

3.044 Lectures

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Abstract

This represents the sum total of lecture material presented in 3.044, *Materials Processing*, in the Spring of 2005. Its style and content are not yet determined, so I'll end here.

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Chapter 1

Introduction

1.1 February 2, 2005

Handouts: Syllabus, Heat conduction

Circulate signup sheet: name, username, course (if not 3)

- Introductions: me, Randy, TA Wanida Pongsaksawad.
- What is covered: review stuff on general overview. Lots of complexity: structure formation, some process engineering, cost modeling.
- Necessary for all classes of materials, draws on wide range of examples:
 - Polymers: synthesis, injection molding, extrusion, membranes
 - Bio: drug delivery, anisotropic diffusion, blood flow
 - Ceramics: glass ceramics, powder separation, drying, sintering
 - Electronic: crystal growth, CVD, diffusion processing
 - Metals: smelting, refining, casting, heat treatment
- Why 3.044 is important: processing-(structure)-properties-performance. We do low-cost, high-quality processing, low environment overhead, which is one of the two important aspects of this triad/tetrahedron.

Sponsors of our work care about two things: low-cost high-quality processes and high performance. They don't care about structure. Andy Groves, chairman of Intel, could care less about the electronic structure of titanium silicide-titanium aluminide diffusion barriers in aluminum interconnects, he wants cheap high-quality processes that result in high performance. Closer to home, parents' eyes glaze over at talk of "Kinetics of eta phase precipitation in nickel superalloys," but not at "Avoiding catastrophic failure of jet engine turbine blades in service." Structure provides an important way to model the relationship between processing and properties, without which a black box, not a science.

Randy New sections on engineering economics: cost modeling, material and process selection, market size. Life cycle analysis. Intro to stuff in new Fall course.

Mechanics

- Discuss grading: HW points and collab, double-session tests, mixed final.
- Little project: suggest on note cards any time.
- Get test conflict dates, aim for Weds. March 9–11 and April 20–22.

- Make sure everyone has a recitation.
- Schedule office hours.
- Discuss travel: out 2/14, David Dussault covering, tradition of having previous TA give a lecture.

Required math

- Vector arithmetic (dot product, cross product, outer product)
- Vector calculus (gradient, divergence, curl)
- Solving homogeneous linear ordinary differential equations, e.g.

$$y'' = k, \quad \text{or} \quad y'' - ky = 0 \quad (1.1)$$

- What partial differential equations look like, e.g.

$$\nabla^2 C = 0 \quad (1.2)$$

- The error function and derivatives:

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-\xi^2} d\xi \quad (1.3)$$

$$\frac{d}{dx} \text{erf}(x) = \frac{d}{dx} \frac{2}{\sqrt{\pi}} \int_0^x e^{-\xi^2} d\xi = \frac{2}{\sqrt{\pi}} e^{-x^2} \quad (1.4)$$

- The substantial derivative: the time derivative in a moving frame.

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{u} \cdot \nabla \quad (1.5)$$

Kind of like moving vector $x(t), y(t), z(t)$:

$$\left. \frac{dC}{dt} \right|_{(x,y,z)} = \frac{\partial C}{\partial t} + \frac{\partial C}{\partial x} \frac{\partial x}{\partial t} + \frac{\partial C}{\partial y} \frac{\partial y}{\partial t} + \frac{\partial C}{\partial z} \frac{\partial z}{\partial t}. \quad (1.6)$$

Previous feedback

- Prof. Powell is cool, lectures are great, double tests are neat!
- Too much busy algebra on problem sets. Okay, will cut quite a bit, some computer.
- Textbook is awful. It covers things in the wrong order, and is hard to read. Changing to set of texts, better readings. Hopefully will cover all material without problems.
- Too much online. But taking it off would only hurt those without Bibles. Sorry, won't do.
- Prof. Powell lets "dumb" questions slow things down. No dumb questions. Very often correct mistakes or omissions, ten others have the same question. If anything, MIT juniors and seniors need to be much more vocal! (Last mid-term evaluation, dreadful lecture...)

Chapter 2

Heat Conduction

2.1 February 4, 2005: Start heat conduction

Mechanics:

- Test conflicts? March 9–11, April 20–22. If no, will get a room.
- Open: Colleen's facility with names, my advisee...

Heat Conduction Analogy to diffusion: Conservation of thermal energy.

$$\text{accumulation} = \text{in} - \text{out} + \text{generation} \quad (2.1)$$

$$V \frac{dH}{dt} = Aq_{\text{in}} - Aq_{\text{out}} + V\dot{q} \quad (2.2)$$

Note on the accumulation term: when temperature changes, enthalpy changes according to the heat capacity, build up units from dT/dt (Kelvin/sec) adding c_p and ρ to get to Joules/sec.

What's heat flux \vec{q} ? Like diffusion goes down the conc gradient (actually, chem potential gradient), heat goes down the temperature gradient, proportionality constant k :

$$\vec{q} = -k\nabla T. \quad (2.3)$$

Using that in-out and that accumulation term, derive the 1-D heat equation, same as diffusion. Simplify constant k , 1-D, so:

$$\rho c_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \dot{q}. \quad (2.4)$$

Define thermal diffusivity $\alpha = k/\rho c_p$, with no gen reduces to diffusion equation, and give 1-D solutions:

- 1-D steady-state: linear temperature. Result: flux $q_x = k\Delta T/L$
- Cylindrical steady-state: different control volumes, $T = A \ln r + B$.

Total flux: $q_r = -k\partial T/\partial r = A/r$, $2\pi r L q_r = 2\pi A L$.

So, T_1 at inside, T_2 at outside, what to do between? Use R_1 and R_2 for inner, outer radii. Fourier's first, assume 1-D, so T is function of r only.

$$q_r = -k \frac{dT}{dr} \quad (2.5)$$

Conservation: in at r , out at $r + \Delta r$, no gen or accum, area $2\pi rL$:

$$0 = [2\pi rLq_r]_r - [2\pi rLq_r]_{r+\Delta r}, \quad (2.6)$$

divide by $2\pi L$, $\Delta r \rightarrow 0$:

$$0 = -\frac{d}{dr}[rq_r] \quad (2.7)$$

Plug in flux:

$$0 = \frac{d}{dr} \left(rk \frac{dT}{dr} \right). \quad (2.8)$$

Now solve:

$$A' = rk \frac{dT}{dr} \quad (2.9)$$

$$\frac{A'}{kr} = \frac{dT}{dr} \quad (2.10)$$

$$T = A \ln r + B \quad (2.11)$$

where $A = A'/k$. From BCs:

$$\frac{T - T_1}{T_2 - T_1} = \frac{\ln(r/R_1)}{\ln(R_2/R_1)} \quad (2.12)$$

Check at R_1 and R_2 , units.

Flux = $-kdT/dr$:

$$q_r = -k \frac{dT}{dr} = -k \frac{d}{dr} \left[T_1 + (T_2 - T_1) \frac{\ln(r/R_1)}{\ln(R_2/R_1)} \right] = k \frac{T_1 - T_2}{\ln(R_2/R_1)} \frac{1}{r}. \quad (2.13)$$

Important result: not flux, but flux times area.

$$Q = Aq_r = -2\pi rLk \frac{dT}{dr} = 2\pi rLk \frac{T_1 - T_2}{\ln(R_2/R_1)} \frac{1}{r}. \quad (2.14)$$

Note rs cancel, so AJ_r is constant for all r . Make sure units work. Cool.

- Spherical steady-state: still another, $T = \frac{A}{r} + B - \dot{q}r^2/6k$.

Note: timescale L^2/D replaced with L^2/α . Different properties for conductivity (flux) and diffusivity (timescale)!

2.2 February 7, 2005: More Conduction

Mechanics:

- Tests 3/9 and 4/20: in-lecture portion
- Handouts: ABET, PS1 due Mon 2/14.
- Interesting lecture: ASM dinner Chiang “Ceramics in Electrochemical Systems” Thu Feb 17; students \$8, RSVP Sam Davis.

Spherical conduction with generation:

$$4\pi r^2 \Delta r \frac{\partial H}{\partial t} = 4\pi r^2 q_r|_r - 4\pi r^2 q_r|_{r+\Delta r} + 4\pi r^2 \Delta r \dot{q} \quad (2.15)$$

$$r^2 \rho c_p \frac{\partial T}{\partial t} = \frac{-r^2 k \frac{\partial T}{\partial r}|_r + r^2 k \frac{\partial T}{\partial r}|_{r+\Delta r}}{\Delta r} + r^2 \dot{q} \quad (2.16)$$

$$r^2 \frac{\partial T}{\partial t} = \frac{k}{\rho c_p} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + \frac{r^2 \dot{q}}{\rho c_p} \quad (2.17)$$

Steady-state solution:

$$A = \alpha r^2 \frac{\partial T}{\partial r} + \frac{\dot{q} r^3}{3\rho c_p} \quad (2.18)$$

$$T = \frac{A}{r} + B - \frac{\dot{q} r^2}{6\rho c_p} \quad (2.19)$$

Multi-layer solid Slides, mention heat transfer coefficient on outside as resistance $1/h$. Final result:

$$q_x = \frac{T_1 - T_{fl}}{\frac{L_1}{k_1} + \frac{L_2}{k_2} + \frac{L_3}{k_3} + \frac{1}{h}} \quad (2.20)$$

Unsteady Solutions Responsible for two:

- 1-D semi-infinite uniform initial, constant T boundary:

$$\frac{T - T_s}{T_\infty - T_s} = \operatorname{erf} \left(\frac{x}{2\sqrt{\alpha t}} \right). \quad (2.21)$$

Example: two blocks of same material at different temperatures, come together (like a diffusion couple)

- 1-D infinite, uniform initial T , heat deposited at $x = 0$: Gaussian

$$T - T_i = \frac{(T_0 - T_i)\delta}{\sqrt{\pi\alpha t}} \exp \left(-\frac{x^2}{4\alpha t} \right). \quad (2.22)$$

Example: resistance welding, brazing, some adhesives... Note $T_0\delta$ can be replaced with $H/\rho c_p$.

Even more on the handout, not responsible for any further than handout (and not asterisks either).

2.3 February 9, 2005: Loose ends, finite differences

Handout: finite differences made using pdftk of Continuum handout.

Cylindrical multilayer wall Slides, mention heat transfer coefficient on outside as resistance $1/h$. Final result:

$$q_x = \frac{T_1 - T_{fl}}{\frac{L_1}{k_1} + \frac{L_2}{k_2} + \frac{L_3}{k_3} + \frac{1}{h}} \quad (2.23)$$

Cylindrical: slightly different

$$Q = 2\pi r L q_r = \frac{2\pi L(T_1 - T_5)}{\frac{1}{k_1} \ln \frac{R_2}{R_1} + \frac{1}{k_2} \ln \frac{R_3}{R_2} + \frac{1}{k_3} \ln \frac{R_4}{R_3} + \frac{1}{R_4 h}} \quad (2.24)$$

Biot Number One layer and a heat transfer coefficient

$$q_x = \frac{T_1 - T_{fl}}{\frac{L}{k} + \frac{1}{h}} \quad (2.25)$$

$$\text{Bi} = \frac{\text{solid conduction resistance}}{\text{fluid BL resistance}} = \frac{hL}{k} \quad (2.26)$$

Also:

$$\text{Bi} = \frac{T_2 - T_1}{T_{fl} - T_2} \quad (2.27)$$

Unsteady Solutions Responsible for two:

- 1-D semi-infinite uniform initial, constant T boundary:

$$\frac{T - T_s}{T_\infty - T_s} = \text{erf} \left(\frac{x}{2\sqrt{\alpha t}} \right). \quad (2.28)$$

Example: two blocks of same material at different temperatures, come together (like a diffusion couple)

- 1-D infinite, uniform initial T , heat deposited at $x = 0$: Gaussian

$$T - T_i = \frac{(T_0 - T_i)\delta}{\sqrt{\pi\alpha t}} \exp \left(-\frac{x^2}{4\alpha t} \right). \quad (2.29)$$

Example: resistance welding, brazing, some adhesives... Note $T_0\delta$ can be replaced with $H/\rho c_p$.

Even more on the handout, not responsible for any further than handout (and not asterisks either).

Finite differences Very often no analytical solution to a system. (Or if there is one, it's impossibly complex.) So, use a computer, make some approximations.

- Discretize space: calculate temperature at a finite number of points on a grid (here 1-D). Choose x_i , calculate T_i . For simplicity, we'll choose evenly-spaced points, so $x_{i+1} - x_i = \Delta x$.
- Discretize time: calculate temperature at a finite number of "timesteps" at times t_n , so with both, we have $T_{i,n}$. For simplicity, Δt uniform.

- Make some approximations about derivatives:

$$\begin{aligned}\frac{\partial T}{\partial t}\Big|_{x_i, t_{n+1/2}} &\simeq \frac{T_{i,n+1} - T_{i,n}}{\Delta t} \\ \frac{\partial T}{\partial x}\Big|_{x_{i+1/2}, t_n} &\simeq \frac{T_{i+1,n} - T_{i,n}}{\Delta x} \\ \frac{\partial^2 T}{\partial x^2}\Big|_{x_i, t_n} &\simeq \frac{\frac{\partial T}{\partial x}\Big|_{x_{i+1/2}, t_n} - \frac{\partial T}{\partial x}\Big|_{x_{i-1/2}, t_n}}{\Delta x} \simeq \frac{T_{i-1,n} - 2T_{i,n} + T_{i+1,n}}{(\Delta x)^2}\end{aligned}$$

So, let's look at the energy equation, and substitute approximations:

$$\begin{aligned}\frac{\partial T}{\partial x} &= \alpha \frac{\partial^2 T}{\partial x^2} + \frac{\dot{q}}{\rho c_p} \\ \frac{T_{i,n+1} - T_{i,n}}{\Delta t} &= \alpha \frac{T_{i-1,n} - 2T_{i,n} + T_{i+1,n}}{(\Delta x)^2} + \frac{\dot{q}}{\rho c_p} \\ T_{i,n+1} &= T_{i,n} + \Delta t \left[\frac{T_{i-1,n} - 2T_{i,n} + T_{i+1,n}}{(\Delta x)^2} + \frac{\dot{q}}{\rho c_p} \right] = T_{i,n} + \text{Fo}_M (T_{i-1,n} - 2T_{i,n} + T_{i+1,n}) + \frac{\Delta t}{\rho c_p} \dot{q}\end{aligned}$$

This is the “forward Euler” algorithm, a.k.a. “explicit” time stepping. Nice, efficient, easy to put in a spreadsheet. Problems: inaccurate because time and space derivatives not co-located, also unstable. Inaccuracy later.

Demonstrate instability for $\text{Fo}_M > \frac{1}{2}$:

$$T_{i,n+1} = T_{i,n}(1 - 2\text{Fo}_M) + 2\text{Fo}_M \frac{T_{i-1,n} + T_{i+1,n}}{2} + \frac{\Delta t}{\rho c_p} \dot{q}$$

So, it's like a weighted average between $T_{i,n}$ and the average of the two (show graphically). When $\text{Fo}_M > \frac{1}{2}$, the $T_{i,n}$ part is negative, so we shoot past it! So, the criterion is that it must be $\leq \frac{1}{2}$, larger timestep means less work, so use $\frac{1}{2}$.

Exercise: cut length step in half, for same total time, how many more timesteps? How much more computational work? Spreadsheet area...

2.4 February 11, 2005: wrap up finite differences; radiation!

Explicit timestepping stability criterion:

$$\text{Fo}_M = \frac{\alpha \Delta t}{(\Delta x)^2} \leq \frac{1}{2} \Rightarrow \Delta t \leq \frac{1}{2} \frac{(\Delta x)^2}{\alpha} \quad (2.30)$$

Exercise: double spatial resolution, how much does timestep size change? Computational work?

2-D: $T_{i,j,n}$ at x_i, y_j, t_n : add another spatial derivative:

$$T_{i,j,n+1} = T_{i,j,n} + \frac{\alpha \Delta t}{(\Delta x)^2} (T_{i-1,j,n} - 2T_{i,j,n} + T_{i+1,j,n}) + \frac{\alpha \Delta t}{(\Delta y)^2} (T_{i,j-1,n} - 2T_{i,j,n} + T_{i,j+1,n}) + \frac{\dot{q} \Delta t}{\rho c_p} \quad (2.31)$$

For $\Delta x = \Delta y$:

$$T_{i,j,n+1} = (1 - 4\text{Fo}_M)T_{i,j,n} + 4\text{Fo}_M \frac{T_{i-1,j,n} + T_{i+1,j,n} + T_{i,j-1,n} + T_{i,j+1,n}}{4} + \frac{\dot{q} \Delta t}{\rho c_p} \quad (2.32)$$

Resulting stability criterion:

$$\text{Fo}_M = \frac{\alpha \Delta t}{(\Delta x)^2} \leq \frac{1}{4} \Rightarrow \Delta t \leq \frac{1}{4} \frac{(\Delta x)^2}{\alpha} \quad (2.33)$$

Handout: enthalpy method for phase changes, finite volume approach to BCs, timestepping approaches which avoid the stability criterion—but are much harder to implement.

Radiation! Def: spontaneous emission of photons from a hot body. Emission, absorption, reflection, transmission. Cosine distribution: hand-waving skin depth explanation.

Happens throughout a body, but surface emission follows a cosine distribution: handwaving explanation of skin depth as a function of angle.

Concept: black body, absorbs all incident radiation, theoretical construct with some practical application. Also emits maximum possible radiation. Handwaving explanation: zero reflection at the interface.

Defs: e is power emitted per unit area, e_b is power emitted by black body per unit area, e_λ is power per unit wavelength per unit area, $e_{b,\lambda}$ is power by black body per unit wavelength per unit area.

Emission spectrum of black body:

$$e_{b,\lambda} = \frac{2\pi h c^2 \lambda^{-5}}{e^{\frac{ch}{k_B \lambda T}} - 1} \quad (2.34)$$

h is Planck's constant, c is light speed, k_B Boltzmann's constant. Graph for different T .

Peak wavelength:

$$\lambda_{max} T = 2.9 \times 10^{-3} \text{m} \cdot \text{K} \quad (2.35)$$

1000K, $2.9 \mu\text{m} = 2900 \text{ nm}$; sun at 5800K is at 500 nm (yellow)—need to be pretty hot to peak in the visible spectrum.

How to get e_b ? Integrate over all wavelengths. Fortunately, it's quite simple:

$$e_b = \int_0^\infty e_{b,\lambda} d\lambda = \sigma T^4 \quad (2.36)$$

The physicists must have jumped for joy when they saw that one. For our purposes, it puts radiation within reach of engineers. Okay, all done, never have to see that first equation again.

Even better:

$$\sigma = \frac{2\pi^5 k_B^4}{15c^2 h^3} = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \cdot \text{K}^4} \quad (2.37)$$

Note: fourth-power dependence on temperature means this is **MUCH** more important at high temperature than low temperature.

New defs: emissivity $\epsilon_\lambda = e_\lambda / e_{b,\lambda}$, the fraction of black body radiation which is emitted; absorptivity $\alpha_\lambda = a_\lambda / a_{b,\lambda}$. Cool result: $\epsilon_\lambda = \alpha_\lambda$, always! Material property. Graph resulting emission spectrum.

2.5 February 16, 2005: Wrapup radiation, dimensionless graphs

Anyone going to Chiang's lecture tomorrow night?

Muddy from last time:

- Why unstable for large Fo_M ? Consider:

$$\frac{dT}{dt} = -T. \quad (2.38)$$

The solution is easy: $T = Ae^{-t}$. But let's try to solve it with finite differences, say $t = 0 \Rightarrow y = 1$. Using $\Delta t = 0.25$ gives $T = 1, .75, .75^2, .75^3 \dots$. With $\Delta t = 1$, we get $T = 1, 0, 0, 0 \dots$. With $\Delta t = 3$, we get $T = 1, -2, 4, -8, 16, \dots$, which is clearly unstable.

- Please number equations on handouts... Are they not numbered?

Recap from last time: radiation is spontaneous emission, e_b etc. Defs: emissivity $\epsilon_\lambda = e_\lambda/e_{b,\lambda}$, the fraction of black body radiation which is emitted; absorptivity $\alpha_\lambda = a_\lambda/a_{b,\lambda}$. Cool result: $\epsilon_\lambda = \alpha_\lambda$, always! Material property. Graph resulting emission spectrum.

Fortunately e_b is quite simple:

$$e_b = \int_0^\infty e_{b,\lambda} d\lambda = \sigma T^4, \sigma = 5.67 \times 10^{-8} \frac{W}{m^2 \cdot K^4} \quad (2.39)$$

Grey body approximation: $\epsilon = \alpha = \epsilon_\lambda = \alpha_\lambda = \text{constant}$. Makes life a lot simpler for us engineers. Superpose grey spectra on previous graph.

Resulting emission: $e = \epsilon \sigma T^4$. Pretty cool. Likewise average absorptivity α .

Averaged properties: $\epsilon = e/e_b$, $\alpha = a/\text{incident}$. Note ϵ will vary with temperature, α depends on wavelength of incident light. Example: global warming, CO_2 absorbs in the infrared, transmits sun in visible.

Little table:

	Wavelength	Total/average
BB Emission	$e_{b,\lambda}$	$e_b = \int_0^\infty e_{b,\lambda} d\lambda$
Actual emission	e_λ	$e(=q) = \int_0^\infty e_\lambda d\lambda$
Emissivity	$\epsilon_\lambda = e_\lambda/e_{b,\lambda}$	$\epsilon(T) = e/e_b$
Absorptivity	$\alpha_\lambda \equiv \epsilon_\lambda$	$\alpha(\text{incident})$

That's as far as we'll go this year

Convective cooling curves Today's motivating example: Thermal spray. Small droplets, very rapid cooling, rapid solidification microstructures, solute trapping.

So, suppose initial condition $T = T_i$, outside fluid at T_{fl} . Boundary conditions: $r = R \Rightarrow q_r = h(T - T_{fl})$. Want to know temperature distribution through time, or temperature history. This requires a Bessel function series!! How to do understand?

- Dimensional analysis!
- Qualitative description of behavior.
- Graphs in text.
- Simplified low Biot number behavior: Newtonian cooling.

Dimensional analysis:

1. Formulation: $T - T_{fl} = f(t, r, R, T_i - T_{fl}, h, k, \rho c_p)$. $n = 8$ parameters!
2. Units: K, s, m, $\frac{W}{m^2 \cdot K}$, $\frac{W}{m \cdot K}$, $\frac{J}{kg \cdot K}$.

3. Base units: K, s, m, kg so $m = 4$.
4. Buckingham pi: four dimensionless parameters.
5. What to eliminate? Want to keep $T - T_{fl}$, t , r ; choose h also. Eliminate R , $T_i - T_{fl}$, k , ρc_p .
6. π_T is easy, as is π_r . π_h : eliminated by k and R . π_t is funny, use k for seconds, ρc_p for Joules, R for remaining meters. Result is the Fourier number, the ratio of t/t_{SS} .
Note: could have used h to eliminate seconds, but result wouldn't have been as cool: $\pi_t = ht/\rho c_p R$.
7. Dimensionless equation:

$$\frac{T - T_{fl}}{T_i - T_{fl}} = f\left(\frac{r}{R}, \frac{\alpha t}{R^2}, \frac{hR}{k}\right). \quad (2.40)$$

2.6 February 18, 2005: Convective cooling curves

Result from last time, dimensionless numbers and the equation:

$$\frac{T - T_{fl}}{T_i - T_{fl}} = f\left(\frac{r}{R}, \frac{\alpha t}{R^2}, \frac{hR}{k}\right). \quad (2.41)$$

Note on dimensional analysis and ambiguity of choice on parameters to keep, eliminate, with example of one layer and heat transfer coefficient. Keeping q_x and h is just more elegant than q_x and k , though the dimensional analysis allows either one.

Now can graph π_T vs. π_r for various π_t , different graphs for different π_h . Large (> 100) reverts to the constant temperature boundary condition $T = T_{fl}$, small (< 0.1) we'll get to in a moment, intermediate Biot number graphs.

The handout (P&G pp. 292-299) takes a different approach to the graphs: π_T vs. π_t for various π_h , graphs at different π_r . Useful for temperature histories like PS2#4 (but skip past the early graphs...), and also for TTT diagrams, like our ceramic thermal spray. But not so useful for uniformity. P. 299 has what we did.

Newtonian cooling Small Biot number (< 0.1): temperture is roughly uniform. Let's say it *is* uniform. Then we just have $T(t)$, $\pi_T(\pi_t, \pi_h)$. Cool.

Balance over the entire object: accumulation = -out.

$$V \frac{dH}{dt} = -Aq_r \quad (2.42)$$

$$V \rho c_p \frac{dT}{dt} = -Ah(T - T_{fl}) \quad (2.43)$$

Rearrange:

$$\frac{dT}{T - T_{fl}} = -\frac{Ah}{V \rho c_p} dt \quad (2.44)$$

Integrate, with initial condition T_i at $t = 0$:

$$\ln(T - T_{fl}) - \ln(T_i - T_{fl}) = -\frac{Aht}{V \rho c_p} \quad (2.45)$$

$$\frac{T - T_{fl}}{T_i - T_{fl}} = \exp\left(-\frac{Aht}{V \rho c_p}\right) \quad (2.46)$$

So far, everything's general, with volume and area, so whether a sphere, rod, plate, or crumpled up piece of paper, it just works.

First, examine terms, timescale, larger/smaller h , rho c_p , V/A . Plug in V/A :

- Sphere: $R/3$
- Cylinder: $R/2$
- Plate: " $R' = L/2$ "
- Other shapes: varies...

Can instead define alternate Biot and Fourier numbers: $Bi' = \frac{hV}{kA}$, $Fo' = \frac{\alpha A^2}{V^2} t$, then:

$$\frac{T - T_{fl}}{T_i - T_{fl}} = \exp\left(-\frac{hV}{kA} \frac{kA^2}{\rho c_p V^2} t\right) = \exp(-Bi'Fo'). \quad (2.47)$$

So, all set for PS2?

Thermal conductivity Diffusion is straightforward: atoms move, right? Well, not quite: gases in straight lines, liquid atoms move in chains, vacancies, interstitials, dislocations, etc. For heat, various mechanisms:

- Collisions
- Phonons
- Photons—radiation, which is spontaneous emission from hot body
- Electrons

On electrons, Wiedmann-Franz law:

$$k_{el} = L\sigma_{el}T, L = \frac{\pi}{3} (k_B/e)^2 = 2.45 \times 10^{-8} \frac{\text{Wohm}}{K^2}$$

where e =electron charge.

Metals: σ_{el} goes down with temperature. What about electrons in semiconductors?

Liquids: water .615 20-100°C, O₂ 3.4×10^{-4} , H₂ 1.77×10^{-3} (both 300K)

Influence of porosity and humidity/water absorption. Gases are very bad conductors, water not quite as bad but has very high specific heat! (PS2 #1d, water has four times c_p of aluminum which is highest there.)

Typical conductivity values: 0.1 to 300 $\frac{\text{W}}{\text{m}\cdot\text{K}}$. Porous—less, metals high, gases *really* small!

Note: at conference, diamond-aluminum composite for microelectronics, 45 vol% diamond but isotropic conductivity of 550 W/mK! Nearly twice copper, squeeze-castable into heat sink parts. Q: why no diamond-iron composite?

Chapter 3

Liquid-Solid Processes

3.1 February 28, 2005: Moving Body

Heat and phase change Another important concept: heat generated/lost at interface due to phase change. If more heat is removed from the solid than put in from the liquid, the interface moves. How much?

$$\vec{q}_s \cdot \hat{n} - \vec{q}_l \cdot \hat{n} = -\rho\Delta H_M \frac{dX}{dt} \quad (3.1)$$

So the melt interface velocity is proportional to the difference in heat fluxes.

Model of casting or injection molding limited by conduction through growing solid, pure material with single T_m . Temperatures: T_{env} environment, T_s metal surface at mold interface, T_m at liq-sol interface. Solid thickness X changing with time. Flux through mold wall and outside BL collapsed into one heat transfer coefficient $|\vec{q}| = h(T_s - T_{env})$. Flux through solid material at steady state: $|\vec{q}| = k(T_m - T_s)/X$. Note that Biot number hX/k is changing with time!

Short time: small X , small Biot, uniform solid temperature, $T_s \sim T_m$. Then $|\vec{q}| = h(T_m - T_{env}) = \text{constant}$, linear growth.

Long time: large X , large Biot, $T_s \sim T_{env}$. Then

$$|\vec{q}| = k(T_m - T_{env})/X = \rho\Delta H_f \frac{dX}{dt} \quad (3.2)$$

$$X = \sqrt{\frac{k(T_m - T_{env})}{\rho\Delta H_f} t} \quad (3.3)$$

Parabolic growth proportional to square root of time.

Analogy to diffusion phase change (silicon oxidation): H is like C , T is like chemical potential μ . Fast growth means proportional to undercooling, like reaction-limitation in oxidation. Slow growth is like diffusion limited growth.

Moving body Example: VAR of titanium alloys, nickel superalloys. Start, during operation. Nickel: 6-8 kA, 17→20"; Ti around 30 kA, 30→36".

Competition: thermal diffusion up vs. drive down. Suggest steady-state, sketch T vs. z .

Temperatures in ingot real complicated, flow, etc. But can analyze electrode now. Question: how much of the electrode is heated? What's the temperature profile?

Choose frame of reference of melt interface on the bottom of the electrode. Solid is moving with respect to frame of reference. Now conductive and convective heat fluxes: $\vec{q} + \rho c_p T \vec{u}$ (not really, but this is valid for the difference).

In and out have motion component! Important thing: in-out. in = $u_z \rho c_p T$, out too. Result when goes to zero:

$$\text{in} - \text{out} = -\frac{\partial}{\partial z}(q_z + \rho c_p T u_z) \quad (3.4)$$

This example: u_z , ρ , c_p are all constant, so we end up with:

$$\rho c_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial z^2} - \rho c_p u_z \frac{\partial T}{\partial z} + \dot{q} \quad (3.5)$$

Rearrange slightly for constant $\rho c_p u_z$, substitute $q_z = -k \partial T / \partial z$:

$$\rho c_p \left(\frac{\partial T}{\partial t} + u_z \frac{\partial T}{\partial z} \right) = k \frac{\partial^2 T}{\partial z^2} + \dot{q} \quad (3.6)$$

Divide by ρc_p :

$$\frac{\partial T}{\partial t} + u_z \frac{\partial T}{\partial z} = \alpha \frac{\partial^2 T}{\partial z^2} + \frac{\dot{q}}{\rho c_p} \quad (3.7)$$

Discuss terms: why proportional to $\partial T / \partial z$, competing effects of positive $\partial^2 T / \partial z^2$ and negative $-\partial T / \partial z$. Graphical explanation.

What introductory math concept does this remind us of? The substantial derivative! Rewrite:

$$\frac{DT}{Dt} = \alpha \frac{\partial^2 T}{\partial z^2} + \frac{\dot{q}}{\rho c_p} \quad (3.8)$$

Note that's the time derivative in the frame of reference of the moving solid. Cool!

3.2 March 2, 2005: Moving Body, Stability

Recall: vacuum arc remelting. Setup, geometry, frame of reference, relative z -velocity $u_z < 0$. Convective flux $\vec{q} = "H\vec{u}"$ or $\rho c_p \vec{u}$, Back up a couple of steps:

$$\rho c_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial z^2} - \rho c_p u_z \frac{\partial T}{\partial z} + \dot{q} \quad (3.9)$$

Cancel ρc_p :

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2} - u_z \frac{\partial T}{\partial z} + \frac{\dot{q}}{\rho c_p} \quad (3.10)$$

Go through terms: regular accumulation, regular second derivative with thermal diffusivity. Next the convective term, discuss in terms of units and derivatives. Rewrite again in terms of substantial derivative:

$$\frac{DT}{Dt} = \alpha \frac{\partial^2 T}{\partial z^2} + \frac{\dot{q}}{\rho c_p} \quad (3.11)$$

Steady-state, no generation: temperature depends only on z , not t :

$$\alpha \frac{d^2 T}{dz^2} - u_z \frac{dT}{dz} = 0 \quad (3.12)$$

Simple solution using the characteristic polynomial, $R = 0, u_z/\alpha$. Result:

$$T = A + B \exp\left(\frac{u_z z}{\alpha}\right) \quad (3.13)$$

Fit to boundary conditions: $z = 0 \Rightarrow T = T_M, z = \infty \Rightarrow T = T_i$ so use erf-style:

$$\frac{T - T_i}{T_M - T_i} = \exp\left(\frac{u_z z}{\alpha}\right) \quad (3.14)$$

Lengthscale = α/u_z . Graph, noting that u_z is negative. Titanium $\alpha = 0.1 \frac{\text{cm}^2}{\text{s}}$, $u_z \sim 5 \frac{\text{cm}}{\text{min}} = \frac{1}{12} \frac{\text{cm}}{\text{s}}$, so $\alpha/u_z = 1.2 \text{cm}$, about 1/2 inch. So only the bottom few centimeters are heated at all, even at this low velocity!

Heat flux into the bottom:

$$q_z = -k \frac{\partial T}{\partial z} = -k(T_M - T_i) \frac{u_z}{\alpha} \exp\left(\frac{u_z z}{\alpha}\right) = -\rho c_p u_z (T_M - T_i) \quad (3.15)$$

Note $\rho c_p (T_M - T_i)$ is the enthalpy per unit volume to heat metal to its melting point. Mult by u_z for enthalpy per unit area to heat metal coming at a rate of u_z , which is a cool result.

This is heat flux into the solid. What about into the liquid? Remember last time:

$$\vec{q}_s \cdot \hat{n} - \vec{q}_l \cdot \hat{n} = -\rho \Delta H_M \frac{dX}{dt} \quad (3.16)$$

Replace dX/dt with u_z and we're done, need to supply the heat of melting and of getting to this temperature. Here larger \vec{q}_l than \vec{q}_s , both positive, so dX/dt positive.

Stability Is the VAR melt front stable? What if we have a bump, or groove?

Solidification: is the growing solid shell stable?

What about a solid particle growing into an undercooled liquid?

What about alloy solidification?

3.3 March 4, 2005: Stability in Alloy Solidification

Muddy from last time:

- I thought arcs were the opposite: small gap leads to small heat and vice versa. Depends on the operating conditions. At constant current, this is right, more gap means higher voltage, more plasma and more heating. At constant voltage, it's the opposite: more gap means lower current. Shape stability: constant voltage. Industry practice: constant current, control using voltage and drip short frequency to estimate melt rate and gap size.

Chapter 4

Fluid Dynamics

4.1 March 7, 2005: Intro, Newtonian Fluids

Fluid Dynamics! Brief introduction to rich topic, of which people spend lifetimes studying one small part. You will likely be confused at the end of this lecture, come to “get it” over the next two or three.

Categories: laminar, turbulent; confined (tubes and channels), free (jets, wakes); compressible, incompressible.

Outcomes: flow rates (define), drag force (integral of normal stress), mixing. Later couple with diffusion and heat conduction for convective heat and mass transfer.

Conservation of math (in one ear, out the other). But seriously, conservation of momentum.

Start: the 3.185 way. Momentum field, “momentum diffusion” tensor as shear stress. Show this using units: momentum per unit area per unit time:

$$\frac{\text{kg} \frac{\text{m}}{\text{s}}}{\text{m}^2 \cdot \text{s}} = \frac{\text{kg}}{\text{m} \cdot \text{s}^2} = \frac{\text{N}}{\text{m}^2} \quad (4.1)$$

Two parallel plates, fluid between, zero and constant velocity. x -momentum diffusing in z -direction, call it τ_{zx} , one component of 2nd-rank tensor. Some conservation of math:

$$\text{accumulation} = \text{in} - \text{out} + \text{generation}$$

Talking about momentum per unit time, $\frac{\text{kg}}{\text{m} \cdot \text{s}^2}$, locally momentum per unit volume $\rho \vec{u}$. Here suppose u_x varies only in the z -direction, no τ_{xx} or τ_{yx} , no u_y or u_z . Three conservation equations for three components of momentum vector, here look at x -momentum:

$$V \cdot \frac{\partial(\rho u_x)}{\partial t} = A \cdot \tau_{zx}|_z - A \cdot \tau_{zx}|_{z+\Delta z} + V \cdot F_x \quad (4.2)$$

Do this balance on a thin layer between the plates:

$$A \Delta z \frac{\partial(\rho u_x)}{\partial t} = A \tau_{zx}|_z - A \tau_{zx}|_{z+\Delta z} + A \Delta z F_x \quad (4.3)$$

Cancel A and divide by Δz , let go to zero:

$$\frac{\partial(\rho u_x)}{\partial t} = -\frac{\partial \tau_{zx}}{\partial z} + F_x \quad (4.4)$$

What’s generation? Body force per unit volume, like gravity. Units: N/m^3 (like τ has N/m^2), e.g. ρg . What’s the constitutive equation for τ_{zx} ? Newtonian fluid, proportional to velocity gradient:

$$\tau_{zx} = -\mu \left(\frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x} \right) \quad (4.5)$$

This defines viscosity μ , which is the momentum diffusivity. Units: $\text{N} \cdot \text{s}/\text{m}^2$ or $\text{kg}/\text{m} \cdot \text{s}$, Poiseuille. CGS units: $\text{g}/\text{cm} \cdot \text{s}$, Poise = 0.1 Poiseuille. Water: .01 Poise = .001 Poiseuille.

So, sub constitutive equation in the conservation equation, with $u_y = 0$:

$$\frac{\partial(\rho u_x)}{\partial t} = -\frac{\partial}{\partial z} \left(-\mu \frac{\partial u_x}{\partial z} \right) + F_x \quad (4.6)$$

With constant ρ and μ :

$$\rho \frac{\partial u_x}{\partial t} = \mu \frac{\partial^2 u_x}{\partial z^2} + F_x \quad (4.7)$$

It's a diffusion equation! Divide by ρ :

$$\frac{\partial u_x}{\partial t} = \nu \frac{\partial^2 u_x}{\partial z^2} + \frac{F_x}{\rho} \quad (4.8)$$

We have the diffusion equation! ν is the momentum diffusivity, like the thermal diffusivity $k/\rho c_p$ before it. Note: units of momentum diffusivity $\nu = \mu/\rho: \frac{\text{kg}/\text{m} \cdot \text{s}}{\text{kg}/\text{m}^3} = \text{m}^2/\text{s}$! Kinematic (ν), dynamic (μ) viscosities.

So at steady state, with a bottom plate at rest and a top plate in motion in the x -direction at velocity U , we have: a linear profile, $u_x = Az + B$.

Note on graphics: velocities with arrows, flipping the graphs sideways to match orientation of the problem. Case 1 today:

- Steady-state, no generation, bottom velocity zero, top U :

$$u_x = \frac{U}{L}z, \quad \tau_{zx} = -\mu \frac{U}{L} \quad (4.9)$$

Shear stress:

$$\tau_{zx} = -\mu \left(\frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x} \right) = -\mu \frac{U}{L} \quad (4.10)$$

Thus the drag force is this times the area of the plate.

4.2 March 11, 2005: Newtonian Shear Flow II

Recap last time: momentum conservation, vector quantity. Shear stress as momentum flux; Newtonian viscosity.

Non-Newtonian fluids: liquid polymers, semi-solid slurries from metals to ceramic-binder systems, both have decreasing apparent viscosity with increasing shear.

Flow between parallel plates:

- Last time: steady-state, no generation, bottom velocity zero, top U :

$$u_x = \frac{U}{L}z, \quad \tau_{zx} = -\mu \frac{U}{L} \quad (4.11)$$

Shear stress:

$$\tau_{zx} = -\mu \left(\frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x} \right) = -\mu \frac{U}{z} \quad (4.12)$$

Thus the drag force is this times the area of the plate.

- Unsteady, no generation, different velocities from $t = 0$.

$$u_x = U \operatorname{erfc} \left(\frac{L-z}{2\sqrt{\nu t}} \right), \quad \tau_{zx} = -\frac{1}{2\sqrt{\nu t}} \frac{2}{\sqrt{\pi}} \exp \left(-\frac{(L-z)^2}{4\nu t} \right) \quad (4.13)$$

- New: steady-state, generation, with θ the inclination angle off-normal so $g_x = g \sin \theta$, y is the distance from the plane. The steady-state equation reduces to:

$$0 = \mu \frac{\partial^2 u_x}{\partial y^2} + F_x \quad (4.14)$$

$$u_x = -\frac{F_x y^2}{2\mu} + Ay + B \quad (4.15)$$

BCs: zero velocity at bottom plate at $y = 0$, free surface with zero shear stress at $y = L$, $F_x = \rho g_x = \rho g \sin \theta$, result: $B=0$, get

$$u_x = \frac{g \sin \theta}{2\nu} (2Ly - y^2) \quad (4.16)$$

Shear stress:

$$\tau_{yx} = -\mu \left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right) = \rho g \sin \theta (L - y) \quad (4.17)$$

This is the weight of the fluid per unit area on top of this layer!

Shear stress as the mechanism of momentum flux, each layer pushes on the layer next to it. Think of it as momentum diffusion, not stress, and you'll get the sign right.

Flow rate: Q , volume per unit time through a surface. If width of the falling film is W , then flow rate is:

$$Q = \int_S \vec{u} \cdot \hat{n} dA = \int_{y=0}^L u_x W dy = \frac{W g \sin \theta}{\nu} \left[\frac{Ly^2}{2} - \frac{y^3}{6} \right] = \frac{W g \sin \theta}{\nu} \frac{L^3}{3} \quad (4.18)$$

Average velocity is Q/A , in this case Q/LW :

$$u_{av} = \frac{Q}{LW} = \frac{g \sin \theta L^2}{3\nu}; \quad (4.19)$$

$$u_{max} = u_x|_{y=L} = \frac{g \sin \theta L^2}{2\nu}. \quad (4.20)$$

So average velocity is 2/3 of maximum for falling film, channel flow, etc.

Also: Mechanics uses displacement for \vec{u} , acceleration is its *second* derivative with time. Simple shear:

$$\rho \frac{\partial^2 \vec{u}}{\partial t^2} = \nabla \cdot \sigma + \vec{F} \Rightarrow \rho \frac{\partial^2 u_x}{\partial t^2} = \frac{\partial \sigma_{xx}}{\partial x^2} + \frac{\partial \sigma_{yx}}{\partial y^2} + \frac{\partial \sigma_{zx}}{\partial z^2} + F_x = G \frac{\partial^2 u_x}{\partial z^2} + F_x. \quad (4.21)$$

Analogue to momentum diffusivity: G/ρ , units m^2/s^2 , $\sqrt{G/\rho}$: speed of sound! (Well, speed of transverse waves.) Remember with a little jig:

*Fluids are diffusive,
With their velocity and viscosity.
But on replacement with displacement,
it will behave, like a wave!*

4.3 March 14, 2005: Wrap up 1-D flows, drag force on a sphere

Mechanics:

- Evals Wednesday
- PS4 due 3/30
- Talk this Friday...

Nice segue into pressure-driven flows. Suppose fluid in a cylinder, a pipe for example of length L and radius R , P_1 on one end, P_2 on other. Net force: $(P_1 - P_2)A_{xs}$, force per unit volume is $(P_1 - P_2)V/A_{xs} = (P_1 - P_2)/L$. Can shrink to shorter length, at a given point, force per unit volume is $\Delta P/\Delta z \rightarrow \partial P/\partial z$. This is the pressure generation term.

So, flow in tube: uniform generation throughout $(P_1 - P_2)/L$ (prove next week), diffusion out to $r = R$ where velocity is zero. Could do momentum balance, but is same as diffusion or heat conduction, laminar Newtonian result:

$$\rho \frac{\partial u_z}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \mu \frac{\partial u_z}{\partial r} \right) + \rho g_z - \frac{\partial P}{\partial z}. \quad (4.22)$$

Here looking at steady-state, horizontal pipe, uniform generation means:

$$u_z = -\frac{F_z r^2}{4\mu} + A \ln r + B = -\frac{P_1 - P_2}{4\mu L} r^2 + A \ln r + B. \quad (4.23)$$

Like reaction-diffusion in problem set 2 (PVC rod): non-infinite velocity at $r = 0$ means $A = 0$ (also symmetric), zero velocity at $r = R$ means:

$$u_z = \frac{P_1 - P_2}{4\mu L} (R^2 - r^2). \quad (4.24)$$

What's the flow rate?

$$Q = \int_0^R u_z 2\pi r dr = \int_0^R \frac{P_1 - P_2}{4\mu L} (R^2 - r^2) 2\pi r dr \quad (4.25)$$

$$Q = \frac{\pi(P_1 - P_2)}{2\mu L} \left[\frac{R^2 r^2}{2} - \frac{r^4}{4} \right]_0^R = \frac{\pi(P_1 - P_2)R^4}{8\mu L}. \quad (4.26)$$

Hägen-Poiseuille equation, note 4th-power relation is extremely strong! 3/4" vs. 1/2" pipe...

Summary of the three phenomena thus far:

	Diffusion	Heat conduction	Fluid flow
What's conserved?	Moles of each species	Joules of energy	kg m/s momentum
Local density	C	$\rho c_p T$	$\rho \vec{u}$
Units of flux	$\frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$	$\frac{\text{W}}{\text{m}^2}$	$\frac{\text{kg} \frac{\text{m}}{\text{s}}}{\text{m}^2 \cdot \text{s}} = \frac{\text{N}}{\text{m}^2}$
Conservation equation*	$\frac{\partial C}{\partial t} = -\nabla \cdot \vec{J} + G$	$\rho c_p \frac{\partial T}{\partial t} = -\nabla \cdot \vec{q} + \dot{q}$	$\frac{\partial(\rho \vec{u})}{\partial t} = -\nabla P - \nabla \cdot \tau + \vec{F}$
Constitutive equation	$\vec{J} = -D \nabla C$	$\vec{q} = -k \nabla T$	$\tau = -\mu [\nabla \vec{u} + (\nabla \vec{u})^T]$
Diffusivity	D	$\alpha = k/\rho c_p$	$\nu = \mu/\rho$
Result**	$\frac{\partial C}{\partial t} = D \nabla^2 C + G$	$\frac{\partial T}{\partial t} = \alpha \nabla^2 T + \frac{\dot{q}}{\rho c_p}$	$\frac{\partial \vec{u}}{\partial t} = -\frac{\nabla P}{\rho} + \nu \nabla^2 \vec{u} + \frac{\vec{F}}{\rho}$
Convective flux	$C \vec{u}$	$\rho c_p T \vec{u}$	$\rho \vec{u} \vec{u}$
New result**	$\frac{DC}{Dt} = D \nabla^2 C + G$	$\frac{DT}{Dt} = \alpha \nabla^2 T + \frac{\dot{q}}{\rho c_p}$	$\frac{D\vec{u}}{Dt} = -\frac{\nabla P}{\rho} + \mu \nabla^2 \vec{u} + \frac{\vec{F}}{\rho}$

*Only considering diffusive fluxes. T in fluid constit. means matrix transpose. **For uniform properties.

New stuff: vector field instead of scalar; very different units; pressure as well as flux/shear stress and force.

Having taken 3.032, shear stress τ relates to stress σ as follows:

$$\sigma = -\tau - PI, \quad P = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \quad (4.27)$$

so $\tau_{xx} + \tau_{yy} + \tau_{zz} = 0$, $\tau_{xy} = \tau_{yx} = -\sigma_{xy} = -\sigma_{yx}$. Note that $\tau_{yx} = \tau_{xy}$ almost always, otherwise infinite rotation...

Flow past a sphere Motivating process: Electron beam melting and refining of titanium alloys. Water-cooled copper hearth, titanium melted by electron beams, forms solid “skull” against the copper. Clean heat source, liquid titanium contained in solid titanium, results in very clean metal. Mystery of the universe: how does liquid Ti sit in contact with solid Cu? Main purpose: removal of hard TiN inclusions often several millimeters across which nucleate cracks and bring down airplanes! (1983 Sioux City, Iowa.)

Set up problem: sphere going one way u_{sphere} , fluid other way u_∞ , local disturbance but relative velocity $U = u_\infty - u_{sphere}$, relative veloc of fluid in sphere frame. Drag force is in this direction.

For a sphere, drag force is slightly different: it has not only shear, but pressure component as well. Traction $\vec{t} = \sigma \cdot \hat{n}$. Stokes flow: ignore the convective terms, result:

$$F_d = 3\pi\mu dV. \quad (4.28)$$

At high velocity, friction factor concept:

$$F_d = fKA = f \cdot \frac{1}{2}\rho U^2 \cdot \frac{1}{4}\pi d^2. \quad (4.29)$$

Low Re (<0.1) means Stokes flow, can ignore all convective terms; analytical result in 3.21 notes, drag force:

$$F_d = 3\pi\mu Ud = f \cdot \frac{1}{2}\rho U^2 \cdot \frac{1}{4}\pi d^2 \Rightarrow f = \frac{24\mu}{\rho Ud} = \frac{24}{\text{Re}}. \quad (4.30)$$

If faster, though not turbulent, f becomes a constant: about 0.44, that’s the drag coefficient for a sphere. Cars as low as 0.17, flat disk just about 1, making dynamic pressure a good estimate of pressure difference.

Note: for bubbles, $F_d = 2\pi\mu Ud$ all the way out to $\text{Re}=10^5$!

Reynolds number Low velocity: shear stress; high velocity: braking kinetic energy. Ratio of forces:

$$\text{Re} = \frac{\text{convective momentum transfer}}{\text{shear momentum transfer}} = \frac{\text{inertial forces}}{\text{viscous forces}} \simeq \frac{\rho u_y \frac{\partial u_x}{\partial y}}{\mu \frac{\partial^2 u_x}{\partial y^2}} \simeq \frac{\rho U U / L}{\mu U / L^2} = \frac{\rho U L}{\mu}. \quad (4.31)$$

4.4 March 16, 2005: Sphere drag and Reynolds number

Mechanics:

- PS4 due 3/30
- Course evals today...

Muddy from last time:

- Flow rate and average velocity. Last time looked at flow through tube, result was Hagen-Poiseuille: equation:

$$Q = \frac{\pi(P_1 - P_2)}{2\mu L} \left[\frac{R^2 r^2}{2} - \frac{r^4}{4} \right]_0^R = \frac{\pi(P_1 - P_2)R^4}{8\mu L}. \quad (4.32)$$

Didn't really discuss units, this is in volume/time, m³/seconds.

Also, gives average velocity in confined flows:

$$u_{av} = \frac{Q}{A_{xs}} = \frac{\frac{\pi(P_1 - P_2)R^4}{8\mu L}}{\pi R^2} = \frac{(P_1 - P_2)R^2}{8\mu L}. \quad (4.33)$$

Recall that the velocity profile was:

$$u_z = \frac{P_1 - P_2}{4\mu L} (R^2 - r^2), \quad (4.34)$$

with a maximum at $r = 0$. So for a tube, average velocity is *half* of maximum velocity.

What about flow down a plane, or channel flow?

$$u_x = \frac{g \sin \theta}{2\nu} (2Ly - y^2) \quad (4.35)$$

Flow rate: Q , volume per unit time through a surface. If width of the falling film is W , then flow rate is:

$$Q = \int_S \vec{u} \cdot \hat{n} dA = \int_{y=0}^L u_x W dy = \frac{Wg \sin \theta}{\nu} \left[\frac{Ly^2}{2} - \frac{y^3}{6} \right] = \frac{Wg \sin \theta L^3}{\nu} \quad (4.36)$$

Average velocity is Q/A , in this case Q/LW :

$$u_{av} = \frac{Q}{LW} = \frac{g \sin \theta L^2}{3\nu}; \quad (4.37)$$

$$u_{max} = u_x|_{y=L} = \frac{g \sin \theta L^2}{2\nu}. \quad (4.38)$$

So average velocity is 2/3 of maximum for falling film, channel flow, etc.

Reynolds number Dimensional analysis:

$$|\vec{F}_d| = f(V, \mu, d, \rho)$$

Five parameters, three base units, so two dimensionless parameters. Four different nondimensionalizations!

Keep	π_F	π_{other}
F, μ	$\frac{F}{\rho V^2 d^2}$	$\pi_\mu = \frac{\mu}{\rho V d}$
F, ρ	$\frac{F}{\mu V d}$	$\pi_\rho = \frac{\rho V d}{\mu}$
F, V	$\frac{F \rho}{\mu^2}$	$\pi_V = \frac{\rho V d}{\mu}$
F, d	$\frac{F \rho}{\mu^2}$	$\pi_d = \frac{\rho V d}{\mu}$

The first is the ratio of total force to the product of dynamic pressure and area, the kinetic energy drag term. The second is the ratio of total force to the viscous drag. The third and last are identical, and relatively useless physically. So, should we use the first or second?

With different shapes, there is very nearly the same behavior at low Reynolds number, but at high Reynolds number there are different curves, roughly proportional to V^2 . If use second, get one flat π_F in Stokes flow, multiple lines for different shapes. If use first, one line for laminar, multiple flats for different shapes. So the first is generally more convenient.

To make it physically relevant, we define f by $F = fKA$ so $f = F/KA$ where K is the kinetic energy density $\frac{1}{2}\rho V^2$ and A the relevant area, here the cross section $\frac{1}{4}\pi d^2$. And by convention we take the reciprocal of the above π_μ which is $\rho Vd/\mu$. This gives: as the ordinate

$$f = f(\text{Re}), \frac{F_d}{\frac{1}{2}\rho V^2 \cdot \frac{1}{4}\pi d^2} = f \left(\frac{\rho V d}{\mu} \right). \quad (4.39)$$

Stokes flow ($\text{Re} < 0.1$) friction factor:

$$F_d = 3\pi\mu dV \Rightarrow f = \frac{F_d}{KA} = \frac{3\pi\mu dV}{\frac{1}{2}\rho V^2 \cdot \frac{1}{4}\pi d^2} = \frac{24\mu}{\rho V d} = \frac{24}{\text{Re}}. \quad (4.40)$$

High Reynolds number friction factor:

$$F_d = c_d \cdot \frac{1}{2}\rho V^2 \cdot \frac{1}{4}\pi d^2 \Rightarrow f = \frac{F_d}{KA} = c_d, \quad (4.41)$$

where c_d is the drag coefficient equal to 0.44 for a sphere.

4.5 March 18: Engineering and society

September 11 The day meant a lot of things to a lot of people. On its anniversaries, the occasion is commemorated in a number of ways, here in Boston, in my hometown of New York City, and around the country and the world. I can't hope to be as profound as some of the speakers at those services, but can talk about a few things it meant to me personally, in particular as I have reflected on my decision to become an engineer, and my purpose in the profession. Perhaps some of it will resonate with one or two of you; I invite your comments or questions, and we'll take as long for this as we have to. The timing may seem odd, coming in late March instead of mid-September, but its reasons will become apparent presently.

I'd like to start nine days before the tragedy, when I was in New York for my sister-in-law's wedding. My wife's parents live in Brooklyn, which is where the ceremony was held, but we were staying with her aunt and uncle in Long Island. At least twice a day in the few days beforehand, we drove the Belt Parkway and Brooklyn-Queens Expressway, wrapping around Brooklyn, passing under the Verazzano bridge and entering New York Harbor, with the view of the Statue of Liberty and the majestic buildings rising ahead, the skyline dominated, of course, by the World Trade Center.

During those drives, I recalled the experience of my High School French teacher Mr. Schwartzbart, an Austrian Jew who survived World War II in a rural Belgian boys' camp which, unknown to him at the time, was made up entirely of Jewish boys, and in fact, was set up to keep them safe throughout the Nazi occupation. He described the terror he felt under the occupation, and then the arrival of the American soldiers, "All of them giants," he said, then pointed to me, "like Adam," they had come to set the continent free.

And he described the journey to America as a young teenager, a transforming experience. Most amazing was the entry of his ship carrying scores of poor immigrants like himself into New York Harbor, this impossibly enormous bridge which just got bigger and bigger as they approached (the Verazzano was the longest span in the world for about 50 years), the tranquility of the harbor within, with the great buildings visible ahead including the Empire State, and the Statue of Liberty to his left as they steamed toward Ellis Island (the World Trade Center's construction was still 20 years away). There was an awe-inspiring sense of the magnitude of this great nation of impossible size which had overwhelmed some of the greatest evil the world had ever known, and his heart swelled with joy at the thought that there was such power on the side of liberty.

These days it is fashionable to reflexively cringe at the identification of this country with freedom, and this teacher in particular very frequently commented cynically on the deficiencies in American culture and education. Having come to know this side of him, when we asked why he came to this country, Mr. Schwartzbart's reply surprised us: "The land of the free and the home of the brave." Then after a pause, "It really is true." His personal experience of this gave great weight to these words.

During these drives along the Belt Parkway, my thoughts also turned toward the fragility of the grand edifices, and in particular to the 1993 bombing of the underground parking lot of one of the Twin Towers. Fortunately the towers withstood that attempt to destroy them, but there would surely be more attempts, and no amount of devastation was too horrible for the perpetrators to dream up. Should anything happen, I was grateful for the opportunity to see this beauty, and even to feel a small piece of what Paul Schwartzbart had felt some fifty years earlier. I thought of how fortunate is his generation which came through the Depression, fought that terrible war, and lived to see the nation preside over such a long and prosperous peacetime as the world had perhaps never before known.

So you can imagine my shock when just nine days later, as I sat in my office, my wife called from home to say that while watching CNN, they announced that a plane had crashed into the World Trade Center. Well, I thought, about 60 years ago a small plane hit the Empire State building, I'm sure there was a lot of damage and many people killed, but the rest of the building should be fine. Just a few minutes later she called again to tell me about the second plane, and suddenly I was afraid. Then the Pentagon, and the missing plane in Pennsylvania. My thoughts turned to the Mid-East, and this administration's policy of deliberate neglect in the Israeli-Palestinian peace process. Then the last call, one tower had collapsed. With her voice choking from the tears, she described its fall as "like a house of cards," and could say little more. Immediately, I logged out, got on my bike, and pedaled home as fast as I could.

I'm sure each of us can tell a story about where we were when it happened. Being from New York, I was immediately concerned for friends and family. My wife's grandmother went to the roof of her building in Queens, from where she saw the second plane hit the south tower, and that tower's collapse. I had shared this view every day growing up as I rode the Roosevelt Island tramway to school and saw these buildings which seemed as permanent as mountains. My wife's best friend in College, who lives in the Prospect Heights section of Brooklyn and works in the southern tip of Manhattan, noticed people in his neighborhood looking up and saw some smoke, but rushed into the subway as he was late for work; the packed subway stopped after it left Brooklyn and waited in the tunnel for about 20 minutes before it turned back and he got out and learned what had happened. My Elementary School best friend worked in the 17th floor of Tower 1, and had a bad back which would have made it painful and difficult to get out—if he hadn't been home sick that day.

Then there was my father's friend whom I know well and whose business had just finished moving into the 89th floor of Tower 1. His staff had been told not to come in that morning until 10 AM, because their carpets, freshly washed during the 1-7 AM shift, would need to finish drying. As he drove north on the New Jersey Turnpike, he saw the first plane crash right through the windows of his new office, then took the next exit and went right back to his daughter's kindergarten class.

The previous Spring and Summer I had a course 6 UROP student in my group. His brother worked above the 90th floor of Tower 2, and on the first and second day afterward without a word to anyone in his family, my student grew panicked, then desparate, then increasingly hopeless. His brother finally called to say that a friend had literally dragged him from the office after the first plane hit, and they ran out of the building together just as the second plane smashed into it. He described bits of the hell that was the area around him, but at the time had no other thought than to get away, go home and lie down in shock, not even thinking about his relatives who were trying to reach him. My student described the moment when they connected as one of the happiest of his life.

Another friend was not so fortunate. Her father worked in an upper floor of Tower 2, and was one of just two in his company who didn't make it out. To make matters worse, she was trapped in L.A. because of grounded planes, unable to get back and try to locate him, so day upon day she was not only uncertain and hurting but frustrated at being far from anyone who could help her. She is still grieving, as it's hard to accept that she lost the closest person to her in the world because a handful of maniacs decided to crash a plane into his building.

There are of course tens of thousands more stories like these, so many people were affected directly or knew someone who was. But even if you were not so directly involved, if you're like me, the tragedy didn't end on that day, but played out over and over again in your mind. I can't count how many mornings in the ensuing months I woke up at 3 AM thinking about the towers' collapse, feeling hurt, afraid, angry, and much as I hate to admit it, somewhat vindictive as we learned of the total destruction of the Al Queda camps and cave complexes in Afghanistan.

Then thoughts turned to my own life. What can I do, what's my role in the world, how can I help?

I turned to the motivations I had for entering science and engineering, and materials science in particular, which I came up with in High School. Motivations for studying these things vary greatly, from interest in the subject matter, elegance of the equations, beauty of nature etc., to being able to earn a stable income and support a household, or perhaps a large income, to serving society in some way. My own motivations fell somewhat in the first category, but if I had followed that alone I would have been Course 6-3 (computer science); it was the last of these categories, serving society, which steered me into Materials Science.

As a high school student, I verbalized this service as follows. As a scientist or engineer, I would be helping to solve the world's little problems, which I listed as:

- Agriculture, to feed a growing planet.
- Medicine, allowing people to lead longer, healthier lives.
- Transportation and communications, to bring people together and lessen the chances of conflict. For example, much of the reason war between France and Germany today is unthinkable is because there

are so many more personal cross-border relationships now than in 1940 or 1914, it's very difficult for a propagandist to castigate an entire people as "the enemy" and it's becoming more difficult every year.

- Human interactions with the environment, for sustainable living.
- A recent addition, information access, with implications for democracy, as the biggest enemy of an authoritarian state is the truth.

All of these are important in themselves, but even more important, if we do our jobs well and make a difference in these areas, we help the artists, politicians, economists, philosophers and theologians to solve the big problems, which I would list as:

- World peace.
- Averting famines, and their relief. Almost all famines can be avoided without resort to international aid, and are the result of poor resource management and the vicious cycle of price increases and hoarding by the few who can afford it.
- Real public health, made available to those who need it around the world.
- Justice, including somewhat equitable economic distribution.
- Truth in journalism and history.
- Human happiness and fulfillment.
- Purpose and meaning for our lives.
- Artistic expression of emotions, of values, of that purpose and meaning.
- Last year Ross Benson added: Tolerance of differences.

An important consequence of this understanding of "little problems" and "big problems" is that being a scientist or engineer requires a lot of *faith*, faith that our knowledge and our inventions will be used wisely, for good and not for evil. The more "sciencey" our contributions, the more faith is necessary, with the ultimate example perhaps being nuclear science, which can be used to produce lots of cheap power or cure diseases, or destroy entire cities in an instant. If we work on weapons, they can of course be used for defense or for aggression.

But even if we're not working on nuclear science or weaponry, one of the lessons of September 11 for me is that no matter how careful we are to focus on purely non-military technologies, this tragedy showed that even a civilian jetliner—built to bring people together—can be abused by people with sufficient hatred as a weapon of mass destruction. This is truly frightening for us, and requires us to have that much more faith in the people, institutions and systems surrounding the technology in whose development we participate.

So what should we do? Shall we abandon technology altogether and go back to rubbing sticks together? Perhaps we should join the peace corps? For some of us that will be the answer, but I think there's a lot more that can be done with the little problems that can help to make a real impact on the big ones. So how can we put ourselves in positions to do as much good as possible?

I can think of a few ways, but at your age and even at mine, perhaps the most important is to take a step back and examine what we're doing and why. I have an advisee taking this class now who took off all of last Spring for that very purpose, and ended up returning to MIT (and in fact to Materials Science) that much more focused than the previous December for the experience. Of course, you don't have to take off a semester to do this, there are very good ways to do some of this right here.

First, the HASS and HASS-D subjects present outstanding opportunities for this kind of exploration. MIT is no longer just about training technology leaders, but also about training world leaders who know about technology, and this school has put enormous resources into building world class departments in the Humanities, Arts and Social Sciences. For example, I've heard tremendous things about our Anthropology

department from a variety of external sources, and even within our department we offer a HASS subject called Materials in the Human Experience (3.094) every Spring.

Second, I've made a point of suggesting to all of my advisees that they get to know the MISTI programs (MIT International Science and Technology Initiatives), which do an outstanding job not just of sending students to companies, universities and government labs in foreign countries, but also preparing them for the trip, even culturally and psychologically.

Third, develop a habit of using your wealth to support organizations and causes which effectively promote what you view as positive values. You may not have much now, but you will later, and getting into this habit is not hard; furthermore, membership in many of these organizations requires a contribution of as little as \$30. If you like I can discuss offline some of the organizations I've given to since my undergraduate years, one even since high school.

Fourth, look for opportunities to participate in the process of improving lives yourselves. Whether tutoring or mentoring, or working in a social justice organization, or writing to Congress, participating in society in a meaningful way is important to making it all work, and I believe important to improving ourselves too. Believe it or not, time is actually one resource which you will *not* have more of later in life than you have now, particularly if children become part of your life.

Fifth and perhaps most importantly, get to know your fellow students. This buzzword is repeated over and over again, but it's worth repeating yet again: because MIT attracts the best and brightest from all over the world, the *diversity* of the students on this campus is truly extraordinary, it's almost certainly broader and deeper than anything you've experienced before college, and almost certainly broader and deeper than anything you will ever experience later in life. That goes for many other universities as well, though somewhat less so on the graduate level and beyond. And by getting to know your colleagues, I don't just mean hanging out and eating pizza, nor even getting to know what spices they use to cook lamb, though food is of course an important part of intercultural social interaction. I'd encourage you to learn something about your friends' lives, their families, their values—and be willing to discuss these aspects of yourselves too.

And given its importance, I'd encourage you to learn something about your friends' faith. Human institutions, organizations, systems and even nations are terrific, but never perfect, as we learned in a powerful way on September 11. Participating in and strengthening them is an important and honorable activity, but I believe that placing all of our hope on them is not viable in the long term. At some point they're going to let us down, as this country has in some ways let down my French teacher Mr. Schwartzbart. Furthermore, evidence abounds for forces at work in the universe beyond those of physics, and even grows with the increase of human knowledge about this universe; perhaps the most significant example is the Anthropic Principle in Cosmology, which some of you may have heard of and I'd be happy to discuss offline.

That concludes what I said last year: the tragedy reminds us that our work here is very important, but must be viewed in context, and done with faith that it will be used for the broad purposes for which we intend it. Since writing this for the Fall of 2002, time has passed and some of the emotions have subsided just a bit, also several important things have happened, or have not happened, causing my own feelings about this to be somewhat more complicated.

For one thing, the message from Washington continues to urge us to live out lives as if nothing had happened, because if we changed anything, we'd be giving the terrorists what they want. But what sense does this make, when important things have changed, and as citizens there are things we can do on a daily basis to improve our country's security, and the silence from Washington has been deafening.

A while ago I saw a book provocatively titled, "When you ride alone, you ride with bin Laden." The cover art was derived from a World War II poster, "When you ride alone, you ride with Hitler," whose point was that the practices of avoiding driving, carpooling, and using public transportation save gasoline needed for the war effort. In that vein, an important thing which has *not* happened is that there has been no effort whatsoever on a national level to reduce our dependence on imported oil, which has been a huge factor in our problems in the Middle East. In fact, we've seen the opposite in this administration's rollback in fuel economy standards, and heard talk about the costs to the auto manufacturers and consumers of requiring increases in efficiency, with no mention whatsoever of the multitude of costs of continuing to burn fossil fuels as extravagantly as we like.

Another thing which has changed my view of the world is the war in Iraq. For months, the administration hyped any evidence at all for Iraqi connections to Al Qaeda and possession or development of weapons of mass destruction (WMD). Then inspections were allowed (to be fair, largely due to U.S. pressure, and no thanks to the posturing of certain countries like France), and one-by-one the inspections eliminated every piece of purported WMD evidence save the rumor about uranium purchase from Niger. And so with that one rumor as justification, we sent an invasion force to Kuwait, and two years ago this Sunday, some two hundred thousand U.S. soldiers—including my brother—crossed the border and destroyed the Iraqi army in about four weeks.

I personally disagree with the war pretty strongly, but today would like to present a somewhat more balanced view than I did in the Fall of 2003, and talk about some lessons we can draw from the experience.

First, unconditional and stubborn opposition (particularly from France) was of no help in encouraging Saddam Hussein to accept inspections. The credible threat of invasion was necessary for him to let inspectors in with open access, and we all learned a lot from those inspections which informed the debate on the eventual start of the war.

As evidence lined up between September 2002 and March 2003, it was overwhelmingly against connections between Iraq and terrorism, and against the presence of WMD or an active WMD program.

The proverb talks about following a “multitude of wise counsel” which in this case was solidly against the war, including three of the five Security Council permanent members, some of our most important allies, and both of our neighbors. The three most prominent foreign policy advisors of the previous Republican administration of Bush Sr. came out strongly against the war during the Fall of 2002 via *New York Times* op-ed pieces. And of course there’s Colin Powell, whose opposition in private stood in strong contrast to his public stance.

Never brag about the lethality of weaponry. Today with over 1000 Americans and some 100,000 Iraqis dead, who is the better for all of that “Shock and Awe”? Those lives lost very nearly included that of my own brother, a Captain in the U.S. Army third infantry division’s second brigade, whose unit was hit by an Iraqi missile just after their capture of downtown Baghdad. Like my Course 6 UROP student more than three years ago, the days between learning of the attack and confirming my brother’s safety were some of the longest of my life. I cannot imagine the terror and grief of hundreds of thousands of loved ones of Iraqi soldiers who did not know for weeks or months whether their sons, brothers, husbands or fathers were dead or alive, nor the pain of those whose worst fears were in the end confirmed.

A great disappointment was the childishness with which the administration spoke of “punishing” the opponents to the war—particularly the French—and then turned around to ask them to contribute money and troops to the occupation and reconstruction to reduce the resource burden on us.

Turning to the other side, that August as my brother’s convoy rolled through southern Iraq on his way to Kuwait and back home, he passed through what had been the home of the Marsh Arabs, victims of Saddam Hussein’s ethnic cleansing which in this case took the form of diverting water away from these areas so they starved. That tyrant is gone, and can we put a price on the ensuing freedom?

In the long term, the most diplomatically problematic aspect of the war is the precedent it sets for accusing a nation of violations of one sort or another, brushing aside international outcry for restraint, and using military superiority to crush the weaker victim. This precedent can easily be abused by, say, Turkey, Syria, Egypt, Jordan and Saudi Arabia against Israel, North Korea against the South, Russia against the former Soviet Republics, China against Taiwan—any nation with a fight to pick can say, “But of course it’s been done before, by the Land of the Free and Home of the Brave!”

And so we are reminded of our duty as citizens to speak out about matters of importance to our country. And in particular, as scientists and engineers we have the duty to speak out with authority on certain issues such as the small cost of reducing energy consumption, and the enormous costs of not doing so. Most of all, in the changed world our need for faith is greater than ever, in our work as well as our outlook for the future. I welcome any comments, contributions, or questions.

4.6 March 28, 2005: Friction factors, boundary layers

Tubes: recall laminar velocity profile

$$u_z = \frac{P_1 - P_2}{4\mu L}(R^2 - r^2), \quad (4.42)$$

shear stress at $r = R$:

$$\tau_{rz} = -\mu \frac{\partial u_z}{\partial r} = \frac{P_1 - P_2}{2L} R \quad (4.43)$$

Average velocity is half maximum:

$$u_{av} = \frac{P_1 - P_2}{8\mu L} R^2, \quad (4.44)$$

so the shear can be given in terms of the average velocity:

$$\tau_{rz} = \frac{4\mu u_{av}}{R} = \frac{8\mu u_{av}}{d}. \quad (4.45)$$

Laminar flow friction factor:

$$f = \frac{\tau}{\frac{1}{2}\rho V^2} = \frac{\frac{8\mu}{d} u_{av}}{\frac{1}{2}\rho V^2} = \frac{16\mu}{\rho V d} = \frac{16}{\text{Re}}. \quad (4.46)$$

To calculate drag force: Reynolds number (and surface roughness) \rightarrow friction factor $f \rightarrow \tau = fK$, $F_d = fKA$.
Difference with sphere: no stagnation, sudden transition to turbulence.

“Boundary layers” in a solid Thought experiment with moving solid: extruded polymer thick plate (like PS2 extruded rod problem). Start at high temp, if thick and well-cooled so large Biot then constant temperature on surface; no generation. Full equation:

$$\frac{DT}{Dt} = \alpha \nabla^2 T. \quad (4.47)$$

Here, $u_y = 0$, and for $\delta_T \ll x$ so boundary layer is thin, then

$$\frac{\partial^2 T}{\partial y^2} \gg \frac{\partial^2 T}{\partial x^2}, \quad (4.48)$$

can simplify to:

$$u_x \frac{\partial T}{\partial x} = \alpha \frac{\partial^2 T}{\partial y^2}. \quad (4.49)$$

Transform: time $t = x/u_x$, becomes diffusion equation, erf solution:

$$\frac{T - T_s}{T_i - T_s} = \text{erf} \frac{y}{2\sqrt{\alpha x/u_x}} \quad (4.50)$$

If we define δ as where we get to 0.99, then $\text{erf}^{-1}(0.99) = 1.8$, and

$$y = \delta \text{ where } \frac{\delta}{2\sqrt{\alpha x/u_x}} = 1.8 \Rightarrow \delta = 3.6\sqrt{\frac{\alpha x}{u_x}}. \quad (4.51)$$

Obviously breaks down at start $x = 0$, but otherwise sound.

Boundary layers in a fluid Now we want to calculate drag force for flow parallel to the plate.

Similar constant IC to solid, infinite BC, call it U_∞ . Difference: BC at $y = 0$: $u_x = u_y = 0$. Have to solve 2-D incompressible steady-state Navier-Stokes:

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} = 0 \quad (4.52)$$

$$u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} = -\frac{\partial p}{\rho \partial x} + \nu \left(\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} \right) \quad (4.53)$$

$$u_x \frac{\partial u_y}{\partial x} + u_y \frac{\partial u_y}{\partial y} = -\frac{\partial p}{\rho \partial y} + \nu \left(\frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial y^2} \right). \quad (4.54)$$

Then a miracle occurs, the Blasius solution for $\delta \ll x$ is a graph of u_x/U_∞ vs. $\beta = y\sqrt{U_\infty/\nu x}$; hits 0.99 at ordinate of 5:

$$\delta = 5.0 \sqrt{\frac{\nu x}{U_\infty}}. \quad (4.55)$$

Why 5.0, not 3.6? Because there must be vertical velocity due to mass conservation (show using differential mass equation and integral box), carries low- x -velocity fluid upward.

Entrance Length For channel flow between two parallel plates spaced apart a distance H , we can define the entrance length L_e as the point where the boundary layers from each side meet in the middle. The twin Blasius functions are close enough to the parabolic profile that we can say it's fully-developed at that point. So we can plug in the boundary layer equation if flow is laminar:

$$x = L_e \Rightarrow \frac{H}{2} = \delta = 5.0 \sqrt{\frac{\nu x}{U_{av}}}, \quad (4.56)$$

$$L_e = \frac{H^2 U_{av}}{100\nu}. \quad (4.57)$$

If $L_e \ll L$, then flow is fully-developed for most of the tube, so the fully-developed part will dominate the drag force and $F_d = \tau \cdot 2\pi RL$.

4.7 March 30, 2005: Plate drag, turbulence

Recall from last time: Blasius solution to 2-D Navier Stokes around flat plate: u_x/U_∞ vs. $\beta = y\sqrt{U_\infty/\nu x}$; hits 0.99 at ordinate of 5. At $y = 0$, slope: 0.332, so viscous drag:

$$\tau_{yx} = -\mu \frac{\partial u_x}{\partial y} = -\mu \frac{\partial u_x}{\partial \beta} \frac{\partial \beta}{\partial y} \quad (4.58)$$

$$\tau_{yx} = -\mu \cdot 0.332 U_\infty \sqrt{\frac{U_\infty}{\nu x}} \quad (4.59)$$

Note: a function of x (larger near leading edge), diverges at $x = 0$! But $\delta \ll x$ does not hold there.

Now set to a friction factor:

$$\tau_{yx} = -0.332 \sqrt{\frac{\rho \mu U_\infty^3}{x}} = f_x \cdot \frac{1}{2} \rho U_\infty^2 \quad (4.60)$$

This time τ is not constant, so we have different $f_x = \tau/K$ and $f_L = F_d/KA$. Let's evaluate both:

$$f_x = 0.664 \sqrt{\frac{\mu}{\rho U_\infty x}} = \frac{0.664}{\sqrt{\text{Re}_x}} \quad (4.61)$$

Lengthwise, global drag force, average friction factor. Neglect edge effects again...

$$F_d = \int \tau_{yx} dA = W \int_{x=0}^L \tau_{yx} dx \quad (4.62)$$

$$F_d = W \int_{x=0}^L 0.332 \sqrt{\frac{\rho \mu U_\infty^3}{x}} dx \quad (4.63)$$

$$F_d = 0.332 W \sqrt{\rho \mu U_\infty^3} \cdot 2\sqrt{L} \quad (4.64)$$

$$F_d = 0.664 W \sqrt{\rho \mu U_\infty^3 L} \quad (4.65)$$

Now for the average friction factor/drag coefficient:

$$f_L = \frac{F_d}{KA} = \frac{0.664 W \sqrt{\rho \mu U_\infty^3 L}}{\frac{1}{2} \rho U_\infty^2 \cdot WL} = 1.328 \sqrt{\frac{\mu}{\rho U_\infty L}} = \frac{1.328}{\sqrt{\text{Re}_L}} \quad (4.66)$$

For a sphere, only defined average/global; for a tube, that and local are the same; but for a BL, they're different.

Also, note dimensionless BL thickness:

$$\delta = 5.0 \sqrt{\frac{\nu x}{U_\infty}} \Rightarrow \frac{\delta}{x} = 5.0 \sqrt{\frac{\nu}{U_\infty x}} = \frac{5.0}{\sqrt{\text{Re}_x}} \quad (4.67)$$

Dimensionless entrance length too:

$$L_e = \frac{H^2 U_{av}}{100\nu} \Rightarrow \frac{L_e}{H} = \frac{U_{av} H}{100\nu} = \frac{\text{Re}_H}{100}. \quad (4.68)$$

Turbulence Started watching the movie, unfortunately didn't finish...

4.8 April 1, 2005: Turbulence

Turbulence Starting instability, energy cascade. Vortices grow in a velocity gradient because of momentum convection, damped due to viscosity; therefore, tendency increases with increasing Re.

Resulting behavior:

- Disorder.
- “Vorticity” in flow, 3-D.
- Lots of mixing, of mass and heat as well as momentum.
- Increased drag due to momentum mixing, as small vortices steal energy from the flow.

Turbulent transport: enhanced viscosity, also enhanced diffusivity, conductivity. $\nu_t \simeq \alpha_t \simeq D_t$.

Energy cascade and the Kolmogorov microscale. Largest eddy $Re=UL/\nu$, smallest eddy Reynolds number $u\ell/\nu \sim 1$. Energy dissipation, W/m^3 ; in smallest eddies:

$$\epsilon = \eta \left(\frac{du}{dx} \right)^2 \sim \eta \frac{u^2}{\ell^2}. \quad (4.69)$$

Assuming most energy dissipation happens there, we can solve these two equations, get smallest eddy size and velocity from viscosity, density and dissipation:

$$u \sim \ell \sqrt{\frac{\epsilon}{\eta}} \Rightarrow \frac{\rho \ell^2}{\eta} \sqrt{\frac{\epsilon}{\eta}} \sim 1, \quad (4.70)$$

$$\ell \sim \left(\frac{\eta^3}{\rho^2 \epsilon} \right)^{\frac{1}{4}}. \quad (4.71)$$

This defines the turbulent microscale. For thermal or diffusive mixing, turbulence can mix things down to this scale, then molecular diffusion or heat conduction has to do the rest. Time to diffusive mixing in turbulence is approximately this ℓ^2/D .

So suppose we turn off the power, then what happens? Smallest eddies go away fast, then larger ones, until the whole flow stops. Timescale of smallest is ℓ^2/ν , largest is L^2/ν_t , turbulent effective viscosity. Get into modeling and structure later if time is available.

[Didn't cover...] Modeling: $K - \ell$ and $K - \epsilon$ modeling ($C_\mu, C_1, C_2, \sigma_K$ and σ_ϵ are empirical constants):

$$K = \frac{1}{2} \rho (u_x'^2 + u_y'^2 + u_z'^2), \nu_t = C_\mu \frac{K^2}{\epsilon}. \quad (4.72)$$

$$\frac{DK}{Dt} = \nabla \cdot \left(\frac{\nu_t}{\sigma_K} \nabla K \right) + \nu_t \nabla \vec{u} \cdot (\nabla \vec{u} + (\nabla \vec{u})^T) - \epsilon. \quad (4.73)$$

$$\frac{D\epsilon}{Dt} = \nabla \cdot \left(\frac{\nu_t}{\sigma_\epsilon} \nabla \epsilon \right) + C_1 \frac{\nu_t \epsilon}{K} \nabla \vec{u} \cdot (\nabla \vec{u} + (\nabla \vec{u})^T) - C_2 \frac{\epsilon^2}{K}. \quad (4.74)$$

Parviz Moin and John Kim, “Tackling Turbulence with Supercomputers,” *Scientific American* January 1997 pp. 62-68.

Turbulence may have gotten its bad reputation because dealing with it mathematically is one of the most notoriously thorny problems of classical physics. For a phenomenon that is literally ubiquitous, remarkably little of a quantitative nature is known about it. Richard Feynman, the great Nobel Prize-winning physicist, called turbulence “the most important problem of classical physics.” Its difficulty was wittily expressed in 1932 by the British physicist Horace Lamb, who, in an address to the British Association for the Advancement of Science, reportedly said, “I am an old man now, and when I die and go to heaven there are two matters on which I hope for enlightenment. One is quantum electrodynamics, and the other is the turbulent motion of fluids. And about the former I am rather optimistic.”

4.9 April 4, 2005: Batch and Continuous Flow Reactors

Questions/Muddy...

- Friction factor role: dimensionless shear stress or drag force.
- Force or shear stress procedure:

$$\left. \begin{array}{l} U \\ L \\ \rho \\ \mu \end{array} \right\} \Rightarrow \text{Re} \Rightarrow f \Rightarrow \tau, F_d \quad (4.75)$$

- Physical modeling, e.g. wind tunnel and water modeling: if the dimensionless parameters are right and the same assumptions are satisfied, then every detail is identical. Here f is only a function of Re.

Batch and Continuous Flow Reactors Examples: catalytic combustion (that dimensional analysis problem in PS3), alveoli/breathing (continuous/batch mixed). Batch: generally better conversion in same volume (see why); continuous: consistent quality, no setup time.

Steelmaking: batch, but folk want to make continuous.

Basic definitions, motivating examples. Economics: batch better for flexibility, continuous for quality and no setup time (always on).

Two types: volumetric and surface reactors. Volume V , generation due to chemical reaction; we'll discuss first-order $A \rightarrow B$, so

$$G = -kC_A. \quad (4.76)$$

For a volume batch reactor, start with C_{A0} , dump into reactor, it goes:

$$\text{accum} = \text{generation} \quad (4.77)$$

$$V \frac{dC_A}{dt} = -VkC_A \quad (4.78)$$

$$\ln(C_A) = -kt + A \quad (4.79)$$

$$\frac{C_A}{C_{A0}} = \exp(-kt) \quad (4.80)$$

For mass transfer-limited surface batch reactor, say

$$\text{accum} = \text{out} \quad (4.81)$$

$$V \frac{dC_A}{dt} = -Ah_D C_A \quad (4.82)$$

$$\frac{C_A}{C_{A0}} = \exp\left(-\frac{h_D A}{V} t\right) \quad (4.83)$$

Two extremes in continuous reactor behavior with flow rate Q : plug flow and perfect mixing.

Plug flow is like a mini-batch with $t_R = V/Q$, draw plug in a pipe, derive:

$$\frac{C'_A}{C_{A0}} = \exp\left(-\frac{kV}{Q}\right) \quad (4.84)$$

With a surface, the V s cancel, left with

$$\frac{C'_A}{C_{A0}} = \exp\left(-\frac{h_D A}{Q}\right) \quad (4.85)$$

Perfect mixing: in, out, gen, no accum, out at C'_A reactor conc:

$$0 = QC_{A0} - QC'_A - kVC'_A \quad (4.86)$$

$$\frac{C'_A}{C_{A0}} = \frac{Q}{Q + kV} = \frac{1}{1 + \frac{kV}{Q}} \quad (4.87)$$

With area:

$$\frac{C'_A}{C_{A0}} = \frac{1}{1 + \frac{hDA}{Q}} \quad (4.88)$$

4.10 April 6, 2005: Chemical reactors, porous media

Recall results for plug flow, perfect mixing:

- Plug flow: homogeneous $C_A/C'_A = \exp(-kV/Q)$, heterogeneous $C_A/C_{A0} = \exp(-k''A/Q)$.
- Perfect mixing: homogeneous $C_A/C'_A = 1/(1+kV/Q)$, heterogeneous $C_A/C_{A0} = 1/(1+kA/Q)$.

How to tell whether plug or mixed? Tracers, Peclet number (more details in the slides).

Porous Media Darcy's Law for seeping flow through a medium:

$$Q = \frac{k_D A \Delta P'}{L} \quad (4.89)$$

($\Delta P'$ includes Δp and gravity), where k_D is the permeability. For a given geometry, we can define specific permeability \mathcal{P} as:

$$k_D = \frac{\mathcal{P}}{\mu}. \quad (4.90)$$

The superficial velocity V_0 is then given by:

$$V_0 = \frac{Q}{A} = -\frac{\mathcal{P}}{\mu} \left(\frac{\partial P}{\partial x} - \rho g \right) \quad (4.91)$$

Tube bundle approximation: average velocity in the pores with volume fraction ω is:

$$\bar{V} = \frac{V_0}{\omega}. \quad (4.92)$$

Then define the hydraulic radius R_h for a fluid volume V_h with wetting surface area A_w as:

$$R_h = \frac{V_h}{A_w}. \quad (4.93)$$

For a porous solid of wetting surface area/total volume ratio S , it's usually useful to define the surface area/solid volume ration S_0 as

$$S_0 = \frac{S}{1-\omega}. \quad (4.94)$$

Then the hydraulic radius becomes:

$$R_h = \frac{V_h/V}{A_w/V} = \frac{\omega}{S} = \frac{\omega}{S_0(1-\omega)}. \quad (4.95)$$

Remember the Hagen-Poiseuille equation:

$$Q = \frac{\pi(P_1 - P_2)}{2\mu L} \left[\frac{R^2 r^2}{2} - \frac{r^4}{4} \right]_0^R = \frac{\pi(P_1 - P_2)R^4}{8\mu L}. \quad (4.96)$$

And average velocity:

$$u_{av} = \frac{Q}{A_{xs}} = \frac{\frac{\pi(P_1 - P_2)R^4}{8\mu L}}{\pi R^2} = \frac{(P_1 - P_2)R^2}{8\mu L}. \quad (4.97)$$

Now relate this back to V_0 and R_h :

$$\bar{V} = K_1 \frac{\Delta P' R_h^2}{L\mu}; \quad V_0 = K_1 \frac{\Delta P' R_h^2 \omega}{L\mu}. \quad (4.98)$$

And substituting R_h :

$$V_0 = K_1 \frac{\nabla P' \omega}{L \mu} \frac{\omega^2}{S_0^2 (1 - \omega)^2}. \quad (4.99)$$

This is the Blake-Kozeny equation.

Relate this back to the Darcy equation:

$$Q = \frac{\mathcal{P}}{\mu} \frac{A \Delta P'}{L} \Rightarrow V_0 = \frac{\mathcal{P} \Delta P'}{\mu L}. \quad (4.100)$$

This gives an expression for \mathcal{P} :

$$\mathcal{P} = K_1 \frac{\omega^3}{S_0^2 (1 - \omega)^2}. \quad (4.101)$$

Note that for packed beds, $K_1 \simeq 1/4.2$.

Now beyond laminar flow, need a f -Re correlation. Define the Reynolds number:

$$\text{Re} = \frac{\rho \bar{V} R_h}{\mu} = \frac{\rho V_0}{\mu (1 - \omega) S_0}, \quad (4.102)$$

Later we'll relate this to a friction factor.

4.11 April 8, 2005: Wrap up porous media, Deformation processing

Porous media: calculating K_1 starting with single tube average velocity:

$$u_{av} = \frac{Q}{A_{xs}} = \frac{\Delta P R^2}{8\mu L}. \quad (4.103)$$

Definitions:

- ω is pore volume fraction (so $1 - \omega$ is solid volume fraction)
- S =area/vol
- S_0 =area/solid vol= $S/(1 - \omega)$
- R_h =hydraulic radius=fluid volume/wetting area $V_h/A_w = \omega/S_0(1 - \omega)$.

Then said average fluid velocity in pores (fluid phase) is like tube flow:

$$\bar{V} = K_1 \frac{\Delta P' R_h^2}{L\mu}; \quad V_0 = K_1 \frac{\Delta P' R_h^2 \omega}{L\mu} = K_1 \frac{\nabla P' \omega}{L\mu} \frac{\omega^2}{S_0^2(1 - \omega)^2}. \quad (4.104)$$

So set \bar{V} equal to u_{av} :

$$K_1 \frac{\Delta P' R_h^2}{L\mu} = \frac{(P_1 - P_2) R^2}{8\mu L} \quad (4.105)$$

$$K_1 \left(\frac{R}{2}\right)^2 = \frac{R^2}{8} \quad (4.106)$$

$$K_1 = \frac{1}{2}. \quad (4.107)$$

For a packed bed of spheres, around 1/4.2 or 1/5, differences in literature.

This works for Stokes flow (laminar in tubes); how to define Reynolds number?

$$\text{Re} = \frac{\rho \bar{V} R_h}{\mu} = \frac{\rho V_0}{\mu(1 - \omega) S_0}, \quad (4.108)$$

For a friction factor, we get:

$$f_c = \frac{F_d}{KA} = \frac{\Delta P' \cdot A_{xs} \omega}{\rho \bar{V}^2 \cdot A_w} = \frac{\Delta P' V}{L} \frac{\omega^3}{\rho V_0^2 S_0(1 - \omega)V} = \frac{\Delta P' \omega^3}{L \rho V_0^2 S_0(1 - \omega)}. \quad (4.109)$$

For slow flow, substitute V_0 expressions to get $f_c = 4.2/\text{Re}$; higher velocities get Ergun equation whose dimensionless version is:

$$f_c = \frac{4.2}{\text{Re}} + 0.292. \quad (4.110)$$

Deformation Processing

- Non-Newtonian fluids, Viscoelasticity
- Deformation mechanisms: metals, polymers
- Stress-strain, sheet forming, stability
- Consolidation processes and mechanisms: sintering, HIP, compression molding

4.12 April 11, 2005: Non-Newtonian flow

Recall 2-D channel flow at steady-state:

$$0 = -\frac{\partial P}{\partial x} - \frac{\partial \tau_{xx}}{\partial x} - \frac{\partial \tau_{yx}}{\partial y} + F_x. \quad (4.111)$$

In the absence of force in the x -direction, and with uniform pressure gradient everywhere $\partial P/\partial x = \Delta P/L$, we get:

$$\tau_{yx} = \frac{\Delta P}{L}y + \text{const.} \quad (4.112)$$

Shear stress is linear regardless of the flow rheology.

Non-Newtonian: graphs of τ_{yx} vs. $\partial u_x/\partial y$. Categories:

- Bingham plastic: finite yield stress, beyond that moves with strain proportional to stress minus yield stress, but up to it nothing. Some heavily-loaded liquids, polymer composites; semi-solid metals, toothpaste bond together then break free above τ_y .

Model: yield stress τ_y , slope μ_P :

$$\text{gamma} = \begin{cases} 0, & |\tau| < \tau_y \\ \frac{\tau - \tau_y}{\mu_P}, & |\tau| > \tau_y \end{cases} \quad (4.113)$$

Result: material in the center moves together uniformly, shear layers on either side. If not enough $\Delta P/L$ then it doesn't move at all.

More than 1-D leads to wierd Tresca, von Mises yield criteria, etc.

- Pseudoplastic (shear-thinning), examples: heavily-loaded semi-solid, many polymers get oriented then shear more easily.

Model: power law, $n < 1$.

Power law relation:

$$\tau_{yx} = \mu_0 \left(\frac{\partial u_x}{\partial y} \right)^n$$

- Dilatant (shear-thickening), example: fluid with high-aspect ratio solid bits; blood. More mixing, momentum mixing, acts like viscosity. Platelet diffusivity, concentration near walls...

Model: power-law, $n > 1$.

Viscoelasticity Frictional damping in an elastic solid. Result: slow time-dependent springback. Especially important in polymers; in metals leads to springback after deformation.

Mechanism: example of loading in polymers:

- When first loaded, can have rapid elastic response due to bond stretching and bending.
- Over time, the polymer slowly (depending on temperature) flows to accomodate stress, orienting its molecules in the process.
- When released, the elastic response is restored right away.
- Then entropy slowly flows the molecules into their original isotropic random (non-aligned) conformation, returning the body to its original shape.

It's "elastic" because the final shape is the same as the initial, "viscous" because the change happens slowly, hence "visco-elastic".

Model: spring in series with (spring and dashpot in parallel). More complex: take 3.064 Polymer Engineering.

4.13 April 13, 2005: Deformation Mechanisms

Metal Deformation Generally by motion of dislocations:

- Glide: simple slip of dislocations.
- Note on obstacles and strengthening, strength \propto distance between precip. Note on fine Cu-Al inter-metallic precipitates in aluminum alloys.
- Climb: (vacancy) diffusion-assisted motion between planes to get around obstacles (slow).
- Multiplication: *e.g.* Frank-Read source.
- Forms dislocation cells, power-law creep, like power-law fluid.
- Result: regimes of strain: elastic, easy glide (I), work hardening with dislocation multiplication (II), recovery as dislocs assemble into cells with something like low-angle GBs (III).

Diffusion of vacancies, also ceramics:

- Nabarro-Herring: diffusion across GBs, rate $\propto 1/d^2$.
- Coble: diffusion within GBs, rate $\propto 1/d^3$.

Increasingly important as features (grains) get smaller, both in ceramics and metals. Metals: small grains mean higher strength by Hall-Petch, if nanocrystalline then vacancy diffusion becomes important.

Note on special boundaries: shut down diffusional creep, stress corrosion cracking. Hall-Petch strengthening? Not yet known.

Superplasticity: grain boundary sliding, up to 1000% deformation!

Polymers Flow of molecules as described last time.

- Necking (E.g. PE, PC): growing region of oriented polymer, high-strength yielded region, large strains to failure followed by higher (engineering) stress.
- Crazeing (e.g. PMMA): little cracks open up with polymer bundles bridging, no real “yielding” but visible damage.

Sensitivity of many polymers to solvents: touch with finger \Rightarrow craze in pattern of fingerprint!

Concave stress-strain curve: $d\sigma/d\epsilon > \sigma/\epsilon$ leads to stability in sheet forming. Thinner sections are stronger, thicker ones yield.

Chapter 5

Vapor-Solid Processes

5.1 April 27: Evaporation Processes

(Supplement to slides)

Evaporation/condensation Clapeyron equation: Gibbs free energy

$$G = H - TS = U + PV - TS \quad (5.1)$$

For two phases in equilibrium, along coexistence curve G changes the same way

$$dG_1 = dG_2,$$

$$V_1 dP_1 - S_1 dT_1 = V_2 dP_2 - S_2 dT_2,$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V}.$$

For evaporation:

$$\Delta V \simeq V_{gas} = \frac{nRT}{P}$$

$$\frac{dP}{dT} = \frac{P \Delta H}{nRT^2}$$

$$\frac{dP}{P} = \frac{\Delta H dT}{nRT^2}$$

$$\ln P = -\frac{\Delta H}{nRT} + B. \quad (5.2)$$

With $\Delta H = mT + b$, get another term $+C \ln T$.

Equilibrium pure vapor pressure: Clausius-Clapeyron equation, one form:

$$\log_{10} p_v = -\frac{A}{T} + B + C \log_{10} T(+DT), \quad (5.3)$$

units: torr, conversion factor. If not pure, then mult by activity. Either way, multiply material flux J by ΔH_{vap} for heat flux influence.

Evaporation rate into a vacuum: Langmuir equation

$$J = \frac{p_v}{\sqrt{2\pi MRT}}. \quad (5.4)$$

Here the units should work, go through.

Evaporation ratio: dilute solution of B in A

$$ER_B = \frac{\text{wt}\%B_{\text{vapor}}/\text{wt}\%A_{\text{vapor}}}{\text{wt}\%B_{\text{melt}}/\text{wt}\%A_{\text{melt}}} \quad (5.5)$$

This ratio will be equal to the equivalent ratio of mole fractions, and the ratio of mole fractions in the vapor is in turn equal to the ratio of Langmuir evaporation rates (equation 5.4), so the evaporation ratio can be rewritten as

$$ER_B = \frac{p_{vB}}{X_B \sqrt{M_B}} \frac{X_A \sqrt{M_A}}{p_{vA}} \quad (5.6)$$

where X_i represents the mole fraction of species i in the melt, p_{vi} its vapor pressure, and M_i its molecular weight. Assuming titanium activity roughly follows Raoult's law, its vapor pressure is the product of the vapor pressure in its pure state and mole fraction in the melt, so we rewrite the evaporation ratio again as

$$ER_B = \frac{p_{vB}}{X_B \bar{p}_{vA}} \sqrt{\frac{M_A}{M_B}} \quad (5.7)$$

where \bar{p}_{vi} represents the vapor pressure of pure species i . We then assume Henrian behavior and use the definition of the activity coefficient $p_{vB} = \gamma_B \bar{p}_{vB} X_B$ to arrive at

$$ER_B = \gamma_B \frac{\bar{p}_{vB}}{\bar{p}_{vA}} \sqrt{\frac{M_A}{M_B}} \quad (5.8)$$

Evaporation into gas: boundary layer, $J = h_D(C_s - C_{bulk})$.

Also for evaporation, heat flux from gas, plasma, radiation incl. laser (below), electron beam, etc. Condensation releases a lot of heat!

5.2 April 29, 2005: Vapor phase transport, structure formation

Knudsen number is λ/L , λ is the mean free path. Derivation: volume of cylinder (approx. volume per particle) divided by area

$$\lambda = \frac{1}{\sqrt{2}\sigma^2\rho_{atoms}} = \frac{kT}{\sqrt{2}\sigma^2P}. \quad (5.9)$$

That was easy. But why the $\sqrt{2}$ in the denominator? I believe it has something to do with the velocity distribution.

Different value of L for different situations. To check continuum approximation validity, use chamber size; sometimes will need feature size; for cosine power deviation, use source diameter (and note the graphs use an inverse Knudsen number).

For low Knudsen number in the chamber, use mass transfer coefficients. Example: chemical vapor deposition chamber, uneven h_D leads to uneven distribution, ramp trick to even out the boundary layer.

Slides on the structure zone model... Basic principle: atoms arrive on one timescale, diffuse on another. Fast arrival with low substrate temperature means they can't diffuse well, shadowing and faceting lead to fibrous structure. Slow arrival and/or high substrate temperature means they diffuse very well, dense grains or even equiaxed structure.

Structure zone followup: textured films, preferential orientation by growth selection and by ion beam interactions.

5.3 May 2, 2005: Patterning, polymer deposition

Structure zone model clarification: Argon pressure correlates with sputtering rate and deposition rate at the substrate.

Masking and patterning: start with polymer thin film, use radiation to alter the structure and etching properties:

- Positive tone: radiation breaks the chain backbone, lowering molecular weight, so exposed regions are easier to dissolve.
- Negative tone: radiation cross-links the polymer, giving it a three-dimensional structure which dissolves more slowly.

Such exposure is followed by etching of the substrate material beneath, or deposition of a new thin film, followed by dissolution of the polymer.

Radiation types:

- Far-UV: resolution limited by wavelength and diffraction around mask features; expose a large area at once.
- Electron beams: very small electron “wavelength” allows extremely fine lines; “writing” a pattern takes a long time.

Balance: use EB to make the mask for far-UV patterning.

Making the polymer film: spin coating, produces uniform film in the same way a rotating plate produces a uniform boundary layer.

Vapor deposition of polymer films “Polymer sputtering” obviously isn’t about vaporizing entire polymer chains, but getting monomers to the substrate where they polymerize in situ. Deposition technologies:

- Plasma-enhanced CVD: use a plasma to radicalize monomers, usable for relatively “stubborn” and insensitive molecules like methyl-methacrylate to make PMMA photoresist films, which need lots of radiation to cross-link.
- Hot filament CVD: lower temperature, controllable between 160 and 500°C to make more delicate polymer films.
- Initiated CVD (iCVD): use a reactive initiator such as tert-butyl peroxide to form radicals, can use very sensitive acrylic polymers such as those with epoxy groups.

5.4 May 4, 2005: Coherent/epitaxial films, nanostructure formation

Coherent films, strained epitaxial films. Epitaxy basically means growing new material with the same lattice spacing. Applications:

- High-quality films of various types: early giant magnetoresistance (GMR) films were alternating Fe/Cr on Al_2O_3 sapphire substrates.
- Heterojunction lasers: deposit together GaAs, AlAs, AlAs layers pump electrons and holes, GaAs has smaller bandgap in middle to let them in in an inverted state. Single crystal really helps conduction. GaAs and AlAs have very close lattice spacing, different band gap.
- III-IV devices on Si-Ge: (Ga,Al)As has lattice spacing between Si and Ge; Si and Ge form solid solution with varying lattice spacing between the two. Eugene Fitzgerald (MIT DMSE) pioneered this.

If deposition is *really* slow, and entropy of roughness really high, and temperature pretty high then can use RHEED to determine when each layer completes, and make alternating layers in a superlattice; pretty cool!

Making nanostructures Different ways to make nano-structured materials:

- Fancy deposition: vapor-liquid-solid, anything from alumina whiskers to GaN nanowires. Start with high-surface energy metal which beads up, nucleates whisker and moves with it as it grows. GaN: JMR 18:2 2003 p. 245; ZnO: JMR 18:3 2003 p. 714. Question: is it really liquid? Nature Materials piece shows good data fitting from a solid diffusion model: Nature Materials Nature Materials 3:10 2004 p. 677.
- Catalytic thermal vapor deposition: CNTs catalyzed by nickel particles.
- Very large strains on small scales: ball milling, friction stir processing. Low temperature keeps it solid, large deformation results in nanoscale grains.
- Surface deformation: surface mechanical attrition. JMR 19 p. 1623 2004.
- Self-assembly: proteins have bits that fit, just fall into place. Microtubule formation by a protein pair. Nanoparticles too: chemical function on the surface can attach them together in ways which form structure.
- Templated self-assembly of block copolymers: Nature Materials 3:11 2004 p. 823 (Anne Mayes, Caroline Ross; Ned Thomas does some of this too).

(JMR = Journal of Materials Research, published by the Materials Research Society.)

5.5 May 6, 2005: Process Selection

Seen materials selection: PS1 thermal properties, Randy's charts. Graph types:

- k vs. ρc_p : thermal diffusivity, unsteady flux.
- E vs. ρ : best stiffness-to-weight for uniaxial tension, rod, plate.
- E vs. σ_y : elastic strain to yield.

Now process selection: visualize process attributes, make intelligent decisions. Ashby: pioneered both types of selection.

Being 2-D thinkers (eyes, screen tech), can make helpful 2-D graphs:

- Hardness vs. melting point: if both high, need powder sintering/HIP or

Moving on: Kirchain materials choice class this Fall.

5.6 May 11, 2006: Miscellaneous

Random topics...

Recyclability and entropy Recyclability example: aluminum, takes energy to extract, just melt and recycle, right? But suppose it's an aluminum film on a polymer, like a potato chip bag. Then you're in trouble, can't just melt it, it will oxidize with the plastic.

So entropy is important too. Reflected in the difficulty of separating materials. Other examples: copper in steel, magnesium and other elements in aluminum. Gooseberry's vs. Anna's Taqueria packaging...

Concept: "exergy" defined as free energy relative to ambient chemical potentials, can be thought of as useful energy. "There cannot be an 'energy crisis', as energy is always conserved. (This is the essence of the first law of thermodynamics.) However exergy is a scarce resource which we are depleting daily." Burning fossil fuels does not reduce energy of system, but does reduce available energy (in fact, greenhouse gases increase energy on earth).

The original paper: Keenan, J.H. "Availability and Irreversibility in Thermodynamics." *Br. J. Appl. Phys.*; 1951; 2.

Questions on the future of 3.044

- What new materials or experiences would be helpful for learning about the processes discussed here? Labs, computation applets, etc.?
- This class has been part analysis/modeling and part process description. Would you say the balance between these has been appropriate, or should there have been more of one or the other?
- How could this course be better tied to 3.042?