PHYS4171-Statistical Mechanics and Thermal Physics
Fall 2017,Assignment #4

Problem 1) Four-state model (Canonical Ensemble): Consider a particle that can occupy four quantum states with energy, $-\varepsilon$,0,0, and ε.

a) (**5 points**) Show that the 1-particle partition function is $Z_1 = \left(2\cosh\left(\beta\varepsilon/2\right)\right)^2$, the average (mean) energy is $\langle E\rangle = -\varepsilon\tanh\left(\beta\varepsilon/2\right)$,and $\frac{\varepsilon}{2k_B T} = \frac{1}{2}\ln\left(\frac{\varepsilon - \langle E\rangle}{\varepsilon + \langle E\rangle}\right)$. Show that the average energy range is $-\varepsilon \le \langle E\rangle \le \varepsilon$.

$Z_1 = \sum \exp\left(-\beta E\right) = \exp\left(\beta\varepsilon\right) + \exp\left(0\right) + \exp\left(0\right) + \exp\left(-\beta\varepsilon\right)$.

$$Z_1 = \exp\left(\beta\varepsilon\right) + 2 + \exp\left(-\beta\varepsilon\right) = \left(\exp\left(\frac{\beta\varepsilon}{2}\right) + \exp\left(-\frac{\beta\varepsilon}{2}\right)\right)^2 = \left(2\frac{\exp\left(\frac{\beta\varepsilon}{2}\right) + \exp\left(-\frac{\beta\varepsilon}{2}\right)}{2}\right)^2,$$

But $\cosh x = \frac{\exp x + \exp -x}{2}$, and hence $Z_1 = \left(2\cosh\left(\beta\varepsilon/2\right)\right)^2$.

In the midterm we showed, $\langle E\rangle = -\left(\frac{\partial \ln Z_1}{\partial\beta}\right)$, $\langle E\rangle = -\left(\frac{\partial \ln\left(\left(2\cosh\left(\beta\varepsilon/2\right)\right)^2\right)}{\partial\beta}\right)$,

$$\langle E\rangle = -2\left(\frac{\partial \ln\left(2\cosh\left(\beta\varepsilon/2\right)\right)}{\partial\beta}\right) = -2\frac{2\sinh\left(\beta\varepsilon/2\right)}{2\cosh\left(\beta\varepsilon/2\right)}\frac{\varepsilon}{2} = -\varepsilon\tanh\left(\frac{\beta\varepsilon}{2}\right), -\frac{\langle E\rangle}{\varepsilon} = \tanh\left(\frac{\beta\varepsilon}{2}\right).$$

Using $\tanh^{-1}\left(x\right) = \frac{1}{2}\ln\left(\frac{1+x}{1-x}\right)$, $\tanh^{-1}\left(\frac{\langle E\rangle}{\varepsilon}\right) = \tanh^{-1}\left(\tanh\left(\frac{\beta\varepsilon}{2}\right)\right)$, which gives

$$\frac{\beta\varepsilon}{2} = \frac{1}{2}\ln\left(\frac{1+\left(-\langle E\rangle/\varepsilon\right)}{1-\left(-\langle E\rangle/\varepsilon\right)}\right) \rightarrow \frac{\varepsilon}{k_B T} = \ln\left(\frac{\varepsilon - \langle E\rangle}{\varepsilon + \langle E\rangle}\right).$$

It is well known that $\tanh x$ varies from -1 at $x = -\infty$, to 0 at x = 0, to $+1$ at $x = \infty$.
Hence, $\langle E\rangle = -\varepsilon\tanh\left(\beta\varepsilon/2\right)$, will vary from ε at $\beta = -\infty$ to 0 at $\beta = 0$ to from $-\varepsilon$ at $\beta = \infty$.

b) (**Graduate Student only, 5 points**) Show that the one-particle entropy is

$$S = \frac{\langle E\rangle}{T} + k_B \ln Z \rightarrow \frac{S}{k_B} = -\left(\frac{\varepsilon + \langle E\rangle}{\varepsilon}\right)\ln\left(\frac{\varepsilon + \langle E\rangle}{2\varepsilon}\right) - \left(\frac{\varepsilon - \langle E\rangle}{\varepsilon}\right)\ln\left(\frac{\varepsilon - \langle E\rangle}{2\varepsilon}\right).$$

Start from $S = \frac{\langle E\rangle}{T} + k_B \ln Z$, and from a), $\frac{1}{T} = \frac{k_B}{\varepsilon}\ln\left(\frac{\varepsilon - \langle E\rangle}{\varepsilon + \langle E\rangle}\right)$ and $\beta\varepsilon = \ln\left(\frac{\varepsilon - \langle E\rangle}{\varepsilon + \langle E\rangle}\right)$.

This give $\exp\left(\frac{\beta\varepsilon}{2}\right)=\left(\frac{\varepsilon-\langle E\rangle}{\varepsilon+\langle E\rangle}\right)^{1/2}$ and $\exp\left(-\frac{\beta\varepsilon}{2}\right)=\left(\frac{\varepsilon+\langle E\rangle}{\varepsilon-\langle E\rangle}\right)^{1/2}$.

From a) $Z_1=\left(\exp\left(\frac{\beta\varepsilon}{2}\right)+\exp\left(-\frac{\beta\varepsilon}{2}\right)\right)^2=\left(\left(\frac{\varepsilon-\langle E\rangle}{\varepsilon+\langle E\rangle}\right)^{1/2}+\left(\frac{\varepsilon+\langle E\rangle}{\varepsilon-\langle E\rangle}\right)^{1/2}\right)^2$. Now multiply

by **one** (doesn't look like 1) $Z_1=\left(\left(\frac{\varepsilon-\langle E\rangle}{\varepsilon+\langle E\rangle}\right)^{1/2}\left(\frac{\varepsilon-\langle E\rangle}{\varepsilon-\langle E\rangle}\right)^{1/2}+\left(\frac{\varepsilon+\langle E\rangle}{\varepsilon-\langle E\rangle}\right)^{1/2}\left(\frac{\varepsilon+\langle E\rangle}{\varepsilon+\langle E\rangle}\right)^{1/2}\right)^2$,

$Z_1=\left[\frac{(2\varepsilon)^2}{(\varepsilon+\langle E\rangle)(\varepsilon-\langle E\rangle)}\right]\rightarrow\ln Z_1=-\ln\left(\frac{\varepsilon-\langle E\rangle}{2\varepsilon}\right)-\ln\left(\frac{\varepsilon+\langle E\rangle}{2\varepsilon}\right)$,

Using $S=\frac{\langle E\rangle}{T}+k_B\ln Z=\frac{k_B\langle E\rangle}{\varepsilon}\ln\left(\frac{\varepsilon-\langle E\rangle}{\varepsilon+\langle E\rangle}\right)-\ln\left(\frac{\varepsilon-\langle E\rangle}{2\varepsilon}\right)-\ln\left(\frac{\varepsilon+\langle E\rangle}{2\varepsilon}\right)$,

$\frac{S}{k_B}=-\frac{\langle E\rangle}{\varepsilon}\ln\left(\frac{\varepsilon+\langle E\rangle}{\varepsilon-\langle E\rangle}\right)-\ln\left(\frac{\varepsilon-\langle E\rangle}{2\varepsilon}\right)-\ln\left(\frac{\varepsilon+\langle E\rangle}{2\varepsilon}\right)$. Now **add zero** and rearrange.

$\frac{S}{k_B}=-\frac{\langle E\rangle}{\varepsilon}\ln\left(\frac{\varepsilon+\langle E\rangle}{\varepsilon-\langle E\rangle}\right)-\ln\left(\frac{\varepsilon+\langle E\rangle}{2\varepsilon}\right)-\ln\left(\frac{\varepsilon-\langle E\rangle}{2\varepsilon}\right)-\frac{\langle E\rangle}{\varepsilon}\ln\frac{1}{2\varepsilon}+\frac{\langle E\rangle}{\varepsilon}\ln\frac{1}{2\varepsilon}$.

$\frac{S}{k_B}=-\frac{\langle E\rangle}{\varepsilon}\ln\left(\frac{\varepsilon+\langle E\rangle}{2\varepsilon}\right)-\ln\left(\frac{\varepsilon+\langle E\rangle}{2\varepsilon}\right)-\left(-\frac{\langle E\rangle}{\varepsilon}\ln\left(\frac{\varepsilon-\langle E\rangle}{2\varepsilon}\right)\right)-\ln\left(\frac{\varepsilon-\langle E\rangle}{2\varepsilon}\right)$.

Rearrange again, $\frac{S}{k_B}=-\frac{\varepsilon+\langle E\rangle}{\varepsilon}\ln\left(\frac{\varepsilon+\langle E\rangle}{2\varepsilon}\right)-\frac{\varepsilon-\langle E\rangle}{\varepsilon}\ln\left(\frac{\varepsilon-\langle E\rangle}{2\varepsilon}\right)$.

Full grade will be **awarded only** if **all algebraic steps** are **shown**.

c) (**5 points**) Using the result of b), find the energy **range** $\langle E\rangle$, when the **temperature** is **positive** and when it is **negative**. By direct differentiation, show that the temperature is infinite, when $\langle E\rangle=0$, and that the temperature is zero when $\langle E\rangle=-\varepsilon,\varepsilon$.

From equation 4.21 and 4.22, $\left(\frac{\partial S}{\partial\langle E\rangle}\right)_{N,V}=\frac{1}{T}$,

$\frac{1}{T}=\left(\frac{\partial S}{\partial\langle E\rangle}\right)_{N,V}=-\frac{1}{\varepsilon}\ln\left(\frac{\varepsilon+\langle E\rangle}{2\varepsilon}\right)+\frac{1}{\varepsilon}\ln\left(\frac{\varepsilon-\langle E\rangle}{2\varepsilon}\right)$, where **both** $\ln\left(\frac{\varepsilon+\langle E\rangle}{2\varepsilon}\right)<0$, and $\ln\left(\frac{\varepsilon-\langle E\rangle}{2\varepsilon}\right)<0$, are **negative**. In the case where $-\varepsilon<\langle E\rangle<0$, the **magnitude** of the **former** is larger $\left|\ln\left(\frac{\varepsilon+\langle E\rangle}{2\varepsilon}\right)\right|>\left|\ln\left(\frac{\varepsilon-\langle E\rangle}{2\varepsilon}\right)\right|$, hence $\frac{1}{T}>0$, so the **temperature** is **positive**, as expected. In the case where $0<\langle E\rangle<\varepsilon$, the magnitude of the **latter** is larger $\left|\ln\left(\frac{\varepsilon-\langle E\rangle}{2\varepsilon}\right)\right|>\left|\ln\left(\frac{\varepsilon+\langle E\rangle}{2\varepsilon}\right)\right|$, hence $\frac{1}{T}<0$, so the **temperature** is **negative**.

At $\langle E\rangle=0$, $\frac{1}{T}=\left(\frac{\partial S}{\partial\langle E\rangle}\right)_{N,V}=-\frac{1}{\varepsilon}\ln\left(\frac{\varepsilon+0}{2\varepsilon}\right)+\frac{1}{\varepsilon}\ln\left(\frac{\varepsilon-0}{2\varepsilon}\right)=0$, and $T=\infty$.

When $\langle E\rangle=-\varepsilon, S\to\infty$, so write $\langle E\rangle\to-\varepsilon+\delta$, where $0<\delta\ll1$ is a **very small positive number**. $\frac{1}{T}=-\frac{1}{\varepsilon}\ln\left(\frac{\delta}{2\varepsilon}\right)+\frac{1}{\varepsilon}\ln\left(\frac{2\varepsilon}{2\varepsilon}\right)$, where we neglect the δ in the last term. $\frac{1}{T}=-\frac{1}{\varepsilon}\underset{\delta\to0}{Lim}\ln\left(\frac{\delta}{2\varepsilon}\right)=+\infty$, or $T=0^+$. When $\langle E\rangle=\varepsilon, S\to\infty$, so write $\langle E\rangle\to\varepsilon-\delta$, where $0<\delta\ll1$ is a **very small positive number**. $\frac{1}{T}=-\frac{1}{\varepsilon}\ln\left(\frac{2\varepsilon}{2\varepsilon}\right)+\frac{1}{\varepsilon}\ln\left(\frac{\delta}{2\varepsilon}\right)$, where we neglect the δ in the first term $\frac{1}{T}=\frac{1}{\varepsilon}\underset{\delta\to0}{Lim}\ln\left(\frac{\delta}{2\varepsilon}\right)=-\infty$, or $T=0^-$.

Problem 2) Graduate Student Only (10 points): In the **micro-canonical** (constant energy) ensemble the entropy is $S=k_B\ln\Omega$, where Ω is the total number of microstates (multiplicities). **Shannon's theorem** states that the entropy is $S=-k_B\sum_i p_i\ln p_i$, where p_i is the probability of the i^{th} state, and the summation is over all states.

a) From textbooks or online, explain the Ergodic hypothesis. Explain in no more than three sentences the meaning of the Ergodic hypothesis. Use this hypothesis to determine the probability p_i of any microstate in the **micro-canonical ensemble**.

Ergodic hypothesis states that, in a micro-canonical ensemble, after a sufficiently long period, all microstates will be visited. In fact, all microstates are equally probable.

b) Use the result of a) to show that $S=k_B\ln\Omega$ is consistent with **Shannon's theorem**.

If all microstates are equally probable, then the occupation probability of a state (say the i^{th} state) is $p_i=1/\Omega$, where Ω is the total number of microstates. Note this relation gives proper **normalization** $\sum_{i=1}^{\Omega} p_i = \sum_{i=1}^{\Omega}(1/\Omega) = (1/\Omega)\sum_{i=1}^{\Omega}(1/\Omega) = (1/\Omega)\Omega = 1$. Now

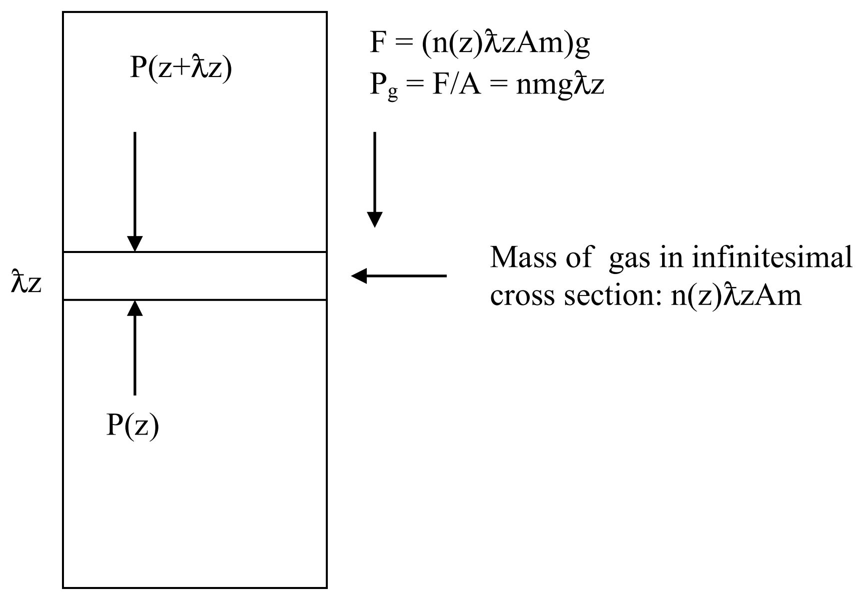
substitute $p_i = \dfrac{1}{\Omega}$ into $S = -k_B \sum_i p_i \ln p_i = -k_B \sum_i \left(\dfrac{1}{\Omega}\right)\ln\left(\dfrac{1}{\Omega}\right) = -k_B\left(\dfrac{1}{\Omega}\right)\left[\ln\left(\dfrac{1}{\Omega}\right)\right]\sum_i (1)$.

Since $\sum_{i=1}^{\Omega}(1) = \Omega$, $S = -k_B\left(\dfrac{1}{\Omega}\right)\left[\ln\left(\dfrac{1}{\Omega}\right)\right]\Omega = -k_B \ln\left(\dfrac{1}{\Omega}\right) \to S = k_B \ln\Omega$, QED.

Problem 3) Problem 1 Chapter 7 (10 points)

Problem 1

a) As discussed in class, the pressure, P(z), pushing upward on the infinitesimal cross-section volume Aƛz, must cancels the downward pressure P(z+ƛz) and P_g.



$P(z) = P(z+\Delta Z) + P_g \to P(z) = P(z+\Delta z) + nmg\Delta z.$

b) Rearranging $P(z+\Delta z) - P(z) = -nmg\Delta z \to \dfrac{P(z+\Delta z) - P(z)}{\Delta z} = -nmg$

Taking the limit $\Delta z \to 0$, $\underset{\Delta z\to\infty}{Lim}\dfrac{P(z+\Delta z) - P(z)}{\Delta z} = \dfrac{dP}{dz} = -nmg$

Using the ideal gas equation $PV = NkT \to P = nkT$, where $n = \dfrac{N}{V}$. It is noted here that $P = P(z)$ and $n = n(z)$ are functions of z. Using $n = \dfrac{P}{kT}$, $\dfrac{dP}{dz} = -\dfrac{Pmg}{kT} \to \dfrac{dP}{P} = \dfrac{mg}{kT}dz$.

Integrating mg we obtain $\ln\dfrac{P}{P_0} = -\dfrac{mgz}{kT} \to P = P_0 e^{-mgz/kT}$.

c) Using $P=nkT$ and $P_0=n_0kT$, where n_0 is the concentration at the surface, we obtain $n=n_0e^{-mgz/kT}$. If at a height z the number density drops to half the value at the surface $n=\frac{n_0}{2}\rightarrow\frac{1}{2}=e^{-mgz/kT}$. Taking the natural logarithm of both sides $\ln\frac{1}{2}=-\frac{mgz}{k_BT}$ which gives $z=\frac{kT}{mg}ln2$. The atomic mass of nitrogen is 14 amu (1 amu $=1.66\times10^{-27}$ kg), and hence the mass of one nitrogen molecule (N_2) is

$m=2\times14\times\left(1.66\times10^{-27}kg\right)=4.65\times10^{-26}kg,\ T=300K\rightarrow$

$$z=\frac{\left(1.381\times10^{-23}J/K\right)\left(300K\right)}{\left(4.65\times10^{-26}kg\right)\left(9.8m/s^2\right)}\ln2=6300m=6.3km.$$

Problem 4) Read section 7.4, then do **Problem 4 Chapter 7 (10 points)**
A) Langmuir Model Summary: In the problem a surface of total area, *A*, can "adsorb" N identical pebbles. Each pebble occupies area A_p, and there are a total of $N_s = A/A_p$. When a pebble is adsorbed onto a site there is an **energy change** of ε. But there is a **counting** component to this. This is a coin toss problem, where there are N_s coin tosses, where N will be heads, and $N_s -$ N tails. The "first" can be in N_s sites, the "second" in $N_s - 1$, and so on. The number of distinct arrangements of N **distinguishable** pebbles

$$N_s\times\left(N_s-1\right)\times....\left(N_s-\left(N-1\right)\right)=\frac{N_s!}{\left(N_s-N\right)!}$$

If the pebbles were **indistinguishable** we would use the binomial coefficient:

$$\frac{N_s}{N!\left(N_s-N\right)!}\quad[1]$$

This would take care of **overcounting**.
In the canonical ensemble, the partition function is $Z=\sum\exp\left(-\beta E\right)$, but here the energy is simply $E=-N\varepsilon$, and the number of distinct state is given above by equation [1], so the partition function is $Z\left(N\right)=\frac{N_s!}{N!\left(N_s-N\right)!}\exp\left(\beta N\varepsilon\right)$, or for adsorbed atoms we have

$Z_{adsorbed}\left(N_{ad}\right)=\frac{N_s!}{N_{ad}!\left(N_s-N_{ad}\right)!}\exp\left(\beta N_{ad}\varepsilon_0\right)$, with $N\rightarrow N_{ad}$ and $\varepsilon\rightarrow\varepsilon_0$.

B) Using Stirling's approximation,
$\ln Z_{adsorbed}\left(N_{ad}\right)=N_s\ln N_s-N_{ad}\ln N_{ad}-\left(N_s-N_{ad}\right)\ln\left(N_s-N_{ad}\right)+\beta N_{ad}\varepsilon_0$,

and equation 7.19, $\mu_{ad}=-k_BT\left(\frac{\partial F}{\partial N}\right)=-k_BT\left(\frac{\partial\ln Z_{adsorbed}}{\partial N}\right)=-\varepsilon_0-k_BT\ln\left(\frac{N_s-N_{ad}}{N_{ad}}\right)$.

From 7.20, the chemical potent of ideal gas is $\mu_{gas} = -k_B T \ln\left(\dfrac{V}{N_{gas}\lambda^3}\right)$.

At equilibrium $\mu_{gas} = \mu_{adsorbed} \rightarrow -k_B T \ln\left(\dfrac{V}{N_{gas}\lambda^3}\right) = -\varepsilon_0 - k_B T \ln\left(\dfrac{N_s - N_{ad}}{N_{ad}}\right)$.

Solving $\dfrac{N_{gas}}{V} = \dfrac{N_{ad}}{N_s - N_{ad}} \dfrac{1}{\lambda^3} \exp\left(-\dfrac{\varepsilon_0}{k_B T}\right)$. Using ideal gas law

$P = \dfrac{N_{gas} k_B T}{V} = \dfrac{N_{ad} k_B T}{N_s - N_{ad}} \dfrac{1}{\lambda^3} \exp\left(-\dfrac{\varepsilon_0}{k_B T}\right)$.

Problem 5) Problem 3 Chapter 8 (10 points)

A) In **classical limit** (8.18) gives $\langle n_\alpha \rangle = \dfrac{1}{\exp\left(\left(\varepsilon_\alpha - \mu\right)/k_B T\right)} \ll 1$, and equation (8.22) gives $\langle n_\alpha \rangle = N \dfrac{\exp\left(-\varepsilon_\alpha / k_B T\right)}{Z_1}$, with $Z_1 = \dfrac{V}{\lambda^3}$, and $\lambda = \dfrac{h}{\sqrt{2\pi m k_B T}}$. Since $\exp\left(-\varepsilon_\alpha / k_B T\right)$ is variable $\langle n_\alpha \rangle \ll 1 \rightarrow \dfrac{N\lambda^3}{V} = \dfrac{Nh^3}{V\left(2\pi m k_B T\right)^{3/2}} \ll 1$.

B) Using 7.20, $\mu = -k_B T \ln\left(\dfrac{V}{N}\dfrac{1}{\lambda^3}\right)$, and from (A), $\dfrac{N\lambda^3}{V} \ll 1 \rightarrow \dfrac{V}{N\lambda^3} \gg 1$. Hence it is clear that $\mu < 0$. In fact the magnitude of μ, which is proportional to T can be quite large.