NPT ensemble

(This first part is not in the movie, but useful)

$\langle V \rangle = V$ is fixed $\to$ Constraint. $\quad \langle \mathcal{E} \rangle = \mathcal{E}$ fixed

Max $\quad S = -k_B \sum_{V, r_V} p_{V, r_V} \ln p_{V, r_V}$

$$f(\{p_{V,r_V}\}) = S - \lambda \underbrace{\sum_{V, r_V} p_{V,r_V}}_{\text{norm. of } p} + k_B \beta P \underbrace{\sum_V V \sum_{r_V} p_{V,r_V}}_{\langle V \rangle} - k_B \beta \underbrace{\sum_V p_{V,r_V} \mathcal{E}_{V,r_V}}_{\langle \mathcal{E} \rangle}$$

$$\frac{\partial f}{\partial p_{V,r_V}} = 0 \Rightarrow -k_B - \lambda - k_B \ln p_{V,r_V} + k_B \beta P V - k_B \beta \mathcal{E}_{V,r_V} = 0$$

$$\Rightarrow \quad p_{V,r_V} = \frac{1}{Q} e^{+\beta P V - \beta \mathcal{E}_{V,r_V}}$$

$$Q = \sum_{V, r_V} e^{\beta P V - \beta \mathcal{E}_{V,r_V}} =$$

$$\int_0^\infty dV\, e^{\beta P V} \underbrace{\sum_{r_V} e^{-\beta \mathcal{E}_{V,r_V}}}_{Z_{can.}}$$

$G = -k_B T \ln Q$

$G(P, T, N)$

cf: $\quad Z_{gr} = \sum_N e^{\beta \mu N} \underbrace{\sum_{r_V} e^{-\beta \mathcal{E}_{N,r_N}}}_{Z_{can.}(N,V,T)}$

Legendre transformation revisited.

$\mathcal{E}(S,V)$ $\quad T = \partial\mathcal{E}/\partial S$ $\quad x = x(y,\xi)$

$f(x,\xi)$; $\quad y = \frac{\partial f}{\partial x}$. Search for $\frac{\partial f}{\partial \xi}(x,\xi) = 0$.

F $\quad$ Then $g(y,\xi) = f(x,\xi) - xy$. $= \mathcal{E} - TS$

$$\frac{\partial g}{\partial \xi} = 0 \to \underbrace{\cancel{\frac{\partial f}{\partial x}}}_{y} \cancel{\frac{\partial x}{\partial \xi}} + \frac{\partial f}{\partial \xi} - \cancel{\frac{\partial x}{\partial \xi} y} = 0.$$

Now we disregard ξ

Legendre transformation

$\to g(x,y) = f(x) - xy \qquad f''(x) < 0$ concave

$g(y) = \max_x \left(f(x) - xy\right)$

So $f'(x) - y = 0$ hence $y = f'(x)$

$$dg = \cancel{f'(x)} dx - \cancel{y\,dx} - x\,dy$$

So $\frac{dg}{dy} = -x$ and $\frac{d^2g}{dy^2} = -\frac{dx}{dy} = -\frac{1}{dy/dx} = -\frac{1}{f''(x)} > 0$

So if f concave (vex) $\to g$ convex. (cave)

Thermo: S is concave

$\mathcal{E}$ is convex as a fction of S, X_r

$F = \mathcal{E} - TS$ is concave as a fction of T

Convex as a fction of V

$G = \mathcal{E} - TS + PV$ concave as a fction of T

" " " " P.

i.e.: $\left.\frac{\partial G}{\partial P}\right)_{T,N} = V \to \left.\frac{\partial^2 G}{\partial P^2}\right)_{T,N} = \left.\frac{\partial V}{\partial P}\right)_{TN} \leq 0$

Example

$f(x) = x^2$: convex.

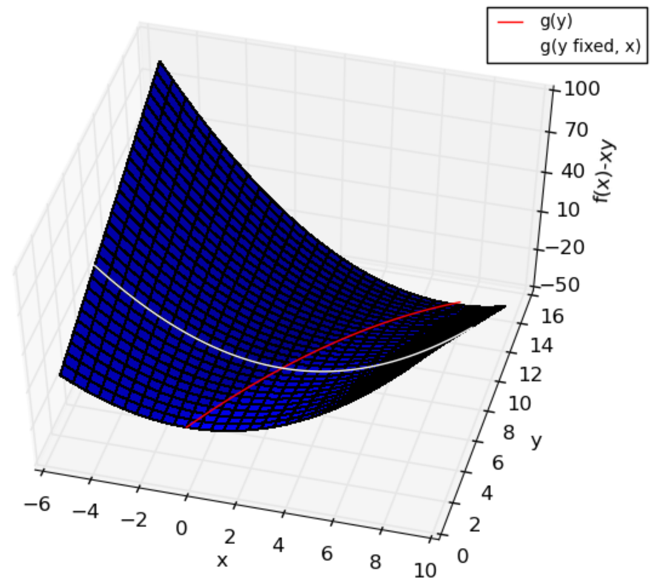
$g(x,y) = f(x) - xy$:

BLUE surface

$g(y) = \min_x g(x,y)$ $y = 2x$; $g(y) = -y^2/4$

RED curve

$\rightarrow$ CONCAVE



HOWEVER: $g(x, y \text{ fixed})$

is convex WHITE curve: convex.

Hence: $F(T,V,N)$ is convex as a fction of V

$G(T,P,N)$ is concave " " " " P

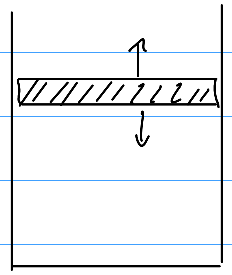
$V = \left.\frac{\partial G}{\partial P}\right)_{T,N}$ defines the equilibrium (RED curve)

However, if V deviates from this: $G(T,P,V,N)$ goes up: WHITE

$\uparrow$ fixed

We usually write $G(T,P,N)$, assuming equilibrium.

However, we can change V from its equilibrium value $V = -\left.\frac{\partial G}{\partial P}\right)_{T,N}$:



P = const (weight of piston / area)

V : varies.

Then: $G(T,P,V,N)$ convex as a fction of V

A legendre transformation turns a convex function into a concave one and vice-versa!

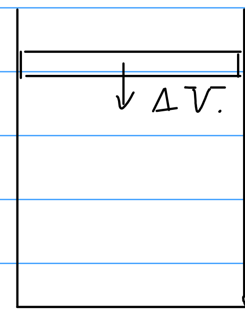
E is a convex function of S, V, N

$F = E - TS \qquad S \xrightarrow{LT} T$

F concave as a function of T.

F is still convex as a fction of V

$G = F + PV \qquad V \xrightarrow{LT} P \qquad P \neq -\left.\frac{\partial F}{\partial V}\right)_{T,N}$



P const.

G is concave as a function of P

If V changes due to a fluctuation, G goes <u>up</u>.

$F(T,V,N) = \alpha (V - V_0)^2 + \beta$

α, β may depend on T, N

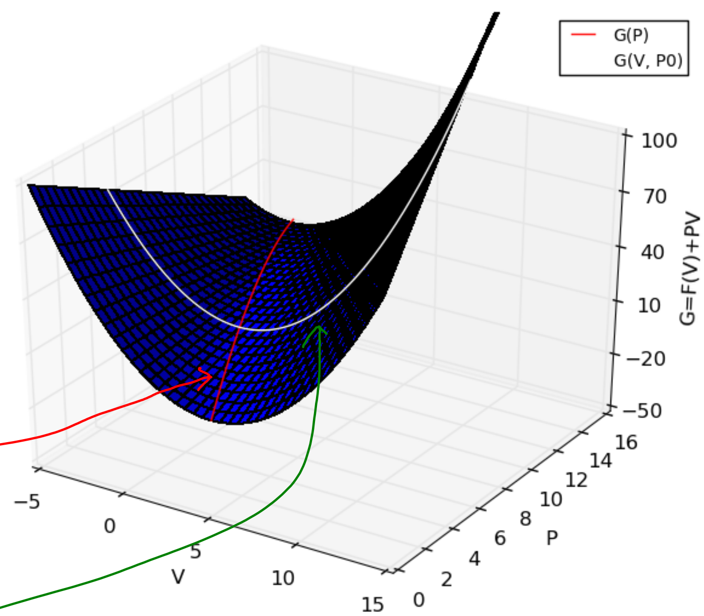
$G(P,V) = F(V) + PV$

leg. transf

$$G(P) = \min_V G(P,V) + PV$$

$$= -\frac{P^2}{4\alpha} + \beta + PV_0$$

concave



However,

fixed

$G(P,V) = \alpha (V - V_0)^2 + \beta + PV$

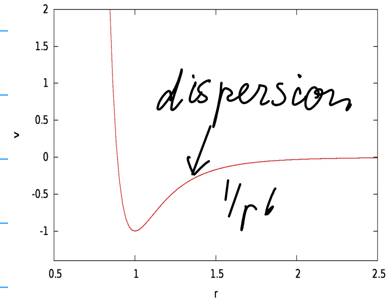
is convex as a function of V.

Van der Waals eqn of state (LN 8.2, Peliti 5.2, 5.3)

Ideal gas law $PV = Nk_BT$

Interaction between particles:

There is a repulsive core of volume $2b$
This reduces the volume available to the particles.



$$V_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$Z_{ideal} = \frac{1}{N!\,h^{3N}} \int e^{-\beta\sum_i p_i^2/2m}\, d^{3N}p \int_{V^N} d^{3N}R$$

$$= \frac{V^N}{N!\,\lambda^{3N}} \qquad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$F_{ideal} = -k_BT \ln Z = -k_BTN(\ln V - 3\ln\lambda - \ln N + 1).$$

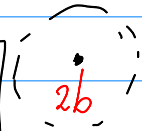
$$P = -\frac{\partial F_{id}}{\partial V} = +k_BT\frac{N}{V}$$

$$\int_{V^N} d^{3N}R \rightarrow \int_{V^N} e^{-\beta U(\underline{r}_1 \dots \underline{r}_N)}\, d^{3N}R$$

$$U(\underline{r}_1 \dots \underline{r}_N) = \sum_{i<j} v(|\underline{r}_i - \underline{r}_j|).$$

Hard core part $\rightarrow$ excluded volume $2b$.

$$\underset{\text{ideal gas.}}{\ln V^N} \Rightarrow \ln\left[V(V-2b)(V-4b)(V-6b)\cdots(V-(N-1)2b)\right]$$



$$\ln V + \ln(V-2b) + \dots + \ln(V-(N-1)2b)$$

$$\approx N \ln(V - Nb).$$

Attractive part.

$$\Delta \mathcal{E}_1 = (N-1) \int_{V-(N-1)2b} v(r) \frac{d^3 r}{V}$$ Potential due to one particle

$$\Delta \mathcal{E}_N = \frac{N(N-1)}{2V} \int v(r) d^3 r = -a \frac{N^2}{V}$$

$$e^{\beta a \frac{N^2}{V}}$$

$$\ln Z = N \ln(V - Nb) + a \frac{N^2}{V} \beta$$

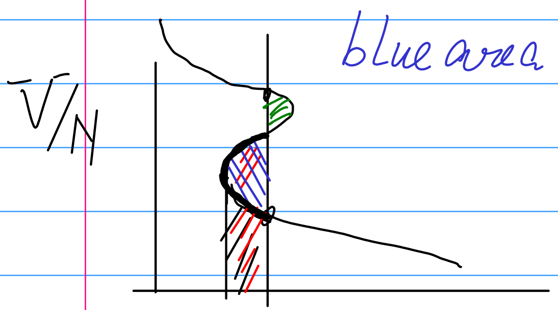
$$F = -k_B T \ln Z = -k_B T N \ln(V - Nb) - a \frac{N^2}{V}$$

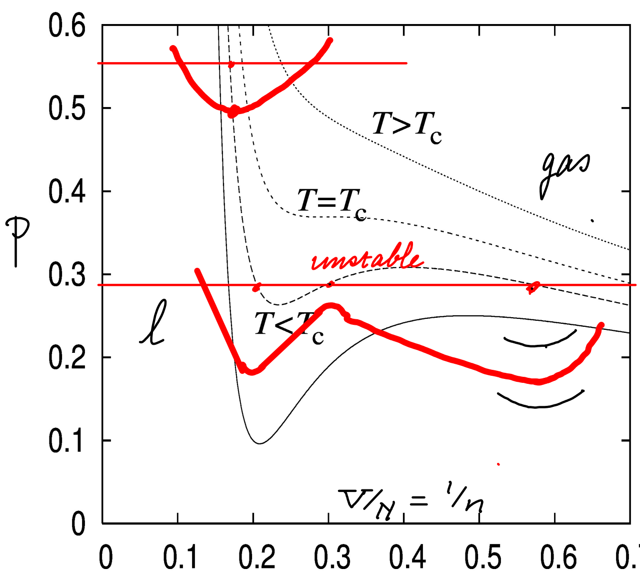
$$P = -\left.\frac{\partial F}{\partial V}\right)_{T,N} = \frac{k_B T N}{V - Nb} - a \frac{N^2}{V^2}$$

$$\left(P + a \frac{N^2}{V^2}\right)(V - Nb) = N k_B T$$

$$\mu_l = \mu_g \qquad \mu_l = \frac{G_l}{N} ; \mu_g = \frac{G_g}{N}$$

$$\Delta G = \int dG = \int -\cancel{S dT} + V dP = 0.$$





Maxwell construction.

$$\int \bar{V}\, dP = \int \bar{V} \left.\frac{\partial P}{\partial \bar{V}}\right)_{H,T} d\bar{V} = \bar{V} P \Big|_{\bar{V}_0 P_0}^{\bar{V}_1 P_0} - \int P\, d\bar{V}$$

red area

blue area + red area