Workshop

Physical Chemistry II

Exercises and Homework Set 10

Conceptional Review

- **i.** Definition of mean values and variances in terms of partition functions total differentials and partial derivatives with and without constraints.
- **ii.** Thermal variables from PF, role of entropy and heat energy, heat capacity,
- **iii.** Grand canonical partition function,
- **iv.** Rotational and vibrational dof,
- **v.** Boltzmann high-T, low state density limit,
- **vi.** Influence of electronic and nuclear spin. L multiplicities.

1. Translational Partition Function

Consider a canonical ensemble of systems, each made of $\boldsymbol{N}$ free, independent particles of mass $\boldsymbol{m}$ in a container of volume $\boldsymbol{V}$. The container is in thermal contact with a heat bath at temperature $\boldsymbol{T}$.

a) Write down the partition function $\boldsymbol{Q_N}$.

b) What mathematical operation on $\boldsymbol{Q_N}$ will generate an expression for the mean expectation value for the mechanical pressure, $\boldsymbol{p}$?

c) Using the operation identified in ***b)***, deduce the mean pressure and its dependence on parameters of system and environment.

d) How does the result in ***c)*** agree with the phenomenological Equation of State of an ideal gas?

2. Free Energy

Consider an ideal gas of mass-$\boldsymbol{m}$ particles in a container of Volume $\boldsymbol{V}$, immersed in a heat bath at temperature $\boldsymbol{T}$. It is subjected to a constant external potential energy $\boldsymbol{U}$.

a) Write down an expression for the appropriate partition function and an operator projecting the entropy from this PF.
b) Using the translational partition function, derive an expression for the relation between Helmholtz free energy ***A*** and mean pressure ***p***.
c) How are the pressure and other thermal variables affected by the external field ***U***?

3. <u>Grand Canonical Ensemble</u> (AC)

A multi-particle system is in thermal equilibrium with a heat bath at temperature ***T*** and in contact with an external particle reservoir of the same kind of particle (mass ***m***). The cost or gain in system energy upon addition of one extra particle is given by the parameter μ.

a) Write down the partition function for this ensemble.
b) Write down the Gibbs free energy and the chemical potential.
c) Write down a compact form of the PF in terms of the free energy.
d) Calculate the mean number $\langle N \rangle$ of particles in such a system.
e) Calculate the variance $\sigma_N^2 = \left(\langle N^2 \rangle - \langle N \rangle^2\right)$ in particle number.
f) Write down an expression for the normalized probability $P(N,T)$.