NANOPHYSIQUE

INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch6 . Density Functional Theory

(classical T>0)

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Lecture 7, 2019-2020

Density Functional Theory

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Le début de la DFT

N particule $\Gamma^{(N)}=(\boldsymbol{q}_1, \boldsymbol{p}_1 \ldots \boldsymbol{q}_N, \boldsymbol{p}_N)$

Hamiltonienne $H^{(N)}=\sum_{i=1}^{N} \frac{p_i^2}{2\mathrm{m}_i}+\sum_{1\leq i<j\leq N} U(q_{ij})+\sum_{i=1}^{N} \phi(\boldsymbol{q}_i)$

Grand-canonical equilibrium distribution

$$\langle O(\boldsymbol{\Gamma})\rangle=\sum_{N=1}^{\infty} \frac{Z_N}{\Xi[\phi]\, N!\, h^{ND}} \exp(\beta\mu N) \int f^{(N)}(\boldsymbol{\Gamma})\, O^{(N)}(\Gamma^{(N)})\, d\Gamma^{(N)}$$

$$f^{(N)}(\Gamma^{(N)})=\frac{1}{Z_N\, N!\, h^{ND}} \exp(-\beta H^{(N)})$$

$$Z_N[\phi]\equiv\exp(-\beta F[\phi])=\frac{1}{N!\, h^{ND}} \int \exp(-\beta H^{(N)})\, d\Gamma^{(N)}$$ Helmholtz energie libre

$$\Xi[\phi]\equiv\exp(-\beta\Omega[\phi])=\sum_{N=0}^{\infty} \frac{1}{N!\, h^{ND}} \int \exp(-\beta(H^{(N)}-\mu N))\, d\Gamma^{(N)}$$

"Grand potential"

Le début de la DFT: Densité locale

$$\Xi[\phi]\equiv\exp(-\beta\Omega[\phi])=\sum_{N=0}^{\infty}\frac{1}{N!\,h^{ND}}\int\exp(-\beta(H^{(N)}-\mu N))\,d\Gamma^{(N)}$$

Definissez la densite locale: $\hat{\rho}(\boldsymbol{r})=\sum_{i=1}^{N}\delta(\boldsymbol{r}-\boldsymbol{q}_i)$

$$H^{(N)}=\sum_{i=1}^{N}\frac{p_i^2}{2\mathrm{m}_i}+\sum_{1\le i<j\le N}U(r_{ij})+\sum_{i=1}^{N}\phi(\boldsymbol{q}_i)=\sum_{i=1}^{N}\frac{p_i^2}{2\mathrm{m}_i}+\sum_{1\le i<j\le N}U(r_{ij})+\int\hat{\rho}(\boldsymbol{r})\phi(\boldsymbol{r})$$

Alors, $\frac{\delta\Omega[\phi]}{\delta\phi(\boldsymbol{r})}=\langle\hat{\rho}(\boldsymbol{r})\rangle\equiv\rho(\boldsymbol{r})$ “Ensemble-averaged density”

$$\frac{\delta^2\Omega[\phi]}{\delta\phi(\boldsymbol{r})\delta\phi(\boldsymbol{r}')}=\langle\hat{\rho}(\boldsymbol{r})\hat{\rho}(\boldsymbol{r}')\rangle-\langle\hat{\rho}(\boldsymbol{r})\rangle\langle\hat{\rho}(\boldsymbol{r}')\rangle$$

$$\frac{\delta\rho(\boldsymbol{r}|\phi)}{\delta\phi(\boldsymbol{r}')}=\langle\hat{\rho}(\boldsymbol{r})\hat{\rho}(\boldsymbol{r}')\rangle-\langle\hat{\rho}(\boldsymbol{r})\rangle\langle\hat{\rho}(\boldsymbol{r}')\rangle=\underbrace{\langle(\hat{\rho}(\boldsymbol{r})-\rho(\boldsymbol{r}))(\hat{\rho}(\boldsymbol{r}')-\rho(\boldsymbol{r}'))\rangle}_{\text{positive definite}}$$

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

Definissez la fonctionales:

$$f_N(\Gamma;[\phi]) = \frac{1}{\Xi[\phi]N!h^{ND}} \exp(-\beta(H^{(N)} - \mu N))$$

$$\Lambda[\phi,\phi_0] \equiv k_B T \sum_{N=0}^{\infty} \int \left(\ln\left(f_N(\Gamma^{(N)};[\phi]) / f_N(\Gamma^{(N)};[\phi_0]) \right) - \ln \Xi[\phi_0] \right) f_N(\Gamma^{(N)};[\phi]) d\Gamma^{(N)}$$

et notez que

$$\Lambda[\phi_0,\phi_0] = -k_B T \ln \Xi[\phi_0] = \Omega[\phi_0]$$

de sorte que

$$\Lambda[\phi,\phi_0] = \Lambda[\phi_0,\phi_0] + k_B T \sum_{N=0}^{\infty} \int f_N(\Gamma^{(N)};[\phi]) \ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])} \right) d\Gamma^{(N)}$$

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

$$\Lambda[\phi,\phi_0]=\Lambda[\phi_0,\phi_0]+k_B T\sum_{N=0}^{\infty}\int f_N(\Gamma^{(N)};[\phi])\ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)d\Gamma^{(N)}$$

$$\Lambda[\phi_0,\phi_0]=-k_B T\ln\Xi[\phi_0]=\Omega[\phi_0]$$

En utilisant $x\ln x\geq x-1$ avec égalité si et seulement si $x=1$

$$\int_N f_N(\Gamma^{(N)};[\phi])\ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)d\Gamma^{(N)}$$

$$=\int f_N(\Gamma^{(N)};[\phi_0])\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)\ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)d\Gamma^{(N)}$$

$$\geq\int f_N(\Gamma^{(N)};[\phi_0])\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}-1\right)d\Gamma^{(N)}=0$$

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

$$f_N(\Gamma;[\phi]) = \frac{1}{\Xi[\phi] N! h^{ND}} \exp(-\beta(H^{(N)} - \mu N))$$

$$\Lambda[\phi,\phi_0] = \Lambda[\phi_0,\phi_0] + k_B T \sum_{N=0}^{\infty} \int f_N(\Gamma^{(N)};[\phi]) \ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right) d\Gamma^{(N)}$$

Donc,

$$\int_N f_N(\Gamma^{(N)};[\phi]) \ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right) d\Gamma^{(N)} \geq 0$$

$$\Rightarrow \Lambda[\phi,\phi_0] \geq \Lambda[\phi_0,\phi_0]$$

avec égalité si et seulement si $f_N(\Gamma^{(N)};[\phi]) = f_N(\Gamma^{(N)};[\phi_0])$

ca veux dire $\phi(\boldsymbol{r}) = \phi_0(\boldsymbol{r}) + \text{constante}$

Mais, avec la forme explicite des distributions,

$$\Lambda[\phi,\phi_0] = \Lambda[\phi,\phi] + \int (\phi(\boldsymbol{r}) - \phi_0(\boldsymbol{r}))\rho(\boldsymbol{r};[\phi])\, d\boldsymbol{r}$$

Donc, $\Lambda[\phi_0,\phi_0] \leq \Lambda[\phi,\phi] + \int (\phi(\boldsymbol{r}) - \phi_0(\boldsymbol{r}))\rho(\boldsymbol{r};[\phi])\, d\boldsymbol{r}$

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

$$\Lambda[\phi_0,\phi_0]\leq\Lambda[\phi,\phi]+\int\left(\phi(\boldsymbol{r})-\phi_0(\boldsymbol{r})\right)\rho(\boldsymbol{r};[\phi])\,d\boldsymbol{r}, \qquad \text{égalité}\Leftrightarrow\phi(\boldsymbol{r})=\phi_0(\boldsymbol{r})+\text{constante}$$

On peut répéter l'argument avec $\phi\Leftrightarrow\phi_0$

$$\Lambda[\phi,\phi]\leq\Lambda[\phi_0,\phi_0]+\int\left(\phi_0(\boldsymbol{r})-\phi(\boldsymbol{r})\right)\rho(\boldsymbol{r};[\phi_0])\,d\boldsymbol{r}$$

Donc,

$$0\leq\int\left(\phi_0(\boldsymbol{r})-\phi(\boldsymbol{r})\right)\left(\rho(\boldsymbol{r};[\phi_0])-\rho(\boldsymbol{r};[\phi])\right)d\boldsymbol{r},$$
$$\text{égalité}\Leftrightarrow\phi(\boldsymbol{r})=\phi_0(\boldsymbol{r})+\text{constante}$$

Conclusion:

$$\phi\neq\phi_0\Rightarrow 0<\int\left(\phi_0(\boldsymbol{r})-\phi(\boldsymbol{r})\right)\left(\rho(\boldsymbol{r};[\phi_0])-\rho(\boldsymbol{r};[\phi])\right)d\boldsymbol{r}$$
$$\Rightarrow\rho(\boldsymbol{r};[\phi])\neq\rho(\boldsymbol{r};[\phi_0])$$

C’est claire que $\rho(\boldsymbol{r};[\phi])\neq\rho(\boldsymbol{r};[\phi_0])\Rightarrow\phi\neq\phi_0$

Donc, la relation est un a un.

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

Conclusion: $\phi \neq \phi_0 \Leftrightarrow \rho(\boldsymbol{r};[\phi]) \neq \rho(\boldsymbol{r};[\phi_0])$

1. La relation entre densité est champ est un a un et, donc, inversible:

$$\rho(\boldsymbol{r};[\phi]) \Leftrightarrow \phi(\boldsymbol{r};[\rho])$$

2.La distribution est une fonctionnel de la densite $f_N(\Gamma;[\phi]) \rightarrow f_N(\Gamma;[\rho])$

3. Il y a un fonctionnel $\Omega[\rho,\phi_0] \equiv \Lambda[\phi[\rho],\phi_0]$ et car $\Lambda[\phi,\phi_0] \geq \Lambda[\phi_0,\phi_0]$

$\Omega[\rho,\phi_0]$ est minimizée par $\rho = \rho_0 \equiv \rho[\phi_0]$

4. $\Omega[\rho_0,\phi_0] = \Omega[\phi_0]$

5. $\Omega[\rho,\phi_0] = F[\rho] + \int (\phi_0(\boldsymbol{r}) - \mu)\rho(\boldsymbol{r})\,d\boldsymbol{r}$ où "F" est indépendant du champ.

Euler-Lagrange equation:

$$\boxed{0 = \frac{\delta\Omega[\rho,\phi_0]}{\delta\rho(\boldsymbol{r})} = \frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})} + \phi_0(\boldsymbol{r}) - \mu}$$

Lutsko, Adv. Chem. Phys. **144**, 1-91 (2010).

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Digression: des quantities du mechanique statistique

1. La distribution un particule est la densite locale:

$$f_N^{(N)}(\Gamma^{(N)};[\phi])=\frac{1}{Z[\phi]N!h^{ND}}\exp(-\beta H^{(N)})$$

$$f_{N-1}^{(N)}(\Gamma^{(N-1)}|\phi)=\int f_N(\Gamma|\phi)\,d\boldsymbol{x}_N,\quad d\boldsymbol{x}_N\equiv d\boldsymbol{q}_N\,d\boldsymbol{p}_N$$

$$f_{N-2}^{(N)}(\Gamma^{(N-1)}|\phi)=\int f_N(\Gamma|\phi)\,d\boldsymbol{x}_{N-1}\,d\boldsymbol{x}_N$$

$$\vdots$$

$$f_1^{(N)}(\boldsymbol{x}_1|\phi)=\int f_N(\Gamma|\phi)\,d\boldsymbol{x}_2\ldots d\boldsymbol{x}_N$$

$$\left(\frac{N}{V}\right)^2 g_2^{(N)}(\boldsymbol{q}_1,\boldsymbol{q}_2|\phi)=\int f_2^{(N)}(\boldsymbol{x}_1,\boldsymbol{x}_2|\phi)\,d\boldsymbol{p}_1\,d\boldsymbol{p}_2$$

$$\frac{N}{V}g_1^{(N)}(\boldsymbol{q}_1|\phi)=\int f_1^{(N)}(\boldsymbol{x}_1|\phi)\,d\boldsymbol{p}_1$$

$$\hat{\rho}(\boldsymbol{r})=\sum_{i=1}^{N}\delta(\boldsymbol{r}-\boldsymbol{q}_i)$$

$$\rho(\boldsymbol{r})\equiv\langle\hat{\rho}(\boldsymbol{r})\rangle=\sum_{N=0}^{\infty}\frac{Z_N[\phi]}{\Xi[\phi]}\exp(\beta\mu)\frac{N}{V}g_1^{(N)}(\boldsymbol{r})\xrightarrow[\text{canonique}]{}\rho(\boldsymbol{r})=\frac{N}{V}g_1^{(N)}(\boldsymbol{r})$$

La probabilité de trouver une particule à la position **r**

Digression: des quantities du mechanique statistique

2. La distribution deux particule (canonique):

$$\frac{N(N-1)}{V^2} g_2^{(N)}(\boldsymbol{q}_1, \boldsymbol{q}_2|\phi) = \frac{N(N-1)}{V^2} \int f_2^{(N)}(\boldsymbol{x}_1, \boldsymbol{x}_2|\phi)\, d\,\boldsymbol{p}_1\, d\,\boldsymbol{p}_2 \;= \langle \hat{\rho}(\boldsymbol{q}_1) \hat{\rho}(\boldsymbol{q}_2) \rangle - \langle \hat{\rho}(\boldsymbol{q}_1) \rangle \delta(\boldsymbol{q}_1 - \boldsymbol{q}_2)$$

4. Direct correlation function

$$g_2^{(N)} - 1$$

Definissez

$$\frac{\delta \rho(\boldsymbol{r}|\phi)}{\delta \beta \phi(\boldsymbol{r}')} = \langle \hat{\rho}(\boldsymbol{r}) \hat{\rho}(\boldsymbol{r}') \rangle - \langle \hat{\rho}(\boldsymbol{r}) \rangle \langle \hat{\rho}(\boldsymbol{r}') \rangle \equiv \langle \hat{\rho}(\boldsymbol{r}) \rangle \delta(\boldsymbol{r} - \boldsymbol{r}') + \langle \hat{\rho}(\boldsymbol{r}) \rangle \langle \hat{\rho}(\boldsymbol{r}') \rangle \underline{h(\boldsymbol{r}, \boldsymbol{r}'|\phi)}$$

$$\frac{\delta \beta \phi(\boldsymbol{r}|\rho)}{\delta \rho(\boldsymbol{r}')} \equiv -\frac{1}{\langle \hat{\rho}(\boldsymbol{r}) \rangle} \delta(\boldsymbol{r} - \boldsymbol{r}') + \underline{\Gamma(\boldsymbol{r}, \boldsymbol{r}'|\rho)}$$

DFT: des quantities du mechanique statistique

4. Direct correlation function

$$\frac{\delta\rho(\boldsymbol{r}|\beta\phi)}{\delta\phi(\boldsymbol{r}')} \equiv \langle\hat{\rho}(\boldsymbol{r})\rangle\delta(\boldsymbol{r}-\boldsymbol{r}')+\langle\hat{\rho}(\boldsymbol{r})\rangle\langle\hat{\rho}(\boldsymbol{r}')\rangle h(\boldsymbol{r},\boldsymbol{r}'|\rho);$$

$$\frac{\delta\beta\phi(\boldsymbol{r}|\rho)}{\delta\rho(\boldsymbol{r}')} \equiv -\frac{1}{\langle\hat{\rho}(\boldsymbol{r})\rangle}\delta(\boldsymbol{r}-\boldsymbol{r}')+\Gamma(\boldsymbol{r},\boldsymbol{r}'|\rho)$$

$$\delta(\boldsymbol{r}-\boldsymbol{r}'')=\int \frac{\delta\rho(\boldsymbol{r}|\phi)}{\delta\phi(\boldsymbol{r}')}\frac{\delta\phi(\boldsymbol{r}'|\rho)}{\delta\rho(\boldsymbol{r}'')}d\boldsymbol{r}' \quad \Rightarrow h(\boldsymbol{r},\boldsymbol{r}'')=\Gamma(\boldsymbol{r},\boldsymbol{r}'')+\int h(\boldsymbol{r},\boldsymbol{r}')\rho(\boldsymbol{r}')\Gamma(\boldsymbol{r}',\boldsymbol{r}'')d\boldsymbol{r}'$$

"Ornstein-Zernike equation"

Euler-Lagrange:

$$0=\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})}+\phi(\boldsymbol{r})-\mu \Rightarrow \phi(\boldsymbol{r}|\rho)=\mu-\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})}$$

$$\Rightarrow \frac{\delta\beta\phi(\boldsymbol{r}|\rho)}{\delta\rho(\boldsymbol{r}')}=-\frac{\delta^2\beta F[\rho]}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')}$$

$$\Rightarrow \frac{\delta^2\beta F[\rho]}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')}=-\Gamma(\boldsymbol{r},\boldsymbol{r}'|\rho)+\frac{1}{\rho(\boldsymbol{r})}\delta(\boldsymbol{r}-\boldsymbol{r}')$$

DFT: lien entre la fonctionalle d'energie et la structure.

Direct correlation function

$$\frac{\delta^2 \beta F[\rho]}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')} = -\Gamma(\boldsymbol{r},\boldsymbol{r}'|\rho) + \frac{1}{\langle\hat{\rho}(\boldsymbol{r})\rangle}\delta(\boldsymbol{r}-\boldsymbol{r}')$$

En generale si $\quad \dfrac{\delta\beta F[\rho]}{\delta\rho(\boldsymbol{r})} = c_1(\boldsymbol{r}|\rho) \quad$ et si $\quad \dfrac{\delta c_1(\boldsymbol{r}_1|\rho)}{\delta\rho(\boldsymbol{r}_2)} = \dfrac{\delta c_1(\boldsymbol{r}_2|\rho)}{\delta\rho(\boldsymbol{r}_1)}$

il s'ensuite que $\quad \beta F[\rho_1] - \beta F[\rho_0] = \int_0^1 d\lambda \int d\boldsymbol{r} \dfrac{\partial\rho_\lambda(\boldsymbol{r})}{\partial\lambda} c_1(\boldsymbol{r}|\rho_\lambda)$

pour tout parametrization, e.g. $\quad \rho_\lambda(\boldsymbol{r}) = \rho_0(\boldsymbol{r}) + \lambda(\rho_1(\boldsymbol{r}) - \rho_0(\boldsymbol{r}))$

Voire, e.g. T. Frankel, *The Geometry of Physics*, Cambridge University Press, Cambridge, UK, 1997.

Donc,

$$\beta F[\rho_1] - \beta F[\rho_0] = \int_0^1 d\lambda \int d\boldsymbol{r} \frac{\partial\rho_\lambda(\boldsymbol{r})}{\partial\lambda} c_1(\boldsymbol{r}|\rho_\lambda)$$
$$- \int_0^1 d\lambda \int_0^\lambda d\lambda' \int d\boldsymbol{r}\, d\boldsymbol{r}' \frac{\partial\rho_\lambda(\boldsymbol{r})}{\partial\lambda} \frac{\partial\rho_{\lambda'}(\boldsymbol{r}')}{\partial\lambda'} \left(\Gamma(\boldsymbol{r},\boldsymbol{r}'|\rho_{\lambda'}) - \frac{1}{\rho_{\lambda'}(\boldsymbol{r})}\delta(\boldsymbol{r}-\boldsymbol{r}')\right)$$

Digression: dans une fluide avec pair-interactions et symetrie spherique

1. Dans l'etat fluide (liquide ou gaz) et sans champ exteriour $\rho(\boldsymbol{r}) \equiv \bar{\rho} = \frac{N}{V}$

(exercise)

2. Pair correlation function

$$g_2^{(N)}(\boldsymbol{q}_1, \boldsymbol{q}_2 | \phi) \rightarrow g_2^{(N)}(|\boldsymbol{r}_1 - \boldsymbol{r}_2|; \bar{\rho}) = 1 + h_2^{(N)}(|\boldsymbol{r}_1 - \boldsymbol{r}_2|; \bar{\rho})$$

"pair correlation function" "structure function"

3. Ornstein-Zernike equation

$$h(r_{12}; \bar{\rho}) = c(r_{12}; \bar{\rho}) + \bar{\rho} \int h(r_{13}; \bar{\rho}) c(r_{32}; \bar{\rho}) \, d\boldsymbol{r}_3$$

"direct correlation function"

4. Liquid-state theory:

$$c(r) = (1 - e^{\beta U(r)}) g(r), \quad \text{Percus-Yevik}$$

$$c(r) = g(r) - 1 - \ln g(r) - \beta U(r), \quad \text{Hypernetted-chain equation}$$

(Diagramatic resummations of cluster expansion.)

Les spheres dure: résoudre (PY)

Percus-Yevik: $c_{PY} = \begin{cases} a_0 + a_1 r + a_3 r^3, & r < d \\ 0, & r > d \end{cases}$

$$g_{HS}(r<d) = 0$$

$$a_0 = -\frac{(1+2\eta)^2}{(1-\eta)^4}, a_1 = \frac{3\eta}{2}\frac{(2+\eta)^2}{(1-\eta)^4}, \quad a_3 = \frac{\eta}{2} a_0$$

$$y(r) = e^{\beta U(r)} g(r)$$

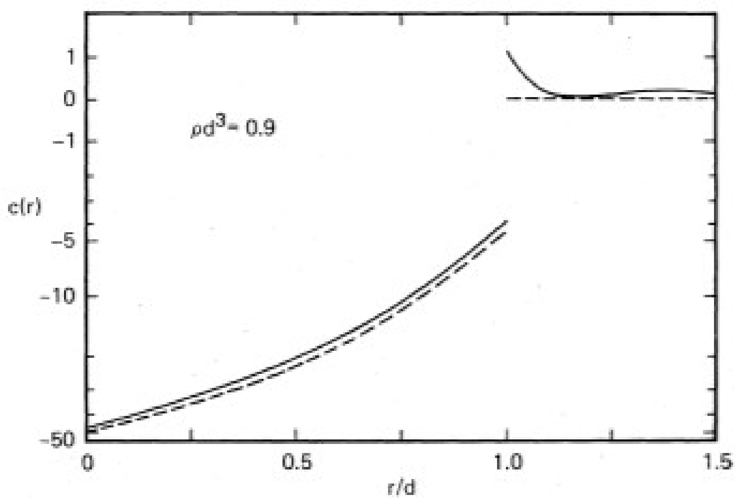

FIG. 18. Direct correlation function of hard spheres at $\rho d^3 = 0.9$. The solid curve gives the semiempirical results of Grundke and Henderson (1972) and the broken curve gives the PY results. The curve is plotted on a $\sinh^{-1}$ scale. This pseudologarithmic scale combines the advantages of a logarithmic scale with the ability to display zero and negative quantities.

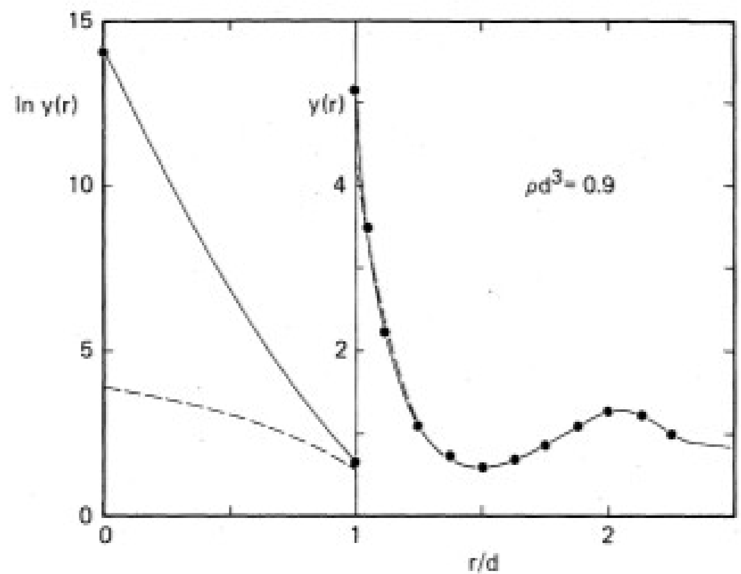

FIG. 17. $y(r)$ of hard spheres at $\rho d^3 = 0.9$. The points give the simulation results of Barker and Henderson (1971a, 1972) and the solid line gives the semiempirical results of Verlet and Weis (1972a) and Grundke and Henderson (1972) and the broken curve gives the PY results.

J.A. Barker and D. Henderson, “What is liquid?”, Rev. Mod. Phys. 48, 587 (1976)

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DFT: gaz parfait

$$\Xi[\phi] \equiv \exp(-\beta\Omega[\phi]) = \sum_{N=0}^{\infty} \frac{1}{N!\,h^{ND}} \int \exp(-\beta(H^{(N)} - \mu N))\, d\Gamma^{(N)}$$

$$= \sum_{N=0}^{\infty} \frac{1}{N!\,h^{ND}} (2\pi k_B T)^{-DN/2} \left(\int \exp(-\beta(\phi(\boldsymbol{r}) - \mu))\, d\boldsymbol{r} \right)^{N}$$

$$= \exp\left(\Lambda^{-D} \int e^{-\beta(\phi(\boldsymbol{r})-\mu)} d\boldsymbol{r} \right) \qquad \Lambda \equiv \frac{h}{\sqrt{2\pi k_B T}}$$

$$\Rightarrow \rho(\boldsymbol{r}|\phi) = \frac{\delta\Omega}{\delta\phi(\boldsymbol{r})} = \Lambda^{-D} \exp(-\beta(\phi(\boldsymbol{r}) - \mu)) \Leftrightarrow \phi(\boldsymbol{r}|\rho) = \mu + \ln \Lambda^{D} \rho(\boldsymbol{r})$$

Euler-Lagrange $$\frac{\delta F_{id}[\rho]}{\delta\rho(\boldsymbol{r})} = \mu - \phi(\boldsymbol{r}|\rho) = k_B T \ln \Lambda^{D} \rho(\boldsymbol{r})$$

DFT: gaz parfait

$$\frac{\delta F_{id}[\rho]}{\delta \rho(\boldsymbol{r})} = \mu - \phi(\boldsymbol{r}|\rho) = k_B T \ln \Lambda^D \rho(\boldsymbol{r})$$

En generale si $\dfrac{\delta \beta F[\rho]}{\delta \rho(\boldsymbol{r})} = c_1(\boldsymbol{r}|\rho)$ et si $\dfrac{\delta c_1(\boldsymbol{r}_1|\rho)}{\delta \rho(\boldsymbol{r}_2)} = \dfrac{\delta c_1(\boldsymbol{r}_2|\rho)}{\delta \rho(\boldsymbol{r}_1)}$

ils ensuite que $\beta F[\rho_2] - \beta F[\rho_1] = \int_0^1 d\lambda \int d\boldsymbol{r} (\rho_2(\boldsymbol{r}) - \rho_1(\boldsymbol{r})) c_1(\boldsymbol{r}|\rho_1 + \lambda(\rho_2 - \rho_1))$

Donc, on trouve que $\boxed{\beta F_{id}[\rho] = \int \left(\rho(\boldsymbol{r}) \ln\left(\Lambda^D \rho(\boldsymbol{r})\right) - \rho(\boldsymbol{r})\right) d\boldsymbol{r}}$

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DFT: Des modèles

$$\beta F_{id}[\rho]=\int\left(\rho(\boldsymbol{r})\ln\left(\Lambda^{D}\rho(\boldsymbol{r})\right)-\rho(\boldsymbol{r})\right)d\boldsymbol{r}$$

$$\beta F[\rho_1]-\beta F[\rho_0]=\int_0^1 d\lambda\int d\boldsymbol{r}\,\frac{\partial\rho_\lambda(\boldsymbol{r})}{\partial\lambda}c_1(\boldsymbol{r}|\rho_\lambda)$$
$$-\int_0^1 d\lambda\int_0^\lambda d\lambda'\int d\boldsymbol{r}\,d\boldsymbol{r}'\,\frac{\partial\rho_\lambda(\boldsymbol{r})}{\partial\lambda}\frac{\partial\rho_{\lambda'}(\boldsymbol{r}')}{\partial\lambda'}\left(\Gamma(\boldsymbol{r},\boldsymbol{r}'|\rho_{\lambda'})-\frac{1}{\rho_{\lambda'}(\boldsymbol{r})}\delta(\boldsymbol{r}-\boldsymbol{r}')\right)$$

Si l'on définit $\beta F[\rho]=\beta F_{id}[\rho]+\beta F_{ex}[\rho]$

il s'ensuite que

$$\beta F_{ex}[\rho_1]=\beta F_{ex}[\rho_0]+\int_0^1 d\lambda\int d\boldsymbol{r}\,\frac{\partial\rho_\lambda(\boldsymbol{r})}{\partial\lambda}c_1(\boldsymbol{r}|\rho_\lambda)$$
$$-\int_0^1 d\lambda\int_0^\lambda d\lambda'\int d\boldsymbol{r}\,d\boldsymbol{r}'\,\frac{\partial\rho_\lambda(\boldsymbol{r})}{\partial\lambda}\frac{\partial\rho_{\lambda'}(\boldsymbol{r}')}{\partial\lambda'}\Gamma(\boldsymbol{r},\boldsymbol{r}'|\rho_{\lambda'})$$

DFT: des modèles

Effective liquid models:

$$\beta F_{ex}[\rho_1] - \beta F_{ex}[\rho_0] = \int_0^1 d\lambda \int d\boldsymbol{r} \frac{\partial \rho_\lambda(\boldsymbol{r})}{\partial \lambda} c_1(\boldsymbol{r}|\rho_\lambda) \qquad (\Gamma \rightarrow c_2)$$

$$- \int_0^1 d\lambda \int_0^1 d\lambda' \int d\boldsymbol{r}\, d\boldsymbol{r}' \frac{\partial \rho_\lambda(\boldsymbol{r})}{\partial \lambda} \frac{\partial \rho_\lambda(\boldsymbol{r}')}{\partial \lambda'} c_2(\boldsymbol{r}, \boldsymbol{r}'|\rho_{\lambda'})$$

$$\rho_0(\boldsymbol{r}) = \bar{\rho}_0 \qquad F[\rho_0] \rightarrow V f(\bar{\rho}_0) \qquad \rho_\lambda(\boldsymbol{r}) = \bar{\rho}_0 + \lambda(\rho_1(\boldsymbol{r}) - \bar{\rho}_0)$$

$$\beta \frac{1}{V} F_{ex}[\rho_1] = \beta f_{ex}(\bar{\rho}_0) + \frac{\partial f_{ex}(\bar{\rho}_0)}{\partial \bar{\rho}_0} (\bar{\rho}_1 - \bar{\rho}_0)$$

$$- \frac{1}{V} \int_0^1 d\lambda \int_0^1 d\lambda' \int d\boldsymbol{r}\, d\boldsymbol{r}' (\rho(\boldsymbol{r}) - \bar{\rho}_0)(\rho(\boldsymbol{r}') - \bar{\rho}_0) c_2(\boldsymbol{r}, \boldsymbol{r}'|\bar{\rho}_0 + \lambda(\rho_1 - \bar{\rho}_0))$$

DFT: des modeles de liquide efficaces

$$\frac{1}{V}\beta F_{ex}[\rho_1]=\beta f_{ex}(\bar{\rho}_0)+\frac{\partial f_{ex}(\bar{\rho}_0)}{\partial\bar{\rho}_0}(\bar{\rho}_1-\bar{\rho}_0)$$
$$-\frac{1}{V}\int_0^1 d\lambda\int_0^1 d\lambda'\int d\boldsymbol{r}\,d\boldsymbol{r}'(\rho(\boldsymbol{r})-\bar{\rho}_0)(\rho(\boldsymbol{r}')-\bar{\rho}_0)c_2(\boldsymbol{r},\boldsymbol{r}'|\bar{\rho}_0+\lambda'(\rho_1-\bar{\rho}_0))$$

Ramakrishnan–Yussouff: Ramakrishnan and Yussouff, Phys. Rev. B 19, 2775 (1979).

$$\bar{\rho}_0=\bar{\rho}_1 \qquad c_2(\boldsymbol{r},\boldsymbol{r}'|\bar{\rho}_0+(1-\lambda)(\rho_1-\bar{\rho}_0))=c_2(|\boldsymbol{r}-\boldsymbol{r}'|;\bar{\rho}_0)+\ldots$$

$$\frac{1}{V}\beta F_{ex}^{(RY)}[\rho_1]=\beta f_{ex}(\bar{\rho}_0)-\frac{1}{2V}\int d\boldsymbol{r}\,d\boldsymbol{r}'(\rho(\boldsymbol{r})-\bar{\rho}_0)(\rho(\boldsymbol{r}')-\bar{\rho}_0)c_2(|\boldsymbol{r}-\boldsymbol{r}'|;\bar{\rho}_0)$$

Generalized Effective Liquid Approx. (GELA)

Lutsko and Baus, Phys. Rev. Lett. 6**4**, 761 (1990); Phys. Rev. A**41**, 6647 (1990).

$$\bar{\rho}_0=0 \qquad c_2(\boldsymbol{r},\boldsymbol{r}'|\bar{\rho}_0+(1-\lambda)(\rho_1-\bar{\rho}_0))=c_2(|\boldsymbol{r}-\boldsymbol{r}'|;\bar{\rho}(\lambda))$$

$$\frac{1}{V}\beta F_{ex}^{(GELA)}[\rho_1]=-\frac{1}{2V}\int_0^1 d\lambda(1-\lambda)\int d\boldsymbol{r}\,d\boldsymbol{r}'\rho(\boldsymbol{r})\rho(\boldsymbol{r}')c_2(|\boldsymbol{r}-\boldsymbol{r}'|;\bar{\rho}(\lambda))$$

$$\frac{1}{V\alpha\bar{\rho}_1}\beta F_{ex}^{(GELA)}(\alpha\bar{\rho}_1)=\frac{1}{\bar{\rho}_{GELA}(\alpha)}\beta f_{ex}(\bar{\rho}_{GELA}(\alpha))$$

DFT: des modeles

Modified Weighted Density Approx. (MWDA):
Denton and Ashcroft, Phys. Rev. A**39** 2909 (1985).

$$\frac{1}{\rho_1} V \beta F_{ex}^{(MWDA)}[\rho] = \frac{1}{\rho_{MWDA}} V \beta F_{ex}(\rho_{MWDA}[\rho])$$

$$\lim_{\rho(\boldsymbol{r}) \to \bar{\rho}} \frac{\delta^2 \beta F_{ex}^{(MWDA)}}{\delta\rho(\boldsymbol{r}_1)\delta\rho(\boldsymbol{r}_2)} = -c(r_{12}; \bar{\rho})$$

$$\Rightarrow \rho_{MWDA}[\rho] = \frac{1}{\bar{\rho} V} \int w(r_{12}; \rho_{MWDA}[\rho]) \rho(\boldsymbol{r}_1) \rho(\boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

$$w(r,\rho) = \frac{-1}{2\beta\psi'(\rho)} \left(c_2(r_{12};\rho) + \frac{1}{V} \rho \beta \psi''(\rho) \right), \quad \psi(\rho) = \frac{1}{\rho} f_{ex}(\rho) = \frac{1}{\rho V} F_{ex}(\rho)$$

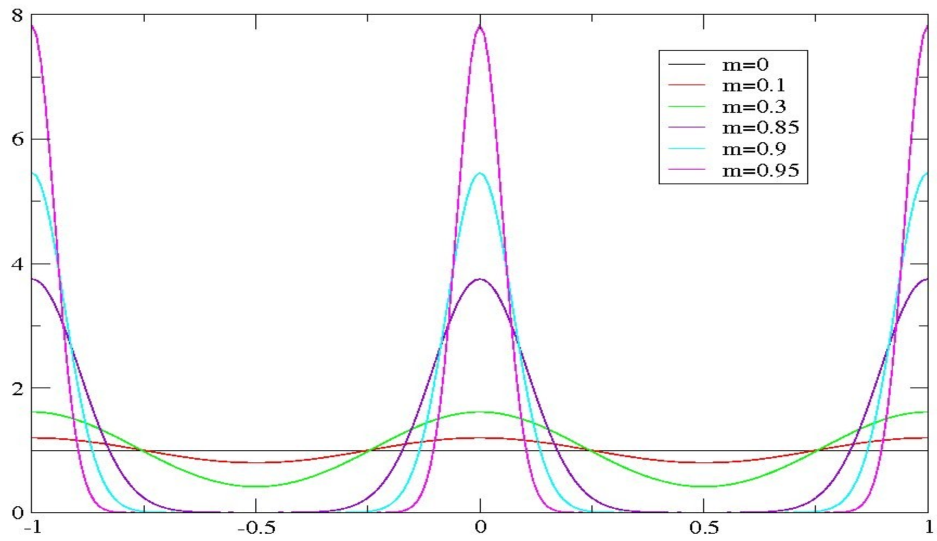
(exercise)

DFT: solides

$$\rho(\boldsymbol{r}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_{\boldsymbol{R}_1 \in lattice\ vectors} \exp\left(-\alpha\left(\boldsymbol{r} - \boldsymbol{R}_i\right)^2\right)$$

$$\rho(\boldsymbol{r}) = \bar{\rho} + \bar{\rho} \sum_{\boldsymbol{K}_i \in \text{recip lattice}} \exp\left(i\,\boldsymbol{K}_i \cdot \boldsymbol{r}\right) \exp\left(-K_i^2/(4\alpha)\right)$$

$$= \bar{\rho} + \bar{\rho} \sum_{\boldsymbol{K}_i \in \text{recip lattice}} \exp\left(i\,\boldsymbol{K}_i \cdot \boldsymbol{r}\right) \chi^{\left(K_i/K_1\right)^2}, \quad \chi = \exp\left(-K_1^2/(4\alpha)\right) \quad \text{"crystallinity"}$$



Lutsko, Adv. Chem. Phys. **144**, 1-91 (2010).

Efficaces théories liquides: gel des sphères dures

TABLE I

Comparison of the Predictions of Various Effective-Liquid DFTs for the Freezing of Hard Spheres to Data from Simulation[a]

Theory	EOS	$\bar{\eta}_{liq}$	$\bar{\eta}_{sol}$	P^*	L
RY[b]	PY	0.506	0.601	15.1	0.06
MWDA[c]	CS	0.476	0.542	10.1	0.097
ELA[d]	PY	0.520	0.567	16.1	0.074
SCELA[e]	CS	0.508	0.560	13.3	0.084
GELA[e]	CS	0.495	0.545	11.9	0.100
WDA[c,f]	CS	0.480	0.547	10.4	0.093
MC[g]	—	0.494	0.545	11.7	0.126

[a]Given are the liquid ($\bar{\eta}_{liq}$) and solid ($\bar{\eta}_{sol}$) packing fractions ($\eta = \pi\rho d^3/6$), the reduced pressure ($P^* = \beta P d^3$), and the Lindemann parameter (L) at bulk coexistence. For each theory, the equation of state used for the fluid, Percus–Yevick (PY), or Carnahan–Starling (CS) is indicated.

[b]From Barrat et al. [49].

[c]From Denton and Ashcroft [41].

[d]From Baus and Colot [37].

[e]From Lutsko and Baus [25].

[f]From Curtin and Ashcroft [40].

[g]From Hoover and Ree [57].

Density Functional Theory

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- 0K DFT
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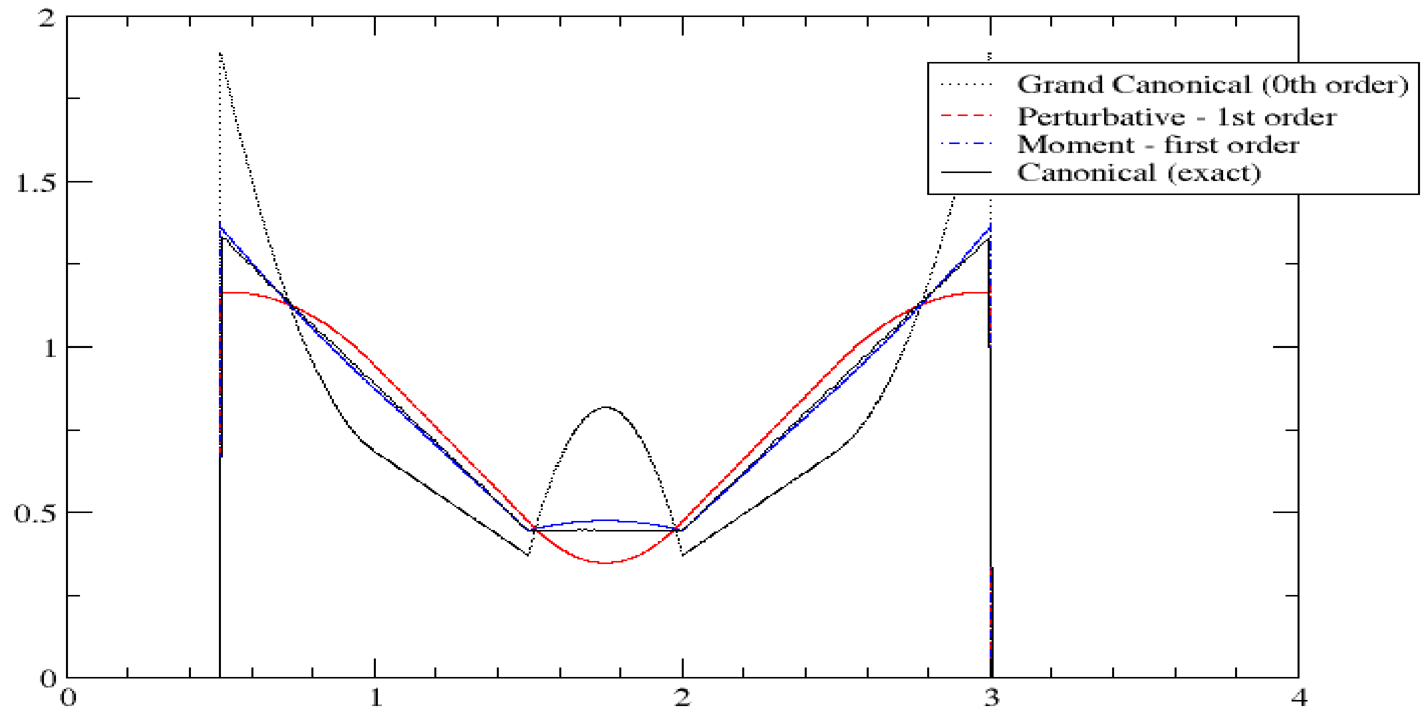
Hard spheres in 1D: hard rods (barres dures)

$$F[\rho]=F_{id}[\rho]-\int_{-\infty}^{\infty}\frac{1}{2}\left(\rho(x+d/2)+\rho(x-d/2)\right)\ln\left(1-\int_{-d/2}^{d/2}\rho(x+y)\,dy\right)dx \qquad \text{(Exact)}$$

Percus, J. Stat. Phys **15**, 505 (1976)



Sphères Dures: FMT

Fundamental Measure Theory (FMT): Généralisation du résultat de Percus à plusieurs dimensions.

Ansatz:

$$F_{ex}[\rho]=\int \Phi(\{n_\alpha(\boldsymbol{r})\})\,d\boldsymbol{r}$$

$$n_\alpha(\boldsymbol{r}|\rho)=\int w_\alpha(|\boldsymbol{r}-\boldsymbol{r}'|)\rho(\boldsymbol{r}')\,d\boldsymbol{r}'$$

Percus:

$$F[\rho]=F_{id}[\rho]-\int_{-\infty}^{\infty}\frac{1}{2}\left(\rho(x+d/2)+\rho(x-d/2)\right)\ln\left(1-\int_{-d/2}^{d/2}\rho(x+y)\,dy\right)dx$$

$$\Phi(\{n_\alpha(\boldsymbol{r})\})=s(x)\ln(1-\eta(x))$$

$$w_s(|x-x'|)=\delta((d/2)-|x-x'|)$$
$$w_s(|x-x'|)=\Theta((d/2)-|x-x'|)$$

Rosenfeld: ansatz + “scaled particle theory”

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

Lutsko, Adv. Chem. Phys. **144**, 1-91 (2010).

Sphères Dures: FMT

$$F_{ex}[\rho]=\int \Phi(\{n_\alpha(\boldsymbol{r})\})d\boldsymbol{r}$$

$$n_\alpha(\boldsymbol{r}|\rho)=\int w_\alpha(\boldsymbol{r}-\boldsymbol{r}')\rho(\boldsymbol{r}')d\boldsymbol{r}'$$

Kierlik and M. L. Rosinberg: insiste que $\lim_{\rho(\boldsymbol{r})\to\bar{\rho}}\frac{\delta^2\beta F^{(FMT)}[\rho]}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')}=-c_2^{(PY)}(|\boldsymbol{r}-\boldsymbol{r}'|;\bar{\rho})$

E. Kierlik and M. L. Rosinberg, Phys. Rev. A **42**, 3382 (1990).

$$\lim_{\rho(\boldsymbol{r})\to\bar{\rho}}\frac{\delta^2\beta F^{(FMT)}[\rho]}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')}=\frac{\partial^2\Phi(\{n_\alpha(\boldsymbol{r})\})}{\partial n_\alpha\partial n_\beta}\sum_{\alpha,\beta}\int w_\alpha(\boldsymbol{r}-\boldsymbol{r}'')w_\beta(\boldsymbol{r}'-\boldsymbol{r}'')d\boldsymbol{r}''$$

Rosenfeld et Kierlik & Rosinberg sont equilvant:

$$\Phi=-\frac{1}{\pi d^2}s\ln(1-\eta)+\frac{1}{2\pi d}\frac{s^2-v^2}{(1-\eta)}+\frac{1}{24\pi}\frac{s^3-3sv^2}{(1-\eta)^2}$$

$$w_\eta(\boldsymbol{r})=\Theta(\frac{d}{2}-r),\quad w_s(\boldsymbol{r})=\delta(\frac{d}{2}-r),\quad \boldsymbol{w}_v(\boldsymbol{r})=\hat{\boldsymbol{r}}\,\delta(\frac{d}{2}-r)$$

Lutsko, Adv. Chem. Phys. **144**, 1-91 (2010).

Sphères Dures: FMT

$$F_{ex}[\rho]=\int \Phi(\{n_\alpha(\boldsymbol{r})\})d\boldsymbol{r}$$

$$n_\alpha(\boldsymbol{r}|\rho)=\int w_\alpha(\boldsymbol{r}-\boldsymbol{r}')\rho(\boldsymbol{r}')d\boldsymbol{r}'$$

Probleme: Rosenberg FMT ne se stabilise pas le solide.

Solution: après beaucoup de travail, exiger des limites plus précises.
(Pour example: une cavité qui peut contenir au plus deux boules.) (exercise)

Afin de satisfaire à toutes les exigences, on a besoin des densités tensorielles:

$$\boldsymbol{w}_T(\boldsymbol{r})=\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}\,\delta\left(\frac{d}{2}-r\right)$$

$$\Phi_3=\frac{1}{24\pi}\frac{s^3-3sv^2}{(1-\eta)^2}\rightarrow\frac{3}{16\pi(1-\eta)^2}\left(\boldsymbol{v}\cdot\boldsymbol{T}\cdot\boldsymbol{v}-sv^2-Tr\left(\boldsymbol{T}^3\right)+s\,Tr\left(\boldsymbol{T}^2\right)\right)$$

P. Tarazona, Phys. Rev. Lett. **84**, 694 (2000).

Lutsko, Adv. Chem. Phys. **144**, 1-91 (2010).

Sphères Dures: FMT

Probleme: Le description de gel de hard-sphere n'etait pas bonne.

Raison: Percus-Yevik pas precise a haut densitie.

Solution: modification heuristique de Tarazona fonctionnel appelé "White Bear".

R. Roth, R. Evans, A. Lang, and G. Kahl, J. Phys. Condens. Matter **14**, 12063 (2002).

TABLE II

Comparison of the Predictions of Various FMT DFTs for the Freezing of Hard Spheres to Data from Simulation[a]

Theory	EOS	$\bar{\eta}_{liq}$	$\bar{\eta}_{sol}$	P^*	L
RSLT[b]	PY	0.491	0.540	12.3	1.06
Tarazona[c]	PY	0.467	0.516	9.93	0.145
White Bear[c,d]	CS	0.489	0.536	11.3	0.132
MC[e]	—	0.494	0.545	11.7	0.126

[a] Given are the liquid, $\bar{\eta}_{liq}$, and solid, $\bar{\eta}_{sol}$, packing fractions, the reduced pressure $P^* = \beta P d^3$ and the Lindemann parameter, L, at bulk coexistence. For each theory, the equation of state used for the fluid, Percus–Yevick(PY) or Carnahan–Starling (CS), is indicated. The Lindemann ratio for all three theories, calculated in the Gaussian approximation, is taken from Ref. 81.

[b] From Rosenfeld et al. [80].

[c] From Tarazona [82].

[d] From Roth et al. [74].

[e] From Hoover and Ree [57].

Lutsko, Adv. Chem. Phys. **144**, 1-91 (2010).

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Interactions de longue portée

Modele moyenne-champ (ou, parfois "van der Waals"):

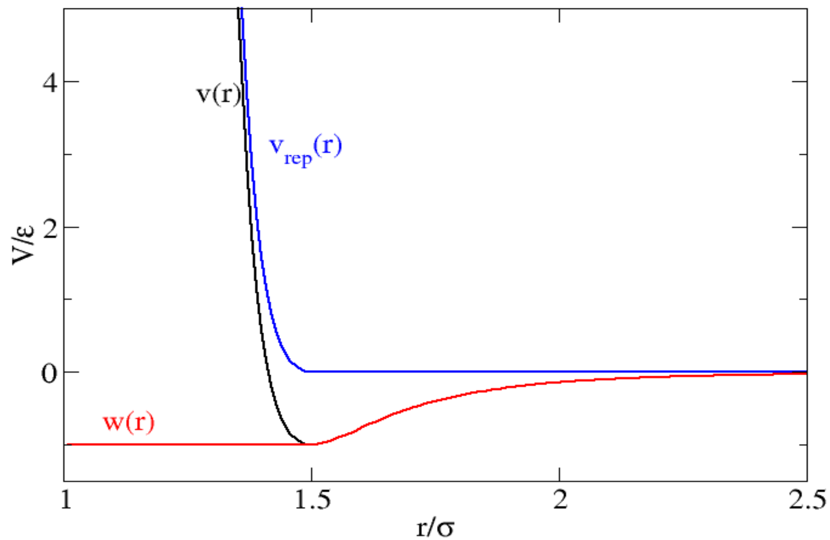
$$v(r) = v_{rep}(r) + w(r)$$

partie répulsive

partie attractive

$$F_{ex}[\rho] = F_{ex}^{HS}(d_{eff}|\rho) + \frac{1}{2}\int \rho(\mathbf{r})\rho(\mathbf{r}')w(\mathbf{r}-\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'$$

$$d_{eff} = \int_0^{r_0}\left(1-\exp\left(-\beta v_{rep}(r)\right)\right)d\mathbf{r}$$



Lutsko, Adv. Chem. Phys. **144**, 1-91 (2010).

Interactions de longue portée

Plus simple:

$$F_{ex}[\rho]=F_{ex}^{HS}(d_{eff}|\rho)+V\left(f_{ex}(\bar{\rho})-f_{ex}^{HS}(\bar{\rho};d_{eff})\right)$$

$$F_{ex}[\rho]=F_{ex}^{HS}(d_{eff}|\rho)+\int\left(f_{ex}(\rho(\boldsymbol{r}))-f_{ex}^{HS}(\rho(\boldsymbol{r});d_{eff})\right)d\boldsymbol{r}$$

$$F_{ex}[\rho]=\int f_{ex}(\rho(\boldsymbol{r}))\,d\boldsymbol{r}$$

"local density model"

$$F_{ex}[\rho]=\int\left(f_{ex}(\rho(\boldsymbol{r}))+K(\nabla\rho(\boldsymbol{r}))^2\right)d\boldsymbol{r}$$

"van der Waals' model"
or "squared-gradient model"

Plus complex et précise:

$$F_{ex}[\rho]=F_{ex}^{HS}(d_{eff}|\rho)+F_{ex}^{core}(d_{eff}|\rho)+\frac{1}{2}\int\rho(\boldsymbol{r})\rho(\boldsymbol{r}')w(\boldsymbol{r}-\boldsymbol{r}')\,d\boldsymbol{r}\,d\boldsymbol{r}'$$

Pour l'application de certaines propriétés de la dcf;
formulées comme FMT

Lutsko, J. Chem. Phys. 128, 184711 (2008).
Lutsko, Adv. Chem. Phys. **144**, 1-91 (2010).

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Applications: Hard-Spheres

TABLE III: The order parameter profile parameters obtained by minimizing the free energy. The profiles studied are the hyperbolic tangents with $B_m = B_p$ (H), the "offset" hyperbolic tangents where $B_m \neq B_{rho}$ (OH), and the hyperbolic tangents with a Gaussian term (HG). Also included are the results from MD simulations of ref [27] and the MC simulations of ref.[28]. In all cases, the last column gives the surface tension.

Theory	Profile	A_m	A_p	B_p	C_p	D_p	E_p	$\gamma\sigma^2/k_BT$
RLST	H	0.61	0.83	*	*	*	*	0.730
RLST	OH	0.67	1.64	-0.70	*	*	*	0.669
RLST	HG	0.68	0.99	*	-0.039	1.27	0.04	0.667
WB	H	0.74	0.84	*	*	*	*	0.754
WB	OH	0.85	2.54	-0.78	*	*	*	0.659
WB	HG	0.88	1.70	*	-0.06	1.97	-0.21	0.656
MD								0.617
MC								0.623

Lutsko, Phys. Rev. E **74**, 021603 (2006)

Applications: Hard-Spheres

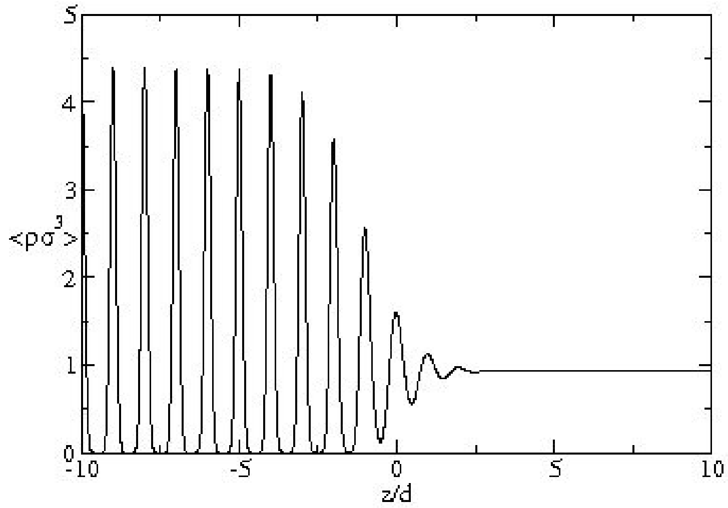


FIG. 3: The atomic density averaged over planes perpendicular to the interface as a function of position, calculated using the RLST theory and the offset hyperbolic tangent parameterization. The position is shown in units of the interplaner spaceing for [100] planes, $d = 0.5a$ where a is the lattice parameter.

Applications: Problems with Hard-Spheres

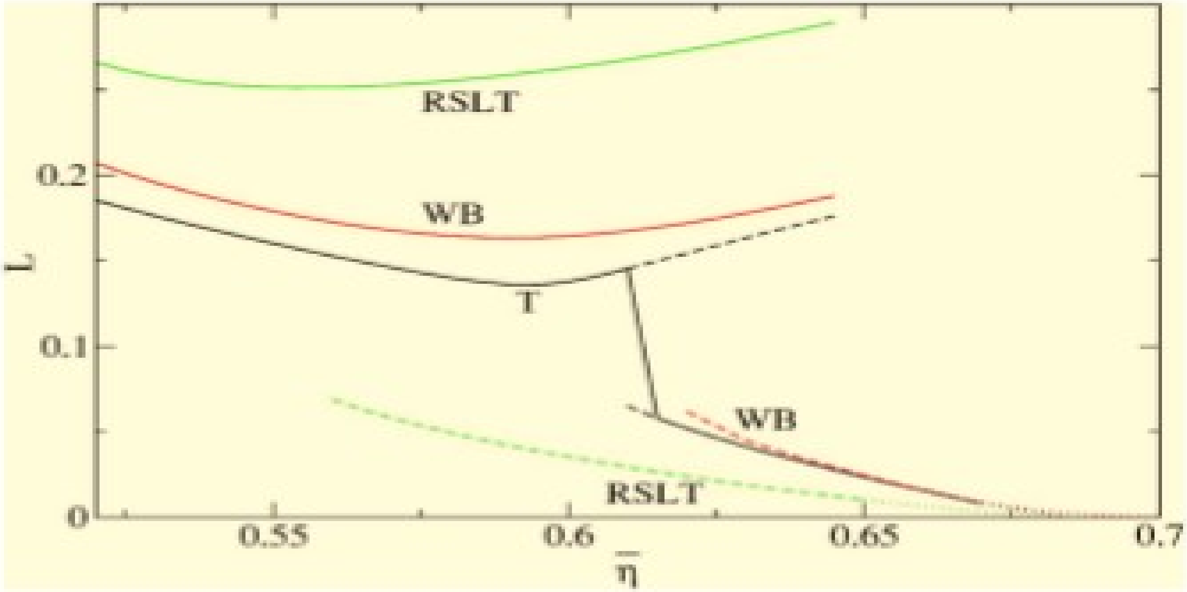
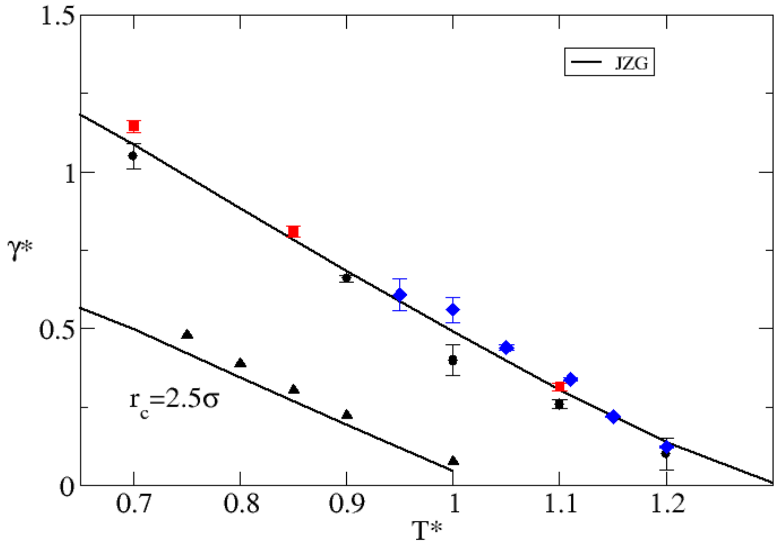


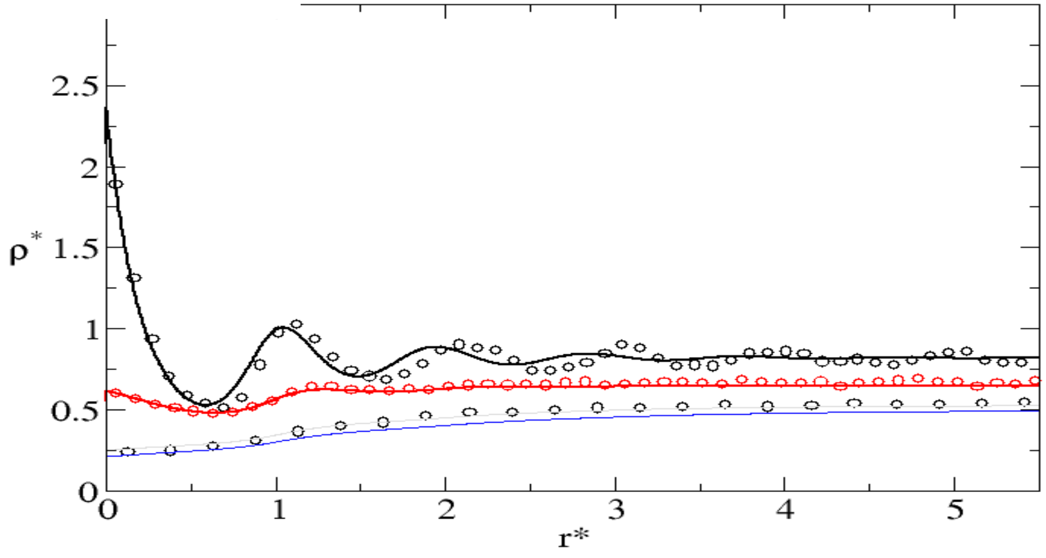
FIG. 4. (Color online) The Lindemann parameter for the bcc phase as a function of packing fraction $\overline{\eta}$ as calculated using the RSLT theory, the Tarazona theory (labeled T) and the White Bear theory (labeled WB). Both the low-α and high-α branches are shown with the stable branch being drawn with full lines and the unstable branch with dashed lines. Also shown as dotted lines are the quadratic interpolation of the curves to $L=0$ based on the data for $\overline{\eta} > 0.60$.

Applications: un fluid simple

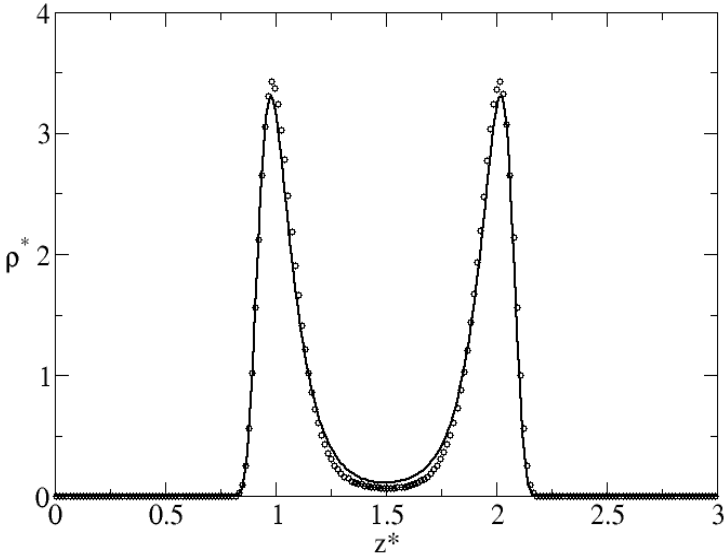


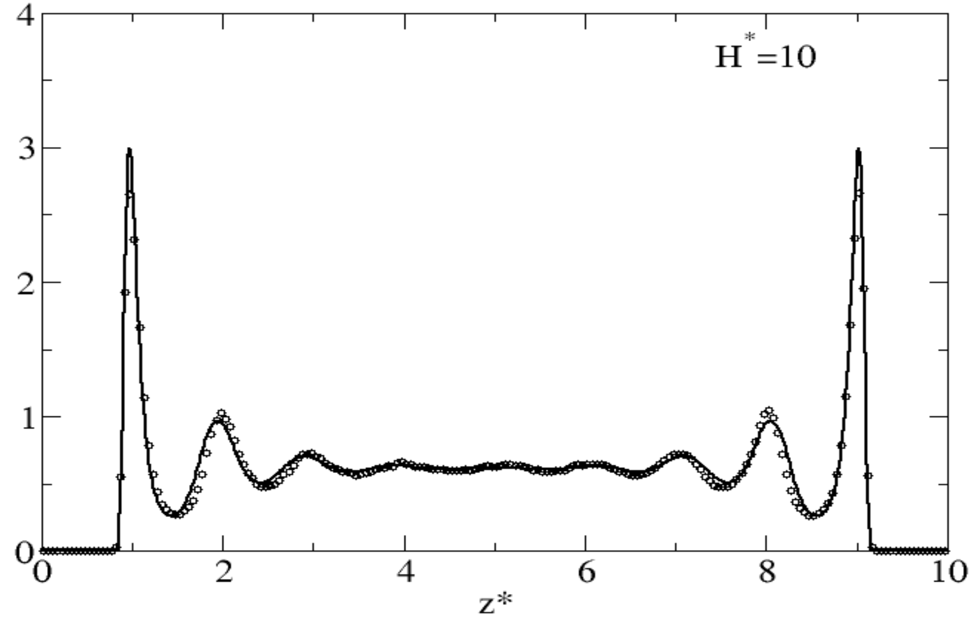
tension superficielle entre liquide et gaz

structure de près d'un mur

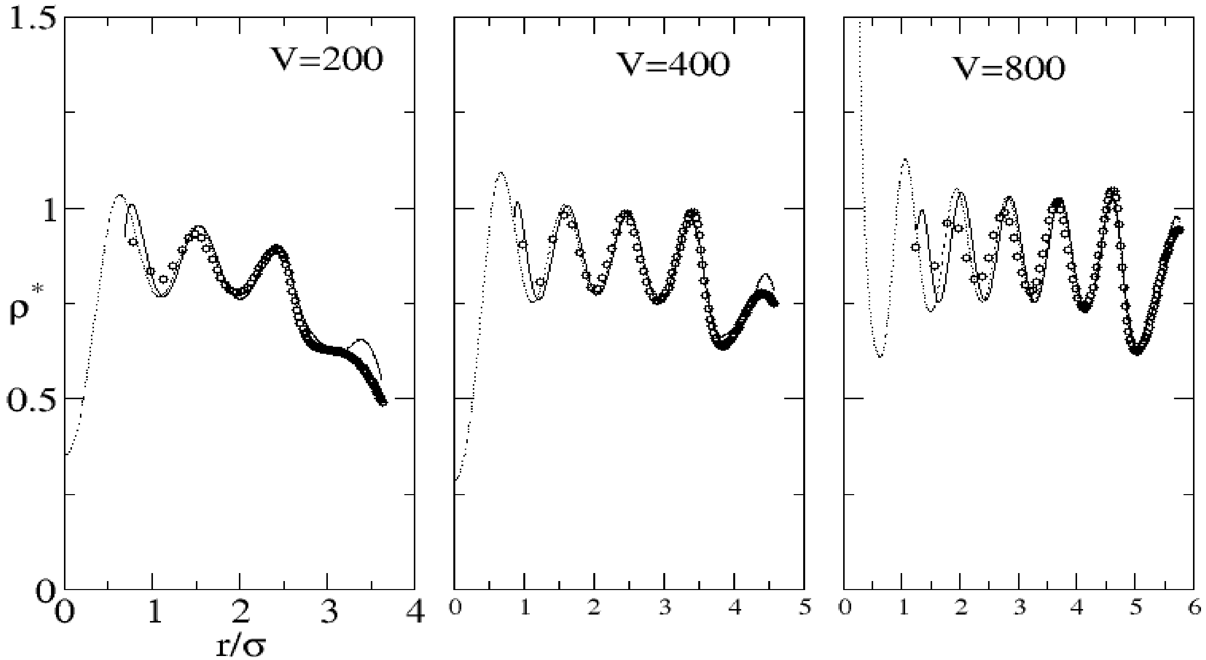


Applications: Slit pores (deux parois parallèles et infinie)





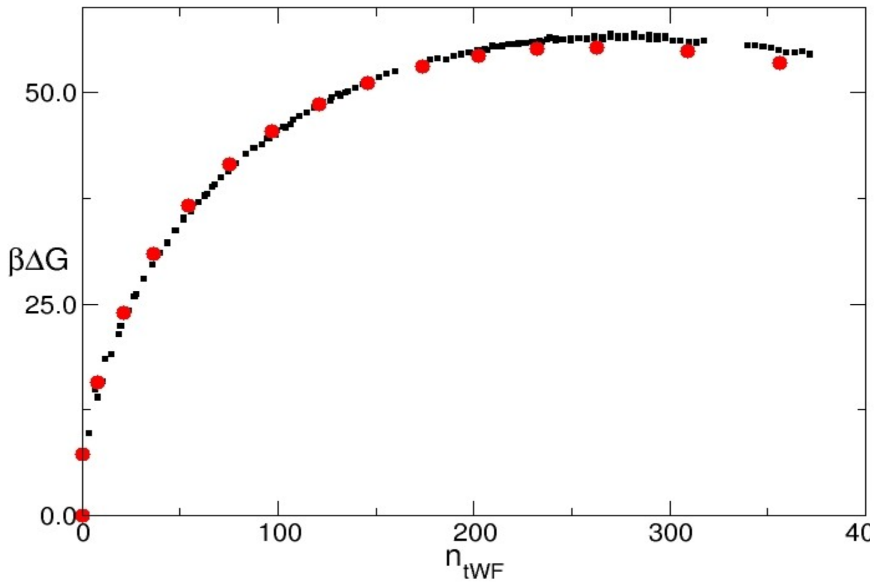
Applications: Confined Clusters

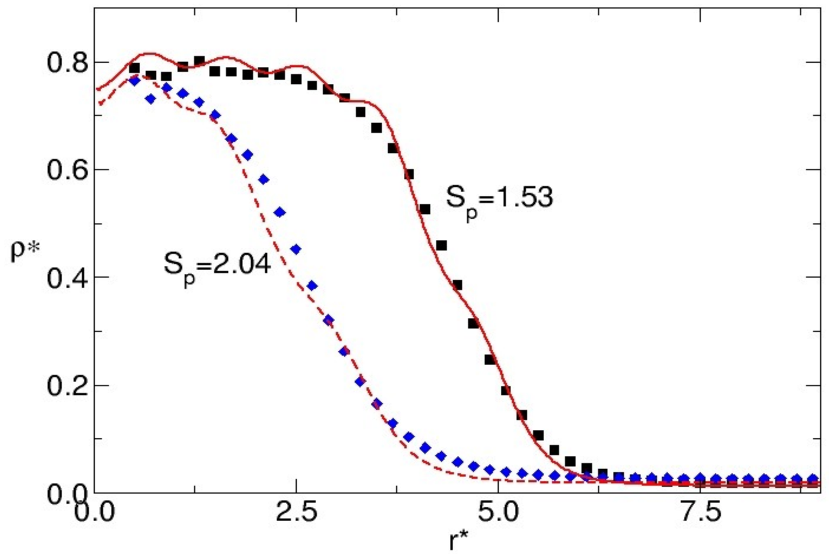


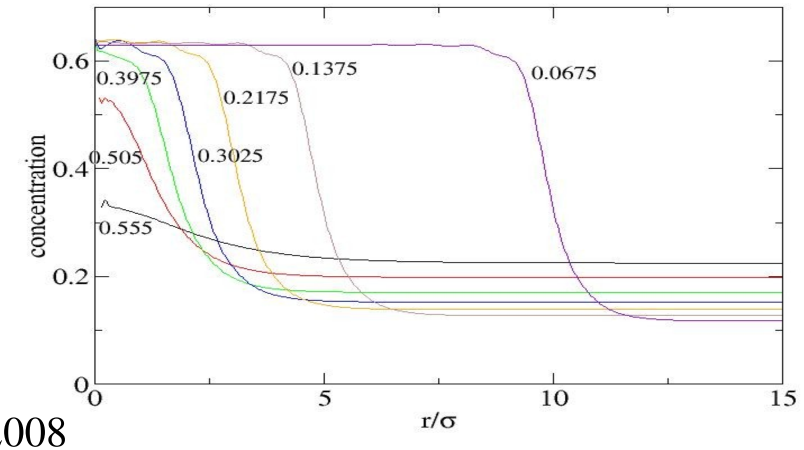
Un liquide confiné à un nano-volume sphérique

Lutsko, Laidet, Grosfils, J. Phys.: Condens. Matter **22** 035101 (2010)

Applications: Liquid-vapor nucleation

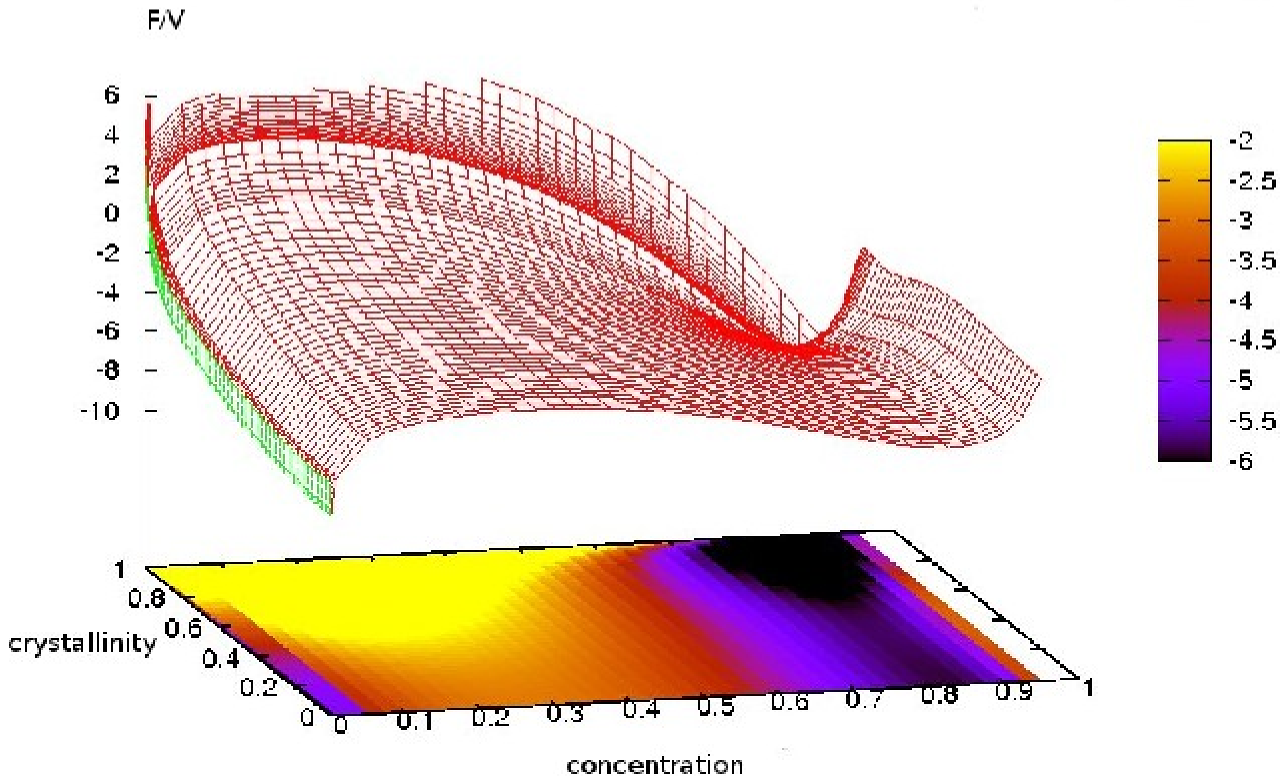






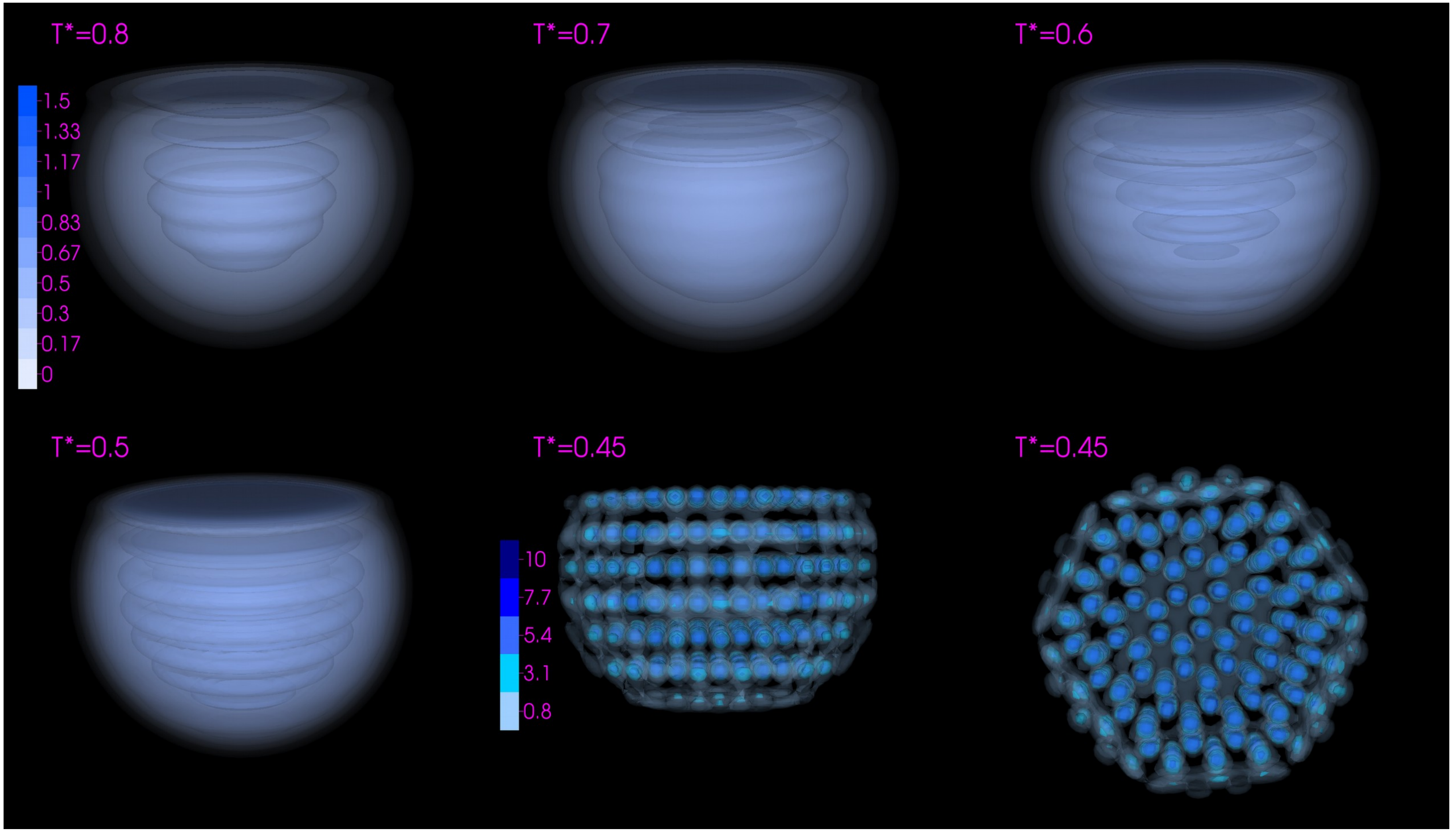
Lutsko, J. Chem. Phys., 129(124):244501+, 2008

Applications: Protein crystallization

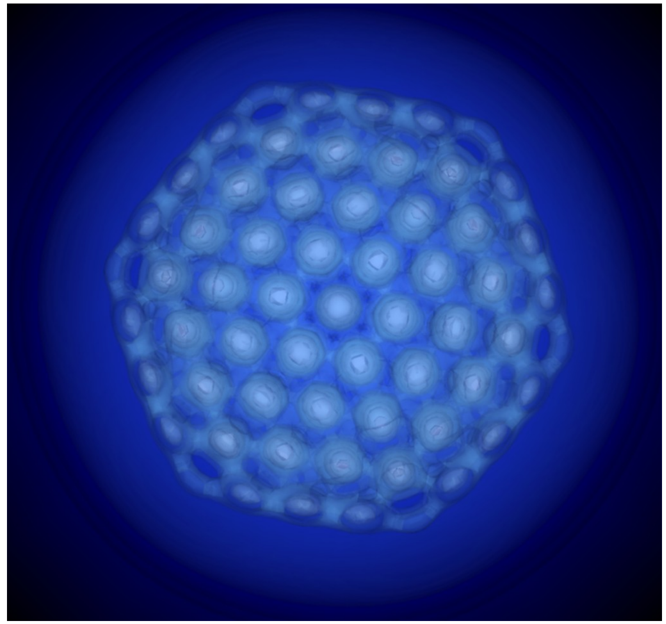


Lutsko and Nicolis, Phys. Rev. Lett. **96**, 046102 (2006)

Applications: Crystallization



Applications: Crystallization



Applications: Crystallization