Massachusetts Institute of Technology

Mathematical Methods for Materials Scientists and Engineers

3.016 Fall 2012

W. Craig Carter

Department of Materials Science and Engineering
Massachusetts Institute of Technology
77 Massachusetts Ave.
Cambridge, MA 02139

Problem Set 4: **Due: Oct. 17**

Individual assigments 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.

Babuza: *eamurphy, kdoolit, mwburr, ldbobbio, cmjoseph*
Baga Sobané: *peteraug, langomas, glau, anniapan, scottste*
Canichana: *selda, dunnwi, jenniez, jennyylu*
Chitimacha: *smarzen, heewoo, erhine, ajaved*
Cumanagoto: *efodor, tjc15, jaburgos, dengd*
Ngbee: *minakh, aqthomas, liherman, nhuynh3*
Pumpokol: *apontec, bjjones, kezi, msuglian*
Qatabanian: *chaoyliu, sdon, lilyg4, juanhp*
Shuadit: *inbar, jzl, jlee2014, dhynbaa*
Tetete: *ahelmick, jherring, mdevoe, trebawa*
Vestinian: *raclark, morenoj, sarith, dlizardo*

Estimation Exercise E4-1

(State your assumptions, identify any source material, and show your reasoning in such a way that it can be easily followed.)

25 points

I propose to promote global cooling by using solar panels to charge single-A batteries and then bury these deep underground in Nevada. Estimate how many moles of solar charged single-A batteries would I need to bury to cool the atmosphere and the top ten meters of the world's oceans by 5 degrees centigrade.

Individual (Handworked) Exercise I4-1

25 points

Find the equations of three distinct lines where each two of the three planes: $z = -2\alpha x + 3y$, $y = 5 - 2\alpha z - 2x$, and $x + y + z = 3$ intersect as a function of α.

Find the point where each of the three lines intersect as a function of α.

Individual Exercise I4-2

25 points

Display the solution to the previous problem graphically.

Individual Exercise I4-3

50 points

This is a famous problem in probability theory called "Buffon's Needle." It is so famous that it is very easy to find the solution to this problem. Our goal is to simulate the problem and see how the statistics gathered by the simulation converge to the known probabilities.

The Buffon's needle problem is the following. Suppose an infinite plane is ruled with parallel straight lines and each is a distance of ℓ from its neighbors. Let a needle of length $\beta\ell$ be tossed at random onto the plane—what is the probability that the needle will cross at least one line?

i: Write a function that takes a measure of the length of the needle returns a 1 if the randomly tossed needle crosses a line and a 0 if not. (Hint, the function `Mod[x,1]` may be very useful.)

ii: Using your function above, write another function that counts the number of crossings for N tosses as a function of needle length. Show that the fraction of "crossing tosses" converges to a constant a N becomes large.

iii: Illustrate how the standard deviation behaves as a function of N and needle length.

Individual Exercise I4-4

75 points

Random Directions with Random Magnitudes *i*: Write a function to produce a three dimensional vector with a random direction, but with a user specified magnitude.

ii: Use your function to plot a bunch of vectors of magnitude 3.

iii: Use your function to plot a bunch of vectors with random magnitude.

iv: For the problem just above (randomly directed vectors with random magnitude), use a sequence of concentric spherical shells and determine a histogram of vectors that lie in each shell. Let the shells be identified by $(0, \Delta r), (\Delta r, \Delta r + \Delta r), (2\Delta r, 2\Delta r + \Delta r), \ldots, (n\Delta r, (n+1)\Delta r)$. Also, normalize your histogram so it becomes a probability distribution. Also, plot the density of atom centers as a function of distance from the center.

Random Positions with Local Excluded Volume Consider a cube that is $10 \times nm$10nm $\times$ 10nm and "hard spheres" that have radius 0.19898nm, find a method to randomly place the "hard spheres" in the cube with none overlapping. Fill the cube to a volume fraction of 1/3 of these hard spheres.

This filling may quite a while on some CPUs. If you find that your code is taking too long, then describe your algorithm and download data here:
`http://pruffle.mit.edu/3.016/Data/x_y_z_coordinates_for_ps3.xls`.
Compute the number, probability, and density distribution of distances from the center of concentric spherical shells about the origin.

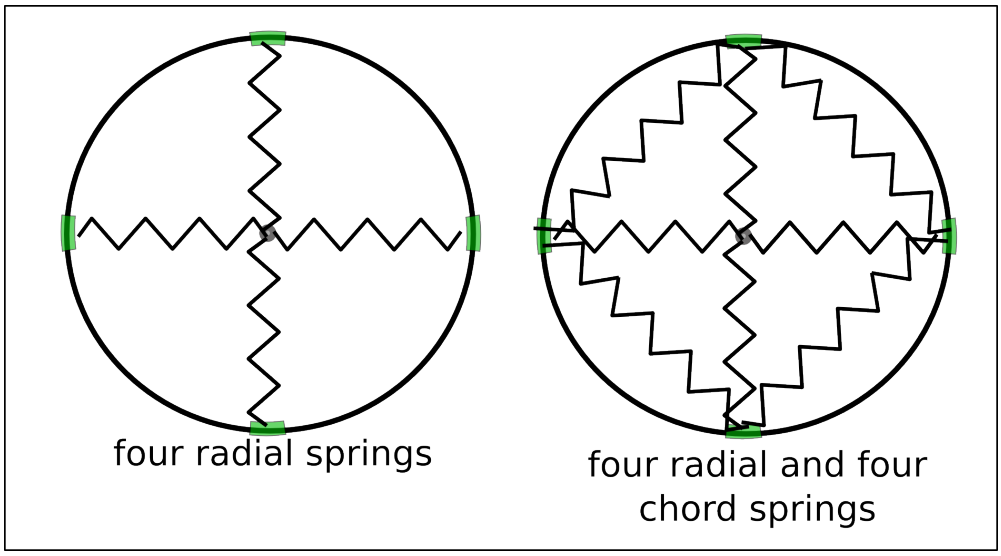
Small Perturbations on a Cubic Lattice Consider a cubic lattice with ten 1nm lattice vectors on each cube edge (i.e., the volume is 10 $\times$ nm $\times$ 10nm $\times$ 10nm). Put the center of an atom on each cube corner, and then perturb each position randomly with a maximum distance of 0.19898nm. Plot the histogram of distances from the center-most atom and its corresponding probability distribution. Plot the probability distribution and the density distribution as well.

Individual Exercise I4-5

125 points

This problem is designed to illustrate the conditions of a structural instability and to draw parallels to phase transitions. The analysis of this problem relies heavily on the concept of of positive definite matrices which necessarily have only positive eigenvalues.

There are similarities to a linear springs problem that was assigned earlier. You can consult that solution—it may be helpful. However, for this problem, you will need to analyze the equilibrium solution and assess whether that equilibrium is stable or not.



On the left, four identical radial springs are attached to a node and their ends are attached to beads that are free to move on a circular ring. On the right, four additional springs are attached to the beads—these springs have the same spring constant as the radial springs. The ring has radius R.

i: For the four radial spring configuration, suppose the springs have a linear force behavior given by $F = -k(\ell - R)$ where ℓ is the length of the spring and k is the spring constant. There are six free variables: the angles θ_i of the beads and the position x, and y of the nodal connection. You may wish to non-dimensionalize this problem by divding all length terms by R.

Find a configuration of beads for which the forces on the beads and the node are all zero.

ii: Is this equilibrium stable or unstable?

iii: In your analysis of stability, you should have found that at least one of the system eigenvalues is zero. What is the *physical meaning* of that zero eigenvalues? Test your hypothesis by fixing the angular position of one of the beads.

iv: For the four-radial/four-chord configuration, suppose that the chord-spring behavior is given by: $F = -k(\ell - \sqrt{2}R)$. Analyze the stability of this configuration.

v: Suppose that ring expands with temperature, T (i.e., it has a coefficient of thermal expansion α, so that $R(\Delta T) = R_o(1 + \alpha\Delta T)$). Analyze the stability of the system as a function of temperature (ΔT can be positive or negative). In other words, illustrate the range of temperatures at which the illustrated configuration remains stable?

Individual Exercise I4-6

75 points

An image of Andy Warhol's *Soup Cans* is displayed below with its image after mapping each pixel with a matrix operation $\underline{M}$ and then translating by adding a vector $\vec{t}$.

Andy Warhol, Soup Cans, 1962 and $\underline{M}$(Soup Cans) $+ \vec{t}$

i: Find the matrix $\underline{M}$. You can use a ruler, or any other means you find convenient.

ii: Find the eigenvectors of $\underline{M}$ and make lines one each image corresponding to the eigenvectors. Comment on what you observe.

iii: How do you interpret the eigenvalues?

Group Exercise G4-1

200 points

In this example, the appearance of energy gaps in the reciprocal space of a one-dimensional crystal will be calculated and visualized. This is an advanced topic that you will learn in 3.023, but we can go through the math now and you will be able to concentrate on the physics later.

There is one mathematical concept that I would like you to notice. Remember that the matrix equation $\underline{A}\vec{x} = \vec{0}$ only has solutions with the determinant of $\underline{A}$ has a zero determinant. Furthermore, this zero determinant condition also led us to the equation for eigenvalues: Det$(\underline{A} - \lambda\underline{I}) = 0$. In this example, the condition for a zero determinant will result values of energy for which solutions exist and don't exist. These energies are the eigenvalues of Shrödinger's equation. There are conditions for which no eigen-energies exist and this produces energy-band gaps. Such energy gaps will be computed in this problem.

Every materials scientist and engineer should be familiar with the behavior of electrons in a periodic lattice of ionized atoms—for example, free electrons in a gold single crystal. The simplest model to illustrate this physics is the Kronig-Penney model. The Kronig-Penney model is one-dimensional and treats the electron potential as a finite well of depth $-V_o$ in a small block of width b near ions and completely free of any potential away from the ions. A very readable description and derivation can be found here (`http://en.wikipedia.org/wiki/Particle_`

in_a_one-dimensional_lattice) and a nice mathematica demo can be found here (http://demonstrations.wolfram.com/TheKronigPenneyModel/). It involves concepts that are covered in 3.023 such as Shrödinger's equation and Bloch's theorem—and these concepts are descrived in enough depth at this url to proceed. However, the derivation at (http://en.wikipedia.org/wiki/Particle_in_a_one-dimensional_lattice leads to a result:

$$\cos(ka) = \cos(\beta b)\cos(\alpha(a-b)) - \frac{\alpha^2+\beta^2}{2\alpha\beta}\sin(\beta b)\sin(\alpha(a-b))$$

where

$$\alpha^2 \equiv \frac{2mE}{\hbar^2} \qquad (1)$$

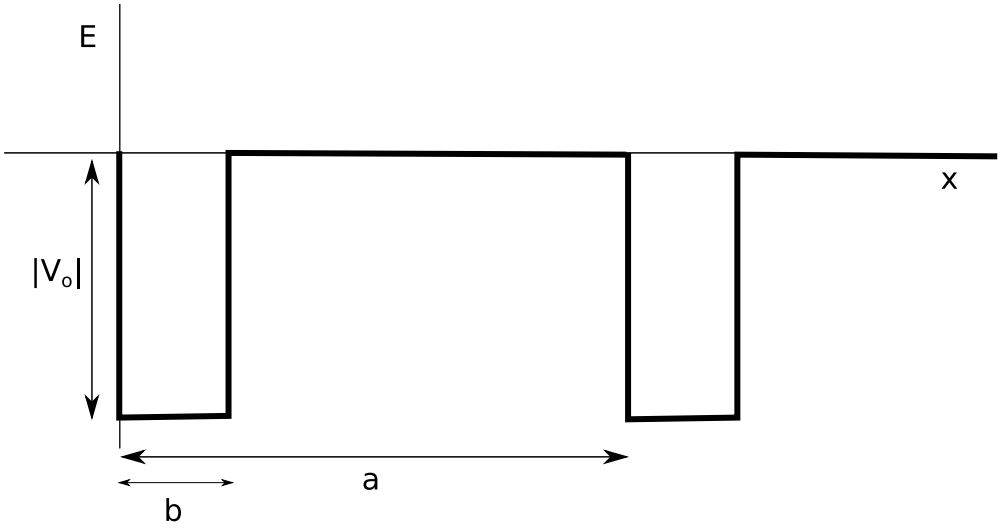
$$\beta^2 \equiv \frac{2m(E+V_o)}{\hbar^2}$$

where k is the position in reciprocal space (this is a concept you should be learning in 3.012, but is not which is not explained or described at the Wiki page above).

Furthermore, this equation is in such a form that it is tedious to extract the band diagram. If you choose, you can do this problem using Eq. 1, or you can proceed with the somewhat modified method described below—this is a problem that begs to be non-dimensionalized and rewritten with a more convenient set of physical parameters.

Let's explore this derivation and the implications of the equation above by working it through. The derivation can be summarized with the following steps:

- Assume the potential is made of "square blocks" with potential $-|V_o|$ (attractive) near the ion cores and 0 a finite distance away from the cores. We expect the electron wave function to be periodic and to become more delocalized from the ion cores as the energy of the electron goes up.



Periodic one-dimensional lattice positively charged atoms sit in the middle of the negative potential region.

$$E(x) = \begin{cases} -|V_o| & 0 < x < b \\ 0 & b < x < a \end{cases} \qquad (2)$$

- The Shrödinger equation in each domain is:

$$\begin{aligned} \frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + |V_o|\psi(x) = E\psi(x) \quad 0 < x < b \\ \frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad b < x < a \end{aligned} \tag{3}$$

By introducing these non-dimensional variables for length, width, potential, ratio of total energy to potential energy (the total energy cannot be less than the ground state energy $-|V_o|$, and wave-vector:

$$\begin{aligned} \xi \equiv x/a \qquad & \text{and} \quad \beta \equiv b/a \quad (\text{thus } 0 < \beta < 1) \\ \nu \equiv \frac{V_o}{\frac{\hbar^2}{2ma^2}} \qquad & \text{and } f \equiv E/|V_o| (\text{thus } -1 < f < \infty) \\ \kappa = ka & \end{aligned} \tag{4}$$

with these non-dimensional variables, the Shrödinger equation in each region becomes:

$$\begin{aligned} \frac{d^2\psi(\xi)}{d\xi^2} = -\nu(1+f)\psi(\xi) \quad 0 < \xi < \beta \\ \frac{d^2\psi(\xi)}{d\xi^2} = -\nu f\psi(\xi) \quad \beta < \xi < 1 \end{aligned} \tag{5}$$

- Assume that the electron wave function $\psi(\xi)$ has the same periodicity as the lattice: $\psi(\xi) = u(\xi)\exp(\imath\kappa\xi)$ where κ is the non-dimensionalized lattice's reciprocal vector (it is related to the electron momentum). Multiplying $\psi(\xi)$ by $\exp(\imath\kappa\xi)$ creates something known as a *Bloch wave*. $\psi(\xi)$ can be a complex valued and $\exp(\imath\kappa x)$ and $u(\xi) = u(\xi + 1)$ guarantees that the electron wave function will be periodic in real space as well as reciprocral space.

- The Shrödinger equation can for the wavefunctions ψ in the two regions (near the ions and away from the ions). The wavefunction are complex functions (i.e., they have real and imaginary parts).

- Each of the two solutions (one for each domain) to the Shrödinger equation has this form:

$$\begin{aligned} \psi_A = A_1\, p_1(\xi; f, \nu) + A_2\, p_2(\xi; f, \nu) \\ \psi_B = B_1\, q_1(\xi; f, \nu) + B_2\, q_2(\xi; f, \nu) \end{aligned}$$

Each ψ has two integration constants (four constants to be determined) that are determined by applying conditions of differential continuity for the wave functions ($\psi_A(\xi)$ and $\psi_B(\xi)$) and Bloch waves ($u_A(\xi) = \exp(-\kappa\xi)\psi_A(\xi)$ and) and Bloch waves $u_B(\xi) = \exp(-\kappa\xi)\psi_B(\xi)$) (i.e., that the functions and their derivatives are perioidic are continuous).

- The resulting system of linear equations is of the form $\underline{M}\vec{b} = \vec{0}$ where $\underline{M}$ contains the constants A_1, A_2, B_1, B_2 and $\vec{b}$ is a vector of four functions. The condition that this system *has a solution* is that the determinant of $\underline{B}$ vanishes leads to a condition that is equivalent to Eq. 1.

- The vanishing determinant produces an equation between E (or f) and k (or κ) that depends on β and ν. This equation has solutions for only for some energies E and no solutions for other E: this is an example of a band gap.

- $E(k)$ (or in non-dimensional form $f(\kappa)$) is a dispersion relation; dE/dk is proportional to the electron's velocity and d^2E/dk^2 is proportional to the electron's *effective mass*

Even if you don't choose to use the non-dimensionalization described above and work directly from Eq. 1, you should do parts *i*, and *vi*–*x*.

i: Derive Eq. 1 (or an equivalent form) using the steps outlined above (you should do this on paper and then typeset your reasoning into your solution).

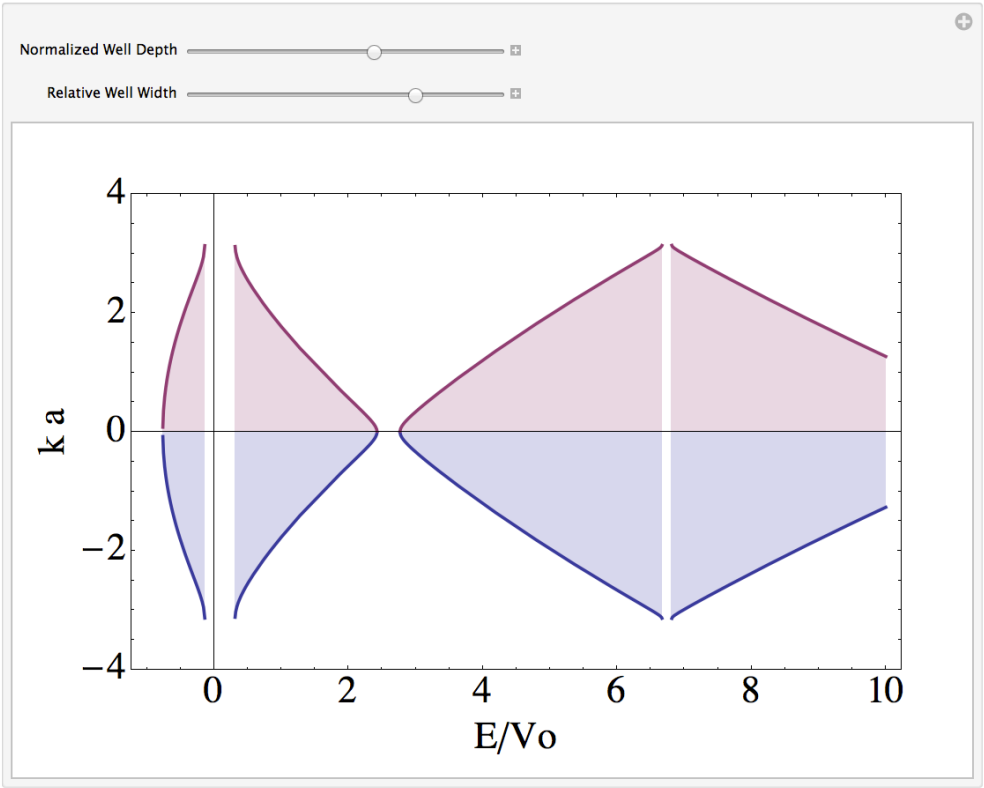
ii: Solve the Shrödinger equation for each domain (you may find that the option to `DSolve`, `GeneratingParameters` could be useful).

iii: Find the the matrix (i.e., such as $\underline{M}$ above) for which the determinant must vanish for solutions to exist. If you use the non-dimensionalized form, you may find it useful to force all the expressions to have the same form by using `ExpToTrig`.

iv: Find the form of the determinant and simplify under the assumptions that $f > -1$ and $0 < \beta < 1$.

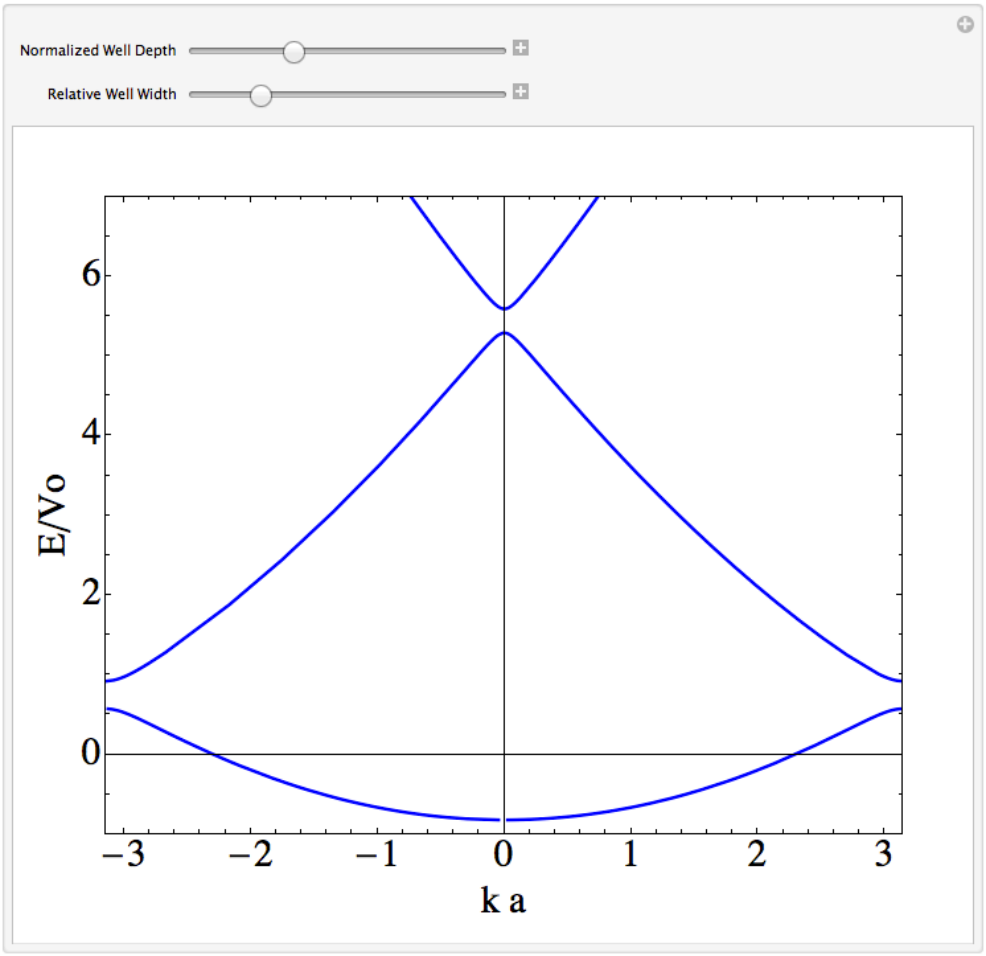
v: Solve for the condition that the determinant vanishes for κ; this will give you a relation between energy and wavevector.

vi: Plot the solutions of wavevector versus energy. They should look something like the following:



An example of the wavevector as a function of energy for a given potential width and depth. Note that there are some energies for which solutions do not exits–these are band gaps.

vii: Electron energy band diagrams are usually drawn as $E(k)$, plot the relationship this way (you may find that `ParametricPlot` is useful). Plot these relationships, they should look something like the following:



An example of a dispersion relation

viii: What is the behavior of electron momentun dE/dk? Make sure that you describe physical aspects of this relationship.

ix: What is the behavior of electron effective mass which is proportional to d^2E/dk? Make sure that you describe physical aspects of this relationship.

x: Summarize your results in a paragraph or two—in other words, continue the Wikipedia description (`http://en.wikipedia.org/wiki/Particle_in_a_one-dimensional_lattice`) that would be useful for an audience just like you.