Workshop -3d

Physical Chemistry II

Exercises and Homework Set 9

Conceptional Review

i. Discuss total differentials and partial derivatives with and without constraints.
ii. Equivalence between probability distributions and partition integrals.
iii. Structure of partition functions spectrum and multiplicity/degeneracy of states.
iv. Product structure of PF for independent degrees of freedom.

1. Internal and Free Energies

According to the first law of thermodynamics, the internal energy $\boldsymbol{U} = \boldsymbol{U}(\mathbf{N},\mathbf{x})$ of an ensemble of $\boldsymbol{N}$ particles with internal structure degree of freedom $\boldsymbol{x}$ is changed by the transfer of heat ($\boldsymbol{dQ}$) between system and environment, by the addition of particles, $\boldsymbol{dG}=\mu\cdot\boldsymbol{dN}$, or by other types of work, $\boldsymbol{dW}=\boldsymbol{F}\cdot\boldsymbol{dx}$, done on or by the system. The internal degree of freedom $\boldsymbol{x}$ is receptive to the force $\boldsymbol{F}$. Hence, $\boldsymbol{dU} = \boldsymbol{dQ} + \boldsymbol{dW} + \mu\cdot\boldsymbol{dN}$.

a) Write down an expression for the system heat capacity, $\boldsymbol{C} = (\boldsymbol{dU/dT})$
b) Derive an expression for the total differential $\boldsymbol{dS}$ of the entropy at constant number $\boldsymbol{N}$ of particles.
c) Derive expressions for the free energy change $\boldsymbol{dG}$ with particle number, temperature, and strength of force.

2. Expectation Values and Fluctuations of Thermal Variables

A partition function $P(T) \triangleq P(\beta)$ is given for a canonical (isothermal) thermodynamic ensemble of particles, at equilibrium and at constant temperature.

a) Follow the procedures discussed in class and derive a method to project the second energy moment $\langle E^2 \rangle$ from the partition function.

b) Develop an expression for the dependence of the fluctuations in average particle energies, $\sigma_E^2 = \left\langle E^2 - \langle E \rangle^2 \right\rangle$, and the heat capacity C_V of the ensemble.

c) Write down an expression for the magnitude of energy fluctuations for an ideal gas.

3. <u>Thermodynamic Variables from Partition Functions</u>

For the following, assume a canonical (isothermal) thermodynamic ensemble of *N* particles, at equilibrium and at constant temperature. Each particle has a discrete *s.p.* spectrum of internal energies, $\{\varepsilon_i\}$ with associated energy degeneracies, $\{\varpi_i\}$.

a) Write down the partition sum ***Z*** for the ensemble.

b) Design a differential operator $\hat{p}_i$ projecting the probability p_i to find a particle in energy state ε_i. Demonstrate its action on ***Z***.

c) Write down the (microscopic) entropy ***S*** for the ensemble.

d) Express the Helmholtz free energy in compact form.