# Midterm Exam I ADDENDUM

Name: Daniel Staros

*Summary of goals:*
Here you will be tested on nearly all of the concepts we have reviewed prior to classical molecular partition functions. This includes Chapters 1-6 in McQuarrie and the corresponding lecture notes.

*Prompt:*
You have one week to solve the following problems and submit your solutions electronically to Canvas. The work you submit must be your own. Be sure to label all figures and *place a box around your final solutions.* All work done in Mathematica must be debugged, clearly commented, and simplified. In your submission *you must include the signed cover page of this exam*, verifying that you agree to honor the following rules.

*Rules:*
This is an open-note, open-textbook exam. However, you are only allowed to use (i) your own personal notes from lecture, (ii) the course materials posted to Canvas, (iii) the textbooks listed in the course syllabus, and (iv) the online Mathematica documentation. You are not allowed to use outside resources, such as other textbooks, solution manuals, or the internet to solve these problems. You are also not allowed to discuss any of the problems with your peers or with anyone outside the course. You may ask Prof. Church clarifying questions during office hours and lecture. By signing below you agree to the rules of the exam. Disregard of these rules will be considered a violation of Brown University's Academic Code and will be reported accordingly.

*Deadline:*
Monday 03/07/2022 at 11:59pm

Sign below to confirm that you agree with and will adhere to the rules and guidelines of the exam as stated above.

Signature: Danny Staros Date: March 14th, 2022

| | |
|---|---|
| Problem I | /10 |
| Problem II | /15 |
| Problem III | /20 |
| Total | /45 |

## Problem I: Statistics of Fermions and Boltzons

Consider $M$ single-particle states. Of these $M$ states there is a nondegenerate ground state of energy 0, and the remaining $M-1$ states have energy $\epsilon > 0$.

1. Draw and label an energy level diagram of the single-particle states. How large is the energy gap? If $N$ structureless fermions are put into this model, what are the energies of the $N$-particle states? What is the degeneracy of each $N$-particle state? Which $N$-particle energy level exhibits higher degeneracy? Draw and label an energy level diagram of the $N$-particle states. How large is the energy gap? (2 points)

2. Write down the fermionic partition function $Q_f$ as a sum over the $N$-particle energies and their degeneracies. Your answer should be in terms of $N$, $M$, $\epsilon$, and $\beta$. (2 points)

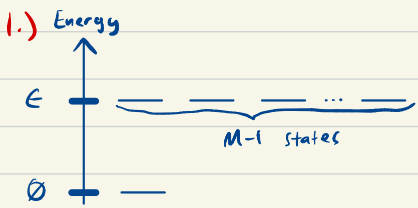
   Talked w/ Professor Church + my original answer was correct; typo in reasoning (see attached)

3. Now use Boltzmann statistics to write down the canonical partition function for this model, call it $Q_{bz}$. Your answer should be in terms of $N$, $M$, $\epsilon$, and $\beta$. (2 points)

4. In what limit of $M$ in relation to $N$ is Boltzmann statistics expected to be valid? Briefly explain. With $N = 10$, use Mathematica to plot the ratio $Q_f/Q_{bz}$ vs. $M$ and interpret the results. In your code you can take $\epsilon = k_BT$. (2 points)

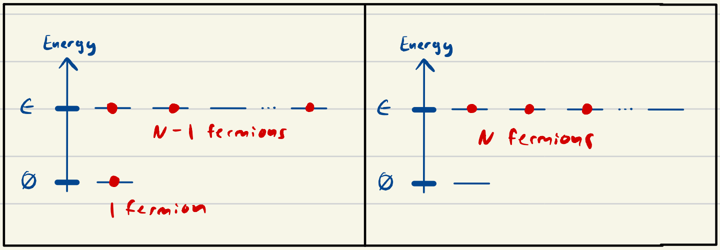
5. Use Mathematica to plot the probabilities of occupying each $N$-particle energy level as a function of temperature $T$ (use $Q_f$ for this calculation). Furthermore, use the Manipulate[] function so that the user can adjust the value of $M$ from $M = 10$ to $M = 300$. Take $N = 10$ and $\epsilon = k_B = 1$. Have your plot extend from $T = 0.05$ to $T = 10$. Discuss your results. (2 points)

# Problem I

1.) 


Energy level diagram

$$\boxed{\text{Energy gap} = (\epsilon - \emptyset) = \epsilon}$$




Option (1.) Option (2.)

→ two possible types of N-particle state

(1.) 1 fermion with $E = \emptyset$, $N-1$ with energy $E = \epsilon$

(2.) N fermions with $E = \epsilon$

$$\boxed{E^1_{TOT} = (N-1)\epsilon}$$
$$\boxed{E^2_{TOT} = N\epsilon}$$

→ structureless (indistinguishable) fermions:

(1.) Number of ways to put N-1 fermions into M-1 single-particle states

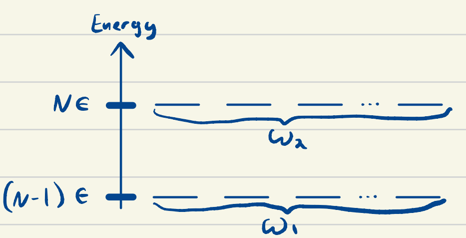
↳ binomial coefficient : $\binom{M-1}{N-1} = \frac{(M-1)!}{(N-1)!((M-1)-(N-1))!} = \frac{(M-1)!}{(N-1)!\,(M-N)!} = \omega_1$

(2.) Number of ways to fill M-1 states with N indist. fermions

↳ binomial coefficient : $\binom{M-1}{N} = \frac{(M-1)!}{N!(M-1)!} = \omega_2$ Typo $\binom{M-1}{N} = \frac{(M-1)!}{N!\,(M-1-N)!}$ equiv.

• Rewriting, degeneracies are: $\boxed{\omega_1 = \frac{1}{(M-N)} \cdot \frac{(M-1)!}{(N-1)!\,(M-N-1)!}}$ $\boxed{\omega_2 = \frac{1}{N} \cdot \frac{(M-1)!}{(N-1)!\,(M-N-1)!}}$

• N-particle state (1.) exhibits higher degeneracy → example in Mathematica




N-particle energy level digram

• N-particle energy gap $\Delta E_N$ is

$$\boxed{\Delta E_N = N\epsilon - (N-1)\epsilon = \epsilon}$$

# Problem I

2.) $$Q_f(N,V,T) = \sum_{i=1}^{2} \omega_i e^{-\beta E_i} = \frac{(M-1)!}{(N-1)!\,(M-N-1)!}\left[\frac{e^{-\beta(N-1)\epsilon}}{M-N} + \frac{e^{-\beta N}}{N}\right]$$

$$\boxed{Q_f(N,V,T) = \frac{(M-1)!}{(N-1)!\,(M-N-1)!}\left[\frac{e^{-\beta(N-1)\epsilon}}{M-N} + \frac{e^{-\beta N}}{N}\right]}$$

3.) $$Q_{bz}(N,V,T) = \frac{q^N}{N!} \quad ; \quad q = \sum_j \omega_j e^{-\beta E_j} = \cancel{(1)e^{-\beta(0)}}^{\,1} + (M-1)e^{-\beta(\epsilon)}$$

$$\boxed{Q_{bz}(N,V,T) = \frac{1}{N!}\left[1 + (M-1)e^{-\beta\epsilon}\right]^N}$$

4.) I expect Boltzmann statistics to be valid when $M \ggg N$. This is because, in the thermodynamic limit there are many more single-particle states possible than number of particles. One should see $Q_f/Q_{bz} \to 1$ as $M$ goes to $M \ggg N$.

5.) Done in Mathematica.

## Problem II: The Heat Capacities of $H_2$ and $D_2$

Review sections 6-4 and 6-5 on homonuclear diatomics in McQuarrie (pg. 101) and the corresponding lecture notes. In particular, review the discussion surrounding Figures 6-8 and 6-9, which plot equilibrium properties of molecular $H_2$ as a function of temperature.

1. Use Mathematica to reproduce Figure 6-8, the %-para composition of gaseous $H_2$ as a function of temperature (from $T = 1$K to $T = 400$K). In the same figure, plot the %-para composition of $D_2$ as a function of temperature. Briefly comment on the two results, and briefly explain the high and low temperature limits. Note that the nuclear spin quantum number of a deuterium nucleus is $I = 1$. (5 points)

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2. Use Mathematica to reproduce the four solid curves of Figure 6-9 for both $H_2$ and $D_2$ over $T = 1$K to $T = 400$K. There are eight curves to plot here, so you will be partly graded on the organization and clarity of your graphic. Use no more than one or two figures. Briefly interpret your results. (8 points)

3. Using your results from part 2, argue why it might be important to monitor nuclear spin composition when storing $H_2$ and $D_2$ at low temperatures, say $T < 200K$. (2 points)

## Problem II ADDENDUM

### Hydrogen

$$q_{para} = I(2I+1)\sum_{j=\emptyset}^{100}(2J+1)e^{-\frac{\theta_r}{T}J(J+1)} = \sum_{j=\emptyset}^{100}(2J+1)e^{-\frac{\theta_r}{T}J(J+1)}$$

$$q_{ortho} = (I+1)(2I+1)\sum_{j=1}^{100}(2J+1)e^{-\frac{\theta_r}{T}J(J+1)} = 3\sum_{j=1}^{100}(2J+1)e^{-\frac{\theta_r}{T}J(J+1)}$$

### Deuterium

$$q_{ortho} = (I+1)(2I+1)\sum_{j=\emptyset}^{100}(2J+1)e^{-\frac{\theta_r}{T}J(J+1)} = 6\sum_{j=\emptyset}^{100}(2J+1)e^{-\frac{\theta_r}{T}J(J+1)}$$

$$q_{para} = I(2I+1)\sum_{j=1}^{100}(2J+1)e^{-\frac{\theta_r}{T}J(J+1)} = 3\sum_{j=1}^{100}(2J+1)e^{-\frac{\theta_r}{T}J(J+1)}$$

1.) Both the $H_2$ + $D_2$ curves exhibit sigmoidal behavior, but $H_2$ starts with majority para compositions at low temperature and ends with majority ortho compositions at high temperature whereas $D_2$ has the opposite trend. At low temperature, only the rotational state $J=\emptyset$ is accessible, which couples with para-$H_2$, but with ortho-$D_2$ because of the half-integer versus integer nuclear spins of the molecules. In the high temperature limit, the statistical weighting of occupied excited rotational states is according to $\%\text{para}^{T\to\infty} = I(2I+1)/(2I+1)^2$ and $\%\text{ortho}^{T\to\infty} = (I+1)(2I+1)/(2I+1)^2$. Thus, we expect $\%\text{para}_{H_2}^{T\to\infty} = 1/4 = 25\%$, $\%\text{ortho}_{H_2}^{T\to\infty} = 3/4 = 75\%$ and $\%\text{para}_{D_2}^{T\to\infty} = 3/9 = 33\%$, $\%\text{ortho}_{D_2}^{T\to\infty} = 6/9 = 66\%$.

## Problem III: Statistical Mechanics of a Phase Equilibrium

For this problem it may be worth reviewing the partition function of the 2D diatomic gas from Problem 3 of Homework 2.

1. Assuming now that the diatomic molecules are *homonuclear* and that the high-T approximation for the rotational partition function is valid, show that the canonical partition function can be expressed as

fixed

$$Q(N, \mathcal{A}, T) = \frac{1}{N!}\left[\mathcal{A}\tilde{q}(T)\right]^N, \tag{1}$$

where $\mathcal{A} = L^2$ is the area of the 2D surface and $\tilde{q}(T)$ is a function of the temperature $T$, the nuclear spin quantum number $I$, and various constants and parameters. You can neglect the electronic partition function. (8 points)

2. Now let's recast the problem. Imagine a cubic vessel of volume $V = L^3$ submerged in a thermal reservoir at fixed temperature $T$. The vessel contains an ideal sample of $N$ homonuclear diatomics. One of the six inner faces of the cubic container (area $\mathcal{A} = L^2$) is made of a material that can adsorb and, after a while, release the diatoms at random. While adsorbed to the 2D surface, the molecules obey the motion described in Problem 3 of Homework 2, but the bond is weaker than when in the 3D phase, so the force constant $k$ is smaller and the moment of inertia is larger. Though the number of diatoms in the 2D phase $N_{(2\text{D})}$ and the number of diatoms in the 3D phase $N_{(3\text{D})}$ are constantly fluctuating, the two phases are in thermodynamic equilibrium. This means $T = T_{(2D)} = T_{(3D)}$, $\mu = \mu_{(2\text{D})} = \mu_{(3\text{D})}$, and etc. Using this information, answer the following:

How would you expect the number density of adsorbed molecules, defined as $\rho_{(2\text{D})} = \frac{N_{(2D)}}{\mathcal{A}}$, to vary with the pressure inside the vessel? Derive (by hand) an expression for $\rho_{(2\text{D})}$ as a function of the pressure inside the vessel. Your answer should also contain the temperature as well as molecular and universal constants. At a given temperature, at what rate does $\rho_{(2\text{D})}$ change as the pressure is increased? How does $\rho_{(2\text{D})}$ change with temperature? Briefly explain. (12 points)

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# Problem III APPENDED

1.) The translational partition function of a 2D homonuclear diatomic gas is given by $q_{trans} = A/\Lambda^2$, and the vibrational by $q_{vib} = \frac{1}{2}\operatorname{csch}\left(\frac{\theta_v}{2T}\right)$.

The rotational partition function of a 2D homonuclear diatomic gas is

$$q^{int}_{rot,nucl}(T) = (I+1)(2I+1)\left(e^{-\theta_r (0)^2/T} + \sum_{j_{even}\neq 0} 2e^{-\theta_r j^2/T}\right) + I(2I+1)\left(1 + \sum_{j_{odd}\neq 0} 2e^{-\theta_r j^2/T}\right)$$

neglecting these      neglecting these

or

$$q^{int/2}_{rot,nucl}(T) = I(2I+1)\left(1 + \sum_{j_{even}\neq 0} 2e^{-\theta_r j^2/T}\right) + (I+1)(2I+1)\left(1 + \sum_{j_{odd}\neq 0} 2e^{-\theta_r j^2/T}\right)$$

for nuclei with integer nuclear spin (int) or half-integer (int/2) respectively.

Under the high-T approximation, $\sum_{j_{even}} \approx \sum_{j_{odd}} \approx \frac{1}{2}\sum_j \implies q_{rot} \approx \frac{1}{\cancel{\chi}}\int_0^\infty \cancel{\chi} e^{-\theta_r j^2/T}\, dj$

↳ gives $q_{rot,nucl} = (2I+1)^2 \int_0^\infty e^{-\theta_r j^2/T}\, dj = (2I+1)^2\sqrt{\frac{\pi T}{4\theta_r}}$ where $\Theta_r = \frac{\hbar^2}{2k_B \mu r^2}$.

**NOTE:** I have neglected these 1's because they are much smaller than the sums.

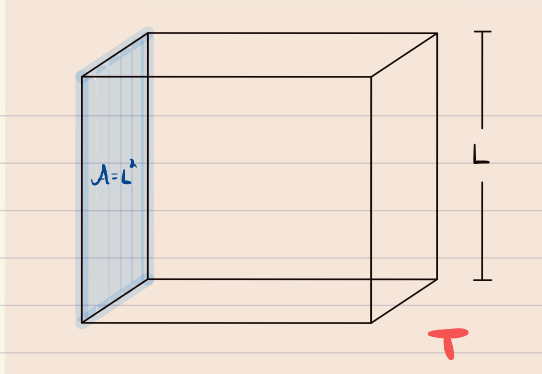
- Since this is an ideal gas which obeys Boltzmann statistics, we have:

$$Q_{2D}(N,A,T) = \frac{\left(q_{trans}(T)\, q_{vib}(T)\, q_{rot,nuc}(T)\right)^N}{N!} = \frac{1}{N!}\left[A\left(\frac{1}{\Lambda^2}\cdot\frac{1}{2}\operatorname{csch}\left(\frac{\theta_v}{2T}\right)(2I+1)^2\sqrt{\frac{\pi T}{4\theta_r}}\right)\right]^N$$

or

$$\boxed{Q_{2D}(N,A,T) = \frac{1}{N!}\left[A\,\tilde{q}(T)\right]^N \quad \text{where} \quad \tilde{q}(T) = \left(\frac{1}{\Lambda^2}\right)\frac{1}{2}\operatorname{csch}\left(\frac{\theta_v}{2T}\right)(2I+1)^2\sqrt{\frac{\pi T}{4\theta_r}}}.$$

# Problem III APPENDED




2.) From previous: $Q_{2D}(N,A,T) = \frac{1}{N!}\left[A\tilde{q}(T)\right]^N$

$$\mu = \mu_{2D} = \mu_{3D}$$
$$T = T_{2D} = T_{3D}$$

I would expect that the number density of adsorbed molecules would <u>increase</u> with pressure.

**DERIVATION**

Noting that $Q_{3D} = \frac{1}{N_{3D}!}\left[Vq^*\right]^{N_{3D}}$ with $q^* = \frac{1}{\Lambda^3}(2I+1)^2 \frac{T}{2\Theta_r^{3D}} \frac{1}{2}\operatorname{csch}\left[\frac{\Theta_v^{3D}}{2T}\right]$,

$$\mu_{2D} = -k_B T\left(\frac{\partial \ln Q_{2D}}{\partial N_{2D}}\right) = -k_B T \frac{\partial}{\partial N_{2D}}\left[N_{2D}\ln[A\tilde{q}] - N_{2D}\ln N_{2D} + N_{2D}\right] = -k_B T \ln\left(\frac{A\tilde{q}}{N_{2D}}\right)$$

$$\mu_{3D} = -k_B T\left(\frac{\partial \ln Q_{3D}}{\partial N_{3D}}\right) = -k_B T \frac{\partial}{\partial N_{3D}}\left[N_{3D}\ln[Aq^*] - N_{3D}\ln N_{3D} + N_{3D}\right] = -k_B T \ln\left(\frac{Vq^*}{N_{3D}}\right)$$

But since $\mu_{2D} = \mu_{3D}$, $\frac{A\tilde{q}}{N_{2D}} = \frac{Vq^*}{N_{3D}}$ and $\rho_{2D} = \frac{N_{3D}}{V}\cdot\frac{\tilde{q}}{q^*}$ or, noting that $V = \frac{N_{3D}k_B T}{P_{3D}}$ for an ideal gas, $\rho_{2D} = \cancel{N_{3D}}\frac{P_{3D}}{\cancel{N_{3D}}k_B T}\cdot\frac{\tilde{q}}{q^*}$ giving $\boxed{\rho_{2D} = \beta P_{3D}\frac{\tilde{q}}{q^*}}$.

Evidently, at fixed $T$, the direct proportionality between $\rho_{(2D)}$ and $P$ suggests that $\rho_{(2D)}$ increases linearly with increased pressure. Further, this proportionality is scaled by the ratio of possible states of the 2D system to those of the 3D system. For fixed pressure, $\rho_{2D}$ varies as

$$\beta\cdot\frac{\left(\frac{1}{\cancel{\Lambda^2}}\right)\cancel{\frac{1}{2}}\operatorname{csch}\left(\frac{\Theta_v^{2D}}{2T}\right)\cancel{(2I+1)^2}\sqrt{\frac{\pi T}{4\Theta_r}}}{\cancel{\frac{1}{\Lambda^3}}_{1/\Lambda}\cancel{(2I+1)^2}\frac{T}{2\Theta_r^{3D}}\cancel{\frac{1}{2}}\operatorname{csch}\left[\frac{\Theta_v^{3D}}{2T}\right]} = \frac{\sqrt{\pi}\cancel{T}^{1/2}}{\cancel{\chi}\Theta_r^{1/2}}\cdot\frac{\cancel{\chi}\Lambda\operatorname{csch}\left(\Theta_v^{2D}/2T\right)\Theta_r^{3D}}{\cancel{T}^{T^{1/2}}\operatorname{csch}\left(\Theta_v^{3D}/2T\right)} = \frac{\sqrt{\pi}\Lambda\operatorname{csch}\left(\Theta_v^{2D}/2T\right)\Theta_r^{3D}}{\sqrt{T}\operatorname{csch}\left(\Theta_v^{3D}/2T\right)\Theta_r^{1/2}}\cdot\frac{1}{k_B T}$$

The factor of $T^{-3/2}$ suggests that there will be fewer molecules adsorbed at higher temperature. The hyperbolic terms contribute a constant since $\Theta_v^{2D}$ + $\Theta_v^{3D}$ do not change with $T$ (even though $\Theta_v^{2D} \neq \Theta_v^{3D}$, + since $\Theta_v$ and $T$ have the same units.

# Midterm Exam II

Name:

*Summary of goals:*
Here you will be tested on nearly all of the concepts we have reviewed so far, up to and including Chapter 12 of McQuarrie.

*Prompt:*
You have one week to solve the following problems and submit your solutions electronically to Canvas. The work you submit must be your own. Be sure to label all figures and clearly indicate your final answers. All work done in Mathematica must be debugged, clearly commented, and simplified. In your submission *you must include the signed cover page of this exam*, verifying that you agree to honor the following rules.

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*Deadline:*
Wednesday 04/20/2022 at 11:59pm

Sign below to confirm that you agree with and will adhere to the rules and guidelines of the exam as stated above.

Signature: Danny Sturos Date: 04/12/22

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|---|---|
| Problem I | /10 |
| Problem II | /2.5 |
| Problem III | /10 |
| Problem IV | /10 |
| Problem V | /10 |
| Problem VI | /2.5 |
| Total | /45 |

## Problem I: Isomerization

Consider the isomerization between states X and Y of a molecule,

$$\mathrm{X} \quad \rightleftarrows \quad \mathrm{Y}, \tag{1}$$

and say $\Delta E$ is the energy difference between the two states.

1. Starting from the equilibrium condition of chemical potentials, show that

$$\frac{\langle N_X \rangle}{\langle N_Y \rangle} = \frac{\omega_X}{\omega_Y} e^{-\beta \Delta E}, \tag{2}$$

where $\omega_j$ is the degeneracy of isomer state $j$.

2. Using Boltzmann statistics the canonical partition function is given by

$$Q = \frac{1}{N!} q^N, \tag{3}$$

where $q$ is the Boltzmann-weighted sum over all single-particle states (i.e. for *both* isomers). Show that $Q$ can also be written as

$$Q = \sum_p e^{-\beta A(N_X, N_Y)}, \tag{4}$$

with

$$-\beta A(N_X, N_Y) = \ln \frac{q_X^{N_X} q_Y^{N_Y}}{N_X! N_Y!}, \tag{5}$$

where $\sum_p$ sums over all the ways of partitioning the $N$ molecules into $N_X$ molecules of type $X$ and $N_Y$ molecules of type $Y$. The molecular partition functions of $X$ and $Y$ are $q_X$ and $q_Y$ respectively.

3. Now use ensemble averages to show that

$$\langle N_X \rangle = q_x \left( \frac{\partial \ln Q}{\partial q_X} \right)_{q_B, N}. \tag{6}$$

Then do the same for $\langle N_Y \rangle$ and show that

$$\frac{\langle N_X \rangle}{\langle N_Y \rangle} = \frac{q_X}{q_Y}. \tag{7}$$

4. Again using ensemble averages, show that the average square fluctuations in $N_X$ is given by

$$\langle [N_X - \langle N_X \rangle]^2 \rangle = q_x \left( \frac{\partial \langle N_X \rangle}{\partial q_X} \right)_{q_Y, N} \tag{8}$$

$$= \frac{\langle N_X \rangle \langle N_Y \rangle}{N}. \tag{9}$$

Repeat for $N_Y$.

## Problem 1

a.) For a general reaction, $\nu_A A + \nu_B B + \ldots \rightleftharpoons \nu_C C + \nu_D D + \ldots$

For this reaction, then: $1X \rightleftharpoons 1Y \Rightarrow 1\mu_X - 1\mu_Y = \emptyset$ and $\mu_X = \mu_Y$ @ equil.

In canonical terms, $\mu_X = -k_BT\left(\frac{\partial \ln Q}{\partial N_X}\right)$ and $\mu_Y = -k_BT\left(\frac{\partial \ln Q}{\partial N_Y}\right)$, necessitating that

$-\cancel{k_B}T\left(\frac{\partial \ln Q}{\partial N_X}\right) = -\cancel{k_B}T\left(\frac{\partial \ln Q}{\partial N_Y}\right)$ for which, since $Q = \frac{q_X^{N_X}}{N_X!}\cdot\frac{q_Y^{N_Y}}{N_Y!}$, we have

$$\frac{\partial}{\partial N_X}\ln(Q) = \frac{\partial}{\partial N_X}\left[N_X \ln q_X - (N_X \ln N_X - N_X)\right] = \left[\ln q_X - (\cancel{1} + \ln N_X - \cancel{1})\right] = \ln\left(\frac{q_X}{N_X}\right)$$

$$= \frac{\partial}{\partial N}\ln(Q) = \frac{\partial}{\partial N}\left[N_Y \ln q_Y - (N_Y \ln N_Y - N_Y)\right] = \left[\ln q_Y - (\cancel{1} + \ln N_Y - \cancel{1})\right] = \ln\left(\frac{q_Y}{N_Y}\right).$$

Exponentiating, $e^{\ln\left(\frac{q_X}{N_X}\right)} = e^{\ln\left(\frac{q_Y}{N_Y}\right)}$ and $\frac{q_X}{N_X} = \frac{q_Y}{N_Y}$, or $\frac{N_X}{N_Y} = \frac{\langle N_X\rangle}{\langle N_Y\rangle} = \frac{q_X}{q_Y}$.

Generally, $q_j = \omega_j e^{-\beta E_j}$, so $\frac{\langle N_X\rangle}{\langle N_Y\rangle} = \frac{q_X}{q_Y} = \frac{\omega_X e^{-\beta E_X}}{\omega_Y e^{-\beta E_Y}} = \frac{\omega_X}{\omega_Y} e^{-\beta(E_X - E_Y)}$ or,

denoting $\Delta E = E_X - E_Y$, $\boxed{\frac{\langle N_X\rangle}{\langle N_Y\rangle} = \frac{\omega_X}{\omega_Y} e^{-\beta\Delta E}}$.

b.) $$Q = \frac{1}{N!}q^N = \frac{1}{N!}(q_X + q_Y)^N = \frac{1}{\cancel{N!}}\sum_{N_X N_Y}^{*}\frac{\cancel{N!}\, q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!} = \sum_{N_X N_Y}^{*}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!} = \sum_{N_X N_Y}^{*} e^{\ln\left(\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!}\right)}$$, or

($\sum^*$: $N_1 + N_2 = N$)

$$\boxed{Q = \sum_P e^{-\beta A(N_X, N_Y)}} = \sum_{N_X N_Y}^{*} e^{\ln\left(\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!}\right)}$$ for $\sum_P = \sum_{N_X N_Y}^{*}$ and $-\beta A(N_X, N_Y) = \ln\left(\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!}\right)$.

c.) $$\boxed{\langle N_X\rangle} = \left(\sum_{N_X N_Y} N_X \frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!}\right)\Big/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!} = \left(q_X \sum_{N_X N_Y}\left(N_X q_X^{N_X - 1}\right)\frac{q_Y^{N_Y}}{N_X!\,N_Y!}\right)\Big/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!} = q_X \sum_{N_X N_Y}\left(\frac{\partial}{\partial q_X}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!}\right)\Big/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!}$$

$$= q_X \frac{\partial}{\partial q_X}\left(\sum_{N_X N_Y}^{*}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!}\right)\Big/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!} = q_X\frac{\partial Q}{\partial q_X}\frac{1}{Q} = \boxed{q_X\frac{\partial \ln Q}{\partial q_X}}.$$

$$\boxed{\langle N_Y\rangle} = \left(\sum_{N_X N_Y} N_Y \frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!}\right)\Big/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!} = \left(q_X \sum_{N_X N_Y}\left(N_Y q_Y^{N_Y - 1}\right)\frac{q_X^{N_X}}{N_X!\,N_Y!}\right)\Big/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!} = q_Y \sum_{N_X N_Y}\left(\frac{\partial}{\partial q_Y}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!}\right)\Big/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!}$$

$$= q_Y \frac{\partial}{\partial q_Y}\left(\sum_{N_X N_Y}^{*}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!}\right)\Big/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X} q_Y^{N_Y}}{N_X!\,N_Y!} = q_Y\frac{\partial Q}{\partial q_Y}\frac{1}{Q} = \boxed{q_Y\frac{\partial \ln Q}{\partial q_Y}}.$$

$$\left.\begin{aligned}\langle N_X\rangle &= q_X\frac{\partial}{\partial q_X}\ln Q = q_X\frac{\partial}{\partial q_X}\ln\left(\frac{1}{N!}(q_X + q_Y)^N\right) = q_X N\frac{\partial}{\partial q_X}(q_X + q_Y) = \frac{q_X N}{q_X + q_Y}\\ \langle N_Y\rangle &= q_Y\frac{\partial}{\partial q_Y}\ln Q = q_Y\frac{\partial}{\partial q_Y}\ln\left(\frac{1}{N!}(q_X + q_Y)^N\right) = q_Y N\frac{\partial}{\partial q_Y}(q_X + q_Y) = \frac{q_Y N}{q_X + q_Y}\end{aligned}\right\}\ \boxed{\frac{\langle N_X\rangle}{\langle N_Y\rangle} = \frac{q_X \cancel{N}}{\cancel{q_X + q_Y}}\cdot\frac{\cancel{q_X + q_Y}}{q_Y\cancel{N}} = \frac{q_X}{q_Y}}$$

2.) $\langle (N_x - \langle N_x\rangle)^2\rangle = \langle (N_x - \langle N_x\rangle)(N_x - \langle N_x\rangle)\rangle = \langle N_x^2 - N_x\langle N_x\rangle - \langle N_x\rangle N_x + \langle N_x\rangle^2\rangle$

$$= \langle N_x^2\rangle - 2\langle N_x\rangle^2 + \langle N_x\rangle^2 = \langle N_x^2\rangle - \langle N_x\rangle^2$$

From previous:

$$\langle N_x\rangle = q_x\left(\frac{\partial \ln Q}{\partial q_x}\right)_{q_Y,N}$$

Show that: $\langle N_x^2\rangle - \langle N_x\rangle^2 = q_x\left(\frac{\partial\langle N_x\rangle}{\partial q_x}\right)_{q_Y,N} = q_x^2\frac{\partial}{\partial q_x}\left(\frac{\partial \ln Q}{\partial q_x}\right) + q_x\frac{\partial \ln Q}{\partial q_x} = q_x^2\frac{\partial}{\partial q_x}\left(\frac{\partial \ln Q}{\partial q_x}\right) + \langle N_x\rangle$

or : $\langle N_x^2\rangle - \langle N_x\rangle^2 = q_x^2\frac{\partial}{\partial q_x}\left(\frac{1}{Q}\frac{\partial Q}{\partial q_x}\right) = q_x^2\frac{1}{Q}\frac{\partial^2 Q}{\partial q_x^2} + q_x^2\frac{\partial Q}{\partial q_x}\left(-\frac{1}{Q^2}\frac{\partial Q}{\partial q_x}\right)$

$$= q_x^2\frac{1}{Q}\frac{\partial^2 Q}{\partial q_x^2} - q_x^2\frac{1}{Q^2}\left(\frac{\partial Q}{\partial q_x}\right)^2 + \langle N_x\rangle$$ by the product rule.

$$\boxed{\langle N_x\rangle^2} = q_x^2\left(\frac{\partial \ln Q}{\partial q_x}\right)^2 = q_x^2\left(\frac{1}{Q}\frac{\partial Q}{\partial q_x}\right)^2 = \boxed{q_x^2\frac{1}{Q^2}\left(\frac{\partial Q}{\partial q_x}\right)^2}$$

$$\boxed{\langle N_x^2\rangle} = \left(\sum_{N_xN_Y}^{*} N_x^2\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!}\right)\Big/\sum_{N_xN_Y}^{*}\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!} = \left[\left(q_x^2\sum_{N_xN_Y}^{*} N_x^2 q_x^{N_x-2}\right)\frac{q_Y^{N_Y}}{N_x!N_Y!}\right]\Big/\sum_{N_xN_Y}^{*}\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!};$$

$$= \left[q_x^2\sum_{N_xN_Y}^{*}\left(\frac{\partial^2}{\partial q_x^2}q_x^{N_x} + N_x q_x^{N_x-2}\right)\frac{q_Y^{N_Y}}{N_x!N_Y!}\right]\Big/\sum_{N_xN_Y}^{*}\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!} = \left[q_x^2\sum_{N_xN_Y}^{*}\left(\frac{\partial^2}{\partial q_x^2}\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!} + N_x\frac{q_x^{N_x-2}q_Y^{N_Y}}{N_x!N_Y!}\right)\right]\Big/\sum_{N_xN_Y}^{*}\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!}$$

$$= \left[\sum_{N_xN_Y}^{*}\left(q_x^2\frac{\partial^2}{\partial q_x^2}\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!} + N_x\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!}\right)\right]\Big/\sum_{N_xN_Y}^{*}\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!}$$

$$= \left[\sum_{N_xN_Y}^{*}q_x^2\frac{\partial^2}{\partial q_x^2}\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!}\right]\Big/\sum_{N_xN_Y}^{*}\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!} + \left[\sum_{N_xN_Y}^{*}N_x\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!}\right]\Big/\sum_{N_xN_Y}^{*}\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!}$$

$$= q_x^2\frac{\partial^2}{\partial q_x^2}\left[\sum_{N_xN_Y}^{*}\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!}\right]\Big/\sum_{N_xN_Y}^{*}\frac{q_x^{N_x}q_Y^{N_Y}}{N_x!N_Y!} + \langle N_x\rangle = \boxed{q_x^2\frac{1}{Q}\frac{\partial^2 Q}{\partial q_x^2} + \langle N_x\rangle}$$

↳ $\langle N_x^2\rangle - \langle N_x\rangle^2 = q_x^2\frac{1}{Q}\frac{\partial^2 Q}{\partial q_x^2} - q_x^2\frac{1}{Q^2}\left(\frac{\partial Q}{\partial q_x}\right)^2 + \langle N_x\rangle$

giving that $\boxed{\langle N_x^2\rangle - \langle N_x\rangle^2 = q_x\left(\frac{\partial\langle N_x\rangle}{\partial q_x}\right)_{q_Y,N}} = q_x^2\frac{1}{Q}\frac{\partial^2 Q}{\partial q_x^2} - q_x^2\frac{1}{Q^2}\left(\frac{\partial Q}{\partial q_x}\right)^2 + \langle N_x\rangle$.

Note: $\boxed{\langle N_x^2\rangle - \langle N_x\rangle^2} = q_x\left(\frac{\partial\langle N_x\rangle}{\partial q_x}\right)_{q_Y,N} = q_x^2\frac{\partial}{\partial q_x}\left(\frac{\partial \ln Q}{\partial q_x}\right) + q_x\frac{\partial \ln Q}{\partial q_x} = q_x^2\frac{\partial}{\partial q_x}\left(\frac{N}{q_x+q_Y}\right) + \frac{q_xN}{q_x+q_Y}$

$$= \frac{q_xN}{q_x+q_Y} - \frac{q_x^2N}{(q_x+q_Y)^2} = \frac{\cancel{q_x^2N} + q_xq_YN - \cancel{q_x^2N}}{(q_x+q_Y)^2} = \frac{1}{N}\left(\frac{q_xN}{q_x+q_Y}\right)\left(\frac{q_YN}{q_x+q_Y}\right) = \boxed{\frac{\langle N_x\rangle\langle N_Y\rangle}{N}}.$$

$$\langle (N_Y - \langle N_Y\rangle)^2\rangle = \langle (N_Y-\langle N_Y\rangle)(N_Y-\langle N_Y\rangle)\rangle = \langle N_Y^2 - N_Y\langle N_Y\rangle - \langle N_Y\rangle N_Y + \langle N_Y\rangle^2\rangle$$
$$= \langle N_Y^2\rangle - 2\langle N_Y\rangle^2 + \langle N_Y\rangle^2 = \langle N_Y^2\rangle - \langle N_Y\rangle^2$$

From previous:
$$\langle N_Y\rangle = q_Y\left(\frac{\partial \ln Q}{\partial q_Y}\right)_{q_X,N}$$

Show that:
$$\langle N_Y^2\rangle - \langle N_Y\rangle^2 = q_Y\left(\frac{\partial\langle N_Y\rangle}{\partial q_Y}\right)_{q_X,N} = q_Y^2\frac{\partial}{\partial q_Y}\left(\frac{\partial \ln Q}{\partial q_Y}\right) + q_Y\frac{\partial \ln Q}{\partial q_Y} = q_Y^2\frac{\partial}{\partial q_Y}\left(\frac{\partial \ln Q}{\partial q_Y}\right) + \langle N_Y\rangle$$

or:
$$\langle N_Y^2\rangle - \langle N_Y\rangle^2 = q_Y^2\frac{\partial}{\partial q_Y}\left(\frac{1}{Q}\frac{\partial Q}{\partial q_Y}\right) = q_Y^2\frac{1}{Q}\frac{\partial^2 Q}{\partial q_Y^2} + q_Y^2\frac{\partial Q}{\partial q_Y}\left(-\frac{1}{Q^2}\frac{\partial Q}{\partial q_Y}\right)$$
$$= q_Y^2\frac{1}{Q}\frac{\partial^2 Q}{\partial q_Y^2} - q_Y^2\frac{1}{Q^2}\left(\frac{\partial Q}{\partial q_Y}\right)^2 + \langle N_Y\rangle$$
by the product rule.

$$\boxed{\langle N_Y\rangle^2 = q_Y^2\left(\frac{\partial \ln Q}{\partial q_Y}\right)^2 = q_Y^2\left(\frac{1}{Q}\frac{\partial Q}{\partial q_Y}\right)^2 = q_Y^2\frac{1}{Q^2}\left(\frac{\partial Q}{\partial q_Y}\right)^2}$$

$$\boxed{\langle N_Y^2\rangle} = \left(\sum_{N_X N_Y}^{*} N_Y^2\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!}\right)\Bigg/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!} = \left[\left(q_Y^2\sum_{N_X N_Y}^{*} N_Y^2 q_Y^{N_Y-2}\right)\frac{q_X^{N_X}}{N_X!\,N_Y!}\right]\Bigg/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!};$$
$$= \left[q_Y^2\sum_{N_X N_Y}^{*}\left(\frac{\partial^2}{\partial q_Y^2}q_Y^{N_Y} + N_Y q_Y^{N_Y-2}\right)\frac{q_X^{N_X}}{N_X!\,N_Y!}\right]\Bigg/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!} = \left[q_Y^2\sum_{N_X N_Y}^{*}\left(\frac{\partial^2}{\partial q_Y^2}\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!} + N_Y\frac{q_Y^{N_Y-2}q_X^{N_X}}{N_X!\,N_Y!}\right)\right]\Bigg/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!}$$
$$= \left[\sum_{N_X N_Y}^{*}\left(q_Y^2\frac{\partial^2}{\partial q_Y^2}\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!} + N_Y\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!}\right)\right]\Bigg/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!}$$
$$= \left[\sum_{N_X N_Y}^{*} q_Y^2\frac{\partial^2}{\partial q_Y^2}\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!}\right]\Bigg/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!} + \left[\sum_{N_X N_Y}^{*} N_Y\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!}\right]\Bigg/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!}$$
$$= q_Y^2\frac{\partial^2}{\partial q_Y^2}\left[\sum_{N_X N_Y}^{*}\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!}\right]\Bigg/\sum_{N_X N_Y}^{*}\frac{q_X^{N_X}q_Y^{N_Y}}{N_X!\,N_Y!} + \langle N_Y\rangle = \boxed{q_Y^2\frac{1}{Q}\frac{\partial^2 Q}{\partial q_Y^2} + \langle N_Y\rangle}$$

$$\hookrightarrow \langle N_Y^2\rangle - \langle N_Y\rangle^2 = q_Y^2\frac{1}{Q}\frac{\partial^2 Q}{\partial q_Y^2} - q_Y^2\frac{1}{Q^2}\left(\frac{\partial Q}{\partial q_Y}\right)^2 + \langle N_Y\rangle$$

giving that
$$\boxed{\langle N_Y^2\rangle - \langle N_Y\rangle^2 = q_Y\left(\frac{\partial\langle N_Y\rangle}{\partial q_Y}\right)_{q_X,N}} = q_Y^2\frac{1}{Q}\frac{\partial^2 Q}{\partial q_Y^2} - q_Y^2\frac{1}{Q^2}\left(\frac{\partial Q}{\partial q_Y}\right)^2 + \langle N_Y\rangle.$$

Note:
$$\boxed{\langle N_Y^2\rangle - \langle N_Y\rangle^2} = q_Y\left(\frac{\partial\langle N_Y\rangle}{\partial q_Y}\right)_{q_X,N} = q_Y^2\frac{\partial}{\partial q_Y}\left(\frac{\partial \ln Q}{\partial q_Y}\right) + q_Y\frac{\partial \ln Q}{\partial q_Y} = q_Y^2\frac{\partial}{\partial q_Y}\left(\frac{N}{q_X+q_Y}\right) + \frac{q_Y N}{q_X+q_Y}$$
$$= \frac{q_Y N}{q_X+q_Y} - \frac{q_Y^2 N}{(q_X+q_Y)^2} = \frac{\cancel{q_Y^2 N} + q_X q_Y N - \cancel{q_Y^2 N}}{(q_X+q_Y)^2} = \frac{1}{N}\left(\frac{q_X N}{q_X+q_Y}\right)\left(\frac{q_Y N}{q_X+q_Y}\right) = \boxed{\frac{\langle N_X\rangle\langle N_Y\rangle}{N}}.$$

## ✓Problem II: Chemical Equilibrium II

Calculate the equilibrium constant for the reaction

$$CO_2 \quad + \quad H_2 \quad \rightleftarrows \quad CO \quad + \quad H_2O, \tag{10}$$

at 900K and 1200K.

$$q_v^{CO_2} = \prod_{j=1}^{4} \frac{1}{2} \operatorname{csch}\left[\frac{\theta_{v,j}}{2T}\right], \quad q_r^{CO_2} = \frac{T}{\sigma\theta_r}, \quad q^e_{CO_2} = e^{D_e/k_BT}; \quad D_e = D_0 + \sum_j \frac{1}{2} h\nu_j = D_0 + \sum_j \frac{1}{2}\theta_{v,j}k_B = 381.5\,\frac{\text{kcal}}{\text{mole}} + \sum_{j=1}^{4} \frac{1}{2}\theta_{v,j}k_B$$

$$\theta_r^{CO_2} = \{0.561\}, \quad \theta_{v,j}^{CO_2} = \{1840, 3360, 954, 954\}$$

$$q_v^{H_2O} = \prod_{j=1}^{3} \frac{1}{2} \operatorname{csch}\left[\frac{\theta_{v,j}}{2T}\right], \quad q_r^{H_2O} = \frac{\pi^{1/2}}{2}\left(\frac{T^3}{\theta_A\theta_B\theta_C}\right), \quad q^e_{H_2O} = e^{D_e/k_BT}; \quad D_e = D_0 + \sum_j \frac{1}{2} h\nu_j = D_0 + \sum_j \frac{1}{2}\theta_{v,j}k_B = 219.3\,\frac{\text{kcal}}{\text{mole}} + \sum_{j=1}^{4} \frac{1}{2}\theta_{v,j}k_B$$

$$\theta_{r,j}^{H_2O} = \{46.1, 20.9, 13.4\}, \quad \theta_{v,j}^{H_2O} = \{5360, 5160, 2290\}$$

$$q_v^{H_2} = \frac{1}{2}\operatorname{csch}\left(\frac{\theta_v^{H_2}}{2T}\right), \quad q_{rn}^{H_2} = \frac{(2I+1)^2 T}{2\theta_r^{H_2}} = \frac{(1+1)^2 T}{2(85.3)}, \quad q_e^{H_2} = \omega_{e1} e^{D_e/k_BT} = 1e^{D_e/k_BT}; \quad D_e^{H_2} = 103.2\,\frac{\text{kcal}}{\text{mole}} + \frac{1}{2}\overbrace{\theta_v^{H_2}}^{=6215\text{ K}} k_B$$

$$\theta_v^{H_2} = 6215 \text{ K}$$

valid since $\theta_r^{H_2} = 85.3$ ; $\frac{\theta_r^{H_2}}{T} = \frac{85}{400} \approx 0.2$

$$q_v^{CO} = \frac{1}{2}\operatorname{csch}\left(\frac{\theta_v^{CO}}{2T}\right), \quad q_r^{CO} = \frac{T}{\theta_r^{CO}}, \quad q_e^{CO} = 1e^{D_e/k_BT}; \quad D_e = 255.8\,\frac{\text{kcal}}{\text{mole}} + \frac{1}{2}\overbrace{\theta_v^{CO}}^{=3103\text{ K}} k_B$$

valid since $\theta_r^{CO} = 2.77$ ; $\frac{\theta_r}{T} = \frac{2.77}{400} \approx 0.0075 \ll 0.2$

Calculation in Mathematica.

## ✓Problem III: Fermi-Gas

Starting from the grand canonical formulas for indistinguishable particles, derive an expression for the thermodynamic energy $E$ of a gas of weakly degenerate fermions as a power series in the density $\rho$. Go as far as $\rho^2$. Briefly discuss your results.

## Problem 3

Since density is $\rho = N/V$, one may start by noting that $N$ in the GCE is:

$$N = \sum_k \langle n_k \rangle = \sum_k \frac{\lambda e^{-\beta\varepsilon_k}}{1+\lambda e^{-\beta\varepsilon_k}} = \frac{\pi}{4}\left(\frac{8mV^{2/3}}{h^2}\right)^{3/2}\int_0^\infty d\varepsilon\, \frac{\lambda \varepsilon^{1/2} e^{-\beta\varepsilon}}{1+\lambda e^{-\beta\varepsilon}} = \frac{\pi}{4}\left(\frac{8mV^{2/3}}{h^2}\right)^{3/2}\sum_{n=\varnothing}(-1)^n\lambda^{n+1}\int_0^\infty d\varepsilon\, \varepsilon^{1/2} e^{-\beta(n+1)\varepsilon}$$

where replacement of the sum by an integral is valid since the eigenenergies, essentially of a particle in a box, are close enough to be interpreted as a density of states:

$$\varepsilon_k = \frac{h^2}{8mV^{2/3}}(n_x^2+n_y^2+n_z^2) \rightarrow \omega(\varepsilon)d\varepsilon = \frac{\pi}{4}\left(\frac{8mV^{2/3}}{h^2}\right)^{3/2}\varepsilon^{1/2}d\varepsilon$$

Thus,

$$N = \frac{\pi}{4}\left(\frac{8mV^{2/3}}{h^2}\right)^{3/2}\sum_{n=\varnothing}(-1)^n\lambda^{n+1}\left(\frac{\pi(k_BT)^3}{4(n+1)^3}\right)^{1/2},$$ after evaluating the integral in Mathematica.

The density is then
$$\rho = \frac{N}{V} = \frac{\cancel{V}}{\cancel{V}}\left(\frac{\pi}{4}\right)^{3/2}\left(\frac{8m}{h^2}\right)^{3/2}(k_BT)^{3/2}\sum_{n=0}\frac{(-1)^n}{(n+1)^{3/2}}\lambda^{n+1} = \left(\frac{\cancel{8}^2\pi m k_BT}{\cancel{4}h^2}\right)^{3/2}\sum_{n=0}\frac{(-1)^n}{(n+1)^{3/2}}\lambda^{n+1}$$

$$= \frac{1}{\Lambda^3}\sum_{n=0}\frac{(-1)^n}{(n+1)^{3/2}}\lambda^{n+1} = \frac{1}{\Lambda^3}\sum_{n=1}\frac{(-1)^{n+1}}{n^{3/2}}\lambda^n = \frac{1}{\Lambda^3}\left\{\varnothing+\lambda-\frac{1}{2^{3/2}}\lambda^2+\frac{1}{3^{3/2}}\lambda^3+\dots\right\}$$

$$= \frac{1}{\Lambda^3}\left\{(a_0+a_1\rho+a_2\rho^2+\dots)-\frac{1}{2^{3/2}}(a_0+a_1\rho+a_2\rho^2+\dots)^2+\frac{1}{3^{3/2}}(a_0+a_1\rho+a_2\rho^2+\dots)^3-\dots\right\}$$

$$= \frac{1}{\Lambda^3}\left\{\left(a_0-\frac{1}{2^{3/2}}a_0^2+\frac{1}{3^{3/2}}a_0^3-\dots\right)\rho^0+\left(a_1-\frac{1}{2^{3/2}}a_0a_1+\frac{1}{3^{3/2}}a_0^2a_1-\dots\right)\rho^1+\left(a_2-\frac{1}{2^{3/2}}(a_0a_2+a_1^2)+\frac{1}{3^{3/2}}(a_0^2a_2+a_0a_1^2)-\dots\right)\rho^2\dots\right.$$

$$= \frac{1}{\Lambda^3}\left\{\varnothing+\lambda-\frac{1}{2^{3/2}}\lambda^2+\frac{1}{3^{3/2}}\lambda^3+\dots\right\} \Rightarrow \frac{1}{\Lambda^3}\left(a_0-\frac{1}{2^{3/2}}a_0^2+\frac{1}{3^{3/2}}a_0^3-\dots\right)=\varnothing,\quad \boxed{a_0=\varnothing}$$

$$\frac{1}{\Lambda^3}\left(a_1-\frac{1}{2^{3/2}}\cancel{a_0}^{\varnothing}a_1+\frac{1}{3^{3/2}}\cancel{a_0^2}^{\varnothing}a_1-\dots\right)=1,\quad \boxed{a_1=\Lambda^3}$$

$$\frac{1}{\Lambda^3}\left(a_2-\frac{1}{2^{3/2}}(\cancel{a_0a_2}^{\varnothing}+a_1^2)+\frac{1}{3^{3/2}}(\cancel{a_0^2a_2}^{\varnothing}+\cancel{a_0a_1^2}^{\varnothing})\right)=-\frac{1}{2^{3/2}}\qquad \boxed{a_2=\frac{1}{2^{3/2}}\Lambda^6}$$

$$\rightarrow \frac{1}{\Lambda^3}\left(a_2-\frac{1}{2^{3/2}}a_1^2\right)=-\frac{1}{2^{3/2}} \rightarrow \frac{a_2}{\Lambda^3}-\cancel{\frac{\Lambda^6}{\Lambda^3}}^{1}\frac{1}{2^{3/2}}=-\frac{1}{2^{3/2}}$$

So, $\lambda = a_0+a_1\rho+a_2\rho^2+\dots = \varnothing+\Lambda^3\rho+\frac{1}{2^{3/2}}(\Lambda^3\rho)^2+\dots = \Lambda^3\rho+\frac{1}{2^{3/2}}(\Lambda^3\rho)^2$ to second order in $\rho$.

Now for energy $E$ in the GCE,

$$E = \sum_k \varepsilon_k\langle n_k\rangle = \sum_k\frac{\varepsilon_k\lambda e^{-\beta\varepsilon_k}}{1+\lambda e^{-\beta\varepsilon_k}} = \frac{\pi}{4}\left(\frac{8mV^{2/3}}{h^2}\right)^{3/2}\int_0^\infty d\varepsilon\,\frac{\lambda\varepsilon^{3/2}e^{-\beta\varepsilon}}{1+\lambda e^{-\beta\varepsilon}} = \frac{\pi}{4}\left(\frac{8m}{h^2}\right.\quad -1)^n\lambda^{n+1}\int_0^\infty d\varepsilon\,\varepsilon^{3/2}e^{-\beta(n+1)\varepsilon}$$

Solve in Mm

$$E = \frac{3}{2}\left[\frac{\pi}{4}\left(\frac{8mV^{2/3}}{h^2}\right)^{3/2}\sum_{n=\varnothing}(-1)^n\lambda^{n+1}\left(\frac{\pi(k_BT)^3}{4(n+1)^3}\right)^{1/2}\frac{k_BT}{n+1}\right] = \frac{3}{2}\frac{k_BT}{\Lambda^3}\sum_{n=0}\frac{(-1)^n}{(n+1)^{5/2}}\lambda^{n+1} = \frac{3}{2}\frac{k_BT}{\Lambda^3}\sum_{n=1}\frac{(-1)^{n+1}}{n^{5/2}}\lambda^n$$

$$= \frac{3}{2}\frac{k_BT}{\Lambda^3}\sum_{n=1}\frac{(-1)^{n+1}}{n^{5/2}}\left(\Lambda^3\rho+\frac{1}{2^{3/2}}(\Lambda^3\rho)^2\right)^n = \frac{3}{2}\frac{k_BT}{\Lambda^3}\left(\Lambda^3\rho+\frac{1}{2^{3/2}}(\Lambda^3\rho)^2\right)-\frac{3}{2^{7/2}}\frac{k_BT}{\Lambda^3}\left(\Lambda^3\rho+\frac{1}{2^{3/2}}(\Lambda^3\rho)^2\right)^2+\dots$$ neglect $> \rho^2$,

$$E = \frac{3}{2}\frac{k_BT}{\cancel{\Lambda^3}}\cancel{\Lambda^3}\rho+\cancel{\frac{3}{2}\frac{k_BT}{\Lambda^3}\frac{1}{2^{3/2}}(\Lambda^3\rho)^2}-\cancel{\frac{3}{2^{7/2}}\frac{k_BT}{\Lambda^3}(\Lambda^3\rho)^2}$$

$$\boxed{E = B_1(T)\rho+B_2(T)\rho^2+\dots \quad \text{with } B_1(T)=\frac{3}{2}k_BT \text{ and } B_2(T)=\varnothing.}$$

Discussion of results in Mathematica

## Problem IV: Real Gases

In class we discussed four different models for $u(r)$, the interatomic potential energy between two atoms of a real gas. These models include the hard sphere model,

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases}, \tag{11}$$

the square-well,

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \leq r \leq \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}, \tag{12}$$

the triangle potential,

$$u(r) = \begin{cases} \infty & r < \sigma \\ \frac{\epsilon}{\sigma(\lambda-1)}(r - \lambda\sigma) & \sigma \leq r \leq \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}, \tag{13}$$

and finally the Lennard-Jones potential,

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{14}$$

Answer the following.

1. Using the parameters for krypton in Table 12-3 of McQuarrie, plot the Lennard-Jones and square-well models for $u(r)/k_B$ on the same figure. Also on the same figure, plot $u(r)/k_B$ for the triangle potential with $\epsilon/k_B = 290\text{K}$, $\lambda = 1.7$, and $\sigma = 3.4\text{Å}$. Make sure your figure is labeled properly. Briefly comment on the similarities and differences.

2. Derive by hand the second virial coefficient for the square-well potential. Your answer should be in terms of $\beta$, $\epsilon$, $\lambda$, and the second virial coefficient for hard spheres $B_2^{\text{HS}}$. Also by hand, solve for the Boyle temperature for the square-well potential.

3. Use Mathematica to plot the second virial coefficient of (a) the square-well potential, (b) the triangle potential, and (c) the Lennard-Jones potential as a function of temperature, all on the same figure. Use the parameters from part 1. Numerically determine the Boyle temperature for (b) and (c). Place a Point[] at the location of each Boyle temperature on your figure. Briefly comment on your results.

## Problem 4

a.) Plotting and discussion of results in Mathematica

b.)

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \le r \le \lambda\sigma \\ \emptyset & r > \lambda\sigma \end{cases} \qquad Z_N = \int dq_1 \dots \int dq_N \, e^{-\beta u(q_1, q_2, \dots)}$$

Sidenote

$$B_2^{HS}(T) = -2\pi \int_0^\sigma dr\, r^2 \left[\cancel{e^{-\infty}}^{\,0} - 1\right] = 2\pi \frac{r^3}{3}\Big|_0^\sigma = 2\pi \frac{\sigma^3}{3}$$

$$B_2(T) = -\frac{1}{2V}(Z_2 - Z_1^2) = -\frac{1}{2V}\int dq_1 \int dq_2 \left[e^{-\beta u(r_{12})} - 1\right] = -\frac{1}{2V}\int dq_1 \int dr_{12}\left[e^{-\beta u(r_{12})} - 1\right]$$

$$\hookrightarrow B_2(T) = -\frac{1}{2}\int dr_{12}\left[e^{-\beta u(r_{12})} - 1\right] = -\frac{1}{2}\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\varphi \int dr\, r^2\left[e^{-\beta u(r)} - 1\right] = -2\pi\int_0^\infty dr\, r^2\left[e^{-\beta u(r)} - 1\right]$$

$$\int_0^\infty dr\, r^2\left[e^{-\beta u(r)} - 1\right] = \int_0^\sigma dr\, r^2\left[e^{-\beta u(r)} - 1\right] + \int_\sigma^{\lambda\sigma} dr\, r^2\left[e^{-\beta u(r)} - 1\right] + \int_{\lambda\sigma}^\infty dr\, r^2\left[e^{-\beta u(r)} - 1\right]$$

$$= \int_0^\sigma dr\, r^2\left[e^{-\infty} - 1\right] + \int_\sigma^{\lambda\sigma} dr\, r^2\left[e^{\beta\epsilon} - 1\right] + \cancel{\int_{\lambda\sigma}^\infty dr\, r^2\left[e^{0} - 1\right]} \to \emptyset$$

$$= \int_\sigma^{\lambda\sigma} dr\, r^2\left[e^{\beta\epsilon} - 1\right] - \int_0^\sigma dr\, r^2 = e^{\beta\epsilon}\int_\sigma^{\lambda\sigma} dr\, r^2 - \int_\sigma^{\lambda\sigma} dr\, r^2 - \frac{r^3}{3}\Big|_{r=\emptyset}^{r=\sigma}$$

$$= \frac{1}{3}\left(e^{\beta\epsilon} r^3\Big|_{r=\sigma}^{r=\lambda\sigma} - r^3\Big|_{r=\sigma}^{r=\lambda\sigma} - r^3\Big|_{r=\emptyset}^{r=\sigma}\right)$$

$$= \frac{1}{3}\left[e^{\beta\epsilon}(\lambda^3\sigma^3 - \sigma^3) - (\lambda^3\sigma^3 - \cancel{\sigma^3}) - (\cancel{\sigma^3})\right]$$

$$\hookrightarrow B_2(T) = -2\pi\frac{\sigma^3}{3}\left[(e^{\beta\epsilon} - 1)\lambda^3 - e^{\beta\epsilon}\right] \quad \text{or} \quad \boxed{B_2(T) = -B_2^{HS}(T)\left[(e^{\beta\epsilon} - 1)\lambda^3 - e^{\beta\epsilon}\right]}$$

Boyle temperature: $B_2(T) = \emptyset = -2\pi\frac{\sigma^3}{3}\left[(e^{\beta\epsilon} - 1)\lambda^3 - e^{\beta\epsilon}\right] \longrightarrow$ finite, $> \emptyset$ for $\sigma$ & $\lambda$

Need $\left[(e^{\beta\epsilon} - 1)\lambda^3 - e^{\beta\epsilon}\right] = \emptyset \longrightarrow e^{\beta\epsilon}\lambda^3 - \lambda^3 - e^{\beta\epsilon} = 0$

Above looks similar to $(e^{\beta\epsilon} - 1)(\lambda^3 - 1) = e^{\beta\epsilon}\lambda^3 - e^{\beta\epsilon} - \lambda^3 + 1$ (equal to above plus 1)

$$\hookrightarrow (e^{\beta\epsilon} - 1)(\lambda^3 - 1) - 1 = \emptyset, \quad e^{\beta\epsilon} - 1 = \frac{1}{\lambda^3 - 1} \to \frac{\epsilon}{k_B T} = \ln\left(\frac{1}{\lambda^3 - 1} + 1\right) \to \frac{k_B}{\epsilon} T = -\ln\left(\frac{1}{\lambda^3 - 1} + 1\right)$$

so $B_2(T) = \emptyset$ at $\boxed{T_{Boyle}^{SW} = -\frac{\epsilon}{k_B}\ln\left(\frac{1}{\lambda^3 - 1} + 1\right)}$

c.) Plotting and discussion of results in Mathematica

## ✓ Problem V: Adsorption Revisited

Consider a 2D surface containing $N$ sites, each of which can adsorb a single gas molecule. The energy of an adsorbed molecule is $-\epsilon_0$ compared to the free state. The adsorbing surface is in contact with an ideal gas. Derive the covering ratio $\theta$, i.e. the ratio of adsorbed molecules $N_s$ to adsorbing sites $N$, as a function of the pressure of the gas. Use the grand canonical ensemble. Briefly discuss your results.

## ✓Problem VI: Heterogeneous Equilibrium

Though molecular iodine $I_2$ is non-polar, it is weakly soluble in water. Consider a flask containing molecular iodine and two immiscible solvents: water and a non-polar solvent. At equilibrium there are two layers in the flask, one aqueous and one non-polar, each with a particular concentration of $I_2$. Therefore we have the following equilibrium

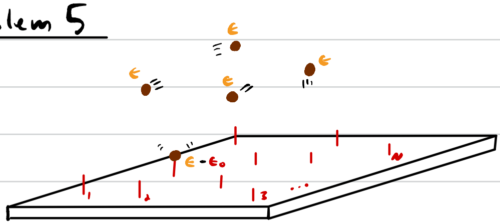
$$\mathrm{I}_{2\ (\mathrm{aq.})} \quad \rightleftarrows \quad \mathrm{I}_{2(\mathrm{n.p.})}, \tag{15}$$

and equilibrium constant,

$$K = \frac{\left[\mathrm{I}_{2\ (\mathrm{n.p.})}\right]}{\left[\mathrm{I}_{2\ (\mathrm{aq.})}\right]}. \tag{16}$$

Based on your knowledge of statistical mechanics, hypothesize (in words) the microscopic information that determines the magnitude of $K$. How is this similar/different to what we have studied so far?

# Problem 5




Dist of energies available to an adsorbed molecule is the same as ideal gas, minus $\epsilon_0$.

$$\underbrace{\sum_j e^{-\beta E_j}}_{gas} \rightarrow \underbrace{\sum_j e^{-\beta(E_j-\epsilon_0)}}_{ads.} = \left(\sum_j e^{-\beta E_j}\right) e^{\beta\epsilon_0}$$

The partition function of the adsorbing surface is:

$$\Xi_{ads} = \sum_{n=\varnothing}^{N}\sum_j e^{-E_{nj}(V)/k_BT} e^{\mu n/k_BT} = e^{\beta\epsilon_0}\sum_{n=0}^{N} Q(n,V,T)_{gas}\, e^{\mu n/k_BT} = e^{\beta(\epsilon_0+\mu)}\sum_{n=0}^{N} Q(n,V,T)_{gas}\, e^{n/k_BT}$$

possible energies for adsorbate with n particles adsorbed

has no $\mu$

Defining $\chi(T) = \sum_{n=0}^{N} Q(n,V,T)_{gas}\, e^{n/k_BT}$, $\Xi_{ads} = e^{\beta(\epsilon_0+\mu)}\chi(T)$ ; no. ads. particles is:

$$N_s = k_BT\left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{V,T} = \frac{pV}{\ln \Xi}\frac{\partial}{\partial \mu}\ln \Xi$$ where the second step comes from $pV = k_BT\ln\Xi$.

$\hookrightarrow$ $\ln \Xi_{ads} = \ln\left(e^{\beta(\epsilon_0+\mu)}\right) + \ln(\chi(T)) = \beta\epsilon_0 + \beta\mu + \ln(\chi(T))$ ; $\frac{\partial \ln \Xi}{\partial \mu} = \beta$

$\hookrightarrow$

**A** $N_s = \frac{pV}{\ln\Xi}\frac{\partial}{\partial\mu}\ln\Xi = \frac{pV}{\epsilon_0 + \mu + k_BT\ln(\chi(T))}$, giving $\boxed{\theta_r = \frac{N_s}{N} = \frac{pV}{\epsilon_0+\mu+k_BT\ln(\chi(T))}\cdot\frac{1}{N}}$

The covering ratio increases linearly with pressure, reflective of the trends $pV = Nk_BT$ and $E = \frac{3}{2}Nk_BT$ of an ideal gas on its own. Pressure is linearly related to particle number and to temperature, as is overall energy. Thus, the fact that the energy shift of any adsorbed molecule is always $\epsilon_0$ less than it was, this linear energy shift relates to $N\cdot T$, and thus directly to pressure. In this context, $\frac{N_s}{N} \propto p$ makes sense.

# Problem 6

The primary microscopic information will be related to the local ordering of the molecules in a polar solvation sphere versus a nonpolar solvation sphere. Most reactions we have studied so far are gaseous reactions where individual translational, vibrational, etc partition functions can be written for molecules that spend a lot of time on average not interacting with other molecules. In solution, all molecules are constantly interacting with several layers of solvation spheres. The nature of solvation / the amount of $I_2$ that can be dissolved will be directly related to the polarizability of the solutes and solvents. Polarizability is essentially a characteristic of the "malleability" of the electron density of a molecule, and would be completely determined by electronic partition functions. In conclusion, electronic contributions are often negligible in the (gas-phase) problems we have done, but likely dominate in a disordered, "gridlocked" setting like a liquid where a solute in any given solvent would have little translational, vibrational, or rotational variability between solvents; differences in miscibility would boil down to these electronic differences.