# Advanced Transport Phenomena II
ChE 548
Department of Chemical Engineering
University of Tennessee, Knoxville
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## Midterm Examination Solutions
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**Problem 1.**

Consider an isothermal binary mixture of A and B with molecular weights, $M_A$ and $M_B$, at a thermodynamic state specified by density, $\rho$, temperature, $T$, and composition, $w_A$. We experimentally measure the average velocity of component A and component B along the axis of a cylindrical tube relative to laboratory frame of reference, $v_A$ and $v_B$, which are constant over the length of the cylinder. Answer the following questions. Assume we choose to measure diffusion relative to the center of mass velocity. Also assume that we will use a form of Fick's law that gives mass flux as a function of gradient in mass fraction.

a. What is the center of mass velocity, $v$, in this system?

$$v = w_A v_A + w_B v_B$$

b. What is the total flux of component A in this system?

$$n_A = \rho w_A v_A$$

c. What is the convective flux of component A in this system?

$$\rho w_A v = \rho w_A (w_A v_A + w_B v_B)$$

d. What is the diffusive flux of component A in this system, given in terms of the variables listed in the problem statement? Give it in the most simplified form.

$$j_A = n_A - \rho w_A v$$

$$j_A = \rho w_A v_A - \rho w_A (w_A v_A + w_B v_B)$$

$$j_A = \rho w_A [v_A - w_A v_A - w_B v_B]$$

$$j_A = \rho w_A [w_B v_A - w_B v_B]$$

$$j_A = \rho w_A w_B (v_A - v_B)$$

e. What form of Fick's law is appropriate for the assumptions listed in the problem statement?

When we assume that (i) diffusion is measured relative to the center-of-mass velocity and that Fick's law relates (ii) a mass flux to (iii) a gradient in the mass fraction, we know that Fick's law must have a form.

$$j_A = -\rho D \nabla w_A$$

$$j_B = -\rho D \nabla w_B$$

Moreover, under these assumptions, we know that the $D$ that appears in the diffusive flux of $A$ is the same $D$ as appears in the diffusive flux of $B$.

f. Assuming we know the diffusivity, $D$, of this system, what is the gradient of the mass fraction of component $A$ in this system?

$$j_A = -\rho D \nabla w_A = \rho w_A w_B (v_A - v_B)$$

$$\nabla w_A = \frac{w_A w_B (v_B - v_A)}{D}$$

g. Using symmetry relations, answer parts (d) and (f) for component $B$.

Interchanging $A$ and $B$ indices,

$$j_B = \rho w_B w_A (v_B - v_A)$$

$$\nabla w_B = \frac{w_B w_A (v_A - v_B)}{D}$$

h. Do your results satisfy the constraint that the sum of the diffusive fluxes must be zero? Why or why not?

$$j_A = \rho w_A w_B (v_A - v_B) \qquad j_B = \rho w_B w_A (v_B - v_A)$$

$$j_A + j_B = 0$$

Yes, the fluxes sum to zero as they must since our frame of reference is the center-of-mass velocity.

i. Do your results satisfy the constraint that the gradient of the mass fraction of $A$ must be equal in magnitude and opposite in sign to the gradient of the mass fraction of $B$?

$$\nabla w_A = \frac{w_A w_B (v_B - v_A)}{D} \qquad \nabla w_B = \frac{w_B w_A (v_A - v_B)}{D}$$

$$\nabla w_A + \nabla w_B = 0$$

Yes, the results satisfy the constraint that the gradient of the mass fraction of A must be equal in magnitude and opposite in sign to the gradient of the mass fraction of B.

j. What is the profile of the mass fraction of A along the cylinder axis?

$$\frac{dw_A}{dz} = \frac{w_A w_B (v_B - v_A)}{D} = \frac{w_A (1 - w_A)(v_B - v_A)}{D}$$

$$\frac{dw_A}{w_A (1 - w_A)} = \frac{(v_B - v_A)}{D} dz$$

$$\int_{w_{A,0}}^{w_A} \frac{dw_A}{w_A (1 - w_A)} = \int_0^z \frac{(v_B - v_A)}{D} dz$$

Use the method of partial fraction expansions to evaluate the integral on left hand side.

$$\int_{w_{A,0}}^{w_A} \left( \frac{1}{w_A} + \frac{1}{1 - w_A} \right) dw_A = \int_0^z \frac{(v_B - v_A)}{D} dz$$

$$\ln \frac{w_A}{w_{A,0}} + \ln \frac{1 - w_{A,0}}{1 - w_A} = \frac{(v_B - v_A)}{D} z$$

$$\frac{w_A}{1 - w_A} = \frac{w_{A,0}}{1 - w_{A,0}} \exp\left[ \frac{(v_B - v_A)}{D} z \right]$$

Solve for the mass fraction. Define a new variable

$$C(z) = \frac{w_{A,0}}{1 - w_{A,0}} \exp\left[ \frac{(v_B - v_A)}{D} z \right]$$

$$\frac{w_A}{1 - w_A} = C(z)$$

$$w_A = C(z)(1 - w_A)$$

$$w_A\left(1+C(z)\right)=C(z)$$

$$w_A=\frac{C(z)}{1+C(z)}$$

$$w_A(z)=\frac{\dfrac{w_{A,0}}{1-w_{A,0}}\exp\left[\dfrac{\left(v_B-v_A\right)}{D}z\right]}{1+\dfrac{w_{A,0}}{1-w_{A,0}}\exp\left[\dfrac{\left(v_B-v_A\right)}{D}z\right]}$$

Simplify

$$w_A(z)=\frac{w_{A,0}}{\left(1-w_{A,0}\right)\exp\left[\dfrac{\left(v_A-v_B\right)}{D}z\right]+w_{A,0}}$$

**Problem 2.**
You have performed a molecular dynamics simulation in the microcanonical ensemble, which maintains a constant number of molecules, N, system volume, V, and total energy, E. You have simulated a relatively dilute gas. You use an initial configuration of a simple cubic lattice. In this initial configuration, there are no molecules within the interaction cut-off distance of each other. You equilibrate using velocity scaling to maintain a constant set temperature for maxeqb steps.

a. What is the initial potential energy?

The short-range contribution to the initial potential energy will be zero since there are no molecules within the interaction cut-off distance of each other. The initial potential energy will consist only of the mean field long-range correction.

b. If at the beginning of the data production stage, your temperature increases beyond the set temperature, what is causing the increase?

Since the potential energy starts off at zero (neglecting the long-range correction which is a constant at all times), it will decrease to some negative value for a dilute gas. If you don't equilibrate long enough, then the potential energy won't reach its equilibrium value. In which case, once you start the microcanonical data production, the total energy will be constant, the potential energy will continue to decrease to its equilibrium value, and the kinetic energy (and the temperature) will be forced to increase, since energy is conserved.

c. How can you fix this problem?

You have to equilibrate longer.

d. You wanted to simulate at a given pressure (say 10 atm) and temperature. You fed that pressure and temperature into an equation of state, and obtained an estimate of the molar density, N/V. You simulated at that N and V and calculated from the simulation a negative pressure. List and explain with text or plots possible reasons for the negative pressure. What does it mean?

A negative pressure indicates an unstable phase. If you consider even the van der Waals equation of state, an isotherm plotted on P-V plot can have negative pressures in the unstable region. The problem with the simulation is that the simulation doesn't agree all that well with your approximate equation of state. In the liquid phase, small differences in density can cause huge differences in pressure. This sort of result is routinely observed. A negative pressure just means that you are simulating an unstable phase, which is possible in an MD simulation. If you really wanted to simulated at a given T and P, then you should simulate in the isobaric-isothermal ensemble.