Phys 362 2020

Lecture 23

Thurs: Read 4.12 ; 6.3

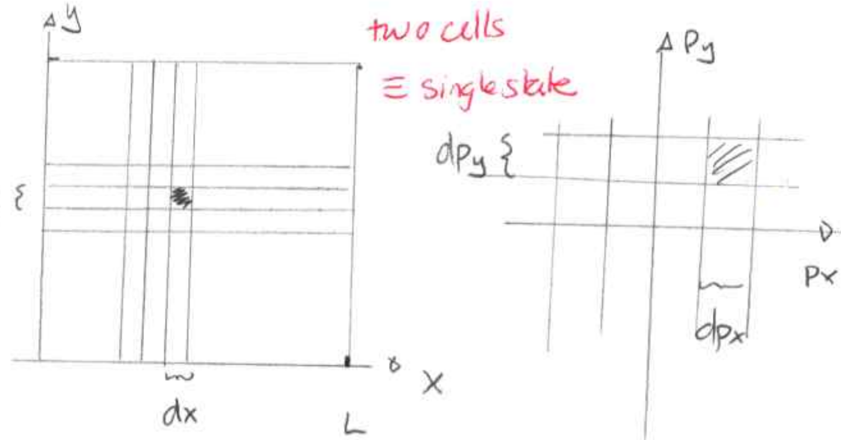
Fri: HW by 6pm

Classical ideal gas via canonical ensemble

The classical statistical physics model for an ideal gas involves partitioning the state space into discrete pieces and constructing the partition function using this.

The energy associated with any state is

$$E = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$



Then the single particle partition function is

$$Z_{\text{single}} = \alpha \underbrace{\int dx \int dy \int dz \int dp_x \int dp_y \int dp_z}_{\text{all allowed states}} e^{-(p_x^2+p_y^2+p_z^2)\beta/2m}$$

where α is a scale factor with units $(\text{kg}\,\text{m}^2\text{s}^{-1})^{-3}$

1 Classical ideal gas: canonical ensemble

a) Determine the single particle partition function for a classical ideal gas. Note that if $a > 0$

$$\int_{-\infty}^{\infty} e^{-ax^2}\,\mathrm{d}x = \sqrt{\frac{\pi}{a}}.$$

b) Determine the partition function for a classical ideal gas consisting of N distinguishable particles.

c) Determine an expression for the mean energy of the gas in terms of T.

d) Starting with the Helmholtz free energy, use classical thermodynamics to show that

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

and use this result and $F = -kT\ln Z$ to determine the pressure equation of state.

e) Describe how one might attempt to obtain the chemical potential. Does this formalism allow for an expression for the chemical potential?

Answer: a) $$Z_{single} = \alpha \underbrace{\int_0^L dx \int_0^L dy \int_0^L dz}_{L^3} \int_{-\infty}^{\infty} e^{-p_x^2\beta/2m}\,dp_x \int_{-\infty}^{\infty} e^{-p_y^2\beta/2m}\,dp_y \int_{-\infty}^{\infty} e^{-p_z^2\beta/2m}\,dp_z$$

$$= \alpha V \int_{-\infty}^{\infty} e^{-\frac{p_x^2\beta}{2m}}\,dp_x \int_{-\infty}^{\infty} e^{-p_y^2\beta/2m}\,dp_y \int_{-\infty}^{\infty} e^{-p_z^2\beta/2m}\,dp_z$$

where V is the volume of the spatial region occupied by the gas

Each Gaussian integral gives $\sqrt{\frac{\pi 2m}{\beta}}$ Thus

$$Z_{single} = \alpha V \left(\frac{\pi 2m}{\beta}\right)^{3/2}$$

b) For distinguishable particles

$$Z = (Z_{single})^N$$

$$= \alpha^N V^N \left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

c) $$\bar{E} = -\frac{\partial}{\partial\beta}[\ln Z] = -\frac{\partial}{\partial\beta} \ln\left[\alpha^N V^N \left(\frac{2\pi m}{\beta}\right)^{3N/2}\right]$$

$$= -\frac{\partial}{\partial\beta}\left\{ \cancel{\ln[\alpha^N]} + \cancel{\ln[V^N]} + \ln\left[\frac{2\pi m}{\beta}\right]^{3N/2} \right\}$$

$$= -\frac{\partial}{\partial\beta}\left\{ \cancel{\ln[(2\pi m)^{3N/2}]} - \ln[\beta^{3N/2}] \right\}$$

$$= \frac{\partial}{\partial\beta} \frac{3N}{2} \ln[\beta]$$

$$= \frac{3N}{2}\frac{1}{\beta}$$

$$\Rightarrow \bar{E} = \frac{3N}{2} kT \qquad \Rightarrow \boxed{\bar{E} = \frac{3}{2} NkT}$$

d) $$F = E - TS$$

$$dF = dE - T\,dS - S\,dT$$

and $$dE = T\,dS - P\,dV + \mu\,dN$$

$$\Rightarrow dF = -P\,dV - S\,dT + \mu\,dN \Rightarrow P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

Then $F = -kT \ln Z$

$$= -kT \ln \left[\alpha^N V^N (2\pi m kT)^{3N/2} \right]$$

$$= -kT \left\{ \ln[\alpha^N] + \underbrace{\ln[V^N]}_{N \ln V} + \ln [2\pi m kT]^{3N/2} \right\}.$$

So

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = -kT \frac{\partial}{\partial V} N[\ln V]$$

$$= -\frac{NkT}{V}$$

and $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \Rightarrow P = \frac{NkT}{V} \Rightarrow PV = NkT$

d) $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \frac{\partial}{\partial N}(-kT \ln Z)$

$$= -kT \frac{\partial}{\partial N} \ln \left[\alpha^N V^N (2\pi m kT)^{3N/2} \right]$$

$$= -kT \frac{\partial}{\partial N} N \ln \left[\alpha V (2\pi m kT)^{3/2} \right]$$

$$= -kT \ln \left[\alpha V (2\pi m kT)^{3/2} \right] - kTN \frac{\partial \alpha}{\partial N}$$

This would require α.

Also note that

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

$$= -\frac{\partial}{\partial T}\left[-kT \ln Z\right]$$

$$= k\frac{\partial}{\partial T}\left[T \ln[\alpha^N V^N (2\pi m kT)^{3N/2}]\right]$$

$$= k\frac{\partial}{\partial T}\left\{T\, N \ln\left[\alpha V (2\pi m kT)^{3/2}\right]\right\}$$

$$= Nk \ln\left[\alpha V (2\pi m kT)^{3/2}\right]$$

$$+ NkT\ \frac{3}{2}\frac{1}{T}$$

$$= \frac{3}{2}Nk + Nk \ln\left[\alpha V (2\pi m kT)^{3/2}\right]$$

This also requires α. Note that it requires α depend on N since if it were not as V and N both double the entropy would not double.

These issues can partly be resolved via a semi-classical particle in a well approach

Semiclassical canonical ensemble approach

In the semiclassical approach we consider a particle in a three dimensional infinite well. Here the energy eigenstates are labeled by $n_x, n_y, n_z = 1, 2, 3, 4, \ldots$ and these have energy

$$E = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

Then the partition function for a single particle is:

$$Z_{single} = \sum_{\text{all states}} e^{-E_s \beta}$$

$$= \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta h^2 n_x^2/8mL^2}\, e^{-\beta h^2 n_y^2/8mL^2}\, e^{-\beta h^2 n_z^2/8mL^2}$$

$$= \sum_{n_x=1}^{\infty} e^{-h^2 n_x^2 \beta/8mL^2} \sum_{n_y=1}^{\infty} \cdots$$

$$= \left[\sum_{n=1}^{\infty} e^{-\beta h^2 n^2/8mL^2}\right]^3$$

We will need to approximate

$$S = \sum_{n=1}^{\infty} e^{-\beta h^2 n^2/8mL^2}$$

with an integral

Then consider

$$\frac{h^2\beta}{8mL^2} = \frac{h^2}{8mkT}\,\frac{1}{L^2}$$

and with

$$\left.\begin{aligned} h &\sim 10^{-33} \\ m &\sim 10^{-26} \\ k &\sim 10^{-23} \\ T &\sim 10^{2} \end{aligned}\right\} \quad \frac{h^2}{8mkT} \approx 10^{-19} \ll 1$$

So letting $\alpha^2 = \dfrac{h^2\beta}{8mL^2}$ i.e. $\alpha = \sqrt{\dfrac{h^2\beta}{8mL^2}}$ we have $\alpha \ll 1$.

So

$$\sum_{n=1}^{\infty} e^{-\alpha^2 n^2} \approx \int_0^{\infty} dn\, e^{-\alpha^2 n^2} = \frac{1}{2}\sqrt{\frac{\pi}{\alpha^2}} = \frac{1}{2\alpha}\sqrt{\pi}$$

Thus

$$S = \frac{1}{2}\sqrt{\frac{8mL^2\pi}{h^2\beta}} = \frac{1}{2}\sqrt{\frac{8mL^2\pi}{(\hbar 2\pi)^2\beta}} = \sqrt{\frac{mL^2}{2\pi\hbar^2\beta}}$$

So

$$Z_{single} = \left(\frac{mL^2}{2\pi\hbar^2\beta}\right)^{3/2} = V\left[\frac{m}{2\pi\hbar^2\beta}\right]^{3/2}$$

Then for the ensemble

$$Z = (Z_{single})^N = V^N\left[\frac{m}{2\pi\hbar^2}\right]^{3N/2} \beta^{-3N/2}$$

Again:

$$\bar{E} = -\frac{\partial}{\partial\beta}\ln Z \quad \Rightarrow \quad \bar{E} = \frac{3}{2}NkT$$

Now

$$F = -kT\ln Z$$

$$= -NkT\left\{\ln V + \ln\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} - \frac{3}{2}\ln\beta\right\}$$

$$= -NkT\left\{\ln V + \ln\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} + \frac{3}{2}\ln(kT)\right\}$$

So

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} \quad \Rightarrow \quad PV = NkT$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} \quad \Rightarrow \quad S = Nk\left\{\ln V + \ln\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} + \frac{3}{2}\ln kT\right\} + \frac{3}{2}Nk$$

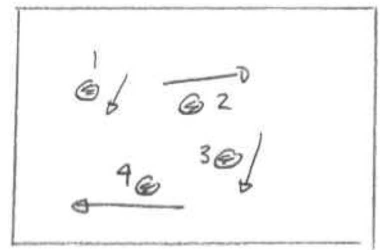
(still not extensive)

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -kT\left\{\ln V + \ln\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} + \frac{3}{2}\ln(kT)\right\}$$

and μ also lacks the property (double V, double N $\Rightarrow$ μ same).

Velocity Probability Distributions.

Consider a gas consisting of many identical molecules. The gas is at a known temperature, T. This is related to the mean energy of the gas which will be related to the kinetic energies of the molecules. Since the average is over an ensemble, the velocities within the gas will fluctuate. We can ask



$$E = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} + \cdots$$

$$\bar{E} = \frac{3}{2} NkT.$$

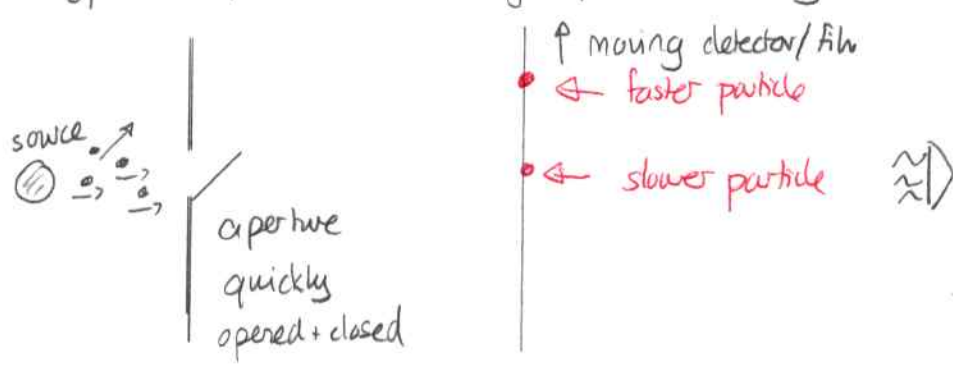
* "What is the distribution of velocities?"
* " " " " " of speeds?"
* " " " the mean speed?"

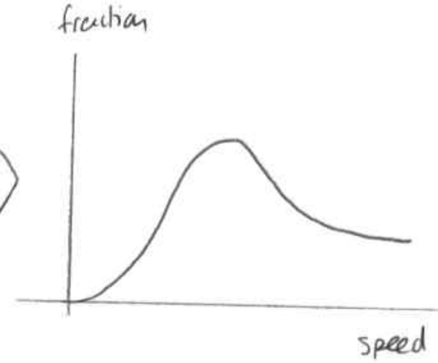
These can be calculated and checked experimentally

Experiments of this type have been done since the 1920s.

1) Eldridge, Phys Rev 30, pg 931 (1927)
2) Stern, Z. Physik, 2, 49 (1920)
3) Zaartman, Phys Rev 37, pg 383 (1931)
4) Miller + Kusch, Phys Rev 99, pg 1314 (1955)

A typical experiment involves gas particles escaping a shutter.





We can use the canonical ensemble formalism to answer these questions. The crucial rule is

> If s is a state of a gas particle and E_s is the associated energy then the probability with which this occurs is
>
> $$P_s = Ae^{-E_s\beta}$$
>
> where $\beta = 1/kT$ and $A = 1/Z$ is a constant (here Z is the partition function

We will eventually establish the key results:

$$\text{Prob}\begin{pmatrix}\text{molecule has velocity} \\ \vec{v} \to \vec{v} + d^3\vec{v}\end{pmatrix} = \left[\frac{m\beta}{2\pi}\right]^{3/2} e^{-(v_x^2+v_y^2+v_z^2)m\beta/2}\, dv_x dv_y dv_z$$

which describes the velocity distribution. The distribution of speeds, regardless of direction is given by

$$\text{Prob}\,(\text{speed in range } v \to v+dv) = 4\pi\left(\frac{m\beta}{2\pi}\right)^{3/2} v^2 e^{-v^2 m\beta/2}\, dv$$

This gives the Maxwell probability distribution for speeds:

$$P(v) = 4\pi\left(\frac{m\beta}{2\pi}\right)^{3/2} v^2 e^{-v^2 m\beta/2}$$

Proof: (velocity / speed distributions)

The states of the molecules are described as for a classical ideal gas

Then

$$\text{Prob}\begin{pmatrix} \text{state} \\ \vec{r} \to \vec{r} + d^3\vec{r} \\ \vec{p} \to \vec{p} + d^3\vec{p} \end{pmatrix} = A e^{-\vec{p}^{\,2}\beta/2m}\, dx\, dy\, dz\, dp_x\, dp_y\, dp_z$$

Normalization gives:

$$\int \text{Prob}(\ldots) = 1 \Rightarrow \quad 1 = A \int dx \int dy \int dz \int dp_x \int dp_y \int dp_z\, e^{-p_x^2\beta/2m} e^{-p_y^2\beta/2m} \cdots$$

$$= A V \left[\frac{\pi 2m}{\beta}\right]^{3/2}$$

$$\Rightarrow \quad A = \frac{1}{V}\left[\frac{\beta}{2\pi m}\right]^{3/2}$$

So

$$\text{Prob}\begin{pmatrix} \text{state} \\ \vec{r} \to \vec{r} + d^3\vec{r} \\ \vec{p} \to \vec{p} + d^3\vec{p} \end{pmatrix} = \frac{1}{V}\left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\vec{p}^{\,2}\beta/2m}\, dx\, dy\, dz\, dp_x\, dp_y\, dp_z$$

We want the probability with which velocities occur regardless of direction. To do so

1) $p_x = m v_x \quad p_y = m v_y \quad \Rightarrow \quad dp_x = m\, dv_x$ etc..

2) eliminate position info: (integrate over all positions)

Thus

$$\text{Prob}\left(\vec{v} \to \vec{v} + d^3\vec{v}\right) = \frac{1}{V}\left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-m\left(v_x^2+v_y^2+v_z^2\right)\beta/2m}\, m^3\, dv_x\, dv_y\, dv_z$$

$$\times \underbrace{\iiint dx\, dy\, dz}_{V}$$

$$= \left(\frac{m\beta}{2\pi}\right)^{3/2} e^{-\left(v_x^2+v_y^2+v_z^2\right)m\beta/2}\, dv_x\, dv_y\, dv_z$$

In order to determine the results for speed we use polar co-ordinates for speed. Then

$$dv_x\, dv_y\, dv_z = v^2 \sin\theta\, dv\, d\theta\, d\phi$$

and we only want Prob $(v \to v+dv)$. So

$$\text{Prob}\left(v \to v+dv\right) = \int_0^{\pi} d\theta \int_0^{2\pi} d\phi \left(\frac{m\beta}{2\pi}\right)^{3/2} e^{-v^2 m\beta/2}\, v^2 \sin\theta$$

$$= 4\pi \left(\frac{m\beta}{2\pi}\right)^{3/2} v^2\, e^{-v^2 m\beta/2}\, dv \qquad \blacksquare$$

This proves the results. We can use these to:

1) determine most probable velocity via $\frac{dP}{dv} = 0$

2) mean velocity $\bar{v} = \int_0^{\infty} v\, P(v)\, dv$

3) mean KE via $\overline{v^2} = \int_0^{\infty} v^2\, P(v)\, dv$

These can be compared to observations Zeitman pg 390