ChE 548: Advanced Transport Phenomena II
Spring, 2009
Midterm

Problem 1. For a single component gas, one can use kinetic theory to estimate the self diffusivity,

$$D_{self,A} = \frac{1}{3}\bar{u}\lambda \tag{I.1}$$

where the mean molecular speed, $\bar{u}$, is

$$\bar{u} = \sqrt{\frac{8k_B T}{\pi m_A}} \tag{I.2}$$

and where the mean free path, λ, is

$$\lambda = \frac{1}{\sqrt{2}\,\pi d_A^2 n} \tag{I.3}$$

where k_B is Boltzmann's constant, T is temperature, m_A is the mass of component A, d_A is the collision diameter of component A and n is the number density of component A.

These numbers may be useful:

k_B = 1.38066x10^{-23} J/K/molecule
N_{AV} = 6.02205x10^{23} molecule/mole
R = 8.31441 J/K/mole
1 amu = 1.66056x10^{-27} kg

name	molecular weight	collision diameter (Å)
propane	44.10	4.934
n-butane	58.12	5.604

(a) Explain, from a molecular level point of view, the qualitative temperature and density dependence of the self diffusivity.
(b) What is the self-diffusivity of propane at 300 K and 1 atm?
(c) At the same temperature and density, is the diffusivity of n-butane higher or lower than that of propane?
(d) For a 50/50 molar mixture of propane and n-butane, use kinetic theory to estimate the Fickian diffusivity at 300 K and 1 atm?

Problem 2. When one obtains transport properties such as the diffusivity from molecular dynamics simulations, one must run the equilibration portion of the simulation sufficiently long that the system is equilibrated at the set point temperature and pressure. Also, one must run the data production portion of the simulation sufficiently long to be in the long-time limit required by the Einstein relation for diffusivity;

$$D_{self} = \frac{1}{2d} \lim_{\tau \to \infty} \frac{\left\langle \left[r(t+\tau) - r(t) \right]^2 \right\rangle}{\tau} \qquad \text{(II.1)}$$

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) How does one determine if the equilibration is sufficiently long to ensure that the system is equilibrated? Provide sketches of qualitative plots if possible. Label axes clearly.
(b) How does one determine if the simulation is sufficiently long to ensure that the transport properties are valid? Again, provide sketches of qualitative plots to demonstrate your point. Label axes clearly.

Problem 3. Consider diffusion in a binary, isothermal system. One can write Fick's law as

$$\mathbf{j}_A = -\rho D \nabla w_A \qquad \mathbf{j}_B = -\rho D \nabla w_B \qquad \text{(III.1)}$$

What three assumptions are implicit in this constitutive equation?