Due: Workshop+1d

Physical Chemistry II

Exercises Set 6

1. Conceptual Questions

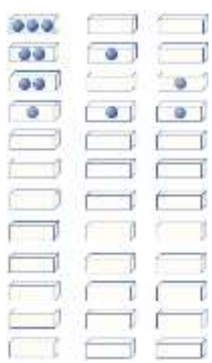
a) Name the main thermodynamic system classes and the prime Laws of Thermodynamics by which they are governed.
b) How does the time evolution of a system's microstates and a given macrostate differ?
c) What qualifies as a thermodynamic ensemble?
d) What does an application of the information-theoretical concept of statistical entropy on a thermodynamic system reveal about the system's actual state?
e) How is the total differential d*f* of a function *f*(x,y) related to its Taylor expansion? How is it influenced by a constraint *g*(x,y)=0

2. Poisson Probability Distribution

On average, 270 people in the U.S. are struck per year, about 10 percent of that number die from the event.

a) Estimate the odds to be struck by lightning in the U.S. during one's lifetime.
b) Does the accident rate with lightning strikes likely follow a Poisson law?
c) Is the recent observation of 293 lightning accidents in the U.S. consistent with expectations or an indication of a new, extreme weather feature?

3. Distributions and Partitions

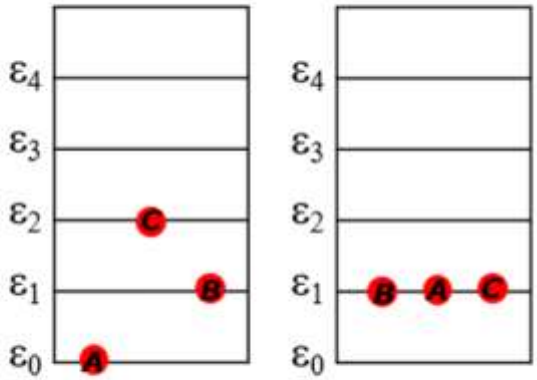


a) A triplet (n_p = 3) of identical particles ("Bosons") is to be distributed among m_b = 3 different containers. Each container can hold any number of such particles. The figure shows 4 of the possible partitions of the triplet. Complete the set.

b) Express the number of all partitions of the particle triplet in terms of n_p and m_b. Consider factorials of combinations of these numbers.

c) Perform a similar calculation for Fermion triplets, where one container can hold only up to two particles.

4. Statistics of Microcanonical Microstates



Consider a large (microcanonical) ensemble of instances for a closed system consisting of $\boldsymbol{N = 3}$ identical particles, ***A***, ***B***, ***C***. The particle energy level scheme is equidistant, with a spacing of ***e***. The ground state is at $\varepsilon_0 = 0$. The total energy

$$E = \sum_{i=0}^{4} \varepsilon_i \cdot n_i = \sum_{i=0}^{4} i \cdot \varepsilon \cdot n_i$$

of the system is fixed at $E = 3e$, where $\boldsymbol{n_i}$ is the number of particles in energy level ***i***. The figure illustrates 2 arrangements of the particle triplet over the energy levels compatible with $E = 3e$. It shows just two of the various microstates available for the ensemble to populate.

a) Write down the relevant partitions $\Pi_k = \{n_0, n_1, n_2, n_3\}_k$ of N and the numbers Ω_k of associated microstates.

b) Calculate the statistical entropy $S = -\sum_{i=0}^{4} p_i Ln(p_i)$ for each partition, where the occupation is given by $p_i = n_i/N$.

c) What is the probability of observing the most likely configuration for this ensemble?

d) Make a sketch for the set of most likely configurations identified in c).

(**Suggestion:** make a table for the relevant partitions Π_k)

	n_0	n_1	n_2	n_3	Ω_k	S
Π_1						

5. System Properties from a Partition Function (AC)

Consider the partition function Q(N,V,T) for a canonical ensemble of statistical systems embedded in a heat bath at constant temperature T. Derive expressions for the first and second moments, $\langle E \rangle$ and σ_E^2, of the system energy distribution $P(E)$.