Workshop -3d

Physical Chemistry II

Exercises and Homework Set 4

Conceptional and Math Review

- **i.** Discuss combinatorics, statistics, and probability. See: Information & Probability.
- **ii.** Sets of random numbers in Excel. Sort random events into discrete bins. CLT
- **iii.** What is the main difference between a cellular automaton (CA#20) and a random walk, each with 2 alternatives/rules?
- **iv.** Explain the meaning of "occupation probability" and Ergodic Theorem for a one-dimensional string of cells (=particle states)? Example of 100 particles and 10^4 cells?
- **v.** Discuss probability binomial and Poisson probability distributions: Normalization and moments, mean expectations and variance.
- **vi.** Functions of random variables.
- **vii.** Series expansion of the exponential $\exp(x) = \sum_{n=0}^{\infty} \frac{1}{n!} x^n$

1. Random Numbers and Central Limit Theorem

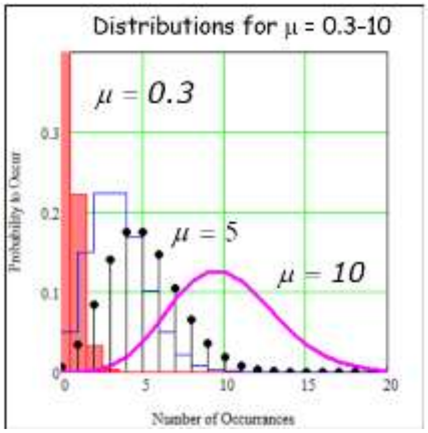
Test experimentally the validity of the Central Limit Theorem. This theorem states that the sums $S(N) = \sum_{i=1}^{N} x_i$ of large numbers of uniformly distributed random numbers $\{x_i,\ i = 1-N\}$ approach a Gaussian "Normal" distribution for large N.

a) Use MS-Excel to generate several (*5*) instances of the mean expectation value $E_N(x) = \frac{1}{N}\sum_{i=1}^{N} x_i$ of random-number sets $\{0 \le x_i \le 1\}$ for $N=10$.

b) Generate and record additional data sets $\{E_N^{(n)}(x),\ n = 1,\dots,5\}$ for N= *50, 100,200*.

c) Compare the average values $\langle E_N^{(n)}(x)\rangle_n$ and the spreads in the sets $\{E_N^{(n)}(x)\}$ for N = *10, 50, 100,200*. Consider the ratio of variance to mean value.

2. Poisson Distribution



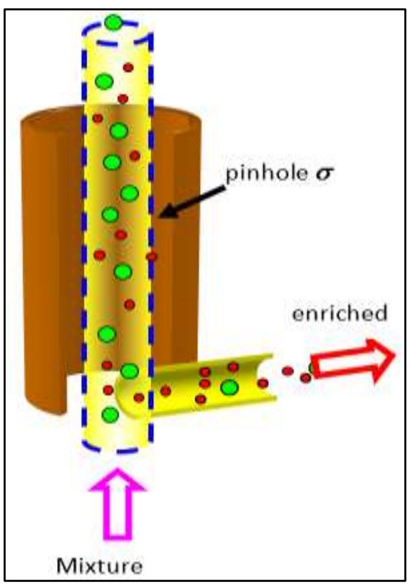
The Poisson distribution for an integer variable *m* (=0,1,2,..) is defined as

$P(m) = \frac{1}{m!} \cdot a^m \cdot e^{-a}$ where ***a*** is a characteristic of the distribution.

a) Show that the Poisson distribution is normalized.

b) Use the series expansion of the exponential function to show that ***a*** is equal to the average expectation value of *m*, i.e., $\langle m \rangle = a$.

3. Isotope Separation through Effusion

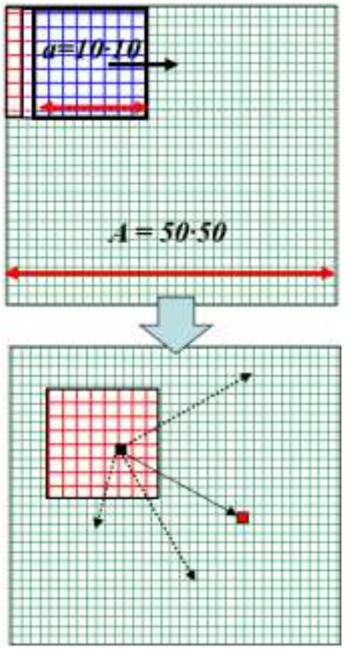


Consider a column of volume *V* and temperature *T* containing an equilibrated mixture of two gases of N_m and N_M particles with masses *m* and *M*, respectively. A simple mode of separating the two kinds of gas particles uses fractionation with a column of the basic design shown in the sketch. The mixture is let into the inner chamber and diffuses through pinholes in the chamber walls. Since the thermal velocities are different for *m* and *M*, one type migrates (effuses) much more readily than the other, one of the substances will become enriched in the concentric outer chamber surrounding the column.

a)Calculate the relative separation efficiency $\varepsilon_1 = \langle \dot{N}_M \rangle / \langle \dot{N}_m \rangle$ for a column with 10^3 pinholes of area σ, where $\langle \dot{N}_i \rangle$ is the rate of particles of type *i* leaving the column.

b) Can one increase the separation efficiency by increasing or decreasing the temperature *T* of the mixture?

3. Dissolution of a Particle Cluster



Consider a 2D space spanned by a grid of A=50·50 single-particle (s.p.) states (=pixels). Initially, the grid contains the configuration of one, closely-packed, multi-particle cluster of a=10·10 individual, non-interacting particles. In time, all particles are capable to reach any of the accessible states on the grid, including the original states assembled in the cluster.

a) Calculate the number $\Omega_C(100)$ of accessible multi-particle cluster states on the grid.

b) Calculate the number $\Omega_C(99)$ of "cluster-minus ***1*** particle" states available on the grid, where 1 particle has left the cluster and populates any of the s.p. states outside the cluster remnant.

c) Calculate the number $\Omega_\mu(1)$ of microstates of the final (asymtotic) equilibrium configurations, where the cluster has completely dissolved into single particles populating random s.p. states on the grid.

d) Calculate the entropies $S/k = Ln\Omega$ of the initial and the final configurations associated with the number Ω of, at least partially, populated s.p. states.