ENERGÍA LIBRE EN MEZCLAS POLIDISPERSAS DE DISCOS DUROS Y ESFERAS DURAS

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VIII Encuentro GET – RSEF, RSEQ

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• **Energía libre de un sistema** ***simple*****:**

$$F(N,V,T) = V f(\rho,T); \quad \rho = \frac{N}{V}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = \rho^2 \left(\frac{\partial (f/\rho)}{\partial \rho}\right)_T$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{N,T} = \left(\frac{\partial f}{\partial \rho}\right)_T$$

• **Energía libre de un sistema** ***multicomponente*****:**

$$F(\{N_i\},V,T) = V f(\{\rho_i\},T); \quad \rho_i = \frac{N_i}{V}$$

$$f(\{\rho_i\},T) = f(\rho,\{x_i\},T); \quad \rho = \sum_i \rho_i, \quad x_i = \frac{\rho_i}{\rho}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{N_i,T} = \rho^2 \left(\frac{\partial (f/\rho)}{\partial \rho}\right)_{x_i,T}$$

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{N_j,T} = \left(\frac{\partial f}{\partial \rho_i}\right)_{\rho_j,T}$$

$$z_i = e^{\mu_i/k_B T} : \text{ fugacidad}$$

• **Energía libre de un sistema** *polidisperso* **(e.g., solución coloidal):**

$$N_i \to N_\sigma d\sigma; \quad \int d\sigma\, N_\sigma = N$$

$$\rho_i \to \rho_\sigma d\sigma; \quad \int d\sigma\, \rho_\sigma = \rho = \frac{N}{V}$$

$$x_i \to x_\sigma d\sigma; \quad \int d\sigma\, x_\sigma = 1; \quad x_\sigma = \frac{\rho_\sigma}{\rho}$$

$$\mu_i \to \mu_\sigma; \quad z_i \to z_\sigma d\sigma = e^{\mu_\sigma/k_B T} d\sigma$$

$$F[N_\sigma|V,T] = V f[\rho_\sigma|T] = V f[x_\sigma|\rho,T]$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{N_\sigma,T} = \rho^2 \left(\frac{\partial (f/\rho)}{\partial \rho}\right)_{x_\sigma,T}$$

$$\mu_\sigma = \left(\frac{\delta F}{\delta N_\sigma}\right)_T = \left(\frac{\delta f}{\delta \rho_\sigma}\right)_T : \text{ derivada } \textit{funcional}$$

• Gas ideal:

$$\mu_\sigma^{\rm id} = k_B T \ln\left(\Lambda_\sigma^d \rho_\sigma\right) \quad (\Lambda_\sigma : \text{longitud de onda térmica})$$

$$z_\sigma^{\rm id} = \Lambda_\sigma^d \rho_\sigma$$

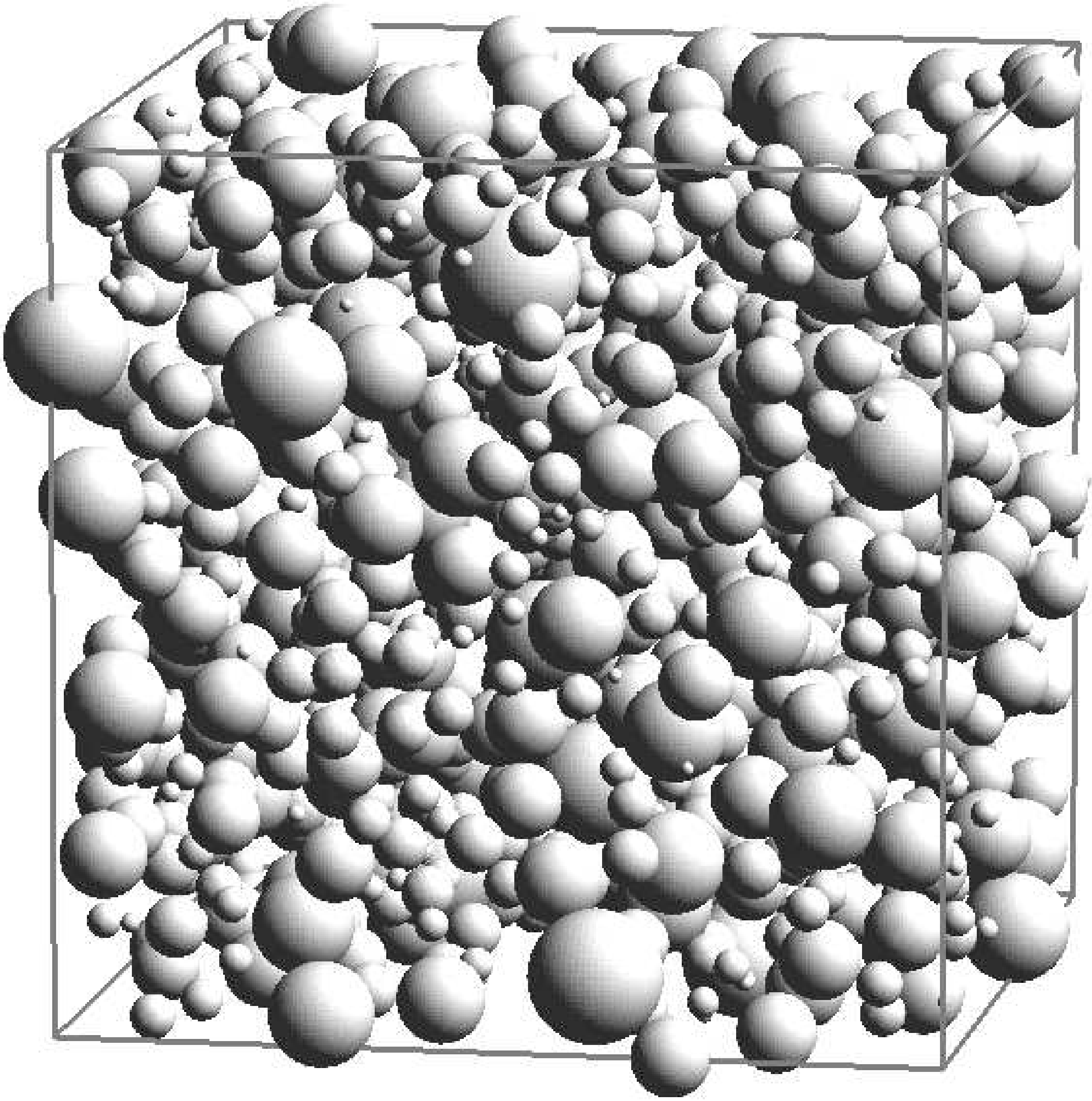
• Valores de exceso:

$$\mu_\sigma = \mu_\sigma^{\rm id} + \mu_\sigma^{\rm ex}$$

$$z_\sigma = z_\sigma^{\rm id} z_\sigma^{\rm ex}; \quad z_\sigma^{\rm ex} = e^{\mu_\sigma^{\rm ex}/k_B T}$$

[Zhang *et al.*, J. Chem. Phys. **110**, 5318 (1999)]

24% de volumen ocupado por las esferas ($\eta = 0.24$)

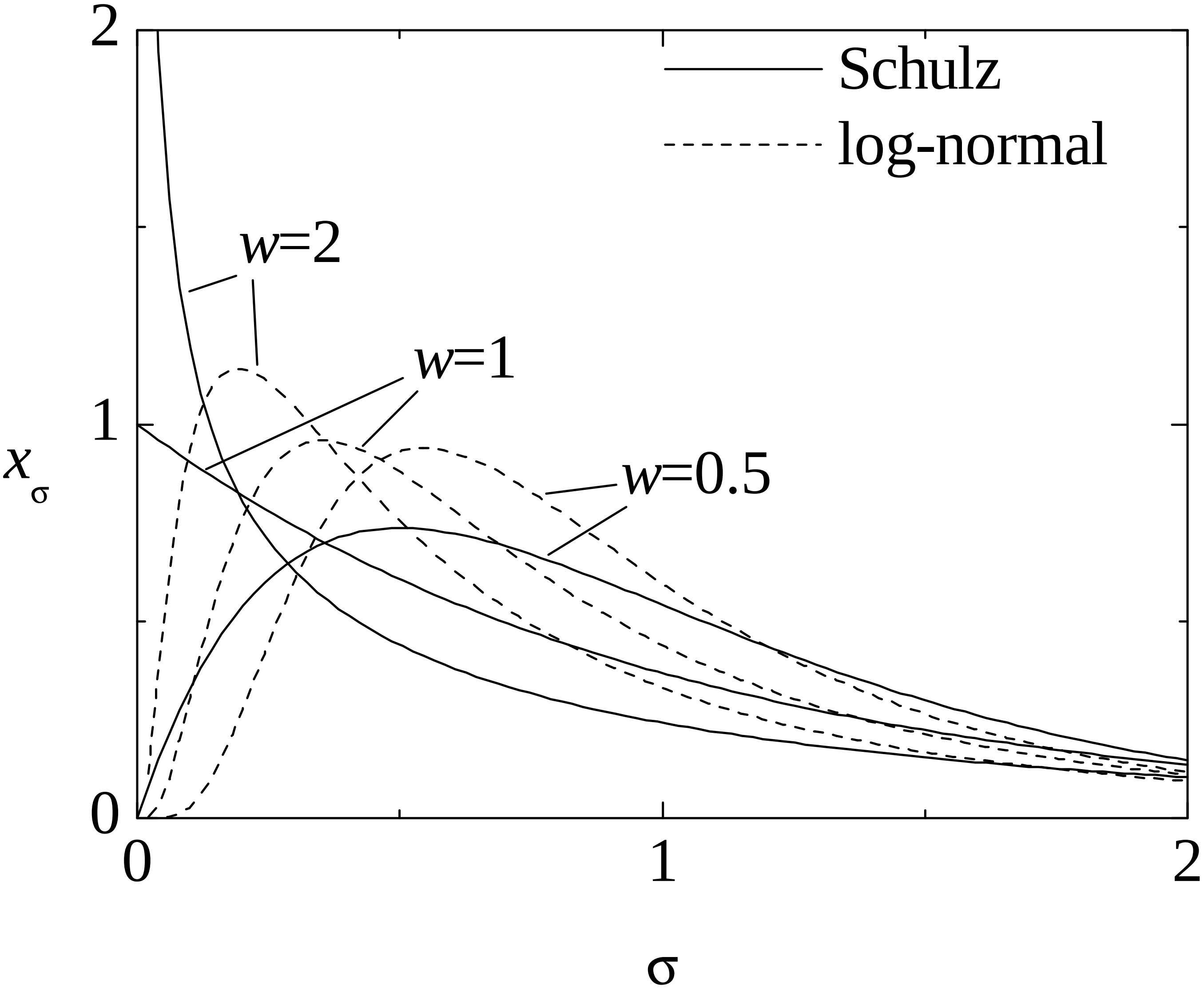


• Distribución de tamaños de Schulz ($\langle\sigma\rangle = 1$, $w \equiv \langle\sigma^2\rangle - \langle\sigma\rangle^2$):

$$x_\sigma = \frac{1}{w\Gamma(w^{-1})}(\sigma/w)^{w^{-1}-1}e^{-\sigma/w}, \quad \langle\sigma^3\rangle = (1+w)(1+2w)$$

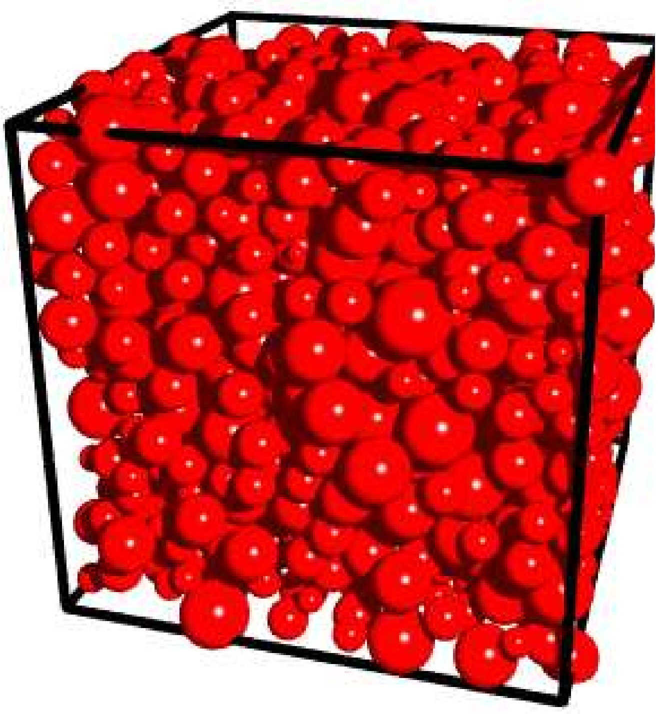
• Distribución de tamaños log-normal ($\langle\sigma\rangle = 1$, $w \equiv \langle\sigma^2\rangle - \langle\sigma\rangle^2$):

$$x_\sigma = \frac{1+w}{\sqrt{2\pi\ln(1+w)}}\exp\left\{-\frac{\ln^2\left[\sigma(1+w)^{3/2}\right]}{\ln(1+w)^2}\right\}, \quad \langle\sigma^3\rangle = (1+w)^3$$

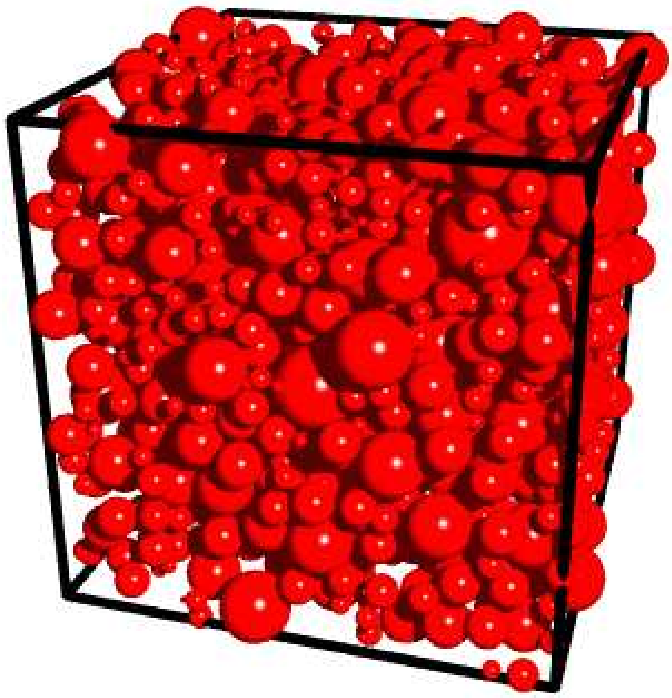


[Wilding and Sollich, J. Chem. Phys. **116**, 7116 (2002)]

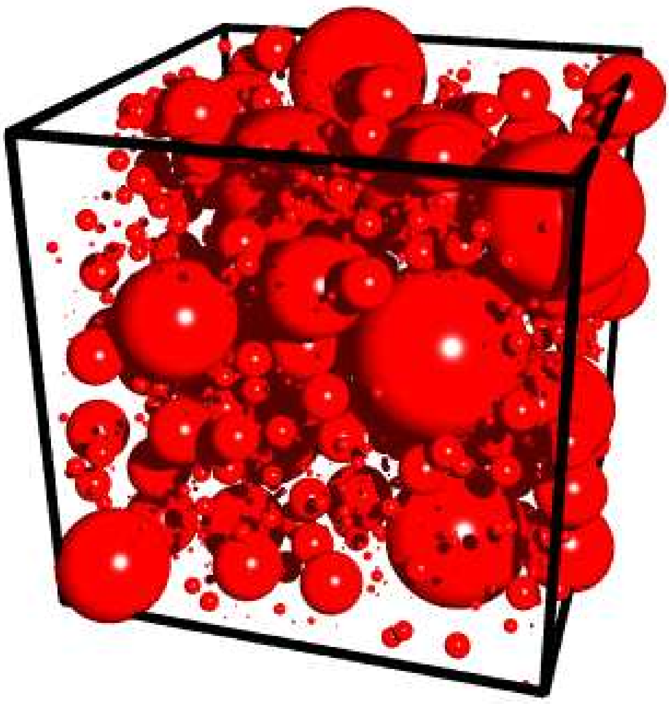
Schulz; $w = 0.0625$, $\eta = 0.43$



Schulz; $w = 0.167$, $\eta = 0.38$



log-normal; $w = 6.25$, $\eta = 0.29$



Sistema polidisperso de esferas duras (en d dimensiones)

- Ecuación del virial:

$$Z \equiv \frac{p}{\rho k_B T} = 1 + 2^{d-1} v_d \rho \int d\sigma \int d\sigma' \, x_\sigma x_{\sigma'} \left(\frac{\sigma + \sigma'}{2} \right)^{d-1} g_{\sigma,\sigma'}$$

$g_{\sigma,\sigma'}$: valor de contacto de la función de correlación espacial para dos esferas de diámetros σ y σ'.

v_d: volumen de una esfera de diámetro unidad.

- Nuestra propuesta [Molecular Physics **96**, 1–5 (1999)]:

$$g_{\sigma,\sigma'} = \frac{1}{1-\eta} + \left(g_{\text{mono}} - \frac{1}{1-\eta} \right) \frac{2\sigma\sigma'}{\sigma + \sigma'} \frac{\langle \sigma^{d-1} \rangle}{\langle \sigma^d \rangle}$$

donde

$\eta \equiv v_d \rho \langle \sigma^d \rangle$: fracción del "volumen" total ocupado por las esferas (fracción de empaquetamiento),

g_{mono}: valor de contacto de la función de correlación espacial en un sistema *monocomponente* con la misma fracción de empaquetamiento η que el sistema polidisperso.

• Energía libre ($k_B T = 1$):

$$f^{\text{ex}}[\rho_\sigma] = f^{\text{ex}}[x_\sigma|\rho] = A[x_\sigma] f^{\text{ex}}_{\text{mono}}(\eta) - B[x_\sigma]\rho \ln(1-\eta)$$

donde

$A[x_\sigma]$, $B[x_\sigma]$: funcionales de la distribución x_σ a través de los primeros d momentos.

$$\text{2D: } A[x_\sigma] = \frac{\langle\sigma\rangle^2}{\langle\sigma^2\rangle}, \quad B[x_\sigma] = 1 - A[x_\sigma]$$

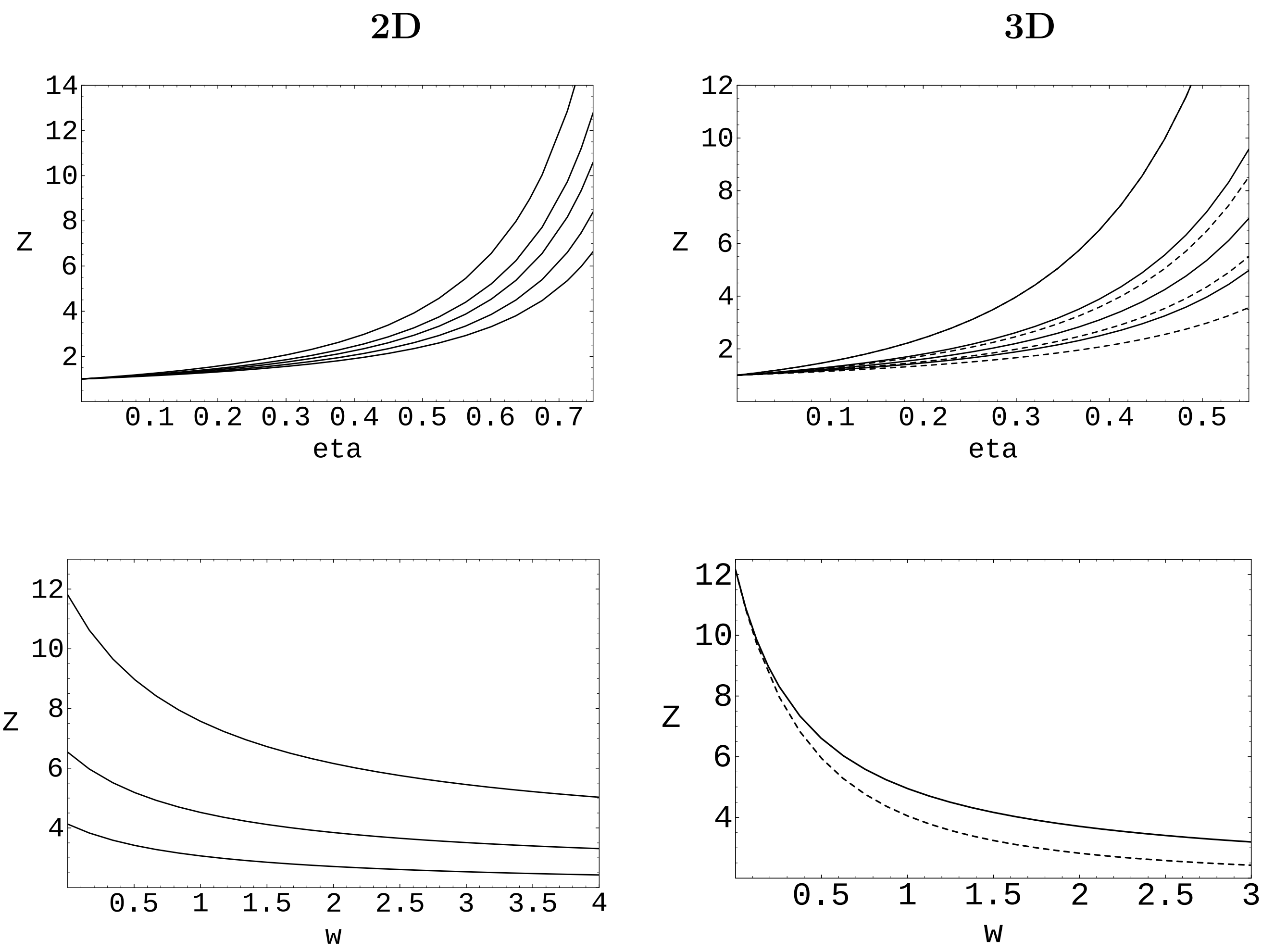
$$\text{3D: } A[x_\sigma] = \frac{\langle\sigma^2\rangle}{2\langle\sigma^3\rangle^2}\left(\langle\sigma^2\rangle^2 + \langle\sigma\rangle\langle\sigma^3\rangle\right), \quad B[x_\sigma] = 1 - \frac{\langle\sigma^2\rangle}{\langle\sigma^3\rangle^2}\left(2\langle\sigma^2\rangle^2 - \langle\sigma\rangle\langle\sigma^3\rangle\right)$$

• Ecuación de estado:

$$Z[\rho_\sigma] - 1 = A[x_\sigma]\left[Z_{\text{mono}}(\eta) - 1\right] + B[x_\sigma]\frac{\eta}{1-\eta}$$

• Potencial químico:

$$\begin{aligned}\mu^{\text{ex}}_\sigma &= \frac{\delta f^{\text{ex}}}{\delta \rho_\sigma} \\ &= \sum_{n=0}^{d} \frac{\partial f^{\text{ex}}}{\partial m_n}\sigma^n, \quad m_n \equiv \int d\sigma\, \rho_\sigma \sigma^n, \quad \langle\sigma^n\rangle = \frac{m_n}{m_0}\end{aligned}$$


2D
3D
Z
eta
0.1 0.2 0.3 0.4 0.5 0.6 0.7
2 4 6 8 10 12 14
0.1 0.2 0.3 0.4 0.5
2 4 6 8 10 12
w
0.5 1 1.5 2 2.5 3 3.5 4
4 6 8 10 12
0.5 1 1.5 2 2.5 3

- Potencial químico:

$$\mu_\sigma^{\mathrm{ex}} = -A\frac{f_{\mathrm{mono}}^{\mathrm{ex}}}{\rho} - \ln(1-\eta) + \sum_{n=1}^{d} \alpha_n \sigma^n + \left(A\mu_{\mathrm{mono}}^{\mathrm{ex}} + B\frac{\eta}{1-\eta}\right)\sigma^d$$

donde

$$\alpha_n = \frac{\partial A}{\partial\langle\sigma^n\rangle}\frac{f_{\mathrm{mono}}^{\mathrm{ex}}}{\rho} - \frac{\partial B}{\partial\langle\sigma^n\rangle}\ln(1-\eta)$$

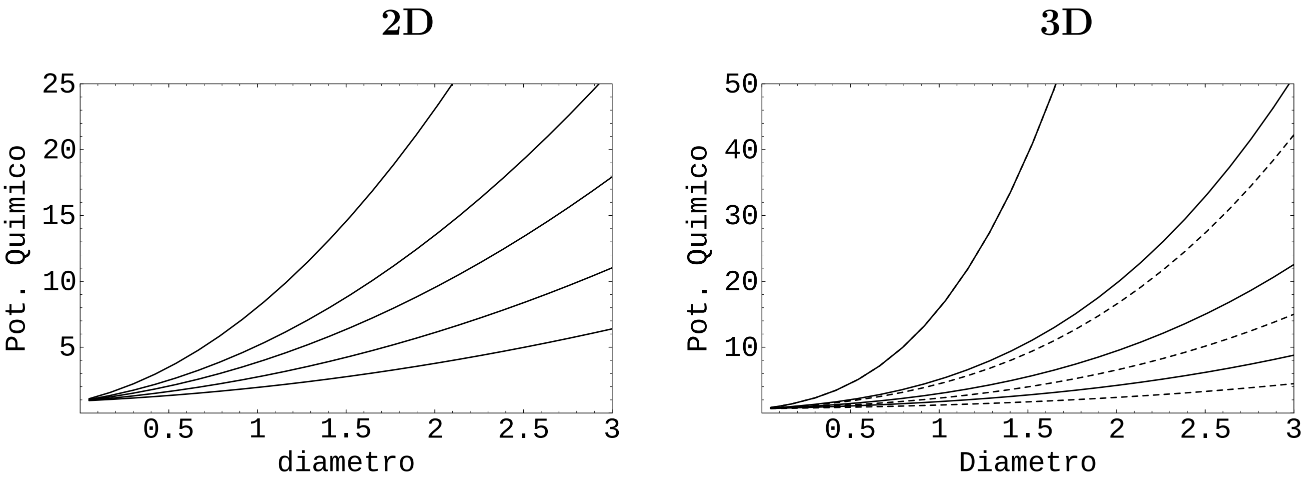
- Efecto "fantasma":

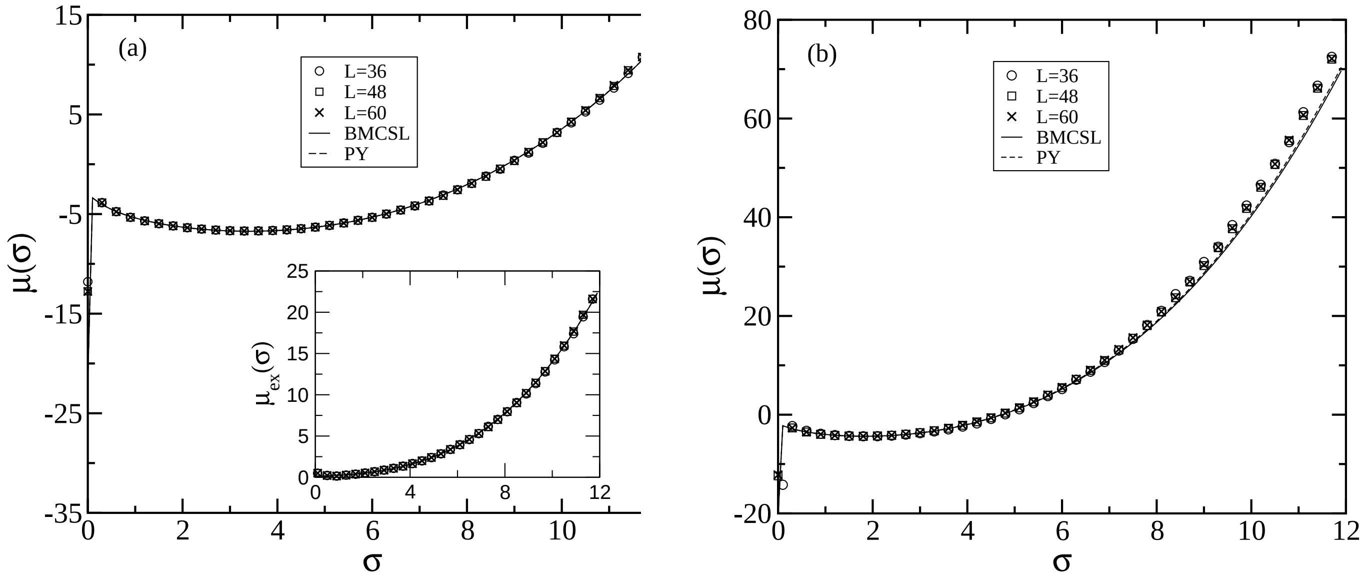
$$x_\sigma \to \delta(\sigma-1) \Rightarrow \mu_\sigma^{\mathrm{ex}} \to \sum_{n=1}^{d} \alpha_n^0(\sigma^n-1) + \mu_{\mathrm{mono}}^{\mathrm{ex}}\sigma^d$$

$$\Rightarrow z_\sigma^{\mathrm{ex}} \to \left(z_{\mathrm{mono}}^{\mathrm{ex}}\right)^{\sigma^d} \prod_{n=1}^{d} e^{\alpha_n^0(\sigma^n-1)}$$

...pero

$$z_\sigma = \Lambda_\sigma^d z_\sigma^{\mathrm{ex}} \rho x_\sigma \to \Lambda_\sigma^d z_\sigma^{\mathrm{ex}} \rho \delta(\sigma-1)$$





log-normal (3D); $w = 6.25$, $\eta = 0.126$

log-normal (3D); $w = 6.25$, $\eta = 0.307$

[Wilding and Sollich, J. Chem. Phys. **116**, 7116 (2002)]