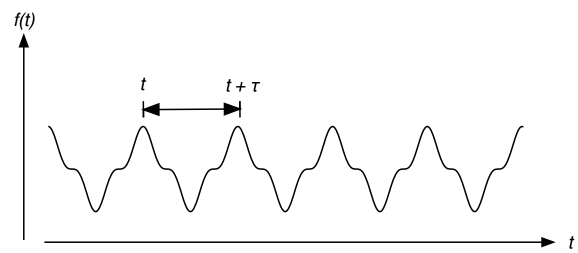
Chemistry 30321 | Fall 2012
Professor J. Daniel Gezelter | Due Fri. 9/7/2012

Problem Set 2 (Classical Wave Equation)

First, a few notes on showing a function has a particular frequency:

If a function $f(t)$ is periodic, it will repeat itself with *period* τ. This means that:

$$f(t+\tau) = f(t)$$



The frequency (ν) is inversely related to the period ($\nu = 1/\tau$), this means that a function with frequency ν will have this property,

$$f(t+\frac{1}{\nu}) = f(t)$$

Many of the problems below ask you to show that a function has a frequency, $\nu = \omega/2\pi$. What you are being asked to do is to prove the following:

$$f(t+\frac{2\pi}{\omega}) = f(t)$$

for the function in question.

Now, on to the problems:

1. Do problem 2-2 in McQuarrie and Simon.
2. Do problem 2-3 in McQuarrie and Simon.

3. Do problem 2-4 in McQuarrie and Simon.
4. Do problem 2-5 in McQuarrie and Simon.
5. Do problem 2-7 in McQuarrie and Simon.
6. Extra Credit (but very difficult). This is worth 1 additional point for each section completed correctly:

   The classical wave equation and the *Ultraviolet Catastrophe*

   a) Use the method of separation of variables to show that the solution to the 3-d wave equation
   $$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}$$
   for electromagnetic waves in a cubic box of side L is given by:
   $$\psi(x,y,z,t) = Ae^{-i\omega t}\sin\frac{l\pi x}{L}\sin\frac{m\pi y}{L}\sin\frac{n\pi z}{L}$$
   with l,m,n integers. The boundary conditions are that $\psi = 0$ at $x,y,z = 0$ and at $x,y,z = L$.

   b) Show that the relation between the values of l,m,n and ω is given by
   $$\frac{\omega^2}{c^2} = \frac{\pi^2}{L^2}(l^2+m^2+n^2)$$

   c) We are interested in a quantity called the *density of states* which is the number of modes of a system that are clustered around the same energy or frequency. We'll call this quantity $u(\nu)$ where ν is the frequency of the wave. To find the density of states, we define
   $$r^2 = l^2+m^2+n^2$$
   and calculate the number of modes $n(r)$ in the range from r to $r+dr$. For large r this is given by the increment in volume of one octant of a sphere going from radius r to $r+dr$ (when $l,m,n > 0$). To help visualize this, take a look at Figure 1 below.
   Use this and the relation between r and ω to show that
   $$n(r)dr = \frac{L^3\omega^2}{2\pi^2c^3}d\omega$$

   d) Use the relationship between linear and angular frequency, $\omega = 2\pi\nu$, to find the energy density of electromagnetic radiation in the box, $u(\nu)$, given in Eq. (1).
   $$En(r)dr = L^3u(\nu)d\nu$$
   $$u(\nu) = \frac{8\pi\nu^2}{2c^3}E \tag{1}$$

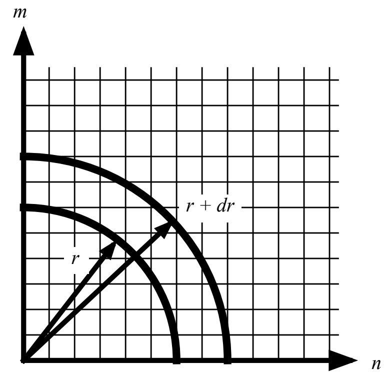


Figure 1: The Rayleigh – Jeans construction of the density of states is easiest to visualize in 2-d. Each intersection in the grid corresponds to one mode (or to one solution of the wave equation). The density of states is related to the number of modes between the quarter circle with radius (r) and another with radius ($r + dr$). In 3-d, the quarter circles become octants of a sphere.

e) We multiply by 2 to account for the two kinds of polarization for each wave, and using equipartition of energy to set $E = kT$, Rayleigh obtained his and Jeans' law for black body radiation which exhibits the "ultraviolet catastrophe",

$$u(\nu) = \frac{8\pi kT}{c^3}\nu^2$$

Describe physically why this is a "catastrophe".

f) What was the fatal flaw in the derivation in parts a)-e)?