DEPARTMENT OF PHYSICS
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PH5080 Statistical Physics **Problem Set 8** **20.3.2022**

1. Write down the first law of thermodynamics for the grand potential Φ. What is the extensivity property of the grand potential? Prove the Euler relation: $\Phi = U - TS - \mu N$. Also show that $\Phi = -PV$.

2. The grand partition function for an ideal gas takes the form

$$Q(T, V, \mu) = \sum_{n=0}^{\infty} \frac{\mathfrak{z}^n}{n!} \left(e^{\beta\mu}\right)^n = \exp\left(\mathfrak{z}\ e^{\beta\mu}\right) \ .$$

   with $\mathfrak{z} = V(2\pi m k_B T/h^2)^{3/2}$ is the canonical partition function for a single particle.

   (a) Compute the average number of particles as well as the variance in the number of particles in the grand canonical ensemble.

   (b) Apply this general formula for the ideal gas.

   (c) Obtain the expression for the chemical potential of an ideal gas with N particles in the canonical ensemble. How does it compare with the above formula for the average number of particles in the grand canonical ensemble?

3. Show that the entropy of a system in the grand canonical ensemble can be written as

$$S(T, V, \mu) = k_B \sum_N \sum_E -p(N, E)\ \log p(N, E) \ ,$$

   where the first sum runs over the number of particles and the second sum runs over all N-particle states with energy E and $p(N, E)$ is the probability of finding the system with N particles and total energy E.

$$p(N, E) = \frac{1}{Q}\ e^{-\beta E + \beta\mu N}$$

   Can you write a similar formula for the entropy in the canonical ensemble?

4. A surface with M adsorption centres can have N ($\leq M$) gas molecules adsorbed on it. Let μ denote chemical potential of the gas molecule and let $a(T)$ denote the canonical partition function of a single molecule that is adsorbed on the surface. Compute the grand canonical partition for the system. Equating N to the average number of adsorbed molecules on the surface, show that one has

$$z = e^{\beta\mu} = \frac{N}{(M - N)\, a(T)} \quad \text{or} \quad \frac{M}{N} = \frac{a(T)\, z}{1 + a(T)\, z} \ .$$

   Can you derive the same expression in the canonical ensemble?