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:

$k_B = 1.38066\text{x}10^{-23}$ J/K/molecule
$N_{AV} = 6.02205\text{x}10^{23}$ molecule/mole
$R = 8.31441$ J/K/mole
1 amu = $1.66056\text{x}10^{-27}$ 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 1 Solution:

(a) Explain, from a molecular level point of view, the qualitative temperature and density dependence of the self diffusivity.

The mean velocity is proportional to the square root of the temperature. This comes from the Maxwell-Boltzmann distribution of velocities. As the velocity (temperature) increases the diffusivity increases.

The mean free path is inversely proportional to the density. As the mean free path decreases, the diffusivity decreases.

(b) What is the self-diffusivity of propane at 300 K and 1 atm?

N_avogadro	6.02E+23	molecules/mole		
kb	1.38E-23	J/K/molec	8.31E+00	J/mole/K
T	300	K	300	K
pressure	1	atm	101325	Pa
pi	3.141592654		3.141593	
m	7.32307E-26	kg/molec	0.0441	kg/mole
MW	44.1		44.1	grams/mole
arg	18003.83247		18003.64	
sqrt	134.1783607	m/s	134.1776	
dA	4.93E+00	Angstroms	4.93E-10	m
1/n	4.09E+04	Angstrom/molecule	2.46E-02	m^3/mole
1/n	4.08782E-26	m^3/molecule		
D	4.78E-06	m2/sec		
u_bar	379.5137148	m/s		
lambda	3.78E-08	m/s		

(c) At the same temperature and density, is the diffusivity of n-butane higher or lower than that of propane?

As the molecular weight increases, diffusivity decreases. As collision diameter increases, diffusivity decreases. For both these reasons, n-butane will have a lower diffusivity than propane. (Calculation for n-butane below.)

N_avogadro	6.02E+23	molecules/mole		
kb	1.38E-23	J/K/molec	8.31E+00	J/mole/K
T	300	K	300	K
pressure	1	atm	101325	Pa
pi	3.141592654		3.141593	
m	9.65117E-26	kg/molec	0.05812	kg/mole
MW	58.12		58.12	grams/mole
arg	13660.85705		13660.71	
sqrt	116.8796691	m/s	116.879	
dA	5.60E+00	Angstroms	5.60E-10	m
1/n	4.09E+04	Angstrom/molecule	2.46E-02	m^3/mole
1/n	4.08782E-26	m^3/molecule		
D	3.23E-06	m2/sec		
u_bar	330.5856265	m/s		
lambda	2.93E-08	m/s		

(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?

Several ways to work this problem. For ideal gas, use kinetic theory for self-diffusivity and Darken equation.

$$D_{FICK} = \left(\frac{\partial \ln a_A}{\partial \ln x_A}\right)_{T,p} \left(x_A D_{self,B} + x_B D_{self,A}\right) = 4.0\,\mathrm{x}10^{-6}\ \mathrm{m^2/s}$$

The thermodynamic factor is unity for an ideal gas.

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;

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

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) 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 2 Solution.

(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.

Examine a property such as potential energy or pressure as a function of simulation time. Make sure that the properties are fluctuating about an average value.

(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.

One must be in the long-time limit required by the Einstein Relation. Make a log-log plot of the mean square displacement vs. observation time. The slope of that log-log plot must be close to unity.

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

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

What three assumptions are implicit in this constitutive equation?

Problem 3 Solution.

1. The diffusive flux is a mass flux.
2. The driving force for diffusion is the gradient in the mass fraction.
3. Diffusion is measured relative to the center-of-mass velocity.