

THE UNIVERSITY OF QUEENSLAND
SCHOOL OF MATHEMATICS AND PHYSICS
PHYS3020/3920/7021 – Statistical Mechanics

Module 3 Worksheet: Grand Canonical Ensembles

Module Problem Set Due Tuesday 4 Oct, 2 pm. Submission portal on Blackboard.

Questions 1, 2, 4, 6, 7 and 8 are for assessment.

1. **[FOR ASSESSMENT] Distribution function for double occupancy statistics**

Let us imagine a new mechanics in which the allowed occupancies of an orbital are 0, 1, and 2. The values of the energy associated with these occupancies are assumed to be 0, E , and $2E$, respectively. Derive an expression for the ensemble average occupancy $\langle N \rangle$, when the system composed of this orbital is in thermal and diffusive contact with a reservoir at temperature T and chemical potential μ .

2. **[FOR ASSESSMENT] Gibbs sum for a two level system**

(a) Consider a system that may be unoccupied with energy zero or occupied by one particle in either of two states, with one of energy zero and one of energy E . Show that the Gibbs sum for this system is

$$\mathcal{Z} = 1 + e^{\mu/k_B T} + e^{(\mu-E)/k_B T},$$

where τ stands for $\tau = k_B T$. Our assumption excludes the possibility of one particle in each state at the same time. Notice that we include in the sum a term for $N = 0$ as a particular state of a system of a variable number of particles.

(b) Show that the thermal average occupancy of the system is

$$\langle N \rangle = \frac{e^{\mu/k_B T} + e^{(\mu-E)/k_B T}}{\mathcal{Z}}.$$

(c) Show that the thermal average occupancy of the state at energy E is

$$\langle N(E) \rangle = \frac{e^{(\mu-E)/k_B T}}{\mathcal{Z}}.$$

(d) Find an expression for the thermal average energy of the system.

(e) Allow the possibility that the orbital at 0 and E may be occupied each by one particle at the same time; show that

$$\begin{aligned} \mathcal{Z} &= 1 + e^{\mu/k_B T} + e^{(\mu-E)/k_B T} + e^{(2\mu-E)/k_B T} \\ &= (1 + e^{\mu/k_B T})(1 + e^{(\mu-E)/k_B T}). \end{aligned}$$

Because \mathcal{Z} can be factored as shown, we have in effect two independent systems and the Gibbs sum for the combined system can be represented as a *product* of the individual Gibbs sums of these two independent systems.

3. **[PRACTICE PROBLEM] Alternative expressions for the chemical potential**

The chemical potential μ is defined as:

$$\mu \equiv \left(\frac{\partial F}{\partial N} \right)_{T,V}. \quad (1)$$

(a) Show that an alternative expression for μ is:

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V}. \quad (2)$$

To derive (2), consider the entropy as a function of the independent variables U , V , and N . The differential

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V,N} dU + \left(\frac{\partial S}{\partial V} \right)_{U,N} dV + \left(\frac{\partial S}{\partial N} \right)_{U,V} dN$$

gives the differential change of the entropy for *arbitrary, independent* differential changes dU , dV , and dN . Let $dV = 0$ for the process under consideration. Further, select the ratios of dS , dU , and dN in such a way that the overall temperature change dT will be zero. If we denote these interdependent values of dS , dU , and dN by $(\delta S)_T$, $(\delta U)_T$, and $(\delta N)_T$, then $dT = 0$ when

$$(\delta S)_T = \left(\frac{\partial S}{\partial U} \right)_N (\delta U)_T + \left(\frac{\partial S}{\partial N} \right)_U (\delta N)_T.$$

After division by $(\delta N)_T$, the ratio $(\delta S)_T/(\delta N)_T$ is $(dS/dN)_T$, and $(\delta U)_T/(\delta N)_T$ is $(dU/dN)_T$, all at constant volume. With the definition of $1/T = (\partial S/\partial U)_N$ we have then

$$\left(\frac{\partial S}{\partial N} \right)_{T,V} = \frac{1}{T} \left(\frac{\partial U}{\partial N} \right)_{T,V} + \left(\frac{\partial S}{\partial N} \right)_{U,V}. \quad (3)$$

By the original definition of the chemical potential, Eq. (1), which can be rewritten using $F = U - TS$, and on comparison with (3) we obtain the required expression Eq. (2).

(b) Show that the third alternative expression for μ is

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V}.$$

4. [FOR ASSESSMENT] Average number of particles and particle number fluctuations in a single-orbital system

(a) Show that the average occupancy of a single-particle orbital σ can be found as

$$\langle N_\sigma \rangle = \frac{\tau}{\mathcal{Z}_\sigma} \frac{\partial \mathcal{Z}_\sigma}{\partial \mu},$$

where

$$\mathcal{Z}_\sigma = \sum_{N_\sigma} \exp[N_\sigma(\mu - E_\sigma)/k_B T]$$

is the Gibbs sum for the single-particle system, N_σ are the respective occupation numbers, and τ denotes $\tau = k_B T$.

(b) Show next that

$$\langle N_\sigma^2 \rangle = \frac{\tau^2}{\mathcal{Z}_\sigma} \frac{\partial^2 \mathcal{Z}_\sigma}{\partial \mu^2}.$$

(c) Hence show that the fluctuation of number of particles or the mean-square deviation $\langle (\Delta N_\sigma)^2 \rangle$ of N_σ from $\langle N_\sigma \rangle$ (where $\Delta N_\sigma \equiv N_\sigma - \langle N_\sigma \rangle$) can be found from:

$$\langle (\Delta N_\sigma)^2 \rangle = \tau \frac{\partial \langle N_\sigma \rangle}{\partial \mu}. \quad (4)$$

Hint: Using the results from parts (a) and (b), show that what you get from Equation (4) is the same as what you get from $\langle (\Delta N_\sigma)^2 \rangle = \langle [N_\sigma - \langle N_\sigma \rangle]^2 \rangle$.

(e) Applying the result of (c) to the Fermi-Dirac, Bose-Einstein, and Boltzmann distribution functions for $\langle N_\sigma \rangle$, show that the particle number fluctuation in an orbital is given by

$$\begin{aligned}\langle (\Delta N_\sigma)^2 \rangle &= \langle N_\sigma \rangle (1 - \langle N_\sigma \rangle) \text{ - for an ideal Fermi gas,} \\ \langle (\Delta N_\sigma)^2 \rangle &= \langle N_\sigma \rangle (1 + \langle N_\sigma \rangle) \text{ - for an ideal Bose gas,} \\ \langle (\Delta N_\sigma)^2 \rangle &= \langle N_\sigma \rangle \text{ - for a classical ideal gas.}\end{aligned}$$

For an ideal Bose gas, if the average occupancy is large, $\langle N_\sigma \rangle \gg 1$, the fluctuations can be enormous, $\langle (\Delta N_\sigma)^2 \rangle \simeq \langle N_\sigma \rangle^2$. For an ideal Fermi gas, on the other hand, the fluctuations can be vanishingly small, for orbitals that have $\langle N_\sigma \rangle \simeq 1$.

5. [PRACTICE PROBLEM] Quantum densities for a non-relativistic ideal gas

Consider a quantum ideal gas of N particles of mass m and spin S confined in:

- (a) a one dimensional potential well of length L ;
- (b) two-dimensional square of area $A = L^2$;
- (c) three-dimensional cubic box of volume $V = L^3$.

Find the density of states $D(E) \equiv dN(E)/dE$ (or the density of single-particle orbitals) as a function of the single-particle energy E in all three cases.

6. [FOR ASSESSMENT] Classical ideal gas in two dimensions

- (a) Find the chemical potential μ of a classical ideal gas in two dimensions, with an average of $N = \langle N \rangle$ atoms confined to a square of area $A = L^2$. (Neglect the spin and assume that the particles are non-relativistic.) The temperature is T .
- (b) Find the total average internal energy U of the gas and the average energy per particle U/N .
- (c) Find the entropy of the gas S .

7. [FOR ASSESSMENT] Quantum density of an ideal gas in the extreme relativistic regime

Consider an ideal gas of spin S particles in the extreme relativistic regime with energies $E \gg mc^2$ (where m is the rest mass of the particle), so that the single-particle energy is given by $E \simeq pc$, where p is the particle momentum. For a particle confined in a cube of volume $V = L^3$, the momentum eigenvalues are exactly the same as in the non-relativistic case $p_{\mathbf{n}} = \pi \hbar n / L$, so that the single-particle states have energies $E_{\mathbf{n}} = \pi \hbar c n / L$, where $\mathbf{n} \equiv (n_x, n_y, n_z)$, n is given by $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$, and the three quantum numbers n_x , n_y , and n_z can take positive integers values ($n_{x,y,z} = 1, 2, 3, \dots$).

Find the density of states $D(E)$.

8. [FOR ASSESSMENT] Quantum versus classical regime for an extreme relativistic gas

Consider an ideal gas of N particles in a volume $V = L^3$ at temperature τ , in the extreme relativistic regime as in Problem 7.

- (a) Write down an explicit integral (which is for the total number of particles), evaluation of which with distribution functions would give the corresponding value of the chemical potential $\mu(T, N)$ of the quantum gas.
- (b) Evaluate the same integral with the classical Boltzmann distribution function $f_C(E) = \exp[-(E - \mu)/k_B T]$ (use $\int_0^\infty dx x^2 \exp(-x) = 2$).
- (c) The classical Boltzmann distribution function closely approximates the quantum Fermi-Dirac and Bose-Einstein distributions in the limit of $\exp[-\mu/k_B T] \gg 1$, i.e. in the classical regime of the gas where the average occupancies of the quantum states are much smaller than one [$f_{F(B)}(E) \ll 1$]. Show that the result found in (b) can be used to rewrite this condition in the form of:

$$n \ll n_Q,$$

where $n = N/V$ is the concentration (or the particle number density), and the (relativistic) quantum concentration n_Q is defined by:

$$n_Q = \frac{1}{\pi^2} \left(\frac{k_B T}{\hbar c} \right)^3 .$$

Accordingly, the quantum regime of a relativistic gas corresponds to densities $n \gtrsim n_Q$, or temperatures $T \lesssim T_Q \equiv \hbar c (\pi^2 n)^{1/3} / k_B$.