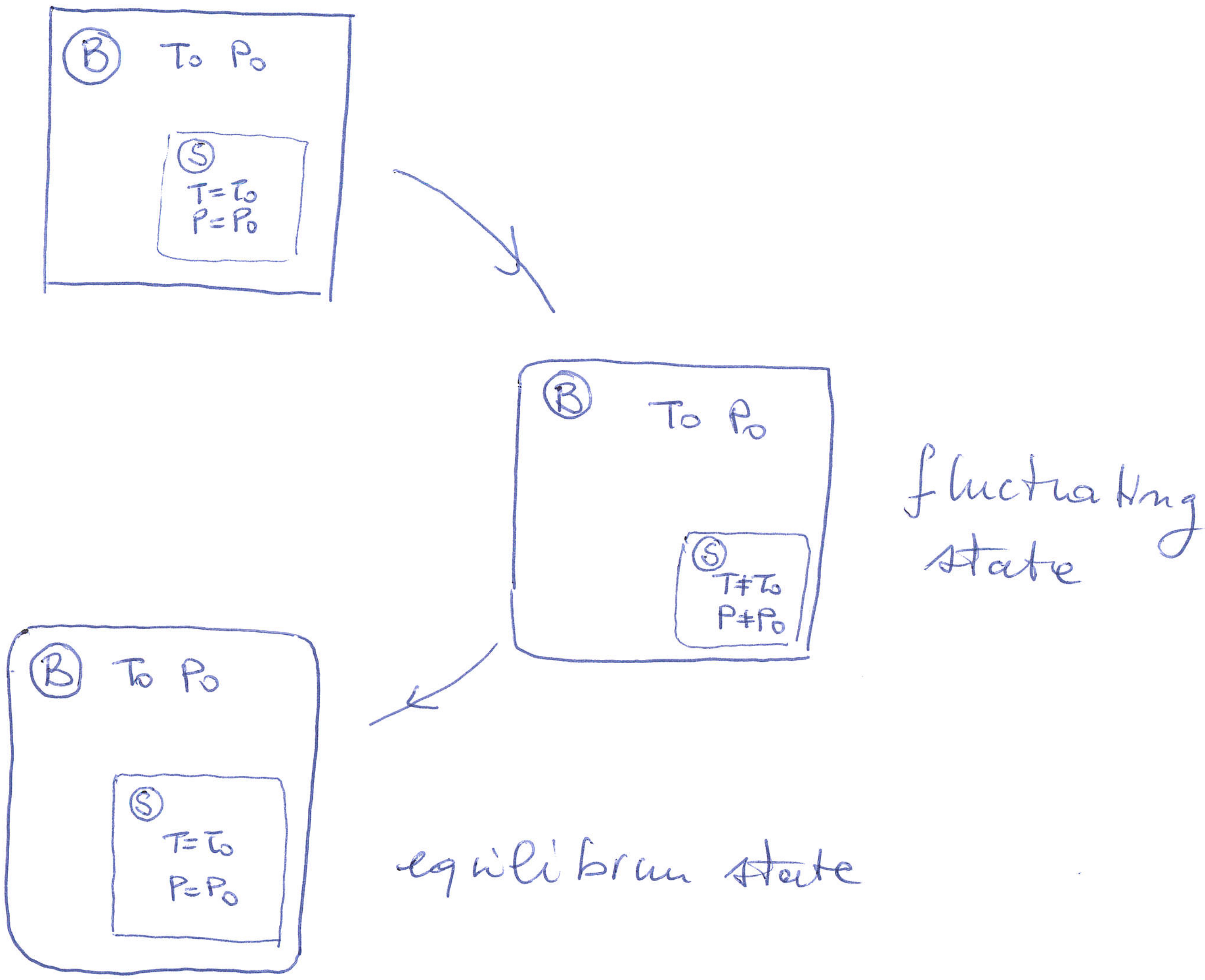
Thermodynamic Fluctuations

Fluctuations as non-equilibrium thermodynamic transformation



Thermodynamic fluctuation
=
Macroscopic fluctuation of a S as a whole

$$\Delta Q \leq T_0 \Delta S$$ system entropy irreversible

$$\Delta Q = -T_0 \Delta S_0$$ bath entropy reversible

$$0 \leq T_0(\Delta S + \Delta S_0) \qquad \Delta S_{tot} = \Delta S + \Delta S_0 \geq 0$$

if $w^* = 0$

$$\Delta A = \underbrace{\Delta U + P_0 \Delta V}_{\Delta Q = -T_0 \Delta S_0} - T_0 \Delta S \leq 0$$

$$\Delta A = -T_0 \underbrace{(\Delta S_0 + \Delta S)}_{\Delta S_{tot}} \leq 0$$

$$\boxed{\Delta A = -T_0 \Delta S_{tot}}$$ ← Availability = Total Entropy

Statistical hypothesis ← external to thermodyn!

$S = k_B \ln P$ ← Statistical Weight

$$\Delta S = k_B \ln \frac{P(B)}{P(A)} = -\frac{\Delta A}{T_0}$$

$$P(B) = P(A)\, e^{-\frac{\Delta A}{k_B T_0}}$$

for small deviations around minima ΔA is quadratic and the distribution of fluctuations is gaussian

Equilibrium

When $T=T_0$ $\quad S=S_0$

$\quad\quad\;\; P=P_0$ $\quad V=V_0$

$$\Delta A = A(S,V) - A(S_0, V_0)$$

fluctuation state (B) $\qquad$ equilibrium state (A)

$$\Delta A = \frac{1}{2}\left[\left(\frac{\partial^2 A}{\partial S^2}\right)_V \Delta S^2 + \left(\frac{\partial^2 A}{\partial V^2}\right)_S \Delta V^2 + 2\frac{\partial^2 A}{\partial V \partial S}\Delta V \Delta S\right]$$

quadratic form btw [...] can be expressed as a Jacobian $\dfrac{\partial(T,-P)}{\partial(S,V)}$

$$\Delta A = \frac{1}{2}\left[\left(\frac{\partial T}{\partial S}\right)_V \Delta S^2 - \left(\frac{\partial P}{\partial V}\right)_S \Delta V^2 + \underbrace{\left(\frac{\partial T}{\partial V}\right)_S \Delta S \Delta V - \left(\frac{\partial P}{\partial S}\right)_V \Delta V \Delta S}_{2\frac{\partial^2 A}{\partial S \partial V} = \frac{\partial^2 A}{\partial S \partial V} + \frac{\partial^2 A}{\partial V \partial S}}\right]$$

$$\Delta A = \frac{1}{2}\left[\Delta S \overbrace{\left(\left(\frac{\partial T}{\partial S}\right)_V \Delta S + \left(\frac{\partial T}{\partial V}\right)_S \Delta V\right)}^{\Delta T} - \Delta V \underbrace{\left(\left(\frac{\partial P}{\partial S}\right)_V \Delta S + \left(\frac{\partial P}{\partial V}\right)_S \Delta V\right)}_{\Delta P}\right]$$

$$\Delta A = \frac{1}{2}\left[\Delta S \Delta T - \Delta V \Delta P\right]$$

expressing variations in different variables allows to diagonalise the quadratic form

T, V variables

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)_V \Delta T + \left(\frac{\partial S}{\partial V}\right)_T \Delta V$$

Maxwell's relation (Helmholtz free Energy)

$$-\frac{\partial^2 F}{\partial V \partial T} = -\frac{\partial^2 F}{\partial T \partial V}$$

$$\Delta P = \left(\frac{\partial P}{\partial T}\right)_V \Delta T + \left(\frac{\partial P}{\partial V}\right)_T \Delta V$$

$$\Delta A = \frac{1}{2}\Big[\underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{c_V/T} \Delta T^2 - \underbrace{\left(\frac{\partial P}{\partial V}\right)_T}_{-\frac{1}{V\kappa_T}} \Delta V^2\Big]$$

$$P(\Delta V, \Delta T) \propto \exp\left(-\frac{\Delta A}{k_B T_0}\right) = \exp\left(-\frac{1}{2}\left(\frac{\partial S}{\partial T}\right)_V \Delta T^2 + \frac{1}{2}\left(\frac{\partial P}{\partial V}\right)_T \Delta V^2\right)$$

ΔT & ΔV are gaussian uncorrelated fluctuations

with

$\sigma_T^2 = \dfrac{k_B T^2}{C_V}$	$\sigma_V^2 = k_B T V \kappa_T$

S, P variables

$$\Delta T = \left(\frac{\partial T}{\partial S}\right)_P \Delta S + \left(\frac{\partial T}{\partial P}\right)_S \Delta P$$

Maxwell's relation (Entalpy)

$$\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial^2 H}{\partial P \partial S}$$

$$\Delta V = \left(\frac{\partial V}{\partial S}\right)_P \Delta S + \left(\frac{\partial V}{\partial P}\right)_S \Delta P$$

$$\Delta A = \frac{1}{2}\Big[\underbrace{\left(\frac{\partial T}{\partial S}\right)_P}_{T/C_P} \Delta S^2 - \underbrace{\left(\frac{\partial V}{\partial P}\right)_S}_{-V\kappa_S} \Delta V^2\Big]$$

$\sigma_S^2 = k_B C_P$
$\sigma_P^2 = \dfrac{k_B T}{V \kappa_S}$

Thermodynamic fluctuations are small

Intensive variables

$$\sigma_T^2 = \frac{k_B T^2}{C_V} \propto \frac{1}{N}$$

Extensive

$$\sigma_T, \sigma_p \propto \frac{1}{\sqrt{N}}$$

$$\sigma_p^2 = \frac{k_B T}{V \kappa_S} \propto \frac{1}{N}$$

extensive

Extensive variables

extensive

$$\sigma_V^2 = k_B T V \kappa_T$$

relative fluctuation $\quad \dfrac{\sqrt{\sigma_V^2}}{V} = \dfrac{\sqrt{k_B T \kappa_T}}{\sqrt{V}} \sim \dfrac{1}{\sqrt{N}}$

Extensive

$$\sigma_S^2 = k_B C_p$$

relative fluctuations $\quad \dfrac{\sqrt{\sigma_S^2}}{S} = \dfrac{\sqrt{k_B C_p}}{S} \sim \dfrac{1}{\sqrt{N}}$

2 thermodynamically macroscopic systems has thermodynamic fluctuations that are independent and scale as $1/\sqrt{N} \sim 1/\sqrt{V}$

Thermodynamic fluctuations & Thermodynamic responses

Extensive variables

$$\sigma_V^2 = k_B T \left(V \kappa_T \right)$$

$\left(-\frac{\partial V}{\partial P}\right)_T$

thermodyn responses

$$(dV)_T = \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\sigma_S^2 = k_B T \left(\frac{C_P}{T} \right)$$

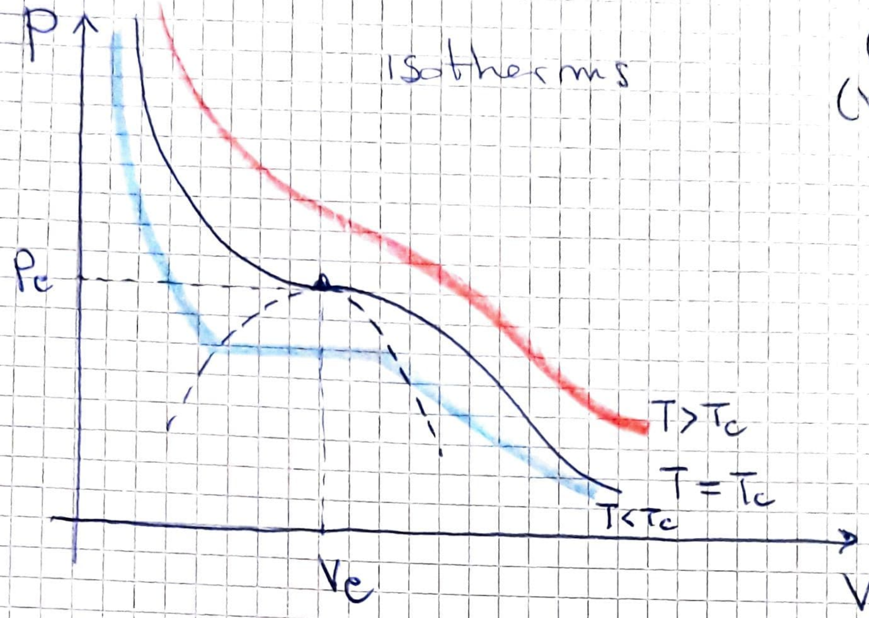
$\left(\frac{\partial S}{\partial T}\right)_P$

$$(dS)_P = \left(\frac{\partial S}{\partial T}\right)_P dT$$

(fluctuations of extensive response) = $k_B T$ (Thermodynamic Response to the conjugate ext force)

Linear Response relations in Thermodynamics

Thermodynamic fluctuations diverge at the critical point



Critical point (Water)

$P_c = 218$ Atm

$T_c = 647$ K

at critical point $\left(\frac{\partial P}{\partial V}\right)_T = 0 \Rightarrow K_T \to +\infty$

$K_T \to +\infty \quad \to \quad \sigma_V^2 \to +\infty$???

$T > T_c$ — neither gas nor liquid
a FLUID

$T = T_c$ — huge response
a small variation of $P \to$ huge var of V
large fluctuation of volume

$T < T_c$ — either gas or liquid or
coexistence