Due: WS+1d

Physical Chemistry II

Exercises 8

1. Conceptual Questions

A) Information theory provides the foundation of the partition function describing the statistical behavior of physical systems, which depends on the energies of the possible configurations. What is the reason for this prominent role of energy? Can you think of other types of systems with complex configuration that may be accessible to similar lines of thought, i.e., which could be studied with similar methods?

B) Consider the partitions of the total probability among possible two-particle configurations, when three single-particle energy levels are available, e_1, e_2, and e_3. What are the energies of the associated microstates,

a) for 2 classical particles,

b) for 2 fermions and

c) for 2 bosons.

2. Interchangeable Math Procedures

The derivation of multi-particle partition functions demonstrated in class relies on the interchangeability (associativity) of summation and multiplication of sums of exponential terms. Illustrate the validity of the procedure for the following finite sums of products of power terms:

a) Show explicitly that $S = \sum_{i=1}^{2} \sum_{k=0}^{1} x^i \cdot y^k = \sum_{i=1}^{2} x^i \cdot \sum_{k=0}^{1} y^k$

b) In the same sense, evaluate the expression $S = \sum_{i=1}^{3} \sum_{k=0}^{2} x^{i+k}$ in two different ways.

c) How many terms do you expect in the explicit evaluation of $S = \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=0}^{2} x^i \cdot y^j \cdot z^k$ and why?

3. Translational Partition Function

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

a) Write down the partition function Q_N.

b) What mathematical operation on Q_N will generate an expression for the mean expectation value for the mechanical pressure, ***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?

4. Free Energy

Consider an ideal gas in a heat bath at temperature ***T*** and exposed to a constant external field ***U***.

a) Using the translational partition function given in class, derive an expression for the relation between Helmholtz free energy ***A*** and mean pressure ***p***.

b) How is the pressure affected by the external field ***U***?

5. Grand Canonical Ensemble (AC)

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

a) Write down the partition function for this ensemble.

b) Calculate the mean number $\langle N \rangle$ of particles in such a system.

c) Calculate the variance $\sigma_N^2 = \left(\langle N^2 \rangle - \langle N \rangle^2 \right)$ in particle number.

d) Write down an expression for the normalized probability $P(N)$.