

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

**Mathematical Methods
for Materials Scientists and Engineers**

3.016 Fall 2010

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PROBLEM SET 5: Out: 12 Oct. AND Due: 25 Oct.

INDIVIDUAL ASSIGNMENTS SHOULD BE A COMBINATION OF YOUR HAND-WORKED SOLUTIONS AND OTHER PRINTED MATERIAL—THEY SHOULD BE PLACED IN THE MAILBOX OUTSIDE PROF. CARTER’S DOOR. EMAIL GROUP ASSIGNMENTS TO 3016-psets(the symbol at)pruffle.mit.edu

For the individual problems indicated as “Handworked”, you should work your solutions by hand and show your work. Print the results of software-worked solutions, and staple them to your hand-worked assignments before turning them in.

The following are this week’s randomly assigned homework groups. The first member of the group is the “Jomework Jefe” who will be in charge of setting up work meetings and have responsibility for turning in the group’s homework notebook. If some some reason, the first member in the list is incapacitated, recalcitrant, or otherwise unavailable, then the second member should take that position. *Attention slackers:* The Jefe should include a line at the top of your notebook listing the group members that participated in the notebook’s production; only those listed will receive credit. Group names are boldfaced text.

Annapurna: *chandrak, tsmickel, jrm90, spuranam*

Dhanwantari: *ronrose, msee, tsarathi, dimitri_*

Durga: *ckopp, jschein, m_gibson, eperry4*

Ganesh: *ezuniga, ssluo, vtrevino, sojung*

Hanuman: *hekopp, bwee, aypark, llena*

Kali: *ernmart, yhelen, pmelo, andy_c*

Lakshmi: *amelanie, elomeli, aliciac, viviand*

Saraswati: *nsinatra, jchenlia, changey, mcjasso, eogorman*

Individual (Handworked) Exercise I5-1

For a thermodynamic system with an equation of state $P(V, T)$, the molar heat capacities at constant volume, c_V and at constant pressure, c_P , can be written in terms of molar free energies and molar entropy as

$$c_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$$
$$c_P = \left(\frac{\partial H}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

(The later relations with entropy S will be the most useful going forward in this problem).

1. Show that

$$c_P - c_V = -T \frac{\left[\left(\frac{\partial V}{\partial T} \right)_P \right]^2}{\left(\frac{\partial V}{\partial P} \right)_T}$$

2. Think about the physical nature of $\left(\frac{\partial V}{\partial P} \right)_T$ in a stable system. What is its sign, positive or negative?
3. Which is greater in a stable system, c_P or c_V .
4. Show that

$$c_P - c_V = -T \frac{\left[\left(\frac{\partial P}{\partial T} \right)_V \right]^2}{\left(\frac{\partial P}{\partial V} \right)_T}$$

as well.

Individual Exercise I5-2

Although we have not covered differential equations yet in 3.016, they are fairly easy to solve and visualize in Mathematica. For the differential equation:

$$t^2 \ddot{y}(t) - t \dot{y}(t) + y(t) = \frac{\log(t)}{t^3}$$

1. Find the general solution to this differential equation. Identify the homogeneous and the heterogeneous (particular) solution.
2. Find the solutions for the initial conditions $y(t = 1) = b$ and $\dot{y}(t = 1) = 0$, and plot them for several values of b .

Individual Exercise I5-3

One place that eigenvalues and eigensystems become very useful is in visualizing the behavior of coupled first-order differential equations. One such system is:

$$\dot{x} = y$$
$$\dot{y} = 2x^3 + x^2 - x$$

This is a non-linear set of equations for which general solutions are difficult to analyze. To explore such systems, one usually explores behavior around “fixed” points. Fixed points are defined by those points x and y for which $\dot{x} = \dot{y} = 0$. If the system is sitting exactly at a fixed point, then it will stay there forever because the time-derivatives are zero.

The system is analyzed with the following steps:

Find the fixed points Find solutions for all of the points x and y . Let each of these fixed point solutions be identified by ξ_i and η_i for $i = 1, \dots$, number of fixed points.

Linearize at the fixed points Consider solutions that are near the fixed points $x = \xi_i + \epsilon_x$ and $y = \eta_i + \epsilon_y$ and expand the original set of differential equations equation around the fixed points to first order in ϵ (i.e., Taylor expand around ξ_i and η_i and neglect terms ϵ_x^2 , $\epsilon_x\epsilon_y$ and ϵ_y^2).

Matrix equations Write the coupled set of differential equations as a matrix equation:

$$\begin{pmatrix} \dot{\epsilon}_x \\ \dot{\epsilon}_y \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} \epsilon_x \\ \epsilon_y \end{pmatrix}$$

Eigenbasis Transform the matrix equation into its eigenbasis. Because the eigenbasis-matrix is diagonal, the two equations are uncoupled in the eigenbasis.

Plot Using the eigenvalues, make parametric plots of $(\epsilon_x(t), \epsilon_y(t))$ at each fixed point for several different initial values $(\epsilon_x(0), \epsilon_y(0))$. This will allow you to visualize the system trajectories near the fixed points.

There are three fixed points for the system of differential equations given above. Analyze all three.

Individual Exercise I5-4

1. Visualize the gradient and the divergence of gradient of

$$f(x, y) = (\operatorname{erf}(x - 1) - \operatorname{erf}(x + 1))(\operatorname{erf}(y - 2) - \operatorname{erf}(y + 2))$$

2. Visualize the divergence and the curl of

$$\vec{v}(x, y) = (\sin(x) \cos(y), \sin(x) \sin(y), \cos(x))$$

Group Exercise G5-1

The purpose of this exercise is to explore how a random walk corresponds to diffusion of a species, and ultimately to the diffusion equation.

Perhaps the simplest example of diffusion is the following. Suppose that a large number of atoms are initially placed at the origin of a coordinate system at time $t = 0$, then the atoms undergo random displacements of some average distance $\langle r \rangle$ at some frequency Γ (steps per time).

The random walk can take place in one- two- or three-dimensions. In one dimension, the problem is equivalent to diffusion along an infinitely long wire where all the diffusing atoms are initially placed at $x = 0$ and they can “hop” to the right (positive x) or the left (negative x) randomly. In two dimensions, the problem is like that of the diffusing atoms being initially placed at the center of an infinitely wide but very thin plate. In three dimensions, the problem is equivalent to an initial state where all the diffusing atoms are placed at the origin of an infinite body.

The diffusion coefficient, D can be related to the hopping rate Γ and $\langle r \rangle$ through a relation like:

$$D = \alpha \Gamma \langle r \rangle^n$$

where α and n are dimensionless constants which *may* depend on the dimensionality of the diffusion problems described above. The average of r is denoted $\langle r \rangle$. One of the goals to this problem is to find the α and the n .

The diffusion equation is a partial differential equation:

$$\begin{aligned} \frac{\partial c}{\partial t} &= D \frac{\partial^2 c}{\partial x^2} && \text{One dimension} \\ \frac{\partial c}{\partial t} &= D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right) && \text{Two dimensions} \\ \frac{\partial c}{\partial t} &= D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) && \text{Three dimensions} \\ \frac{\partial c}{\partial t} &= D \nabla^2 c && \text{In general} \end{aligned}$$

where c is the concentration that is a function of position and time: $c(x, y, z, t)$, or $c(\vec{r}, t)$. The concentration is a *continuized variable* representing the number of atoms in a small, but finite, volume; the volume is located at a point in space. The concentration at that point in space changes as a function of time, t .

For the three physical problems described above, the solutions to the diffusion equation can be shown to be:

$$\begin{aligned} c(x, t) &= \frac{N}{(4\pi Dt)^{1/2}} e^{-x^2/(4Dt)} && \text{One dimension} \\ c(x, y, t) &= \frac{N}{4\pi Dt} e^{-|\vec{r}|^2/(4Dt)} && \text{Two dimensions} \\ c(x, y, z, t) &= \frac{N}{(4\pi Dt)^{3/2}} e^{-|\vec{r}|^2/(4Dt)} && \text{Three dimensions} \end{aligned} \tag{1}$$

where N is the number of atoms diffusing in the infinite line, plane, or space. For practical problems, N is a large number so that “continuization” makes sense.

Continuum Exploring the diffusion equation.

- 1-a** What are the units of $c(\vec{r}, t)$ in each of the three cases?
- 1-b** Show that the number of diffusing atoms in the system is conserved—that is, it doesn't change in time.
- 1-c** Show that each of the three concentration fields in Eq. 1 satisfy the diffusion equations.
- 1-d** Visualize the solutions to the diffusion equations.

Discrete Simulating a random walk.

- 2-a** Simulate a random walk in one dimension by iterating a single random walk step many times. At each iteration, an atom will hop a distance $|\vec{b}|$ in the plus- or minus- x direction. Do this for enough atoms and a series of times so that you can plot distributions of random walker positions at several times. You can associate the time with the number of iterations, so that Γ will have units of $(\text{length})^n/(\text{time per iteration})$
- 2-b** Compare your distributions to the continuum solution to the diffusion equation.
- 2-c** Use your distributions as data to fit to Eqs. 1 so that you can find estimates to the coefficients α and n in Γ for one dimensional diffusion.
- 2-d,e,f** Repeat the above exercises a, b, and c for the two-dimensional diffusion case.
- 2-g,h,i** Repeat the above exercises a, b, and c for the three-dimensional diffusion case.