

AMT Homework 8 Supplement ANSWERS
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The purpose of this supplement is to illustrate some of the ways in which probability distributions associated with continuous outcomes are handled mathematically. Specifically, the Maxwell-Boltzmann speed distribution for gaseous molecules and the Bose-Einstein distribution for photons are considered.

1. Suppose that we have 5×10^{20} atoms, each of which are free to occupy any one of three accessible energy states with energies of $0, \varepsilon$, and 5ε .

- (a) What configuration will give the largest entropy if we do not have to restrict the total energy of the system? What is the entropy of this configuration?

One third in each state... entropy is

$$(N \ln 3 - \ln(2\pi N) + (3 \ln 3)/2) k_B \approx 5.493 \times 10^{20} k_B.$$

- (b) Determine the temperature of the system if the total energy is fixed at $2 \times 10^{20} \varepsilon$. Give your result as a decimal multiple of ε/k_B . How many atoms will be in each state under this restriction, and what will be the resulting entropy?

We solve the equation $2 \times 10^{20} \varepsilon = \frac{\varepsilon e^{-\beta\varepsilon} + 5\varepsilon e^{-5\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-5\beta\varepsilon}} \cdot 5 \times 10^{20}$, or

$23x^5 + 3x - 2 = 0$, with $x = e^{-\beta\varepsilon}$. This gives $x = 0.477$ and a temperature of $1.35 \varepsilon/k_B$. The fractions are 66.585% in the zero energy, 31.77% in the next state, and 1.646% in the highest energy state. The entropy is $3.513 \times 10^{20} k_B$.

- (c) Determine the temperature of the system if the total energy is fixed at $7 \times 10^{20} \varepsilon$. Give your result as a decimal multiple of ε/k_B . How many atoms will be in each state under this restriction, and what will be the resulting entropy?

The equation is now $7 = \frac{e^{-\beta\varepsilon} + 5e^{-5\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-5\beta\varepsilon}} \cdot 5$, or $18x^5 - 2x - 7 = 0$. This gives

$x = 0.865$, and a temperature of $6.91 \varepsilon/k_B$. The fractions are 42.55% in the lowest state, 36.815% in the next, and 20.637% in the highest. The entropy is $5.2855 \times 10^{20} k_B$.

- (d) Determine the temperature of the system if the total energy is fixed at $20 \times 10^{20} \varepsilon$. Give your result as a decimal multiple of ε/k_B . How many atoms will be in each state under this restriction, and what will be the resulting entropy? What's different about this situation?

The equation is now $20 = \frac{e^{-\beta\varepsilon} + 5e^{-5\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-5\beta\varepsilon}} \cdot 5$, or $5x^5 - 15x - 20 = 0$. This gives

$x = 1.5383$, and a temperature of $-2.322 \varepsilon/k_B$. The fractions are 8.966% in the lowest state, 13.793% in the next, and 77.24% in the highest. The entropy is $3.445 \times 10^{20} k_B$. The difference between this part and the previous ones is that the temperature is *negative*. Temperature is defined as the change in internal energy divided by change in entropy at constant volume. Increasing the entropy in this case forces us to remove atoms from the highest state, lowering the internal energy.

- (e) Suppose that the temperature is fixed at $7\epsilon/k_B$. How many atoms are in each state? What is the total energy of the system? What is the resulting entropy? This case is much simpler than the last ones. The Boltzmann factor is given explicitly by $\exp(-\alpha/7)$ for a state with energy $\alpha\epsilon$, so we have 42.44% in the lowest, 36.79% in the next, and 20.775% in the highest. This is very close to the results of part (c), so everything makes sense. As the temperature increases, the number of atoms in states with probabilities *larger* than that associated with maximum entropy decreases while that in states with smaller probabilities increases... we are attempting to achieve maximum entropy... at maximum entropy, the derivative $(\partial S/\partial S)_V$ vanishes so the temperature is without bound.

2. When considering gases on a larger scale, we need to include the gravitational force. The potential energy associated with a molecule of mass m at height h above the surface of the Earth can be taken as $U_G = mgh$, where $g = 9.8$ meters per square second. In the following, we will ignore the contributions pressure makes to the potential energy of a gas molecule and the fact that the atmosphere is *not* at constant temperature.

- (a) Write a normalized distribution for the probability of finding a gas molecule of mass m at height h above the surface of the Earth, taking the atmosphere in thermal equilibrium at temperature T .

$$P(h, h+dh) = \frac{mg}{k_B T} \exp(-mgh/k_B T) dh.$$

- (b) Determine the average height of a gas molecule of mass m in equilibrium at Kelvin temperature T . Find the average height of a helium, chlorine, argon, and oxygen molecule/atom in thermal equilibrium at 300 Kelvin, in kilometers, then determine the probability that each of these will be found above 100 kilometers.

$\langle h \rangle = k_B T / mg$. Units make the rest of the problem tricky. The average height can be

manipulated to read $\langle h \rangle = RT/Mg$, where R is the ideal gas constant and M is the molar mass (in KILOGRAMS). For the probability, we re-write the integral as

$$\frac{Mg}{RT} \int_{100\text{km}}^{\infty} \exp(-Mgh/RT) dh = \int_{(Mg100\text{km})/RT}^{\infty} e^{-u} du = \int_{117.867M/T}^{\infty} e^{-u} du = e^{-117.867M/T},$$

with M in GRAMS and T in kelvin. Helium gives an average height of 63.63 km and a probability of 20.77%. Chlorine is diatomic, so gives 3.59 km and $7.967 \times 10^{-11}\%$.

Argon gives 6.37 km and $1.53 \times 10^{-5}\%$, and oxygen gives 7.95 km and $3.466 \times 10^{-4}\%$.

3. The Maxwell-Boltzmann distribution is based on the idea that the probability that a state of energy E will be populated in a system in equilibrium at Kelvin temperature T is proportional to $e^{-\beta E}$, where $\beta = 1/k_B T$. The Boltzmann constant $k_B \approx 1.38 \times 10^{-23} \text{ J/K}$ can be thought of as a conversion constant between Kelvin and Joules. One of the simplest applications of this distribution involves the sharing of kinetic energy between gaseous molecules in thermal equilibrium.

- (a) The kinetic energy of a molecule with mass m and speed v is given by $K = \frac{1}{2}mv^2$.

Ignoring other contributions to the energy of a system of gaseous molecules with mass m , write an expression proportional to the probability that a molecule will have a velocity lying between (v_x, v_y, v_z) and $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$.

$$e^{-mv^2/2k_B T} dv_x dv_y dv_z.$$

- (b) The probability that a molecule will have *some* speed between 0 and ∞ is 1. Use this fact to normalize the probability distribution found in (a). You may want to use spherical coordinates to evaluate the integral.

$$\int_0^\infty e^{-mv^2/2k_B T} 4\pi v^2 dv = \left(\frac{2\pi k_B T}{m} \right)^{3/2}, \text{ so the normalized probability is}$$

$$4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} v^2 dv, \text{ or } \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} dv_x dv_y dv_z.$$

- (c) Use your normalized probability distribution to determine the average speed and the average square of the speed for molecules of mass m in thermal equilibrium at temperature T . Again, you may want to use spherical coordinates.

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}. \quad \langle v^2 \rangle = \frac{3k_B T}{m}.$$

- (d) Determine the mean speed and root-mean-square speed ($v_{rms} \equiv \sqrt{\langle v^2 \rangle}$) of hydrogen,

nitrogen, and carbon dioxide molecules in thermal equilibrium in our atmosphere at a temperature of 300 K. For comparison, the escape speed of the Earth is approximately 11,200 m/s.

Mean speeds are 1782 m/s for hydrogen, 476 m/s for nitrogen, and 380 m/s for carbon dioxide. Rms speeds are 1934 m/s, 517 m/s, 412 m/s, respectively.

- (e) Find an expression for the probability that a molecule of mass m in thermal equilibrium at temperature T has a speed lying between v and $v + \Delta v$. Use this to determine the probability that the speed of a hydrogen, nitrogen, and carbon dioxide molecule will be found between 400 and 500 meters per second at 300 K. What is the probability that the speed will be *larger* than 600 m/s?

$$\int_v^{v+\Delta v} 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mu^2/2k_B T} u^2 du. \text{ This is better re-written as}$$

$$\frac{4}{\sqrt{\pi}} \int_{v/\sqrt{m/2k_B T}}^{(v+\Delta v)/\sqrt{m/2k_B T}} x^2 e^{-x^2} dx. \text{ The probabilities are 1.07\% for hydrogen, 19.33\% for}$$

nitrogen, and 19.94\% for carbon dioxide. Speeds larger than 600 m/s have probabilities of 96.2\% for hydrogen, 25.7055\% for nitrogen, and only 9.575\% for carbon dioxide. This illustrates the difference between the meaning of the probabilities found above. Nitrogen's peak lies on the larger side of the interval while carbon dioxide's lies on the smaller side. This is reflected in the probabilities for speeds above 600 m/s.

4. Explain how the following quantities could be obtained experimentally. Your explanation can be qualitative, but it should indicate what the experimentalist needs to do in order to determine the quantity. Say whether the determination of this quantity is relatively easy, hard, or in-between, and whether normal materials (like water or an ideal gas) will exhibit a positive or negative value for this quantity. Explain the reasons for your answers. Then, use Maxwell relations to re-express the quantity in terms of the heat capacity at constant pressure, $C_p = T(\partial S/\partial T)_p$, the isothermal bulk modulus, $B = -V(\partial p/\partial V)_T$, and the thermal expansion coefficient $\alpha = (\partial V/\partial T)_p/V$. If this is not possible, explain why.

- (a) $(\partial p/\partial T)_V$. We keep the material in a fixed volume and heat it, measuring the change in pressure. This is usually easy to do for gases, but liquids and solids often buck the constant volume requirement. This quantity is almost always positive. It is given by αB , as can fairly easily be shown by examining the differential dV expressed in terms of dp and dT .
- (b) $(\partial S/\partial p)_T$. We add a small amount of heat to the system and measure its change in pressure while it is in thermal contact with a heat reservoir. This is not easily accomplished, but materials on isotherms usually expand as heat is added. This decreases the pressure, so we expect it to be negative. Appealing to the differential of Gibbs' free energy, $dG = -SdT + Vdp$, we can be certain that $(\partial S/\partial p)_T = -\alpha V$.
- (c) $(\partial E/\partial p)_T$. We increase the pressure of the material and measure the change in energy, making sure that the material is always in full thermal contact with a heat reservoir. This increase in pressure usually leads to a decrease in volume and net energy given to the material. With no change in temperature, however, the material must also give off heat. This quantity will be zero for an ideal gas, and may be positive or negative for other materials, depending on whether or not the energy of the system favors higher pressure. To determine its value, we divide the differential of energy by that of pressure and take the temperature as constant:
 $(\partial E/\partial p)_T = T(\partial S/\partial p)_T - p(\partial V/\partial p)_T$. Both of these quantities are accessible, owing to our work in part (b), so we have $(\partial E/\partial p)_T = V(p/B - \alpha T)$. This will likely be positive at high pressure and negative at high temperature.
5. The behavior of photons is vastly different from that of molecules partly because the number of photons that exist is not constant – photons will be created as the temperature is increased and destroyed as the temperature is decreased. This changes our normalization convention, as we cannot require that the total number of photons is constant. In order to handle this difficulty, we employ the idea of a *phase space*. This idea allows us to determine the number of states that are available within a specific momentum window. A standard analysis gives the result that the number of states per unit volume available to photons with momentum lying between \mathbf{p} and $\mathbf{p} + d\mathbf{p}$ is given by d^3p/h^3 , where $h \approx 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ is Planck's constant. Assuming *isotropy* (the direction of the photon does not matter), this gives a *state density* of $4\pi p^2 dp/h^3$ for photons with momentum whose magnitude lies between p and $p + dp$. The energy of a photon is related to its momentum via $E = cp$, so this translates to a state density of $4\pi E^2 dE/c^3 h^3$ for photons with energy lying between E and $E + dE$. The Blackbody radiation spectrum experimentally gives the probability that a state of energy E is occupied as $\frac{2}{e^{\beta E} - 1}$, with the factor of 2 coming from the two different polarization states available to each photon.
- (a) Determine the total number of photons per unit volume in thermal equilibrium at Kelvin temperature T . How many photons are there in a cubic centimeter of gas in thermal equilibrium at 273 Kelvin? Give your answer to three significant digits, and compare it to the number of *atoms* present in a volume of 1 cubic centimeter of an ideal gas at STP. What happens to this comparison if the temperature is 40,000 K? Give the ratio of number of photons to number of atoms in thermal equilibrium at pressure P and temperature T .

Note that the pressure exerted by the photons is independent of that associated with the atoms; these two pressures are referred to as *partial pressures* for this reason.

There are $16\pi\zeta(3)(k_B T/hc)^3 \Delta V$ photons in a volume ΔV of space in thermal equilibrium at temperature T . One cubic centimeter at 273 K contains 412.2 million photons. The number of atoms present under these conditions is

$p\Delta V/k_B T = 2.6895 \times 10^{19}$. At 40,000 K, this changes to 1.2966×10^{15} photons and 1.8356×10^{17} atoms. In general, the ratio of photons to atoms is given by

$N_\gamma/N_{\text{atom}} = 16\pi(k_B T/hc)^3 k_B T \zeta(3)/p = 2.7958 \times 10^{-16} T^4/p$, with everything given in SI units.

- (b) Determine the total energy per unit volume held by photons in thermal equilibrium at Kelvin temperature T . How much energy per unit volume is held by photons interacting with gas in thermal equilibrium at 273 Kelvin? Give your answer to three significant digits, and compare it to the energy held by the atoms present in 1 cubic meter of an ideal gas at STP. What happens to this comparison if the temperature is 40,000 K? Give the ratio of energy held by photons to energy held by atoms in thermal equilibrium at pressure P and temperature T . At what temperature will helium atoms at 1 atm, 100 atm, and 500 atm become radiation dominated?

The total energy held per unit volume is $\frac{8\pi^5}{15} \left(\frac{k_B T}{hc} \right)^3 k_B T = 7.55 \times 10^{-16} T^4$, where

everything is given in SI units. At 273 K, we have $4.19 \mu\text{J}/\text{m}^3$. An ideal monatomic gas contains energy per unit volume $3p/2$, or $1.52 \times 10^5 \text{ J}/\text{m}^3$. This energy density depends only on pressure, so as the photon density will certainly catch up as temperature increases at constant pressure. At 40,000 K, the photon energy density is given by $1930 \text{ J}/\text{m}^3$, about 80 times smaller than the energy density associated with matter. The ratio is $5.03 \times 10^{-16} T^4/p$ in SI units, and the temperature at which this ratio becomes 1 is given by $T = 6675 \sqrt[4]{p} \text{ K}$, or 119,100 K for 1 atm, 376,600 K for 100 atm, and 563,150 K at 500 atm. Above these temperatures, the majority of the energy density is associated with photons instead of matter.

- (c) A hydrogen molecule consists of two hydrogen atoms bonded to each other with a bond of energy 432 kJ/mol, or $7.17 \times 10^{-19} \text{ J}/\text{molecule}$. How many photons exist per unit volume with energy exceeding this binding energy at 1000 K, 3000 K, 6000 K, and 12,000 K? How does this compare to the number of atoms present per unit volume at 1 atm? What does this mean in terms of our expectation of the state of hydrogen under these conditions?

The key to this problem is the following scaling substitution:

$$N_{>E_0} = \frac{8\pi}{(hc)^3} \int_{E_0}^{\infty} \frac{E^2 dE}{e^{\beta E} - 1} = 8\pi \left(\frac{k_B T}{hc} \right)^3 \int_{\beta E_0}^{\infty} \frac{u^2 du}{e^u - 1}. \text{ For our energy } E_0 = 7.17 \times 10^{-19} \text{ J},$$

we have $\beta E_0 = 5.2 \times 10^4 \text{ K}/T$. The integral therefore gives extraordinarily small values unless the temperature is of order $5.2 \times 10^4 \text{ K}$. We can estimate these values by using an

asymptotic expansion, $\int_x^{\infty} \frac{u^2 du}{e^u - 1} \approx (x^2 + 2x + 2)e^{-x}$, so there are approximately 6.2×10^{-4}

photons exceeding this energy per cubic meter at 1000 K, 2.27×10^{12} at 3000 K, 3.0×10^{16} at 6000 K, and 5.66×10^{18} at 12,000 K. The matter numbers are 7.34×10^{24} atoms per volume at 1000 K, 2.43×10^{24} at 3000 K, 1.22×10^{24} at 6000 K, and 6.12×10^{23} at 12,000 K. At each of these temperatures, the matter numbers are much higher than the radiation numbers, though the radiation numbers increase dramatically as the temperature increases. From only this analysis, we may expect that hydrogen gas will largely consist of molecules rather than atoms at all of these temperatures. This is actually *not* true, mainly because entropy favors atoms over molecules. The dissociation of the molecules does not happen instantaneously, but at one atmosphere we can be relatively certain that most of the matter will be present as atoms rather than molecules at temperatures exceeding 3000 K or so. Higher pressures favor molecules, so the temperature needs to be higher in order to observe the same fraction of dissociation.

- (d) What is the average energy held by photons in thermal equilibrium at Kelvin temperature T ? What is the most probable energy held by these photons? Calculate the frequency and wavelength associated with these energies at a temperature of 5800 K, the temperature at the surface of the Sun, using the fact that the energy of a photon with frequency ν is given by $E = h\nu$. How do your results compare with Wien's displacement law? Remember that this law can be determined by thinking of the distribution of *wavelengths* instead of *energies*. What fraction of the total energy output of the Sun lies within the visible part of the electromagnetic spectrum (wavelengths from 400 – 700 nm)?

The total energy held by photons per volume is $\frac{8\pi^5}{15} \left(\frac{k_B T}{hc} \right)^3 k_B T$ and the number of

photons holding this energy is $16\pi\zeta(3) \left(\frac{k_B T}{hc} \right)^3$, so the 'average' energy is given by

$$\langle E \rangle = \frac{\pi^4}{30\zeta(3)} k_B T = 2.7 k_B T. \text{ The most probable energy is given by setting the derivative}$$

of the distribution function to zero. Numerically, it comes out to $E_{mp} = 1.5936 k_B T$. At 5800 K, we have $\langle E \rangle = 2.16 \times 10^{-19} \text{ J} = 1.349 \text{ eV}$ and $E_{mp} = 1.2755 \times 10^{-19} \text{ J} = 0.796 \text{ eV}$.

The frequencies are 3.26 and $1.925 \times 10^{14} \text{ Hz}$, and the wavelengths are 920 and 1560 nm, both firmly in the infrared region of the spectrum. Wien's result, by contrast, gives a most probable wavelength of 500 nm. The difference is associated with the effective window, dE in the first case and $d\lambda = -hcdE/E^2$ in the Wien case. The effective window size dE is therefore suppressed for the Wien calculation when the energy is small, leading to a larger energy and smaller wavelength for the peak. This again indicates the largely unphysical role of the photon itself. Questions like the last one that involve entirely physical parameters are much more well-defined. The fraction of the total energy output of

the Sun that lies in the visible range is given by $\frac{15}{\pi^4} \int_{\beta hc/700 \text{ nm}}^{\beta hc/400 \text{ nm}} \frac{u^3 du}{e^u - 1} = 0.36754$. The

fraction lying in the infrared is 0.50867, and that lying in the ultraviolet is 0.123787. Our results for the maximum intensities can be thought of as indicating this result: the largest share of the energy coming from the Sun lies in the infrared. This will persist until the temperature reaches about 7000 K, at which time the majority briefly is taken by the visible spectrum until about 8600 K, where the ultraviolet takes over. These answers are the same in both the energy and the Wien scheme, as they are completely independent of the idea of a *photon*.