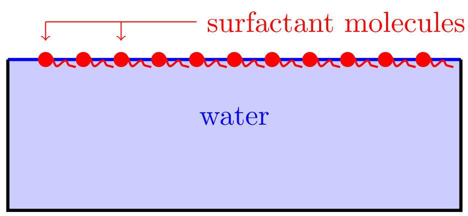
Surfactants

A **surfactant** is a compound that lowers the surface tension on the surface of a liquid. Surfactants find great usage in a variety of chemical applications, such as paints, inks, detergents, adhesives and shampoo; a typical surfactant is a molecule with both a hydrophilic and a hydrophobic component. In this problem, we will explore the statistics of a collection of a surfactant molecules on the surface of a liquid, such as water.

N surfactant molecules of mass m are trapped on the surface of a body of water at temperature T. The area of the surface is A. The Hamiltonian of the surfactant molecules is given by

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i{}^2}{2m} + \frac{1}{2}\sum_{i\neq j} V_0(|\mathbf{r}_i - \mathbf{r}_j|),$$

where $V_0(r)$ is the rough interaction energy between two surfactants. Approximate that each surfactant molecule is a hard sphere of radius R; two hard spheres therefore cannot overlap.



(a) Write down an exact expression for Z, involving only integrals over $\mathbf{r}_i$.

(b) Ignoring the interaction term, and treating the surfactant molecules as hard spheres, show the allowed volume in position phase space for the system is given by approximately

$$V_{\mathbf{r}} \approx (A - 2\pi R^2)^N.$$

Now, assume that

$$-u_0 = \int_{2R}^{\infty} (2\pi r\mathrm{d}r) V_0(r).$$

Approximate that the density of surfactant molecules on the surface is approximately a constant, $n = N/A$; this will make the calculation tractable.

(c) What is the approximate potential energy U_T due to the interactions?

(d) Combining parts (b) and (c), find an approximation for Z not involving any integrals.

(e) Show that the surface tension of the water is given by

$$\sigma(n, T) \approx \sigma_0 - nk_\mathrm{B}T + \frac{1}{2}n^2 u_0.$$

(f) Why does the approximate result of part (e) break down at low temperatures? Guess what happens to the film of surfactants at low temperatures.