Fri: HW by 5pm

Final: Tues 12 May 10am - noon:30

* Will be at home
* Exam emailed at 10am
* Drop in D2L Box
* Comprehensive — similar to previous exams.

  - 2016 Final All Q
  - 2019 Final All Q

Grand Canonical Ensemble formalism for ideal gas

We aim to apply the grand canonical formalism to an ideal gas to determine

1) energy equation of state

2) entropy

3) pressure equation of state

4) chemical potential.

The crucial facts about the grand canonical ensemble are:

1) list single particle states $\sim$ labeled "j"

$\sim$ energy ϵ_j

2) obtain the mean occupation numbers for each state

$$\bar{n}_j \equiv \bar{n}_j(\epsilon_j)$$

3) mean energy is

$$\bar{E} = \sum_j \bar{n}_j \epsilon_j$$
all single particle
states j

4) mean particle number:

$$\bar{N} = \sum \bar{n}_j$$
single particle states

5) entropy is:

$$S = k \sum_j \ln[Z_{Gj}] + \frac{1}{T}(\bar{E} - \mu\bar{N})$$

We can consider three distributions:

1) Bose - Einstein
$$\bar{n}_j(\epsilon_j) = \frac{1}{e^{+(\epsilon_j - \mu)\beta} - 1}$$

2) Fermi - Dirac
$$\bar{n}_j(\epsilon_j) = \frac{1}{e^{+(\epsilon_j - \mu)\beta} + 1}$$

3) Maxwell Boltzmann (if $\bar{n}_j \ll 1$)
$$\bar{n}_j(\epsilon_j) = e^{-(\epsilon_j - \mu)\beta}$$

When using the Maxwell Boltzmann distribution we get

$$\bar{S} = k\bar{N} + \frac{1}{T}(\bar{E} - \mu\bar{N})$$

$$\bar{S} = \left(k - \frac{\mu}{T}\right)\bar{N} + \frac{1}{T}\bar{E}$$

When we apply this to the ideal gas we will find that it is more convenient to label the states in terms of energy ϵ that a state label "j." The immediate issue is that there will be many states with the same energy and we will have to rephrase the sums to account for this.

Mean energies and particle numbers in terms of state energies

The mean particle number + energy are:

$$\bar{N} = \sum_j \bar{n}_j(\epsilon_j)$$

$$\bar{E} = \sum_j \epsilon_j \, \bar{n}_j(\epsilon_j)$$

We want to express these as sums over energies. There are two cases

Non-degenerate case	Degenerate case
No two states have same energy	There are at least two states with the same energy
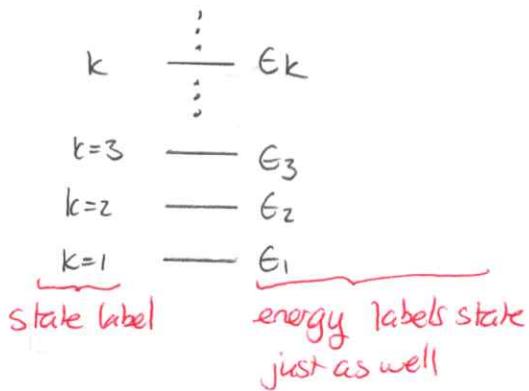
Non-degenerate case:

$$k \; \vdots \; \epsilon_k$$
$$k=3 \; — \; \epsilon_3$$
$$k=2 \; — \; \epsilon_2$$
$$k=1 \; — \; \epsilon_1$$

$\underbrace{\text{state label}}$ $\underbrace{\text{energy labels state just as well}}$

$$\bar{N} = \sum \bar{n}(\epsilon)$$

all single particle energies ϵ

$$\bar{E} = \sum \epsilon \, \bar{n}(\epsilon)$$

all single particle energies ϵ

Degenerate case:

$$k=3 \quad k=4 \quad k=5 \quad \epsilon_3 \quad \gamma(\epsilon_3)=3$$
$$\epsilon_1 \quad \gamma(\epsilon_1)=2$$
$$k=1 \quad k=2$$
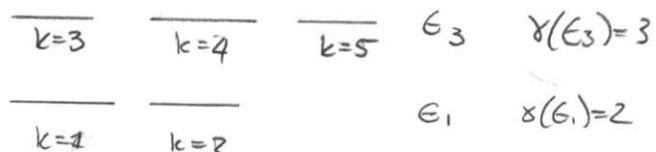
Energy does not label states but
$$\bar{n}_1(\epsilon_1) = \bar{n}_2(\epsilon_2)$$
$$\bar{n}_3(\epsilon_3) = \bar{n}_4(\epsilon_4) = \bar{n}_5(\epsilon_5)$$

means, with
$$\gamma(\epsilon) = \text{number states with energy } \epsilon$$

$$\bar{N} = \sum \gamma(\epsilon)\bar{n}(\epsilon) \qquad \bar{E} = \sum \epsilon \, \gamma(\epsilon) \bar{n}(\epsilon)$$

energies   energies

We can again do this accounting with an energy density of states function, $g(\epsilon)$, such that

| number of states with energy $\epsilon \to \epsilon + d\epsilon$ | $=$ | $g(\epsilon)\, d\epsilon$ |

Then:

$$\bar{N} = \int \bar{n}(\epsilon)\, g(\epsilon)\, d\epsilon$$

$$\bar{E} = \int \epsilon\, \bar{n}(\epsilon)\, g(\epsilon)\, d\epsilon$$

So we need

Consider single particle states
- $\to$ list possible energies
- $\to$ obtain energy density of states function, $g(\epsilon)$

Do particles obey
- * Bose-Einstein
- * Fermi-Dirac
- * Maxwell-Boltzmann statistics?

$\to$ gives $\bar{n}(\epsilon)$

Determine $\bar{N} = \int \bar{n}(\epsilon)\, g(\epsilon)\, d\epsilon$

$$\bar{E} = \int \epsilon\, \bar{n}(\epsilon)\, g(\epsilon)\, d\epsilon$$

$$S = ??$$

Semi-classical model of an ideal gas

The model for an ideal gas is:

1) identical, indistinguishable particles in a three dimensional cubic well with sides L

2) sufficiently dilute so that $\bar{n}(\epsilon) \ll 1$ for any state

Then we need to provide energies and obtain the energy density of states.

From quantum physics

Possible single particle states are labeled by $n_x, n_y, n_z = 1, 2, 3, 4 \ldots$
and have energy

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2ML^2} \left(n_x^2 + n_y^2 + n_z^2 \right)$$

This is clearly degenerate. In order to obtain the energy density of states we note that energy only depends on

$$n = \sqrt{n_x^2 + n_y^2 + n_z^2}$$

and

$$E(n) = \frac{\hbar^2 \pi^2}{2ML^2} n^2$$

To get $g(\epsilon)$ we follow:

Find $\Gamma(n) =$ number states where $\sqrt{n_x^2 + n_y^2 + n_z^2} \leq n$ ⟶ "n" density of states $g(n) = \frac{d\Gamma(n)}{dn}$

energy density of states $g(\epsilon) = g(n) \frac{dn}{d\epsilon}$

Since

$g(\epsilon) d\epsilon = \underbrace{g(\epsilon) \frac{d\epsilon}{dn}}_{g(n)} dn$

$\hookrightarrow g(n) = g(\epsilon) / \left(\frac{dn}{d\epsilon} \right)$

Statistical and Thermal Physics: Class 26

7 May 2020

1 Ideal gas: semi-classical grand canonical ensemble treatment part 2

For the three dimensional well and the usual indices, let

$$n = \sqrt{n_x^2 + n_y^2 + n_z^2}$$

a) Express the energy of the state ϵ in terms of n.

b) Determine the number of single particle states for which $\sqrt{n_x^2 + n_y^2 + n_z^2} \leqslant n$, i.e. determine $\Gamma(n)$.

c) Determine $g(n)$ and use this to determine the energy density of states.

d) Determine the mean energy and the mean particle number for the ideal gas, assuming · that it obeys Maxwell-Boltzmann statistics.

e) Combine these to determine the energy equation of state for the ideal gas.

f) Determine an expression for the chemical potential in terms of particle number, volume and temperature.

g) Determine an expression for the entropy in terms of particle number, volume and temperature. Verify that it is extensive.

Note that a useful integral is that for any positive integer, k

$$\int_0^\infty x^{k/2} e^{-ax} \, dx = \frac{\Gamma[k/2 + 1]}{a^{k/2+1}}$$

whenever $a > 0$. The Gamma function satisfies

$$\Gamma(1/2) = \sqrt{\pi}$$
$$\Gamma(1) = 1$$
$$\Gamma(n + 1) = n \, \Gamma(n).$$

Answer: a)

$$E = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

b) Use the geometrical construction.
   Each point occupies volume 1

   $\Rightarrow$ number of states = volume sphere:

$$\Gamma'(n) = \frac{1}{8} \frac{4}{3} \pi n^3$$

$$\Gamma(n) = \frac{\pi}{6} n^3$$

1st octant

radius n
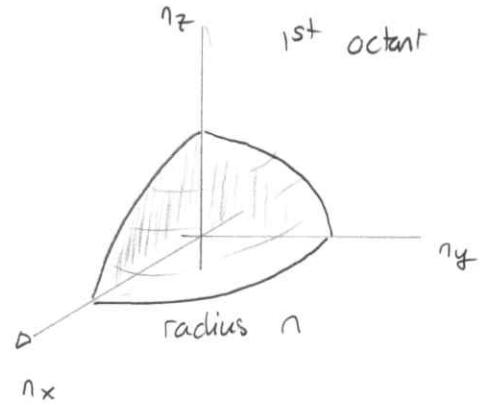
c) $$g(n) = \frac{d\Gamma}{dn} = \frac{\pi}{2} n^2$$

$$g(\epsilon) = g(n) \frac{dn}{d\epsilon}$$

$$= \frac{\pi}{2} n^2 \frac{dn}{d\epsilon}$$

But $$n = \sqrt{\frac{2mL^2}{\hbar^2 \pi^2}} \sqrt{\epsilon}$$

$$n^2 = \frac{2mL^2}{\hbar^2 \pi^2} \epsilon$$

$$\Rightarrow \quad \frac{dn}{d\epsilon} = \sqrt{\frac{2mL^2}{\hbar^2 \pi^2}} \frac{1}{2} \frac{1}{\sqrt{\epsilon}}$$

$$\Rightarrow \quad g(\epsilon) = \frac{\pi}{2} \frac{2mL^2}{\hbar^2 \pi^2} \epsilon \sqrt{\frac{2mL^2}{\hbar^2 \pi^2}} \frac{1}{2} \frac{1}{\sqrt{\epsilon}}$$

$$= \frac{1}{4\pi^2} \left(\frac{2mL^2}{\hbar^2} \right)^{3/2} \sqrt{\epsilon}$$

$$= \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} L^3 \sqrt{\epsilon}$$

$$\llcorner_{\circ V}$$

$$\Rightarrow \quad g(\epsilon) = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} V \sqrt{\epsilon}$$

d) $\quad \bar{E} = \int_0^\infty \epsilon g(\epsilon) \, \bar{n}(\epsilon) \, d\epsilon$

$\quad\quad = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} V \int_0^\infty \epsilon \, e^{-(\epsilon-\mu)\beta} \sqrt{\epsilon} \, d\epsilon$

$\quad\quad = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} V \, e^{\mu\beta} \underbrace{\int_0^\infty e^{-\epsilon\beta} \, \epsilon^{3/2} \, d\epsilon}$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad \Gamma\left(\frac{3}{2}+1\right) \Big/ \beta^{5/2}$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad \hookrightarrow \; \Gamma\left(\frac{5}{2}\right) = \Gamma\left(\frac{3}{2}+1\right) = \frac{3}{2} \Gamma\left(\frac{3}{2}\right)$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad = \frac{3}{2} \frac{1}{2} \cdot \Gamma\left(\frac{1}{2}\right)$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad = \frac{3}{4} \sqrt{\pi}$

$\bar{E} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} V \, e^{\mu\beta} \, \frac{3}{4} \sqrt{\pi} \, \beta^{-5/2}$

$$\boxed{\bar{E} = \frac{3}{16} \left(\frac{2m}{\pi\hbar^2}\right)^{3/2} e^{\mu\beta} V \beta^{-5/2}}$$

$\bar{N} = \int_0^\infty \bar{n}(\epsilon) g(\epsilon) \, d\epsilon \quad = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} V e^{\mu\beta} \underbrace{\int_0^\infty e^{-\epsilon\beta} \, \epsilon^{1/2} \, d\epsilon}$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \Gamma\left(\frac{1}{2}+1\right) \beta^{-3/2}$

$\quad\quad\quad\quad\quad\quad\quad = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} V e^{\mu\beta} \, \frac{1}{2} \sqrt{\pi} \, \beta^{-3/2}$

$=0 \quad \boxed{\bar{N} = \frac{1}{8} \left(\frac{2m}{\pi\hbar^2}\right)^{3/2} e^{\mu\beta} V \beta^{-3/2}}$

e) We can see that

$$\bar{E} = \frac{3}{2} \bar{N} \beta^{-1} \qquad =\!\!\!\triangleright \quad \boxed{\bar{E} = \frac{3}{2} \bar{N} kT}$$

$$=\!\!\!\triangleright \quad \boxed{\boxed{E = \frac{3}{2} NkT}}$$

redenergy eqn of state

f) From $\quad \bar{N} = \frac{1}{8} \left(\frac{2m}{\pi\hbar^2} \right)^{3/2} e^{\mu\beta} V \beta^{-3/2}$

$$e^{\mu\beta} = 8 \left(\frac{\pi\hbar^2}{2m} \right)^{3/2} \beta^{3/2} \frac{\bar{N}}{V}$$

$$=\!\!\!\triangleright \quad \mu\beta = \ln\left[8 \left(\frac{\pi\hbar^2}{2m} \right)^{3/2} \beta^{3/2} \frac{\bar{N}}{V} \right]$$

$$=\!\!\!\triangleright \quad \mu = \frac{1}{\beta} \ln[\ldots]$$

$$=\!\!\!\triangleright \quad \mu = kT \ln\left[8 \left(\frac{\pi\hbar^2}{2m} \right)^{3/2} \frac{\bar{N}}{V} \left(\frac{1}{kT} \right)^{3/2} \right]$$

$$=\!\!\!\triangleright \quad \boxed{\mu = kT \ln\left[\frac{\bar{N}}{V} \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2} \right]}$$

g) For M-B statistics:

$$S = \left(k - \frac{\mu}{T} \right) \bar{N} + \frac{1}{T} \bar{E}$$

$$= \left\{ k - k \ln\left[\frac{\bar{N}}{V} \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2} \right] \right\} \bar{N} + \frac{1}{\cancel{T}} \frac{3}{2} \bar{N} k \cancel{T}$$

$$=\!\!\!\triangleright \quad S = \bar{N} k \left\{ \frac{5}{2} - \ln\left[\frac{\bar{N}}{V} \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2} \right] \right\}$$

$\Rightarrow$ $$S = \bar{N}k\left\{\frac{5}{2} + \ln\left[\frac{V}{N}\right] - \frac{3}{2}\ln\left[\frac{2\pi\hbar^2}{mkT}\right]\right\}$$

This is the entropy which is now clearly extensive since

$$\bar{N} \rightarrow \lambda\bar{N}$$
$$V \rightarrow \lambda\bar{V}$$
$\left.\right\} \Rightarrow$ $S \rightarrow \lambda S$

Finally we would like to obtain the pressure equation of state.
One way would be to use

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,E}$$

This requires $S = S(E, V, N)$. So the variable T must be replaced.
Here

$$\frac{3}{2}NkT = E \quad \Rightarrow \quad kT = \frac{2}{3}\frac{E}{N}$$

$\Rightarrow$

$$S = Nk\left\{\frac{5}{2} + \ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left[\frac{2mE}{3N}\frac{1}{2\pi\hbar^2}\right]\right\}$$

Then

$$\frac{P}{T} = \frac{\partial S}{\partial V} = \frac{Nk}{V} \qquad \Rightarrow \qquad \boxed{PV = NkT}$$

Thus

The grand canonical ensemble formalism plus a semiclassical model for an ideal gas yields: energy + pressure equations of state, entropy that is extensive, chemical potential

Notes:

1) <u>chemical potential</u> The chemical potential depends on T, V, N

$$\mu = kT \ln\left[\frac{N}{V}\left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2}\right]$$

a) Thus if T is fixed μ increases as particle number density increases. So particles will flow from a more dense to a less dense region

more dense	less dense
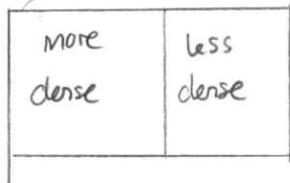
b) If T is fixed an particle number density is fixed then μ increases as particle mass decreases. So less massive particles tend to flow to region with more massive particles.

2) <u>entropy</u> We found that

$$S = Nk\left\{\frac{5}{2} + \ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln T \underbrace{- \ln\left[\left(\frac{2\pi\hbar^2}{m}\right)^{3/2}\right]}_{S_0}\right\}$$

The entropy depends on $\hbar, m$ via S_0. But the change in entropy is unaffected by these (so the quantum aspect does not matter in this regard)