Statistical Mechanics

Hard rods

A collection of N asymmetric molecules in two dimensions may be modeled as a gas of rods, each of length $2l$ and lying in a plane. A rod can move by translation of its center of mass and rotation about latter, as long as it does not encounter another rod. Without treating the hard-core interaction exactly, we can incorporate it approximately by assuming that the rotational motion of each rod is restricted (by the other rods) to an angle θ, which in turn introduces an excluded volume $\Omega(\theta)$ (associated with each rod). The value of θ is then calculated self consistently by maximizing the entropy at a given density $n = N/V$, where V is the total accessible area.

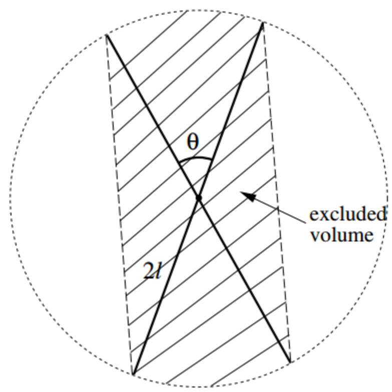


Figure 1: Schematic diagram of a rod

(a) Show that the total non-excluded volume available in the positional phase space of the system of N rods is given by $(V - N\Omega/2)^N$

- The joint phase space of rods with excluded volume can be estimated by summing them up one by one. The first one can occupy the whole volume V, while the second rod explore only $V - \Omega$. Neglecting three body effects, the area available to the third particle is $(V - 2\Omega)$ and similarly $(V - n\Omega)$ for the $n-$th particle. Hence the joint excluded volume in this limit is given by
$$V(V-\Omega)(V-2\Omega)...(V-(N-1)\Omega) \approx (V - N\Omega/2)^N \tag{1}$$

(b) Express the entropy in terms of N, n, Ω, and $A(\theta)$, the entropy associated to the rotational freedom of a single rod. (You may ignore the momentum contributions throughout, and consider the large N limit.)

- Including both forms of entropy, translational and rotational, one will get

$$S = k_b \ln\left[\frac{1}{N!}\Big(V - \frac{N\Omega(\theta)}{2}\Big)^N A(\theta)^N\right] \approx Nk_b\left[\ln\Big(n^{-1} - \frac{\Omega(\theta)}{2}\Big) + 1 + \ln A(\theta)\right] \tag{2}$$

(c) Extremizing the entropy as a function of θ, show that the density n can be expressed as

$$n = \frac{2A'}{\Omega A' + \Omega' A} \tag{3}$$

where Ω', A' denotes the derivatives with respect to θ.

- By applying the extremum condition $\partial S/\partial\theta = 0$ to Equation (1), one will have

$$\frac{\Omega'}{2n^{-1} - \Omega} = \frac{A'}{A} \tag{4}$$

where the primes represent derivatve with respect to θ. Solving for density,

$$n = \frac{2A'}{\Omega A' + \Omega' A} \tag{5}$$

(d) Express the excluded volume Ω in terms of θ and sketch n as a function of $\theta \in [0, \pi]$, assuming $A \propto \theta$

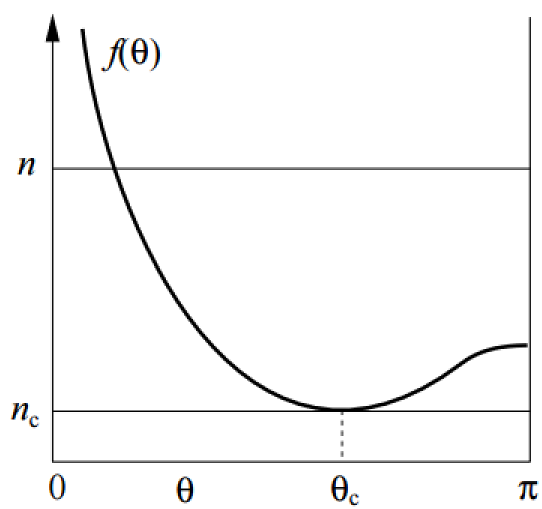
- From Figure (1), with elementary geometry, one can derive the excluded volume to be

$$\Omega = l^2(\theta + \sin\theta) \tag{6}$$

Along with the assumption that A $\propto \theta$, the equilibrium condition becomes

$$n = f(\theta) = \frac{2}{l^2}[\theta(1 + \cos\theta) + \sin\theta]^{-1}) \tag{7}$$

The sketch of $f(\theta)$ is as follows



(e) Describe the equilibrium state at high densities. Can you identify a phase transition as the density is decreased? Draw the corresponding critical density n_c on your sketch. What is the critical angle θ_c at the transition? You don't need to calculate θ_c explicitly, but give an (implicit) relation defining it. What value does θ adopt at $n < n_c$?

- At high densities $\theta << 1$, the equilibrium condition reduces to

$$N \approx \frac{V}{2\theta l^2} \tag{8}$$

the angle θ is as open as allowed by the close packing. The equilibrium value of θ increases as the density is decreased, up to its "optimal" value θ_c at n_c, and $\theta(n < n_c) = \theta_c$. The transition occurs at the minimum of $f(\theta)$, whence θ_c satisfies

$$\frac{d}{d\theta}[\theta(2 + \cos\theta) + \sin\theta] = 0, \tag{9}$$

i.e.

$$2(1 + \cos\theta_c) = \theta_c \sin\theta + c \tag{10}$$

Actually, the above argument tracks the stability of a local maximum in entropy (as density is varied) which becomes unstable at θ_c. There is another entropy maximum at $\theta = \pi$, corresponding to freely rotating rods, which becomes more advantageous (i.e. the global equilibrium state) at a density slightly below θ_c.