$$\Rightarrow \mu = kT \ln\left[\frac{\Lambda^3 \langle N\rangle}{V}\right]$$

Grand potential

$$G = -kT \frac{Vz}{\Lambda^3}$$

Pressure $P = -\dfrac{\partial G}{\partial V} = kT \dfrac{z}{\Lambda^3} = kT \dfrac{\langle N\rangle}{V} \Rightarrow$ EOS

Can also do S, F, etc. $\Rightarrow$ consistent with canon & micro when $V \to \infty$

3.4) Thermodynamics

3.4.1) Thermodynamic variables

3 extensive variable, E, V, N & 3 intensive ones, T, p, μ.

$\Rightarrow 2^3 - 1 = 7$ ensembles with at least one extensive observable.

All these ensembles lead to thermodynamic potentials

$$\left.\begin{array}{l} (E,V,N) \to S_m \\ (T,V,N) \to F \\ (T,V,\mu) \to G \end{array}\right\} \text{etc.}$$

In the large size limit, all ensembles lead to consistent thermodynamics provided the variables are related by the saddle point relations*.

e.g. $\dfrac{1}{T} = \left.\dfrac{\partial S}{\partial E}\right|_U \Rightarrow U(T,V,N)$ relates the variables.

$F = U - TS \Rightarrow$ the Legendre transform constrains the potentials.

$\Rightarrow$ Thermodynamic variables/Functions are NOT independent.

Experiments: what you can measure

Ensemble: what you can predict

* & the thermo potentials have the right convexity properties.

The evil crime of thermodynamics.

In the thermodynamic limit, each observable can be expressed in terms of different variables.

E.g. $S_m(E,V,N)$, $S_c(T,V,N)$, $S_{GC}(T,V,\mu)$, ...

and we have seen that

$$S_{GC}(T,V,\mu) = S_C(T,V,N^*(T,V,\mu)) = S_m(E^*(T,V,\mu),V,N^*(T,V,\mu))$$

Nobody want to write that! But $\frac{\partial S}{\partial V}$ can refer to $\frac{\partial S_m}{\partial V}$, $\frac{\partial S_c}{\partial V}$, $\frac{\partial S_{GC}}{\partial V}$

that are different functions so we need to do something

Solution: $\left.\frac{\partial S}{\partial V}\right)_{X,Y}$ $\Rightarrow$ means we talk about $S(V,X,Y)$ $\Rightarrow$ unambiguous!

Using a single name makes notation light & computations difficult...

So we have many functions with the same name & dependent variables... let's see how to deal with this...

The modified chain rule

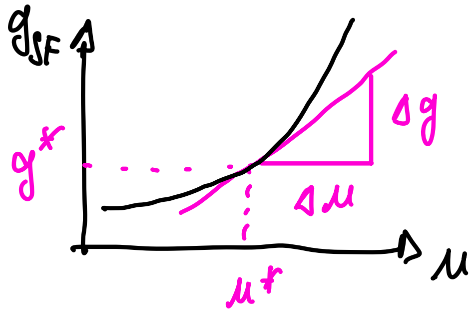
Thermodynamics relations $\Rightarrow$ dependent variables

e.g. $F = U - TS$ $\Rightarrow$ at fixed T, F, U & S are not independent

$\Leftrightarrow$ We can write this as $g(U,S,F)=0$ where $g(x,y,z) = x - Ty - z$

$$\Rightarrow dg = 0 = \frac{\partial g}{\partial u}\,du + \frac{\partial g}{\partial S}\,dS + \frac{\partial g}{\partial F}\,dF \qquad (*)$$

At fixed S & F, $g(u,S,F) = g_{SF}(u)$ is a $1d$ function



$$\frac{\partial g}{\partial \mu}\Big|_{\mu^*} = \frac{\Delta g}{\Delta \mu}$$

but also $\frac{\partial \mu}{\partial g}\Big|_{g^*} = \frac{\Delta \mu}{\Delta g} = \left(\frac{\partial g}{\partial \mu}\Big|_{\mu^*}\right)^{-1}$

$(*) \times \frac{\partial \mu}{\partial g}\Big|_{S,F} \Rightarrow d\mu = -\frac{\partial \mu}{\partial g}\Big|_{S,F}\frac{\partial g}{\partial S}\Big|_{\mu,F} dS - \frac{\partial \mu}{\partial g}\Big|_{S,F}\frac{\partial g}{\partial F}\Big|_{S,\mu} dF$

$$\Rightarrow \frac{\partial \mu}{\partial S}\Big)_{F,T} = -\frac{\partial \mu}{\partial g}\Big)_{S,F}\frac{\partial g}{\partial S}\Big)_{\mu,F}$$

Similarly ⇒ $\frac{\partial S}{\partial F}\Big)_{\mu,T} = -\left(\frac{\partial S}{\partial g}\Big)_{\mu,F}\right)^{-1}\frac{\partial g}{\partial F}\Big)_{S,\mu}$

⇒ $\frac{\partial F}{\partial \mu}\Big)_{S,T} = -\left(\frac{\partial F}{\partial g}\Big)_{S,\mu}\right)^{-1}\left(\frac{\partial g}{\partial \mu}\Big)_{S,F}\right)^{-1}$

$$\boxed{\frac{\partial \mu}{\partial S}\Big)_{F,T}\cdot\frac{\partial S}{\partial F}\Big)_{\mu,T}\cdot\frac{\partial F}{\partial \mu}\Big)_{S,T} = -1}$$

This looks like the wrong chain rule!

Also $\frac{\partial S}{\partial \mu}\Big)_{F,T} = -\frac{\partial S}{\partial F}\Big)_{\mu,T}\cdot\frac{\partial F}{\partial \mu}\Big)_{S,T}$

Proof: at fixed T $\quad dF = d\mu - T dS \Rightarrow \frac{\partial F}{\partial \mu} = 1\,;\ \frac{\partial S}{\partial F} = -\frac{1}{T}\,;\ \frac{\partial \mu}{\partial S} = T$

The standard chain rule

$$S_c(T,N,V) = S_m(E(T,V,N),N,V) \quad \text{thanks to} \quad \frac{\partial S(E,V,N)}{\partial E} = \frac{1}{T}$$

$$\Rightarrow \underbrace{\frac{\partial S_c}{\partial V}\Big)_{T,N}}_{\text{"Obvious" that this is the canonical } S} = \underbrace{\frac{\partial S_m}{\partial V}\Big)_{E,N} + \frac{\partial S_m}{\partial E}\Big)_{N,V}}_{\text{"obvious" that it is } S_m \text{ since } E,N,V \text{ are the variables}}\cdot\frac{\partial E}{\partial V}\Big)_{T,N}$$

$$\Rightarrow \frac{\partial S}{\partial V}\Big)_{T,N} = \frac{\partial S}{\partial V}\Big)_{E,N} + \frac{\partial S}{\partial E}\Big)_{N,V}\frac{\partial E}{\partial V}\Big)_{T,N}$$

$\Rightarrow$ Be careful with the functions & the variables involved!

3.4.2) Thermodynamic relations

How do we derive thermodynamic relations?

(i) chain rules

(ii) The 1st law $dU = TdS - pdV + \mu dN \Leftrightarrow dS = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN$

relate the change in energy/entropy to change in extensive variables

Comment: We can use this to change variables. If we want $U(T,V,N)$

We need to get rid of $dS \Rightarrow dS = \frac{\partial S}{\partial T}\Big|_{N,V} dT + \frac{\partial S}{\partial N}\Big|_{V,T} dN + \frac{\partial S}{\partial V}\Big|_{N,T} dV$

$$\Rightarrow dU = T\frac{\partial S}{\partial T}\Big|_{N,V} dT + \left(T\frac{\partial S}{\partial V}\Big|_{N,T} - p\right)dV + \left(T\frac{\partial S}{\partial N}\Big|_{V,T} + \mu\right)dN$$

(iii) Saddle point & Legendre transform

$F = U - TS$; $G = U - TS + \mu N$; etc.

$\Rightarrow$ from the ensembles.

(iv) Extensivity

$E(\lambda S, \lambda V, \lambda N) = \lambda E(S,V,N)$ [also works for $E(\lambda S, \lambda V, \mu)$ $= \lambda E(S,V,\mu)$]

$\frac{\partial}{\partial \lambda}$ & $\lambda = 1$

$$S\underbrace{\frac{\partial E}{\partial S}\Big|_{V,N}}_{T} + V\underbrace{\frac{\partial E}{\partial V}\Big|_{S,N}}_{-P} + N\underbrace{\frac{\partial E}{\partial N}\Big|_{SV}}_{\mu} = E(S,V,N)$$

1st principle $\Rightarrow \boxed{E = ST - PV + \mu N}$ (**)

Similarly $G(T, \lambda V, N) = \lambda G(T,V,N)$

$$\Rightarrow V \underbrace{\frac{\partial G}{\partial V}\Big|_{T,N}}_{-P} = G(T,V,N) \Rightarrow \boxed{G = -PV}$$

$\rightarrow$ fastest way to compute P!

Application: Gibbs Duhem relation

Use $(**)$ & 1st law $\Rightarrow$ $S\,dT - V\,dP + N\,d\mu = 0$

relates variations of intensive parameters.

V) Maxwell relations

For any function $X(A,B,C)$, $\frac{\partial^2 X}{\partial A \partial B} = \frac{\partial^2 X}{\partial B \partial A}$

With our notations $\frac{\partial}{\partial A}\left(\frac{\partial X}{\partial B}\Big|_{A,C}\right)\Big|_{B,C} = \frac{\partial}{\partial B}\left(\frac{\partial X}{\partial A}\Big|_{B,C}\right)\Big|_{A,C}$

Ex: $\frac{\partial E}{\partial S}\Big|_{V,N} = T$ & $\frac{\partial E}{\partial N}\Big|_{S,V} = \mu \Rightarrow \frac{\partial T}{\partial N}\Big|_{V,S} = \frac{\partial \mu}{\partial S}\Big|_{V,N}$

Application: Number fluctuations & compressibility

Grand canonical

T, V fixed $\langle N^2 \rangle_c = kT \frac{\partial \langle N \rangle}{\partial \mu}\Big|_{T,V}$ $\Rightarrow$ how to measure the r.h.s.?

Modified chain rule $\frac{\partial N}{\partial \mu}\Big|_{V,T} = -\underbrace{\frac{\partial N}{\partial V}\Big|_{\mu,T}}_{\text{extensivity} \Rightarrow \rho_0} \frac{\partial V}{\partial \mu}\Big|_{T,N} = -\rho_0 \underbrace{\frac{\partial V}{\partial P}\Big|_{T,N} \cdot \frac{\partial P}{\partial \mu}\Big|_{T,N}}_{\text{standard chain rule}}$

$\left.\frac{\partial V}{\partial p}\right|_{T,N} \Rightarrow$ measurable in experiments! Compressibility $K_T = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_{T,N}$

Maxwell relation to reexpress $\frac{\partial p}{\partial \mu}$ $\begin{matrix} \rightarrow \text{fct}^\circ \Rightarrow V \text{ variable} \\ \rightarrow \text{variable} \end{matrix}$ $\Big\}$ grand canonical

$$dG = -SdT - pdV - Nd\mu \Rightarrow \frac{\partial p}{\partial \mu} = \frac{\partial N}{\partial V} = \rho_0$$

$$\left.\frac{\partial N}{\partial \mu}\right|_{V,T} = \rho_0^2 V K_T = \frac{N^2}{V} K_T \Rightarrow \frac{\langle N^2 \rangle}{\langle N \rangle^2} = \frac{kT}{V} K_T \Rightarrow \text{can be measured!}$$

Outlook: With this, you can look at transformations brought to systems & not simply their static properties, i.e. how system evolves when the external constraints changes.

Now relevant observables:

Heat: "Energy exchanged with the environment that is not work"

$$\delta Q = dU - dW = dU - pdV - \mu dN \Rightarrow \delta Q = TdS$$

Something hard to understand precisely. Stat mech helps: canonical ensemble: energy exchange with the reservoir. Actually: work done by the degrees of freedom of the thermostat...

Study of transformation from microscopic perspective: stochastic thermodynamics.

Applications to heat engines $\Rightarrow$ thermodynamic books.