PHYS4171-Statistical Mechanics and Thermal Physics
Fall 2017
Assignment #2

Assigned on Friday January 19, 2007. Due on Friday February 2, 2007.
Read Chapter 2 of textbook, and the Math Appendix 1 sent to you earlier.
Graduate Student must do **all questions**. **Undergraduate students do not have to do** Exercise 3A and 3B, and exercise 4.
DUE on Monday October 2, 2017

Exercise 1) Consider again the coin-tossing problem discussed in class. The coins can land as Heads (H) or Tails (T). For the case where there are N coins, the total number of microstates (i.e. the # of different arrangements of heads and tails) is 2^N. This is consistent with the result in class where the total number of microstates for 3 coins is $2^3 = 8$. It was shown that the number of microstates, also called the multiplicity, of a macrostate with n heads (in a coin tossing experiment of N coins) is:

$$\Omega_N(n) = \frac{N!}{n!(N-n)!}.$$

Now consider a coin tossing experiment of 4 coins.

a) Just as in class, make a table to count all the possible microstates of the experiment. Count the total number of microstates. Is it consistent with the formula 2^N?

Microstate #	Coin 1	Coin 2	Coin 3	Coin 4	# of heads
1	H	H	H	H	4
2	H	H	H	T	3
3	H	H	T	H	3
4	H	T	H	H	3
5	T	H	H	H	3
6	H	H	T	T	2
7	H	T	H	T	2
8	H	T	T	H	2
9	T	H	H	T	2
10	T	H	T	H	2
11	T	T	H	H	2
12	H	T	T	T	1
13	T	H	T	T	1
14	T	T	H	T	1
15	T	T	T	H	1
16	T	T	T	T	0

In all there are 16 microstates, consistent with the formula $2^4 = 16$.

b) In such an experiment where 4 coins are tossed what is the most probable number of heads? Briefly justify your response.

Of course, the answer is 2 H and 2T. Anytime you toss a coin it is equally probable that it is either head or tail.

c) Using the given formulas, calculate the probabilities that a toss of all four coins gives: i) 4H, 0T; ii) 3H, 1T; iii) 2H, 2T; iv) 1H 3T; v) 0H, 4T.

i) 4H, 0T, n = 4, $\Omega_4(n) = \frac{4!}{4!0!} = 1$, note $0! = 1$.

ii) 3H, 1T, n = 3, $\Omega_4(3) = \frac{4!}{3!1!} = 4$

iii) 2H, 2T, n = 2, $\Omega_4(2) = \frac{4!}{2!2!} = 6$

iv) 1H 3T, n = 1, $\Omega_4(1) = \frac{4!}{1!3!} = 4$

v) 0H, 4T, n = 0, $\Omega_4(0) = \frac{4!}{0!4!} = 1$

Note that the result is consistent with the table of part (a)

d) Using the result of c) what is the most probable outcome of a coin toss experiment? Is this consistent with your answer in b) ?

The n = 2 macrostate (2H and 2T) includes 6 microstates ($\Omega_4(2) = 6$), the most of any macrostates. All microstates having equal probabilities of occurring means that the macrostate with 2H and 2T (n = 2) is the most likely. This occur with the probability $\Omega_4(2)/16 = 6/16 = 3/8$, where we've used the fact that there are 16 microstates in total (part a). For comparisons, the other probabilities are $\Omega_4(4)/16 = 1/16$ for n =2, $\Omega_4(3)/16 = 4/16 = 1/4$ for n = 3, $\Omega_4(1)/16 = 4/16 = 1/4$ for n = 1, and $\Omega_4(0)/16 = 1/16$ for n = 0. Hence the macrostate with n = 2 has the largest probability of occurring. This is consistent with the result of part a.

Exercise 2) Warped Coin and Dice toss

a) Consider a **warped coin** that has probability of 0.6 that it will land Head (H), every tike it is tossed. Use the **binomial theorem**, done in class, to calculate the probability that 20 tosses (n = 20) of the **warped coin** will results in the **four** H (k = 4).

Use the binomial theorem $P(k;n,p) = \binom{n}{k} p^k (1-p)^{n-k}$ with, p = 0.6, n = 20, k = 4,

$$P(4;20,0.6) = \binom{20}{4} (0.6)^4 (0.4)^{14} = \frac{20!}{4!16!} (0.6)^4 (0.4)^{16} = 2.7 \times 10^{-4}$$

b) Use the **generalized binomial theorem**, done in class, to calculate the probability that 100 rolls (n = 100) of a six-sided die will land with **three** (3) side up 20 times (k = 20). This is really like the last question, but with p = 1/6. The probability is

$$P\left(20;100,\frac{1}{6}\right) = \binom{100}{20} \left(\frac{1}{6}\right)^{20} \left(\frac{5}{6}\right)^{80} = \frac{100!}{20!80!} \left(\frac{1}{6}\right)^{20} \left(\frac{5}{6}\right)^{80}$$

Probability is $\frac{1.3 \times 10^{39}}{2.43 \times 10^{18}} \times 2.73 \times 10^{-16} \times 4.6 \times 10^{-7} = 0.067$.

Exercise 3) **<u>Sackur-Tetrode Relation</u>**

A) **Graduate Student Only**. In class to prove the relation for the d-dimension hypersphere, A_d, we use the **relation**, $\int_0^\pi d\theta \sin^n\theta = \sqrt{\pi}\frac{\Gamma\left(\frac{n}{2}+\frac{1}{2}\right)}{\Gamma\left(\frac{n}{2}+1\right)}$. Prove this **relation**.

In Class we showed $\Gamma(\mu)\Gamma(v) = 2\Gamma(\mu+v)\int_0^{\pi/2}\cos^{2\mu-1}\theta\sin^{2v-1}\theta d\theta$. **Students do not** need to **show** this for this **exercise**.

Let $\mu = \frac{1}{2} \to 2\mu - 1 = 0$ and $v = \frac{n}{2}+\frac{1}{2} \to 2v-1 = n$, which gives

$\Gamma(\mu)\Gamma(v) = 2\Gamma(\mu+v)\int_0^{\pi/2}\cos^{2\mu-1}\theta\sin^{2v-1}\theta d\theta \to$

$\Gamma\left(\frac{1}{2}\right)\Gamma\left(\frac{n}{2}+\frac{1}{2}\right) = 2\Gamma\left(\frac{n}{2}+1\right)\int_0^{\pi/2}\cos^0\theta\sin^n\theta d\theta = 2\Gamma\left(\frac{n}{2}+1\right)\int_0^{\pi/2}\sin^n\theta d\theta$.

Since $\sin\theta$ is symmetric (even) about $\theta = \pi/2$, over the interval $0 < \theta < \pi$, we can see that $\int_0^{\pi/2}\sin^n\theta d\theta = \frac{1}{2}\int_0^\pi \sin^n\theta d\theta$. This gives

$\Gamma\left(\frac{1}{2}\right)\Gamma\left(\frac{n}{2}+\frac{1}{2}\right) = \Gamma\left(\frac{n}{2}+1\right)\int_0^\pi \sin^n\theta d\theta$.

Now what about $\Gamma\left(\frac{1}{2}\right)$? Use the definition

$\Gamma(v) = \int_0^\infty \exp(-x)x^{v-1}dx \to \Gamma\left(\frac{1}{2}\right) = \int_0^\infty \exp(-x)x^{1/2}dx$, and make the substitution

$x = y^2, dx = 2ydy$, $\Gamma\left(\frac{1}{2}\right) = 2\int_0^\infty \exp(-y^2)dy$. I am sure in one of your classes it is shown that $\int_0^\infty dx\exp(-x^2) = \sqrt{\pi}/2$, hence $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$, which gives finally

$\Gamma\left(\frac{1}{2}\right)\Gamma\left(\frac{n}{2}+\frac{1}{2}\right) = \Gamma\left(\frac{n}{2}+1\right)\int_0^\pi \sin^n\theta d\theta \to \int_0^\pi \sin^n\theta d\theta = \sqrt{\pi}\frac{\Gamma\left(\frac{n}{2}+\frac{1}{2}\right)}{\Gamma\left(\frac{n}{2}+1\right)}$. **QED**

B) Graduate Student Only. In the appendix, we showed $\Omega_N \simeq \left(\frac{\partial \Sigma_N}{\partial p}\right)\Delta_p$, with

$\Sigma_N = \frac{V^N}{N!h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!}(2mE)^{3N/2}$. Show that $\Omega_N \simeq 3N\Sigma_N \frac{\Delta_p}{\sqrt{2mE}}$, where $p = \sqrt{2mE}$.

$\left(\frac{\partial \Sigma_N}{\partial p}\right) = \left(\frac{\partial \Sigma_N}{\partial E}\right)\frac{dE}{dp}$, with $E = \frac{p^2}{2m} \rightarrow \frac{dE}{dp} = \frac{p}{m}$, and

$$\left(\frac{\partial \Sigma_N}{\partial E}\right) = \frac{V^N}{N!h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!}(2m)^{3N/2}\frac{dE^{3N/2}}{dE} = \frac{V^N}{N!h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!}(2m)^{3N/2}\frac{3N}{2}E^{\frac{3N}{2}-1}.$$

Rearranging $\left(\frac{\partial \Sigma_N}{\partial E}\right) = \left[\frac{V^N}{N!h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!}(2mE)^{3N/2}\right]\frac{3N}{2}\frac{1}{E} = \Sigma_N \frac{3N}{2}\frac{1}{E}$,

Combining $\Omega_N \simeq \left(\frac{\partial \Sigma_N}{\partial p}\right)\Delta_p = \left(\frac{\partial \Sigma_N}{\partial E}\right)\frac{dE}{dp}\Delta_p = \Sigma_N 3N\frac{p}{2mE}\Delta_p$. Using $p = \sqrt{2mE}$ gives

$$\Omega_N = 3N\Sigma_N \frac{\Delta_p}{\sqrt{2mE}}.$$

C) **All students**. Use the Stirling's approximation that for very large N, $\ln N! = N\ln N - N$, and also that N is so large that $N \gg \ln N$, and that $\Delta_p \ll \sqrt{2mE}$ is relatively small, to obtain the Sackur-Tetrode Equation $S = k_B \ln \Omega_N = Nk_B\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mE}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$.

From part B, $S = k_B \ln \Omega_N = k_B \ln\left[3N\Sigma_N \frac{\Delta_p}{\sqrt{2mE}}\right]$, with $\Sigma_N = \frac{V^N}{N!h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!}(2mE)^{3N/2}$.

$$S = k_B\left[N\ln\left(V\left(\frac{2\pi mE}{h^2}\right)^{3/2}\right) - \ln N! - \ln\left(\frac{3N}{2}\right)! - \ln\sqrt{2mE} + \ln\Delta_p + \ln 3N\right],$$

Using Stirling's approximation $-\ln N! - \ln\left(\frac{3N}{2}\right)! = -\frac{3N}{2}\ln\frac{3N}{2} + \frac{3N}{2} - N\ln N + N$, or

$-\ln N! - \ln\left(\frac{3N}{2}\right)! = N\left(-\ln N - \ln\left(\frac{3N}{2}\right)^{3/2}\right) + \frac{5N}{2}$, which gives

$S = k_B\left[N\ln\left(\frac{V}{N}\left(\frac{2\pi mE}{Nh^2}\right)^{3/2}\right) + \frac{5}{2}N - \ln\sqrt{2mE} + \ln\Delta_p + \ln 3N\right]$. The first to terms are of order N, which is very large, while $\ln\sqrt{2mE} \sim \ln\sqrt{N} \ll N$, $\ln\sqrt{2mE} \ll \ln\Delta_p$, and $\ln 3N \ll N$ so the last three terms are negligible, which gives the final result.

D) **All Students.** Compare this with equation 2.16 in the textbook. Are the two entropy relations consistent? **HINT:** Use the equi-partition theorem.

Using the equi-partition theorem for monatomic ideal gas $E=\frac{3}{2}Nk_BT$, which gives

$$S=k_B\ln\Omega_N=Nk_B\left[\ln\left(\frac{V}{N}\left(\frac{2\pi mT}{h^2}\right)^{3/2}\right)+\frac{5}{2}\right]=Nk_B\left[\ln VT^{3/2}+f(N)+\frac{5}{2}\right],$$ where

$f(N)=Nk_B\ln\left(\frac{1}{N}\left(\frac{2\pi m}{h^2}\right)^{3/2}\right)$, or $S\sim k_B\ln\left(V^NT^{3N/2}\right)+Nk_Bf(N)+5Nk_B/2$, which is the same as 2.16 in the textbook.

E) **All Students.** Use the relation of part C to calculate the entropy (in J/K) of one mole of helium at one atmospheric pressure, and room temperature (300K).

For helium use ideal gas equation

$$PV=Nk_BT\rightarrow V=\frac{6.023\times10^{23}\times1.381\times10^{-23}J/K\times300K}{1.0132\times10^5Pa}=0.025m^3$$

Mass of helium, $m=4\times1.67\times10^{-27}kg=6.7\times10^{-27}kg$, $h=6.626\times10^{-34}J\bullet s$, one mole is $N=6.023\times10^{23}$, and $k_B=1.381\times10^{-23}J/K$, which gives

$Nk_B=\left(6.023\times10^{23}\right)\left(1.381\times10^{-23}J/K\right)=8.32J/K$.

$$S=\left(8.32\frac{J}{K}\right)\left[\ln\left(\frac{0.025m^3}{6.023\times10^{23}}\left(\frac{4\pi\left(6.7\times10^{-27}kg\right)4000J}{3\times6.023\times10^{23}\left(6.626\times10^{-34}J\bullet s\right)^2}\right)^{3/2}\right)+\frac{5}{2}\right],$$ which

gives $S=127J/K$.

Exercise 4) <u>Sackur-Tetrode Relation for 2D ideal gas</u>

Graduate Student Only. Consider N non-interacting particles in two dimensions (2D). Use the same method as for Exercise 3 to find the entropy. Do the problem for the case where the particles are identical and indistinguishable (need factor 1/N!), then for the case where they are distinguishable (no need for factor).

Use the exercise 3 trick, $\Omega_N\simeq\left(\frac{\partial\Sigma_N}{\partial p}\right)\Delta_p$, and math appendix

$$\Sigma_N=\frac{1}{N!}\frac{(\text{Position Volume})(\text{Momentum Volume})}{h^{2N}}=\frac{1}{N!}\frac{\int d^{2N}r\int d^{2N}p}{h^{2N}}$$, valid for 2D. It is easy to see $\int d^{2N}\vec{r}=A^N$, where $A=L^2$ is the surface area. The momentum integration is

all "volume" in the hypersphere, $p_1^2+p_2^2+......+p_N^2 \le \left(\sqrt{2mE}\right)^2$ in 2D, which using the math appendix $\int_{p_1^2+p_2^2+..p_N^2<\left(\sqrt{2mE}\right)^2} d^{3N}p = \frac{\pi^{2N/2}}{(2N/2)!}(2mE)^{2N/2}, \Sigma_N = \frac{A^N\pi^N}{N!h^{2N}N!}(2mE)^N$. Using the same approach as in exercise 3, $\Omega_N = 2N\frac{A^N\pi^N}{N!h^{2N}N!}(2mE)^N\frac{\Delta_p}{\sqrt{2mE}}$.

$S = k_B\left[N\ln\left(V\left(\frac{2\pi mE}{h^2}\right)\right) - 2\ln N! - \ln\sqrt{2mE} + \ln\Delta_p + \ln 2N\right]$. Using Stirling's approximation, and $\ln\sqrt{2mE} \sim \ln\sqrt{N} \ll N$, $\ln\sqrt{2mE} \ll \ln\Delta_p$, and $\ln 2N \ll N$,

$S = Nk_B\left[\ln\left(\frac{V}{N}\left(\frac{2\pi mE}{Nh^2}\right)\right) + 2\right]$.

Do problems 5, 6, and 8 in Chapter 2.

Problem 5) chapter 2

a) Helium is a monatomic gas, for which the multiplicity is $\Omega =$ constant $V^N T^{3N/2}$. For this constant volume (V) process, using $T_i = 400K$, $T_F = 403K$, and $N = 10^{24}$. The multiplicity change by a factor of

$$\frac{\Omega_F}{\Omega_i} = \frac{\text{constant } V^N T_F^{3N/2}}{\text{constant } V^N T_i^{3N/2}} = \left(\frac{T_F}{T_i}\right)^{3N/2} = \left(\frac{403K}{401K}\right)^{1.5\times10^{24}} = a \text{ very large number}.$$

b) The entropy of helium is $S = k\,\ell n\left(\text{constant } V^N T^{3N/2}\right)$. In a very slow (quasistatic) compression process in which the entropy does not change, the quantity $V^N T^{3N/2} = \text{constant}$. Hence the entropy loss due to the decrease in the volume (V) is offset by the entropy gain due to the increase in temperature (T).

It should be noted that such a constant entropy process is also called an adiabatic process which is described by the equation $TV^{\gamma-1} = \text{constant}$, where for helium $\gamma - 1 = \frac{2}{f} = \frac{2}{3} \rightarrow TV^{2/3} = \text{constant} \rightarrow VT^{3/2} = \text{constant}$, where it is noted that the constants in the equations are not all the same, but nevertheless they are all still constants. Taking the last of these equations to the power of N, we obtain $V^N T^{3N/2} = \text{constant}$, which is the same equation obtained requiring that the entropy remains constant.

Problem 6) chapter 2

a) Start with the thermodynamics definition of entropy: $\Delta S \ge \frac{Q}{T}$. In the sublimation process of this problem heat flow of $Q = \left(10^{-3}g\right)\left(3000J/g\right) = 3J$ transforms ice to water vapour at **constant temperature** of $T=260^{\circ}K$. The change in entropy is $\Delta S=\frac{3J}{260^{\circ}K}=0.0115J/K$. But we also have the Statistical Physics formula $S=k\ln\Omega$, where Ω is the multiplicity. The change in entropy is $\Delta S=S_F-S_i=k\ln\frac{\Omega_F}{\Omega_i}$, where Ω_i and Ω_F are the initial (ice) and final (vapour) multiplicity, respectively. Combining the two equations:

$$0.0115J/K=\Delta S=k\ln\frac{\Omega_F}{\Omega_i}\to\frac{\Omega_F}{\Omega_i}=\frac{0.0115J/K}{1.381\times10^{-23}J/K}=8.33\times10^{20}=10^{21}$$. Hence the multiplicity changes by a factor of 10^{21}.

Gas molecules have translational freedom, which manifested itself in the dependence of volume (V) in the entropy formula $S=\text{ k }\ell\text{n}\left(\text{constant } V^N T^{3N/2}\right)$. The solid phase of matter does not possess this translational freedom, and consequently have lower significantly lower entropy.

Problem 8) chapter 2

a) The entropy of a monatomic gas is $S=\text{ k }\ell\text{n}\left(\text{constant } V^N T^{3N/2}\right)$. Initially the gas is at temperature T, Volume V_0 and entropy $S_i=\text{ k }\ell\text{n}\left(\text{constant } V_0^N T^{3N/2}\right)$. In the final state the gas change in still at temperature T, and its volume is reduced 2% to $0.98V_0$, and its entropy is $S_F=\text{ k }\ell\text{n}\left(\text{ constant } \left(0.98V_0\right)^N T^{3N/2}\right)$. The change in entropy is

$$\Delta S=S_F-S_i=\text{k ln}\left(\text{ constant } \left(0.98V_0\right)^N T^{3N/2}\right)-\text{ k ln}\left(\text{constant } \left(0.98V_0\right)^N T^{3N/2}\right)$$

$$\Delta S=\text{k ln}\left(\frac{\left(0.98V_0\right)^N}{V_0^N}\right)=\text{Nkln}0.98=\left(3\times10^{22}\right)\left(1.381\times10^{-23}J/K\right)\ln\left(0.98\right)=-0.0084J/K$$

b) Using the first law of thermodynamics $Q=\Delta E+W$ and the fact that $\Delta E=0$, we obtain $W=Q$. In an isothermal process the formula $\Delta S=\frac{Q}{T}\to Q=T\Delta S$ is valid. Combining the work done on the gas is $W=Q=T\Delta S$. Using $T=300K$ and $\Delta S=-0.0084J/K$, $W=T\Delta S=\left(300K\right)\left(-0.0084J/K\right)=-2.51J$. So – 2.51 J of work is done by the gas, and 2.51 J of work is done on the gas by us.

c) From part b) the amount of heat flow into the gas is $Q=W=-2.51J$. Basically 2.51 J of heat flow out of the gas. The amount of heat flow into the environment $-Q=2.51J$. Basically 2.51 J of heat flow into the environment.

d) The change of entropy of the environment is $\Delta S=\frac{-Q}{T}=\frac{2.51J}{300K}=0.0084J/K$.