

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

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

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

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

where  $\mu$  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  $\sigma_w$  and  $\epsilon_w$  may differ from  $\sigma$  and  $\epsilon$ . 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  $\omega(h) \equiv \Omega(h)/area$  ( $\Delta F(h)/A$  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.