Universidade Federal
do Rio de Janeiro

Applied Thermodynamics and Molecular Simulation
ATOMS
Termodinâmica Aplicada e Simulação Molecular

Self-Consistent Perturbative Density Functional Theory

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Rio de Janeiro, 14 de maio de 2021

Density Functional Theory (DFT) Clássico

O grand potencial $\Omega[\rho(\boldsymbol{r})]$ é um funcional da densidade local de partículas $\rho(\boldsymbol{r})$

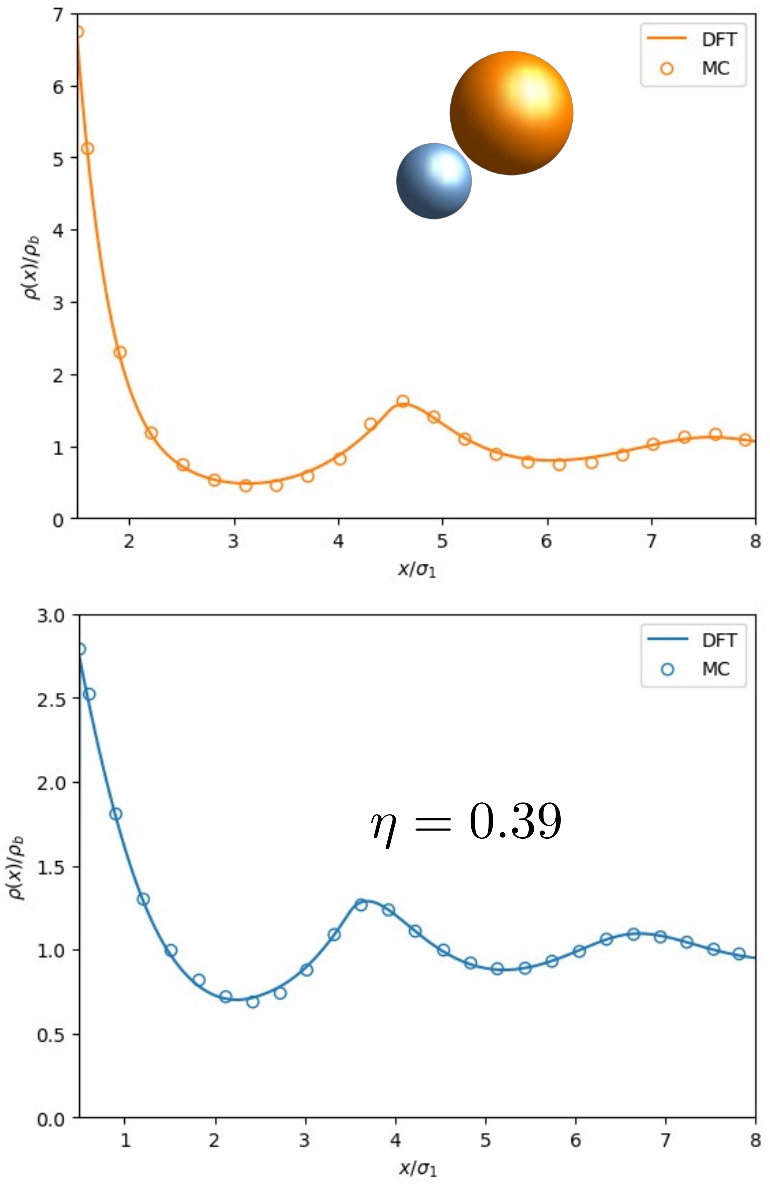
$$\Omega[\rho(\boldsymbol{r})] = F[\rho(\boldsymbol{r})] + \int \mathrm{d}\boldsymbol{r}\,[V_{\text{ext}}(\boldsymbol{r}) - \mu]\rho(\boldsymbol{r})$$

A distribuição de densidade no equilíbrio termodinâmico é dada pelo extremo do grand potencial:

$$\left.\frac{\delta\Omega[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})}\right|_{\mu,T} = \frac{\delta F[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})} + V_{\text{ext}}(\boldsymbol{r}) - \mu$$

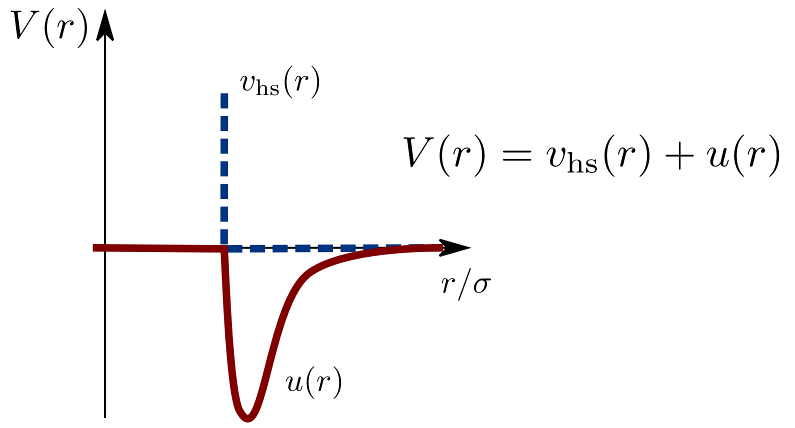
Funcional de energia livre

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



Evans, R. (2009). Lectures at 3rd Warsaw School of Statistical Physics.
Evans, R., Oettel, M., Roth, R., & Kahl, G. (2016). Journal of Physics: Condensed Matter, 28(24), 240401.

Teorias de Perturbação



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

Expansão de Taylor no parâmetro de acoplamento:

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

Coupling Parameter Expansion PT

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

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

Barker-Henderson PT

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

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

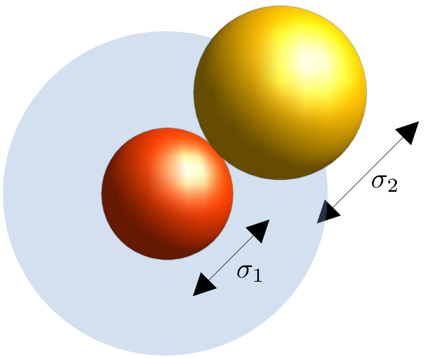
S. Zhou, Physical Review E 74, 031119 (2006).
S. Zhou, The Journal of Chemical Physics 125, 144518 (2006).
J. A. Barker and D. Henderson, The Journal of Chemical Physics 47, 2856-2861 (1967).
J. A. Barker and D. Henderson, The Journal of Chemical Physics 47, 4714-4721 (1967).

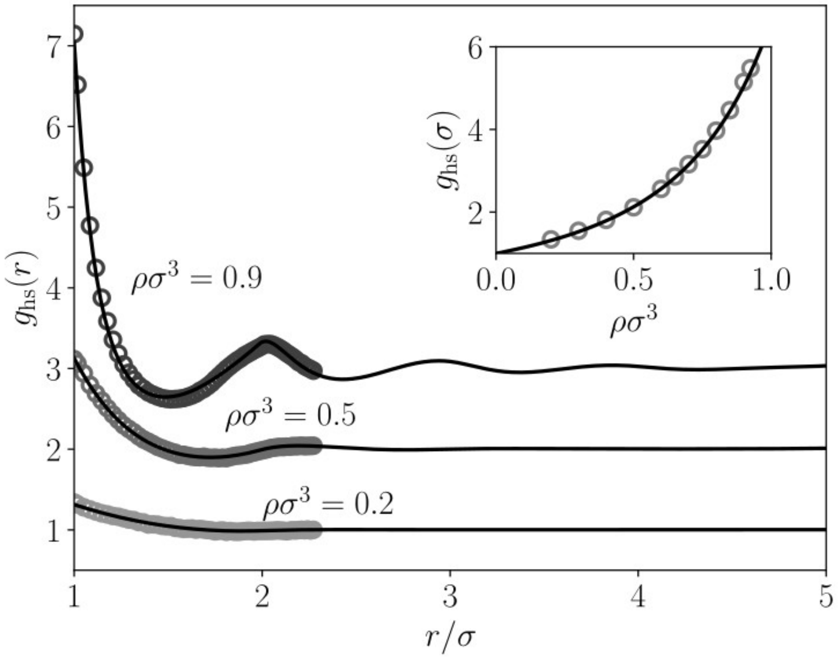
Funcional para Esferas Rígidas

$$\beta F_{\text{hs}}[\rho(\boldsymbol{r})] = \int \mathrm{d}\boldsymbol{r} \left\{ f_1(n_3)n_0 + f_2(n_3)(n_1 n_2 - \boldsymbol{n}_{v1}\cdot\boldsymbol{n}_{v2}) + f_3(n_3)(n_2^3 - 3n_2\boldsymbol{n}_{v2}\cdot\boldsymbol{n}_{v2}) \right\}$$

Densidades ponderadas

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





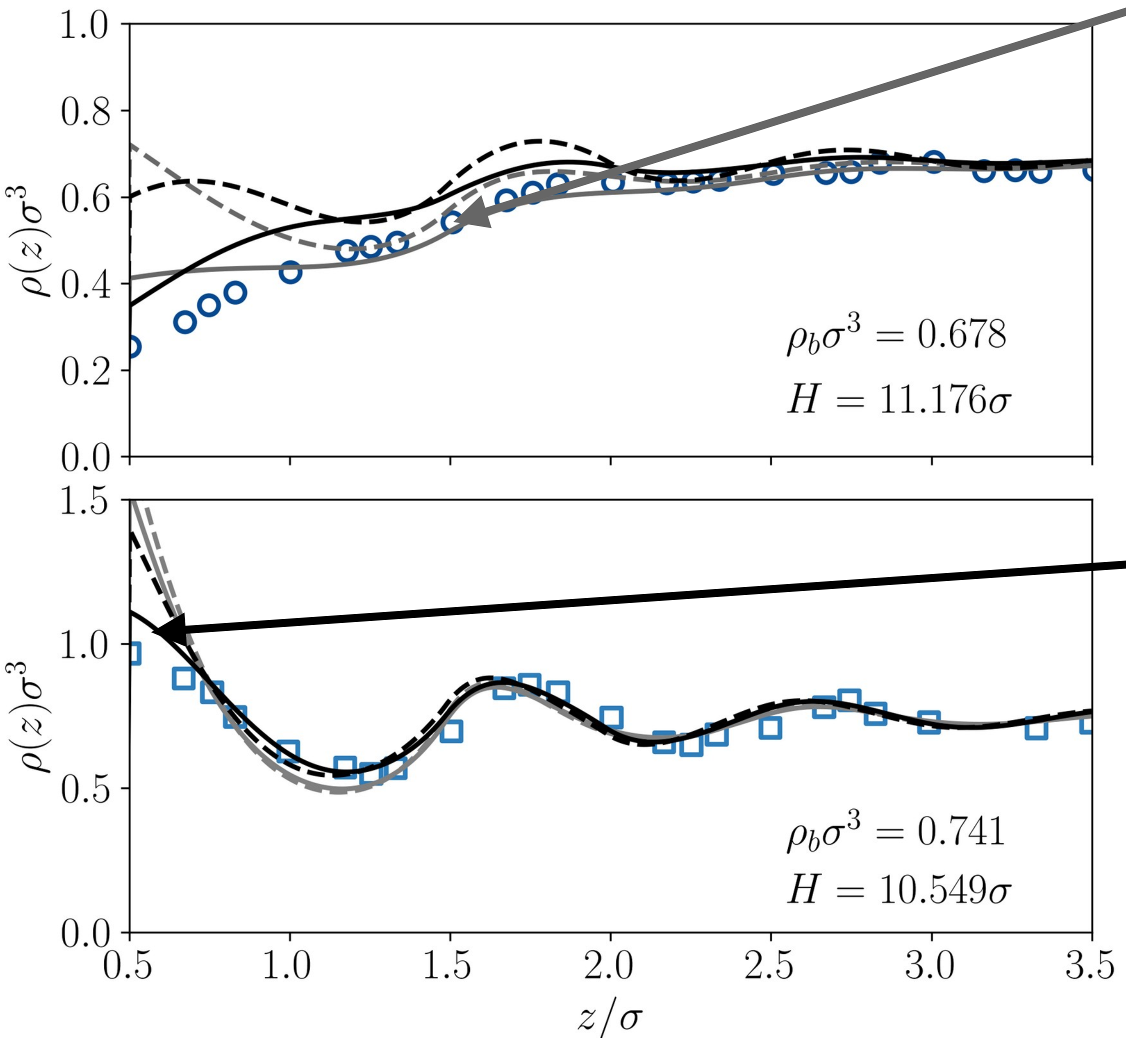
Distribuições peso

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

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

Roth, R. (2010). Journal of Physics: Condensed Matter, 22(6), 063102.

Diferentes sabores de DFT



Modified Weigthed approximation

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

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

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

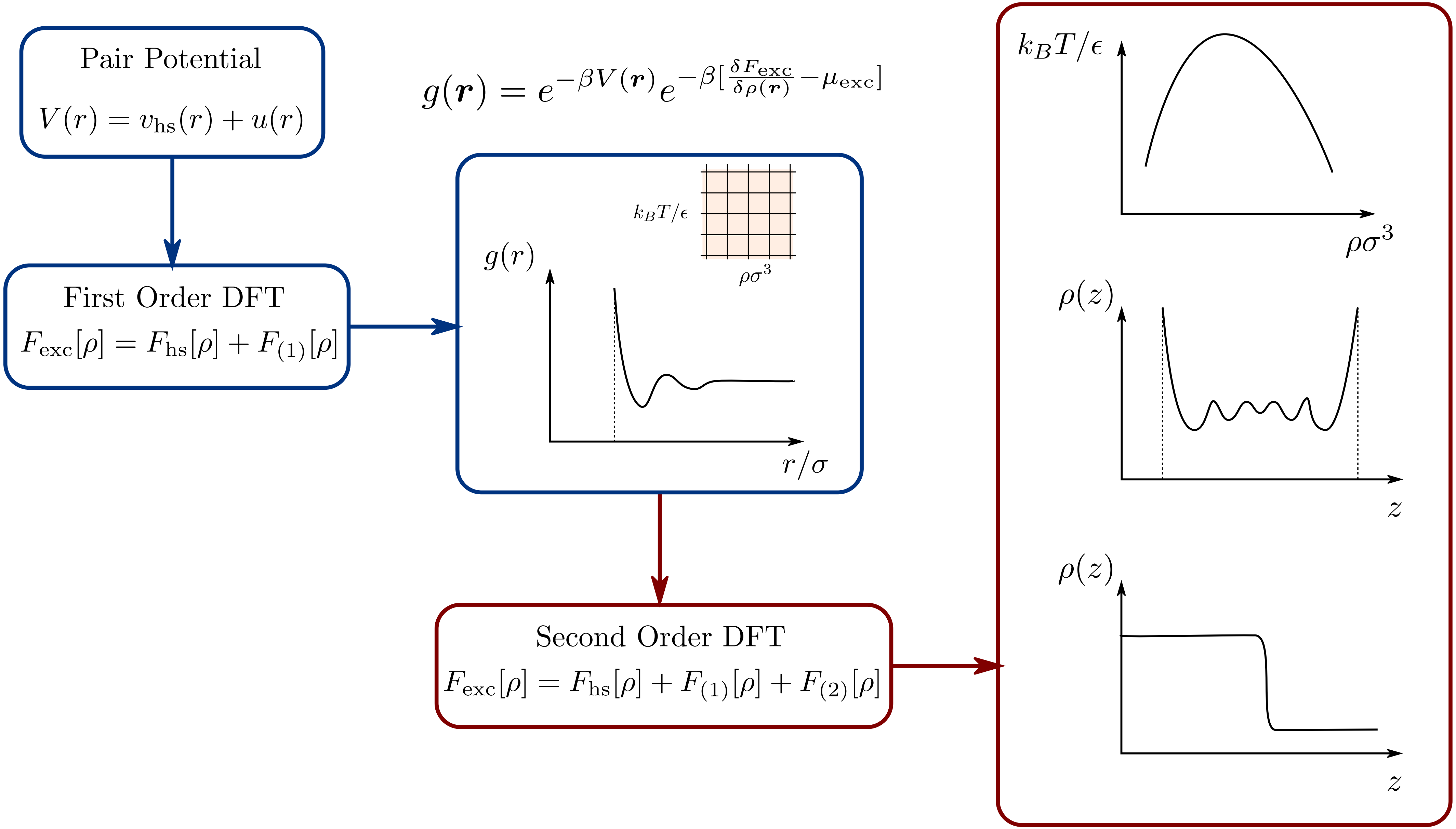
Modified Mean-Field Theory

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

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

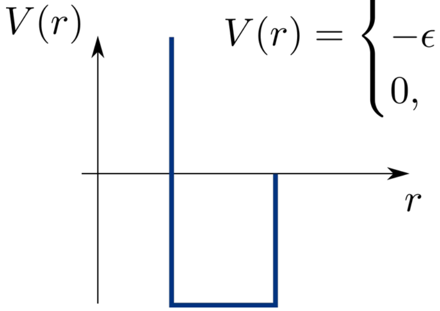
$$F_{\text{corr}}[\rho(\boldsymbol{r})] = \int \mathrm{d}\boldsymbol{r}\, \overline{\rho}(\boldsymbol{r}) f_{\text{corr}}(\overline{\rho}(\boldsymbol{r}), T),$$

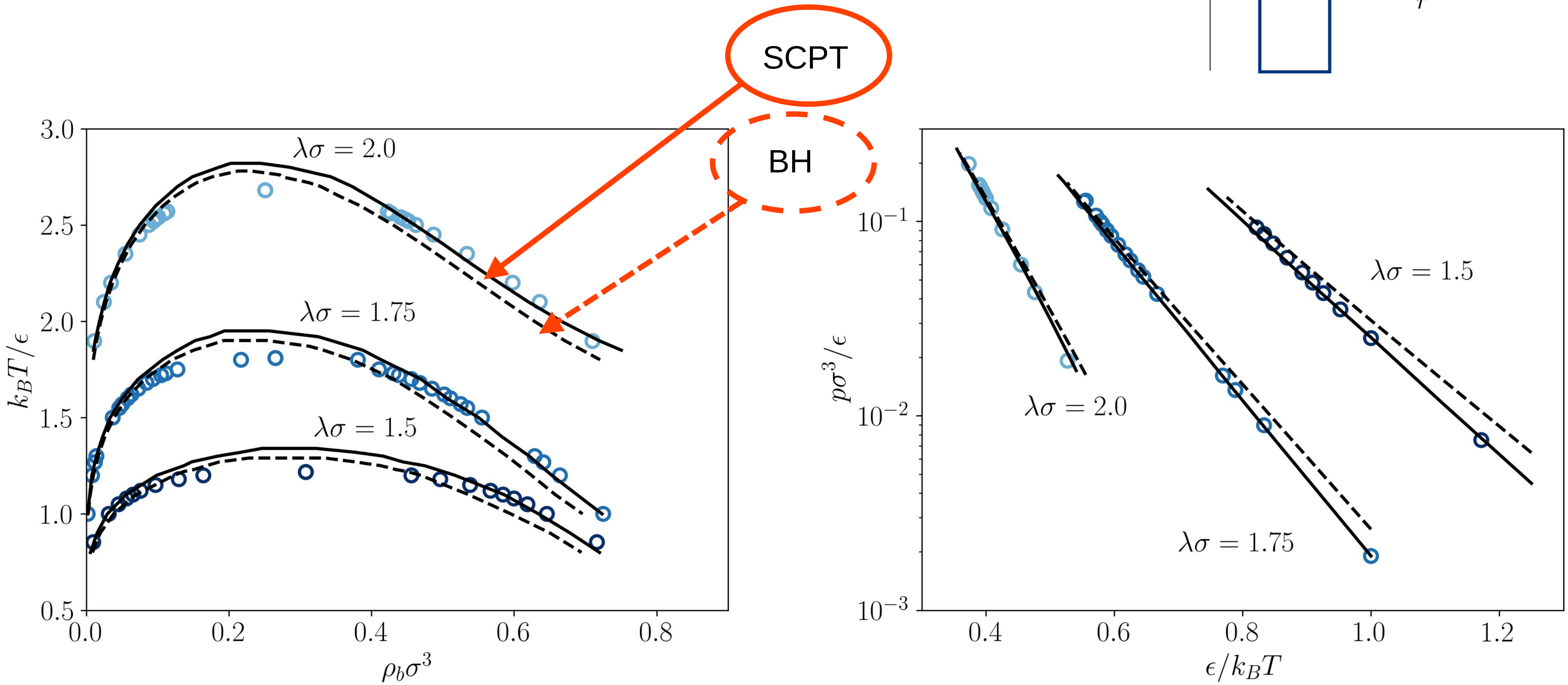
Self-consistent DFT



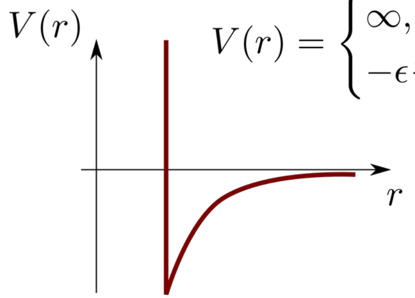
Fluido de Poço Quadrado

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

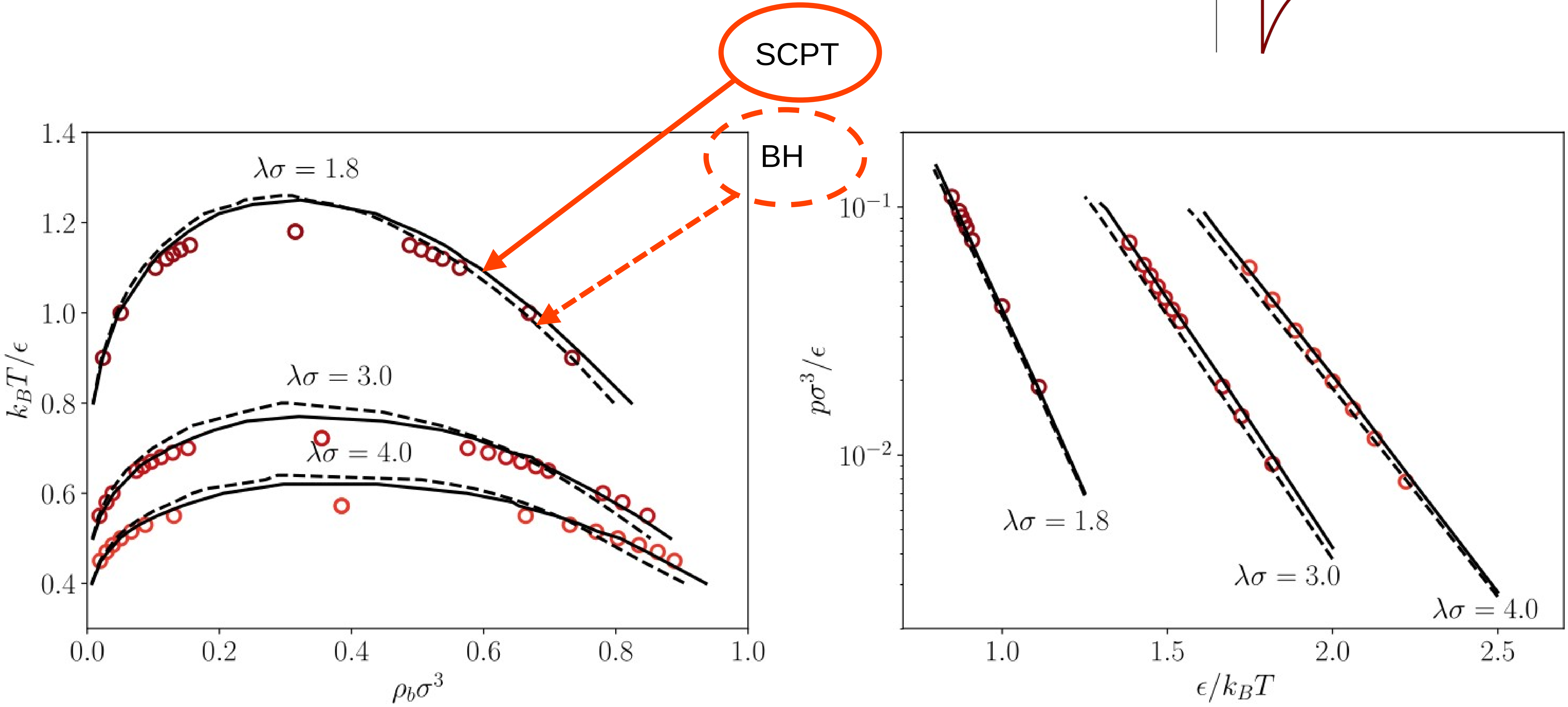




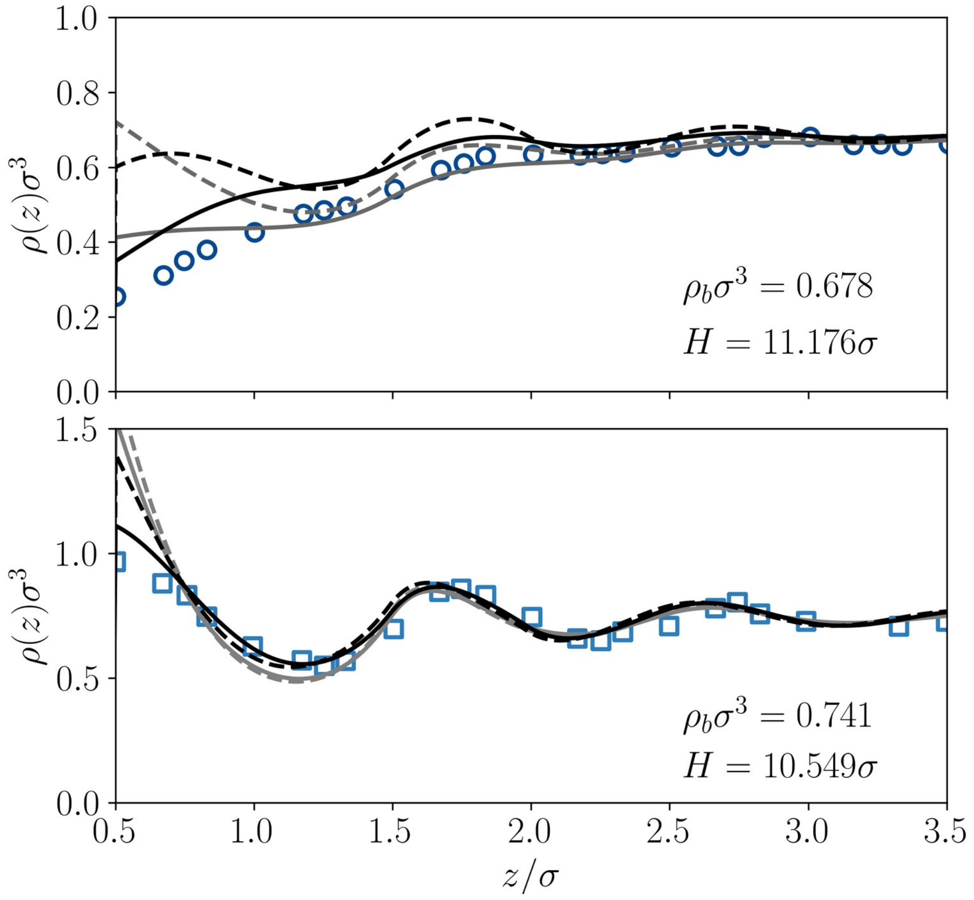
Fluido de Yukawa

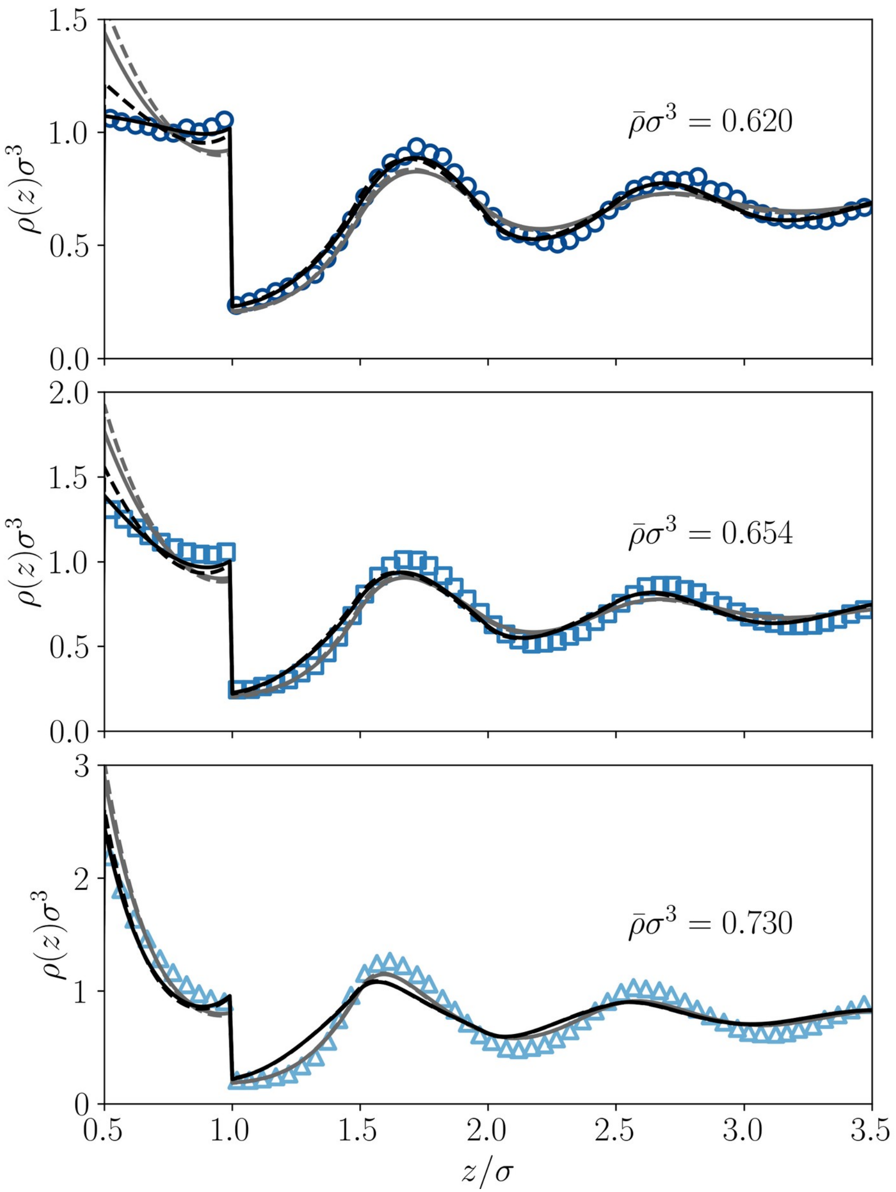


$$V(r) = \begin{cases} \infty, & r \leq \sigma \\ -\epsilon \frac{e^{-\lambda(r-\sigma)}}{r}, & r > \sigma \end{cases}$$



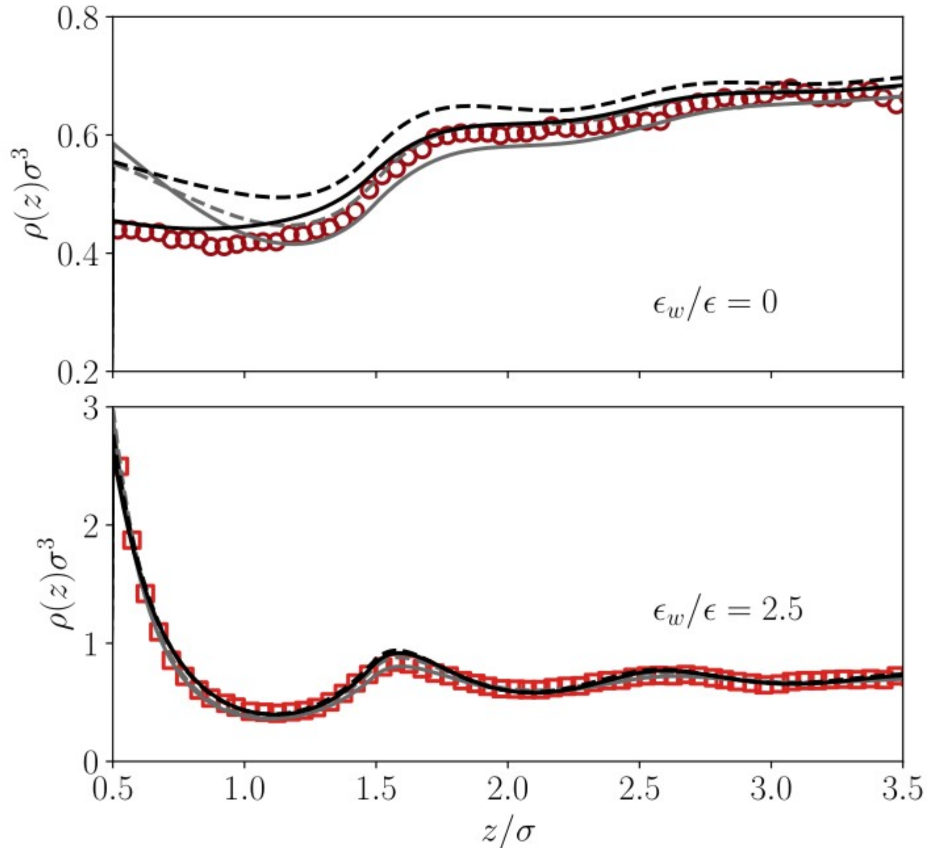
Fluido próximo à Parede

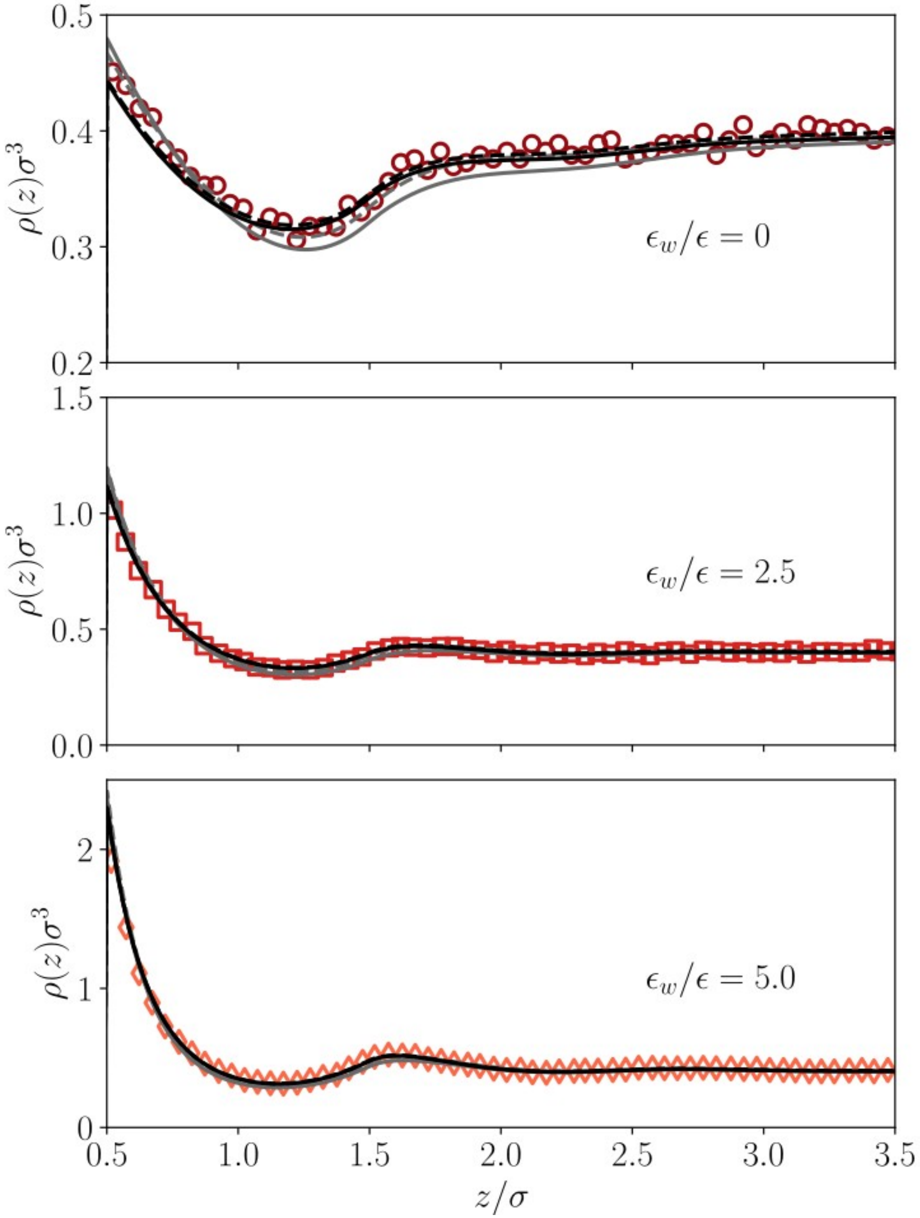




$$V_{\text{ext}}(z) = \begin{cases} \infty, & z < \sigma/2 \\ -\epsilon_w, & \sigma/2 < z < \lambda\sigma - \sigma/2 \\ 0, & z > \lambda\sigma - \sigma/2 \end{cases}$$

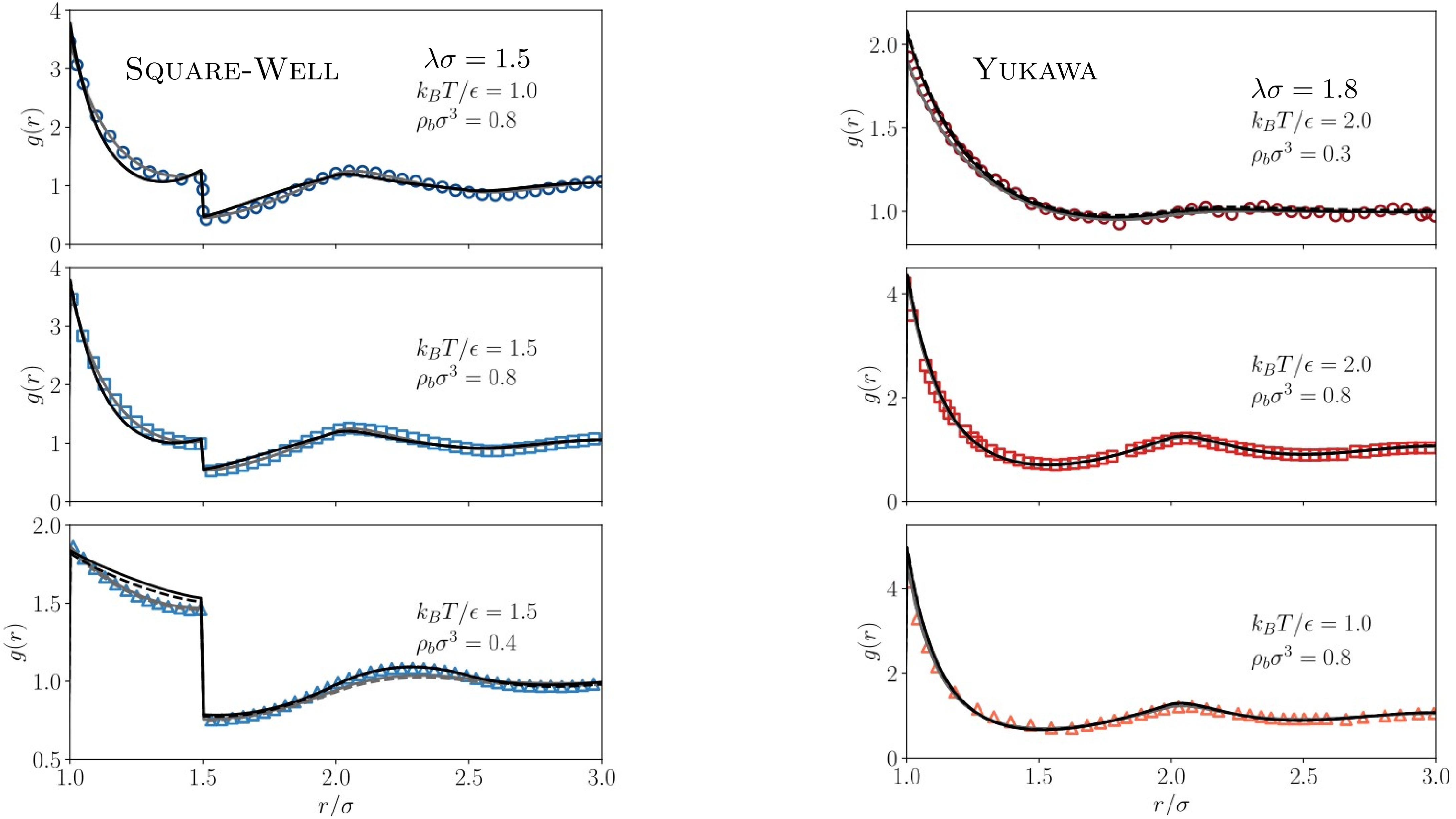
Fluido próximo à Parede



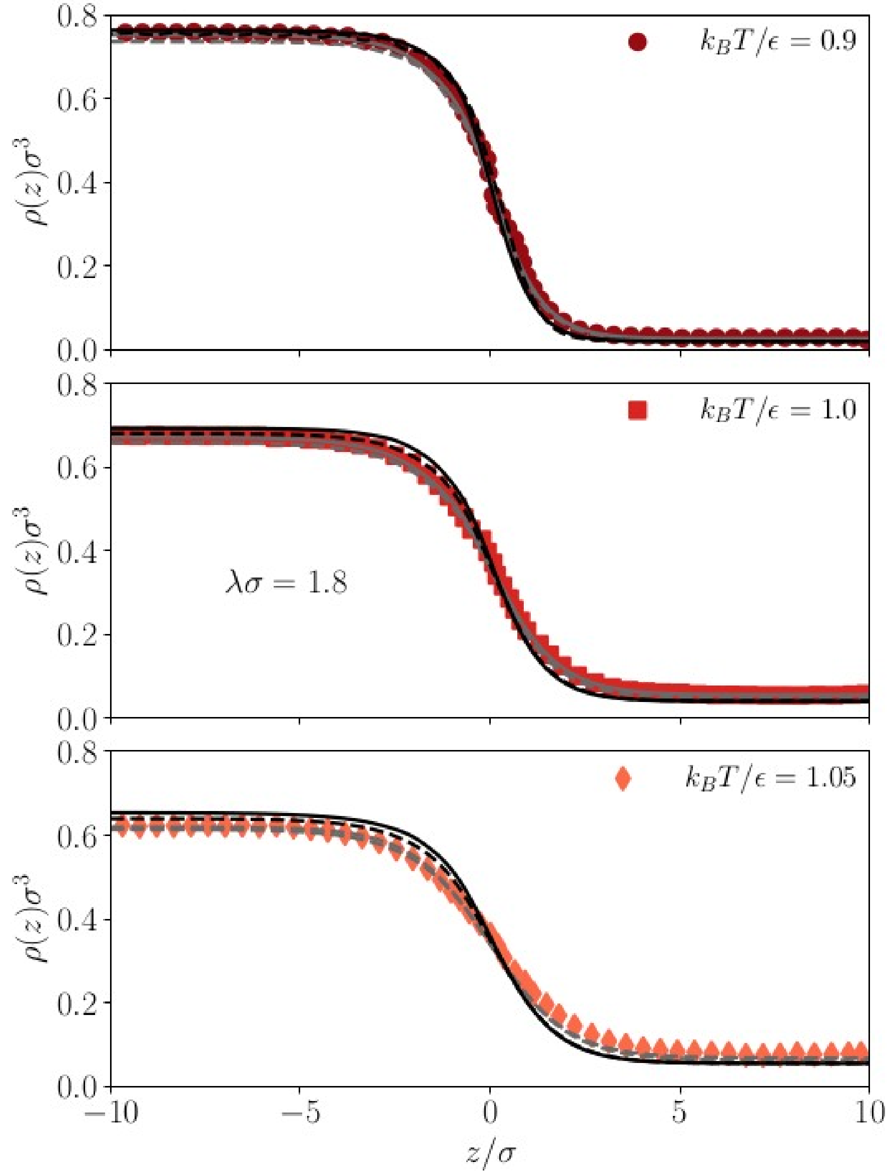


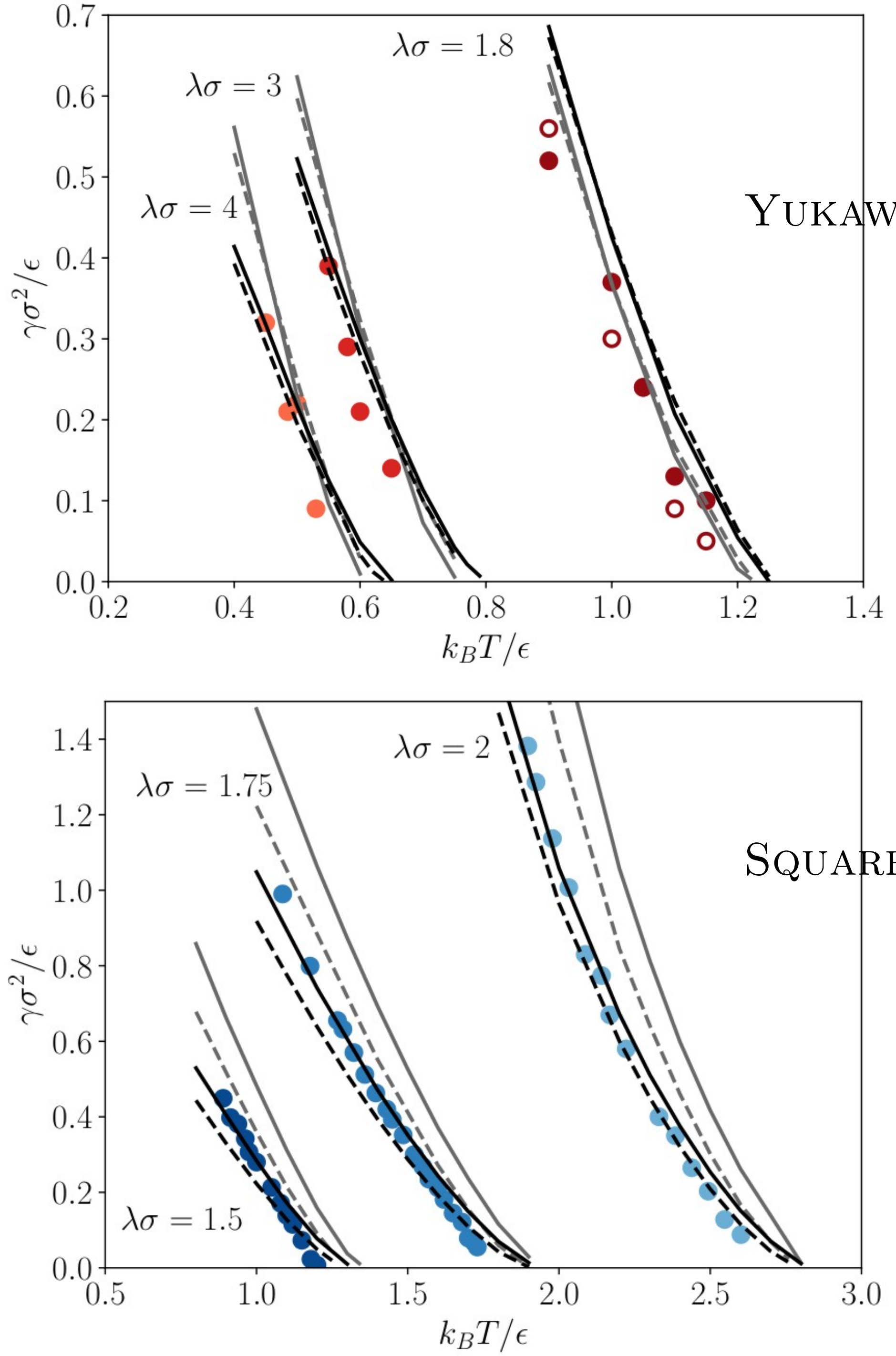
$$V_{\text{ext}}(z) = \begin{cases} \infty, & z < \sigma/2 \\ -\epsilon_w e^{-\lambda(z-\sigma/2)}, & z > \sigma/2 \end{cases}$$

Função de Distribuição Radial



Tensão Interfacial





Yukawa

Square-Well

Submetido para Fluid Phase Equilibria

A self-consistent perturbative density functional theory for hard-core fluids: phase diagrams, structural and interfacial properties

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[1)] *Engenharia de Processos Químicos e Bioquímicos (EPQB), Escola de Química, Universidade Federal do Rio de Janeiro, 21941-909, Rio de Janeiro, RJ, Brazil*

[2)] *Programa de Engenharia Química (PEQ), COPPE, Universidade Federal do Rio de Janeiro, 21945-970, Rio de Janeiro, RJ, Brazil*

(Dated: 22 April 2021)

The classical Density functional theory (DFT) has become a powerful tool to describe the microscopic structure of fluids as the radial distribution function. One of its particular capabilities is to express the thermodynamic properties of those fluids even under the influence of external potentials, such as fluid-solid interaction. However, good models for the Helmholtz free-energy functionals are necessary to improve the results. In this work, we present a self-consistent thermodynamic perturbation theory for the excess Helmholtz free-energy from the DFT applied to hard-core fluids. The new perturbation theory is solved self-consistently without any closure relation to solving the Ornstein–Zernike equation explicitly. We compare the performance of our self-consistent perturbation theory with the results obtained with the well-known second-order Barker-Henderson perturbation theory for the hard-core Yukawa and square-well fluids. Moreover, we propose two versions of the DFT to describe the perturbative contribution: one based on the weighted density approximation theory and another from a modified mean-field theory. The present results confirm the modified mean-field theory as a better option to calculate the thermodynamic and structural properties of hard-core fluids.

Pararemos por aqui?

Termo de correlação baseado em FMT

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

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

Termo de correlação

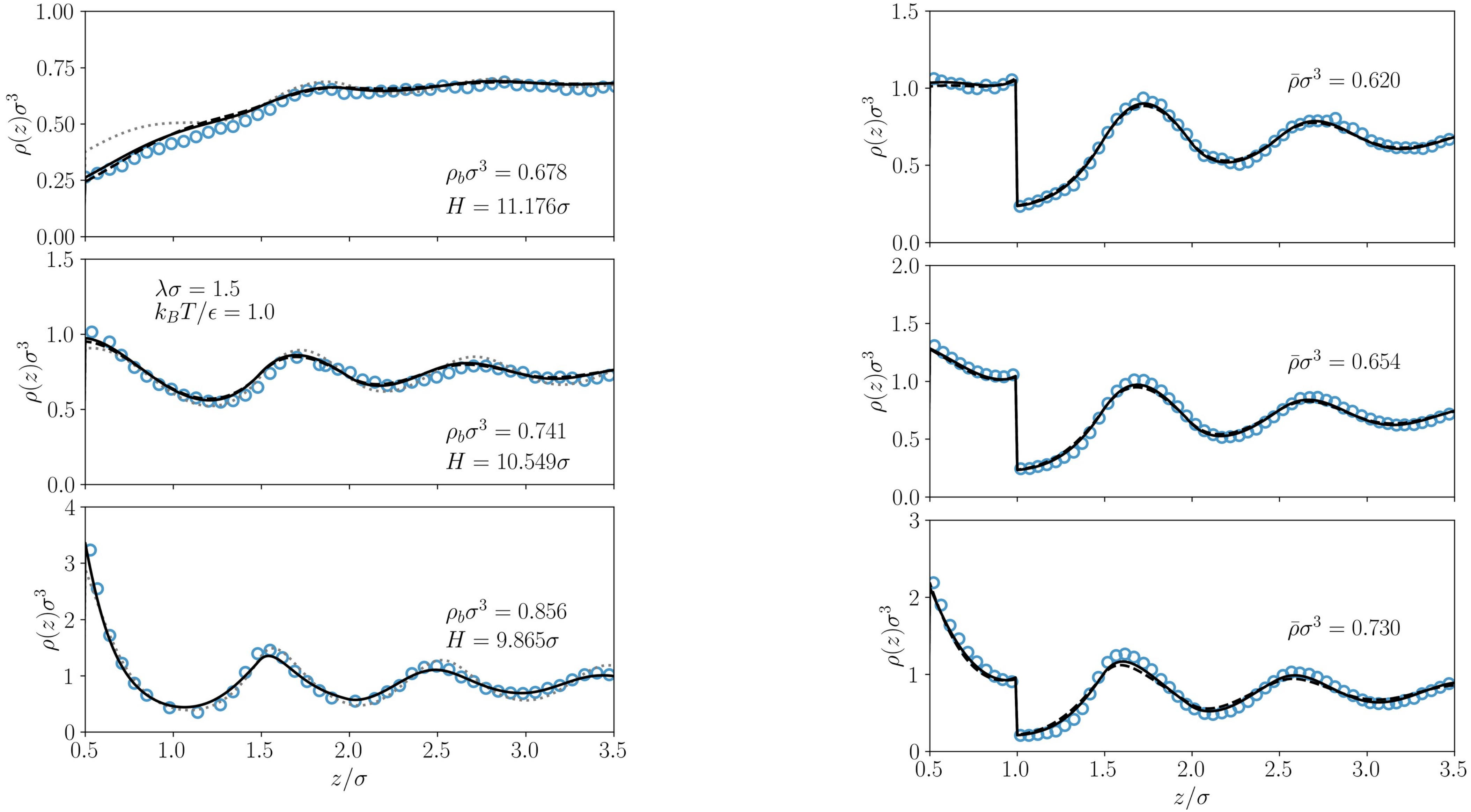
$$F_{\text{corr}}[\rho(\boldsymbol{r})] = \int \mathrm{d}\boldsymbol{r}\,a_{\text{corr}}(n_3(\boldsymbol{r}),T)\,[n_0(\boldsymbol{r})n_3(\boldsymbol{r}) + n_1(\boldsymbol{r})n_2(\boldsymbol{r}) - \boldsymbol{n}_{v1}\cdot\boldsymbol{n}_{v2}]$$

Motivação:

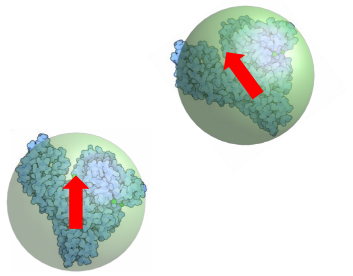
$$\frac{1}{2}\int \mathrm{d}\boldsymbol{r}\int \mathrm{d}\boldsymbol{r}'\,\rho(\boldsymbol{r})\Theta(\sigma-|\boldsymbol{r}-\boldsymbol{r}'|)\rho(\boldsymbol{r}') = \int \mathrm{d}\boldsymbol{r}\,[n_0(\boldsymbol{r})n_3(\boldsymbol{r}) + n_1(\boldsymbol{r})n_2(\boldsymbol{r}) - \boldsymbol{n}_{v1}\cdot\boldsymbol{n}_{v2}]$$

Rosenfeld, Y. (1989). Physical Review Letters, 63(9), 980-983.

Termo de correção baseado em FMT



DFT para SAXS/SANS de Proteínas



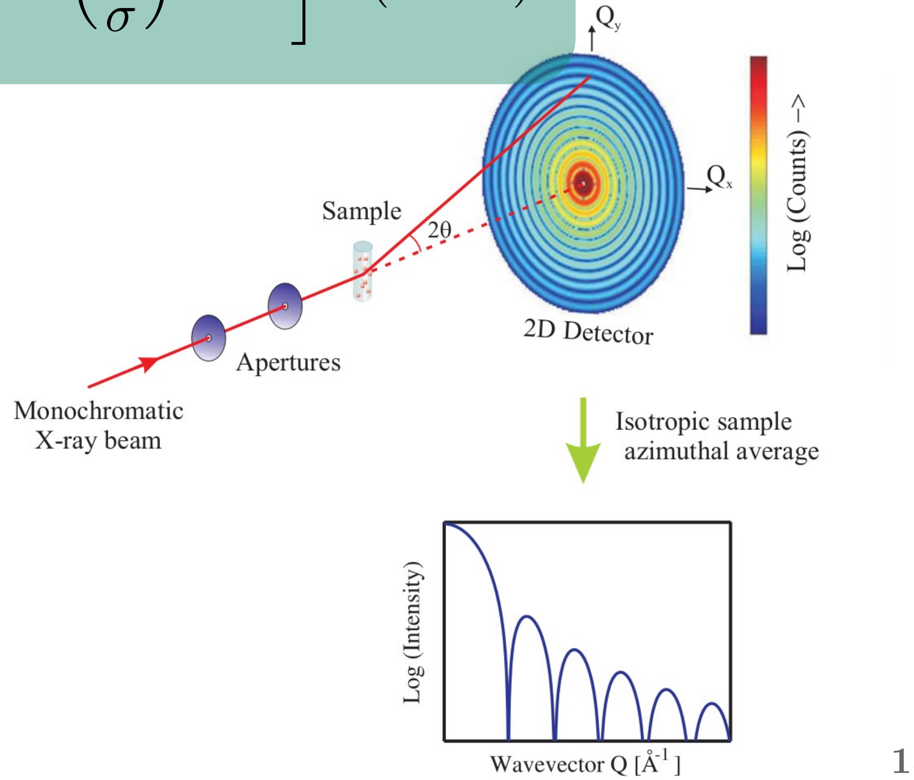
$$F_{\text{exc}}[\rho(\boldsymbol{r})] = F_{\text{hs}}[\rho(\boldsymbol{r})] + F_{\text{mft}}[\rho(\boldsymbol{r})] + F_{\text{corr}}[\rho(\boldsymbol{r})]$$

Função de correlação direta

$$c(r) = -\beta\frac{\delta^2 F_{\text{exc}}}{\delta\rho^2} = c_{\text{hs}}(r) - \beta u(r) - \beta\frac{\partial^2(\rho f_{\text{corr}})}{\partial\rho^2}\frac{3\sigma^3}{\pi}\left[\left(\frac{r}{\sigma}\right)^3 - 3\left(\frac{r}{\sigma}\right)^2 + 2\right]\Theta(\sigma - r)$$

Potencial de interação entre proteínas:

$$u(r) = u_{\text{hs}}(r) + u_{\text{vdW}}(r) + u_{\text{DH}}(r) + u_{\text{carga-dip}}(r) + u_{\text{dip-dip}}(r)$$

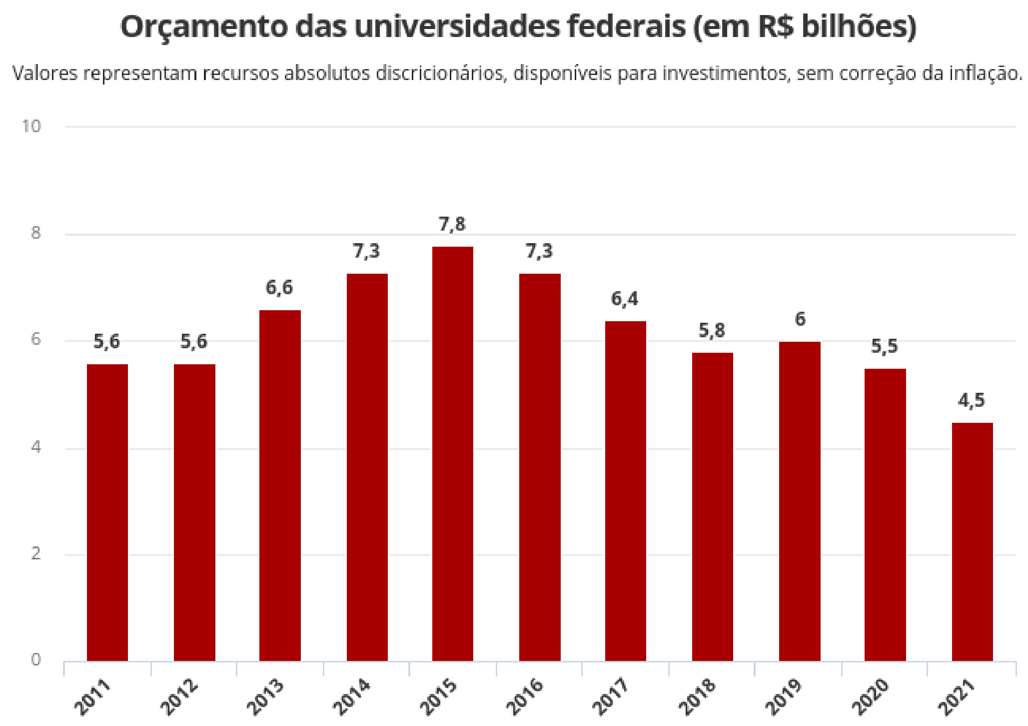


Intensidade de raio-X espalhado

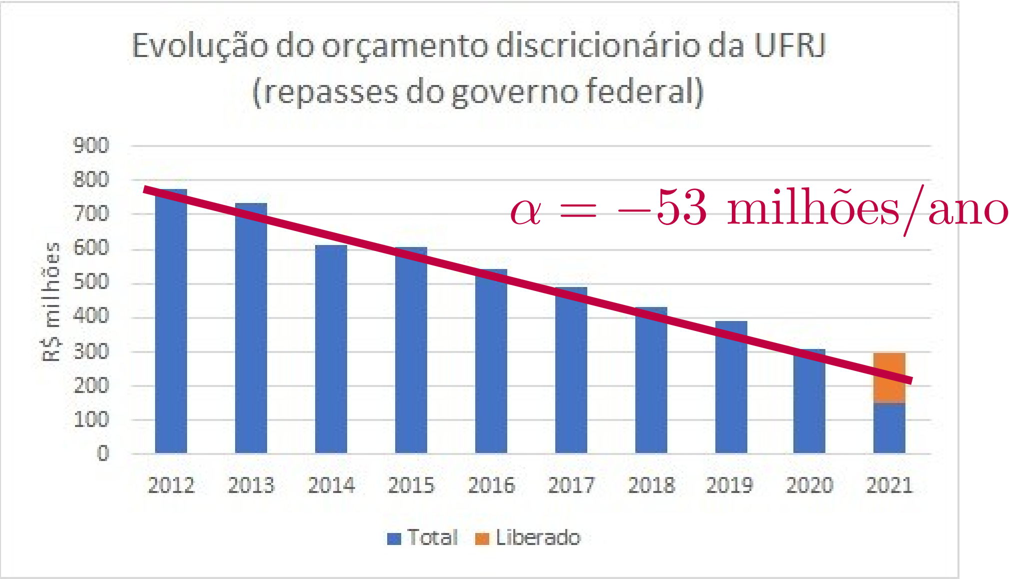
$$I(q) = AP(q)S(q) + B \qquad \text{com} \qquad S(q) = \frac{1}{1 - \rho\tilde{c}(q)}$$

Futuros trabalhos ou em andamento

- SCPT para fluidos com soft-core
- SCPT para eletrólitos
- SCPT com renormalização
- DFT com correlação para misturas de SW
- DFT com correlação para PC-SAFT
- DFT com correlação para dados de interação de proteínas



Fonte: Andifes



Fonte: Prof. Marta Castilho (UFRJ)

≡ O GLOBO

OPINIÃO

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Universidade fica inviável

06/05/2021 • 00:00

Por Denise Pires de Carvalho* e Carlos Frederico Leão Rocha**

A pandemia da Covid-19 revelou a importância da ciência no enfrentamento de questões de risco para a sociedade. Conhecimento

Fonte: https://g1.globo.com

Em defesa do orçamento da UFRJ

APG UFRJ criou este abaixo-assinado para pressionar Ministério da educação e 1 outro

NOTA DOS ESTUDANTES DA UFRJ EM DEFESA DO ORÇAMENTO DA UNIVERSIDADE E DA EDUCAÇÃO PÚBLICA

Entidades representativas estudantis da graduação e da pós-graduação da UFRJ vêm a público condenar a decisão do MEC

138.823 pessoas já assinaram. Ajude a chegar a 150.000!

Lydia Salgado assinou este abaixo-assinado

José de Oliveira assinou há 5 minutos

Hana Silveira assinou há 5 minutos

Elvis

do Amaral Soares

elvis.asoares@gmail.com

Concordo que APG UFRJ possa entrar em contato comigo no futuro

Exibir minha assinatura e meu comentário neste abaixo-assinado

Assinar este abaixo-assinado

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- Fechar 13 museus,
- Mais de 1.450 laboratórios
- 45 bibliotecas
- Mais de 500 cursos de graduação, EAD, PG Stricto e Lato Sensu
- Parque Tecnológico com startups
- Pesquisa de duas Vacinas Nacionais.

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