ChE 548

January 12 & January 14, 2005

Course Introduction:
Lecture Notes for the first two lectures.

LECTURE ONE.

I. Undergraduate Approaches to Teaching Transport Phenomena

I.A. Application-Oriented Approach (used at UT)

momentum: fluid flow in pipes (ChE 240)
energy: heat exchangers (ChE 240)
mass: diffusion in chemical engineering unit operations (ChE 340)

advantages: very practical

disadvantages: very limited, not very fundamental, extension to new systems is not straightforward

I.B. Theoretical Approach (a la BSL)

General Balance Equation Approach (used many other places)
write out general mass, momentum and energy balances
simplify equations (striking out unnecessary terms) to describe a specific system

advantages: very general, extension to new systems is emphasized

disadvantages: a common criticism: “Look at the problems we can solve, not necessarily the problems that are useful to solve.”
BSL’s approach relies a lot on intuition and experience
BSL’s approach pursuit of analytical solutions obfuscates some of the underlying physics

II. Graduate Approach to Teaching Transport Phenomena

Follow BSL in their approach to mathematically rigorous solution techniques.
Understand how to derive and write mass, momentum and energy balances.
But do not overly aggressively pursue analytical solutions. Turn to numerical solutions where necessary.

III. Equilibrium vs Nonequilibrium Thermodynamics

III.A. Equilibrium Thermodynamics

If you have

a mechanical equation of state P(V,T,**x**) e.g. van der Waals equation of state
a thermal equation of state U(V,T,**x**), e.g. polynomial expression for the heat capacity
a reference entropy

then you know everything about the equilibrium thermodynamics of the material at every thermodynamic state characterized by (V,T,**x**)

III.B. Nonequilibrium Thermodynamics

This general field links thermodynamics to transport phenomena. It includes both areas. Traditionally transport phenomena is limited to material, momentum, and energy balances. Nonequilibrium Thermodynamics adds an entropy balance. With this entropy balance, we have a theoretical framework within which we can rigorously describe irreversible processes such as diffusion, viscous dissipation, thermal conduction, and electrical conduction.

Nonequilibrium Thermodynamics requires that in addition to the three pieces of information required by equilibrium thermodynamics, there is additional information that must be known to completely specify the state of this system. This information includes “field strength”, i.e. the gradient of the driving force for the irreversible process, such as a gradient in the mass fraction due to diffusion, or a gradient in the pressure for mass transfer due to convection, or a gradient in the velocity for momentum transfer, or a gradient in the temperature for energy (heat) transfer. In addition to knowing the “field strength”, you must also know “phenomenonological coefficients” that provide proportionality constants between the field strength and the flux of mass, momentum or energy.

IV. Phenomenological Coefficients

What are phenomenological coefficients?

Some examples:

Example 1. The mass balance of component A in a reactive, binary mixture.

$$\rho\frac{\partial w_A}{\partial t}=-\rho\mathbf{v}\cdot\nabla w_A+\nabla\cdot\left(\rho D\nabla w_A\right)-k_r\rho w_A$$

The diffusivity (or diffusion coefficient) and the reaction rate constant are functions of more basic phenomenological coefficients.

Example 2. The momentum balance of a Newtonian fluid.

$$\frac{\partial\rho\mathbf{v}}{\partial t}=-\nabla\cdot\left(\rho\mathbf{v}\mathbf{v}\right)-\nabla p-\nabla\cdot\left(\mu\left(\nabla\mathbf{v}+\left(\nabla\mathbf{v}\right)^T\right)\right)+\rho\mathbf{g}$$

The shear viscosity is a function of a more basic phenomenological coefficient.

Example 3. The energy balance of a single component fluid.

$$\frac{\partial\rho C_p\left(T-T_{ref}\right)}{\partial t}=-\nabla\cdot\left(\rho C_p\left(T-T_{ref}\right)\mathbf{v}\right)+\nabla\cdot\left(k_c\nabla T\right)$$

The thermal conductivity is a function of a more basic phenomenological coefficient.

IV. Constitutive Equations

IV.A. Example of Constitutive Equations

Phenomenological coefficients enter material, momentum and energy balances through the invocation of constitutive equations.

Example 1. The mass balance of component A in a reactive, binary mixture.

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A - \nabla \cdot \mathbf{j}_A - k_r \rho w_A$$

This expression is rigorously true and contains $\mathbf{j}_A$, the diffusive flux of component A relative to the center-of-mass velocity. We don't know this quantity. Therefore, we invoke a constitutive equation, known as Fick's law.

$$\mathbf{j}_A = -\rho D \nabla w_A$$

which states that a linear proportionality exists between the diffusive flux of component A relative to the center-of-mass velocity and the driving force, the gradient of the mass fraction of component A.

Other common constitutive equations include

Newton's law of viscosity: $\tau_{xy} = \mu \frac{\partial v_x}{\partial y}$

Fourier's law of heat conduction: $\mathbf{q} = -k_c \nabla T$

Ohm's law of current conduction: $I = \sigma V = \frac{1}{R} V$

IV.B. Basis of Constitutive Equations

There is no theoretical basis for these linear consitutive laws. They are based solely on empirical evidence.

IV.C. Exceptions to the Linear Constitutive Equations

The most common exception to the linear constitutive equation is the shear-thinning fluid. Many other exception exist when field strengths are high.

Calling these constitutive equations linear is something of a misnomer anyway since the phenomenological coefficients are absolutely functions of the local thermodynamics state, (V,T,**x**), i.e.

$$\mathbf{j}_A = -\rho D(\rho, T, \mathbf{w}) \nabla w_A$$

As noted above, in addition to being functions of the thermodynamic state, the phenomenological coefficients can also be functions of the field strength.

IV.D. The Precise Functional Form of the Constitutive Equation is Arbitrary

The functional form of the constitutive equation is arbitrary. For example,

$$\mathbf{j}_A = -\rho D(\rho, T, \mathbf{w}) \nabla w_A$$

$$\mathbf{j}_A = -D(\rho, T, \mathbf{w}) \nabla \rho_A$$

are both equally valid, but the diffusivity that appears in each of these equations is different. They are not independent of each other but they are not the same.

LECTURE TWO.

IV.E. Three Choices Define the Constitutive Equation

1. define the flux
    - for mass transport: mass flux or molar flux
2. define the field or driving force
    - gradient of the concentration of A
    - gradient of the density of A
    - gradient of the mole fraction of A
    - gradient of the mass fraction of A
    - gradient of the chemical potential of A
    - gradient of the specific chemical potential of A
3. define the frame of reference for diffusion
    - diffusion relative to the mass-averaged motion of the system
    - diffusion relative to the mole-averaged motion of the system
    - diffusion relative to the volume-averaged motion of the system

$$\mathbf{j}_A = -\rho D \nabla w_A$$

Example

First, we stated that we would work the problem with mass fluxes. Second, we stated that we would measure the diffusive mass flux relative to the mass-averaged velocity. Third, we defined the driving force of Fick’s law as the gradient in the mass fraction. These three choices define our diffusivity. If we change any of these assumptions, then we will have to compute a different numerical value of the diffusivity.

IV.F. There is only one diffusivity describing diffusion in a binary mixture under isothermal conditions

Regardless of the choice of the three definitions above, there is only one diffusivity describing diffusion in a binary mixture under isothermal conditions.

proof:

See masstransferbasics_part5.pdf

IV.G. Different forms of Fick’s law lead to different diffusivities

Different choices of the three assumptions above will lead to different diffusivities. It is useful to comment on one alternate choice of definitions.

Example 1. Work problem entirely in mass
Example 2. Work problem entirely in moles
Example 3. Work problem in mass/moles hybrid

Example 4. Show equivalence of Example 1 and 2.

See masstransferbasics_part5.pdf up through page 12.