Chemistry 4300, Autumn Semester 2017 , Exam 1

Name:____

1. **[20 points]** The potential energy of a pair of hydrogen atoms separated by a large distance x is given by $V(x) = -C_6/x^6$, where C_6 is a positive constant. What is the force that one atoms exerts on the other? Is the force attractive or repulsive?

The force is given as

$$F = -\frac{dV}{dx}$$

so inserting our potential into this equation we find that

$$\begin{aligned} F &= -\frac{dV}{dx} \\ &= -\frac{d}{dx}\left(-\frac{C_6}{x^6}\right) \\ &= C_6\frac{d}{dx}x^{-6} \\ &= -6C_6x^{-7} \\ &= -\frac{6C_6}{x^7} \end{aligned}$$

This force is attractive.

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2. **[35 points]** During a meteor shower, meteors fall at the rate 15.7 per hour. What is the probability of observing less than 5 in a given period of 30 minutes?

In the problem, we're told that meteors fall at a rate of 15.7 per hour. We're then asked to find the probability of observing less than 5 in a given period of 30 minutes. We'll be using Poisson's Probability distribution to solve this problem; however, we must first find the rate of meteors falling per thirty minutes (to relate to our probability). Taking into consideration the fact that 30 minutes is 0.5 of one hour:

$$15.7\ \frac{\text{meteors}}{\text{hour}} \times \frac{0.5\ \text{hour}}{30\ \text{minutes}} = 7.85\ \frac{\text{meteors}}{30\ \text{minutes}}$$

This marks the average number of meteors that fall within 30 minutes. Given this average, we can use Poisson's Distribution in order to calculate the probability of observing no meteors, 1 meteor, 2 meteors, 3 meteors, and 4 meteors. To find the probability of observing less than five meteors, we then add up all the probabilities we calculated:

$$P_{poisson}(r, \lambda) = \frac{\lambda^r}{r!} e^{-\lambda}$$

$$\begin{aligned} P_{(0\text{ meteors})} &= \frac{7.85^0}{0!} e^{-7.85} \\ &= 0.000396 \end{aligned}$$

$$\begin{aligned} P_{(1\text{ meteor})} &= \frac{7.85^1}{1!} e^{-7.85} \\ &= 0.00311 \end{aligned}$$

$$\begin{aligned} P_{(2\text{ meteors})} &= \frac{7.85^2}{2!} e^{-7.85} \\ &= 0.0122 \end{aligned}$$

$$\begin{aligned} P_{(3\text{ meteors})} &= \frac{7.85^3}{3!} e^{-7.85} \\ &= 0.0319 \end{aligned}$$

$$\begin{aligned} P_{(4\text{ meteors})} &= \frac{7.85^4}{4!} e^{-7.85} \\ &= 0.0626 \end{aligned}$$

The probability of observing less than 5 is then:

$$\begin{aligned} P &= P_{(0\text{ meteors})} + P_{(1\text{ meteor})} + P_{(2\text{ meteors})} + P_{(3\text{ meteors})} + P_{(4\text{ meteors})} \\ &= 0.110 \text{ or } 11.0\% \end{aligned}$$

There's a probability of 11.0% that you will observe less than five meteors in the provided meteor shower.

3. **[30 points]** The atmosphere of Mars is mostly CO_2 (molar mass 44.0 g/mol) under a pressure of 650 Pa, which we shall assume remains constant. In many places the temperature varies from 0.0°C in summer to −100°C in winter. Over the course of a Martian year, what are the ranges of (a) the rms speeds of the CO_2 molecules and (b) the density (in mol/m^3) of the atmosphere?

(a) Use

$$c_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

Here, I'll use the second form of the equation for connivence from the information provided.

$$\begin{aligned} c_{\text{rms, winter}} &= \sqrt{\frac{3RT}{M}} \\ &= \sqrt{\frac{3(8.314\text{ J/K mole})(173\text{ K})}{44.0\text{ g/mol} \times 10^{-3}}} \\ &= 313.16\text{ m/s} \end{aligned}$$

and

$$\begin{aligned} c_{\text{rms, summer}} &= \sqrt{\frac{3RT}{M}} \\ &= \sqrt{\frac{3(8.314 \text{ J/K mole})(273 \text{ K})}{44.0 \text{ g/mol} \times 10^{-3}}} \\ &= 393.38 \text{ m/s} \end{aligned}$$

so the c_{rms} ranges from 313.16 m/s to 393.38 m/s.
(b) Using now,

$$p = \rho RT$$

we can solve for the density ρ in terms of pressure, p, and the temperature, T. This is,

$$\rho = \frac{p}{RT}$$

now we see that

$$\begin{aligned} \rho_{\text{winter}} &= \frac{650 \text{ Pa} \times \left(\frac{1 \text{ atm}}{101325 \text{ Pa}}\right)}{(8.205 \times 10^{-5} \text{ m}^3 \text{ atm/K mol})(173 \text{ K})} \\ &= 0.4519 \text{ mol/m}^3 \end{aligned}$$

and in the summer

$$\begin{aligned} \rho_{\text{summer}} &= \frac{650 \text{ Pa} \times \left(\frac{1 \text{ atm}}{101325 \text{ Pa}}\right)}{(8.205 \times 10^{-5} \text{ m}^3 \text{ atm/K mol})(273 \text{ K})} \\ &= 0.2863 \text{ mol/m}^3 \end{aligned}$$

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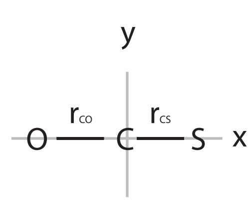
4. **[35 points]** Show that the moment of inertia in the linear OCS molecule is give by

$$I = \left[m_{\text{O}} m_{\text{C}} r_{\text{CO}}^2 + m_{\text{C}} m_{\text{S}} r_{\text{CS}}^2 + m_{\text{O}} m_{\text{S}} (r_{\text{CO}} + r_{\text{CS}})^2\right] / m$$

where m is the total mass $m_{\text{O}} + m_{\text{C}} + m_{\text{S}}$.



Before starting, let's take a moment to write out the coordinates of each atom in our system. Taking the right hand side of the x axis as positive and the upward direction of y axis as positive, we can write the coordinates of the atoms as follows:

#	atom	mass	x	y	z
1	C	m_C	0	0	0
2	S	m_S	r_{CS}	0	0
3	O	m_O	$-r_{CO}$	0	0

First, we start by finding the center of mass for our molecule. Using the formula:

$$X = \frac{\sum_i x_i m_i}{\sum_i m_i}$$
$$Y = \frac{\sum_i y_i m_i}{\sum_i m_i}$$
$$Z = \frac{\sum_i z_i m_i}{\sum_i m_i}$$

We obtain:

$$X = \frac{(0)(m_C) + (r_{CS})(m_S) + (-r_{CO})(m_O)}{m_C + m_O + m_S} = \frac{m_S r_{CS} - m_O r_{CO}}{m}$$
$$Y = \frac{(0)(m_C) + (0)(m_S) + (0)(m_O)}{m_C + m_O + m_S} = 0$$
$$Z = \frac{(0)(m_C) + (0)(m_S) + (0)(m_O)}{m_C + m_O + m_S} = 0$$

Now that we have our center of mass, we can use the formulas for the moment of inertia tensor elements. Before diving in, we should take note of the molecule we're working with. Specifically, we should notice that OCS is a linear molecule. That means if we're working in the principal axis system, $I_a = 0$ and $I_b = I_c$. The coordinate system was chosen in this problem so that the x and y axes lie along the rotational axes of our molecule, signifying the moment of inertia tensor will be diagonal when we calculate it. Thus, we need to only consider the diagonal elements. This is done below:

$$I_{xx} = \sum_{i}^{N} m_i(y_i^2 + z_i^2) - M(Y^2 + Z^2)$$

$$= m_C((0)^2 + (0)^2) + m_S((0)^2 + (0)^2) + m_O((0)^2 + (0)^2) - m((0)^2 + (0)^2)$$
$$= 0$$

$$I_{yy} = \sum_{i}^{N} m_i(x_i^2 + z_i^2) - M(X^2 + Z^2)$$
$$= m_C((0)^2 + (0)^2) + m_S((r_{CS})^2 + (0)^2) + m_O((-r_{CO})^2 + (0)^2) - m((\frac{m_S r_{CS} - m_O r_{CO}}{m})^2 + (0)^2)$$
$$= m_S r_{CS}^2 + m_O r_{CO}^2 - \frac{(m_S r_{CS} - m_O r_{CO})^2}{m}$$
$$= m_S r_{CS}^2 + m_O r_{CO}^2 - \frac{(m_S r_{CS})^2 - m_S m_O r_{CS} r_{CO} - m_S m_O r_{CS} r_{CO} + (m_O r_{CO})^2}{m}$$
$$= \frac{(m) m_S r_{CS}^2 + (m) m_O r_{CO}^2 - \left[(m_S r_{CS})^2 - m_S m_O r_{CS} r_{CO} - m_S m_O r_{CS} r_{CO} + (m_O r_{CO})^2\right]}{m}$$
$$= \frac{(m) m_S r_{CS}^2 + (m) m_O r_{CO}^2 - (m_S r_{CS})^2 + 2 m_S m_O r_{CS} r_{CO} - (m_O r_{CO})^2}{m}$$
$$= \frac{(m_O + m_C + m_S) m_S r_{CS}^2 + (m_O + m_C + m_S) m_O r_{CO}^2 - (m_S r_{CS})^2 + 2 m_S m_O r_{CS} r_{CO} - (m_O r_{CO})^2}{m}$$
$$= \frac{m_S^2 r_{CS}^2 + m_O m_S r_{CS}^2 + m_C m_S r_{CS}^2 + m_S m_O r_{CO}^2 + m_O^2 r_{CO}^2 + m_C m_O r_{CO}^2 - m_S^2 r_{CS}^2 + 2 m_S m_O r_{CS} r_{CO} - m_O^2 r_{CO}^2}{m}$$
$$= \frac{m_O m_S r_{CS}^2 + m_C m_S r_{CS}^2 + m_S m_O r_{CO}^2 + m_C m_O r_{CO}^2 + 2 m_S m_O r_{CS} r_{CO}}{m}$$
$$= \frac{m_S m_O (r_{CS}^2 + 2 r_{CS} r_{CO} + r_{CO}^2) + m_C m_S r_{CS}^2 + m_C m_O r_{CO}^2}{m}$$
$$= \frac{m_C m_S r_{CS}^2 + m_C m_O r_{CO}^2 + m_S m_O (r_{CS} + r_{CO})^2}{m}$$

Since we're working with a linear molecule, we know that in this case $I_{xx} = I_a = 0$ and thus $I_{yy} = I_{zz}$. Thus, we have shown that the moment of inertia is the quantity that we set out to prove.

5. **[35 points]** Scientists have used a highly sensitive technique to measure the mass of a vaccinia virus (the kind used in smallpox vaccine). The procedure involved measuring the frequency of oscillation of a tiny sliver of silicon (just 30 nm long) with a laser, first without the virus and then after the virus had attached itself to the silicon. The difference in mass caused a change in the frequency. We can model such a process as a mass on a spring.
(a) Show that the ratio of the frequency with the virus attached (f_{S+V}) to the frequency without the virus (f_S) is given by

$$\frac{f_{S+V}}{f_S} = \frac{1}{\sqrt{1 + m_V/m_S}}$$

where m_V is the mass of the virus and m_S is the mass of the silicon sliver. Notice that it is not necessary to know or measure the force constant of the spring.
(b) In some data, the silicon sliver has a mass of 2.10×10^{-16} g and a frequency of 2.00×10^{15} Hz without the virus and 2.87×10^{14} Hz with the virus. What is the mass of the virus, in grams and in femtograms?

(a) The frequency in the absence of the virus is in units of the natural oscillation frequency is

$$\omega_{0,S} = f_S = \sqrt{\frac{\kappa_f}{m_S}}$$

Similarly, we can write down an equation describing the frequency of vibration for the virus attached

$$\omega_{0,S+V} = f_{S+V} = \sqrt{\frac{\kappa_{\mathrm{f}}}{m_{S+V}}}$$

now, forming the ratio f_{S+V}/f_S we find

$$\begin{aligned} \frac{f_{S+V}}{f_S} &= \frac{\sqrt{\frac{\kappa_{\mathrm{f}}}{m_{S+V}}}}{\sqrt{\frac{\kappa_{\mathrm{f}}}{m_S}}} \\ &= \sqrt{\frac{m_S}{m_S + m_V}} \end{aligned}$$

dividing everything under the radical by m_S we obtain that

$$\frac{f_{S+V}}{f_S} = \frac{1}{\sqrt{1 + m_V/m_S}}$$

(b) Using the formula we just derived we can compute the mass of the virus

$$\begin{aligned} \frac{f_{S+V}}{f_S} &= \frac{1}{\sqrt{1 + m_V/m_S}} \\ \left(\frac{f_{S+V}}{f_S}\right)^2 &= \frac{1}{1 + m_V/m_S} \\ \left(\frac{f_S}{f_{S+V}}\right)^2 &= \frac{1 + m_V/m_S}{1} \\ \left(\frac{f_S}{f_{S+V}}\right)^2 &= 1 + \frac{m_V}{m_S} \\ m_S\left[\left(\frac{f_S}{f_{S+V}}\right)^2 - 1\right] &= m_V \\ 2.10 \times 10^{-16}\ \mathrm{g}\left[\frac{2.00 \times 10^{15}\ \mathrm{Hz}}{2.87 \times 10^{14}\ \mathrm{Hz}} - 1\right]^2 &= m_V \\ m_V &= 9.99 \times 10^{-15}\ \mathrm{g} = 9.99\ \text{fentograms} \end{aligned}$$

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6. **[30 points]** A sample of methane gas is heated from 300 K to 390 K. Calculate the percent increase in its kinetic energy.

Methane is a non-linear polyatomic molecule and on a per molecule basis has energy

$$\bar{\epsilon} = 3(X - 1)\left(k_B T\right)$$

where X is the number of atoms in the molecule. We find then by taking the ratio

$$\begin{aligned} \frac{\bar{\epsilon}_{390\ \mathrm{K}}}{\bar{\epsilon}_{300\ \mathrm{K}}} &= \frac{3(X-1)\left(k_B(390\ \mathrm{K})\right)}{3(X-1)\left(k_B(300\ \mathrm{K})\right)} \\ &= \frac{390\ \mathrm{K}}{300\ \mathrm{K}} \\ &= 1.3 \end{aligned}$$

this is a 30% increase in the kinetic energy.

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7. **[35 points]** Calculate the average interaction energy, in J/mol, between a water molecule ($\mu = 1.85$ D) and a benzene molecule ($\alpha_0 = 10 \times 10^{-30}$ m^3) separated by 1.0 nm.

Here we use the orientationally averaged formula for a dipole induced dipole. This is

$$\langle V \rangle = -\frac{2\boldsymbol{\alpha}\mu^2}{(4\pi\epsilon_0\kappa)^2}\frac{1}{r^6}$$

First let's convert to SI units

$$1.85 \text{ D} = \frac{3.33664 \times 10^{-30} \text{ C m}}{1 \text{ D}} = 6.17 \times 10^{-30} \text{ C m}$$

now, lets find $\boldsymbol{\alpha}$ from α_0 by the formula

$$\alpha_0 = \frac{\boldsymbol{\alpha}}{4\pi\epsilon_0}$$

so this means that

$$\boldsymbol{\alpha} = 4\pi\epsilon_0\alpha_0$$

now we can plug everything into our formula and find

$$\begin{aligned}\langle V \rangle &= -\frac{2(4\pi\epsilon_0\alpha_0)(6.17 \times 10^{-30} \text{ C m})^2}{(4\pi\epsilon_0\kappa)^2}\frac{1}{(1 \times 10^{-9} \text{ m})^6} \\ &= -\frac{\alpha_0(6.17 \times 10^{-30} \text{ C m})^2}{2\pi\epsilon_0\kappa^2}\frac{1}{(1 \times 10^{-9} \text{ m})^6} \\ &= -\frac{10 \times 10^{-30} \text{ m}^3(6.17 \times 10^{-30} \text{ C m})^2}{2\pi(8.854 \times 10^{-12} \text{ C}^2/(\text{N} \cdot \text{ m}^2)(1)^2}\frac{1}{(1 \times 10^{-9} \text{ m})^6} \\ &= -6.84 \times 10^{-24} \text{ J}\end{aligned}$$

so multiplying by Avogadro's number we find

$$\begin{aligned}\langle V \rangle &= -6.84 \times 10^{-24} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1} \\ &= -4.12 \text{ J/mol}\end{aligned}$$

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8. **[30 points]** The motion of ripples of short wavelength (≤ 1 cm) on water is controlled by surface tension, γ. The phase velocity of such ripples is given by

$$v_p = \left(\frac{2\pi\gamma}{\rho\lambda}\right)^{1/2}$$

where ρ is the density of water.

(a) Show that the group velocity for a disturbance made up of wavelengths close to a given λ is equal to $3v_p/2$.

(b) What does this imply about the observed motion of a group of ripples traveling over a water surface?

(a) First use the relationship that $k = 2\pi/\lambda$ and find that

$$\begin{aligned}v_p &= \left(\frac{2\pi\gamma}{\rho\lambda}\right)^{1/2} \\ &= \left(\frac{2\pi\gamma}{\rho\left(\frac{2\pi}{k}\right)}\right)^{1/2} \\ &= \left(\frac{\gamma k}{\rho}\right)^{1/2}\end{aligned}$$

we also know that $v_p k = \omega$ so we can find ω by

$$\begin{aligned}\omega &= v_p k \\ &= \left(\frac{\gamma k}{\rho}\right)^{1/2} k \\ &= k^{3/2}\left(\frac{\gamma}{\rho}\right)^{1/2}\end{aligned}$$

the group velocity is defined as

$$v_g = \frac{\partial \omega}{\partial k}$$

so taking the k derivative with respect to ω we find t

$$\begin{aligned}\frac{\partial \omega}{\partial k} &= \frac{\partial}{\partial k} k^{3/2}\left(\frac{\gamma}{\rho}\right)^{1/2} \\ &= \frac{3}{2}\left(\frac{\gamma k}{\rho}\right)^{1/2} \\ &= \frac{3}{2} v_p\end{aligned}$$

(b) The group moves at a different rate than the phase (in fact faster than the phase).