ChE 548: Advanced Transport Phenomena II
Spring, 2008
Midterm

Problem 1. Consider diffusion in a binary, isothermal system. You have been provided the diffusivity of component A in B, D°_{AB}, with the understanding that (i) diffusion is measured relative to the center of mass velocity, **v**, (ii) the units of the diffusive flux of A, , are mass of A per area per time, $\mathbf{j}_A$, and (iii) the driving force for diffusion is the molar concentrations, C_A and C_B, with a constitutive equation given by,

$$\mathbf{j}_A = -m_A D^{\circ}_{AB} \nabla C_A \qquad \mathbf{j}_B = -m_B D^{\circ}_{BA} \nabla C_B \tag{1}$$

where m_A and m_B are the respective molecular weights of components A and B. Answer the following questions.

(a In this case, do the diffusive fluxes sum to zero? Provide the proof.
(b) Derive the relationship between D°_{BA} and D°_{AB}.
(c) Consider the traditional case in which (i) diffusion is measured relative to the center of mass velocity, **v**, (ii) the units of the diffusive flux of A, , are mass of A per area per time, $\mathbf{j}_A$, and (iii) the driving force for diffusion is the mass fractions, w_A and w_B, with a constitutive equation given by,

$$\mathbf{j}_A = -\rho D \nabla w_A \qquad \mathbf{j}_B = -\rho D \nabla w_B \tag{2}$$

Find the relationship between D and D°_{AB}.

Problem 2. In a molecular dynamics simulation, the long-time behavior of the mean square displacement as a function of time gives rise to the self-diffusivity via the Einstein relation,

$$D_{self} = \frac{1}{2d} l\, \underset{\tau \to \infty}{im} \frac{\left\langle \left[r(t+\tau) - r(t) \right]^2 \right\rangle}{\tau} \tag{II.1}$$

where d is the dimensionality of the system, r is a particle position, t is time, τ is elapsed time, and the angled brackets indicate an average over both all particle trajectories as well as all times, t.
(a) Sketch a qualitative plot of MSD vs elapsed time. Indicate how one obtains the self-diffusivity from this plot.
(b) Sketch a qualitative plot of ln(MSD) vs ln(elapsed time). Indicate how one uses such a plot to determine if the simulation has indeed reached the infinite-time limit required by the Einstein relation.