Homework 19 (Due Tuesday, May 1st)

1. Consider monatomic particles with hard core repulsion. (a) Given that all of the energy of the particles is kinetic energy, show that the pressure may be obtained from

$$p = T\left(\frac{\partial S}{\partial V}\right)_{T,N}$$

(b) Find the pressure for a gas of such particles by using the *micro-canonical ensemble* with the simple construction that the volume of the system may be partitioned into $M = V/v_0$ boxes, where v_0 is the volume occupied by a single particle ($M \gg N$). Show that your result may be written as

$$p = \frac{NkT}{V - bN}$$

and determine the constant b in terms of v_0.

(c) Find the heat capacities C_v and C_p.

2. Consider an equilibrium classical fluid of N hard rods confined to move on a line of length L; the length of each rod is ℓ. The number density is $\rho = N/L$ and $\rho_{\mathrm{CP}} = 1/\ell$ is the close packed number density. Assume that the system is periodic so $x = 0$ and $x = L$ are the same point.[1]

(a) Define the pair distribution function $g(\Delta x)$ as the average density of rods at position x given that a rod is at the origin, normalized by the mean density. Note that Δx can be positive or negative and that $g \to 1$ for $\Delta x \gg \ell$. Make a hand-drawn sketch showing the high density ($\rho \approx \rho_{\mathrm{CP}}$) and low density ($\rho \approx 0$) limits of $g(\Delta x)$.

(b) For $\rho \to \rho_{\mathrm{CP}}$, compute the value of the integral

$$\int_0^{\alpha\ell} dx\, g(x)$$

where α is a positive constant.

(c) As a function of N, ρ, and T, determine the average kinetic energy of a rod.

(d) Assume that the pressure may be written as

$$P = \frac{\rho kT}{1 - b\rho}$$

where b is independent of density. Relate b to the second virial coefficient.

(e) Explain why the Helmloltz free energy for this system may be written as,

$$A = -kT\ln\left[\frac{1}{N!\lambda^N}\int_0^L dx_1 \ldots \int_0^L dx_N e^{-\beta U(x_1,\ldots,x_N)}\right]$$

[1] Imagine this one-dimensional system to be like a closed loop.

and why the pressure may be written as

$$P = -\left(\frac{\partial A}{\partial L}\right)_{T,N}$$

(f) Use the results from part (e) to get an expression for pressure in the form given in part (d).

3. Using the approximation that the pair correlation function is $g(r) \approx e^{-\beta \upsilon(r)}$ find the second virial coefficient for:

(a) Hard core potential:

$$\upsilon(r) = \begin{cases} \infty & r < r_{min} \\ 0 & r \geq r_{min} \end{cases}$$

(b) Square-well potential:

$$\upsilon(r) = \begin{cases} \infty & r < r_{min} \\ -\epsilon & r_{min} < r < r_{well} \\ 0 & r \geq r_{well} \end{cases}$$

4. (a) Find an integral expression for the second virial coefficient, $B_2(T)$, for the Lennard–Jones potential,

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

and show that it may be written as,

$$B_2(T^*) = -3B_2^{\mathrm{HC}} \int_0^\infty x^2 \left\{\exp\left[-\frac{4}{T^*}(x^{-12} - x^{-6})\right] - 1\right\} dx$$

where $T^* = kT/\epsilon$ and B_2^{HC} is the second virial coefficient for hard core exclusion of radius $r_{min} = \sigma$.
(b) Evaluating the integral numerically and produce a graph of $B_2(T)$ for nitrogen ($\epsilon/k = 95$ K, $\sigma = 0.375$ nm) in the range of temperatures from 50 K to 400 K. From your graph, estimate the Boyle temperature, T_B, defined as $B_2(T_B) = 0$.