

**ChE 548**  
**Final Exam**  
**Spring, 2005**

**Problem 1.**

Explain with texts and accompanying sketches how one determines if a molecular dynamics simulation has been run long enough to obtain a reliable self-diffusivity. What will you expect if you have not run the simulation long enough? Given the same temperature, should you have to run longer for a liquid or gas?

**solution:**

Plot the mean square displacement as a function of time on a log-log plot. compute the exponent. The exponent will be unity if you have reached the long-time limit required by the Einstein relation for the self-diffusivity.

If you haven't run the simulation long enough, the exponent will be between 1 and 2.

You need to run longer for a gas because the time between collisions is longer in a gas.

**Problem 2.**

Consider an incompressible fluid composed of two components A and B. Write out the material, momentum, and energy balances that describe the steady state profile of material under the following boundary conditions.

$$\rho(z = 0) = \rho_o$$

$$w_A(z = 0) = w_{Ao}$$

$$v(z = 0) = 0$$

$$T(z = 0) = T_{low}$$

$$w_A(z = L) = w_{AL}$$

$$T(z = L) = T_{high}$$

You will need to invoke Fick's law and Fourier's law. Write out the equations for each of three cases below. For each case, solve as far as possible for  $\rho(z)$ ,  $w_A(z)$ ,  $v(z)$ , and  $T(z)$ .

Case A. This is a general case in which the diffusivity and the thermal conductivity are arbitrary functions of composition and temperature

$$D = D(w_A, T) \quad \text{and} \quad k_c = k_c(w_A, T)$$

Case B. This is a specific case where the diffusivity is a function of temperature, but not composition, and the thermal conductivity is constant.

$$D = D(T) = D_o \exp\left(-\frac{E_a}{RT}\right) \quad \text{and} \quad k_c = k_c$$

where  $D_o$ ,  $E_a$ , and  $R$  are constants.

Case C. This is a specific case where both the diffusivity and the thermal conductivity are constant.

$$D = D \quad \text{and} \quad k_c = k_c$$

Show all work involved in each step of the derivation. State any additional assumptions that you make.

You may find the following integral useful.

$$\int_{x_{low}}^{x_{high}} \exp\left(\frac{a}{x}\right) dx = x_{high} \exp\left(\frac{a}{x_{high}}\right) - x_{low} \exp\left(\frac{a}{x_{low}}\right) + a \left[ Ei\left(1, -\frac{a}{x_{high}}\right) - Ei\left(1, -\frac{a}{x_{low}}\right) \right]$$

where the well-known exponential integral is defined as

$$Ei(n, x) \equiv \int_1^{\infty} \frac{\exp(-xt)}{t^n} dt .$$

(It is perfectly acceptable to write a solution in terms of Ei.)

**solution:**

The total mass balance for the system is given by the continuity equation

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}), \quad (1)$$

The mass balance on component A is given by

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A - \nabla \cdot \mathbf{j}_A . \quad (2)$$

The constitutive equation used to obtain the total diffusive flux is

$$\mathbf{j}_A = -\rho D \nabla w_A \quad (3)$$

where  $D$  is Fickian diffusivity for the binary system. So our material balance for component A is

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A + \nabla \cdot \rho D \nabla w_A \quad . \quad (4)$$

Our next evolution equation is a momentum balance, which we will write in a general form as

$$\frac{\partial \rho \mathbf{v}}{\partial t} = -\nabla \cdot (\rho \mathbf{v} \mathbf{v}) - \nabla p - \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{g} \quad . \quad (5)$$

Here  $p$  is the pressure,  $\boldsymbol{\tau}$  is the extra stress tensor, and  $\mathbf{g}$  is an external field, e.g. a gravitational field.

The energy balance will have the form

$$\frac{\partial \rho \left( \frac{1}{2} v^2 + \hat{H} + \hat{\Phi} \right)}{\partial t} - \frac{\partial p}{\partial t} = -\nabla \cdot \rho \left( \frac{1}{2} v^2 \cdot \mathbf{v} + \hat{H} \mathbf{v} + \hat{\Phi} \mathbf{v} \right) - \nabla \cdot \mathbf{q} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) \quad , \quad (6)$$

Case A. The general case

Because the fluid is incompressible, the density is constant.

$$\rho(z) = \rho_o \quad (7)$$

For our incompressible fluid at steady state, the total mass balance becomes:

$$0 = -\rho \nabla \cdot \mathbf{v} \quad , \quad (8)$$

As a consequence the velocity is constant. Since our boundary conditions set the velocity to zero, there is no velocity anywhere in the system.

$$\mathbf{v}(z) = 0 \quad , \quad (9)$$

At steady state, the mass balance on A becomes,

$$0 = \rho \nabla \cdot D \nabla w_A \quad . \quad (10)$$

where the accumulation term dropped out because we were at steady state and the convection term dropped out because the velocity is zero.

At steady state and in the absence of convection, the energy balance becomes

$$0 = -\nabla \cdot \mathbf{q} \quad , \quad (11)$$

Substituting in Fourier's law we have

$$0 = \nabla \cdot (k_c \nabla T) , \quad (12)$$

Therefore, for the general case where the thermal conductivity and the diffusivity are functions of composition and temperature, our solution for  $\rho(z)$ ,  $w_A(z)$ ,  $\nu(z)$ , and  $T(z)$  is given by equations (7), (9), (10), and (12).

Case B. Specific case with diffusivity temperature dependent and thermal conductivity constant.

$$D = D(T) = D_o \exp\left(-\frac{E_a}{RT}\right) \quad \text{and} \quad k_c = k_c$$

We have these two ODEs.

$$0 = \rho \nabla \cdot D \nabla w_A . \quad (10)$$

$$0 = \nabla \cdot (k_c \nabla T) , \quad (12)$$

The temperature ODE is easy to solve because the thermal conductivity is constant.

$$0 = \frac{\partial^2 T}{\partial z^2} , \quad (13)$$

We can easily integrate this and fit the constants to match the boundary conditions given. The solution is a straight line that passes through both boundary conditions.

$$T(z) = T_{low} + \left(\frac{T_{high} - T_{low}}{L}\right)z , \quad (14)$$

We can now examine the composition balance.

$$0 = \rho \nabla \cdot D \nabla w_A = \nabla \cdot D_o \exp\left(-\frac{E_a}{RT}\right) \nabla w_A = \nabla \cdot \exp\left(-\frac{E_a}{RT}\right) \nabla w_A . \quad (15)$$

For our one dimensional problem we have

$$\frac{\partial}{\partial z} \left( \exp\left(-\frac{E_a}{RT}\right) \frac{\partial w_A}{\partial z} \right) = 0 . \quad (16)$$

If the gradient is zero, then the quantity is constant, c.

$$\exp\left(-\frac{E_a}{RT}\right) \frac{\partial w_A}{\partial z} = c \quad (17)$$

$$\frac{\partial w_A}{\partial z} = c \exp\left(\frac{E_a}{RT}\right) \quad (18)$$

Integrate.

$$w_A(z) - w_{Ao} = \int_{z=0}^z c \exp\left(\frac{E_a}{RT}\right) dz \quad (19)$$

Let's integrate over  $T$  instead of  $z$ . From (14) we have

$$dT = \left(\frac{T_{high} - T_{low}}{L}\right) dz, \quad (20)$$

$$w_A(z) - w_{Ao} = \int_{z=0}^z c \exp\left(\frac{E_a}{RT}\right) \left(\frac{L}{T_{high} - T_{low}}\right) dT \quad (21)$$

$$w_A(z) - w_{Ao} = c \left(\frac{L}{T_{high} - T_{low}}\right) \int_{T_{low}}^T \exp\left(\frac{E_a}{RT}\right) dT \quad (22)$$

$$\int_{x_{low}}^{x_{high}} \exp\left(\frac{a}{x}\right) dx = x_{high} \exp\left(\frac{a}{x_{high}}\right) - x_{low} \exp\left(\frac{a}{x_{low}}\right) + a \left[ Ei\left(1, -\frac{a}{x_{high}}\right) - Ei\left(1, -\frac{a}{x_{low}}\right) \right] \quad (23)$$

where the well-known exponential integral is defined as

$$Ei(n, x) \equiv \int_1^{\infty} \frac{\exp(-xt)}{t^n} dt \quad (24)$$

so

$$w_A(z) - w_{Ao} = c \left(\frac{L}{T_{high} - T_{low}}\right) \left[ T(z) \exp\left(\frac{E_a}{RT(z)}\right) - T_{low} \exp\left(\frac{E_a}{RT_{low}}\right) + \frac{E_a}{R} \left[ Ei\left(1, -\frac{E_a}{RT(z)}\right) - Ei\left(1, -\frac{E_a}{RT_{low}}\right) \right] \right] \quad (25)$$

where the  $T(z)$  is given by equation (14) and  $c$  must be made to fit the second boundary condition.

$$c = \frac{w_{AL} - w_{Ao}}{\left( \frac{L}{T_{high} - T_{low}} \right) \left[ T_{high} \exp\left( \frac{E_a}{RT_{high}} \right) - T_{low} \exp\left( \frac{E_a}{RT_{low}} \right) + \frac{E_a}{R} \left[ Ei\left( 1, -\frac{E_a}{RT_{high}} \right) - Ei\left( 1, -\frac{E_a}{RT_{low}} \right) \right] \right]} \quad (26)$$

We see that the solution is a function of boundary conditions and the activation energy for diffusion.

### Case C. Both diffusivity and thermal conductivity are constant.

$$D = D \quad \text{and} \quad k_c = k_c$$

We have these two ODEs.

$$0 = \rho \nabla \cdot D \nabla w_A \quad . \quad (10)$$

$$0 = \nabla \cdot (k_c \nabla T) \quad , \quad (12)$$

The temperature ODE is easy to solve because the thermal conductivity is constant.

$$0 = \frac{\partial^2 T}{\partial z^2} \quad , \quad (13)$$

We can easily integrate this and fit the constants to match the boundary conditions given. The solution is a straight line that passes through both boundary conditions.

$$T(z) = T_{low} + \left( \frac{T_{high} - T_{low}}{L} \right) z \quad , \quad (14)$$

We can now examine the composition balance. It is also easy to solve because the diffusivity is constant.

$$w_A(z) = w_{Ao} + \left( \frac{w_{AL} - w_{Ao}}{L} \right) z \quad , \quad (27)$$

Both the composition and temperature profiles are linear and are functions only of the boundary conditions. They are not functions of the diffusivity or thermal conductivity.