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,

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

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,

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

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

Solution:

(a) In this case, do the diffusive fluxes sum to zero? Provide the proof.

Whether or not the diffusive fluxes sum to zero is based only on the first two assumptions given above, (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, $\mathbf{j}_A$. It is independent of the choice of constitutive equations. For these two assumptions, the diffusive fluxes will sum to zero. Proof below.

total mass flux of each component relative to stationary laboratory frame of reference

$$\mathbf{n}_A = \rho w_A \mathbf{v}_A \qquad \mathbf{n}_B = \rho w_B \mathbf{v}_B \qquad (I.5)$$

mass-averaged (or center-of-mass) velocity relative to laboratory frame of reference

$$\mathbf{v} = w_A \mathbf{v}_A + w_B \mathbf{v}_B \qquad (I.6)$$

convective mass flux of each component relative to stationary laboratory frame of reference

$$\chi_A = \rho w_A \mathbf{v} \qquad \chi_B = \rho w_B \mathbf{v} \tag{I.7}$$

diffusive flux of each component relative to mass-averaged velocity

$$\mathbf{j}_A = \mathbf{n}_A - \chi_A \qquad \mathbf{j}_B = \mathbf{n}_B - \chi_B \tag{I.8}$$

Substitution of (I.5) and (I.7) into (I.8) yields

$$\mathbf{j}_A = \rho w_A (\mathbf{v}_A - \mathbf{v}) \qquad \mathbf{j}_B = \rho w_B (\mathbf{v}_B - \mathbf{v}) \tag{I.9}$$

Substitution of (I.6) into (I.9) yields

$$\mathbf{j}_A = \rho w_A w_B (\mathbf{v}_A - \mathbf{v}_B) \qquad \mathbf{j}_B = \rho w_A w_B (\mathbf{v}_B - \mathbf{v}_A) \tag{I.10}$$

Consequently,

$$\mathbf{j}_A + \mathbf{j}_B = 0 \tag{I.11}$$

Q.E.D.

(b) Derive the relationship between D°_{BA} and D°_{AB}.

Substitution of equation (1) into equation (I.11) yields

$$\mathbf{j}_A + \mathbf{j}_B = 0 \tag{I.11}$$

$$-m_A D^{\circ}_{AB} \nabla C_A - m_B D^{\circ}_{BA} \nabla C_B = 0 \tag{1.12}$$

$$D^{\circ}_{BA} = -\frac{m_A}{m_B}\left(\frac{\partial C_A}{\partial C_B}\right) D^{\circ}_{AB} \tag{1.13}$$

This thermodynamic partial derivative that appears in equation (I.13) can be rendered into more familiar terms, given that we understand that the total concentration is a sum of the component concentrations,

$$C_A + C_B = C_{TOT} \tag{I.14}$$

$$\frac{\partial C_A}{\partial C_B} = \frac{\partial C_{TOT}}{\partial C_B} - \frac{\partial C_B}{\partial C_B} = \frac{\partial C_{TOT}}{\partial C_B} - 1 \tag{I.15}$$

$$C_B \equiv C_{TOT} x_B \tag{I.16}$$

$$\frac{\partial C_B}{\partial C_{TOT}} = \frac{\partial C_{TOT} x_B}{\partial C_{TOT}} = C_{TOT} \frac{\partial x_B}{\partial C_{TOT}} + x_B \frac{\partial C_{TOT}}{\partial C_{TOT}} = C_{TOT} \frac{\partial x_B}{\partial C_{TOT}} + x_B \qquad \text{(I.17)}$$

Subsitution of (I.17) into (I.15) yields

$$\frac{\partial C_A}{\partial C_B} = \frac{1}{C_{TOT} \frac{\partial x_B}{\partial C_{TOT}} + x_B} - 1 = \frac{x_A + C_{TOT} \frac{\partial x_A}{\partial C_{TOT}}}{x_B + C_{TOT} \frac{\partial x_B}{\partial C_{TOT}}} \qquad \text{(I.18)}$$

The partial derivatives that now appear in equation (I.18) are related to the familiar partial molar volume of a mixture.

(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,

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

Find the relationship between D and D°_{AB}.
In this case the diffusive mass fluxes are relative to the same reference velocity and they have the same units, so they can be equated.

$$\mathbf{j}_A = -\rho D \nabla w_A = -m_A D^{\circ}_{AB} \nabla C_A \qquad \mathbf{j}_B = -\rho D \nabla w_B = -m_B D^{\circ}_{BA} \nabla C_B \qquad \text{(I.19)}$$

Solving for D yields,

$$D = \frac{m_A}{\rho}\left(\frac{\partial C_A}{\partial w_A}\right) D^{\circ}_{AB} \qquad D = \frac{m_B}{\rho}\left(\frac{\partial C_B}{\partial w_B}\right) D^{\circ}_{BA} \qquad \text{(I.20)}$$

Taken with equation (I.13), these expressions are equivalent.

$$D = \frac{m_A}{\rho}\left(\frac{\partial C_A}{\partial w_A}\right) D^{\circ}_{AB} \qquad D = \frac{m_A}{\rho}\left(\frac{\partial C_A}{\partial w_A}\right) D^{\circ}_{AB} \qquad \text{(I.21)}$$

Additional notes, not necessary for exam solution:
Again, this thermodynamic partial derivative can be expressed in a more familiar way as

$$\frac{\partial C_A}{\partial w_A} = \frac{\partial C_{TOT} x_A}{\partial w_A} = \frac{\partial C_{TOT} x_A}{\partial x_A}\frac{\partial x_A}{\partial w_A} = \left(C_{TOT} + x_A \frac{\partial C_{TOT}}{\partial x_A}\right)\frac{\partial x_A}{\partial w_A} \qquad \text{(I.22)}$$

Since, for a binary system,

$$\frac{\partial x_A}{\partial w_A} = \frac{x_A x_B}{w_A w_B} \qquad \text{(I.23)}$$

substitution of (I.23) into (I.22) yields

$$\frac{\partial C_A}{\partial w_A} = \left(C_{TOT} + x_A \frac{\partial C_{TOT}}{\partial x_A}\right)\frac{x_A x_B}{w_A w_B} \qquad \text{(I.24)}$$

substitution of (I.24) into (I.21) yields

$$D = \frac{m_A}{\rho}\left(C_{TOT} + x_A \frac{\partial C_{TOT}}{\partial x_A}\right)\frac{x_A x_B}{w_A w_B} D_{AB}^{\circ} \qquad \text{(I.25)}$$

Again, the missing partial derivative is related to the partial molar volume of the mixture.

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,

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

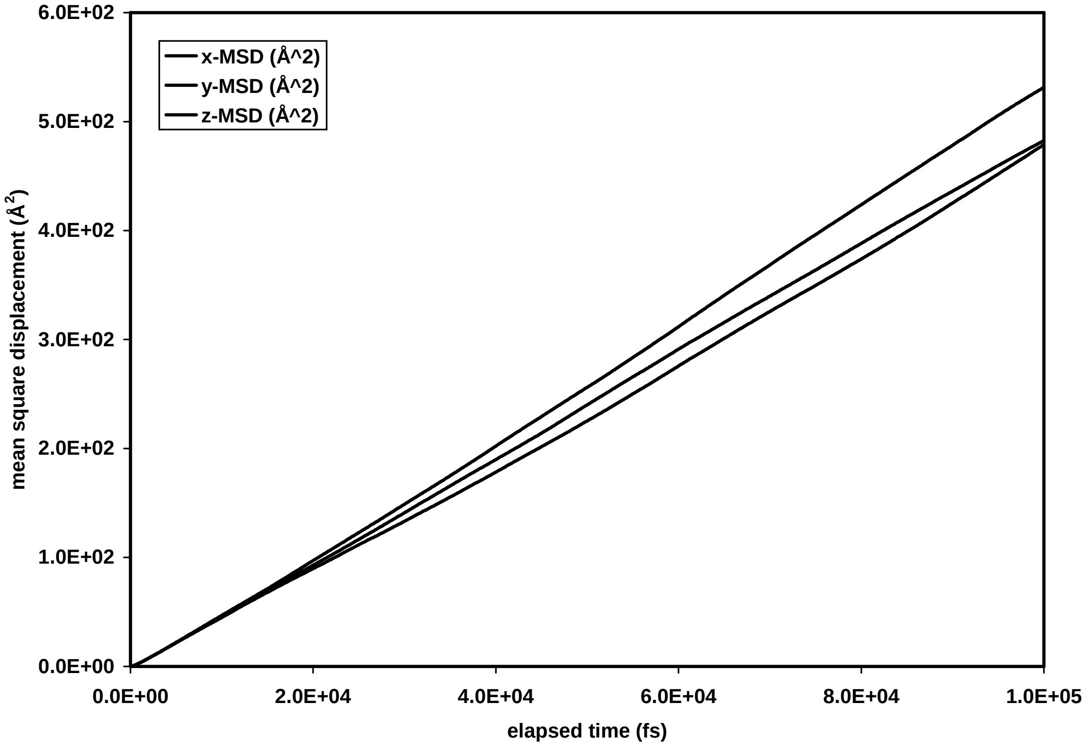
where d is the dimensionality of the system, r is a particle position, t is time, τ is elapsed time, and the angled brackets indicate an average over both all particle trajectories as well as all times, t.

(a) 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.

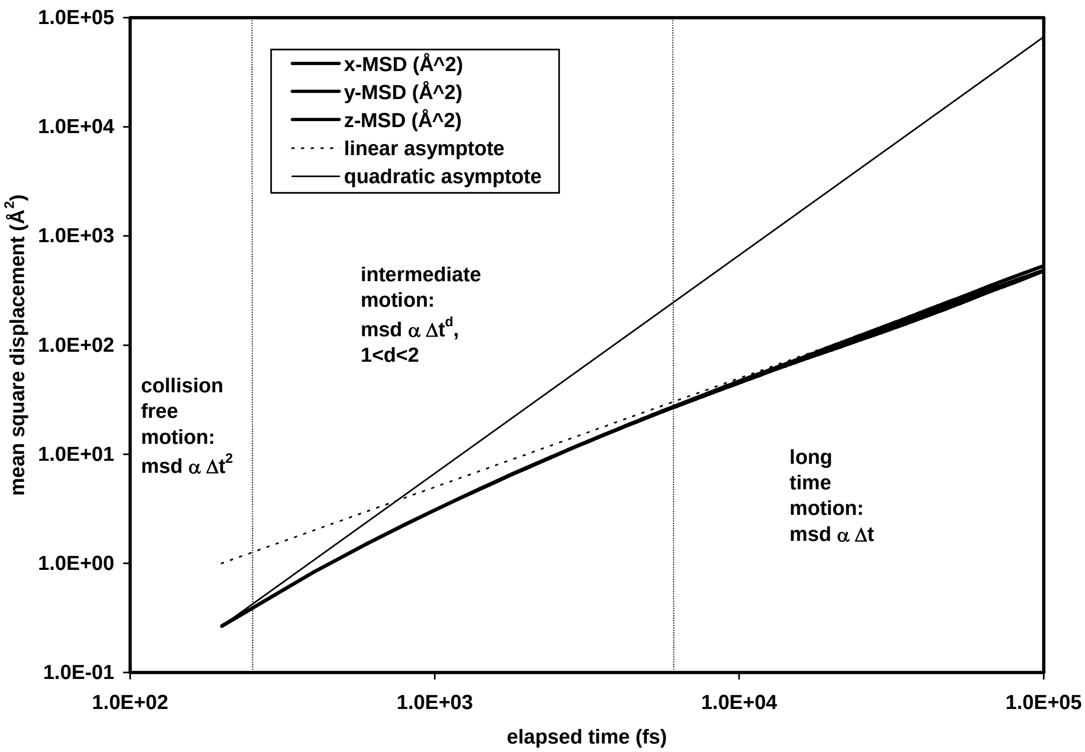
Solution:

(a) Sketch a qualitative plot of MSD vs elapsed time. Indicate how one obtains the self-diffusivity from this plot.



In this plot, you observe nonlinear behavior at short time and linear behavior at long times. The variation between x, y and z in an isotropic material is an indication of the uncertainty in the measurement. The slope of the long-time linear part of these curves is 2D. The dimensionality here is considered as one since we analyze the three dimensions independently.

(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.



In this log-log plot, we can more clearly observe the exponent relating the elapsed time to the MSD. At short times, the curves follows a quadratic (m=2) limit. At long times, the curves follow a linear (m=1) limit.