Massachusetts Institute of Technology

Mathematical Methods for Materials Scientists and Engineers

3.016 Fall 2010

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Problem Set 8: **Out: 15 Nov.** and **Due: 22 Nov.**

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.

Cackle: *llena, hekopp, aypark, ckopp*

Chortle: *viviand, yhelen, tsarathi, tsmickel*

Chuckle: *jschein, msee, ezuniga, elomeli*

Giggle: *spuranam, jrm90, dimitri_, jchenlia*

Guffaw: *ernmart, changey, ronrose, aliciac*

Howl: *chandrak, eperry4, nsinatra, mcjasso*

Snicker: *bwee, pmelo, ssluo, sojung*

Snigger: *vtrevino, andy_c, m_gibson, amelanie*

Individual Exercise I8-1

In this problem, you will explore a simple variation of the "electron-in-a-box" solution to the the time-independent Shrödinger equation. The "electron-in-a-box" problem is described in many places including `http://hyperphysics.phy-astr.gsu.edu/Hbase/quantum/pbox.html`.

Background Material

The time-independent Shrödinger equation is:

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{x}) + V(\vec{x})\psi(\vec{x}) = E\psi(\vec{x})$$

where $\hbar$ is Planck's constant divided by 2π, m is the particle's mass, $V(\vec{x})$ is the potential energy of a particle at a position $\vec{x}$. The wave-function of the particle, $\psi(\vec{x})$ describes the state of the particle, and in quantum mechanics a particle has wave characteristics. A fundamental property of the wavefunction is that $\psi(\vec{x})\psi^\star(\vec{x})$ is the probability of finding a particle at the position $\vec{x}$; $\psi^\star$ is the complex conjugate of ψ which can be a complex function: $\psi(\vec{x}) = \mathcal{R}\rceil(\psi(\vec{x})) + i\mathcal{I}\Updownarrow(\vec{x}))$ and $\psi^\star(\vec{x}) = \mathcal{R}\rceil(\psi(\vec{x})) - i\mathcal{I}\Updownarrow(\vec{x}))$.

The right-hand-side of the time-independent Shrödinger equation plays a very important role: the equation places *conditions* on E for solutions $\psi(\vec{x})$ to exist.

Note that $\phi(\vec{x}) = 0$ always satisifies the Shrödinger equation—this is called the trivial solution. For the trivial solution, there is no particle anywhere and the problem is not interesting. Below, we are only interested in the non-trivial solutions where the particle exists with probability equal to one:

When solutions exist, E is the energy associated with that solution—the E for which solutions exist are often called the eigenvalues of the Shrödinger equation. There can be multiple solutions $\psi_i(\vec{x})$ and each one has its own energy E_i. The E_i are generally quantized (i.e., they form a discrete non-continuous set); they are the quantum energies. All other energies except for the E_i represent forbidden energies: there is no particle that could have that energy.

The one-dimensional "electron-in-a-box" is a simple first example that is taught in introductory quantum mechanics lectures. The idea is the following: an electron exists (i.e., $\psi(x) \neq 0$) in a finite region $-L/2 < x < L/2$ where the potential is zero ($V(-L/2 < x < L/2) = 0$) Outside this finite region, the potential is infinite and the electron cannot exist outside the region: $\psi(x \leq -L/2) = 0 = \psi(x \geq L/2)$.

Thus, one needs to solve the following differential equation and boundary conditions

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)\psi(x = -L/2) = \psi(x = L/2) = 0.$$

which can be shown to have quantum energies proportional to the integers squared ($E_n \propto n^2$ for $n = 0, 1, 2, \ldots$), and $\psi_n \propto \cos(\sqrt{2E_n m}z/\hbar)$.

Here is some mathematica code to show this:

```
SchroEqBox = -(hbar^2*D[psi[z],{z,2}])/(2*mass) == ELevels*psi[z]

dsol = DSolve[{SchroEqBox }, psi[z], z]

bc1 = psi[z] //. Flatten[{dsol[[1]], z -> -L/2}]
bc2 = psi[z] //. Flatten[{dsol[[1]], z -> L/2}]

Simplify[
```

```
  Reduce[
     bc1 == 0 && bc2 == 0 && mass > 0 && hbar > 0  && L > 0, ELevels, Reals
  ],
  Assumptions -> mass > 0 && hbar > 0 && ELevels > 0 && L > 0 && C[2] == 0 && C[1] != 0
]
```

End of Background Material

In this problem, you will give a *pedagogical description* of the *steps* required to solve the "electron-in-a-sphere" spherically symmetric solution to the Shrödinger equation:

$$\frac{-\hbar^2}{2m}\nabla^2\psi(r) = E\psi(r)$$

where r is the radius in spherical coordinates and with boundary condition $\psi(r = R_s) = 0$ and $\psi(0 \leq r \leq R_s) < \infty$.

1. What is the form of the solutions?
2. What are the conditions that are imposed by the boundary condition: $\psi(0 \leq r \leq R_s) < \infty$?
3. How would one find the quantized energies, E_i, of the "electron-in-a-sphere"?
4. The wave-functions, $\psi_i(r)$ are completely determined by the condition that the probability of finding the electron within the sphere of radius R_s is equal to one. How would one go about using this condition to find the form of the wave-functions?

Individual Exercise I8-2

Suppose a A-B binary alloy (i.e., a solution of A and B) has the following form of the molar Gibbs free energy:

$$\overline{G}(X_B, T) = 2\Omega(2X_A^2 + X_A X_B) + RT(X_A \log(X_A) + X_B \log(X_B))$$

where Ω is an interaction energy per mole and the X are mole fractions of components A and B.

1. Plot $\overline{G}(X_B, T)$ over $0 \leq X_B \leq 1$ for several values of the constants to get a sense of what this function looks like.
2. What is the free energy of one mole of pure A? What is the free energy of one mole of pure B?

   Suppose that a system has two moles of pure A and three moles of pure B. What is the total free energy of the system if pure A and pure B are not mixed? What is the total free energy if the A and B are mixed together and form a solution?
3. The change in the molar free energy due to mixing is the difference between the molar free energy of two pure components minus the molar free energy of a solution of A and B. Find an expression for this molar free energy of mixing $\Delta\overline{G}$.

4. The critical temperature is defined as the highest temperature at which $\Delta\overline{G}$ has a vanishing second derivative with respect to a mole fraction. Find this critical temperature.

5. Use this critical temperature to define a dimensionless temperature and then normalize (non-dimensionalize) the molar free energy of mixing.

6. Plot the molar free energy of mixing as a function of mole fraction for several temperatures around the critical temperature.

7. The chemical potential of the A-component ($\mu_A(X_B, T)$) is given by the famous tangent construction: draw a line which is tangent to the curve $\Delta\overline{G}(X_B, T)$ at $X = X_B$; the chemical potential of the A-component ($\mu_A(X_B, T)$) is given by the intersection of this line with the vertical axis at $X_A = 1$. Likewise, the chemical potential of the B-component ($\mu_B(X_B, T)$) is given by the intersection of this line with the vertical axis at $X_B = 1$. Find expressions for these chemical potentials and plot them as function of mole fraction for several temperatures around the critical temperature.

   Does the behavior of $\mu_A(X_B, T)$ remind you of anything you have seen in the 3.016 problem sets?

8. The common tangent construction gives the values of mole fraction at the limits of solubility (i.e., the tie-line of the two-phase region on a binary phase diagram). The common tangent is the line which is tangent to the curve $\Delta\overline{G}(X_B, T)$ at two different points X_B^α and X_B^β simultaneously at some temperature T. Write a function that finds the common tangent points X_B^α and X_B^β as a function of temperature. You may have to use numerical solution methods such as NSolve or FindRoot, but you do know that $0 < X_B^\alpha < X_B^\beta < 1$.

9. Plot the common tangent points X_B^α and X_B^β as a function of temperature.

Group Exercise G8-1

This is an interesting quantum mechanics problem for a single particle in a gravitational potential field.

Suppose the gravitational potential of a particle at a height z is given by mgz where $g > 0$. The particle is prevented from penetrating into the region $z \leq 0$ by an infinite barrer (i.e., $V(-\infty < z \leq 0) = \infty$)

This particle will have quantized energies. Find the smallest ten energies and visualize the probability of finding a particle at one of these energies.

You may find it useful to introduce a characteristic energy quantity $E_c = (\hbar^2 g^2 m)^{(1/3)}$ and a characteristic length $\ell_c = (gm^2/\hbar^2)^{(-1/3)}$ (what are the MKS sizes of these quantities for a neutron in earth's gravity?).