3.4) Thermodynamics throughout ensembles

energy in thermo

Micro: 3 control parameters T/U, P/V, μ/N.

thermodynamic potentials S, F, G

Thermodynamic limits: Saddle point $\Rightarrow$ thermodynamic relations

Dependent variables: The thermodynamic variables are NOT independent. There are 3 control parameters $(U/T, P/V, \mu/N)$ & the other variables are enslaved to these. (If you add observables, e.g. magnetization M & magnetic field h, you can increase the number of independent variables.)

Ensemble equivalence: upon enforcing the right relations, the microscopic origin becomes irrelevant & we can manipulate all these quantities independently of their microscopic origin.

The evil crime of thermodynamics

In the thermodynamic limit, each observable can be expressed using a wide range of variables.

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

Mathematically, these functions are all distinct, but they yield the same values thanks to the thermodynamic relations. Nobody wants to keep such a heavy notation and, instead, one writes

$S(T,V,\mu) = S(T,V,N) = S(U,V,N)$ assuming the thermodynamic relations hold. The variables define the function. But then $\frac{\partial S}{\partial V}$ can correspond to many <u>different</u> functions $\Rightarrow$ solution is to write $\left.\frac{\partial S}{\partial V}\right)_{U,N}$ to say that this is $\frac{\partial}{\partial V} S(U,V,N)$ and not $\frac{\partial}{\partial V} S(T,V,N)$. The notation is light, but it makes mathematics painful.

The standard chain rule

$S_c(T,N,V) = S_m(U(T,V,N), N, V)$ thanks to $\frac{\partial S_m}{\partial U} = \frac{1}{T}$

$$\frac{\partial S_c}{\partial V} = \frac{\partial S_m}{\partial V} + \frac{\partial S_m}{\partial U}\cdot\frac{\partial U}{\partial V} \Leftrightarrow \underbrace{\left.\frac{\partial S}{\partial V}\right)_{N,T}}_{S(V,N,T)=S_c} = \underbrace{\left.\frac{\partial S}{\partial V}\right)_{N,U}}_{S(V,N,U)=S_m} + \left.\frac{\partial S}{\partial U}\right)_{N,V}\cdot \underbrace{\left.\frac{\partial U}{\partial V}\right)_{N,T}}_{U(N,V,T)=E^*}$$

"Obviously",

The modified chain rule

Let us show that another type of chain rule exist, that reads:

!!!

$$\left.\frac{\partial S}{\partial T}\right)_{N,V} = -\left.\frac{\partial S}{\partial N}\right)_{T,V} \cdot \left.\frac{\partial N}{\partial T}\right)_{S,V} \qquad (mc_1)$$

or

$$\left.\frac{\partial S}{\partial N}\right)_{T,V} \cdot \left.\frac{\partial N}{\partial T}\right)_{S,V} \cdot \left.\frac{\partial T}{\partial S}\right)_{N,V} = -1 \qquad (mc_2)$$

S, T, N, V are 4 variables, and thus not independent. We now that $S(U,N,V)$, which can be inverted in $U(S,N,V)$

then $T = \frac{\partial U(S,N,V)}{\partial S}$ relates T, S, N, V

We write this as $g(T,S,N,V)=0$, where $g = T - \frac{\partial U(S,N,V)}{\partial S}$

and we work at fixed V so that T,S,N are not independent any more

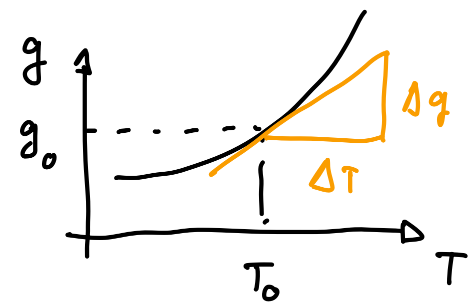
Their variations indeed have to satisfy $dg=0$ so that

$$dg = \left.\frac{\partial g}{\partial T}\right)_{S,N} dT + \left.\frac{\partial g}{\partial S}\right)_{T,N} dS + \left.\frac{\partial g}{\partial N}\right)_{S,T} dN = 0 \qquad (*)$$

Let us show that $\left.\frac{\partial T}{\partial g}\right)_{S,N} \cdot \left.\frac{\partial g}{\partial T}\right)_{S,N} = 1$.

At fixed S, N, V, $g(T,S,N,V)$ is a 1d function $g(T)$

$$\frac{\partial g}{\partial T}(T_0) = \frac{\Delta g}{\Delta T} \quad \& \quad \frac{\partial T}{\partial g}(g_0) = \frac{\Delta T}{\Delta g}$$



$$\Rightarrow \frac{\partial g}{\partial T}(T_0) = \left(\frac{\partial T}{\partial g}(g_0)\right)^{-1}$$

Take (*) & multiply by $\left.\frac{\partial T}{\partial g}\right)_{S,N}$

$$dT = -\left.\frac{\partial T}{\partial g}\right)_{S,N} \left.\frac{\partial g}{\partial S}\right)_{T,N} dS - \left.\frac{\partial T}{\partial g}\right)_{S,N} \left.\frac{\partial g}{\partial N}\right)_{S,T} dN$$

From these, we get

$$\left.\frac{\partial T}{\partial S}\right)_{N,V} = -\left.\frac{\partial T}{\partial g}\right)_{S,N} \left.\frac{\partial g}{\partial S}\right)_{T,N} \quad (1)$$

which one of the 3 factors entering mc_2. We can repeat this for the other variable

$T \to N$; $S \to T$; $N \to S$ to get $\left.\frac{\partial N}{\partial T}\right)_{S,V} = -\left.\frac{\partial N}{\partial g}\right)_{T,S} \left.\frac{\partial g}{\partial T}\right)_{N,S}$ (2)

$$\& \quad \left.\frac{\partial S}{\partial N}\right)_{T,V} = -\left.\frac{\partial S}{\partial g}\right)_{N,T} \left.\frac{\partial g}{\partial N}\right)_{T,S} \quad (3)$$

(1)×(2)×(3) $\left.\frac{\partial T}{\partial S}\right)_{N,V} \cdot \left.\frac{\partial N}{\partial T}\right)_{S,V} \cdot \left.\frac{\partial S}{\partial N}\right)_{T,V} = - \left.\frac{\cancel{\partial T}}{\cancel{\partial g}}\right)_{S,N} \left.\frac{\cancel{\partial g}}{\partial S}\right)_{T,N} \left.\frac{\partial N}{\cancel{\partial g}}\right)_{T,S} \left.\frac{\partial g}{\cancel{\partial T}}\right)_{N,S}$

$$\times \left.\frac{\cancel{\partial S}}{\partial g}\right)_{N,T} \cdot \left.\frac{\partial g}{\cancel{\partial N}}\right)_{T,S} = -1$$

$\Rightarrow$ shows (mc$_2$)

Multiplying by $\left.\frac{\partial S}{\partial T}\right)_{N,V}$ shows (mc$_1$).

The dependency by the variable lead to useful but weird formula...

3.4.2) Thermodynamic relations

What are the tools that we can use to navigate thermodynamics?

(i) chain rule (modified & standard)

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

relates the change in energy / entropy to changes in extensive variables.

Comments: We can use this to change variables

If we want $U(T,V,N)$, we need to get rid of $dS \Rightarrow S(T,V,N)$ so that

$$dS = \left.\frac{\partial S}{\partial T}\right)_{V,N} dT + \left.\frac{\partial S}{\partial V}\right)_{T,N} dV + \left.\frac{\partial S}{\partial N}\right)_{T,V} dN$$

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

(III) Saddle points & Legendre transform

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

(IV) Extensivity

$* \; E(\lambda S, \lambda V, \lambda N) = \lambda E(S,V,N)$ Taking $\frac{\partial}{\partial \lambda}$ & setting $\lambda = 1$

$$\underbrace{\underbrace{S\frac{\partial E}{\partial S}}_{T} + \underbrace{V\frac{\partial E}{\partial V}}_{-P} + \underbrace{N\frac{\partial E}{\partial N}}_{\mu}}_{1^{st}\text{ law}} = E(S,V,N) = TS - PV + \mu N \qquad (1)$$

$$\Rightarrow \mu N = E - TS - PV = F - PV$$

<u>Application:</u> Gibbs Duhem relation

Using (1) & first law: $S\,dT - V\,dP + N\,d\mu = 0$

This relates variations of intensive parameters.

$$* \; G(T,\mu,\lambda V) = \lambda G(T,\mu,V) \Rightarrow \underbrace{V\frac{\partial G}{\partial V}\Big)_{T,\mu}}_{-P} = G \Rightarrow \boxed{G = -PV}$$

$\Rightarrow$ Very useful to compute the pressure.

(V) Maxwell relations

For any function $X(A,B,C)$, $\frac{\partial^2 X}{\partial A \partial B} = \frac{\partial^2 X}{\partial B \partial A} \Leftrightarrow \frac{\partial}{\partial A}\left(\frac{\partial X}{\partial B}\Big)_{A,C}\right)_{B,C} = \frac{\partial}{\partial B}\left(\frac{\partial X}{\partial A}\Big)_{B,C}\right)_{A,C}$

Ex: $\left.\frac{\partial E}{\partial S}\right)_{V,N} = T$ & $\left.\frac{\partial E}{\partial N}\right)_{S,V} = \mu \Rightarrow \left.\frac{\partial T}{\partial N}\right)_{S,V} = \left.\frac{\partial \mu}{\partial S}\right)_{N,V}$

Applications: Number fluctuations & compressibility

Grand canonical: At fixed V&T, $\langle N^2\rangle_c = kT \left.\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V}$

How can we measure the right hand side? By relating it to measurable observables: $\rho_0 = \frac{N}{V}$ & $\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right)_{T,N}$ the compressibility

(i) modified chain rule at fixed T

$$\left.\frac{\partial N}{\partial \mu}\right)_{V,T} = -\left.\frac{\partial N}{\partial V}\right)_{\mu,T}\left.\frac{\partial V}{\partial \mu}\right)_{N,T}$$

(ii) Extensivity $\quad N(\lambda V,\mu,T) = \lambda N(V,\mu,T) \Rightarrow V\left.\frac{\partial N}{\partial V}\right)_{\mu,T} = N \Rightarrow \left.\frac{\partial N}{\partial V}\right)_{\mu,T} = \rho_0$

(iii) Standard chain rule $\quad V(\mu,N,T) = V(P(\mu,N,T),N,T)$

$$\left.\frac{\partial V}{\partial \mu}\right)_{N,T} = \left.\frac{\partial V}{\partial P}\right)_{N,T}\left.\frac{\partial P}{\partial \mu}\right)_{N,T}$$

(iv) Gibbs Duhem

$$0 = SdT - VdP + Nd\mu \overset{\text{fixed } T}{\Rightarrow} dP = \frac{N}{V}d\mu \Rightarrow \left.\frac{\partial P}{\partial \mu}\right)_{V,T} = \rho_0$$

All in all $\left.\frac{\partial N}{\partial \mu}\right)_{V,T} = -\rho_0^2(-V K_T) = \rho_0^2 K_T V = \frac{N^2}{V} K_T \simeq \frac{\langle N\rangle^2}{V} K_T$

$$\Rightarrow \frac{\langle N^2\rangle}{\langle N\rangle^2} = \frac{kT}{V} K_T \Rightarrow \text{which can be measured!}$$

Outlook: Heat engines

With all these tools & formalism, one can now study what happens when transformations are brought to a system.

In the canonical ensemble, energy is exchanged with a thermostat that may not solely happen through work $\Rightarrow$ Heat $\delta Q = dE - dW$

When the process is slow, the system remains in equilibrium and

$$dE = TdS - pdV = TdS - dW \text{, one finds } \delta Q = TdS.$$

Studying these transformations from a microscopic perspective is the goal of stochastic thermodynamics. An important application is the study of heat engines $\Rightarrow$ thermodynamics book.