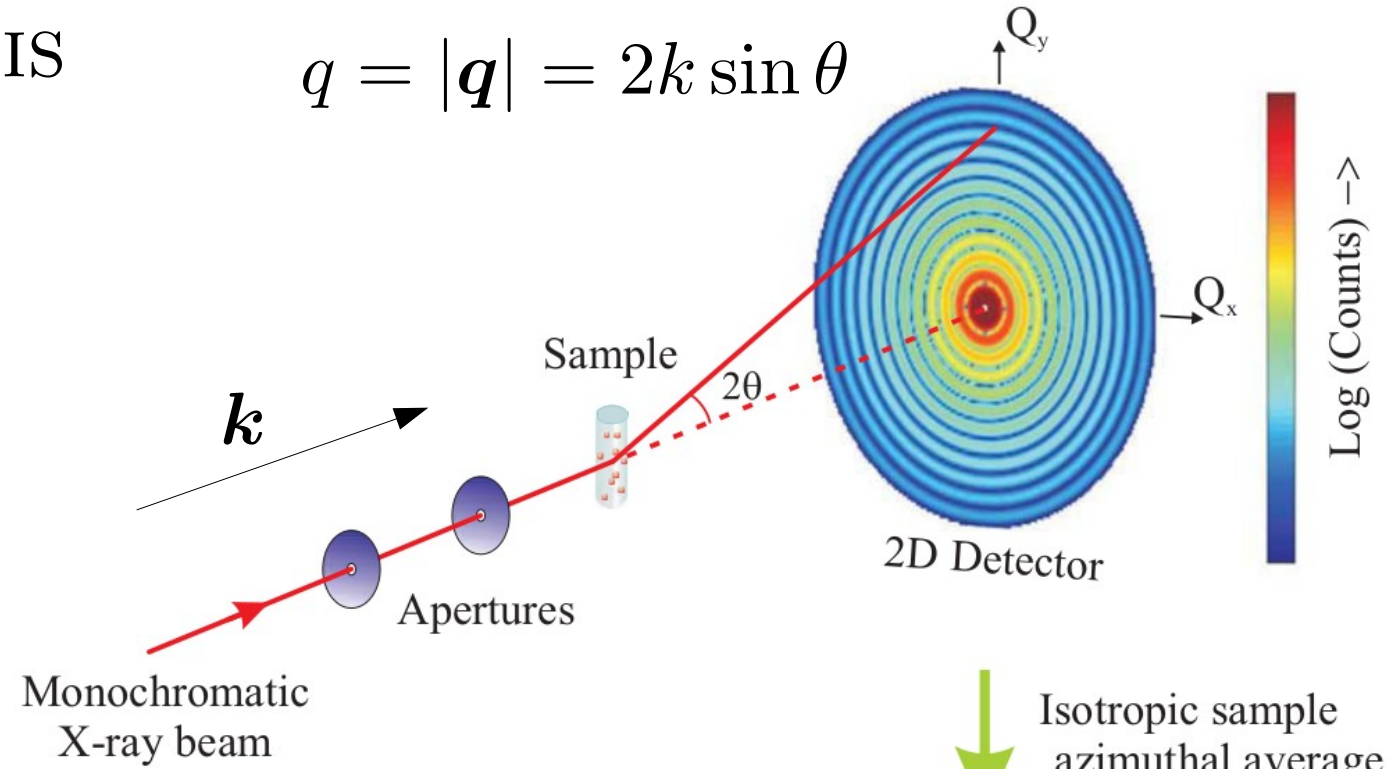
molecule/particle ...

Israelachvili, J. N. Intermolecular and surface forces, 3rd ed.; Academic Press: Burlington, MA, 2011.

SAXS/SANS Analysis

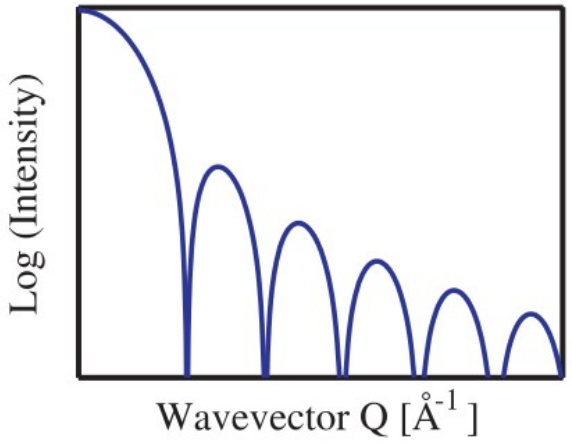
$$q = |\boldsymbol{q}| = 2k \sin\theta$$





Isotropic sample azimuthal average

$$k = \frac{2\pi}{\lambda}$$

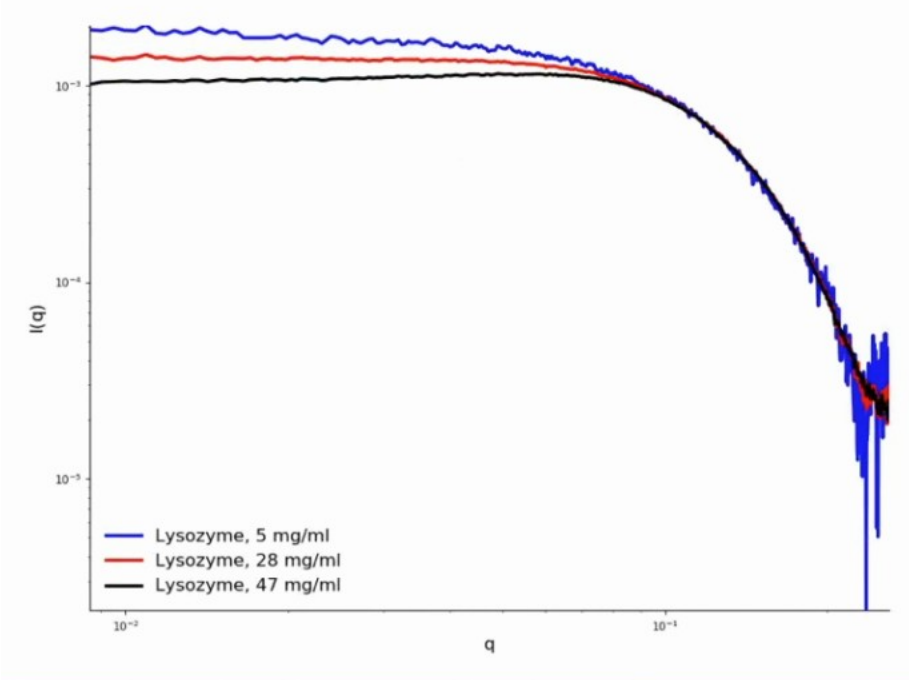


X-ray Intensity

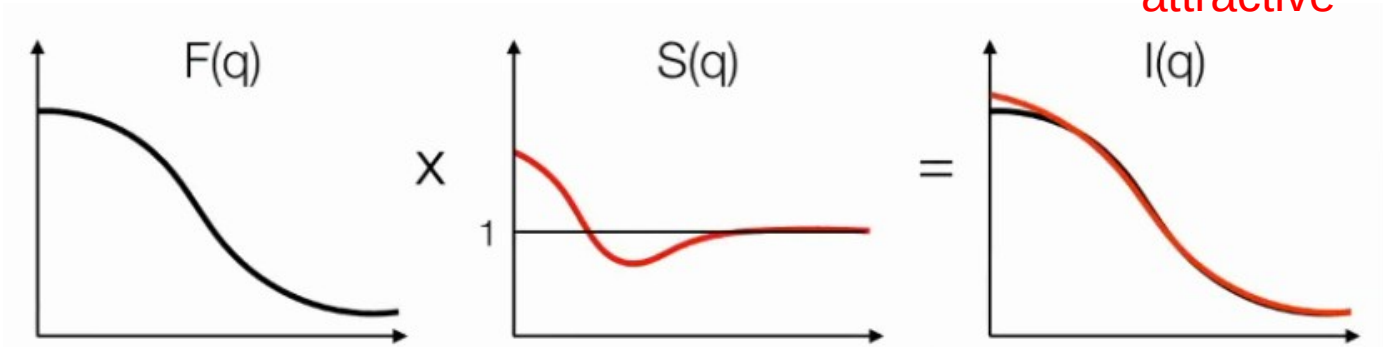
$$I(q) = A|F(q)|^2 S(q) + B$$

Als-Nielsen, Jens, and Des McMorrow. Elements of modern X-ray physics. John Wiley & Sons, 2011.

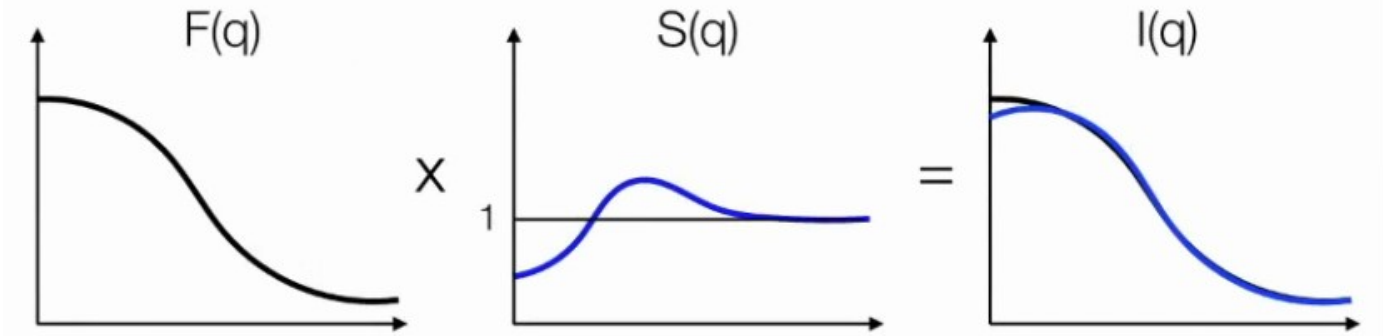
Interparticle interaction



attractive



repulsive

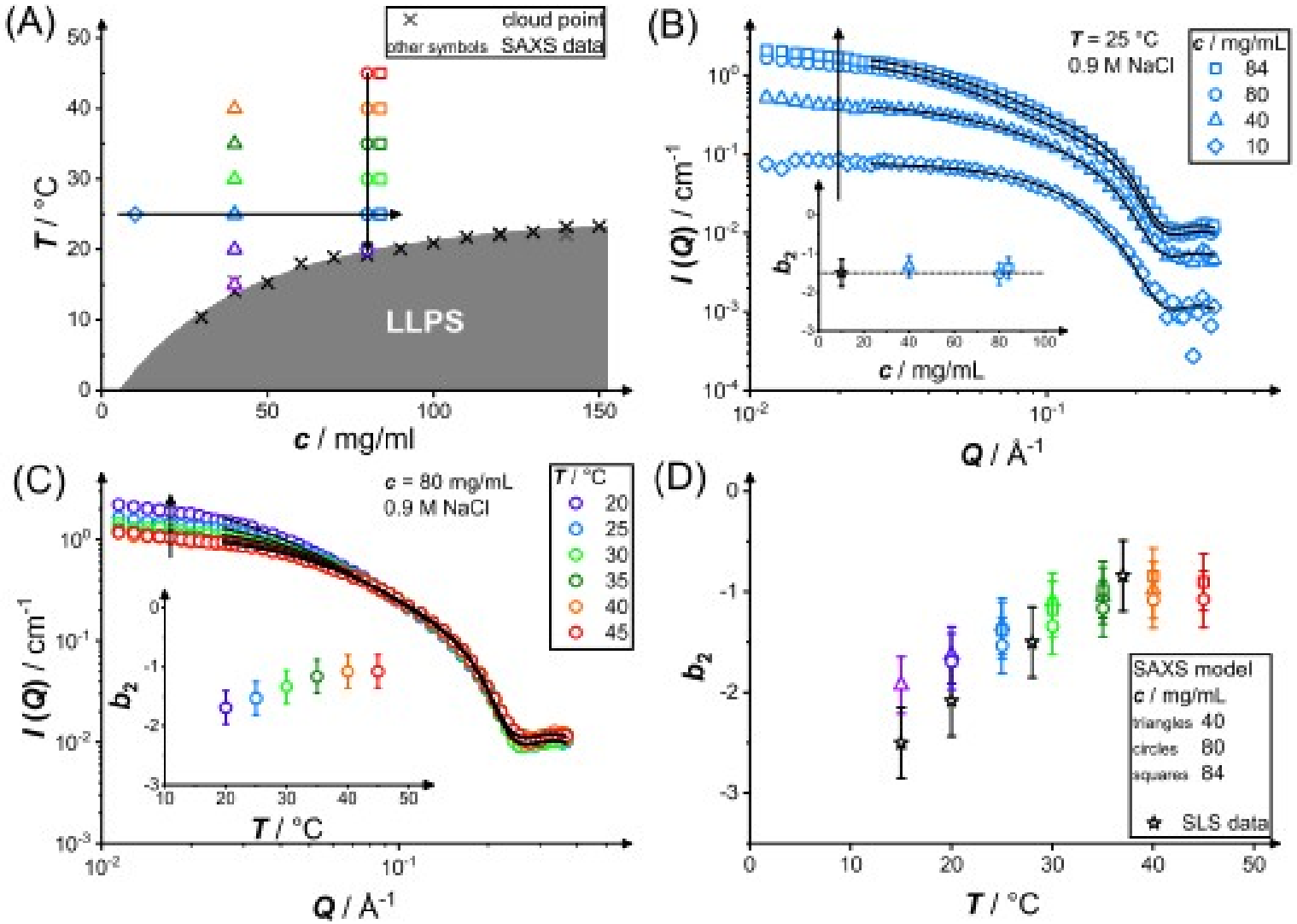


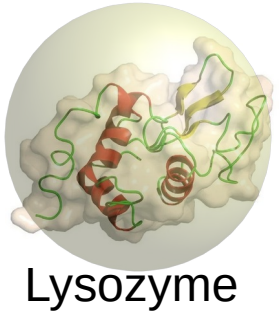
$$S(q) = \frac{1}{1 - \rho\widetilde{c}(q)} = \frac{1}{1 + \rho\beta\widetilde{u}(q)}$$

(Random Phase Approximation)

Hansen, Jean-Pierre, and Ian Ranald McDonald. Theory of simple liquids. Academic Press, 2013.

LIQUID-LIQUID PHASE SEPARATION





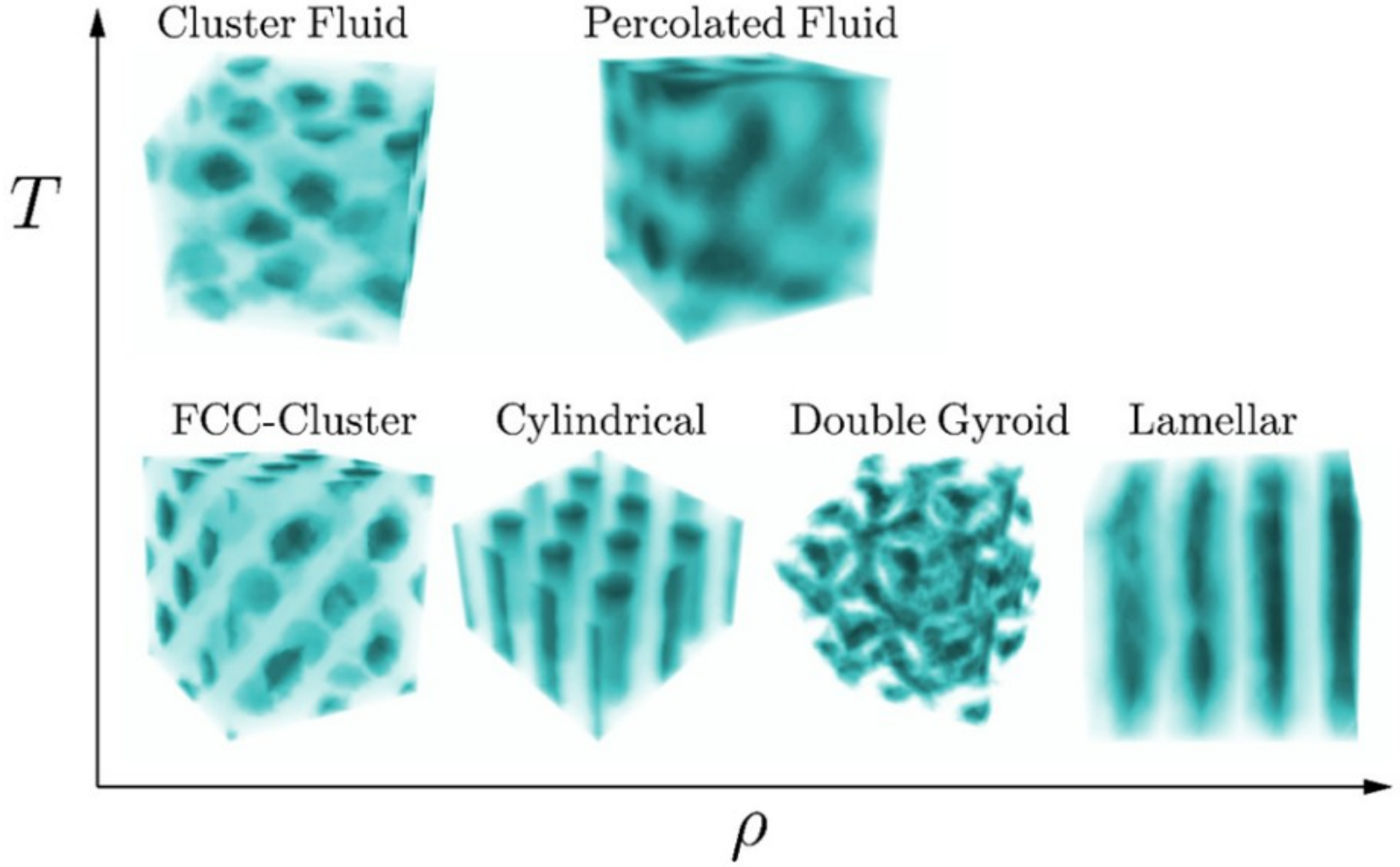
2º Virial Coefficient

$$b_2(T) = 2\pi \int_0^\infty \left[1 - e^{-\beta u(r)}\right] r^2 \, \mathrm{d}r$$

Hansen, J., Pedersen, J. N., Pedersen, J. S., Egelhaaf, S. U., & Platten, F. (2022). The Journal of Chemical Physics.

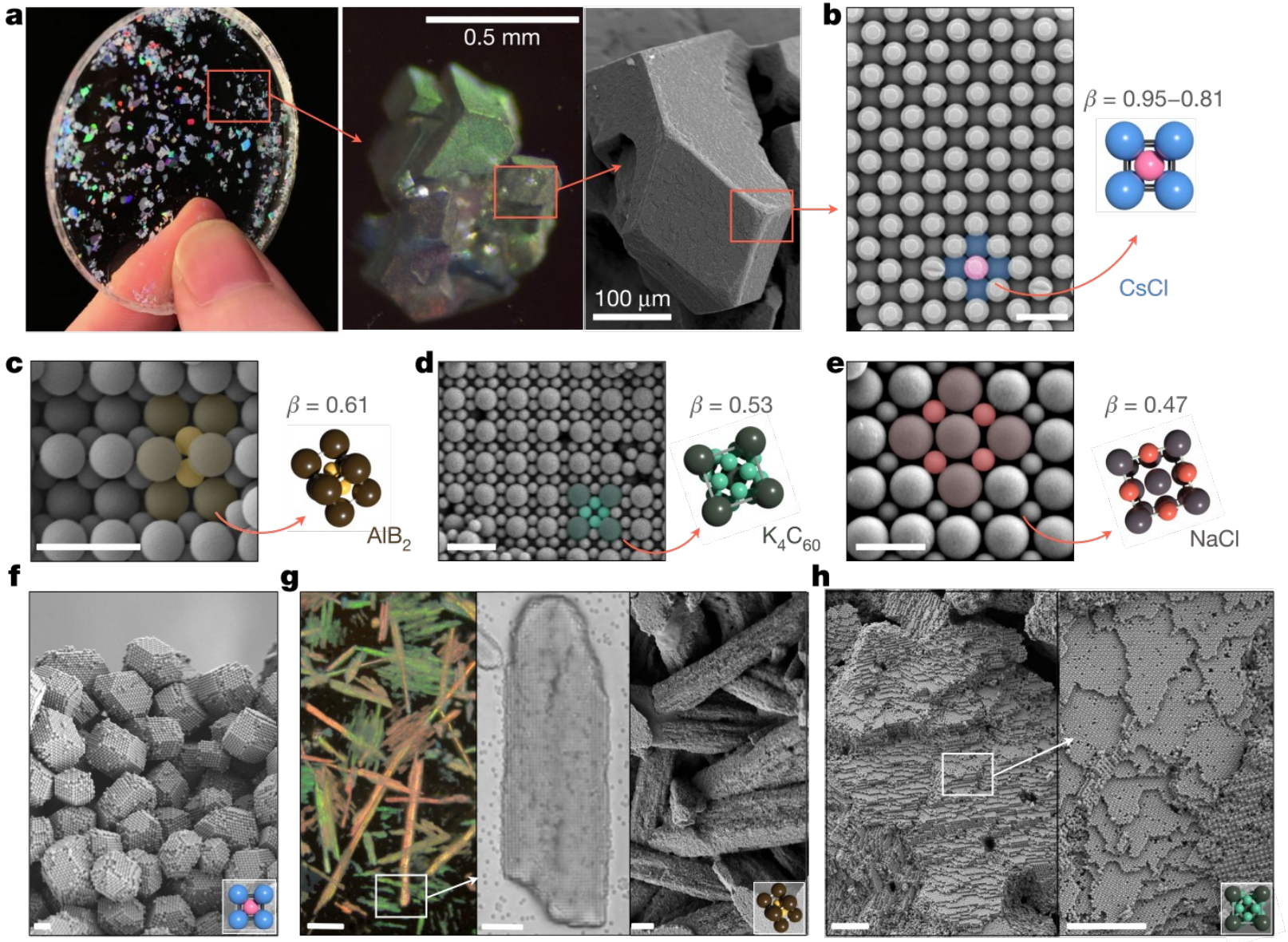
SALR Structures

SALR = **S**hort-Range **A**ttraction and **L**ong-Range **R**epulsion



Zhuang, Yuan, and Patrick Charbonneau. 2016. The Journal of Physical Chemistry B 120 (32): 7775-82.

Colloid Crystal



Hueckel, T., Hocky, G. M., Palacci, J., & Sacanna, S. 2020. Nature, 580(7804), 487-490.

Phase-Field Models

Gradient Expansion

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 28, NUMBER 2 FEBRUARY, 1958

Free Energy of a Nonuniform System. I. Interfacial Free Energy

JOHN W. CAHN AND JOHN E. HILLIARD
General Electric Research Laboratory, Schenectady, New York
(Received July 29, 1957)

Relative Density deviation

$$\rho(\boldsymbol{r}) = \rho_{\text{ref}}[1 + \psi(\boldsymbol{r})]$$

Free-energy functional

$$F[T, \rho] = \int \mathrm{d}\boldsymbol{r}\, f(\rho(\boldsymbol{r}))$$

Cahn-Hilliard Equation

$$\frac{\partial \rho}{\partial t} = M\nabla^2\left(\frac{\delta F}{\delta \rho}\right)$$

Excess free-energy functional

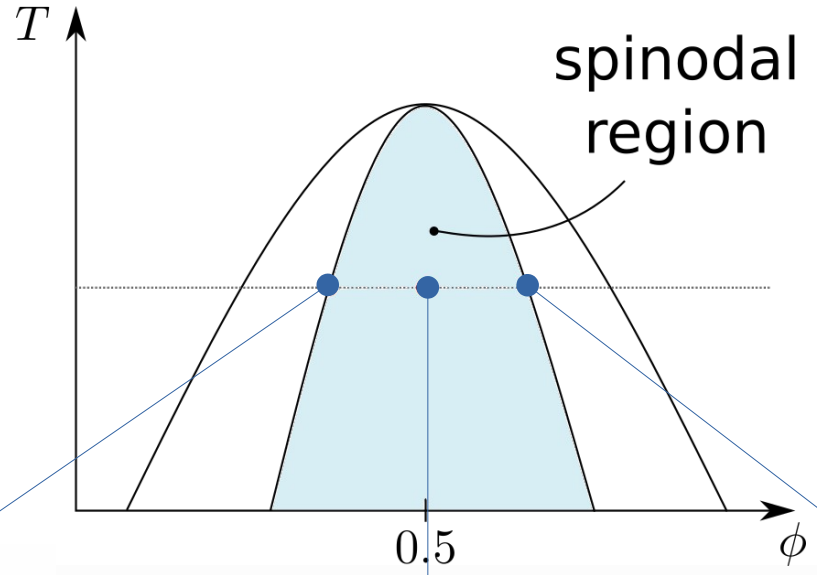
$$\tilde{c}^{(2)}(\boldsymbol{k}) = \tilde{c}_0^{(2)} + \tilde{c}_2^{(2)}\boldsymbol{k}^2 + \tilde{c}_4^{(2)}\boldsymbol{k}^4 + \cdots \longrightarrow c^{(2)}(\boldsymbol{r}) = c_0^{(2)} + c_2^{(2)}\nabla^2 + c_4^{(2)}\nabla^4 + \cdots$$

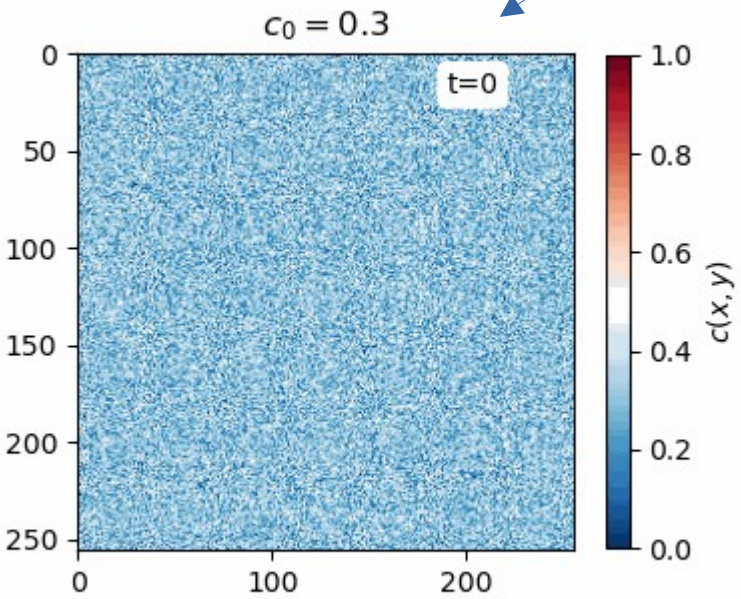
$$F_{\text{exc}}[T, \rho] = F_{\text{exc}}^{(0)} - \frac{\rho_{\text{ref}}}{2} k_B T \int \mathrm{d}\boldsymbol{r}\, \left(B_1\psi^2 + B_2\psi\nabla^2\psi + B_3\psi\nabla^4\psi\right)$$

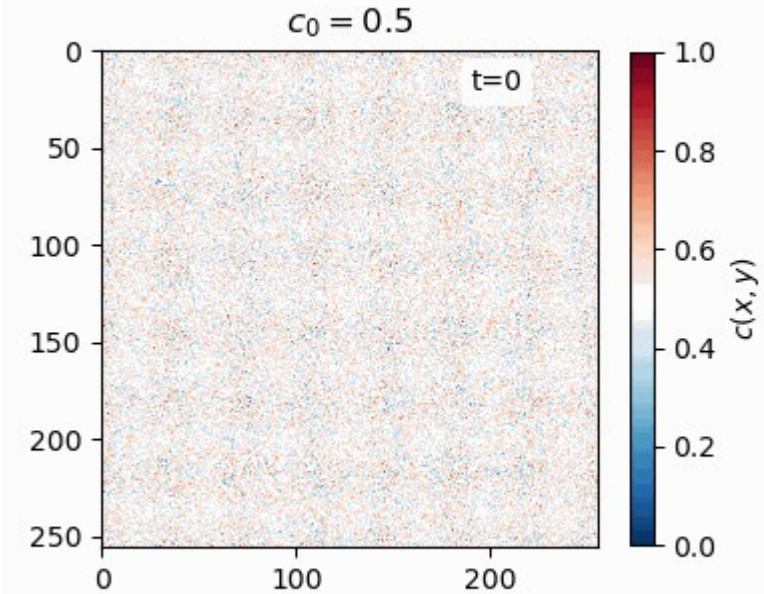
$$\frac{\partial \rho(\boldsymbol{r}, t)}{\partial t} = M\nabla^2\left(2C_1\rho + 2C_2\nabla^2\rho + C_3\nabla^4\rho + f'(\rho)\right)$$

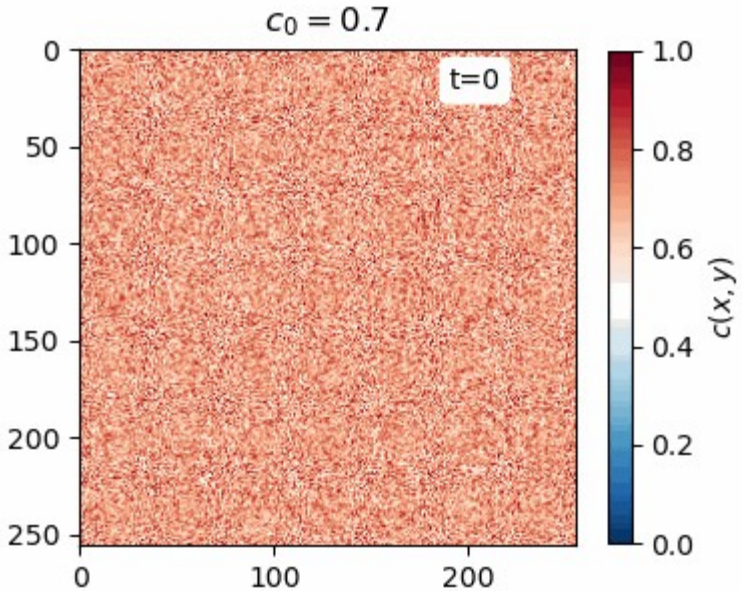
Emmerich et al. (2012). Advances in Physics, 61(6), 665-743.

Phase separation

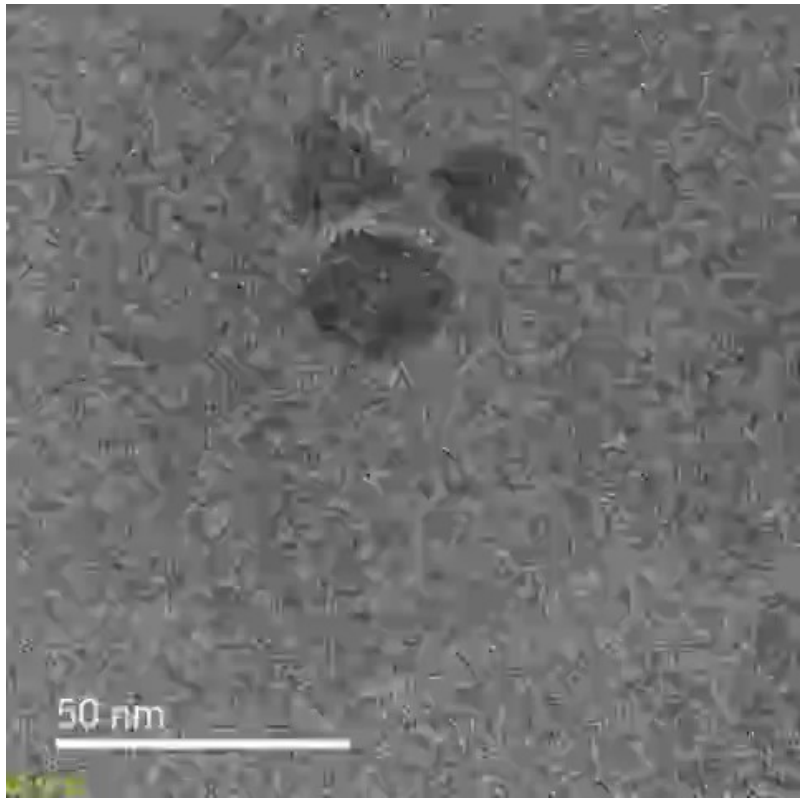






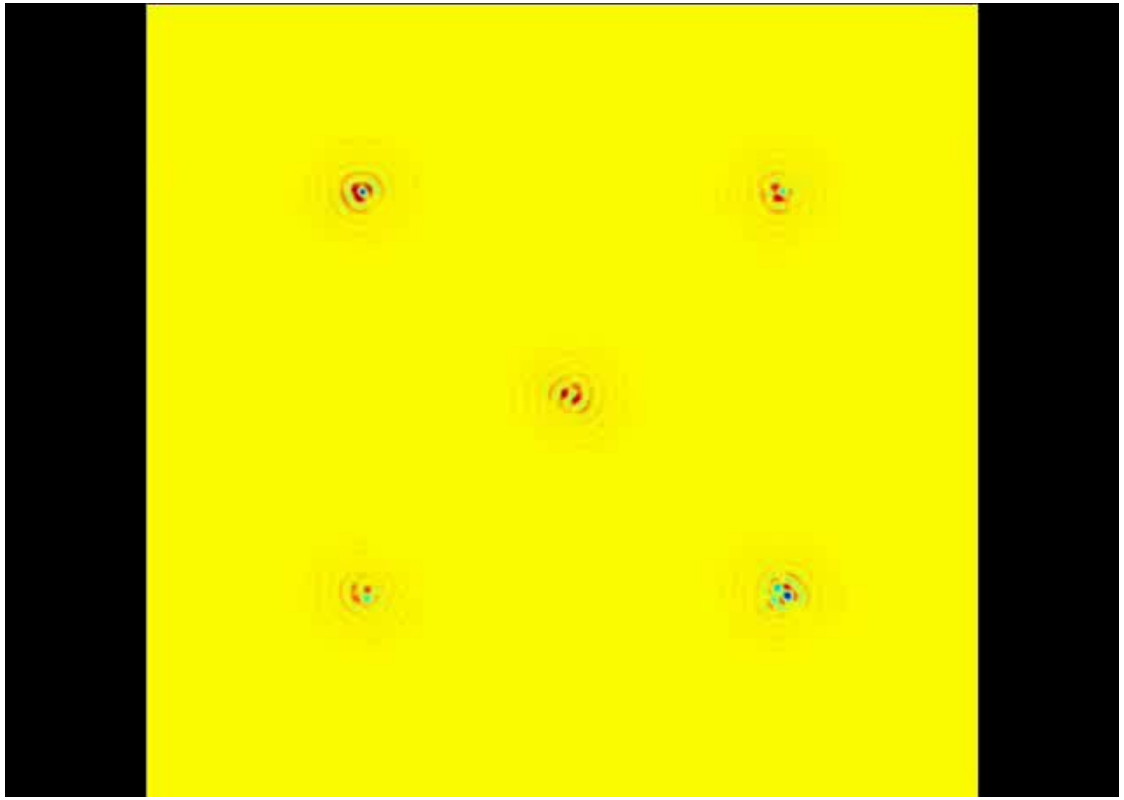


Crystal Nucleation and Growth – TEM in situ

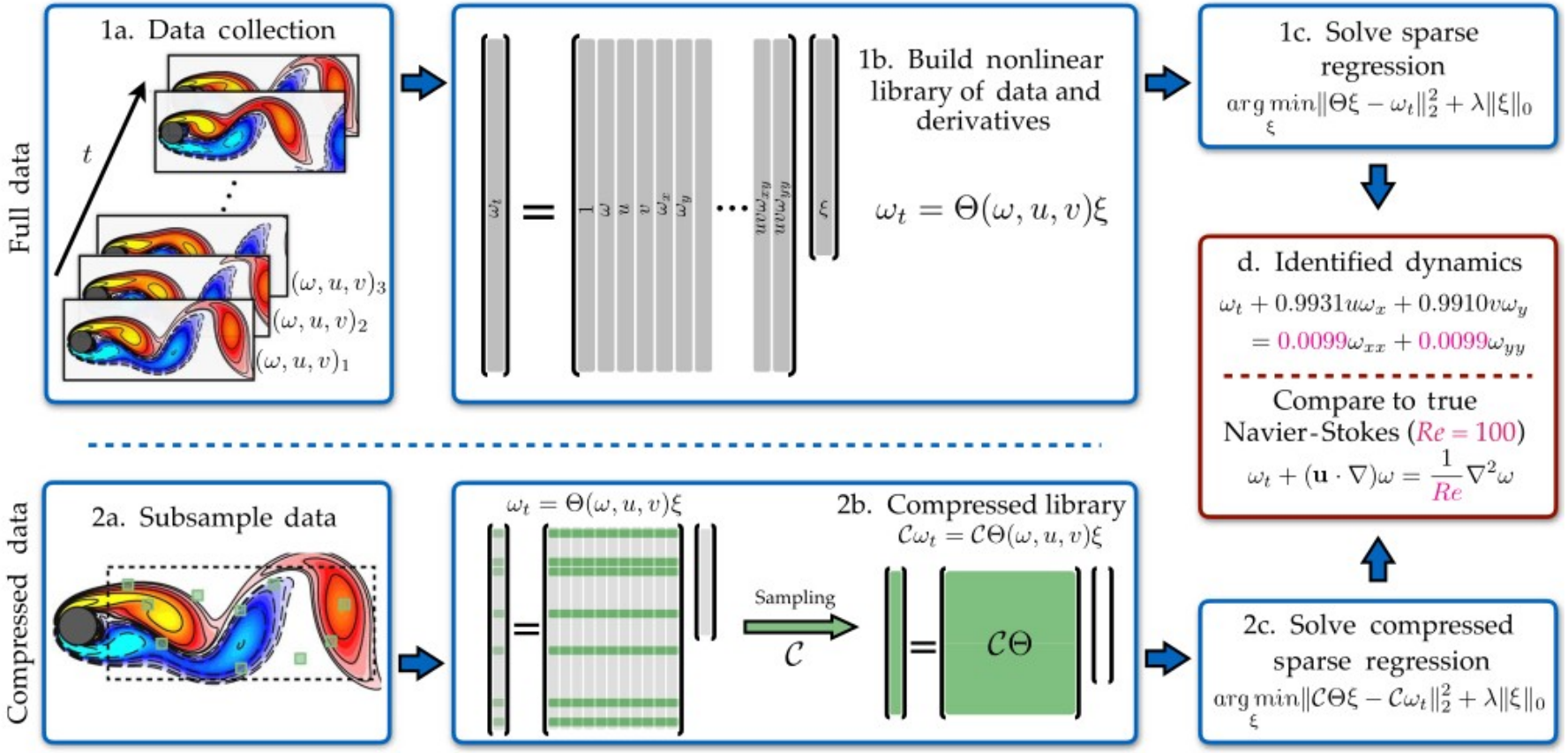


Longuinho, M.M. et al, 2022. CrystEngComm, 24(14), pp.2602-2614.

Crystal Nucleation and Growth – PFC



PDE functional identification of nonlinear dynamics



Correct PDE	$\omega_t = 0.01\omega_{xx} + 0.01\omega_{yy} - u\omega_x - v\omega_y$
Identified PDE (clean data)	$\omega_t = 0.00988\omega_{xx} + 0.00990\omega_{yy} - 0.990u\omega_x - 0.987v\omega_y$
Identified PDE (1% noise)	$\omega_t = 0.0107\omega_{xx} + 0.0083\omega_{yy} - 0.988u\omega_x - 0.983v\omega_y$

Can we identify functionals?!

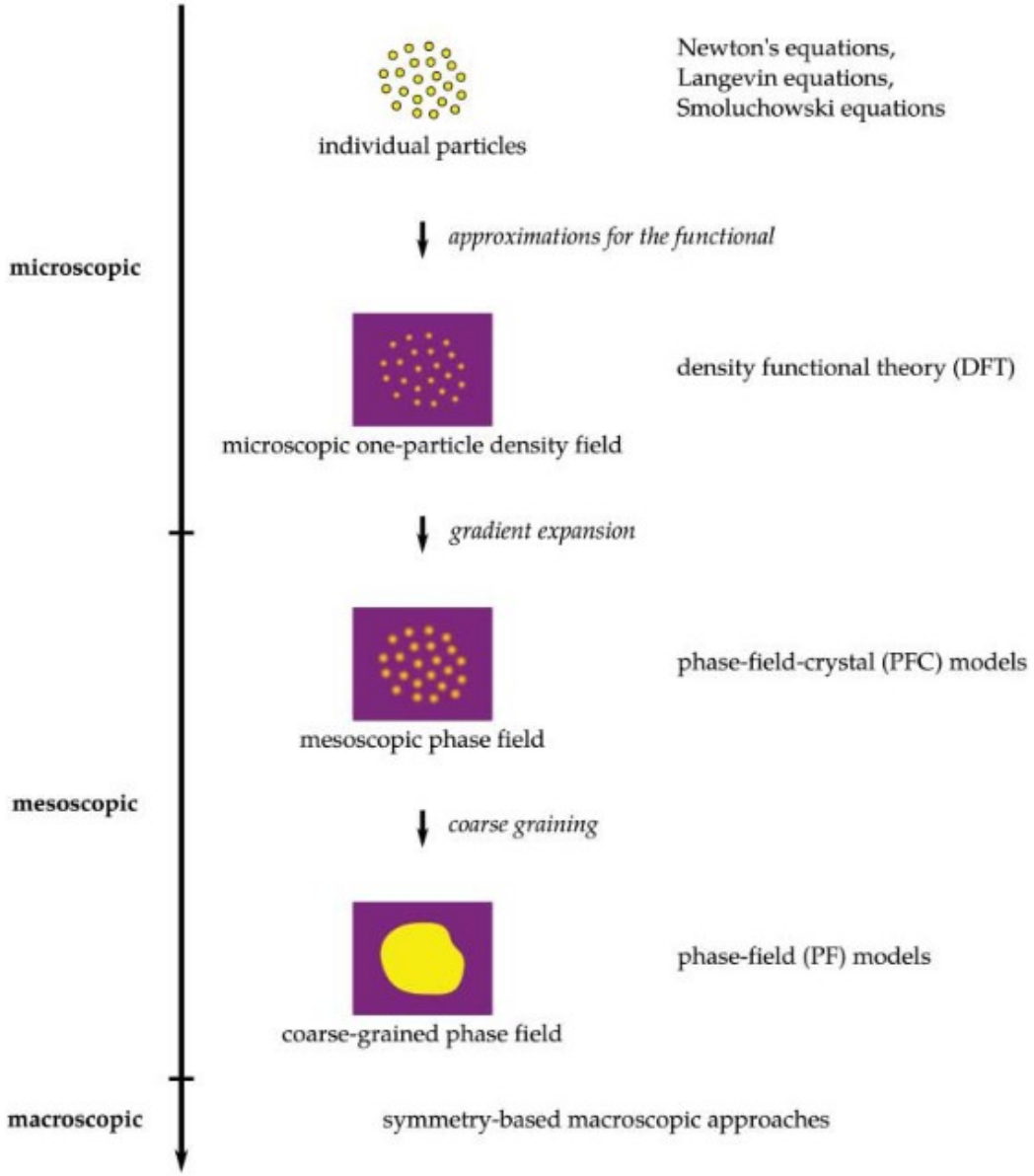
Rudy, S. H. et al. Data-driven discovery of partial differential equations. Sci. Adv. 3, 1-7 (2017).

Conclusions and Perspectives

Conclusions

- The **size and electrostatic correlations are very important** to describe the high concentration systems;
- The **colloid-colloid interactions can be described** by the DFT with thermodynamics and structural properties;
- The connection **DFT-PFC is awesome!**

- **Future works:**
  - Extensions to associative interactions, solvent explicit systems, chain-like systems (e.g., ionic liquids).
  - Quantum DFT? Chemisorption
  - Machine-learning functionals



Acknowledgments

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www.elvissoares.com.br

CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

CAPES

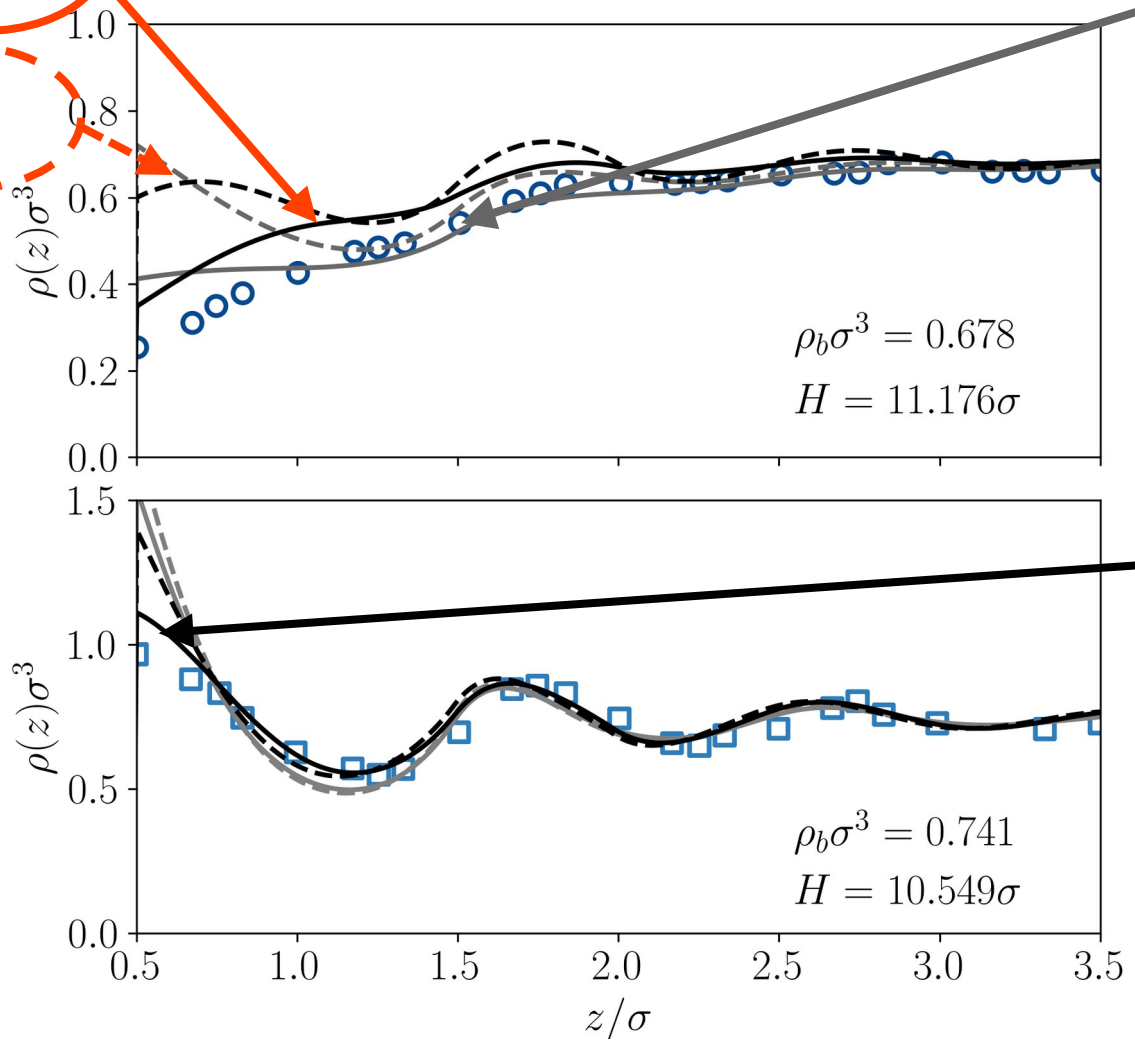
PETROBRAS

Back-Up Slides

Different "flavors" of DFT

SCPT

BH



Modified Weigthed approximation

$$F_{\text{pert}}[\rho(\boldsymbol{r})] = \int \mathrm{d}\boldsymbol{r}\, \overline{\rho}(\boldsymbol{r}) f_{\text{pert}}(\overline{\rho}(\boldsymbol{r}), T)$$

$$\overline{\rho}(\boldsymbol{r}) = \frac{3}{4\pi\psi^3\sigma^3} \int \mathrm{d}\boldsymbol{r}'\, \rho(\boldsymbol{r}')\Theta(\psi\sigma - |\boldsymbol{r} - \boldsymbol{r}'|)$$

Modified Mean-Field Theory

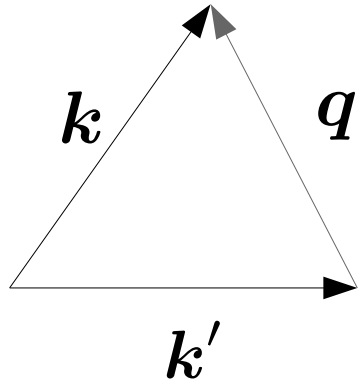
$$F_{\text{pert}}[\rho(\boldsymbol{r})] = F_{\text{mft}}[\rho(\boldsymbol{r})] + F_{\text{corr}}[\rho(\boldsymbol{r})]$$

$$F_{\text{mft}}[\rho(\boldsymbol{r})] = \frac{1}{2} \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r}) \int \mathrm{d}\boldsymbol{r}'\, \rho(\boldsymbol{r}') u(|\boldsymbol{r} - \boldsymbol{r}'|)$$

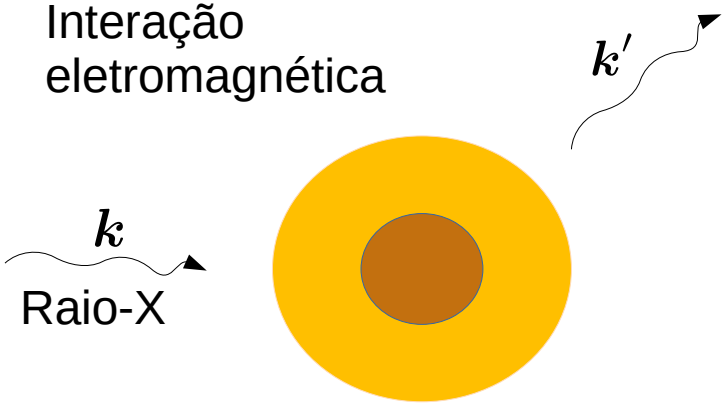
$$F_{\text{corr}}[\rho(\boldsymbol{r})] = \int \mathrm{d}\boldsymbol{r}\, \overline{\rho}(\boldsymbol{r}) f_{\text{corr}}(\overline{\rho}(\boldsymbol{r}), T),$$

Soares, E. do A., Barreto, A. G. & Tavares, F. W. Fluid Phase Equilib. 542–543, 113095 (2021).

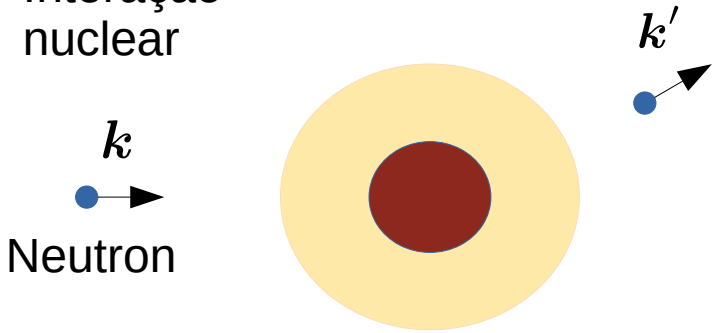
Teoria de Espalhamento



Interação eletromagnética



Interação nuclear



Intensidade espalhada

Fator de Estrutura

$$I(q) = nV_p^2 \Delta\rho_e^2 |F(q)|^2 S(q) + B(q)$$

Densidade de partículas

Volume da partícula

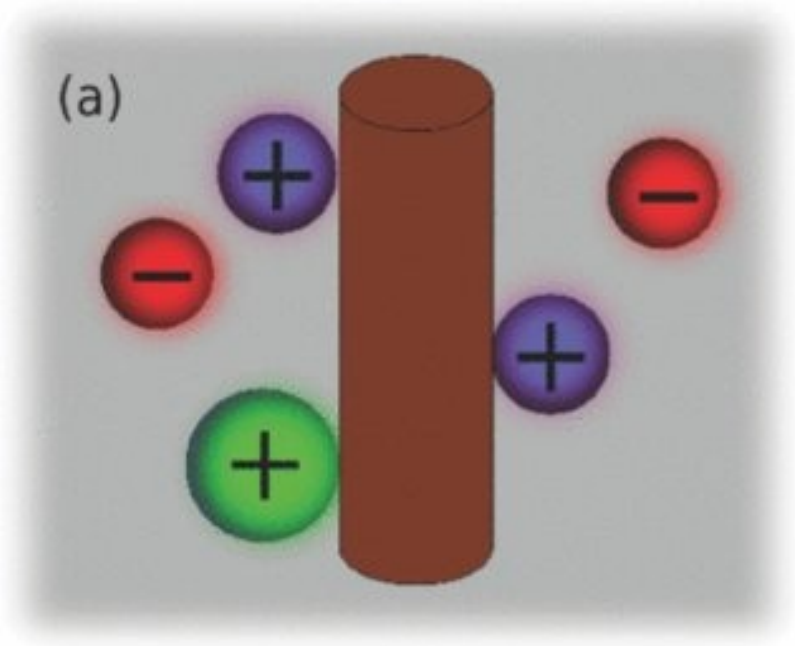
Diferença de densidade *específica* entre a partícula e o solvente

Fator de forma

Background

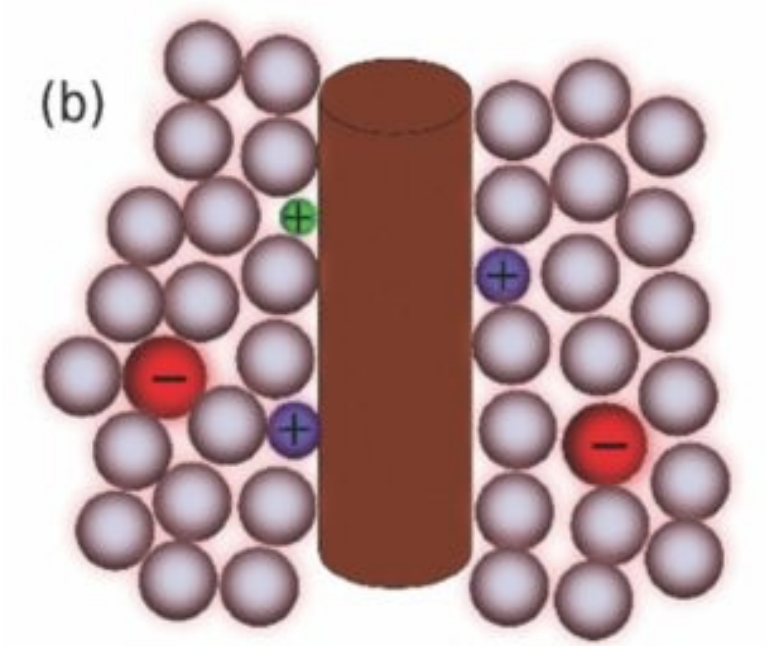
Electrolyte Solution Theories

Primitive Model



- Solvent is implicit (continuum medium)
- Hydrated size of ions
- Ion-ion interactions only

Non-primitive Model



- Solvent is explicit (particle)
- Pauli size of ions
- Ion-ion, Ion-solvent, solvent-solvent interactions

Kontogeorgis, G. M., & Folas, G. K. (2009). Thermodynamic models for industrial applications. John Wiley & Sons.
Ovanesyan, Z. et al (2014). The Journal of Chemical Physics, 141(22), 225103.

Ornstein-Zernike Equation

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

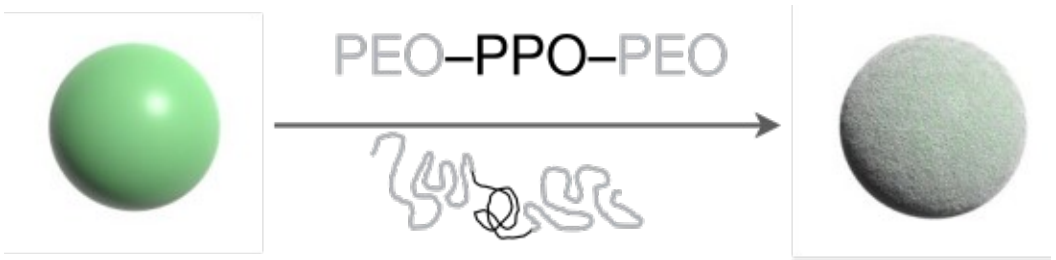
Relation with pair potential

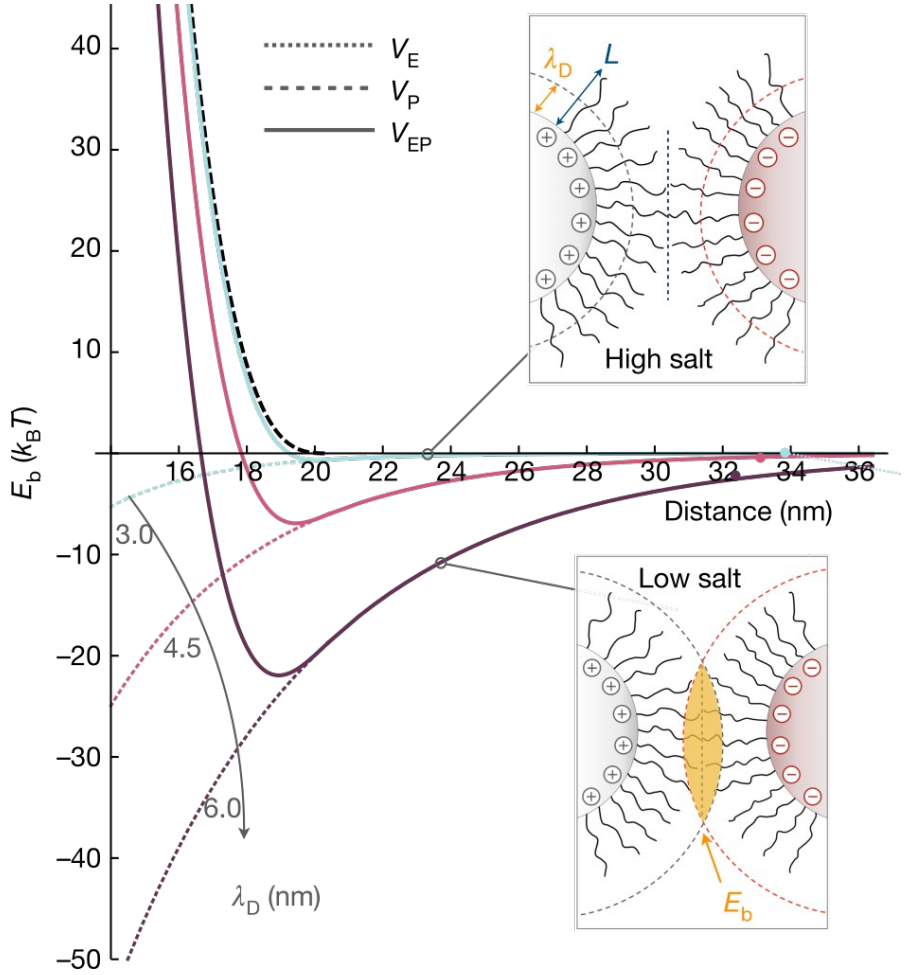
Closure relations:

- **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**yper**n**eted-**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).

Polymer-attenuated Coulombic self-assembly





Electrostatic interaction

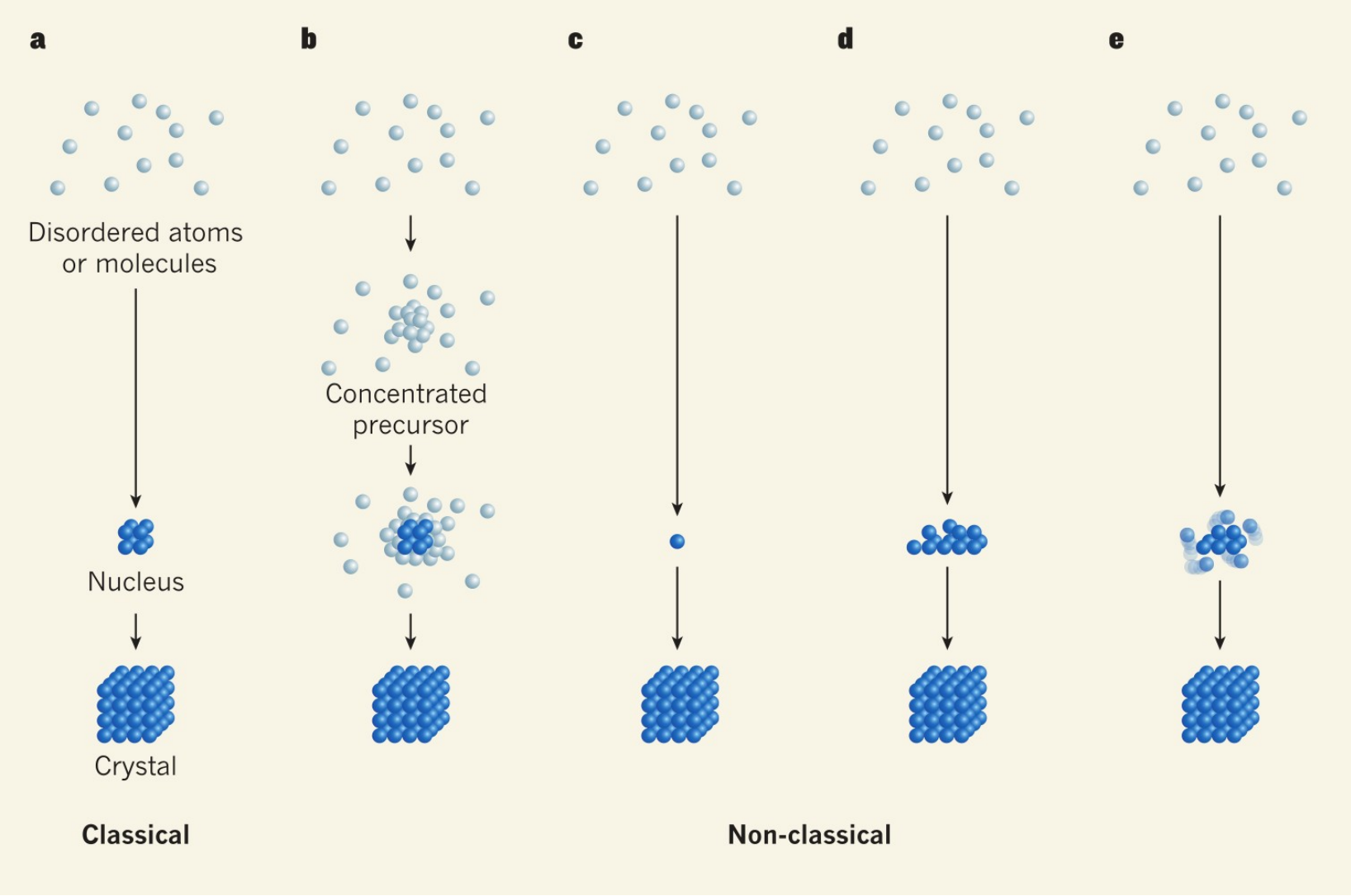
$$u_{\text{ele}}(r) = \frac{Z_+ Z_- e^2}{4\pi\epsilon_0\epsilon_r r} \frac{\exp[-\kappa(r-\sigma)]}{(1+\frac{1}{2}\kappa\sigma)^2}$$

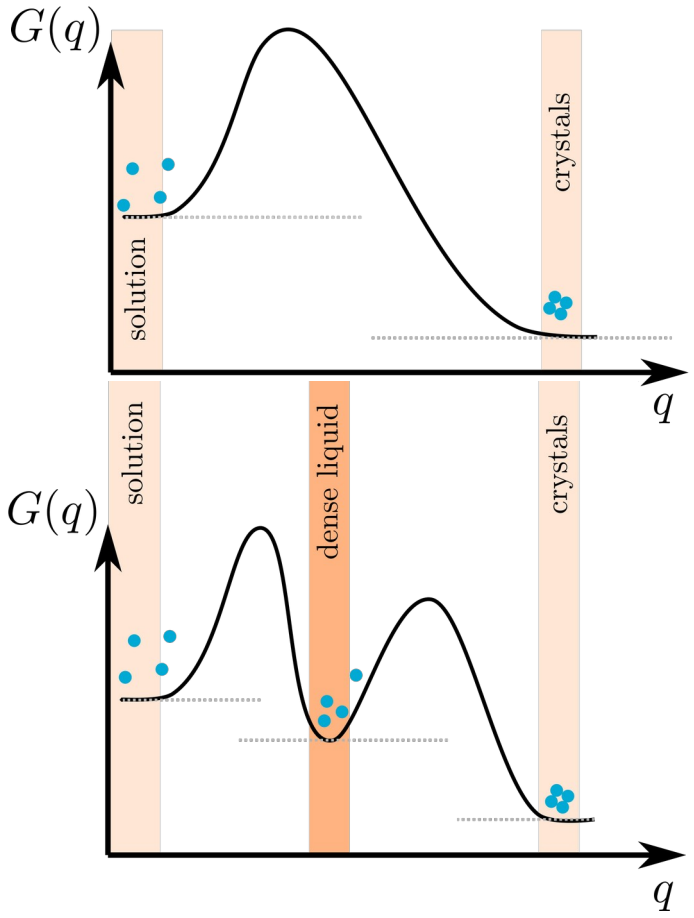
Alexander-de Gennes polymer brush model

$$u_{\text{poly}}(r) = \frac{4\pi d l^2 \sigma_P^{3/2}}{35}\left[28\left(\left(\frac{2l}{h}\right)^{1/4} - 1\right) + \frac{20}{11}\left(1 - \left(\frac{2l}{h}\right)^{-11/4}\right) + 12\left(\frac{h}{2l} - 1\right)\right]$$

Hueckel, T., Hocky, G. M., Palacci, J., & Sacanna, S. (2020). Nature, 580(7804), 487-490.

Multi-Step Nucleation





Vekilov, P. G. (2019). Nature, 570(7762), 450-452.

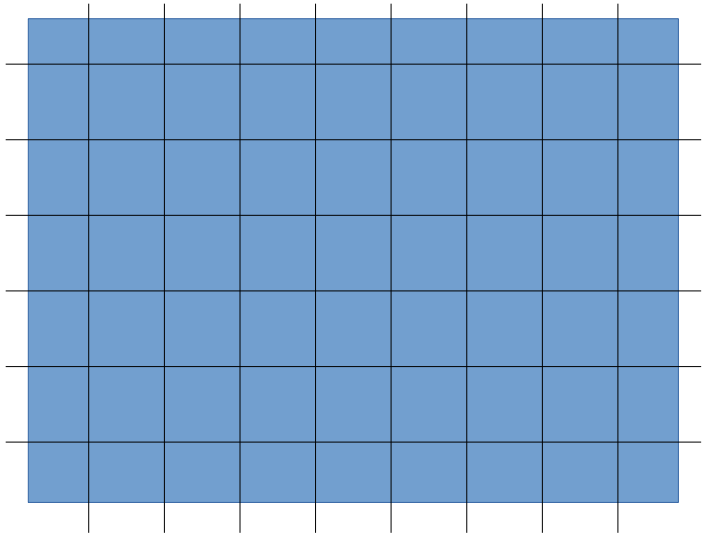
Pseudospectral Methods

$$c(\boldsymbol{r},t) = \frac{1}{V}\sum_{\boldsymbol{k}} \hat{c}_{\boldsymbol{k}}(t) e^{i\boldsymbol{k}\cdot\boldsymbol{r}},$$

$$\frac{\partial c}{\partial t} = M\nabla^2\left[-\kappa\nabla^2 c + f'(c)\right]$$

$$\frac{\partial \tilde{c}_{\boldsymbol{k}}(t)}{\partial t} = M\left[-k^2\mathcal{FT}\{f'\} - (2Wk^2 + \kappa k^4)\tilde{c}_{\boldsymbol{k}}(t)\right]$$

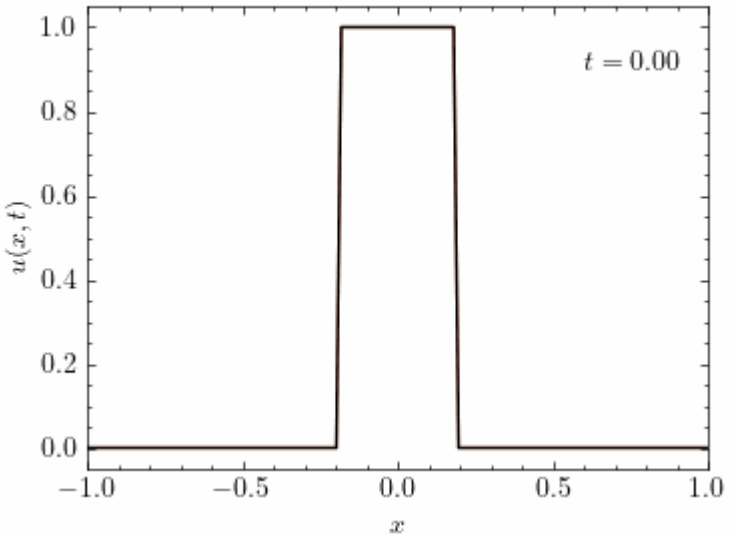
$$\hat{c}_{\boldsymbol{k}}^{n+1} = \frac{\hat{c}_{\boldsymbol{k}}^{n} - k^2\mathcal{FT}\{f'_{\mathrm{nl}}(c_{\boldsymbol{x}}^{n})\}M\Delta t}{1 + M\Delta t(2Wk^2 + \kappa k^4)}$$



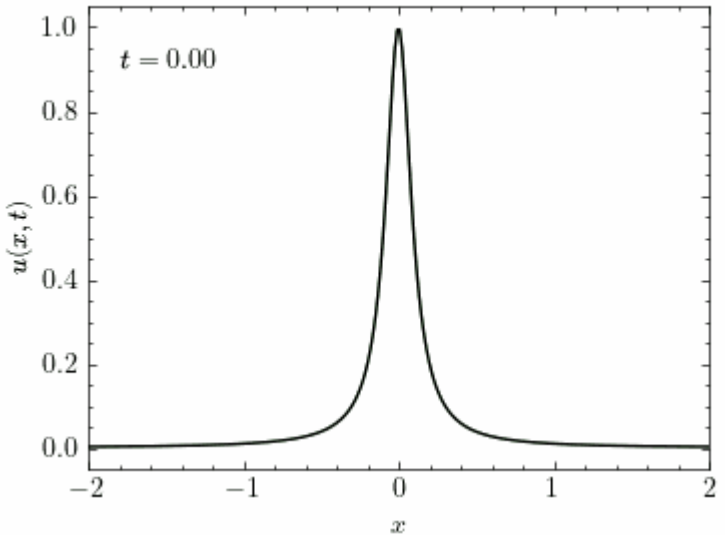
$$k_{\min} = \frac{2\pi}{L}$$

$$k_{\max} = \frac{\pi}{\Delta x}$$

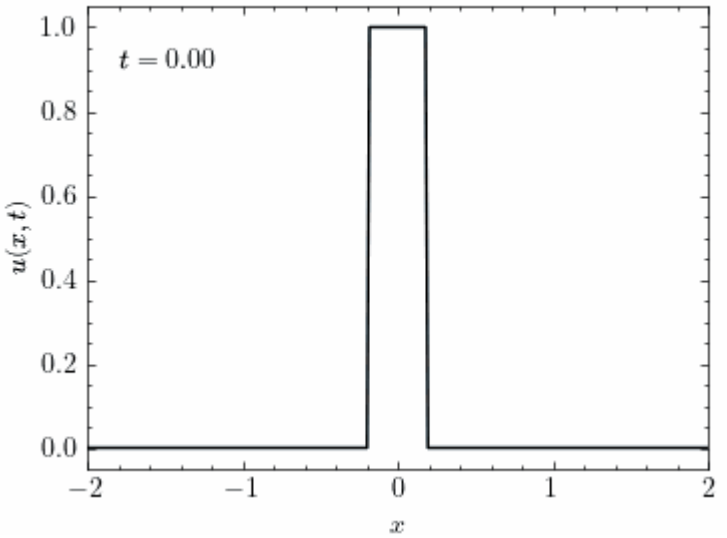
Pseudospectral Methods



Diffusion



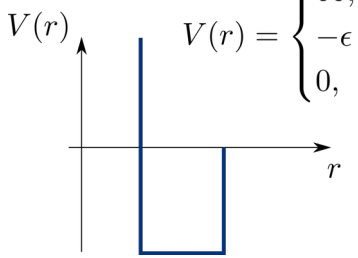
Advection



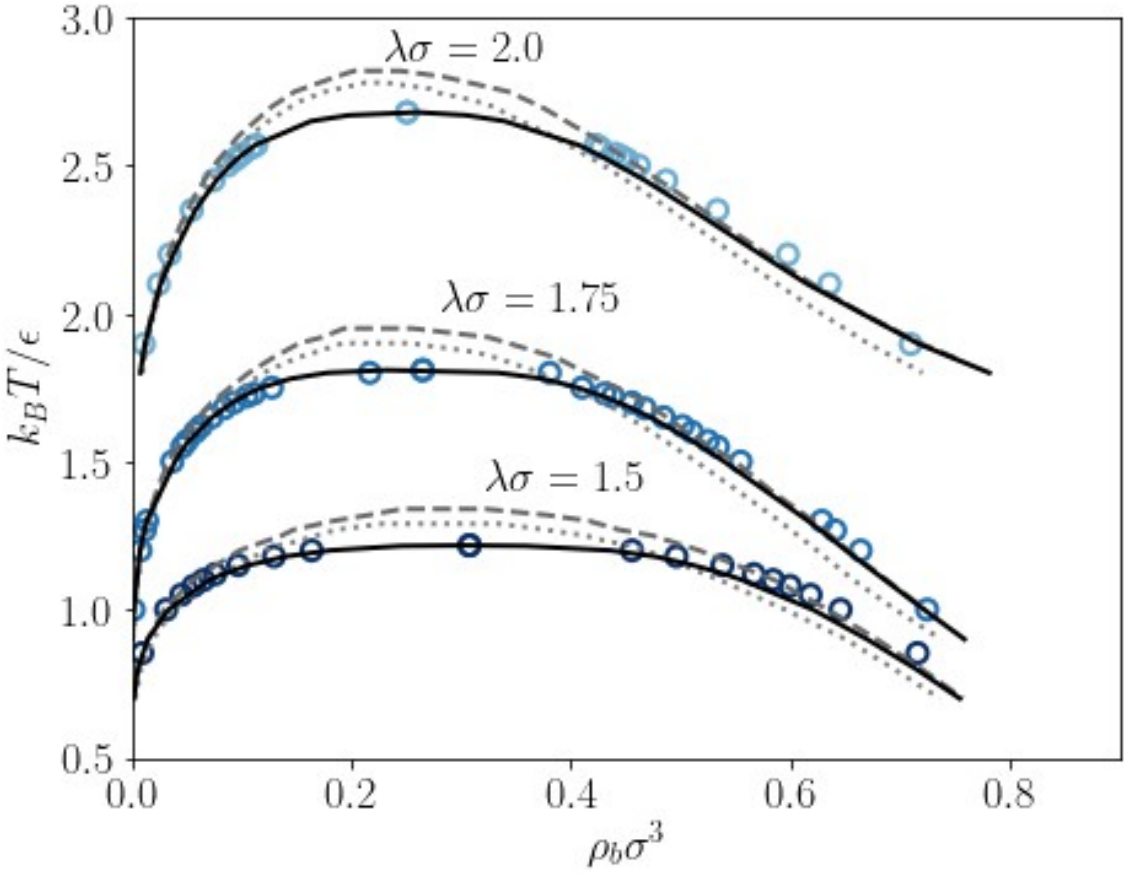
Burgers

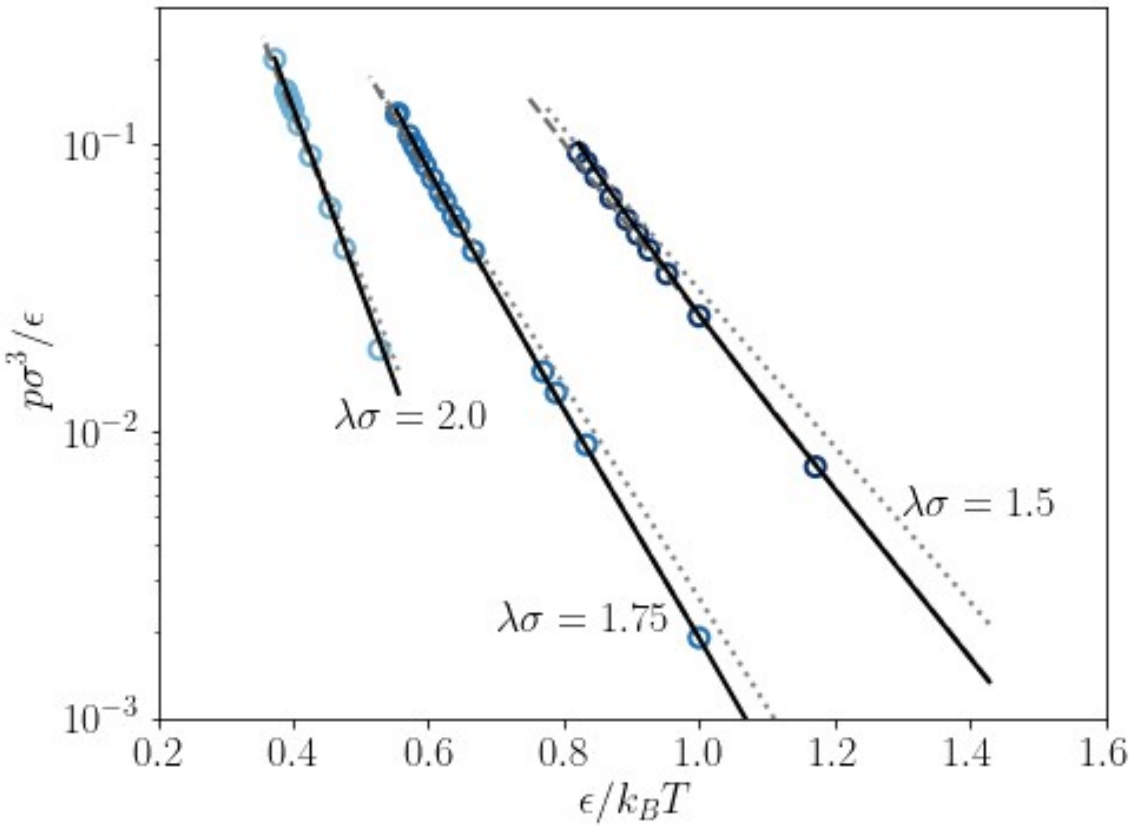
Renormalization

Square-well fluid



$$V(r) = \begin{cases} \infty, & r \leq \sigma \\ -\epsilon & \sigma < r \leq \lambda\sigma \\ 0, & r > \lambda\sigma \end{cases}$$





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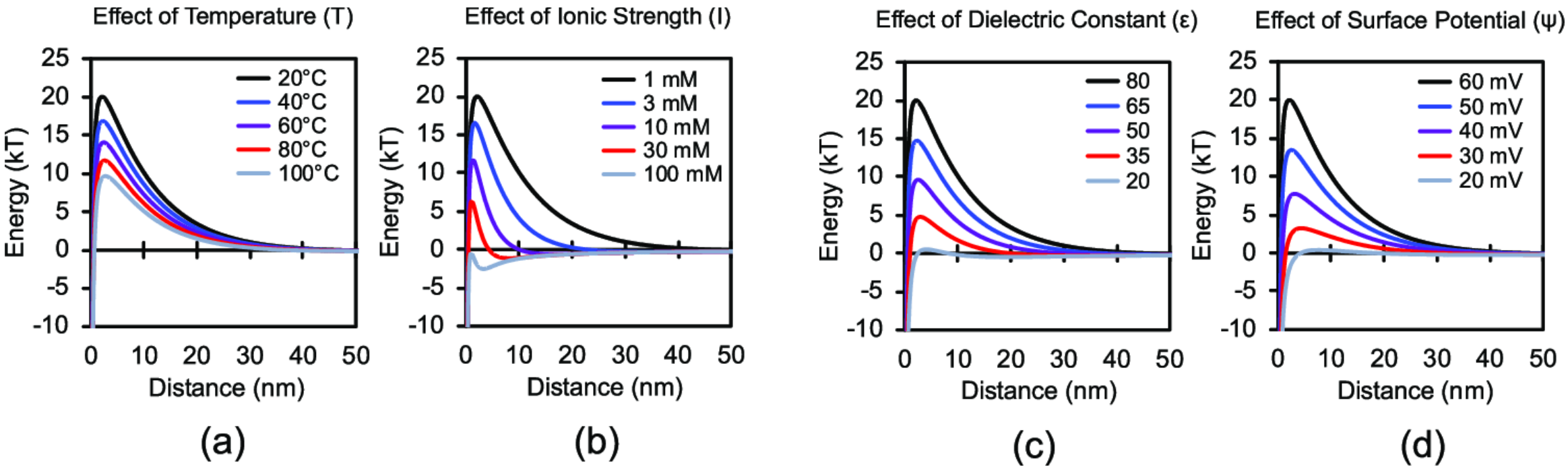
DLVO Theory

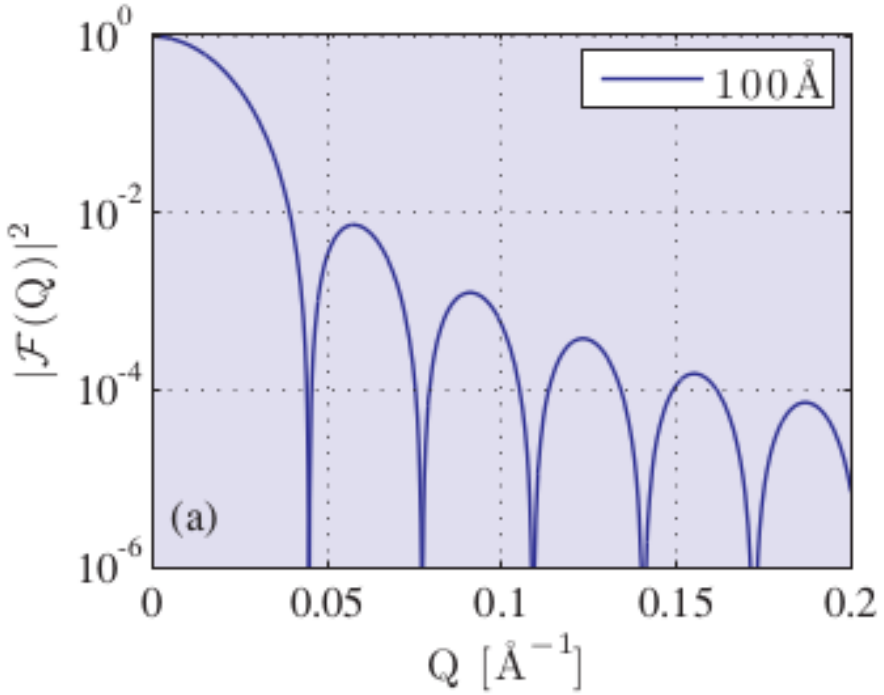

Effect of Temperature (T)
Effect of Ionic Strength (I)
Effect of Dielectric Constant (ε)
Effect of Surface Potential (ψ)
Energy (kT)
Distance (nm)
20°C
40°C
60°C
80°C
100°C
1 mM
3 mM
10 mM
30 mM
100 mM
80
65
50
35
20
60 mV
50 mV
40 mV
30 mV
20 mV
(a)
(b)
(c)
(d)

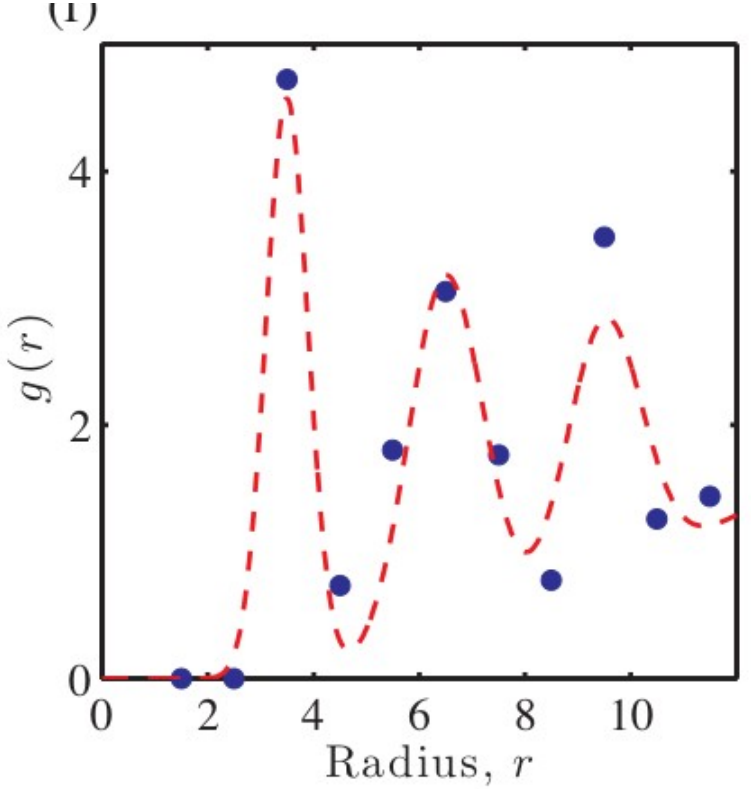
Form and Structure Factors

From Interactions

$$F(q) = \frac{1}{V_p} \int_{V_p} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \, \mathrm{d}V_p$$

$$S(q) = 1 + \rho \int (g(r) - 1) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \, \mathrm{d}r^3$$





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