8.11) Hard problem. I recommend getting quantitative with this problem (although that does not seem to be the text author’s intent). Consult the Lecture 29. Assume the monomer is a prolate ellipsoid with major semi-axis length $a$ and minor semi-axis length $b$. Then the axial ratio $P = \frac{a}{b}$. Assume if the dimer is an “end-to-end” dimer...then the dimer is a prolate ellipsoid with axial ratio is $P = \frac{2a}{b}$. Assume if the dimer is side-by-side it a a prolate ellipsoid with axial ratio $P = \frac{a}{2b}$. Compute (or estimate) the ratio of the frictional coefficients for monomer and dimer for each dimer model.

Solution: The sedimentation coefficient $s \propto \frac{m}{f}$. Then

$$\frac{s_{monomer}}{s_{dimer}} = \frac{m_{monomer}}{f_{monomer}} \cdot \frac{f_{dimer}}{m_{dimer}} \cdot \frac{m_{monomer}}{2m_{monomer}} = \frac{f_{dimer}}{2f_{monomer}}$$

For a hard rod of length $2a$ and radius $b$... $f = f_0 \left( \frac{2}{3} \right)^{1/3} \frac{P^{2/3}}{\ln(2P) - 0.30} \approx f_0 \left( \frac{2}{3} \right)^{1/3} \frac{P^{2/3}}{\ln(P)}$, if $P \gg 2$, where the axial ratio $P = \frac{a}{b}$ and $f_0 = 6\pi \eta R_0 = 6\pi \eta \left( \frac{3ab^2}{2} \right)^{1/3}$ (see Lecture 29).

- Suppose the dimer is end-to-end. Assume an end-to-end dimer has a length $4a$ and a radius of $b$. Then $P_{dimer} = \frac{2a}{b} = 2P_{monomer}$,

$$f_{0,dimer} = 6\pi \eta R_{0,dimer} = 6\pi \eta \left( \frac{3(2a)b^2}{2} \right)^{1/3} = 2^{1/3} f_{0,monomer}, \text{ and}$$

$$f_{dimer} = f_{0,dimer} \frac{\left( \frac{2}{3} \right)^{1/3} \frac{P_{dimer}^{2/3}}{\ln(2 P_{dimer}) - 0.30}}{2^{1/3} f_{0,monomer} \frac{\left( \frac{2}{3} \right)^{1/3} \frac{P_{monomer}^{2/3}}{\ln(4 P_{monomer}) - 0.30}}}{= 2^{1/3} f_{0,monomer} \frac{\left( \frac{2}{3} \right)^{1/3} \frac{P_{monomer}^{2/3}}{\ln(2) + \ln(2 P_{monomer}) - 0.30}}{\ln(P_{monomer})}} \approx 2^{1/3} f_{0,monomer} \frac{\left( \frac{2}{3} \right)^{1/3} \frac{P_{monomer}^{2/3}}{\ln(P_{monomer})}}{2^{1/3} f_{0,monomer} \frac{\left( \frac{2}{3} \right)^{1/3} \frac{P_{monomer}^{2/3}}{\ln(P_{monomer})}}}{2^{1/3} f_{0,monomer}} = 2 f_{monomer}$$

Then $\frac{s_{monomer}}{s_{dimer}} = \frac{f_{dimer}}{2f_{monomer}} = 2 f_{monomer}$

- Suppose the dimer is side-to-side. Assume the length of this dimer is $2a$ and the radius is $2b$. Then $f_{0,dimer} = 6\pi \eta R_{0,dimer} = 6\pi \eta \left( \frac{3a(2b)^2}{2} \right)^{1/3} = 2^{2/3} f_{0,monomer}$. Also, the
axial ratio of this side-to-side dimer is \( P_{\text{dim,er}} = \frac{a}{2b} = \frac{P_{\text{monomer}}}{2} \). Then

\[
f_{\text{dim,er}} = f_{0,\text{dim,er}} \left( \frac{2}{3} \right)^{1/3} \left( \frac{2}{3} \right)^{2/3} P_{\text{monomer}}^{2/3} \frac{\ln(2P_{\text{dim,er}}) - 0.30}{\ln(P_{\text{monomer}}) - 0.30} = 2^{2/3} f_{0,\text{monomer}} \frac{(2/3)^{1/3} P_{\text{monomer}}^{2/3}}{\ln(P_{\text{monomer}})} \approx f_{0,\text{monomer}} \left( \frac{2}{3} \right)^{1/3} P_{\text{monomer}}^{2/3} = f_{\text{monomer}}
\]

Then

\[
\frac{s_{\text{monomer}}}{s_{\text{dim,er}}} = \frac{f_{\text{dim,er}}}{2f_{\text{monomer}}} = \frac{f_{\text{monomer}}}{2f_{\text{monomer}}} = \frac{1}{2}
\]

- Any other models (partial side-by-side overlap, or a flexible dimer) will likely yield \( \frac{s_{\text{monomer}}}{s_{\text{dim,er}}} \) values between 0.5 and 1.0.

- The experimental ratio is \( \frac{s_{\text{monomer}}}{s_{\text{dim,er}}} = \frac{1.74S}{2.36S} = 0.737 \) so we probably have partial side-by-side overlap, or a flexible dimer.

11.2) \( E = \frac{3}{2} k_B T = \frac{3}{2} \left( 1.38 \times 10^{-23} \text{ J/K } \right) \left( 298 \text{ K} \right) = 6.2 \times 10^{-21} \text{ J} \)

\( h\nu = E \Rightarrow \nu = \frac{E}{\hbar} = \frac{6.2 \times 10^{-21} \text{ J}}{6.626 \times 10^{-34} \text{ J/s}} = 9.4 \times 10^{12} \text{ s}^{-1} \)

\( \lambda = \frac{c}{\nu} = \frac{3 \times 10^8 \text{ m/s}}{9.4 \times 10^{12} \text{ s}^{-1}} = 3.2 \times 10^{-5} \text{ m }. \text{ Infrared.} \)

11.3) Visible region is about 600 nm. Then according to the Wien equation

\( T = \frac{2.9 \times 10^6}{600} = 5000 \text{ K} \) for visible light.

For infrared, wavelength is 10000 nm. Then… \( T = \frac{2.9 \times 10^6}{10000} = 300 \text{ K} \)

11.6) \( \log \left( \frac{I_0}{I} \right) = \varepsilon c l \Rightarrow 0.88 = \varepsilon \left( 3.4 \times 10^{-5} \text{ M} \right) (0.1 \text{ m}) \)

\( \therefore \varepsilon = 2.6 \times 10^5 \text{ M}^{-1} \text{ m}^{-1} \)

11.10) a) Using equations 11.12 and 11.19 we conclude the energy of a thin square box is

\( E = \frac{\hbar^2}{8mL^2} \left( n_x^2 + n_y^2 \right) \)
b) and c)

<table>
<thead>
<tr>
<th>n_x , n_y</th>
<th>Energy (units of ( h^2/8mL^2 ))</th>
<th>Number of electrons (one pair per energy state)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>1,2 and 2,1</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>2,2</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>1,3 and 3,1</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>3,2 and 2,3</td>
<td>13</td>
<td>4</td>
</tr>
<tr>
<td>4,1 and 1,4</td>
<td>17</td>
<td>4</td>
</tr>
<tr>
<td>3,3</td>
<td>18</td>
<td>2</td>
</tr>
<tr>
<td>4,2 and 2,4</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>4,3 and 3,4</td>
<td>25</td>
<td>0</td>
</tr>
</tbody>
</table>

The highest energy filled state is \( E=20 \). This has \((n_x,n_y)=(4,2)\) and \((2,4)\).

d) Let \( E_{nx,ny} \) be the energy corresponding to quantum numbers of \( n_x \) and \( n_y \). Then

\[
\Delta E = E_{4,3} - E_{4,2} = \frac{h^2}{8mL^2} (25 - 20) = \frac{5h^2}{8mL^2}
\]

\[
= \frac{(5)(6.62 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(8)(9.11 \times 10^{-31} \text{ kg})(10^{-9} \text{ m})^2} = 3 \times 10^{-19} \text{ J}
\]

\[
\therefore \frac{\Delta E}{h} = \frac{3 \times 10^{-19} \text{ J}}{6.62 \times 10^{-34} \text{ J} \cdot \text{s}} = 4.53 \times 10^{14} \text{ s}^{-1}
\]

and \( \lambda = \frac{c}{\nu} = \frac{3 \times 10^8 \text{ m/s}}{4.53 \times 10^{14} \text{ s}^{-1}} = 660 \times 10^{-9} \text{ m} \)

Additional Problems: Note TWO problems will be graded for 20 points.

1) Answer this question using force balance arguments and the definition of the surface tension pressure \( P = \frac{2\gamma}{L} \). As an aid in forming your arguments…imagine an ideal sausage…with two radii of curvature \( R_1>>R_2 \). Decompose the force exerted on a patch of sausage skin into two components as shown. Which component is larger? That is the component that will cause the sausage skin to rip apart. What direction does it have?

a) Imagine heating a sausage. The sausage skin doesn’t expand much and as the meat inside expands the skin will eventually rip. Along which direction will it split?
Answer: As the meat in the sausage expands, it exerts a force that is tangentially directed along the surface of the sausage skin, as pictured, above right. This force can be decomposed into two components, long the short axis and the long axis. The force to rip open the sausage is opposed by the surface tension of the skin. The skin will rip where the force is largest, and this is where the surface tension is largest. The surface tension has the form \( F = \frac{2\gamma}{L} \) where \( L \) is the distance on the surface over which this force is exerted. The opposition to the short force above has the form \( F_1 = \frac{2\gamma}{2\pi R_1} \) and the opposition to the long force is \( F_2 = \frac{2\gamma}{2\pi R_2} \). Because \( R_1 < R_2 \), then \( F_1 > F_2 \). This means the short force builds up to a larger value than the long force, so the skin will rip along the length of the sausage.

b) As a result of the surface tension, the vapor pressure \( P \) of water in a droplet is dependent on the size of the droplet and is greater than the vapor pressure of water with an uncurved surface (=\( P_0 \)). The relationship between the ratio of the vapor pressure \( P \) for water in a droplet of radius \( r \) and the vapor pressure for water with a flat surface (i.e. \( 1/r=0 \)) is given by the Kelvin equation \( \ln \left( \frac{P}{P_0} \right) = \frac{2M\gamma}{2RT\rho r} \) where \( M \) is the molecular weight of the liquid, \( \rho \) is its density, and \( \gamma \) is its surface tension. Calculate the vapor pressure of water at \( T=293 \) in a droplet of radius \( r=0.001 \) mm. The vapor pressure of water with an uncurved surface at \( T=293K \) is 17.5 torr where 760 torr = 1 atm.

Solution: Note error of 2 in denominator...

\[
\ln \left( \frac{P}{P_0} \right) = \frac{2M\gamma}{2RT\rho r} = \frac{2(0.018kg/mole)(0.07275Nt/m)}{(8.31J/mole\cdot K)(293K)(10^3kg/m^3)(10^{-6}m)} = 0.001
\]

\[ \therefore \frac{P}{P_0} = 1.001 \Rightarrow P = (1.001)17.5torr = 17.52torr \]
2) Consider a quantum mechanical particle in a box. The wave function is
\[ \psi_n = \frac{2}{\sqrt{L}} \sin \left( \frac{n \pi x}{L} \right), \quad n=1,2,3,\ldots \]

a) Calculate the average position of the particle for \( n=1 \). Do these results agree with the results of classical mechanics? Explain. Hint: Recall that an average value of a quantity \( O \) in quantum mechanics is \( \langle O \rangle = \frac{\int \psi^* (x) O \psi (x) dx}{\int \psi^* (x) \psi (x) dx} \). The following integral formulae will be helpful...

\[
\int \sin^2 (ax) \, dx = \frac{a}{2} \left[ \frac{ax}{2} - \frac{\sin(ax) \cos(ax)}{2} \right]
\]

\[
\int x \sin^2 (ax) \, dx = \frac{1}{a^2} \left[ \frac{a^2 x^2}{4} - \frac{ax \sin(2ax)}{4} - \frac{\cos(2ax)}{8} \right]
\]

\[
\int \cos(ax) \sin(ax) \, dx = \frac{\sin^2(ax)}{2a}
\]

All integrals are performed with limits between 0 and L.

**Answer:** For the average position \( O=x \) so for \( n=1 \)... 

\[
\langle x \rangle = \frac{\int \psi^* (x) x \psi (x) dx}{\int \psi^* (x) \psi (x) dx}
\]

\[
= \left( \frac{\pi}{L} \right) \frac{\int_0^L x \sin^2 \left( \frac{\pi x}{L} \right) \, dx}{\int_0^L \sin^2 \left( \frac{\pi x}{L} \right) \, dx} = \left( \frac{\pi}{L} \right) \frac{L/2}{L/2} = \frac{L}{2} = \frac{L}{2}
\]

These results agree with our classical intuition. If the particle has as much chance to be anywhere in the right versus the left hand side its average position is clearly in the middle, i.e. at \( x=L/2 \).

b) For \( n=1 \) and 2, calculate the probability of finding the particle between \( x=L/3 \) and \( x=2L/3 \).

**Answer.** Now in this case the equation is given by the chance of finding the particle between one value of \( x \) and another. So the integration is between \( L/3 \) and \( 2L/3 \). The square of the wave function is the probability of locating the particle at \( x \) is the chance of finding the particle between \( x=L/3 \) and \( /=2L/3 \) is

\[
\int_{L/3}^{2L/3} \psi^2 (x) \, dx \text{ . For } n=1 \text{ this is }
\]
\[
\int_{L/3}^{2L/3} \sin^2 \left( \frac{\pi x}{L} \right) \, dx = \left[ \frac{\pi x}{2L} \sin \left( \frac{\pi x}{L} \right) \cos \left( \frac{\pi x}{L} \right) \right]_{L/3}^{2L/3} - \frac{\pi}{6} + \frac{\pi}{4} - \frac{(0.866)(-0.5)}{4} = \frac{\pi}{6} - 0.217 = 0.306
\]

For \( n=2 \) this is…
\[
\int_{L/3}^{2L/3} \sin^2 \left( \frac{2\pi x}{L} \right) \, dx = \left[ \frac{2\pi x}{2L} \sin \left( \frac{2\pi x}{L} \right) \cos \left( \frac{2\pi x}{L} \right) \right]_{L/3}^{2L/3} - \frac{2\pi}{6} + \frac{2\pi}{4} - \frac{(0.866)(-0.5)}{4} = \frac{2\pi}{6} - 0.217 = 0.830
\]

c) The wave function for the linear harmonic oscillator in its ground state is
\[
\psi_0(q) = \left( \frac{\omega}{\sqrt{\pi}} \right)^{1/2} e^{-q^2/2} \quad \text{where} \quad q = \sqrt{\alpha} x \quad \text{and} \quad \alpha = \frac{2\pi \omega M}{\hbar} .
\]
Calculate the root-mean-square displacement of the oscillator \( x_{rms} = \sqrt{x^2} \) in the ground state. The integral
\[
\int_0^\infty x^2 e^{-r^2x^2} \, dx = \frac{\sqrt{\pi}}{4r^3} \quad \text{will be helpful.}
\]
Answer. I did not give you the integral in the denominator, but it has already occurred in this course and in the homework…
\[
\int_{-\infty}^{\infty} e^{-r^2x^2} \, dx = 2 \int_0^\infty e^{-r^2x^2} \, dx = \frac{\sqrt{\pi}}{r} ;
\]
\[ x_{\text{rms}} = \sqrt{\langle x^2 \rangle} \]
\[ \therefore \langle x^2 \rangle = \frac{\int \psi^* (x)x^2 \psi (x) \, dx}{\int \psi^* (x) \psi (x) \, dx} \]
\[ = \frac{\int_{-\infty}^{\infty} x^2 e^{\alpha x^2} \, dx}{\int_{-\infty}^{\infty} e^{\alpha x^2} \, dx} = \frac{2\int_{0}^{\infty} x^2 e^{\alpha x^2} \, dx}{\int_{0}^{\infty} e^{\alpha x^2} \, dx} = \frac{\alpha^{1/2}}{2\alpha^{3/2}} = \frac{1}{2\alpha} = \frac{h}{4\pi \omega M} \]

3) The average energy for a quantum mechanical one dimensional harmonic oscillator is
\[ E = \hbar \nu \left( e^{\hbar \nu / k_B T} - 1 \right)^{-1} = \frac{\hbar \nu}{e^{\hbar \nu / k_B T} - 1}. \]

a) Plot the average quantum mechanical energy as a function of temperature from \( T=1 \)K to \( T=1000 \)K in increments of 50K. Plot also the average classical energy \( E_{\text{classical}} = k_B T \).
Assume \( \nu = 10^{14} \) sec\(^{-1} \).

Answer: The average energy of a classical one dimensional oscillator is \( k_B T \). The average energy of a quantum mechanical oscillator is
\[ \frac{\hbar \nu}{e^{\hbar \nu / k_B T} - 1} = \left( 6.62 \times 10^{-24} \text{ J} \cdot \text{s} \right) \left( 10^{14} \text{ s}^{-1} \right) \exp \left( \frac{6.62 \times 10^{-20}}{1.38 \times 10^{-23}} \right) \exp \left( -\frac{4797}{T} \right) \]
\[ = \left( 6.62 \times 10^{-20} \right) \exp \left( -\frac{6.62 \times 10^{-20}}{1.38 \times 10^{-23}} \right) \exp \left( -\frac{4797}{T} \right) \]
So the classical quantity is a straight line with slope \( k_B = 1.38 \times 10^{-23} \) J/K. In units of \( k_B \) the classical energy is 1 at \( T=1 \)K, 100 at \( T=100 \)K, 200 at \( T=200 \)K, etc…1000 at \( T=1000 \)K and 4797 at \( T=4797 \)K.

The quantum result depends very strongly on temperature. In units of \( k_B \) it is almost zero at \( T=1 \), about \( 10^{-17} \) at \( T=100 \)K, 1.83 \times 10^{-7} at \( T=200 \)K, 5.45 \times 10^{-4} at \( T=300 \)K, 0.029 at \( T=400 \)K, 0.327 at \( T=500 \)K, 1.62 at \( T=600 \)K, 5.05 at \( T=700 \)K, 11.93 at \( T=800 \)K. Even at \( T=1000 \)K the quantum result of 39.5 does not get close to the classical result of 1000. In fact you have to get to a temperature much higher than 4797K to get close to the classical result.

b) Using your expression for the average energy, given above, and using the definition of the heat capacity \( C_v = \frac{\partial E}{\partial T} \) confirm that the average heat capacity for a quantum harmonic oscillator is \( k_B x^2 e^{-x} \left( 1 - e^{-x} \right)^{-2} \) where \( x = \frac{\hbar \nu}{k_B T} \).
Solution: \( E = h\nu \left( e^{\frac{hv}{k_B T}} - 1 \right)^{-1} = \frac{hv}{e^{\frac{hv}{k_B T}} - 1} \). So

\[
\overline{C}_V = \frac{\partial \overline{E}}{\partial T} = \frac{\partial}{\partial T} \left( h\nu \left( e^{\frac{hv}{k_B T}} - 1 \right)^{-1} \right) = h\nu \frac{\partial}{\partial T} \left( e^{\frac{hv}{k_B T}} \right) \frac{\partial}{\partial T} \left( e^{\frac{hv}{k_B T}} - 1 \right)^{-1}
\]

\[= -\frac{(hv)^2}{k_B T^2} \left( e^{\frac{hv}{k_B T}} \right) \left( e^{\frac{hv}{k_B T}} - 1 \right)^{-2} = k_B \left( \frac{hv}{k_B T} \right)^2 \left( e^{\frac{hv}{k_B T}} \right) \left( e^{\frac{hv}{k_B T}} - 1 \right)^{-2}
\]

c) Plot the vibrational heat capacity for a quantum mechanical one dimensional linear harmonic oscillator from \( T=1K \) to \( T=1000K \) in increments of 50K. At what temperature does the heat capacity come within 20% of its classical value? Assume \( \nu=10^{14} \) sec\(^{-1}\).

Solution: You want the behavior of the function \( \left( \frac{hv}{k_B T} \right)^2 \left( e^{\frac{hv}{k_B T}} \right) \left( e^{\frac{hv}{k_B T}} - 1 \right)^{-2} \).

The ratio \( \frac{hv}{k_B} \) has units of temperature. For \( \nu=10^{14} \) sec\(^{-1}\) we have:

\[\frac{hv}{k_B} = \left( 6.67 \times 10^{-34} \text{ J} \cdot \text{s} \right) \left( 10^{14} \text{ s}^{-1} \right) = 4833K \text{ Then we are interested in the function}
\]

\[
\left( \frac{hv}{k_B T} \right)^2 \left( e^{\frac{hv}{k_B T}} \right) \left( e^{\frac{hv}{k_B T}} - 1 \right)^{-2} = \left( \frac{hv}{k_B T} \right)^2 \left( e^{-\frac{hv}{k_B T}} \right) \left( 1 - e^{-\frac{hv}{k_B T}} \right)^{-2}
\]

\[= \left( \frac{4833K}{T} \right)^2 \left( e^{-\frac{4833K}{T}} \right) \left( 1 - e^{-\frac{4833K}{T}} \right)^{-2} = \left( \frac{4833K}{T} \right)^2 \left( e^{-\frac{4833K}{T}} \right) \left( 1 - e^{-\frac{4833K}{T}} \right)^{-2}
\]

A graph of \( C_v \) in units of \( k_B \) appears below as a function of \( T/4833 \). By 4833K he het capacity is well within 20% of its classical value.