Lecture

Pressure

The goal is to introduce the notion of pressure as a thermodynamic variable. Remember that the variation in terms of the thermodynamic variables of the internal energy was (in the grand canonical distribution)

$$dU = \underbrace{T\,ds}_{} + \underbrace{\mu\,d\langle N\rangle}_{} + \underbrace{\sum_{states} P_j\,dE_j}_{}$$

these two terms are already expressed in terms of averaged values; that is they are in a thermodynamic form

This terms still exhibit the probabilities P_j. We want to write this term in terms of some (still to find!) average values.

To guide our way towards the final resolution of $\sum\limits_{States} P_j \, d\bar{E}_j$, lets remember two types of energy spectra:

(1) For a <u>free</u> particle in 3-dimensions

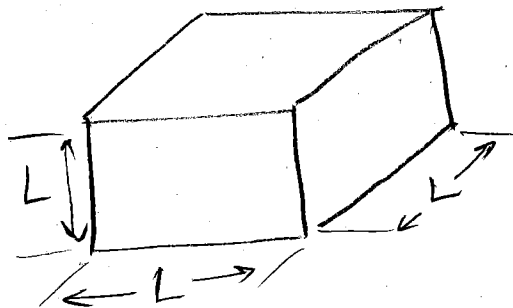$$E_j = \frac{h^2}{8mL^2} \left(n_1^2 + n_2^2 + n_3^2 \right)$$

with $j = (n_1, n_2, n_3)$

and $n_1 = 1, 2, 3, \cdots$
$n_2 = 1, 2, 3, \cdots$
$n_3 = 1, 2, 3, \cdots$

Here m is the mass of the particle which is ia a 3-dimensional box of side L

Because the volume of the box is

$$V = L^3$$

we can express the energy in terms of the volume V

$$E_j = \frac{h^2}{8m \, V^{\frac{3}{2}}} \left(n_1^2 + n_2^2 + n_3^2 \right)$$

Conclusion : E_j is a function of the volume

$$E_j (V)$$

the Volume is a thermodynamic parameter

(2) For a paramagnet, the energy was

$$E_j = - \left(\dot{J}_1 + \dot{J}_2 + \cdots + \dot{J}_N \right) B$$

with $\quad \dot{J} = \left(\dot{J}_1, \dot{J}_2, \cdots, \dot{J}_N \right)$

$$\dot{J}_k = \pm \mu \quad , \quad k = 1, \cdots, N$$

Conclusion E_j is a function of the magnetic
field B

$$E_j (B)$$

and B is a thermodynamic parameter

For other systems, the energy E_j will depend on both the volume V and the magnetic field B

$$E_j (V, B).$$

We can extend the list of thermodynamic parameters to include the electric field, for example.

$$E_j (V, B, \underbrace{x_1, x_2, \cdots, x_M})$$

other thermodynamic parameters.

Now we can go to $\sum_j P_j \, dE_j$ and put it in a form of an average value

$$\sum_j P_j \, dE_j = \sum_j P_j \left(\frac{\partial E_j}{\partial V} \, dV + \frac{\partial E_j}{\partial B} \, dB + \frac{\partial E_j}{\partial x_1} \, dx_1 + \right.$$

$$\left. + \cdots + \frac{\partial E_j}{\partial x_R} \, dx \right) =$$

$$= \left\langle \frac{\partial E_j}{\partial V} \right\rangle_{GC} dV + \left\langle \frac{\partial E_j}{\partial B} \right\rangle_{GC} dB + \left\langle \frac{\partial E_j}{\partial x_1} \right\rangle_{GC} dx_1 + \cdots +$$

$$+ \left\langle \frac{\partial E_j}{\partial x_R} \right\rangle_{GC} dx_M$$

grand canonical probability distribution

the term $\left\langle \dfrac{\partial E_j}{\partial B} \right\rangle_{GC}$ has a physical meaning:

It is $\left\langle \dfrac{\partial}{\partial B} \left[-(j_n + \cdots + j_N) B \right] \right\rangle_{GC} =$

$= -\left\langle j_n + \cdots j_N \right\rangle_{GC} = -\langle M \rangle_{GC} =$

average magnetization
in the grand canonical distribution

Likewise, the term $\left\langle \dfrac{\partial E_j}{\partial V} \right\rangle_{GC}$ has a physical meaning (a very important one!). To find its meaning, notice its contribution to the variation of the internal energy U

$$dU = Tds + \mu \, d\langle N \rangle_{GC} + \boxed{\left\langle \dfrac{\partial E_j}{\partial V} \right\rangle_{GC} dV} - \langle M \rangle_{GC} \, dB +$$

$$+ \left\langle \dfrac{\partial E_j}{\partial x_n} \right\rangle_{GC} dx_n + \cdots + \left\langle \dfrac{\partial E_j}{\partial x_R} \right\rangle dx_R$$

When we change the volume (dV) the energy will change with

$$\left\langle \frac{\partial E_j}{\partial V} \right\rangle_{GC} dV$$

From practice we know that a change in volume is related to the _pressure_ applyed to the system. Also we know that if $dV < 0$ (we reduce the volume) the energy dU increases, $dU > 0$. We will identify the _thermodynamic_ _pressure_ p with

$$\boxed{p = - \left\langle \frac{\partial E_j}{\partial V} \right\rangle_{GC}}$$

Thus

$$dU = Tds + \mu d\langle N \rangle \boxed{- pdV} - \langle M \rangle_{GC} dB +$$

$$+ \left\langle \frac{\partial E_j}{\partial x_n} \right\rangle dx_n + \cdots + \left\langle \frac{\partial E_j}{\partial x_R} \right\rangle dx_R$$

these terms will acquire a physical meaning when you give a physical meaning for $x_n, \cdots, x_R$ (which depends on your specific problems)

Important property for pressure
and grand canonical partition
function

$$pV = kT \log \Lambda$$

(*)

We will show that (*) is correct in
what follows. Before that, notice the
value of this relation. Once you computed
the grand canonical partition function Λ
and thus retain only the thermodynamic
variables, that is

$$\Lambda = \text{function of } T, \mu \text{ and } V$$

you will have a _relation between the
thermodynamic variables_

$$(\quad P \quad , \quad V \quad , T \quad , \mu \qquad)$$
$$\quad \text{pressure} \qquad \text{Volume} \quad \text{temperature} \quad \text{chemical potential}$$

You can use such a relation to find
the pressure if you know V, T, μ; or to
find μ if you know P, V and T. Such a
relation is called an _equation of state
in thermodynamics_ (of course here "state"
means a thermodynamic state P, V, T, μ, and
not a microstate).

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Now lets show that $pv = kT \log \Lambda$.

From the definition of $\Lambda(T, \mu, V)$

$$\Lambda(T, \mu, V) = \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{j_N} e^{-\beta E_{j_N}}$$

and from the fact that the energy E_{j_N} depends on the volume V, it follows that

$$\frac{\partial \Lambda}{\partial V} = \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{j_N} -\beta \frac{\partial E_{j_N}}{\partial V} e^{-\beta E_{j_N}}$$

Notice that the independent variables in Λ are T, μ and V. That is, μ and T are independent of the volume V so the derivative will act only on $E_{j_N}(V)$.

To get an average value, we devide by Λ

$$\frac{1}{\Lambda} \frac{\partial \Lambda}{\partial V} = -\sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{j_N} -\beta \frac{\partial E_{j_N}}{\partial V} \frac{e^{-\beta E_{j_N}}}{\Lambda} =$$

$$= \beta \sum_{\substack{grand \\ states}} - \frac{\partial E_{\substack{grand \\ states}}}{\partial V} \underbrace{P_{grand\,states}}_{\substack{grand \ canonical \\ probabilities}}$$

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So

$$\frac{\partial \log \Lambda}{\partial V} = \beta \left\langle - \frac{\partial E_{grand\,states}}{\partial V} \right\rangle_{GC}$$

$$\underbrace{\qquad\qquad\qquad\qquad}_{pressure}$$

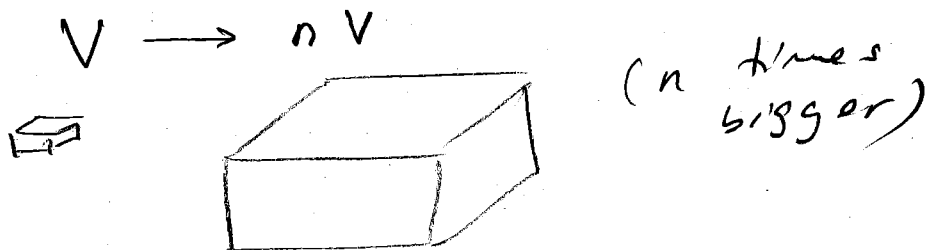$$\frac{\partial \log \Lambda}{\partial V} = \frac{1}{kT} p$$

or

$$\boxed{p = kT \frac{\partial \log \Lambda}{\partial V}}$$

this is also a good formula to find the thermodynamic equation of state. However, we can go even further to show that

$$\frac{\partial \log \Lambda}{\partial V} = \frac{\log \Lambda}{V} \qquad (**)$$

Before we show this, we will talk about the meaning of (**). It says that the grand partition function scales very simple with the volume. that is, if you increase the volume n times

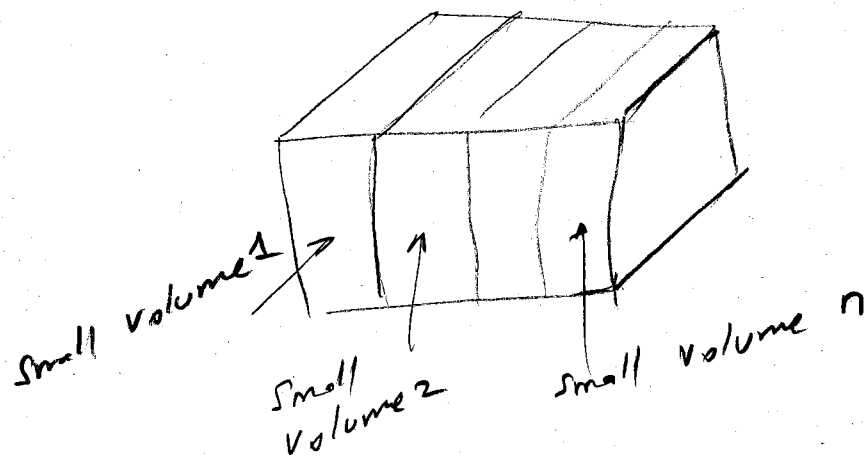$$V \longrightarrow nV$$

(n times bigger)

the logarithm of the grand canonical
partition function also increases n
times

$$\log \Delta (T, \mu, nv) = n \log \Delta (T, \mu, v)$$

In other words:

$$\log \Delta (\text{big volume}) = \sum_{\text{subsystems}} \log \Delta (\text{small volumes})$$

subsystems
of the big system

small volume 1

small volume 2

small volume n

Now (**) comes out of this scaling behavior.
Indeed, write

$$\log \Delta (T, \mu, nv) = n \log \Delta (T, \mu, v)$$

in terms of

$$V_{big} = nv$$

$$V_{small} = v$$

$$\log \Lambda (T, \mu, V_{big}) = \frac{V_{big}}{V_{small}} \log \Lambda (T, \mu, V_{small})$$
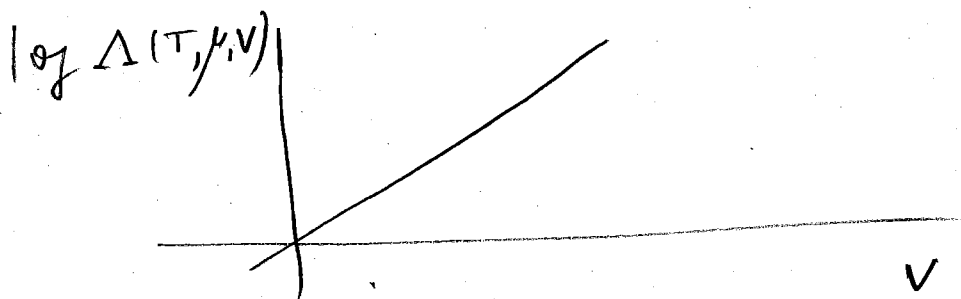
Now take $V_{small} = 1 \, m^3$ (the unit volume)

$$\log \Lambda (T, \mu, V_{big}) = V_{big} \log \Lambda (T, \mu, 1)$$

and get rid of the index "big".

For any volume V we have

$$\boxed{\log \Lambda (T, \mu, V) = V \log \Lambda (T, \mu, 1)}$$

In other words $\log \Lambda (T, \mu, V)$ is p...

simply proportional with the volume V

the result is very simple. The argument

of scaling is worth to remember.

Now the relation

$$\frac{\partial \log \Lambda (T, \mu, V)}{\partial V} = \frac{\log \Lambda (T, \mu, V)}{V}$$

is very easy to prove because of the linearity

in V.

$$\frac{\partial \log \Lambda(T, \mu, V)}{\partial V} = \log \Lambda(T, \mu, 1) = \frac{\log \Lambda(T, \mu, V)}{V}$$

To finish the proof of

$$pV = kT \log \Lambda$$

we need to show that $\log \Lambda$ has the scaling property. The argument for the scaling property is as follows.

Let us divide the volume V into n parts of equal volume $\frac{V}{n}$ by inserting walls which can transmit both heat and particles. The total system is in contact with a heat-particle source with fixed μ and T (of course, because we are in the grand canonical distribution). The macroscopic properties are not affected by the insertion of the walls. One can regard each part as independent, assuming the interaction between the system and the walls, as well as the interactions between the parts, to be weak. therefore, when $N_1, N_2, \cdots$ are distributed in the respective parts, the canonical partition function of the whole system $Z(N_1, N_2, \cdots, T, V)$ is equal to the product of the canonical partition

function of each part (see also the homework):

$$Z(N_1, N_2, \cdots, T, V) = Z(N_1, T, \tfrac{V}{n}) Z(N_2, T, \tfrac{V}{n}) \cdots$$

Substituting this into the definition of the grand canonical partition function Λ, we have

$$\Lambda(T, \mu, V) = \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{N_1 + N_2 + \cdots = N} Z(N_1, N_2, \cdots, T, V) =$$

$$= \sum_{N=0}^{\infty} e^{\beta \mu (N_1 + N_2 + \cdots)} \sum_{N_1 + N_2 + \cdots = N} Z(N_1, T, \tfrac{V}{n}) Z(N_2, T, \tfrac{V}{n}) \cdots =$$

$$= \left[\sum_{N_1 = 0}^{\infty} e^{\beta \mu N_1} Z(N_1, T, \tfrac{V}{n}) \right] \left[\sum_{N_2 = 0}^{\infty} e^{\beta \mu N_2} Z(N_2, T, \tfrac{V}{n}) \right] \cdots$$

$$= \left[\Lambda(T, \mu, \tfrac{V}{n}) \right]^n$$

So

$$\boxed{\log \Lambda(T, \mu, V) = n \log \Lambda(T, \mu, \tfrac{V}{n})}$$

If the assumptions of weak interactions that we used in proving the scaling argument are not realized in some system, then we will use

$$p = kT \frac{\partial \log \Lambda}{\partial V} \qquad (1)$$

Instead of

$$p = kT \frac{\log \Lambda}{V} \qquad (2)$$

Remember that (1) was found without the scaling argument.

More about pressure

The pressure was defined as the grand canonical average value of $-\frac{\partial E_{grand\ state}}{\partial V}$

$$P_{GC} = \left\langle - \frac{\partial E_{grand\ state}}{\partial V} \right\rangle_{GC} =$$

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{j_N} - \frac{\partial E_{j_N}}{\partial V} \frac{e^{-\beta E_{j_N}}}{\Lambda} =$$

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$$= \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{1}{\Lambda} Z_N \sum_{j_N} -\frac{\partial E_{j_N}}{\partial V} \frac{e^{-\beta E_{j_N}}}{Z_N} =$$

by inserting Z_N here we try
to get towards the canonical
distribution

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{1}{\Lambda} Z_N \left\langle -\frac{\partial E_{j_N}}{V} \right\rangle_{canonical, N}$$

So

$$\boxed{P_{grand\ canonical} = \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{Z_N}{\Lambda} P_{canonical, N}} \quad (3)$$

pressure in
the grand
canonical distribution

pressure in a canonical
distribution, for a system
with fixed N particles

We conclude that, when the system does
not exchange particles with the exterior
(canonical distribution) we need to use $P_{canonical}$

The pressure in the cononical distribution can be obtained from the canonical partition function $Z(T, V, N)$ (notice that we do not have the chemical potential μ as a variable here)

$$Z(T, V, N) = \sum_{\substack{\text{Cononical} \\ \text{states}}}' e^{-\beta E_{\text{cononical states}}}$$

So

$$\frac{\partial Z}{\partial V} = \sum_{\substack{\text{Cononical} \\ \text{states}}}' -\beta \frac{\partial E_{\text{cononical states}}}{\partial V} e^{-\beta E_{\text{Cononical states}}}$$

Divide by Z to obtain probabilities on the right side

$$\frac{1}{Z} \frac{\partial Z}{\partial V} = \beta \sum_{\substack{\text{Cononical} \\ \text{states}}}' - \frac{\partial E_{\text{cononical states}}}{\partial V} \underbrace{\frac{e^{-\beta E_{\text{cononical states}}}}{Z}}_{P_{\text{cononical state}}}$$

$$\frac{\partial \ln Z}{\partial V} = \beta \underbrace{\left\langle - \frac{\partial E_{\text{cononical states}}}{\partial V} \right\rangle_{\text{cononical}}}_{P_{\text{cononical}}}$$

So

$$\boxed{P_{\text{cononical}} = kT \frac{\partial \ln Z}{\partial V}} \qquad (4)$$

In microcanonical case, the energy is constant

$$E = \text{Constant}$$

For example, for the free particle in a box

$$E = \frac{h^2}{8MV^{\frac{2}{3}}} \cdot (n_1^2 + n_2^2 + n_3^2)$$

$$n_1 = 1, 2, - -$$
$$n_2 = 1, 2, - -$$
$$n_3 = 1, 2, - -$$

and fixing E, we can find $\Omega(E)$, the number of states (n_1, n_2, n_3) such that

$$n_1^2 + n_2^2 + n_3^2 = E \cdot \frac{8MV^{\frac{2}{3}}}{h^2} \qquad (5)$$

Because we talk about pressure now, the volume V which was fixed up to now, must be consider a parameter which can be varied. Keeping E fixed, when we vary the volume V, the radius of the sphere (5) will change, so that the number of states (n_1, n_2, n_3) that obeys (5) will depend on volume also!

$$\Omega(E, V).$$

Looking at the microconanical distribution as an approximation of the cononical one we have

$$Z \cong \Omega(E,V)\, e^{-\beta E}$$

Now the Cononical pressure can be approximated as follows

$$P_{Cononical} = kT\, \frac{\partial \ln Z}{\partial V} \underset{approximation}{\overset{\sim}{=}} kT\, \frac{\partial}{\partial V}\left(\ln \Omega(E,V) - \beta E \right) =$$

$$= kT\, \frac{\partial \ln \Omega(E,V)}{\partial V}$$

This term dissapears because $E = $ constant in microconanical distribution.

We can thus define

$$P_{microcononical} = kT\left(\frac{\partial \ln \Omega(E,V)}{\partial V} \right)_{E,N}$$

keep E and N constant