1. Thermal ionization of hydrogen at low densities

(a) Consider a proton and an electron confined inside a cubical box of edge length L and volume $V = L^3$; L is much larger than the Bohr radius and the thermal wavelength of the protons. The particles and box are at equilibrium at temperature T.
Write expressions for the probabilities that the electron and the proton

- form an atom in its ground state
- form an atom in an excited but bound state,
- are ionized (not bound)

Express your results in terms of the size of the box (L), and the ratio $\epsilon = E_0/k_BT$ where E_0 is the hydrogen atom ground state ionization energy (13.6 eV). You may leave your results in the form of sums.
You may ignore interactions between the proton and electron for the unbound states, ignore fine and hyperfine effects, and consider the motion of all particles to be nonrelativistic.

(b) Now consider the situation of (a), with the additional information that $k_BT << E_0$. Evaluate the sums of (a) using a suitable expansion in $e^{-\epsilon}$, to obtain approximate formulae for the three cases of (a) (ground state, excited bound state, ionized).
Sketch the probabilities of finding the atom in its ground state, in any excited but bound state, and in an ionized state, all as a function of L.

(c) Use your results of (b) to explain what happens to a *gas* of hydrogen atoms (N atoms in a box of volume $V = L^3$) as you gradually expand its volume, keeping its temperature fixed as in (b) ($k_BT/E_0 << 1$).
You may ignore interactions between the atoms and ionized electrons and protons.

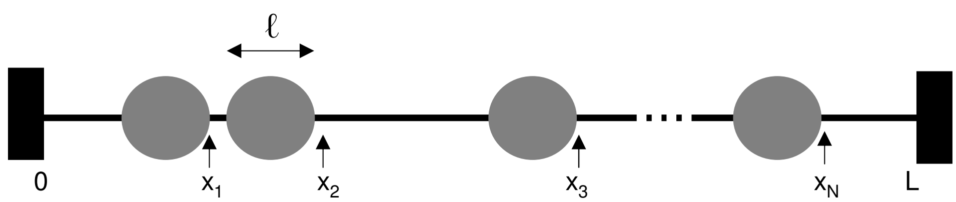
(d) Suppose the gas of (c) is cooled to very low temperature, at a low enough density that it remains a gas. What is the entropy of the gas in the zero-temperature limit? Explain your answer.

2. One-dimensional gas

(a) Consider a ideal gas of N identical point particles each of mass m confined to a one-dimensional box of length L at a temperature where you may ignore their quantum statistics (you may consider them to be spinless particles if you wish). In all the parts of this problem you should consider $N >> 1$ so as to use the thermodynamic limit to simplify your results.
Compute the canonical partition function for the gas, and use it to find the derivative of the Helmholtz free energy with L, $\partial F/\partial L$.
What is the physical meaning of $\partial F/\partial L$?

(b) Now consider the gas of (a), but now where the box length L can fluctuate, by adding a term fL to the energy (*i.e.*, consider the fluctuating-box-length ensemble). You then should integrate over fluctuations of L between 0 and ∞.
Find the thermal average of L as a function of f, N and k_BT.
Explain the relation between f and the derivative you calculated in (a).

(c) Now make the particles of (b) have diameters ℓ and suppose they interact via hard-particle interactions (meaning the interaction energy is zero except when for overlapping configurations, for which the interaction energy is infinite, see figure below).



The particles cannot pass one another, so we can label them 1 through N, where their right-edge positions satisfy $\ell \leq x_1 < x_2 < \cdots < x_{N-1} < x_N < L$. The excluded-volume interactions therefore enforce the constraints $x_{i+1} - x_i \geq \ell$ (for the left-most particle you may suppose that $x_0 = 0$ is the left edge of the box).

Find $\langle L \rangle$ as a function of f, N, ℓ and k_BT.

Hint: you will find it useful to change variables from x_i's to $y_i = x_i - x_{i-1}$.

3. Magnet

(a) Consider N spins (spin-1/2) in an external magnetic field pointing along the z direction. The spins are localized at the vertices of a crystal lattice, *i.e.*, they do not have translational degrees of freedom. To simplify your calculations, take $s_{z,i} = \pm 1$ and take the magnetic moment of the spins to be unity as well (this amounts to making the energy of spin i equal to $E_i = -Hs_{z,i}$, with $s_{z,i} = \pm 1$).
The magnetization is the sum of the z-components of the spins,

$$M = \sum_i s_{z,i}$$

Compute the thermal average of M as a function of magnetic field H.

(b) Now consider the states of fixed magnetization; note that M takes on $N+1$ possible values: $-N, -N+2, -N+4, \cdots, N-4, N-2, N$. Find the entropy as a function of magnetization, using the large-N limit to simplify your calculation.

(c) Compute the probability distribution of magnetization as a function of external magnetic field, and show that the most probable value of M coincides with the result of (a). Again use the large-N limit to simplify your results.

Hint: $\tanh^{-1} x = \frac{1}{2} \ln[(1+x)/(1-x)]$

(d) Now suppose there is a ferromagnetic interaction that acts between every pair of spins, giving a total interaction energy of

$$E_{\text{int}} = -\frac{J}{N} \sum_{1 \le i < j \le N} s_{z,i} s_{z,j}$$

where $J > 0$ is a constant with units of energy.
For zero external magnetic field, find the most probable value(s) of magnetization as a function of J and $k_B T$. Sketch your result for $k_B T >> J$ and for $k_B T << J$.
What new low-temperature property of the magnetization distribution is introduced by the interaction J?

Hint:

$$\sum_{1 \le i < j \le N} s_{z,i} s_{z,j} = \frac{1}{2} \left[\left(\sum_{i=1}^{N} s_{z,i} \right) \left(\sum_{j=1}^{N} s_{z,j} \right) - N \right] = \frac{M^2 - N}{2}$$

Constants

$k_B = 1.381 \times 10^{-23}$ J/K $\quad h = 6.626 \times 10^{-34}$ J·sec $\quad c = 2.998 \times 10^8$ m/sec
$m_p = 1.673 \times 10^{-27}$ kg $\quad m_n = 1.675 \times 10^{-27}$ kg $\quad m_e = 9.109 \times 10^{-31}$ kg
$e = 1.602 \times 10^{-19}$ C $\quad G = 6.67 \times 10^{-11}$ N m^2/kg^2

At room temperature $T = 300$ K and $k_BT = 4.1 \times 10^{-21}$ J

Integrals

$$\int_{-\infty}^{\infty} dx \ \exp\left[-\frac{x^2}{2\sigma^2}\right] = \sqrt{2\pi\sigma^2}$$

$$\frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dx \ x^n \ \exp\left[-\frac{x^2}{2\sigma^2}\right] = 1 \cdot 3 \cdot 5 \cdots (n-1)\sigma^n$$

for $n = 2, 4, 6 \cdots$

$$\int_0^{\infty} dx \ x^n \ e^{-x} = n!$$

Series

$$1 + 2 + 3 + \cdots + N = \frac{N(N+1)}{2}$$

$$1 + x + x^2 + \cdots x^{P-1} = \frac{1 - x^P}{1 - x} \qquad \text{(geometric series)}$$

$$\sum_{n=1}^{\infty} \frac{x^n}{n} = -\ln(1-x) \qquad \sum_{n=0}^{\infty} \frac{x^n}{n!} = e^x$$

$$\sum_{n=1}^{\infty} \frac{1}{n^s} = \zeta(s) \quad \text{Zeta function} \quad \zeta(2) = \sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6} \quad \zeta(4) = \sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{90}$$

$$\zeta(1) = \sum_{n=1}^{\infty} \frac{1}{n} = \infty \qquad \zeta(3) = \sum_{n=1}^{\infty} \frac{1}{n^3} = 1.202056 \cdots$$

Hyperbolic functions

$$\sinh x = \frac{e^x - e^{-x}}{2} \qquad \cosh x = \frac{e^x + e^{-x}}{2} \qquad \tanh x = \frac{\sinh x}{\cosh x}$$

$$\frac{d}{dx}\sinh x = \cosh x \qquad \frac{d}{dx}\cosh x = \sinh x \qquad \cosh^2 x - \sinh^2 x = 1$$

$$\tanh^{-1} x = \frac{1}{2}\ln\frac{1+x}{1-x}$$

Stirling's approximation for log of factorial

$$\ln n! = n\ln n - n + \mathcal{O}(1)$$

Combinations

$$C_n^N = \frac{N!}{n!(N-n)!}$$