

7.4 Density fluctuations in the grand canonical ensemble

Just as we calculated $\langle \delta^2 \rangle - \langle \delta \rangle^2$ for the canonical ensemble, we can calculate $\langle N^2 \rangle - \langle N \rangle^2$ for grand canonical ensemble.

One finds (see pp. 152/153 of text):

$$\overline{(\delta N)^2} = \langle N^2 \rangle - \langle N \rangle^2 \\ = \bar{N} kT \chi_T \frac{1}{v}$$

where $\chi_T = \frac{1}{v} \left(-\frac{\partial P}{\partial v} \right)_T$ and $v = \frac{V}{N}$

↗
isothermal
compressibility

Then: $\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2} = \frac{1}{\bar{N}} kT \chi_T \frac{1}{v}$

provided this is finite (should be away from first-order phase transition), the expression vanishes in thermodynamic limit (fluctuations go to zero)

energy fluctuation: susceptibility is specific heat at constant volume

number fluctuation: susceptibility is isothermal compressibility at fixed T

One can show (in the grand canonical ensemble):

$$\overline{(\Delta E)^2} = \langle (\Delta E)^2 \rangle_{\text{can.}} + \left\{ \left(\frac{\partial u}{\partial N} \right)_{T, V} \right\}^2 \overline{(\Delta N)^2}$$

$\underbrace{\quad}_{\text{What one would get in canonical ensemble}}$

$\underbrace{\quad}_{\text{piece arising from the particle number fluctuations}}$

near phase transitions, large fluctuations can occur

The expressions given here for the fluctuations are special forms of the fluctuation-dissipation theorem.

$\underbrace{\quad}_{\text{theorem allows one to make statements about non-equilibrium properties by analyzing fluctuations of system in equilibrium}}$

Recall: Non-equilibrium situations are beyond statistical mechanics.

→ however:

certain coefficients such as diffusion coefficients that apply to non-equilibrium situations can be derived from equilibrium situation

Near phase transitions, we can do something different:

$$z^N Q_N(T, V) = e^{\beta g N} e^{-\beta A(N, V, T)}$$

probability that a system in the grand-canonical ensemble has N particles

For small density fluctuations, set $N = \bar{N}$ in last eq.:

$$\Rightarrow A(\bar{N}, V, T) = \mathcal{E}T \bar{N} \log z - \mathcal{E}T \log Q$$

$$z \text{ can be eliminated via } \bar{N} \text{ eq.} \quad \mathcal{E} = \mathcal{E}(z, V, T)$$

$$\bar{N} \text{ eq.: } \bar{N} = z \frac{\partial}{\partial z} \log(Q(z, v, T))$$

We have $U = A + TS$

$$\Rightarrow dU = dA + TdS + SdT$$

$$\Rightarrow dA + SdT = dU - TdS \quad (**)$$

Use $(**)$ in $(*)$: $dU = -PdV + TdS + \mu dN$

let $\mu > 0$: lowering of energy (negative dU)

implies reducing # of particles

let $\mu < 0$: lowering of energy (negative dU)

implies increasing # of particles

Gibbs free energy $G = A + PV$

$$\Rightarrow dG = dA + PdV + VdP$$

$$\text{or } dA = dG - PdV - VdP \quad (***)$$

Set $(*)$ and $(***)$ equal:

$$\underline{-PdV - SdT + \mu dN} = dG - \underline{PdV} - VdP$$

Rearranging:

$$dG = V dP \xrightarrow{\text{text has typo}} -SdT + \mu dN$$

Compare with

$$dA = -P dV - SdT + \mu dN$$

$$\Rightarrow \left(\frac{\partial G}{\partial N} \right)_{P,T} = \left(\frac{\partial A}{\partial N} \right)_{V,T}$$

this is one of
Maxwell's relations

Let's apply this to ideal gas:

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{V,T} = \frac{\partial}{\partial N} (-kT \log Q_N)$$

$$e^{-\beta A} = Q_N$$

$$\hookrightarrow -\beta A = \log(Q_N)$$

$$A = -kT \log(Q_N)$$

missing in text

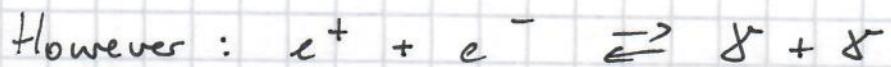
$$\left(\frac{\partial A}{\partial N}\right)_{V,T} = \dots$$

$$\Rightarrow \mu = kT \log(\lambda^3 n)$$

[87]

Conservation of particle number viewpoint:

If we have a bunch of atoms, it makes sense to speak of a definite # of atoms.



process creates / destroys electrons
and positrons (process occurs
in the interior of stars)

we have average N_{e^+} and average N_{e^-}

if N_{e^-} goes up by one, so does N_{e^+}
(and vice versa)

$\Rightarrow N_{e^-} - N_{e^+}$ is conserved and
determined by initial conditions

Use the following effective Hamiltonian:

$$\mathcal{H} = \mathcal{H}_{e^-} + \mathcal{H}_{e^+} - \mu (N_{e^-} - N_{e^+})$$



Lagrange multiplier:

introduced to enable us

to treat N_{e^-} and N_{e^+} as

"unconstrained particles"

(i.e., their values can
change)

We assume absence of interactions (note: this implies that the conversion of particles happens via "magic"):

$$\Omega = \sum_{N_{e^-}=0}^{\infty} \sum_{N_{e^+}=0}^{\infty} Q_{e^-} Q_{e^+} e^{\beta \mu (N_{e^-} - N_{e^+})}$$

$$Q_{e^-} = e^{-\beta A_{e^-}} \quad \sum_{N_{e^-}=0}^{\infty} \sum_{N_{e^+}=0}^{\infty} \exp \left[-\beta (A_{e^-} + A_{e^+} - \mu (N_{e^-} - N_{e^+})) \right]$$

$Q_{e^+} = \dots$

Conditions for equilibrium:

$$\left(\frac{\partial A_{e^-}}{\partial N_{e^-}} \right)_{T,V} = \mu$$

$$\left(\frac{\partial A_{e^+}}{\partial N_{e^+}} \right)_{T,V} = -\mu$$

these two equations determine N_{e^-} and N_{e^+}

So, we need to calculate the Helmholtz free energy:

→ we should use relativistic kinematics

→ well, we use $E = mc^2 + \frac{p^2}{2m}$ instead

$$m_{e^+} = m_{e^-} = m$$

needs to be included
since energy and
mass can be con-
verted into each
other

↑
non-rela-
tivistic

Then: $\mu = kT \log(d^3 n_{e^-}) + mc^2$

$$-\mu = kT \log(d^3 n_{e^+}) + mc^2$$

$\underbrace{\hspace{10em}}$ ideal (non-relativistic) + rest energy
 $\underbrace{\hspace{10em}}$ gas result

Where do the conditions

$$\frac{\partial A_{e^-}}{\partial N_{e^-}} = \mu \quad \text{and} \quad \frac{\partial A_{e^+}}{\partial N_{e^+}} = -\mu$$

for equilibrium come from?

Start w/ $\mathcal{G}_T = \sum_{N_{e^-}=0}^{\infty} \sum_{N_{e^+}=0}^{\infty} \exp[-\beta(A_{e^-} + A_{e^+} - \mu(N_{e^-} - N_{e^+}))]$

**

Calculate $\frac{\partial \mathcal{G}}{\partial N_{e^-}}$ and $\frac{\partial \mathcal{G}}{\partial N_{e^+}}$ and set to zero:

$$\sum_{N_{e^-}} \sum_{N_{e^+}} \left[\left(\frac{\partial A_{e^-}}{\partial N_{e^-}} \right)_{T, V} - \mu \right] e^{-\beta(A_{e^-} + A_{e^+} - \mu(N_{e^-} - N_{e^+}))} = 0$$

$$\sum_{N_{e^-}} \sum_{N_{e^+}} \left[\left(\frac{\partial A_{e^+}}{\partial N_{e^+}} \right)_{T, V} + \mu \right] e^{-\beta(A_{e^-} + A_{e^+} - \mu(N_{e^-} - N_{e^+}))} = 0$$

Keeping only the largest term in the summand, we

have: $\left(\frac{\partial A_{e^-}}{\partial N_{e^-}} \right)_{T, V} = \mu$ of Eq. (**)

$$\left(\frac{\partial A_{e^+}}{\partial N_{e^+}} \right)_{T, V} = -\mu$$

Adding the last two equations, we find

$$\text{or } \left. \begin{aligned} kT \log (\lambda^6 n_e - n_{e+}) &= -2mc^2 \\ \lambda^6 n_e - n_{e+} &= e^{-2mc^2/kT} \end{aligned} \right\}$$

What does this mean?

Rest energy of electron $\approx 6 \cdot 10^9 \text{ K}$.

\Rightarrow r. h. s. is essentially zero for ordinary temperatures

\Rightarrow either n_e^- or n_{e+} essentially zero

Thus: we can ignore anti-particles when $kT \ll mc^2$!

\leadsto this nicely confirms our intuition ...

Chemical equilibrium viewpoint:

Let's look at first second of the Universe ($T > 10^{10} \text{ K}$)

[we will be done w/this example on page 95]

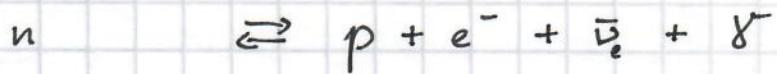
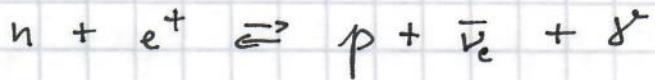
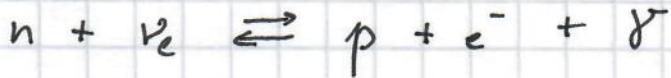
 this is before neutrons and protons combined into nuclei

$$T \approx 10^{11} \text{ K}$$

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→ there existed a so-called thermal

Beta-equilibrium mediated by the weak interactions:



neutrons and protons in equilibrium with each other and in equilibrium with photons, neutrinos, anti-neutrinos, electrons, and positrons.

We should consider μ_n , μ_p , μ_g , μ_{e^-} , μ_{e^+} , μ_{ν_e} , $\mu_{\bar{\nu}_e}$

It turns out: $\mu_8 = 0$ (zero mass particle).

$$\mu_{e^+} \approx \mu_{e^-} \approx \mu_{\nu_e} \approx \mu_{\bar{\nu}_e} = 0$$

hand waving argument: Since there were a lot more photons than baryons, $n_{e^+} \approx n_{e^-}$

Treating this as chemical equilibrium process: [92]

$$\mu_n = \mu_p$$

Again, use classical non-relativistic ideal gas
(this is pretty well justified at $T = 10^{11}$ K):

$$\mu_p = m_p c^2 + kT \log(n_p d_p^3) - \frac{1}{2}kT \log(2)$$

extra factor due
to spin- $\frac{1}{2}$
nature of proton

$$\mu_n = m_n c^2 + kT \log(n_n d_n^3) - \frac{1}{2}kT \log(2)$$

due to spin- $\frac{1}{2}$
nature of neutron

$$\text{We have: } m_n c^2 - m_p c^2 = \Delta E \approx 1.293 \text{ MeV}$$

Setting μ_p and μ_n equal, ignoring the mass difference in the thermal de Broglie wave length but keeping the mass difference in the rest energy, we find

$$m_p c^2 + \frac{1}{2}kT \log(n_p) = m_n c^2 + \frac{1}{2}kT \log(n_n)$$

$$\Rightarrow \Delta E = kT \log \left(\frac{n_p}{n_n} \right)$$

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or $\left\{ \frac{n_p}{n_n} = \exp \left(\frac{\Delta E}{kT} \right) \right\}$

We can rewrite this in terms of the baryon density n_{baryon} :

$$n_{\text{baryon}} = n_n + n_p$$

$$\Rightarrow \text{Equilibrium neutron fraction } q = \frac{n_n}{n_{\text{baryon}}} = \frac{n_n}{n_n + n_p}$$

$$= \frac{1}{1 + \frac{n_p}{n_n}}$$

$\Rightarrow \left\{ q = \frac{1}{1 + \exp \left(\frac{\Delta E}{kT} \right)} \right\}$

Boltzmann constant $k = 1.381 \cdot 10^{-23} \text{ J/K}$

$$k = 8.617 \cdot 10^{-5} \text{ eV/K} \quad (*)$$

$$k = 1.381 \cdot 10^{-16} \text{ erg/K}$$

Using (*), we find $\frac{\Delta E}{k} \approx 1.50 \cdot 10^{10} \text{ K}$

$$\left\{ \begin{array}{l} \text{For } T = 1.5 \cdot 10^{10} \text{ K}, \\ \exp(\Delta E/kT) = 1 \\ (1 + \exp(\Delta E/kT))^{-1} = 0.27 \end{array} \right\}$$

call this "crossover temperature"

for $T = 10^{11} \text{ K} \Rightarrow q \approx 46\%$

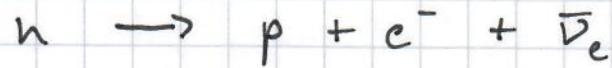
for $T = 9 \cdot 10^9 \text{ K} \Rightarrow q \approx 16\%$

$$kT \approx 0.86 \text{ MeV}$$

When the temperature fell below 10^{10} K , the weak interaction rate began to fall behind the cooling rate of the Universe

\Rightarrow baryons fell out of equilibrium w/ neutrinos

From that time onward, the neutrons began to beta decay:



natural radioactive decay
lifetime of $T_n = 886 \text{ seconds}$

Neutron fraction fell exponentially:

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$$q \approx 0.16 \exp\left(-\frac{t - t_1}{T_n}\right) \text{ for } t \geq 1s$$

with $t_1 \approx 1s$

recall: we treated
the first second
of Universe as
equilibrium process

After about 3.7 minutes, q had dropped
to 0.12.

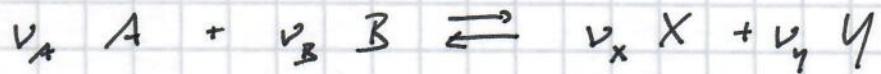
At that point, the remaining neutrons
bond with protons to form deuterons and
other light nuclei

this is referred to as
nucleosynthesis

this completes the example
we started on page 90

Let's look at chemical equilibrium condition from a more general perspective:

Let species A and B undergo the following chemical reaction



e.g.:



$$\begin{aligned} v_A &= 2; A = \text{H}_2; v_B = 1 \\ B &= \text{O}_2; v_X = 2; X = \text{H}_2\text{O}; v_Y = 0 \end{aligned}$$

species X and Y also undergo chemical reaction

v_A, v_B, v_X, v_Y are called stoichiometric coefficients

Let's say, we initially have N_A^0 atoms/molecules/particles of species A.

Similarly for N_B^0, N_X^0, N_Y^0 .

After K chemical reactions:

$$\text{Case 1: } N_A = N_A^0 - v_A K$$

$$N_B = N_B^0 - v_B K$$

$$N_x = N_x^0 + v_x K$$

$$N_y = N_y^0 + v_y K$$

→ reaction proceeds
in "positive
direction"

$$\text{Case 2: } N_A = N_A^0 + v_A K$$

$$N_B = N_B^0 + v_B K$$

→ reaction proceeds
in "negative
direction"

$$N_x = N_x^0 - v_x K$$

$$N_y = N_y^0 - v_y K$$

Let's assume that the reactions happen
at fixed temperature and fixed pressure.

Change of Gibbs free energy $G(N_A, N_B, N_x, N_y, P, T)$
is, for case 1:

$$\begin{aligned} \Delta G = & \left(-v_A \underbrace{\left(\frac{\partial G}{\partial N_A} \right)_{T,P}}_{\mu_A} - v_B \underbrace{\left(\frac{\partial G}{\partial N_B} \right)_{T,P}}_{\mu_B} \right. \\ & \left. + v_x \underbrace{\left(\frac{\partial G}{\partial N_x} \right)_{T,P}}_{\mu_x} + v_y \underbrace{\left(\frac{\partial G}{\partial N_y} \right)_{T,P}}_{\mu_y} \right) K \end{aligned}$$

In chemical equilibrium $\Delta G = 0$

Important: See page 24 of text

- For a system kept at a constant temperature and pressure, the Gibbs free energy or Gibbs potential never increases (i.e., it remains the same or decreases). $\Delta G \leq 0$
- For a system kept at constant temperature and pressure, the state of equilibrium is the state of minimum Gibbs potential or with minimal Gibbs free energy.

$$\Rightarrow \boxed{v_A \mu_A + v_B \mu_B = v_x \mu_x + v_y \mu_y} \quad (*)$$

It's easy to see that case 2 gives the same result.

Note 1: Equation $(*)$ is what we used on page 92, top, when we "demanded" $\mu_n = \mu_p$.

Note 2: We can add a catalyst to both sides of the equation

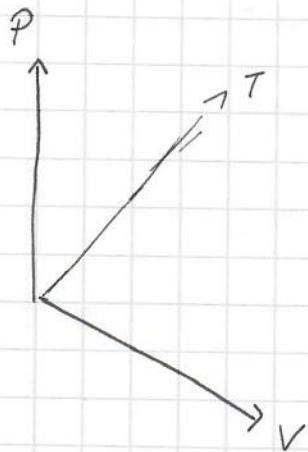


Adding the catalyst on both sides would speed up the equilibration process but would not modify the equilibrium condition $(*)$.

Ideal gas :

99a

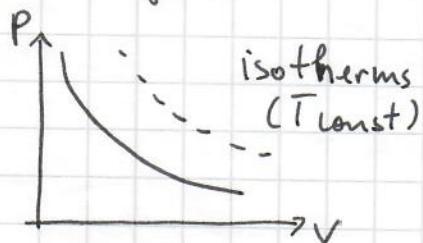
$$P V = N k T$$



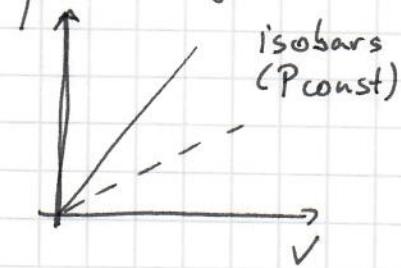
We can plot PVT surface or pressure as function of T and V

(I cannot draw this...)

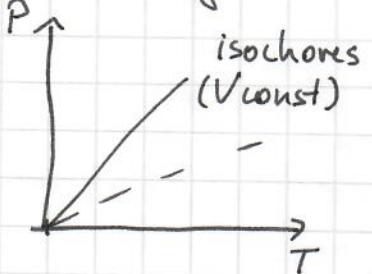
PV diagram



TV diagram



PT diagram



A bit of a detour...(this first detour ends
on page 104)

What is an "equation of state"?

The equation of state constraints the smallest number of observables required to characterize a given "state" or phase of a given substance.

E.g.: Pressure and temperature of any given gas are related to its density in thermodynamic equilibrium by a simple formula.

$$\rightsquigarrow \text{ideal gas } P V = N k T$$

$$\frac{P}{kT} = n$$

Once two variables are specified, the third one is as well

$$\text{more generally: } \frac{P}{kT} = n f(n, T)$$

↗
some, in general, un-known function

Immediate consequence:

$\frac{\partial V}{\partial P}$ and $\frac{\partial V}{\partial T}$ are not independent

(this is just one example)

Let's fix N . A generic equation of state of a gas can then be written as

$$f(P, V, T) = 0$$

 this is not the same f as on previous page!

Now, let's change P by dP , V by dV , and T by dT . $\Rightarrow f$ changes by df :

$$df = \left(\frac{\partial f}{\partial P}\right)_{V,T} dP + \left(\frac{\partial f}{\partial V}\right)_{P,T} dV + \left(\frac{\partial f}{\partial T}\right)_{V,P} dT$$



must be zero: we can think of $f(P, V, T) = 0$ as the equation that constraints to a hyper-surface in the three-dimensional P, V, T space. By definition of e-o-s, the system is in equilibrium only on this hyper-surface.

Thus: the condition $d\mathfrak{f} = 0$ constraints the variables to this hypersurface and ensures that all changes occur under conditions of thermodynamic equilibrium.

Let's imagine that P is constant:

$$\Rightarrow dP = 0$$

from *

$$\Rightarrow \left(\frac{\partial \mathfrak{f}}{\partial V} \right)_{P,T} dV + \left(\frac{\partial \mathfrak{f}}{\partial T} \right)_{V,P} dT = 0$$
$$\Rightarrow \underbrace{\left(\frac{\partial V}{\partial T} \right)_P}_{=} = \left[\left(\frac{\partial T}{\partial V} \right)_P \right]^{-1} = - \underbrace{\frac{\left(\frac{\partial \mathfrak{f}}{\partial T} \right)_{V,P}}{\left(\frac{\partial \mathfrak{f}}{\partial V} \right)_{P,T}}}_{}$$

Let's imagine that V is constant:

$$\Rightarrow \left(\frac{\partial \mathfrak{f}}{\partial P} \right)_{V,T} dP + \left(\frac{\partial \mathfrak{f}}{\partial T} \right)_{V,P} dT = 0$$

$$\Rightarrow \underbrace{\left(\frac{\partial T}{\partial P} \right)_V}_{=} = - \frac{\left(\frac{\partial \mathfrak{f}}{\partial P} \right)_{V,T}}{\left(\frac{\partial \mathfrak{f}}{\partial T} \right)_{V,P}}$$

Last, let's imagine that T is constant:

$$\Rightarrow \left(\frac{\partial f}{\partial P} \right)_{V,T} dP + \left(\frac{\partial f}{\partial V} \right)_{P,T} dV = 0$$

$$\Rightarrow \boxed{\left(\frac{\partial P}{\partial V} \right)_T = - \frac{\left(\frac{\partial f}{\partial V} \right)_{P,T}}{\left(\frac{\partial f}{\partial P} \right)_{V,T}}}$$

Multiply the l.h.s.'s and the r.h.s.'s of the last three equations in boxes:

$$\boxed{\left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_V \left(\frac{\partial P}{\partial V} \right)_T = -1}$$

this is a very general and useful "chain rule result"
(will be used on HW)

In this example, P , V , and T form an assembly.

Assembly: set of thermodynamic parameters on which a system depends.

Let x, y, z be an assembly. Then:

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

$$\left(\frac{\partial}{\partial z} \left(\left(\frac{\partial y}{\partial x}\right)_z \right)\right)_x = \left(\frac{\partial}{\partial x} \left(\left(\frac{\partial y}{\partial z}\right)_x \right)\right)_z$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

$$\left(\frac{\partial x}{\partial y}\right)_w = \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_w$$

Sometimes, the equations involving partial derivatives are referred to as "Four Famous Formulae".

They make it "easy" to derive thermodynamic relations in one assembly or to convert relations from one assembly to another.

A different but related detour...

this is a long detour - will be done on page 114

Consider internal energy U as a state function.

Independent variables are $S, V, \{N_j\}$

N_j : particle # of the j^{th} component

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, \{N_j\}} dS + \left(\frac{\partial U}{\partial V}\right)_{S, \{N_j\}} dV + \sum_j \left(\frac{\partial U}{\partial N_j}\right)_{S, V, \{N_{k+j}\}} dN_j$$

$$= T dS - P dV + \sum_j \mu_j dN_j$$

μ_j : chemical potential of j^{th} component

Internal energy U describes

adiabatic, isochoric, closed assembly.

fixed S fixed V fixed N
Some books use isentropic ($S=\text{const}$) and isochorral ($V=\text{const}$)

$$T = \left(\frac{\partial U}{\partial S}\right)_{V, N_i \neq j}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S, \{N_k\}}$$

$$\mu_j = \left(\frac{\partial U}{\partial N_j}\right)_{V, S, \{N_{k \neq j}\}}$$

$$\left(\frac{\partial}{\partial z} \left(\left(\frac{\partial y}{\partial x} \right)_z \right) \right)_x = \left(\frac{\partial}{\partial x} \left(\left(\frac{\partial y}{\partial z} \right)_x \right) \right)_z$$

We can now use the second of the "Four Famous Formulæ" to write down the Maxwell relations for the internal energy:

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

$$\left(\frac{\partial T}{\partial N_j}\right)_{S, V, \{N_{k \neq j}\}} = \left(\frac{\partial \mu_j}{\partial S}\right)_{V, \{N_k\}}$$

$$\left(\frac{\partial P}{\partial N_j}\right)_{S, V, \{N_{k \neq j}\}} = -\left(\frac{\partial \mu_j}{\partial V}\right)_{S, \{N_k\}}$$

It is not always useful or convenient to use the extensive variables $S, V, \{N_j\}$.

What if we wanted to use T, V , and $\{N_j\}$ instead?

Use $A = U - TS$

Helmholtz free energy ↑ want to get rid of
 want to bring in

$$dA = dU - d(TS)$$

$$= dU - SdT - TdS$$

$$dU = TdS - PdV + \sum_j \mu_j dN_j$$

$$+ \sum_j \mu_j N_j$$

this tells us that

$$A = A(T, V, \{N_j\})$$

We have transformed from U to A via a Legendre transformation.

The Helmholtz free energy describes an isothermal, isochoric, closed assembly.

/ / |
fixed T fixed V fixed $\{N_i\}$

From the above: $S = - \left(\frac{\partial A}{\partial T} \right)_{V, \{N_i\}}$

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T, \{N_i\}}$$

$$\mu_j = \left(\frac{\partial A}{\partial N_j} \right)_{V, T, \{N_{i \neq j}\}}$$

Maxwell relations for the Helmholtz free energy A

are: $\left(\frac{\partial S}{\partial V} \right)_{T, \{N_i\}} = \left(\frac{\partial P}{\partial T} \right)_{V, \{N_i\}}$

$$\left(\frac{\partial S}{\partial N_j} \right)_{T, V, \{N_{i \neq j}\}} = - \left(\frac{\partial \mu_j}{\partial T} \right)_{V, \{N_i\}}$$

$$\left(\frac{\partial P}{\partial N_j} \right)_{T, V, \{N_{i \neq j}\}} = - \left(\frac{\partial \mu_j}{\partial V} \right)_{T, \{N_i\}}$$

Connection of Helmholtz free energy to canonical ensemble :

$$A(T, V, \{N_j\}) = -\underbrace{kT \ln Q(T, V, \{N_j\})}$$

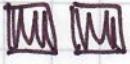
if we have only one species, we write this as

$$Q_N(T, V)$$

$$\text{where } Q(T, V, \{N_j\}) = \frac{1}{h^{3N}} \int e^{-\beta \mathcal{H}} d^{3N} p d^{3N} q \frac{1}{N_1! \dots N_n!}$$

$$\text{with } \sum_j N_j = N$$

What if we wanted to use $T, P, \{N_j\}$ instead?

 Use Gibbs free energy $G = A + PV$

want to bring in want to get rid of

$$dG = dA + d(PV)$$

$$= dA + P dV + V dP$$

$$\begin{aligned} dA &= -SdT - PdV + \sum_i \mu_i dN_i \\ &= -SdT + VdP + \sum_i g_i dN_i \end{aligned}$$

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$$\text{this tells us: } G = G(T, P, \{N_i\})$$

We have transformed from A to G via a Legendre transformation.

The Gibbs free energy describes an isothermal, isobaric, closed assembly.

$$\begin{array}{ccc} / & | & | \\ \text{fixed } T & \text{fixed } P & \text{fixed } \{N_i\} \end{array}$$

$$\text{From the above: } S = -\left(\frac{\partial G}{\partial T}\right)_{P, \{N_i\}}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{T, \{N_i\}}$$

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T, P, \{N_{i \neq i}\}}$$

Maxwell relations for the Gibbs free energy:

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

(11)

$$\left(\frac{\partial S}{\partial N_j}\right)_{T, P, \{N_{i \neq j}\}} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P, \{N_i\}}$$

$$\left(\frac{\partial V}{\partial N_j}\right)_{T, P, \{N_{i \neq j}\}} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T, \{N_i\}}$$

Aside: If we define an "isobaric partition function"

This is assuming that we have a single component system.

$$Y_N(T, P) = \frac{1}{V} \int_0^\infty e^{-\beta PV} Q_N(V, T) dV,$$

then we have

$$G(T, P, N) = -kT \log(Y_N(T, P)).$$

A few more comments on G (assume that we have only a single component):

G depends on exactly one extensive quantity, namely N .

↳ it plays an important role in phase transitions!

We will now proof $G_i = \mu N$

$$\text{Start w/ } dU = T dS - P dV + \mu dN$$

Multiply all extensive quantities by λ (e.g.,

$\lambda=2$ means doubling the size of the system):

$$d(\lambda U) = T d(\lambda S) - P d(\lambda V) + \mu d(\lambda N)$$

$$\Rightarrow \lambda \left[dU - (T dS - P dV + \mu dN) \right] = 0$$

$$= d\lambda \left[U - (TS - PV + \mu N) \right]$$

$$\text{So: } d\lambda \left[U - (TS - PV + \mu N) \right] = 0$$

Since $d\lambda$ is arbitrary, we must have

$$U - (TS - PV + \mu N) = 0$$

$$\underbrace{A}_{A = U - TS}$$

$$\Rightarrow A + PV - \mu N = 0$$

$$\underbrace{G}_{G}$$

$$\Rightarrow G_i = \mu N, \text{ which is what we wanted to show.}$$

What if we wanted to use $S, P, \{N_j\}$ instead?

Use enthalpy $H = G + TS$

want to get rid of
want to bring in

$$\begin{aligned} dH &= dG + d(TS) \\ &= dG + SdT + TdS \end{aligned}$$

$$dG = -SdT + VdP + \sum_j \mu_j dN_j$$

this tells us $H = H(S, P, \{N_j\})$

We have transformed from G to H via a Legendre transformation.

The enthalpy describes an adiabatic, isobaric, closed assembly.

/	/	/
fixed S	fixed P	fixed N_j

From the above: $T = \left(\frac{\partial H}{\partial S}\right)_{P, \{N_i\}}$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S, \{N_i\}}$$

$$\mu_j = \left(\frac{\partial H}{\partial N_j}\right)_{P, S, \{N_{i \neq j}\}}$$

Maxwell relations for the enthalpy:

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

$$\left(\frac{\partial T}{\partial N_j}\right)_{P, S, \{N_{i \neq j}\}} = \left(\frac{\partial \mu_j}{\partial S}\right)_{P, \{N_i\}}$$

$$\left(\frac{\partial V}{\partial N_j}\right)_{P, S, \{N_{i \neq j}\}} = \left(\frac{\partial \mu_j}{\partial P}\right)_{S, \{N_i\}}$$

The enthalpy is often used to analyze chemical reactions that occur at constant pressure.