

## Physics 176: Midterm Exam Solutions

March, 2011

Most of the following answers are more detailed than what was necessary to get full credit. I hope the details will help you improve your problem solving skills and understand the physics better.

### Problems That Require Writing

1. Black holes are simple pure objects in that, no matter what kind of matter collapsed to form the black hole, only three numbers are needed to define its macrostate: the black hole's mass  $M$ , its electrical charge  $Q$ , and its angular momentum  $\mathbf{L}$ . For an electrically-neutral non-rotating black hole ( $Q = 0$ ,  $\mathbf{L} = \mathbf{0}$ ), the black hole's entropy  $S$  depends only on  $M$  and is given by

$$S = \left( \frac{8\pi^2 kG}{hc} \right) M^2 \quad (1)$$

where  $k$  is Boltzmann's constant,  $G$  is the gravitational constant,  $h$  is Planck's constant, and  $c$  is the speed of light.

- (a) **(5 points)** Given that the energy of a black hole is its relativistic rest mass  $U = Mc^2$ , derive a formula for the temperature  $T$  of a black hole in terms of its mass  $M$ . Does decreasing the mass of a black hole make it hotter or colder?

**Answer:** The temperature can be deduced from the dependence of the entropy  $S(U)$  on the system's energy  $U$  using the standard formula. We have:

$$\frac{1}{T} = \frac{\partial S}{\partial U} \quad (2)$$

$$= \frac{\partial S}{\partial M} \times \frac{dM}{dU} \quad (3)$$

$$= \left( \frac{8\pi^2 kG}{hc} \right) \cdot 2M \times \frac{1}{c^2} \quad (4)$$

$$= \frac{16\pi^2 kG}{hc^3} M, \quad (5)$$

so the answer is

$$T = \frac{hc^3}{16\pi^2 GkM} \propto M^{-1}. \quad (6)$$

Note how the entropy and temperature of a black hole involve fundamental constants from four different areas of physics: thermal physics ( $k$ ), gravity ( $G$ ), quantum mechanics ( $h$ ), and special relativity ( $c$ ). This makes black holes intriguing indeed.

Since  $T \propto M^{-1}$  and mass is always a positive quantity (any material object resists acceleration), the temperature must also be positive for a black hole. Black holes are exotic objects but they can't have a negative temperature like a paramagnet.

Because  $T \propto M^{-1}$ , the smaller the mass of a black hole, the hotter it is. A sufficiently small black hole (about the mass of the Earth's moon or less,  $10^{22}$  kg) will become hotter than 3K the temperature of the cosmic blackbody radiation. We would then expect energy to transfer from the black hole to the surrounding photon gas if the black hole could transfer energy. This has been predicted to be possible by the physicist Stephen Hawking, who heuristically applied relativistic quantum mechanics to Einstein's classical gravity theory to predict that all black holes emit light radiation from their event horizon (called "Hawking radiation") and so can evaporate away into light if hotter than their surroundings. Further, the smaller the mass of a black hole, the faster it loses mass by Hawking radiation. The tiny small mass black holes predicted to occur

in the Large Hadron Collider (based on the assumption that there are more than three spatial dimensions) are super hot and disappear within  $10^{-10}$  s of their appearance, in a burst of gamma rays which would be the signature for their appearance. You can learn more about Eq. (6), called the Hawking radiation temperature, from the Wikipedia article with title “Hawking Radiation”.

- (b) **(5 points)** Estimate to the nearest power of ten the temperature  $T$  of a black hole whose mass is one solar mass,  $M \approx 10^{30}$  kg.

**Answer:** As described earlier in the course, I strongly recommend substituting the raw numbers into some formula, then round and simplify. Using the values given at the end of the quiz (except for  $k \approx 1.4 \times 10^{-23}$  J/K which you had to know from memory), we find:

$$T = \frac{hc^3}{16\pi^2 G k M} \quad (7)$$

$$\approx \frac{7 \times 10^{-34} \cdot (3 \times 10^8)^3}{16 \cdot \pi^2 \cdot 7 \times 10^{-11} \cdot 1 \times 10^{-23} \cdot 10^{30}} \quad (8)$$

$$\approx \frac{10 \times 10^{-34} \cdot 3^3 \times 10^{24}}{10 \cdot 10 \cdot 10 \times 10^{-11} \cdot 10^{-23} \cdot 10^{30}} \quad (9)$$

$$\approx 10^{1-34+1+24-1-1-1+11+23-30} \quad (10)$$

$$\approx 10^{-7} \text{ K}, \quad (11)$$

which is cold. (The answer to one significant digit is  $2 \times 10^{-7}$  K so the above approximations lead to the correct nearest power of ten.)

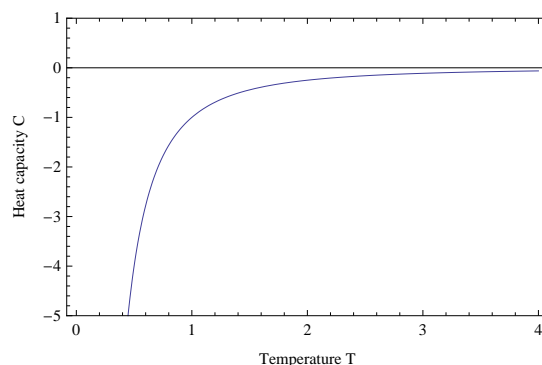
Here I rounded  $7 \approx 10$ ,  $16 \approx 10$  and  $\pi^2 \approx 3^2 \approx 10$ . I did *not* approximate  $3 \times 10^8 \approx 10^8$  because the speed of light is being cubed and one should always cube the digits and then round to the nearest power of ten since cubes (and other powers) can produce one to two powers of ten. So  $(3 \times 10^8)^3 = 3^3 \times 10^{24} = 27 \times 10^{24} \approx 10 \times 10^{24}$ .

- (c) **(5 points)** Qualitatively sketch how the heat capacity  $C(T)$  of the black hole varies with the black hole’s temperature  $T$  for  $T \geq 0$ , and discuss whether  $C(T)$  is compatible with the third law of thermodynamics.

**Answer:** The answer can be obtained most quickly by using proportionality and Eq. (6):

$$U \propto M \propto T^{-1} \Rightarrow C = \frac{dU}{dT} \propto -T^{-2}. \quad (12)$$

So the heat capacity  $C(T)$  for a black hole looks qualitatively like the function  $-a/T^2$  for some positive constant  $a$  which you could set to 1 for the sake of plotting, i.e., it looks like this:



You have seen negative capacities before when you solved Schroeder Problem 1.55 on page 36-37 about the heat capacities of stars, so perhaps it is not too surprising that the heat capacity of a

black hole, which arises from a collapsed star and is gravitationally bound, might also have this property.

2. A kilogram of ice ( $T_1 = 0^\circ \text{C}$ ) and a kilogram of boiling water ( $T_2 = 100^\circ \text{C}$ ) at atmospheric pressure are mixed together in a thermally isolated container and allowed to come to thermodynamic equilibrium.

- (a) **(5 points)** To one significant digit, calculate the final temperature  $T_f$  in Celsius inside the container and describe what you will find in the container if you open it up.

Note: The specific heat of water at constant pressure  $c_P \approx 4.2 \times 10^3 \text{ J}/(\text{kg} \cdot \text{K})$ , and the latent heat of fusion (for converting ice to water) is  $L \approx 3.4 \times 10^5 \text{ J/kg}$ .

**Answer:** First solve this problem conceptually: heat from the boiling water will first melt the ice with a constant temperature  $T_1 = 0^\circ \text{C}$ . If the boiling water has not cooled down to temperature  $T_1$  after the ice has all melted, the remaining heat will warm the melted water at temperature  $T_1$  to the common final temperature  $T_f$  of the melted water and boiling water.

To make more clear the role of ice and boiling water, let's assume that the mass of the ice is  $m_i$  and the mass of the boiling water is  $m_b$ , both in kilograms.

The condition for ice to remain after equilibrium is reached would be that the total heat obtained from the boiling water,  $m_b c_P (T_2 - T_1)$ , when the boiling water has cooled down to the temperature  $T_1$  of ice, is less than the energy needed to melt the ice,  $m_i L$ :

$$m_b c_P (T_2 - T_1) < m_i L, \quad (13)$$

or

$$\frac{m_b}{m_i} < \frac{L}{c_P (T_2 - T_1)}. \quad (14)$$

The right side is approximately equal to  $3.4/4.2 \approx 3.2/4 \approx 0.8$ . Since the masses are assumed equal, Eq. (14) is not satisfied and we conclude that all the ice must melt and the final temperature  $T_f$  must be greater than  $T_1$ : only water will be observed in the container when it is opened after reaching equilibrium.

Conservation of energy requires that the heat from the boiling water  $m_b c_P (T_2 - T_f)$ , must equal the energy needed to melt the ice  $m_i L$  plus the energy  $m_i c_P (T_f - T_1)$  needed to raise the temperature of the water from the ice to the final temperature  $T_f$ :

$$m_b c_P (T_2 - T_f) = m_i L + m_i c_P (T_f - T_1). \quad (15)$$

We can then solve for the final temperature  $T_f$  in terms of given quantities:

$$T_f = \frac{m_i c_P T_1 + m_b c_P T_2 - m_i L}{(m_i + m_b) c_P} = \frac{m_i T_1 + m_b T_2}{m_i + m_b} - \frac{m_i}{m_i + m_b} \frac{L}{c_P}. \quad (16)$$

The term  $(m_i T_1 + m_b T_2) / (m_i + m_b)$  is what we would expect if there were no phase transition of ice to water, it is just a weighted average of the initial temperatures by the corresponding amounts of mass. The final temperature is lower however by the amount  $(-m_i / (m_i + m_b))(L / c_P)$  because heat is needed to melt the ice first.

For the given values  $m_b = m_i = 1 \text{ kg}$ , Eq. (16) becomes:

$$T_f = \frac{T_1 + T_2}{2} - \frac{1}{2} \frac{L}{c_P} \quad (17)$$

$$\approx \frac{0 + 100}{2} - \frac{1}{2} \frac{34}{4.2} \times 10 \approx 50 - \frac{32}{4} \times \frac{10}{2} = 50 - 40 \approx 10^\circ \text{C}, \quad (18)$$

to one significant digit. The fact that the final temperature is much closer to that of ice nicely shows how a lot of energy is needed to melt a kilogram of ice compared to raising the temperature of water at  $0^\circ \text{C}$  to a higher temperature.

One student in the class found a particularly efficient way to solve this problem by asking how much the temperature of the boiling water will drop after melting all of the ice to water with temperature  $T_1$ :

$$c_P(T_2 - T_f) = L \quad \Rightarrow \quad T_2 - T_f = \frac{L}{c_P} \approx 80^\circ \text{C}. \quad (19)$$

So the boiling water will be at a temperature of  $100 - 80 = 20^\circ \text{C}$  after melting all the ice but before warming any of the water from the melted ice. Because there are equal amounts of melted ice and cooled boiling water remaining, the final temperature is just the average of the two temperatures,  $T_1 = 0^\circ \text{C}$  and  $20^\circ \text{C}$  so  $T_f = 10^\circ \text{C}$ .

- (b) **(5 points)** In terms of the quantities  $T_1$ ,  $T_2$ ,  $T_f$ ,  $c_P$ , and  $L$ , find a mathematical expression (which you do *not* have to evaluate numerically) for the total change in entropy of the ice-water mixture after the mixture has reached equilibrium.

**Answer:** The total entropy change  $\Delta S_{\text{total}}$  will consist of the three contributions: melting the ice with constant temperature  $T_1$ , raising the temperature of the melted water with temperature  $T_1$  to the final temperature  $T_f$ , and lowering the temperature of the boiling water to the final temperature  $T_f$ . Assuming the general case of masses  $m_b$  and  $m_i$  for the boiling water and ice respectively, we can write:

$$\Delta S_{\text{total}} = \frac{m_i L}{T_1 + 273} + \int_{T_1+273}^{T_f+273} \frac{m_i c_P}{T} dT + \int_{T_2+273}^{T_f+273} \frac{m_b c_P}{T} dT \quad (20)$$

$$= \frac{m_i L}{T_1 + 273} + m_i c_P \ln \left( \frac{T_f + 273}{T_1 + 273} \right) + m_b c_P \ln \left( \frac{T_f + 273}{T_2 + 273} \right), \quad (21)$$

since we have assumed that the specific heat  $c_P$  of water is approximately constant from melting to boiling.

Note the important point that *we have to switch to absolute temperatures in the entropy formulas* since the integrands  $c_p(T) dT/T$  involve a  $1/T$  factor which is meaningful only for  $T$  measured on an absolute temperature scale. Since  $T_1$  and  $T_2$  were given in Celsius, we have to convert these temperature to kelvin as indicated to get the right answer.

For the case  $m_i = m_b = 1 \text{ kg}$ , Eq. (21) takes on the simpler form

$$\Delta S_{\text{total}} = \frac{L}{T_1 + 273} + c_P \ln \left[ \frac{(T_f + 273)^2}{(T_1 + 273)(T_2 + 273)} \right], \quad (22)$$

which was the answer I was looking for.

The numerical values of the three terms in Eq. (21) for  $m_1 = m_2 = 1 \text{ kg}$  are

$$\Delta S_{\text{total}} \approx (1245 + 151 - 1160) \frac{\text{J}}{\text{K}} \quad (23)$$

$$\approx (1396 - 1160) \frac{\text{J}}{\text{K}} \quad (24)$$

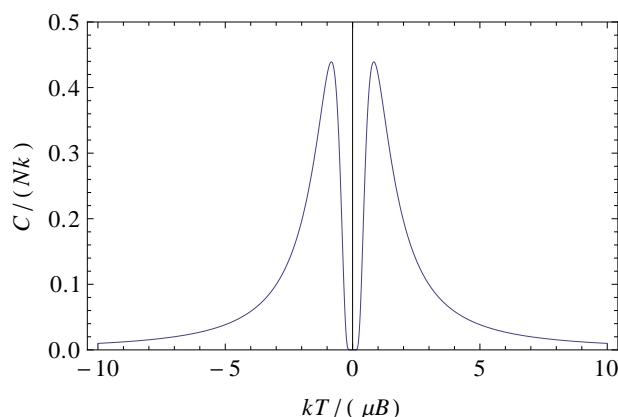
$$\approx 240 \frac{\text{J}}{\text{K}}. \quad (25)$$

Most of the entropy increase,  $1245 \text{ J/K}$ , arises from melting the ice to water, only a small entropy increase  $151 \text{ J/K}$  arises from raising the temperature of the melted water to the final temperature of  $T_f = 10^\circ \text{C}$ . The cooling of the boiling water to  $T_f$  causes a large *decrease* in the entropy,  $-1160 \text{ J/K}$ , but not enough to overcome the entropy increase of melting and warming. The total entropy change of  $240 \text{ J/K}$  is therefore positive (as it should be), and its magnitude of order  $100 \text{ J/K}$  is typical for temperature changes near room temperature for hand-size objects.

3. **(8 points)** Draw the qualitative form of the temperature-dependence of the heat capacity,  $C(T)/(Nk)$  vs  $kT/(\mu B)$ , for a paramagnet consisting of  $N$  spin-1/2 magnetic dipoles of strength  $\mu$  that has been placed in an homogeneous external magnetic field of magnitude  $B$ . Give the approximate numerical values on the horizontal and vertical axes for any interesting features of the curve, and explain whether your plot is consistent with the equipartition theorem.

Note: this problem does not require any derivations or formulas.

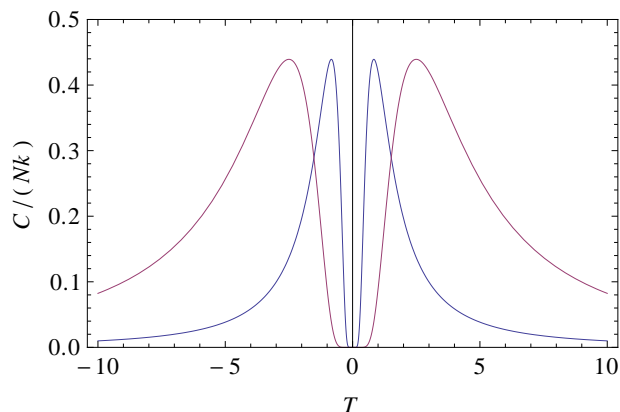
**Answer:** The qualitative form of the heat capacity was worked out during a class project several lectures ago, in which you started with the qualitative form of the entropy  $S(U)$  for a paramagnet, an upside-down U (see Fig. 3.8 on page 101 of Schroeder), then sketched  $T = dU/dS$  vs  $U$ , then rotated and flipped the  $T$  vs  $U$  curve to get  $U$  vs  $T$ , then you sketched  $C = dU/dT$  vs  $T$ . The result, combined with the requirement that  $C \rightarrow 0$  as  $T \rightarrow 0$ , leads to the left panel of Fig. 3.10 on page 103 of Schroeder for the positive temperature part of the plot, and you have to reflect this curve about  $T = 0$  to get the negative temperature part of the heat capacity. The final answer therefore has the form:



decaying to zero as  $T \rightarrow \infty$  and decaying to zero as  $T \rightarrow 0$ . There is a peak of magnitude 1 (actually of height 0.44 but 1 is fine for the order of magnitude) around  $kT/(\mu B) \approx 1$  (the precise location is  $kT/(\mu B) \approx 0.83$ ). If one chooses appropriate units such as  $Nk$  for  $C$  and  $k/(\mu B)$  for  $T$ , one generally expects interesting features to occur when the units have magnitude about one. (And if interesting features occur for large deviations away from one, that is a sign that something interesting and unexpected is occurring, an unsuspected extra scale exists.)

The paramagnet's heat capacity varies (strongly!) with temperature, which contradicts the most obvious prediction of the equipartition theorem: since  $U = Nf(kT/2)$  where  $f$  is the number of quadratic terms that appear in the energy for a microscopic component of the system, the heat capacity  $C = Nf(k/2)$  is independent of temperature.

Given this plot, we can quickly answer a related question namely for a fixed temperature  $T$ , how does the heat capacity  $C$  of a paramagnet change with magnetic field strength? Because the magnetic field strength enters all the physical equations through the single quantity  $kT/(\mu B)$ , increasing the magnetic field strength  $B$  simply stretches the curve  $C/(Nk)$  horizontally when plotted versus  $T$  (not plotted versus  $kT/(\mu B)$ ) since a larger temperature  $T$  is needed for the quantity  $kT/(\mu B)$  and so for  $C(kT/(\mu B))$  to have the same value as before. For example, if we increase the magnetic field strength by a factor of 3,  $B \rightarrow 3B$ , the new heat capacity curve becomes the purple curve in this plot:



with the peak now appearing at a three-times higher temperature than before. From this plot, you can see that increasing the magnetic field with the temperature fixed always causes the heat capacity to increase at large temperatures, to decrease for sufficiently small temperatures, and can increase or decrease at intermediate temperatures. Can you use physical reasoning to justify these conclusions?

4. **(8 points)** For  $x$  a real number whose magnitude is small and for constants  $a$  and  $b$ , find a second-order accurate approximation  $c_0 + c_1x + c_2x^2$  to the expression

$$\frac{1}{1 + \exp(ax + bx^2)}. \quad (26)$$

**Answer:** Please take the time to justify the following steps so you can become a guru of Taylor series approximations, in which you obtain useful approximations without having to evaluate any derivatives:

$$\frac{1}{1 + \exp(ax + bx^2)} \approx \frac{1}{1 + \left[1 + (ax + bx^2) + \frac{1}{2}(ax + bx^2)^2\right]} \quad (27)$$

$$\approx \frac{1}{2 + ax + (b + a^2/2)x^2} \quad (28)$$

$$= \frac{1}{2} \times \frac{1}{1 + (a/2)x + (b/2 + a^2/4)x^2} \quad (29)$$

$$\approx \frac{1}{2} \times \left(1 - [(a/2)x + (b/2 + a^2/4)x^2] + [(a/2)x + (b/2 + a^2/4)x^2]^2\right) \quad (30)$$

$$\approx \frac{1}{2} \left[1 - \frac{a}{2}x + \left(-\left(b/2 + a^2/4\right) + a^2/4\right)x^2\right] \quad (31)$$

$$\approx \frac{1}{2} - \frac{a}{4}x - \frac{b}{4}x^2. \quad (32)$$

Eq. (32) is the intended answer. One can verify this using Mathematica by typing say:

`Series[ 1 / (1 + Exp[a x + b x^2]) , {x, 0, 4} ]`

which produces the output up to fourth-order in  $x$ :

$$\frac{1}{2} - \frac{a}{4}x - \frac{b}{4}x^2 + \frac{a^3}{48}x^3 + \frac{a^2b}{16}x^4 + O(x^5). \quad (33)$$

As tempting as it looks, it would have been wrong to treat  $\exp(ax + bx^2)$  as a small quantity  $\epsilon$  and use the approximation  $1/(1 + \epsilon) = 1 - \epsilon + \epsilon^2$  since, for  $x$  small in magnitude,  $\exp(x) \approx 1$  is not small.

5. The thermodynamic processes corresponding to a gasoline combustion engine can be roughly modeled by a so-called Otto cycle, which consists of the following four successive steps applied to air. (For this problem, you can think of air as an ideal gas consisting of diatomic nitrogen molecules that each have  $f$  degrees of freedom.)

- step 1, adiabatic compression: The gas with initial values  $(V_1, P_1)$  for the volume and pressure is compressed adiabatically by a piston to a smaller volume  $V_2 < V_1$  so that the gas parameters are now  $(V_2, P_2)$ .
- step 2, constant volume heating by combustion: The piston is then locked into place (which makes the volume of the gas constant) and an amount of heat  $Q_0 > 0$  is transferred to the gas by combustion of gasoline droplets mixed with the air. The heat increases the pressure to a new value  $P_3 > P_2$  so that the gas parameters are now  $(V_2, P_3)$ .
- step 3, adiabatic expansion: The piston is released and the gas now expands adiabatically, doing useful work, until the volume has return to the starting volume  $V_1$ . The gas parameters are now  $(V_1, P_4)$ .
- step 4, constant volume cooling: the piston is again locked in place and the gas is cooled with constant volume until the state of the gas has returned to its starting value of  $(V_1, P_1)$ .

Please answer the following questions:

- (a) **(12 points)** Draw the four steps of an Otto cycle on a  $PV$  diagram. On your plot
- i. shade the area that corresponds to the total work done during one cycle.
  - ii. indicate with an arrow and label where the temperature of the gas is highest along the cycle.
  - iii. indicate with an arrow and label where the temperature of the gas is lowest along the cycle.
  - iv. indicate with an arrow and label which of the four steps generates the most entropy.

Note: you need to justify your answers briefly so that I understand that you understand how you got your answers.

**Answer:** Figure 4.5 on page 131 of Schroeder shows the qualitative form of an Otto cycle on a  $PV$  diagram, and you should read Schroeder's words of wisdom about the Otto cycle on pages 131-132. The area enclosed by the closed loop is the work done by the Otto cycle during one cycle and is what you should have shaded.

The point labeled "1" in Fig. 4.5 is the coldest part of the cycle. The temperature increases from point 1 to point 2 since you are adiabatically compressing for which  $TV^{\gamma-1} = TV^{2/f} = \text{constant}$  which implies  $T$  must get bigger if  $V$  becomes smaller. (The new temperature at the end of step 1 is in fact  $T_2 = (V_1/V_2)^{\gamma-1}T_1$ .) The ignition step from 2 to 3 adds energy to the gas (via combustion of fuel) so the temperature must increase even more.

Step 3 from point 3 to point 4 is an adiabatic expansion which means that the temperature must drop, so we conclude that point 3 of the Otto cycle is the location of the highest temperature along the cycle. Step 4, from point 4 back to point 1, involves cooling the gas so the temperature at point 4 must be higher than point 1.

Since heat does not flow into or out of the gas during the two adiabatic processes step 1 and step 3, we conclude that the heat input  $Q_0$  during step 2 from combustion is the total heat input  $Q_h$  over the Otto cycle since heat is removed during step 4. So  $Q_h = Q_0$  and calculating the efficiency of the Otto cycle reduces to calculating  $W/Q_0$  where  $W$  is the total work done by the gas during the cycle.

As discussed in lecture, the entropy  $S(U, V, N)$  of an equilibrium system is a state function that depends only on the current values of  $U$ ,  $V$ , and  $N$ . This implies that the total entropy change for any closed cycle in the  $PV$  diagram is zero (provided that all the processes along the cycle are carried out quasistatically, so the system is always arbitrarily close to being in equilibrium). Since entropy does not change during an adiabatic process (no heat flows in or out of the gas so  $dS = Q/T = [C(V)dT]/T = 0$  over some small change in temperature  $dT$ ), the entropy change is zero after the adiabatic compression (step 1) and after the adiabatic expansion (step 3). Since

the total entropy change is zero, the entropy change during step 2, heating by combustion, must be the step that creates the largest amount of entropy, while step 4, cooling at constant volume, must create an exactly opposite decrease in entropy so that the sum of the entropy changes adds up to zero.

If we wanted to calculate the entropy increase during step 2, we would use the formula for a constant volume process and could try assuming that equipartition of the gas holds over the temperature range of the Otto cycle. We would then have:

$$\Delta S_{\text{step-2}} = \int_{T_2}^{T_3} \frac{C_V(T)}{T} dT = \left( \frac{Nfk}{2} \right) \ln \left( \frac{T_3}{T_2} \right), \quad (34)$$

with

$$T_2 = \left( \frac{V_1}{V_2} \right)^{\gamma-1} T_1 = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \frac{P_1 V_1}{Nk} \quad \text{and} \quad T_3 = T_2 + \frac{2Q}{Nfk}, \quad (35)$$

the final result is not a particularly concise or insightful expression.

(b) **(10 points)** Given that the efficiency  $e$  of a heat engine is defined to be

$$e = \frac{W}{Q_h}, \quad (36)$$

where  $W$  is the total work done by the system during one cycle and  $Q_h$  is the total amount of heat that enters the system during one cycle, show for an Otto cycle that

$$e = 1 - \left( \frac{V_2}{V_1} \right)^{\gamma-1}, \quad (37)$$

where  $\gamma = (f+2)/f$  is the adiabatic exponent (so  $\gamma - 1 = 2/f$ ). Increased efficiency therefore requires making the compression ratio  $V_2/V_1$  smaller; actual engines have a compression ratio of about 1/8.

Hint: You can deduce  $P_2$  in terms of the given quantities  $V_1$ ,  $V_2$ , and  $P_1$  from the relation  $P_1 V_1^\gamma = P_2 V_2^\gamma$  since step 1 is an adiabatic process. Next, figure out how to express  $P_3$  in terms of  $Q_0$ ,  $P_1$ ,  $V_1$ , and  $V_2$ . Finally, calculate  $W$  for the entire cycle by evaluating an appropriate integral between  $V_2$  and  $V_1$ .

**Answer:** Thinking about the successive steps of the Otto cycle led to the conclusion that  $Q_h = Q_0$  so we need to calculate the total work  $W$  done by the gas during one cycle to calculate the efficiency Eq. (36). The pressure  $P_3$  right after the combustion step 2 can be determined by conservation of energy

$$\Delta U = Q + W = Q, \quad (38)$$

since  $W = 0$ , no work is done on the gas during a constant volume process. We are given the value  $Q_0$  (this is determined by the amount of energy released by combusting the gasoline with air so varies with the amount of gas injected into the engine during this step) and so have:

$$Q_0 = \Delta U = \frac{f}{2} \Delta(PV) = \frac{f}{2} (P_3 V_2 - P_2 V_2) = \frac{f V_2}{2} (P_3 - P_2), \quad (39)$$

or

$$P_3 - P_2 = \frac{2Q_0}{fV_2}. \quad (40)$$

Equation (40) allows us to calculate the total work  $W_{\text{total}}$  done by the gas (which is the negative of the work done on the gas). This is the area between the upper pressure curve  $P_{\text{upper}}(V) = (P_3 V_2^\gamma)/V^\gamma$  and the lower curve  $P_{\text{lower}} = (P_2 V_2^\gamma)/V^\gamma$ , where I have used the fact that the upper and lower curves are adiabats that satisfy  $PV^\gamma = \text{constant}$  and the constant is trivially determined



by substituting the values for any point along the curve, e.g.,  $(P_2, V_2)$  for the lower curve and  $(P_3, V_2)$  for the upper curve. The area between the two curves is:

$$W_{\text{total}} = \int_{V_2}^{V_1} P_{\text{upper}}(V) dV - \int_{V_2}^{V_1} P_{\text{lower}}(V) dV \quad (41)$$

$$= \int_{V_2}^{V_1} [P_{\text{upper}}(V) - P_{\text{lower}}(V)] dV \quad (42)$$

$$= \int_{V_2}^{V_1} \left[ \frac{P_3 V_2^\gamma}{V^\gamma} - \frac{P_2 V_2^\gamma}{V^\gamma} \right] dV \quad (43)$$

$$= (P_3 - P_2) V_2^\gamma \int_{V_2}^{V_1} \frac{dV}{V^\gamma} \quad (44)$$

$$= \left( \frac{2Q_0}{fV_2} \right) V_2^\gamma \left[ \frac{V_1^{1-\gamma} - V_2^{1-\gamma}}{1-\gamma} \right] \quad (45)$$

$$= Q_0 \left[ 1 - \left( \frac{V_2}{V_1} \right)^{\gamma-1} \right], \quad (46)$$

which gives the desired answer Eq. (37) after dividing both sides by  $Q_0 = Q_h$ , and after observing that  $(2/f)/(1-\gamma) = -1$  since  $\gamma - 1 = f/2$ .

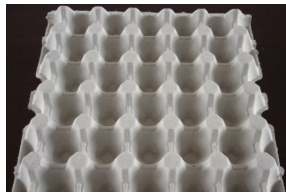
- (c) **(5 points)** By rewriting Eq. (37) in terms of the temperatures that occur at the start and end of step one, explain briefly why the Otto cycle does not attain the maximum possible efficiency allowed by the second law of thermodynamics  $e = 1 - T_c/T_h$ , where  $T_c$  and  $T_h$  are respectively the coldest and hottest temperatures that occur during the Otto cycle.

**Answer:** Using the fact that  $TV^{\gamma-1} = \text{constant}$  for an adiabatic process (this equation was given to you at the end of the quiz), we see that Eq. (37) can be rewritten as

$$e = 1 - \left( \frac{V_2}{V_1} \right)^{\gamma-1} = 1 - \frac{T_1}{T_2}. \quad (47)$$

We have already observed that  $T_1$  is the coldest part of the Otto cycle so this is the temperature that would occur in an optimally efficient Carnot cycle. But the denominator  $T_2$  is not the hottest temperature, it would be the temperature  $T_3$  that occurs right after step 2 at point  $(V_2, P_3)$ . So the Otto cycle is necessarily less efficient than the optimal Carnot cycle that would operate between the highest and lowest temperatures present in the Otto cycle. In fact, the more energy created by combustion (the higher  $T_3$ ), the less efficient the Otto cycle becomes.

6. An important process in many areas of science and engineering is adsorption, the binding of a molecule to the surface of a substance. For many surfaces, a qualitatively useful model of adsorption is an “egg-carton” model in which the surface is assumed to be a set of uniformly spaced and identical concavities like an egg carton:



The concavities are the locations where a molecule can adsorb. The egg carton model assumes that once a molecule adsorbs to the surface, it can not move around, and also that molecules do not interact with one another on the surface, so that adsorption of one molecule does not affect the adsorption of other molecules.

- (a) **(5 points)** The macrostate of a surface with adsorbed atoms can be characterized by the number  $N$  of adsorbed atoms while a microstate of the surface would be some particular arrangement of  $N$  atoms on the surface. Explain why the multiplicity  $\Omega(N)$  of a macrostate with  $N$  atoms is given by the expression

$$\Omega(N) = \binom{M}{N}, \quad (48)$$

where  $M$  is the total number of adsorption sites.

**Answer:** From the information given, you can think of a surface as consisting of  $M$  slots (concavities) where an adatom can bind to the surface. The geometric arrangement of the binding sites is irrelevant since we are assuming that the ability to bind to a given site is not affected by whether other sites already have adatoms or not. (This assumption is not true for big enough molecules that bind to a surface, when the sites start to fill up so there is a high probability of two adatoms being near each other and influencing one another.)

If we have a surface macrostate consisting of  $N$  adatoms, the total number of accessible microstates will be the number of different ways that these adatoms can be assigned to  $N$  slots out of the  $M$  available, which is precisely the number given by the binomial coefficient Eq. (48).

- (b) **(10 points)** Assuming that  $M$  and  $N$  are large integers, use Stirling's formula to obtain a simplified expression for the entropy  $S(N) = k \ln \Omega(N)$  and then obtain an expression for the chemical potential  $\mu_{\text{surface}}$  of adatoms on the surface.

**Answer:** Using Stirling's formula in the given form  $\ln(x) \approx x \ln(x) - x$  and assuming  $M, N \gg 1$ , we use Eq. (48) to find:

$$S/k = \ln \Omega \quad (49)$$

$$= \ln \left( \frac{M!}{N!(M-N)!} \right) \quad (50)$$

$$= \ln(M!) - \ln(N!) - \ln[(M-N)!] \quad (51)$$

$$= M \ln(M) - M - [N \ln(N) - N] - [(M-N) \ln(M-N) - (M-N)] \quad (52)$$

$$= M \ln(M) - N \ln(N) - (M-N) \ln(M-N). \quad (53)$$

This is exactly analogous to calculating the entropy of a spin-1/2 paramagnet for which  $M$  would be the total number of spins,  $N$  would be the number of up spins, and  $M-N$  would be the number of down spins, so your knowledge from the paramagnet should have guided you to Eq. (53).

From the thermodynamic identity  $dU = TdS - PdA + \mu dN$  for a surface of area  $A$ , we deduce that the chemical potential of the adatoms on the surface is given by

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,A}, \quad (54)$$

where  $U$  is the energy of the adatoms bound to the surface. Differentiating Eq. (53) with respect to  $N$  and holding  $M$  constant, we find

$$\mu_{2D} = -kT \left[ -\ln(N) - N \left( \frac{1}{N} \right) - (-1) \ln(M-N) - (M-N) \frac{1}{M-N} (-1) \right] \quad (55)$$

$$= -kT \ln \left( \frac{M-N}{N} \right) \quad (56)$$

$$= -kT \ln \left( \frac{1}{\theta} - 1 \right), \quad (57)$$

where  $\theta = N/M$  is the surface number density of adatoms, often called the surface coverage in the context of surface physics.

- (c) **(5 points)** Assume that the two-dimensional system of adatoms is in thermodynamic equilibrium with a surrounding ideal gas of identical atoms whose temperature and pressure are  $T$  and  $P$  respectively. Given that the chemical potential of the surrounding gas is

$$\mu_{\text{gas}} = -kT \ln \left[ \frac{kT}{P} \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \right], \quad (58)$$

show that the surface density  $\theta = N/M$  of adatoms (with  $0 \leq \theta \leq 1$ ) is related to the pressure  $P$  of the surrounding gas by the expression:

$$\theta(P) = \frac{P}{P_0 + P}, \quad (59)$$

where  $P_0 = P_0(T)$  is some combination of constants and of the temperature that has units of pressure. You should give the mathematical form of  $P_0$  explicitly.

**Answer:** Equating the chemical potential Eq. (57) of the two-dimensional adatoms to the chemical potential Eq. (58) of the three-dimensional gas gives us a necessary condition for thermodynamic equilibrium to occur between the surface and gas:

$$-kT \ln \left( \frac{1}{\theta} - 1 \right) = -kT \ln \left[ \frac{kT}{P} \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \right]. \quad (60)$$

Dividing both sides by  $-kT$  and exponentiating both sides gives

$$\frac{1}{\theta} - 1 = \frac{P_0}{P}, \quad (61)$$

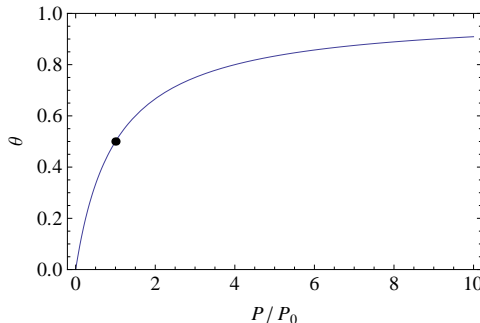
where

$$P_0 = \left( \frac{2\pi m}{h^2} \right)^{3/2} k^{5/2} T^{5/2}. \quad (62)$$

It is easy to see that Eq. (61) leads directly to the answer Eq. (59) with  $P_0$  given by Eq. (62). This is a famous, and useful result known as the Langmuir isotherm, which explains how the surface coverage  $\theta$  varies with pressure of the surrounding gas in thermodynamic equilibrium.

- (d) **(5 points)** Sketch the curve  $\theta$  vs  $P$  as given by Eq. (59) and indicate where the point corresponding to  $P = P_0$  lies on your curve. Discuss whether the values of  $\theta$  make scientific sense in the limits of small and large gas pressures  $P$ .

**Answer:** The curve looks qualitatively like this:



The coverage increases linearly with pressure  $P$  for  $P \ll P_0$ , then starts to saturate to a maximum value of 1 for  $P \gg P_0$ . The coverage is exactly  $1/2$  when  $P = P_0$ .

You can deduce this qualitative shape by asking how the expression Eq. (59) behaves in the limits of small and large  $P$ . For  $P \ll P_0$ , the denominator is roughly constant  $P_0 + P \approx P_0$  and so  $\theta \approx P/P_0$ , which increases linearly with slope  $1/P_0$ . For large  $P$  such that  $P \gg P_0$ ,  $P_0 + P \approx P$  and  $\theta \approx P/P = 1$  becomes independent of  $P$ . Differentiating the curve  $P/(P + P_0)$  with respect to  $P$  gives  $\theta'(P) = P_0/(P + P_0)^2$  which is always positive, so  $\theta$  must be an always increasing function, with no extrema. Combining these observations with the fact that  $\theta(P_0) = 1/2$  gives the qualitative features of the surface coverage as shown.

With more time, you could also use Taylor series approximations to study how Eq. (59) behaves for  $P$  small and large. For example, for  $P \ll P_0$ , we could write

$$\theta = \frac{P}{P_0 + P} \quad (63)$$

$$= 1 - \frac{P_0}{P_0 + P} \quad (64)$$

$$= 1 - \frac{1}{1 + P/P_0} \quad (65)$$

$$\approx 1 - [1 - P/P_0 + (P/P_0)^2 - \dots] \quad (66)$$

$$\approx \frac{P}{P_0} - \left(\frac{P}{P_0}\right)^2, \quad (67)$$

to obtain the leading two terms in an expansion in the small quantity  $P/P_0$ . Similarly, for  $P \gg P_0$ , we can write directly

$$\theta = \frac{1}{1 + P_0/P} \approx 1 - \frac{P_0}{P}, \quad (68)$$

which tells us that  $\theta$  “decays” towards its asymptote of 1 rather slowly as  $1/P$  as  $P \rightarrow \infty$ .

In the most recent homework assignment, you solved this same problem—equating the chemical potential of a two-dimensional medium with the chemical potential of a surrounding three-dimensional gas—but you assumed that the adatoms were point particles that moved around freely on the surface, in exact analogy to how molecules move around in a gas. In that problem, you discovered that  $\theta \propto P$ , the surface coverage increases without limit with increasing gas pressure  $P$ . This can not be physically correct because adatoms have a finite size and one can only pack a finite number of adatoms into a given surface area  $A$ .

This exam problem shows how starting with the assumption of a fixed number of adsorption sites gives a physically more reasonable curve ( $\theta$  saturates to value 1 with increasing pressure) and Eq. (59) is in fact a more accurate description of many actual surfaces to which adatoms bind. Real surfaces are somewhat intermediate between the two models: there are indeed a finite number of surface binding sites but many adatoms are mobile on a surface and can diffuse around from location to location, although not quite as free particles, the surface is more like low ridges that particles have to have enough energy to hop over. Surface science is a rich important interdisciplinary field encompassing chemistry, engineering, and physics, and continues to be an important frontier.

### True or False Questions (2 points each)

For each of the following statements, please circle **T** or **F** to indicate whether a given statement is true or false respectively.

1. **T / F** It is possible for a liquid to have a negative temperature  $T$ .

**Answer: F** Only a system whose elements have no kinetic energy such as a spin-1/2 paramagnet can have an entropy that reaches a maximum and then starts to decrease as the thermal energy  $U$

is increased over some range, a necessary condition for a negative temperature to occur. Liquids and gases can not have negative temperatures.

2. **T / F** Blowing on a hot marshmallow to cool it is an example of energy transfer by work.

**Answer: F** The air coming out of one's mouth is about body temperature, which is about  $37^{\circ}\text{C}$ . This is colder than the temperature of a hot marshmallow (we know this because putting the hot marshmallow in your mouth will burn your mouth) so blowing on it cools the marshmallow by transfer of heat between two systems of different temperature. Although your body has to do work to produce the breath (contract muscles to squeeze your lungs), what is thermodynamically relevant is the temperature of the air coming in contact with the marshmallow.

So why not just let the marshmallow cool in the surrounding air, which is even cooler than the breath from your mouth ( $20^{\circ}\text{C} = 293\text{K}$  vs  $40^{\circ}\text{C} = 313\text{K}$ )? Without blowing, a layer of warm air builds up around the marshmallow which decreases the heat transfer from the marshmallow to the surrounding cooler air. Blowing on the marshmallow carries the warm air near the marshmallow away, effectively making the surface of the marshmallow (at least the surface in contact with your breath) a constant temperature colder surface.

3. **T / F** Expanding an ideal gas always increases its entropy.

**Answer: F** An adiabatic expansion causes no change in the entropy of the gas. Although the volume  $V$  increases, which by itself would cause an increase in entropy, the energy  $U$  of the gas decreases so as to exactly compensate the increase in entropy caused by increasing the volume.

4. **T / F** The magnetic field strength  $B$  is an extensive thermodynamic variable.

**Answer: F** The magnetic field strength of some external magnetic field is an *intensive* thermodynamic variable since it is unchanged if some sample of interest in the magnetic field is varied in size.

5. **T / F** It is possible for heat to be exchanged between two systems with different temperatures even if the systems are not in physical contact with one another.

**Answer: T** Radiative transfer, e.g., involving light energy from the Sun impinging on the Earth's surface, would be an example of energy transfer between two objects of different temperatures that are not in physical contact with one another. We will discuss this case in a few weeks, in the context of blackbody radiation of light from an opaque warm object.

6. **T / F** During a quasistatic adiabatic process, the entropy does not change.

**Answer: T** No heat flows in or out of a system during an adiabatic transition. Provided the adiabatic process is carried out quasistatically so that the system and its environment are always close to thermodynamic equilibrium, the entropy does not change.

7. **T / F** Compressing an ideal gas always increases its temperature.

**Answer: F** An isothermal compression would be an example of a compression for which the temperature does not remain constant. It is true though that many compressions will cause the temperature to increase, e.g., an adiabatic compression.

Can you identify a process applied to an ideal gas that causes its temperature to drop as it is being compressed to a smaller volume?

8. **T / F** For a large integer  $N \gg 1$ , the Gaussian that approximates the function  $(xe^{-x})^N$  will have the form

$$Ae^{-NBx^2}, \quad (69)$$

where  $A$  and  $B$  are positive constants.

**Answer: F** The function  $f(x) = xe^{-x}$  is the product of a function  $x$  that is increasing times a function  $e^{-x}$  that is decreasing as  $x$  itself increases. This means that  $xe^{-x}$  must have a local maximum for some  $x_{\max} > 0$  that is not centered on the origin  $x = 0$  (it is easy to see by solving  $f' = 0$  that  $x_{\max} = 1$ ) and so the Gaussian that approximates  $[f(x)]^N$  must be centered about  $x_{\max} = 1$ . But the given expression is centered about  $x = 0$  so the answer is false.

The following data and formulas may be useful:

$$h \approx 7 \times 10^{-34} \text{ J} \cdot \text{s}, \quad G \approx 7 \times 10^{-11} \text{ N} \cdot \text{m}^2/\text{kg}^2, \quad c \approx 3 \times 10^8 \text{ m/s}, \quad T_{\text{absolute}} = -273^\circ\text{C}.$$

$$dU = TdS - PdV + \mu dN, \quad \Delta U = Q + W, \quad U = Nf \frac{kT}{2} = \frac{f}{2}PV, \quad W = - \int_{V_1}^{V_2} P(V) dV.$$

$$PV^\gamma = \text{const}, \quad TV^{\gamma-1} = \text{const}, \quad \gamma = \frac{f+2}{f}.$$

$$C = \frac{Q}{\Delta T}, \quad C_V = \left( \frac{\partial U}{\partial T} \right)_V, \quad C_P = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P, \quad L = \frac{Q}{m}.$$

$$S = k \ln \Omega, \quad \Delta S = \frac{Q}{T}, \quad \Delta S = \int_{T_1}^{T_2} \frac{C(T)}{T} dT, \quad S = Nk \left( \frac{5}{2} + \ln \left[ \frac{V}{N} \left( \frac{4\pi m}{3h^2} \frac{U}{N} \right)^{3/2} \right] \right).$$

$$\ln(x!) \approx x \ln(x) - x, \quad e^x = \exp(x) \approx 1 + x + \frac{1}{2}x^2, \quad \frac{1}{1+x} \approx 1 - x + x^2, \quad \ln(1+x) \approx x - \frac{1}{2}x^2.$$