Midterm Exam Due at 9 am on April 16 Tue

This is your last chance to review the first part of basic statistical thermodynamics.

You must not discuss with your fellow students. Each of you may send drafts of at most two problems electronically to YO for comments. There will be extra office hours.

1. [Very elementary questions] (cf. 2.10, 2.11, 5.10)

(1) If you convert the kinetic energy of a jet plane of mass 50 t with a speed of 800 km/hr to thermal energy, what is the increase of the temperature of the water in the 50 m pool of size 20m × 50 m × 2 m? What is the significance of your result for humankind?

(2) There is a gas whose density is 13.3 kg/m³. What is the root mean square translational speed of its molecules, if the pressure is 1 atm?

(3) There is a mixed ideal gas consisting of two kinds of molecule whose molecular masses are \( M_1 \) and \( M_2 \), respectively. The mean square relative velocity of the two molecules of different species is three times as large as that for the (on the average) slower molecule whose mass is \( M_1 \). What is \( M_1/M_2 \)?

Soln.

(1) The kinetic energy \( K \) of the plane is

\[
K = \frac{1}{2}(50 \times 10^3) \left( \frac{800 \times 10^3}{3600} \right)^2 = 2.5 \times 10^4(222)^2 = 1.2 \times 10^9 \text{ J}.
\] (M1)

The heat capacity of the water in the pool is (for water \( C = 4.2 \text{ J/K.g} \))

\[
C = (20 \times 50 \times 2) \times 4.2 \times 10^6 = 8.4 \times 10^9 \text{ J/K}.
\] (M2)

Thus, the temperature goes up by only 0.14 K.

This means that if even a very small fraction of thermal energy around us can be converted into a systematic motional energy, a tremendous mechanical effect can be created. Thus, there is no wonder that the industrial revolution was inseparably coupled with Watt’s invention.

(2) According to D. Bernoulli’s result the monatomic ideal gas consisting of \( N \) particles obeys

\[
PV = \frac{2}{3}NK,
\] (M3)

where \( K \) is the average translational kinetic energy of a single particle: \( K = (m/2)\langle v^2 \rangle \), if the mass of the molecule is \( m \) and its speed is \( v \). Therefore,

\[
PV = \frac{1}{3}Nm\langle v^2 \rangle \Rightarrow \frac{3PV}{Nm} = \frac{3P}{\rho} = \langle v^2 \rangle,
\] (M4)

\[\text{1}\text{augmented on April 25; important additions are marked with * in 7-9.}\]
where \( \rho \) is the density of the gas. For our gas, this gives

\[
\langle v^2 \rangle = \frac{3 \times 10^5}{13.3} = 150.2^2.
\] (M5)

Thus, about 150 m/s. This is the order of the sound speed in gases, and is a realistic value.

(3) We need two ingredients: the equipartition of kinetic energy and the statistical independence of two individual particles:

\[
\frac{1}{2} M_1 \langle v_1^2 \rangle = \frac{1}{2} M_2 \langle v_2^2 \rangle = \frac{3}{2} k_B T,
\] (M6)

\[
\langle v_1 \cdot v_2 \rangle = 0.
\] (M7)

Thus, \( M_1 > M_2 \), since particle 1 is on the average slower. Let \( w = v_2 - v_1 \). Then,

\[
\langle w^2 \rangle = \langle (v_2 - v_1)^2 \rangle = \langle v_2^2 \rangle + \langle v_1^2 \rangle = 3\langle v_1^2 \rangle.
\] (M8)

That is

\[
2\langle v_1^2 \rangle = \langle v_2^2 \rangle.
\] (M9)

We know

\[
M_1 \langle v_1^2 \rangle = M_2 \langle v_2^2 \rangle,
\] (M10)

so \( M_1/M_2 = 2 \).

2. [Elementary probability] (cf. 3A, Q3.1, Disc 7.5)

(1) There are 5 doors, but behind only one of them is a prize. You are assured that all the doors have the same probability (1/5) to hide the prize.

The moderator allows you to choose two doors. Then, the moderator opens two of the unselected doors to show you that there is no prize behind them and tells you that you may keep the already chosen two doors or, instead, switch to choose the one not selected yet.

If you wish to maximize the chance to get the prize, what will you do?

(2) There is a box containing 1 mole of gas. Then, its volume is accurately halved by a membrane. This is a convenient example to explain why almost accurate 1/2 division of the particles is overwhelmingly likely if the number of involved particles is huge. In some elementary textbooks the explanation goes as follows: for \( N_A(0.5 - x) \) particles to be on one side is with probability

\[
\left( \frac{N_A}{N_A(0.5 - x)} \right)^{2-N_A}.
\] (M11)

Indeed, this apparently explains the overwhelming likelihood of almost exact even bisection, since \( \sqrt{N_A} \ll N_A \).

A student objected this explanation: since all the particles are indistinguishable, this explanation is totally wrong. Therefore, the student tried to correct the argument as follows:

The total number of ways to distribute the particles is \( (\frac{N_A+2-1}{N_A}) \) instead of \( 2^{N_A} \), because
the problem is to put indistinguishable particles into 2 distinguishable containers. Thus, there are \( N_A \) ways. The number of ways to put \( M \) particles on one side is just one, because particles are indistinguishable. Therefore, the probability to find \( \sim 0.5 - x \) moles on one side is probabilistically indistinguishable from the even \( \sim 0.5 \) case. That is, if the particles are indistinguishable, it is not hard to observe large fluctuations!

You must think the answer is crazy, and you are perfectly correct. What is wrong with this student’s argument?

**Soln**

(1) Since all the doors give you an even chance to win, your initial chance is 2/5. Thus, there is probability 3/5 chance to miss the prize. Now, after knowing the two empty doors, the remaining door should hide the prize with probability 3/5, because the moderator ‘concentrated’ the possibilities of success distributed evenly behind three doors into one door. Thus, you should switch your choice from the original two doors to the remaining 1 door.

(2) Neither a particular particle to be in the right half nor in the left is a single one particle state. Therefore, regarding a particle being on one side as a single one particle state is totally wrong (you may say it is an error of confusing micro and macrostates). The easiest remedy is to divide the space into small cells that can accommodate only one particle and then distribute indistinguishable \( N_A \) particles into these cells. If \( v \) is the number of such cells in one half of the box, we need

\[
\binom{v}{N_A(0.5 - x)} \binom{v}{N_A(0.5 + x)}, \tag{M12}
\]

where \( v \gg N_A \). Thus, the problem is exactly the one(s) you encountered in Discussion.

3 [Easy Boltzmann factor questions] (cf. 5.11, 20.2, 20.9)

(1) [Vapor pressure of silicon]

The chemical potential \( \mu_s \) of the atom in a solid is essentially given by the binding energy \( \Delta \) of atom in the solid (= work needed to excavate an atom): \( \mu_s = -\Delta \). Obtain the formula for the equilibrium vapor pressure of solid, and estimate the vapor pressure at 1,000 K of silicon for which \( \Delta = 3 \) eV. [Note that \( k_B = 8.6 \times 10^{-5} \text{ eV/K} \)]

**Soln.**

This is a typical Physics 100 level question. We may assume that the gas is ideal, so its chemical potential is given by \( \mu = k_B T \log(n/n_Q) \), which we obtained as \( G = N \mu \) in Discussion. The chemical potential of the atom in the solid is \( -\Delta \). Therefore the equilibrium condition (the identity of chemical potentials in two phases) gives

\[
n = n_Q e^{-\beta \Delta} \Rightarrow P = k_B T n. \tag{M13}
\]

Here, the so-called quantum number density \( n_Q \) is defined as \( m = \hat{m} \times 10^{-3}/N_A \), where \( \hat{m} \) is the molecular weight

\[
n_Q = \left( \frac{\sqrt{2\pi mk_BT}}{\hbar} \right)^3 = \hat{m}^{3/2} T^{3/2} \left( \frac{\sqrt{2\pi k_B} \times 10^{-3}/N_A}{\hbar} \right)^3 \tag{M14}
\]
\[ \dot{m}^{3/2} T^{3/2} \left( \frac{\sqrt{2\pi} \times 1.38 \times 10^{-23} \times 10^{-3} / 6.02 \times 10^{23}}{6.62 \times 10^{-34}} \right)^3 \]  
\[ = \dot{m}^{3/2} T^{3/2} \left( \frac{3.79 \times 10^{-25}}{6.62 \times 10^{-34}} \right)^3 = 1.88 \times 10^{26} \dot{m}^{3/2} T^{3/2}, \]  
(M15)

which is sometimes written as

\[ n_Q = \dot{m}^{3/2} \left( \frac{T}{300} \right)^{3/2} \times 10^{30}. \]  
(M16)

We know \( \dot{m} = 28 \)

\[ n_Q = 28^{3/2} \times (3.33)^{3/2} \times 10^{30} \simeq 9 \times 10^{32}. \]  
(M17)

Therefore,

\[ P = k_B T n_Q e^{-\beta \Delta} = 1.38 \times 10^{-23} \times 1,000 \times 9 \times 10^3 e^{-3/0.086} \]  
\[ = 1.24 \times 10^{13} \times 7.1 \times 10^{-16} = 8.8 \times 10^{-3} \text{ Pa}. \]  
(M18)

(2) There is a ‘three one-particle state’ system: one state is the (one-particle) ground state\(^2\) (energy 0), and the other two are with the same energy \( \epsilon \) such that \( \beta \epsilon = 2 \). There are two indistinguishable particles

(i) Suppose the particles are fermions. What is the probability of microstates with energy \( 2\epsilon \)?

(ii) Suppose the particles are bosons. What is the probability of microstates with energy \( 2\epsilon \)?

**Soln.**

For both the cases, all the microstates are illustrated in Fig. M.1:

\[ \begin{array}{c}
(i) \epsilon | \bullet \bullet \bullet \bullet \bullet \bullet \bullet \bullet \bullet \bullet \\
\epsilon \quad \epsilon \quad 2\epsilon \\
\hline
(ii) \epsilon | \bullet \bullet \bullet \bullet \bullet \bullet \bullet \bullet \bullet \bullet \\
0 \quad \epsilon \quad \epsilon \\
\hline
\end{array} \]

**Figure M.1:** All the microstates for 3(2). The red shaded microstates are of our interest.

\(^2\)Do not confuse the one particle ground state and the ground microstate, that is the ground state of the whole system.
(i) The normalization constant $Z$ (the canonical partition function!) is

$$Z = 2e^{-2} + e^{-4} = 0.289.$$  \hspace{1cm} (M21)

Therefore,

$$P(2\epsilon) = \frac{1}{Z}e^{-4} = 0.063.$$  \hspace{1cm} (M22)

(ii) The normalization constant $Z$ is

$$Z = 1 + 2e^{-2} + 3e^{-4} = 1.326.$$  \hspace{1cm} (M23)

Therefore,

$$P(2\epsilon) = \frac{1}{Z} \times 3e^{-4} = 0.0414.$$  \hspace{1cm} (M24)

4 [\textbf{Delta function}] (cf 5.17-22)

(1) Compute the following integrals:

(i) \hspace{1cm} \int_{-\infty}^{\infty} dx \delta(x^2 - x - 2) \sin \frac{\pi}{x}.

\hspace{1cm} (M25)

(ii) \hspace{1cm} \int_{-\infty}^{\infty} dx \delta(4x^2 - 3x - 1)(x - 1)(x + 2).

\hspace{1cm} (M26)

(iii) \hspace{1cm} \int_{-\infty}^{\infty} dx \delta(3 - e^x) \cosh x.

\hspace{1cm} (M27)

\textbf{Soln.}

The basic formula we need is

$$\int_{I} dx \delta(f(x))g(x) = \int_{I} dx \sum_{\{y \mid f(y) = 0, y \in \mathbb{R}\}} \delta(x - y) \frac{g(x)}{|f'(x)|}.$$  \hspace{1cm} (M28)

(i) $x^2 - x - 2 = (x - 2)(x + 1)$, so

$$\int_{-\infty}^{\infty} dx \delta(x^2 - x - 2) \sin \frac{\pi}{x} = \int_{-\infty}^{\infty} dx \frac{1}{2x - 1}[\delta(x-2) + \delta(x+1)] \sin \frac{\pi}{x} = \frac{1}{3} \left( \sin \frac{\pi}{2} - \sin(-\pi) \right) = \frac{1}{3}.$$  \hspace{1cm} (M29)
(ii) \(4x^2 - 3x - 1 = (4x + 1)(x - 1)\), so
\[
\int_{-\infty}^{\infty} dx \, \delta(4x^2 - 3x - 1)(x - 1)(x + 2) = \int_{-\infty}^{\infty} dx \, \frac{1}{|8x - 3|} \left[ \delta(x + 1/4) + \delta(x - 1) \right] (x - 1)(x + 2)
\]
\[
= \frac{1}{5} \left( \frac{-1}{4} - 1 \right) \left( -\frac{1}{4} + 2 \right) = \frac{1 - 5}{4} = -\frac{7}{4}.
\] (M30)

Here, in (M30) \(\delta(x + 1/4)\) instead of \(\delta(4x + 1)\), which is wrong.

(iii) \(e^x = 3\) implies \(x = \log 3\), so
\[
\int_{-\infty}^{\infty} dx \, \delta(3 - e^x) \cosh x = \int_{-\infty}^{\infty} dx \, e^{-x} \delta(x - \log 3) \frac{e^x + e^{-x}}{2}
\]
\[
= \int_{-\infty}^{\infty} dx \, \frac{1 + e^{-2x}}{2} \delta(x - \log 3) = \frac{1 + 1/9}{2} = \frac{5}{9}.
\] (M32)

Instead, you could proceed as follows as well:
\[
= \int_{-\infty}^{\infty} dx \, e^{-x} e^x \delta(3 - e^x) \frac{e^x + e^{-x}}{2} = \int_{0}^{\infty} dy \, \frac{1}{y} \delta(3 - y) \frac{1 + y}{2} = \frac{3 + 1/3}{6}.
\] (M34)

(2) Find the most probable de Broglie wavelength \(\lambda_{\text{mode}}\) for a particle of mass \(m\) in a gas in equilibrium at temperature \(T\).

Is it the same as \(h/p_{\text{mode}}\)?

**Soln.**

The Maxwell distribution (density distribution for the momentum \(p\)) reads
\[
f(p) = \left( \frac{1}{2\pi mk_B T} \right)^{3/2} e^{-p^2/(2mk_B T)}.
\] (M35)

Since
\[
\lambda = h/|p|,
\] (M36)

we get the density distribution function for de Broglie wavelength \(\lambda\) formally (= mechanically) as\(^3\)
\[
\phi(\lambda) = \int_{\mathbb{R}^3} d^3p \, \delta(\lambda - h/p) \left( \frac{1}{2\pi mk_B T} \right)^{3/2} e^{-p^2/(2mk_B T)}
\]
\[
= 4\pi \int_0^{\infty} dp \, p^2 \delta(\lambda - h/p) \left( \frac{1}{2\pi mk_B T} \right)^{3/2} e^{-p^2/(2mk_B T)}
\] (M37)
\[
= 4\pi \int_0^{\infty} dp \, p^2 \delta(p - h/\lambda) \frac{p^2}{h} \left( \frac{1}{2\pi mk_B T} \right)^{3/2} e^{-p^2/(2mk_B T)}
\] (M38)
\[
= 4\pi \left( \frac{h^2}{2\pi mk_B T} \right)^{3/2} \frac{1}{\lambda^2} e^{-h^2/(2mk_B T)}
\] (M39)
\[
= 4\pi \left( \frac{h^2}{2\pi mk_B T} \right)^{3/2} \frac{1}{\lambda^2} e^{-h^2/(2mk_B T)}
\] (M40)

\(^3\)Of course, you need not use \(\delta\)-functions and use your brain a bit harder, but here I like a mechanical way.
Therefore, the mode is
\[
\frac{d}{d\lambda} \left( -4 \log \lambda - \frac{h^2}{2m\lambda^2k_B T} \right) = -\frac{4}{\lambda} + \frac{h^2}{m\lambda^3k_B T} = 0,
\] (M42)
or
\[
\lambda_{\text{mode}} = \frac{h}{\sqrt{4mk_B T}}.
\] (M43)

We know \( p_{\text{mode}} = \sqrt{2mk_B T} \), so \( \lambda_{\text{mode}} < \frac{h}{p_{\text{mode}}} \).

5. [Brownian motion; \( N_A \)] (cf. 7.11, 7.13, 18.10)

(1) One experiment replicating Perrin’s experiment in a modern setting uses polystyrene particles of diameter (i.e., \( 2a \)) 0.54 \( \mu \)m suspended in a buffer solution of viscosity \( \eta = 1.04 \times 10^{-3} \) Pa-s at \( T = 290 \) K. A horizontal two-dimensional stage was recorded by a microscope with a CCD camera, and its \( x \) and \( y \) coordinates are measured as functions of time. The mean square average displacement after \( t \) s in \( x \) is observed as \( \langle x^2 \rangle = 15.6 \times 10^{-13} t \) m\(^2\) and in \( y \) is observed as \( \langle y^2 \rangle = 14.8 \times 10^{-13} t \) m\(^2\). Assuming that you know the gas constant \( R = 8.31 \) J/mol-K, estimate Avogadro’s constant \( N_A \).

**Soln.**

The relation we use is
\[
\langle x^2 + y^2 \rangle = 4Dt
\] (M44)
in 2-space (‘4’ in the formula is 2\( \sigma \)) and the Einstein-Stokes relation \( D = k_B T/6\pi a \eta \) may be used.\(^4\) Therefore,
\[
k_B = \frac{6\pi a \eta D}{T} = \frac{6\pi a \eta \langle x^2 + y^2 \rangle}{4dT} = \frac{3\pi a \eta}{2T} \times (15.6 \times 10^{-13} + 14.8 \times 10^{-13}) \]
\[
= 0.456 \times 10^{-11} \times 30.4 \times 10^{-13} = 1.386 \times 10^{-23}
\] (M45)
or
\[
N_A = \frac{R}{k_B} = 5.99 \times 10^{23}.
\] (M46)

Probably too good.

(2) There is a Brownian particle starting from the center (black dot in Fig. M.2; ignore the tube inside for the time being) of the sphere.

On the average it takes 35 seconds to reach the spherical shell.

Next, as in the figure, a thin tube is placed along the diameter, and the same particle starts from the origin again. On the average how long will it take for the particle to reach an end of the tube? You may assume that, although the tube is very thin, still its diameter

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\(^4\)You might worry whether we can use 3D fluid dynamics to get the Stokes relation \( \zeta = 6\pi a \eta \), the liquid layer is practically thick enough.
Figure M.2: Diffusion in the tube or out of the tube.

is ‘macroscopic’ (say > 1 μm).

\textbf{Soln.}
Notice that
\[ \langle R^2 \rangle = 2dDt. \] (M48)

Therefore, the average time required to traverse distance \( R \) in \( d \)-space is \( t = \langle R^2 \rangle / 2dD \).
Thus, in our case
\[ t_{\text{sphere}}/t_{\text{tube}} = 1/3. \] (M49)

That is, in the tube it takes, on the average, 105 sec. Why? Only once in ‘three’ trials can the particle move in the movable direction. Thus, it take three times as long as the 3D case.

(3) There is a rod-like macromolecule whose length \( L \) fluctuates. According to the measurement \( \langle \delta L^2 \rangle = 23 \text{ nm}^2 \). What is the Hooke’s constant \( k \) (i.e., force = \( k \times \) length change) at temperature 300 K? Get it in pN/nm. Use the fluctuation-response relation.

\textbf{Soln.}
Notice that \( k_B T = 4.14 \text{ pN-nm} \) at 300 K. The relevant fluctuation-response relation is (cf. \( fE = TdS + FdL \))
\[ \langle \delta L^2 \rangle = k_B T \left( \frac{\partial L}{\partial F} \right)_T = \frac{k_B T}{k}. \] (M50)

Therefore,
\[ k = \frac{k_B T}{\langle \delta L^2 \rangle} = 4.14/23 = 0.18 \text{ pN/nm}. \] (M51)

\[ \text{6 [Entropy and information]} \ (\text{cf. 11.5, 11.8, 15.2-6}) \]

(1) There are 9 containers. The \( i \)th container contains \( n_i = np_i \) moles of a monatomic ideal gas, where \( \sum_i p_i = 1 \). The pressure and the temperature of the \( i \)th container is \( P_i \) and \( T_i \). We measure the entropy change after connecting all the containers so that gases can mix freely. In case A, all the gases are chemically distinct and the entropy increase is \( \Delta S_A \). In case B all the gases are identical and the entropy increase is \( \Delta S_B \). Needless to say, \( \Delta S_A > \Delta S_B \).
What is the difference? You must justify your answer.

**Soln.**
In both cases the final $T$ and $P$ are the same. There are two ways to answer this question. A traditional approach is to follow the process explained in Fig. M.3.

The step P prepares all the compartments to have the same $T$ and $P$ as the final state. At this step whether chemicals are distinguishable or not does not matter, obviously. The step Q removes all the separating walls. For B nothing happens, but for A it is the ‘pure’ mixing process, so the system entropy increases by the amount of the mixing entropy. Thus, $\Delta^2 S = \Delta S_A - \Delta S_B$ is the mixing of \{n_i\} moles in the same $T$, $P$ state. Thus, (I do not repeat the argument similar to that given in ‘Information addendum’ lecture note (posted))

$$\Delta^2 S = \sum_{i=1}^{9} p_i \log p_i.$$  \(	ext{(M52)}\)

The other method, that I prefer to the above, is information-theoretical. Because particles do not interact, the difference in the amounts of the required information in specifying the ‘particle state’ between the pure case and the mixture case is due to the existence/absence of the chemical species difference. The information we need for this is obviously given by the Shannon formula per particle. Therefore, $\Delta^2 S$ must be (M52).

(2) [Statistical mechanics of golf green] A golf green consists of a large flat circular lawn and a small deep hole. Thus, we can consider a system with a one particle of mass $m$ moving around in the ‘green’ consisting of two portions with a large volume $V$ without any potential energy (the green state) and with a small volume $V_0$ with a potential energy $-U$ ($U > 0$) (the hole state) (See Fig. M.4).\(^5\)

If you prepare an ensemble consisting of numerous copies of this system, you can handle the ensemble by a canonical ensemble approach at temperature $T$. Everything occurs in liquid, so you need not pay attention to the volume change. That is, the free energy can be either

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\(^5\)This is a caricature of protein folding. The ‘green state’ corresponds to the denatured state dominated by entropy, and the ‘hole’ state a folded state (natural state).
Figure M.4: Statistical mechanics of ‘golf green model’

A or G. There is no practical difference.

(i) What is the free energy difference between the ‘green’ state and the ‘hole’ state (per particle/system)?

(ii) If you prepare numerous copies of this system, you can discuss the phase transition. What is the phase transition temperature (where the free energy difference between the green and the hole states vanishes) between the green and the hole state?

Suppose $V = 10V_0$ and $U/k_B = 705$ K. What is the transition temperature?

(iii) If you have 1 bit of information about the location of the particle in the green state, because some portion of green is made inaccessible, what happens to the phase transition point?

Soln.

(i) The entropy difference is due to the volume difference, so

$$\Delta S = S_{\text{green}} - S_{\text{hole}} = k_B \log \frac{V}{V_0}.$$  (M53)

The number of microstate for the particle is proportional to the volume, so entropy is naturally related to its logarithm. Therefore, since $A = E - TS$,

$$\Delta A = A_{\text{green}} - A_{\text{hole}} = U - k_B T \log \frac{V}{V_0}.$$  (M54)

If you wish to do it ‘more statistical mechanically,’ you could compute the canonical partition functions for these phases as

$$Z_{\text{green}} = V,$$  (M55)

$$Z_{\text{hole}} = V_0 e^{\beta U}.$$  (M56)

Therefore, we get $A_{\text{green}} = -k_B T \log V$ and $A_{\text{hole}} = -k_B T \log V_0 - U$.

(ii) $\Delta A = 0$ is the phase transition condition. Therefore,

$$T = U/k_B \log(V/V_0) = 705/\log 10 = 306.$$  (M57)

That is, 33 °C.

(iii) Now $\Delta S = S_{\text{green}} - S_{\text{hole}}$ must be 1 bit less. That is, $k_B \log 2$ less in the usual unit per

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Footnote: For the protein case chaperones do this. A chaperone tells the protein where the ‘hole’ is likely to be and facilitates folding.
particle. This is of course natural, since $V$ is halved. Therefore,

$$T = 705 / \log 5 = 438,$$

That is, 165 °C.

7 [Elementary thermodynamics] (cf. 10.7, 10.12, 10.15, Q10.2)

(1) We wish to operate a heat pump driven by an engine working with the burner temperature $T_B$. The heat pump operates between the outdoor (temperature $T_O$) and the room of temperature $T_R$. Needless to say, $T_O < T_R \ll T_B$ (see Fig. M.5). Let $Q_O$ be the heat imported to the room from the outside, and $Q_B$ be the heat produced by the burner (per one engine cycle). What is the upper bound of $Q_O/Q_B$ which we wish to maximize?

If $T_B = 1500$ K, and $T_O = 270$ K, what do you expect to make yourself comfortable?

![Figure M.5: Heat pump: E is the engine to drive the heat pump H. Use the sign convention: + in the arrow direction. Thus, e.g., $-Q_R$ is imported to the engine.](image)

(2)

(i) What is the entropy change if you throw in a 1 liter of 20 °C water into 10 liters of 70 °C of water? [Some care may be required to get a reasonable numerical value.]

(ii) If the amount of 70°C water ($V$ liters) is increased, can you say something general about $\Delta S$?

**Soln.**

(1) We wish to save energy to warm up the room as much as possible, so the engine should work between $T_B$ and the room temperature $T_R$. We know, thanks to Carnot,

$$\frac{W}{Q_B} \leq \left(1 - \frac{T_R}{T_B}\right).$$

For the heat pump conservation of energy implies (in this problem the sign convention is + in the arrow direction in Fig. M.5)

$$W + Q_O - Q'_R = 0$$

and Clausius’ inequality tells us

$$0 \geq -\frac{Q'_R}{T_R} + \frac{Q_O}{T_O}.$$
Therefore,

\[ 0 \geq -\frac{W + Q_O}{T_R} + \frac{Q_O}{T_O} = -\frac{W}{T_R} + Q_O \left( \frac{1}{T_O} - \frac{1}{T_R} \right). \]  

(M62)

That is,

\[ \frac{W}{Q_O} \geq \left( \frac{T_R}{T_O} - 1 \right). \]  

(M63)

Taking the ratio of (M59) and (M63), we obtain

\[ \frac{Q_O}{Q_B} \leq \left( 1 - \frac{T_R}{T_B} \right) / \left( \frac{T_R}{T_O} - 1 \right) = \left( 1 - \frac{T_R}{T_B} \right) \frac{T_O}{T_R - T_O}. \]  

(M64)

If you like \( T_R = 300 \) K, we see

\[ \frac{Q_O}{Q_B} \leq \left( 1 - \frac{300}{1500} \right) \frac{270}{300 - 270} = \frac{36}{5} = 7.2. \]  

(M65)

This means that you can save a lot of heating expense.

You could straightforwardly mimic Q10-2. The answer is ‘the same’ with proper translation: \( H \iff B, M \iff R \) and \( L \iff O \).

(2) (i) We need the final equilibrium state, and a quasiequilibrium process (in our case very slow reversible heating) to the final state. The final state is 11 liters of \( \frac{720}{11} \approx 65.45^\circ C \). Therefore,

\[ \Delta S = \int_{293}^{338.45} \frac{4200}{T} \, dT + \int_{343}^{338.45} \frac{42000}{T} \, dT = 4200 \log \frac{338.45}{293} + 42000 \log \frac{338.45}{343} \]

(M66)

\[ = 605.7 - 560.87 = 44.8 \, \text{J/K}. \]  

(M67)

(ii) Let \( T(V) = \frac{293 + 343V}{1 + V} \) be the final temperature. Then, the general formula is

\[ \Delta S(V) = \int_{293}^{T(V)} \frac{4200}{T} \, dT + V \int_{343}^{T(V)} \frac{4200}{T} \, dT. \]  

(M68)

Therefore,

\[ \frac{d}{dV} \Delta S(V) = \frac{4200}{T(V)} (1 + V) \frac{dT(V)}{dV} + \int_{343}^{T(V)} \frac{4200}{T} \, dT. \]  

(M69)

Removing 4200, this reads

\[ (1 + V) \frac{d}{dT} \log T(V) + \log \frac{T(V)}{343} = (1 + V) \left( \frac{343}{293 + 343V} - \frac{1}{1 + V} \right) + \log \frac{T(V)}{343} \]

(M70)

\[ = \frac{343 - 293}{293 + 343V} - \log \frac{343 + 343V}{293 + 343V} \]  

(M71)

\[ = \frac{343 - 293}{293 + 343V} - \log \left( 1 + \frac{343 - 293}{293 + 343V} \right) > 0, \]  

(M72)
because $x - \log(1 + x) > 0$ for $x > 0$. Therefore, $\Delta S(V)$ increases monotonically to the $V \to \infty$ limit.

<table>
<thead>
<tr>
<th>$V$</th>
<th>$\Delta S(V)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>45.4</td>
</tr>
<tr>
<td>20</td>
<td>47.4</td>
</tr>
<tr>
<td>40</td>
<td>48.4</td>
</tr>
<tr>
<td>80</td>
<td>48.9</td>
</tr>
<tr>
<td>160</td>
<td>49.2</td>
</tr>
<tr>
<td>320</td>
<td>49.4</td>
</tr>
<tr>
<td>1200</td>
<td>49.46</td>
</tr>
</tbody>
</table>

(M73)

Notice that

$$\lim_{V \to \infty} V \int_{343}^{T(V)} \frac{4200}{T} dT = \frac{4200}{343} (273 - 343),$$

(M74)

independent of $V$ as expected.

* Perhaps a better answer is to divide the heat bath into two pieces, $V_1$ and $V_2$. Instead of connecting the system to $V_1 + V_2$, first connect the system to $V_1$ only. Then, connect system+$V_1$ with $V_2$. Each step increases the entropy of the world. The end.\footnote{inspired by the solution due to Mr. S. Pani.}

8. \textbf{[Independent spins in B-field]} (cf. 13.2, 17.16, 18.9, 18.10)\footnote{See also the posted Lecture 14 Feb 26 Thermodynamic derivation of canonical formalism.}

This is a continuation of HW 9 3. The collection of $N$ free spins have no internal energy (or we could say $E = 0$), but there is one more thermodynamic coordinates $M$.

(1) Write down the microcanonical partition function $W(M)$ (we will not write the fixed $E$) and obtain the entropy $S(M)$ of the system consisting of $N \pm 1$ spins. Here, $M = \mu \sum_{i=1}^{N} s_i$, where $s_i$ is the $i$th spin value.

(2) We know the Gibbs relation ($dE$ is suppressed in (M75); $dE = TdS + BdB = 0$ is the Gibbs relation as consistent with (M75)):

$$dS = -\frac{B}{T} dM.$$  \hspace{1cm} (M75)

Find $M$ as a function of $B/T$.

(3) We may introduce the (generalized) enthalpy $\tilde{H} = E - MB$ or $-\tilde{H} = \max_{M}[MB]$ (because $E = 0$). Its Gibbs relation reads $d\tilde{H} = TdS - MdB$. We may further Legendre transform this to obtain the (generalized) Gibbs free energy $\tilde{G} = \tilde{H} - ST$ ($-\tilde{G} = \max_{S}[ST - \tilde{H}]$).\footnote{If you prefer entropy} Write down the most convenient partition function $Y(T, B)$ that gives the Gibbs free energy directly as $\tilde{G} = -k_B T \log Y$. Then, compute $\tilde{G}$.

$$-\tilde{G}/T = \max_{H}[(1/T)\tilde{H} - (-S)] = \max_{M}[MB/T + S]$$

under the $B$ constant condition. Using the rightmost form is probably the most convenient for our purpose of getting $Y$.\footnote{If you prefer entropy}
We can demonstrate the ensemble equivalence, computing various quantities explicitly as done in HW9. Here, show that the difference between $\tilde{G}$ obtained directly from $Y$ and $\tilde{H} - TS$ computed microcanonically are no more different than $O[\log N]$. (That is, write the ‘max-sum’ correspondence in a mathematically respectable fashion.)

Some (most?) parts of this problem can be copied from easily accessible sources. Even in that case, however, you must reconstruct your storyline in your answer.

**Soln.**

(1) $W(M)$ is the total number of microstates (= the configurations of spins) with $M/\mu = N_+ - N_-$, where $N_+$ (resp., $N_-$) is the number of up (resp., down) spins. Since $N_+ + N_- = N$, we have

$$N_\pm = \frac{1}{2}(N \pm M/\mu).$$

Therefore,

$$W(M) = \binom{N}{N_+} = \binom{N}{(N + M/\mu)/2}.$$  \hspace{1cm} (M76)

Boltzmann’s principle tells us that

$$S(M) = -k_B N \log \left( \frac{1}{2} \right) \frac{N + M/\mu}{2N} \log \left( \frac{N + M/\mu}{N} \right) + \frac{N - M/\mu}{2N} \log \left( \frac{N - M/\mu}{N} \right).$$  \hspace{1cm} (M78)

(2) The Gibbs relation (M75) gives

$$-\frac{B}{T} = \frac{dS}{dM} = -k_B N \log \left( \frac{1}{2} \right) \frac{N + M/\mu}{2N} - \frac{1}{2} \frac{N - M/\mu}{2N} \log \left( \frac{N - M/\mu}{N} \right).$$  \hspace{1cm} (M79)

Therefore,

$$e^{2\beta B} = \frac{N + M/\mu}{N - M/\mu}.$$  \hspace{1cm} (M81)

Thus,

$$(1 - M/\mu N)e^{2\beta B} = (1 + M/\mu N) \Rightarrow (M/\mu N)(e^{2\beta B} - 1) = e^{2\beta B} - 1$$  \hspace{1cm} (M82)

or

$$M = \mu N \frac{e^{2\beta B} - 1}{e^{2\beta B} + 1} = \mu N \tanh \beta B.$$  \hspace{1cm} (M83)

Because $E = 0$, $T$ cannot appear independently from $B$ for our ‘over-idealized’ model.

(3) We can use the ‘max-sum’ correspondence, starting from the entropic form of the Legendre transformation (see footnote 7)

$$e^{-\beta \tilde{G}} = \max_M [e^{\beta BM + S/k_B}] = \max_M [W(M)e^{\beta BM}] = \sum_M \binom{N}{(N + M/\mu)/2} e^{\beta BM} = Y.$$  \hspace{1cm} (M84)
This is easier to calculate in terms of $N_\pm (M = \mu(N_+ - N_-))$ than in terms of $M$:

$$e^{-\beta \tilde{G}} = \sum_{N_+} \left( \frac{N}{N_+} \right) e^{\beta \mu B(N_+ - N_-)} = \left( e^{\beta \mu B} + e^{-\beta \mu B} \right)^N = Y.$$  \hfill (M85)

Therefore,

$$\tilde{G} = -N k_B T \log \left( e^{\beta \mu B} + e^{-\beta \mu B} \right).$$  \hfill (M86)

We must have $\tilde{G} = \tilde{H} - ST = -MB - ST$.

(4) Our partition function $Y$ is a sum of positive terms, so it obviously satisfies

$$\max_M W(M) e^{\beta BM} \leq Y \leq \max_M W(M) e^{\beta BM} \times N,$$  \hfill (M87)

because there are $N + 1 \simeq N$ terms. This implies

$$\max_M (S + \beta MB) \leq \log Y \leq \max_M (S + \beta MB) + O[\log N].$$  \hfill (M88)

$\max_M (S + \beta MB)$ is nothing but thermodynamically computed $-\beta \tilde{G}$ from the microcanonically obtained $S$. Thus, the discrepancy is at most $O[\log N]$.

* If you calculate $S$, $Y$ and $M$ in this model explicitly, you will find any discrepancy. This is because your calculations have already ignored conveniently the small discrepancies. As you can see from (M87) there must definitely be discrepancies (the sum and the largest summand cannot be the same). It is often the case that the use of Stirling’s formula ignores the $O[\log N]$ error:

$$\log N! = N \log N - N + \frac{1}{2} \log N + O[1].$$  \hfill (M89)

Thus, your explicit results exhibit no discrepancies.

9. **[Canonical ensemble]** (cf. 14.11)

Suppose that a (3D) classical mechanical system (a fluid system) has the following Hamiltonian

$$H = \sum_{k=1}^{N} a_k |p_k + c_k|^s$$  \hfill (M90)

where $a_k (k = 1, \ldots, N)$ and $s$ are positive constants $c_k$ are constant 3D vectors. Without any explicit integration (use, e.g., dimensional analysis) compute the specific heat.

**Soln.**

The partition function $Z$ reads

$$Z = \frac{V^N}{N! h^{3N}} \prod_k \int d^3 p_k e^{-\beta a_k |p_k + c_k|^s}.$$  \hfill (M91)

First of all, $c_k$ may be ignored by shifting the integration ranges. You could use the scaled variable $\lambda$ defined by $\beta a_k p_k = \lambda^s_k$ for each integral. However, I recommend you to use
Dimensional Analysis.

My solution begins here. First I eliminate \( c_k \) by shifting \( p_k \): \( \beta a_k p_k^s \) is dimensionless, so

\[
[p] = [\beta a_k]^{-1/s}. \tag{M92}
\]

On the other hand,

\[
[\frac{Z_N^{3N}}{V^N}] = [p]^{3N} \propto [\beta^{-3N/s}] = (k_B T)^{3N/s}. \tag{M93}
\]

Therefore, even the internal energy (the Gibbs-Helmholtz relation):

\[
E = \frac{\partial \beta A}{\partial \beta} = -\frac{\partial \log \beta^{-3N/s}}{\partial \beta} \tag{M94}
\]

is independent of \( a_k \), so is \( C \). We get \( E = 3Nk_B T/s \) and \( C = 3Nk_B /s \).

\* Another solution\(^{10} \) is to use the equipartition of energy (suitably generalized in the following form for classical canonical partition functions (see 14.13):

\[
\left\langle \sum_{i \in \{x, y, z\}} p_i \frac{\partial H_i}{\partial p_i} \right\rangle = k_B T \delta_{ij}. \tag{M95}
\]

In our case, since we may ignore \( c_k \), for \( H_i = a_i |p_i|^s \) (\( p_i = 0 \) is removed from the following argument; this exclusion does not change the result.)

\[
\left\langle \sum_{i \in \{x, y, z\}} p_i \frac{\partial H_i}{\partial p_i} \right\rangle = sH_i = 3k_B T, \tag{M96}
\]

so \( \langle H_i \rangle = 3k_B T/s \). This immediately gives the correct answer.

10 [Fluctuation, stability] (cf. 18.10, 19.3)\(^{11} \)

Consider a magnet whose Gibbs relation for the internal energy reads \( dE = TdS + BdM \), where \( B \) is in the \( z \)-component of the magnetic field and \( M \) the \( z \)-component of the magnetization.

(1) Write down the fluctuation-response relation for the isothermal magnetic susceptibility.

(2) Write down the adiabatic magnetic susceptibility in terms of various fluctuation variances.

(3) Which is larger the constant magnetic field specific heat \( \chi_S \) or the constant magnetization specific heat \( \chi_T \)? Demonstrate the inequality with the aid of (1) and (2) [See Discussion 9].

Soln.

(1) Under \( T \) constant we already know

\[
\chi_T = \left( \frac{\partial M}{\partial B} \right)_T = \beta \langle \delta M^2 \rangle. \tag{M97}
\]

---

\(^{10}\)Reminded by Mr Yusen Ye.

\(^{11}\)A very similar Discussion was given.
\( \chi_S = \left( \frac{\partial M}{\partial B} \right)_S. \)  
(M98)

Therefore, if we can choose \( B \) and \( S \) as basic variables, then the statistical independence of \( \delta B \) and \( \delta S \) (because they are non-conjugate extensive-intensive quantity pair) allows us to compute \( \langle \delta B^2 \rangle \) with the aid of Einstein’s fluctuation theory. We have

\[
P(\delta) \propto \exp \left[ -\frac{1}{2k_B T} (\delta S \delta T + \delta B \delta M) \right] = \exp \left[ -\frac{1}{2k_B T} \left( \frac{\partial M}{\partial B} \right)_S \delta B^2 \right].
\]  
(M99)

Thus,

\[
\langle \delta B^2 \rangle = k_B T / \left( \frac{\partial M}{\partial B} \right)_S.
\]  
(M100)

Thus,

\[
\chi_S = k_B T / \langle \delta B^2 \rangle.
\]  
(M101)

(3) Cauchy’s inequality means

\[
\langle \delta M \delta B \rangle^2 \leq \langle \delta M^2 \rangle \langle \delta B^2 \rangle,
\]  
(M102)

so positivity of susceptibilities imply

\[
(k_B T)^2 \leq (k_B T \chi_T)(k_B T / \chi_S) \Rightarrow \chi_S \leq \chi_T.
\]  
(M103)

This is a le Chatelier-Braun principle.