Workshop -3d

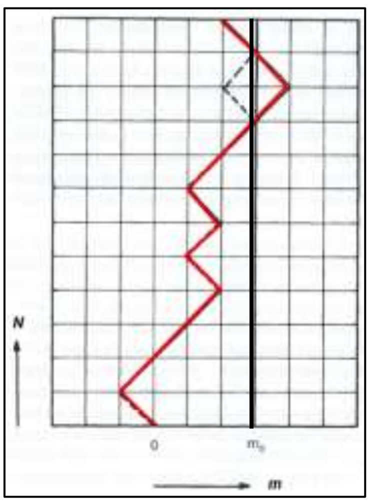
Physical Chemistry II

Exercises and Homework Set 6

Conceptional Review

- **i.** Discuss the meaning of thermodynamic ensembles, fundamental laws of thermodynamics, equivalence of phenomenological and microscopic expression for entropy.
- **ii.** Relation between randomness and entropy, randomness and spontaneity of transitions. Reversible and irreversible processes.
- **iii.** Isothermal and adiabatic equations of state (EoS) of dilute (ideal) gases. Internal energy of gases. Simple isothermal and adiabatic p-V transformations. Heat capacities.
- **iv.** Circular Carnot processes forward and reverse.
- **v.** Relation between entropy (function) and Free Energy.
- **vi.** Effects of particle interactions on EoS, van Der Waals model. ifference between ideal

1. Wall Effects in Transport



A non-biased random, diffusion-like particle transport process occurs in a sequence of ***N*** elementary steps in time intervals of $\Delta t = \tau$ and displacements of length $|\Delta \boldsymbol{m}| = \ell$ in lateral direction. The process occurs in a confinement, where particles may collide with a containment wall at $\Delta m = m_0$ which could either ideally reflect or totally absorb such particles. The graph shows an undisturbed trajectory (solid red) and one (dashed) that illustrates reflection at the wall.

a) Calculate mean and variance of the distribution ***P*(*m*)** of displacements without any wall.

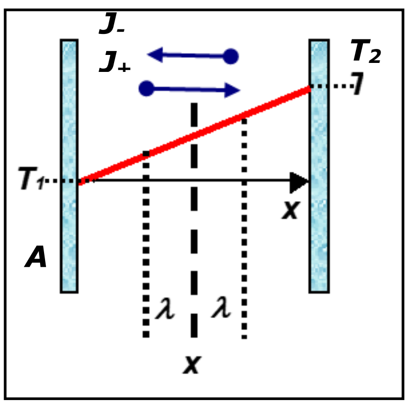
b) Express the variables obtained in a) in terms of drift and diffusion coefficients, ***v*** and ***D***, respectively.

c) Write down an expression for the time dependent probability distribution ***P*(*m*,*t*)** with the time expressed in terms of the interval length $\Delta t = \tau$.

d) Consider the additive probabilistic effect of an ideally reflective, mirror-like confinement wall on the *m*-distribution representing the sum probability $P_{refl}(m,t)$.

e) Consider the additive probabilistic effect of an ideally absorbent confinement wall on the *m*-distribution representing the sum probability $P_{abs}(m,t)$.

2. <u>Heat Convection</u>



Modern, energy-efficient windows have double-pane glass. These double-pane windows often contain an inert gas between the glass layers, which enhances thermal insulation of an inside living area provided by the windows. The sketch depicts 2 panes at different (Winter) temperatures ($T_2 - T_1 = 20^0 C$). The insulating gas has an approximately linear temperature gradient dT/dx. Fluxes J_+ and J_- of gas particles with mean speed $\langle u \rangle$ and mean free path λ moving in positive or negative x-direction, respectively, provide heat exchange between the panes.

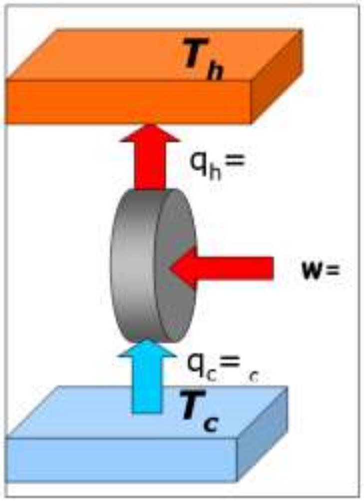
a) Calculate the mean speed of gas particles between the panes with an outside temperature around the freezing point of $0^0 C$.

b) Write down and expression for the thermal fluxes $J_+ \approx J_-$

c) Assuming the given linear temperature gradient of the gas between the panes write down an expression for the net transfer flux of heat, $J_Q(x) = J_+ \langle E_+ \rangle - J_- \langle E_- \rangle$ to first order, where the quantities $\langle E_\pm \rangle$ are the mean kinetic energies picked up in collisions left and right of position ***x***.

d) Given a choice between insulating gases like He, Ne, N_2, Ar, Kr, which would provide the best insulation, i.e., lowest heat exchange and why?

3. <u>Inverse Carnot Engine</u>



An ideal thermodynamic engine can be driven in reverse, i.e., cooling a cold (***T=T***$T=T_c$) body and heating a warm ($T=T_h>T_c$) reservoir further. As shown in the sketch, this requires externally provided energy (work ***w***). The illustrated branched energy flow can be modelled in terms of a stream of entropy ***S*** carrying energy from the inputs to the destination reservoir.

a) Express the magnitudes of heat and work converted in the pictured engine in terms of entropy and temperatures. Note the sign of each energy transfer.

b) What kind of work is required for the process, e.g., isothermal or adiabatic, compression or expansion work?

c) What design efficiency can be achieved?