Advanced Transport Phenomena II
ChE 548
Department of Chemical Engineering
University of Tennessee, Knoxville
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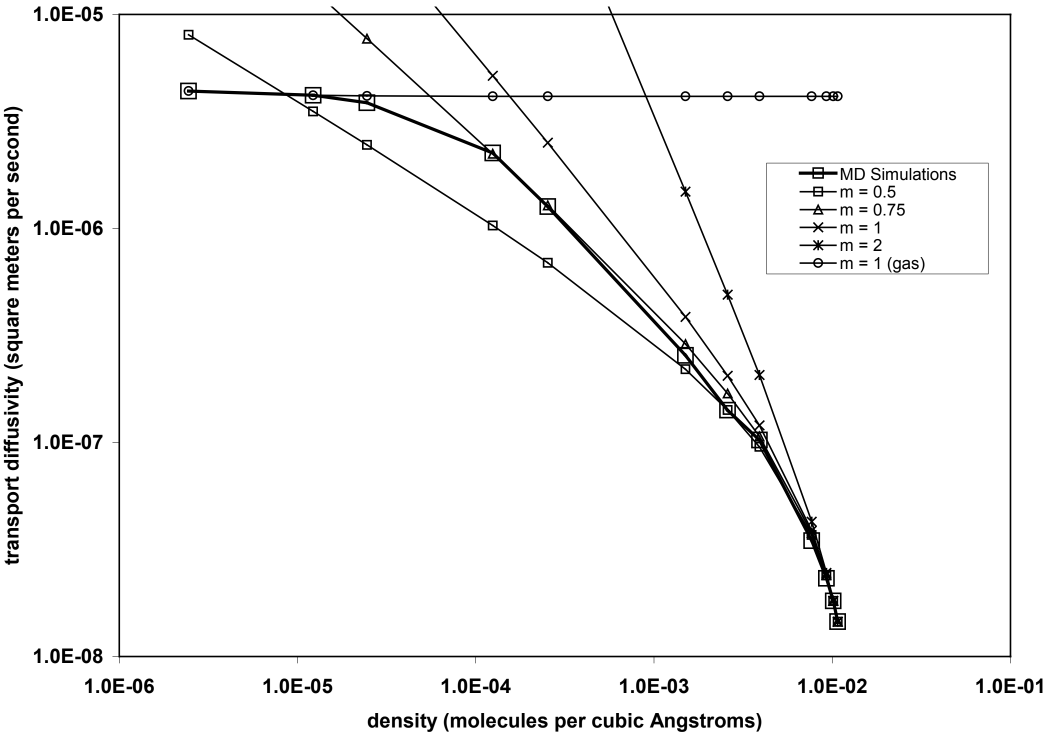
Final Examination
Administered: May 2, 2002

Problem 1. (30 points)
Kinetic theory tells us that the diffusivity of an ideal gas is proportional to the inverse of the total molar density,

$$D = b_0 + b_1 \left(\frac{1}{n} \right)^m$$

so that in this case, the exponent, m, is one. (b_0 and b_1 are empirical constants.) Consider an equimolar binary mixture of methane and ethane at 300 K. The single, binary transport diffusivity, obtained by using MD simulations for the self-diffusivities and the Lennard-Jones equation of state for the thermodynamic correction factors, is plotted below as a function of total density (on a log-log scale). Also plotted are several asymptotes with the function form of the equation given above. At the low density (ideal gas limit), the m = 1 equation fits well. At the high density, several different values of m are plotted.



Answer the following questions based on this plot and on your understanding of the molecular-level mechanisms for diffusion in gases and liquids.

(a) What is the molecular-level mechanism for diffusion in gases that gives rise to m=1 behavior?

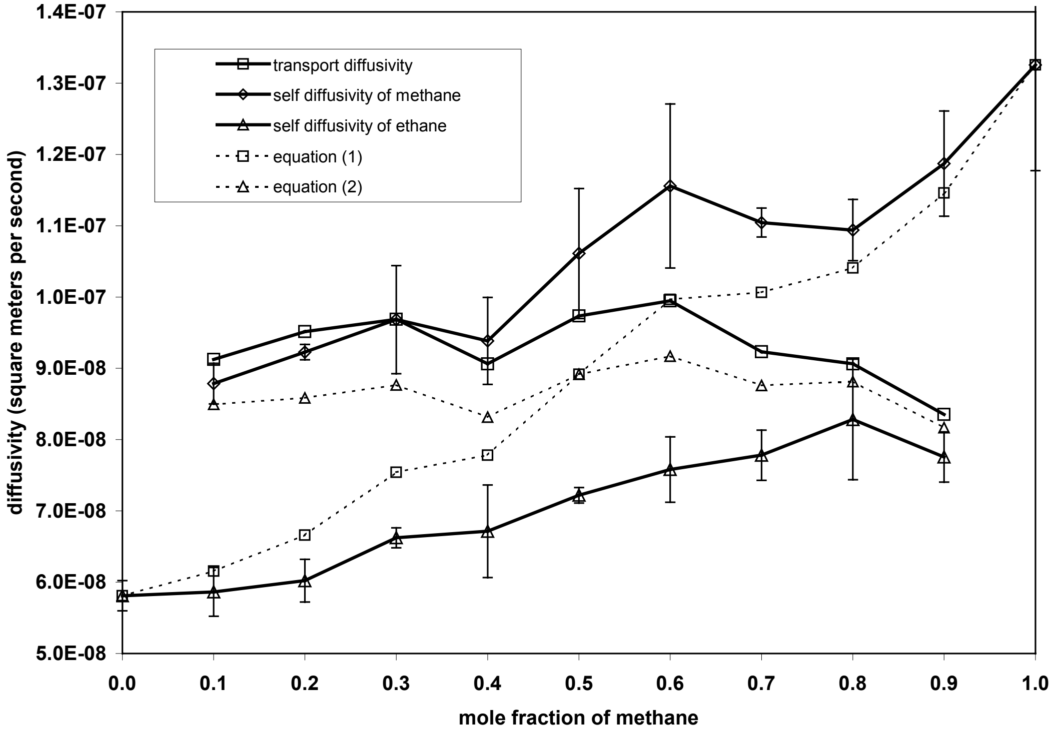
(b) What value of m models the high-density (liquid) density-dependence of the diffusivity best?

(c) What is the molecular-level mechanism for diffusion in liquids that gives rise to the m value selected in part (b)?

Problem 2. (30 points)
The single, binary transport diffusivity of a liquid is obviously a function of composition. Consider a binary mixture of methane and ethane at 300 K and at a density of 3.907×10^{-3} molecules/Å^3 (a liquid density). The single, binary transport diffusivity, obtained by using MD simulations for the self-diffusivities and the Lennard-Jones equation of state for the thermodynamic correction factors, is plotted below as a function of mole fraction of methane (on a log-log scale). Also plotted are the self diffusivities from MD simulations. Also plotted are two equations.

$$D = x_{Me} D_{self,Me} + x_{Et} D_{self,Et} \tag{1}$$

$$D = x_{Me} D_{self,Et} + x_{Et} D_{self,Me} \tag{2}$$



(a) Explain why the self diffusivity of methane is greater than the self diffusivity of ethane at the same temperature and density.

(b) The self diffusivities of methane and ethane generally increase with mole fraction of methane. Why?

(c) The self diffusivities of methane and ethane are not strictly monotonically increasing with mole fraction of methane. In your opinion, do the local non-monotonicities reflect real trends or, rather, are they within the noise of the simulation?

(d) In this data, the transport diffusivity is bound by the two self-diffusivities at all compositions. Must this behavior always be true?

(e) If you believe that the approximate physics of your simulations (such as the approximation of the Lennard-Jones potential) are only good to generate transport properties to +/- 10%, is it a legitimate approximation to assume a constant mean value of the transport diffusivity for use in a process modeling application?

(f) The transport diffusivity is clearly better modeled by equation (2) than by the molar-weighted mean self diffusivity (equation (1)). Explain.

Problem 3. (40 points)
Consider a two-component ideal mixture with constant molar volume in a perfectly insulated one-dimensional system of length L. The boundary conditions of the system are such that at z=0, the composition is fixed at $x_{\alpha,0}$, and at at z=L the composition is fixed at $x_{\alpha,L}$. Since the system is insulated, there is no heat flux at the boundaries, $q = 0$. Initially the temperature is constant. at the thermodynamic reference temperature. The enthalpy of component α at the reference temperature is positive (e.g. CH_4). The enthalpy of component β at the reference temperature is zero (e.g. N_2). In this system, no reaction takes place. You cannot ignore the enthalpy transfer due to the mass flux. (You must use the following form of the heat flux.)

$$q = -k\frac{\partial T}{\partial z} + \sum_{\alpha=1}^{n_c} \overline{H}_\alpha J_\alpha^*$$

As usual, q is the heat flux, k is the thermal conductivity, nc is the number of components (2), $\overline{H}_\alpha$ is the partial molar enthalpy of component α, and J_α^* is the molar flux of component α relative to the molar average velocity, v*.

In this problem, you may assume that the thermal conductivity and diffusivity are constants with respect to temperature, density, and composition. Assume the convection term is zero at steady state.

(a) Express q for an ideal mixture.
(b) Write out the total unsteady state mole balance, the balance on moles of α, and the energy balance.
(c) Derive the steady state profile of the concentration.
(d) Derive the steady state profile of the mole fraction of a. Sketch it.
(e) Derive the steady state profile of the temperature. Sketch it.
(f) If $x_{\alpha,L} > x_{\alpha,0}$, what is the relationship between T(z=L) and T(z=0)?

On the next page, you will find a list of equations, some of which you will certainly find useful in solving this problem.

Note: This problem is much easier to solve if you assume that the heat capacities of α and β are equal. It is acceptable to make this assumption for this problem.

molar flux: $J^*_\alpha = -cD_{\alpha\beta}\frac{\partial x_\alpha}{\partial z}$

$$J^*_\beta = -cD_{\alpha\beta}\frac{\partial x_\beta}{\partial z}$$

for binary systems:

$$x_\alpha + x_\beta = 1$$

$$N = N_\alpha + N_\beta$$

$$\left(\frac{\partial x_\alpha}{\partial N_\alpha}\right)_{T,p,N_\beta} = \frac{1}{N_\alpha + N_\beta} - \frac{N_\alpha}{(N_\alpha + N_\beta)^2} = \frac{N_\beta}{(N_\alpha + N_\beta)^2} = x_\beta\frac{1}{N}$$

$$\frac{\partial x_\beta}{\partial z} = -\frac{\partial x_\alpha}{\partial z}$$

$$x_\alpha = \frac{N_\alpha}{N} = \frac{N_\alpha}{N_\alpha + N_\beta}$$

$$\left(\frac{\partial N}{\partial N_\alpha}\right)_{T,p,N_\beta} = 1$$

$$\left(\frac{\partial x_\beta}{\partial x_\alpha}\right)_{T,p,N_\beta} = \left(\frac{\partial \frac{N_\beta}{N_\alpha + N_\beta}}{\partial N_\alpha}\right)_{T,p,N_\beta}\left(\frac{\partial N_\alpha}{\partial x_\alpha}\right)_{T,p,N_\beta} = -\frac{N_\beta}{(N_\alpha + N_\beta)^2}\frac{1}{x_\beta\frac{1}{N}} = -1$$

pure component enthalpy

$$H_\alpha(T) = \int_{T_{ref}}^{T} C_{p,\alpha}(T)dT + H_\alpha(T_{ref})$$

mixture enthalpy

$$H_{mix}(T,\underline{x}) = x_\alpha H_\alpha(T) + x_\beta H_\beta(T)$$

partial molar enthalpy for an ideal mixture (derived)

$$\overline{H}_\alpha(T,\underline{x}) \equiv \left(\frac{\partial NH_{mix}}{\partial N_\alpha}\right)_{T,p,N_\beta} = N\left(\frac{\partial H_{mix}}{\partial N_\alpha}\right)_{T,p,N_\beta} + H_{mix}\left(\frac{\partial N}{\partial N_\alpha}\right)_{T,p,N_\beta}$$

$$\overline{H}_\alpha(T,\underline{x}) = N\left(\frac{\partial H_{mix}}{\partial x_\alpha}\right)_{T,p,N_\beta}\left(\frac{\partial x_\alpha}{\partial N_\alpha}\right)_{T,p,N_\beta} + H_{mix} = x_\beta\left(\frac{\partial H_{mix}}{\partial x_\alpha}\right)_{T,p,N_\beta} + H_{mix}$$

$$\left(\frac{\partial H_{mix}}{\partial x_\alpha}\right)_{T,p,N_\beta} = H_\alpha(T) + H_\beta(T)\left(\frac{\partial x_\beta}{\partial x_\alpha}\right)_{T,p,N_\beta} = H_\alpha(T) - H_\beta(T)$$

$$\overline{H}_\alpha(T,\underline{x}) = x_\beta\left[H_\alpha(T) - H_\beta(T)\right] + H_{mix} = (1 - x_\alpha)\left[H_\alpha(T) - H_\beta(T)\right] + H_{mix} = H_\alpha(T)$$

$$\overline{H}_\beta(T,\underline{x}) = x_\alpha\left[H_\beta(T) - H_\alpha(T)\right] + H_{mix} = \overline{H}_\alpha(T,\underline{x}) + \left[H_\beta(T) - H_\alpha(T)\right] = H_\beta(T)$$