

Using a simple coarse-grained classical Density Functional theory, cDFT, we can write the grand potential per unit area, Ω , for a simple Lennard-Jones fluid confined between two planar Lennard-Jones surfaces, located at $z = 0$ and $z = h$, as

$$\begin{aligned}\Omega &= k_B T \int_0^h n(z) \ln\left[\frac{n(z)}{1 - n(z)\sigma^3}\right] - n(z)dz + \\ &\quad \frac{1}{2} \int_0^h n(z) \int_0^h n(z') \phi_{LJ}(|z - z'|) dz' dz + \int_0^h n(z) (V_{ex}(z; h) - \mu) dz\end{aligned}(1)$$

where $k_B T$ is the thermal energy and the mean-field Lennard-Jones potential (integrated along x and y) is

$$\phi_{LJ}(|z|) = \begin{cases} \frac{4\pi\epsilon\sigma^2}{5} \left[\frac{1}{z} \left(\frac{\sigma}{z} \right)^{10} - \frac{1}{2} \left(\frac{\sigma}{z} \right)^4 \right] & |z| > \sigma \\ -\frac{6\pi\beta\epsilon\sigma}{5}, & |z| \leq \sigma \end{cases} \quad (2)$$

where μ is the bulk chemical potential. The wall potential (per unit area), $V_{ex}(z; h)$ can be written as $V_{ex}(z; h) = w(z) + w(h - z)$, with

$$w(z) = 2\pi\epsilon \left[\frac{2}{45} \left(\frac{\sigma_w}{z} \right)^9 - \frac{1}{3} \left(\frac{\sigma_w}{z} \right)^3 \right] \quad (3)$$

where σ_w and ϵ_w may differ from σ and ϵ . Write a code that solves the Euler-Lagrange equation to obtain the equilibrium density profile ($n(z)$) via Picard iterations. Input parameters are the Lennard-Jones parameters $\epsilon, \epsilon_w, \sigma, \sigma_w$, the bulk density n_b , the surface separation h , and the temperature T . Use system parameters as described in *J. Chem. Phys.* **79**, 4431 (1983), although you do not have to use separate “coarse-grained” and “fine-grained” densities (a local density $n(z)$ will suffice). Once the code works, conduct the following tasks:

- Set $T^* = kT/\epsilon = 1.2$. Establish equilibrium density distributions $n_{eq}(z)$ for a range of different surface separations, $h/\sigma = 4 \Rightarrow 10$, with increments of 0.2 ($6/0.2 = 30$ separations). Calculate the free energy per unit area at each separation, to obtain $\omega(h) \equiv \Omega(h)/\text{area}$ ($\Delta F(h)/A$ in the notation used in the publication (see eq. (11)). Also calculate the solvation force, $F_s = -\partial\omega/\partial h$ at each separation (eq. (26)) to generate $F_s(h)$. Verify that $F_s(h)$ agrees with the discrete free energy derivative, $-\Delta\omega/\Delta h$. How is the large separation value of $\omega(h)$ related to a well-known thermodynamic quantity, at a single surface?
- Now run the same analyses as above, but at $T^* = kT/\epsilon = 1.0$. Comment on any differences (especially qualitative differences).
- Extra task, if time permits: run the same analyses but with “coarse-grained” and “fine-grained” densities i.e. with a model identical to that described in the article (the use of such “weighted” densities will allow non-local excluded volume effects to be handled, which in turn facilitates a realistic description of “packing”, such as density oscillations).
- Feel free to run with completely different parameters (bulk density etc.) if you wish (not mandatory)

Discuss results, approximations, and possible ways to improve these.