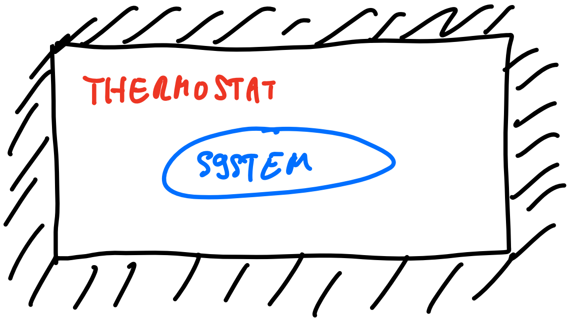



$$\boxed{P(\varphi) = \frac{1}{Z} e^{-\beta E(\varphi)}}$$

with $\beta = \frac{1}{k_B T_{th}}$ and $Z = \sum_{\varphi} e^{-\beta E(\varphi)}$

## Large systems

$$\boxed{P(E) = \frac{e^{-\frac{(E-E^*)^2}{2 k_B T^2 C_V}}}{\sqrt{2\pi C_V k_B T^2}}}$$

where $E^*$ such that

$$\boxed{\left.\frac{\partial S_m}{\partial E}\right|_{E^*} = \frac{1}{T_{th}}}$$

Since $C_V \propto N$, $\lim_{N \to \infty} P(E) = \delta(E - E^*)$

## Ensemble equivalence

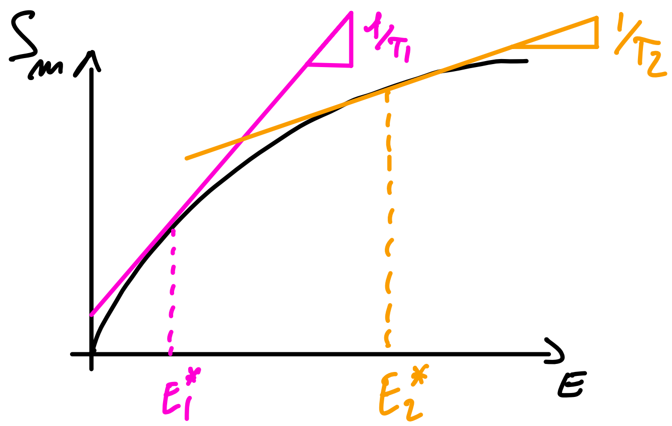
The canonical distribution at temperature $T$ converges to the microcanonical distribution at energy $E^*$ as $N \to \infty$, with $\left.\frac{\partial S}{\partial E}\right|_{E^*} = \frac{1}{T}$.

# Ensemble inequivalence

Can one find $T$ such that $P_{\text{cano}}(E) \sim \delta(E-E^*)$ for any value of $E^*$?

* Yes, if $S(E)$ is concave $\quad \frac{\partial^2 S_m}{\partial E^2} < 0 \Leftrightarrow -\frac{1}{T^2}\frac{\partial T}{\partial E} < 0 \Leftrightarrow \frac{\partial T}{\partial E} > 0$

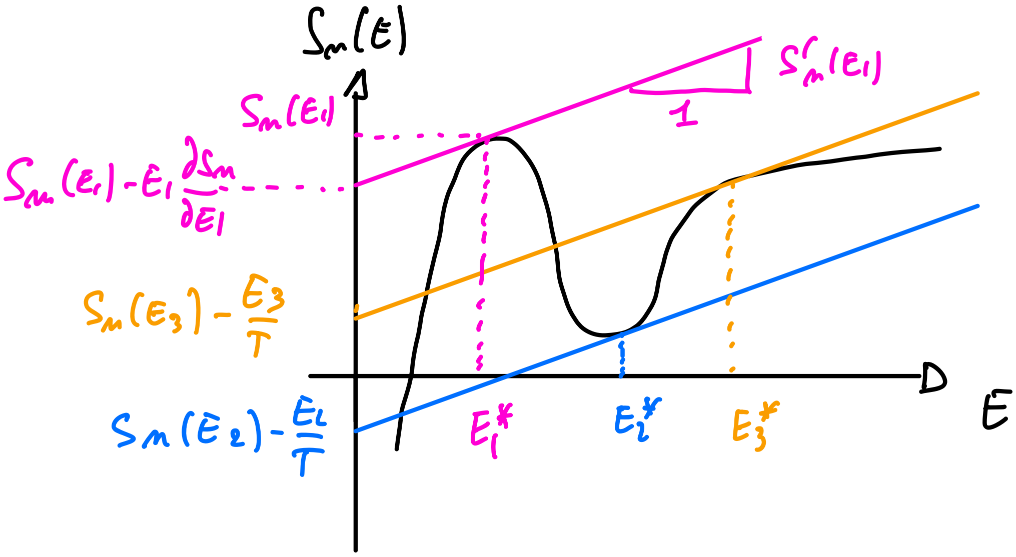
$\Rightarrow T(E)$ is then a one-to-one mapping.




As $E^*$ varies, we can vary $T$ continuously such that $\left.\frac{\partial S_m}{\partial E}\right|_{E^*} = \frac{1}{T}$

* Not for all values of $E^*$ if $S(E)$ is not convex.

Some systems, e.g. with long-range interactions, have non-concave entropies. Then, for ONE value of $T$, there might be several $E^*$ such that $\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{E^*}$

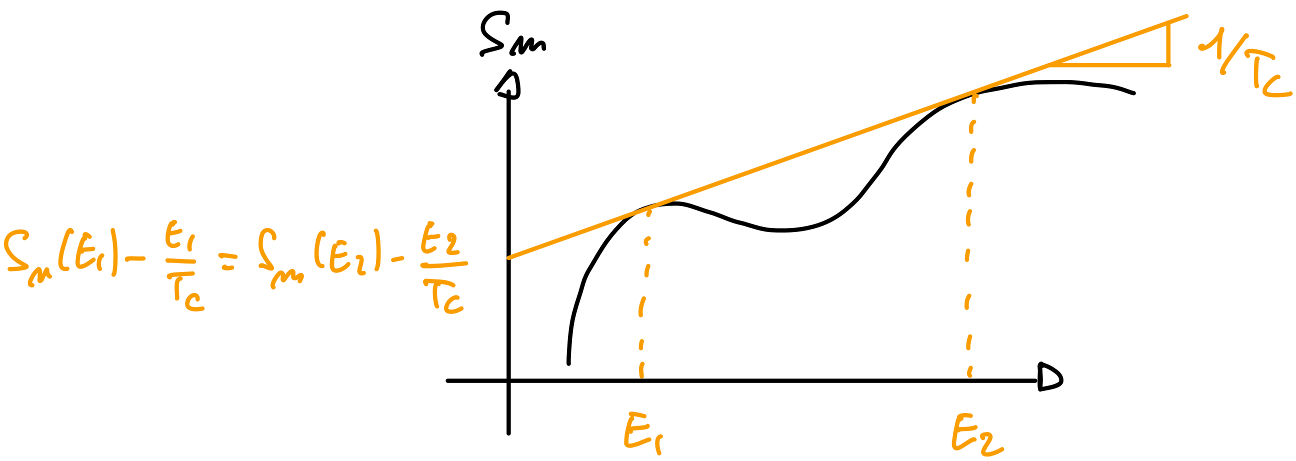



$$Z(T) = \int dE \, e^{\frac{1}{k_B}\left(S - \frac{E}{T}\right)} = e^{\frac{1}{k_B}\left(S(E^*) - \frac{E^*}{T}\right)}$$

$$E^* = \arg\max_E \left(S(E) - \frac{E^*}{T}\right)$$

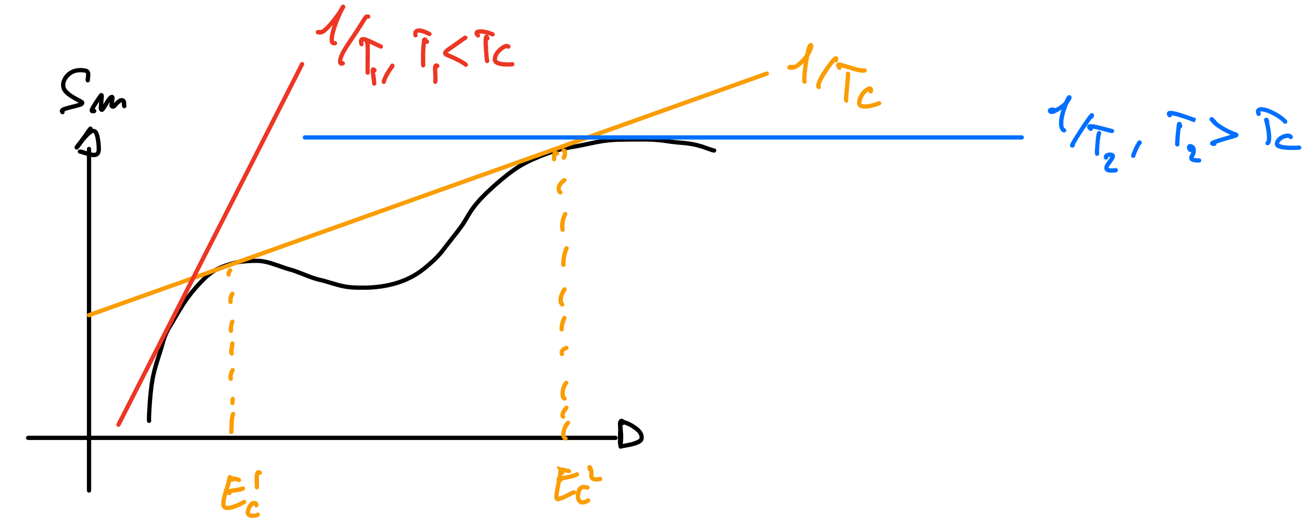
select the maximum, and not all extrema $\Rightarrow E^* = E_1^*$ in the example above

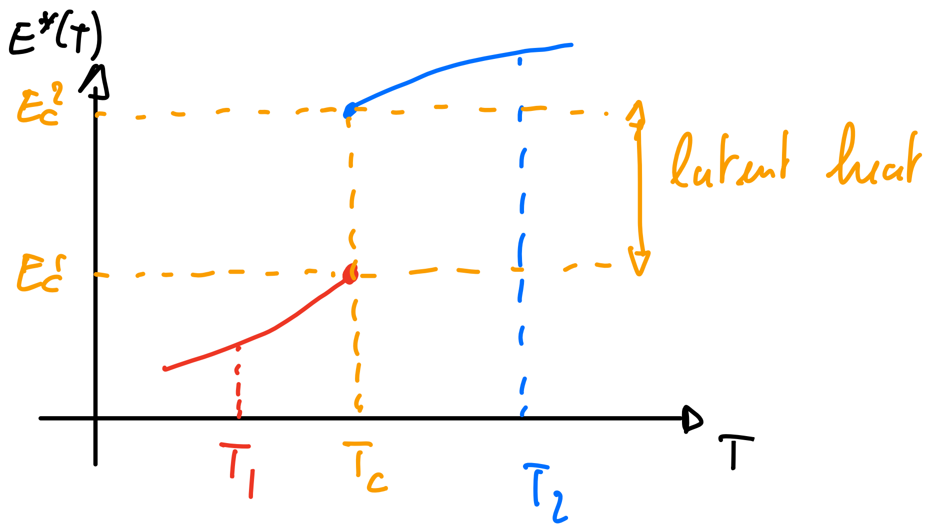
## Temperature of coexistence




When $\frac{1}{T_c}$ is tangent in two values $E_1$ & $E_2$ to $S_m(E)$, both values of the energy are equiprobable (up to the prefactors).

## Phase diagram:




As $T$ increases through $T_c$, the energy of the system discontinuously jump from $E_c^1$ to $E_c^2$.

The range of energies in $[E_c^1, E_c^2]$ are inaccessible in the canonical ensemble. [CAMPA, DAUXOIS, RUFFO, PHYS REP 480:57-159, 2009]

Ensemble inequivalence is interesting but exceptional &, from now on, we focus on the case of ensemble equivalence.

# Helmoltz free energy & Gibbs / Boltzmann entropy

Macrostate $\{q \mid E(q)=E\} \Rightarrow$ | restricted partition function
| conditional
| state

$$Z_T(E) = \sum_{q \mid E(q)=E} e^{-\beta E(q)} = \Omega(E)\, e^{-\beta E} = e^{-\beta(E - TS(E))}$$

We define $F_L(E) = E - TS(E) = -k_T \ln Z_T(E)$ the Helmoltz free energy of the macrostate $E$ or the Landau free energy of $E$ at temperature $T$.

$Z(T) = \int dE\, \omega(E)\, e^{-\beta E}$ is the Laplace transform of $\omega(E)$.

$$\simeq \int dE\, e^{-\beta F_L(E)} \underset{\text{saddle point}}{\sim} e^{-\beta F_L(E^*)}$$

$\Rightarrow F(T) = F_L(E^*)$ where $E^* = \operatorname{argmin} F_L(E)$

The free energy of the system at temperature $T$ is the Landau free energy of the macrostate with the smallest ________________. One often hears that the system has "minimized" its free energy $\Rightarrow$ that $F_L(E)$, not $F(T)$, which is fixed.

Note that, as a result $F(T) = E^* - TS(E^*)$, as in thermodynamics.

Legendre transform: $\varphi(x)$ is the Legendre transform of $\phi(y)$ if

$$\varphi(x) = \sup_y \left[ xy - \phi(y) \right]$$

Because of the saddle point,

$$-\beta F(T) = \sup_E \left[ -\beta E + \frac{S_m(E)}{k} \right] \Rightarrow$$ "$-\beta F$ is the Legendre transform of $-\frac{S_m(E)}{k}$ with respect to $-E$ ... Again, the signs & factors of $\beta$ are unfortunate... (some books use the Massieu function $\Psi = -\frac{F}{T}$ to try & fix that)

The saddle point in stat mech is why one does Legendre transform in thermodynamics $\Rightarrow$ there are microscopic systems behind these bizarre mathematical relations.

Ensemble equivalence If the entropy is concave, we can invert the relationship between F & S:

$$-k^{-1} S_m(E) = \sup_\beta \left[ \beta F(\beta) - \beta E \right]$$

More on the mathematics of ensemble equivalence in

[H. Touchette, arxiv: 0804.0327, The large deviation approach to Stat. Mech.]

## Gibbs entropy

In chapter 1, we encountered Gibbs-Shannon entropy

$$S_G = -k_B \sum_q P(q) \ln P(q)$$

In the microcanonical ensemble, $S_G = S_m$. What about here?

$$S_G(T) = -\frac{k_B}{Z} \sum_q e^{-\beta E(q)} \left[-\beta E(q) - \ln Z\right]$$

$$S_G(T) = \frac{1}{T} \langle E(q) \rangle - \frac{1}{T} F(T)$$

$S_G(T)$ is thus different from $S_m(E)$, which is not surprising: not even the same argument!

**Large N:** $\langle E \rangle \to E^*$ & $S_G(T) = \frac{E^* - F(T)}{T} = \frac{E^* - (E^* - T S_m(E^*))}{T}$

$$= S_m(E^*)$$

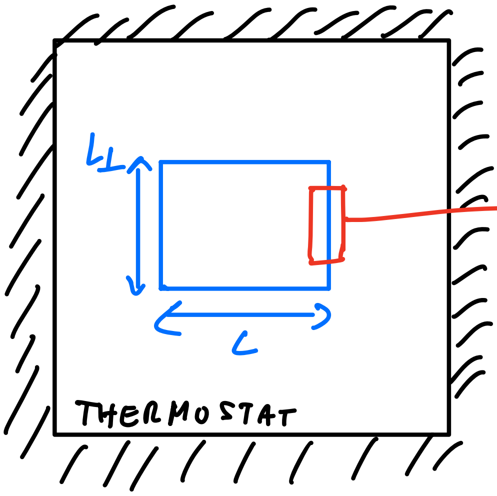
$\Rightarrow$ In the large size limit, $S_G(T)$ & $S_m(E)$ agree, provided

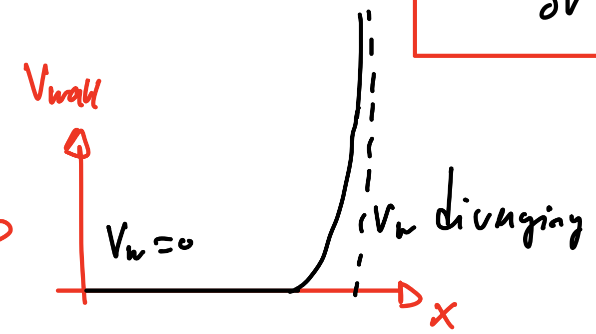
$$\frac{1}{T} = \left.\frac{\partial S_m}{\partial E}\right|_{E^*}$$

More broadly, if microcanonical & canonical ensembles are equivalent, we should be able to construct the same thermodynamics from both of them.

## 3.2.3) Thermodynamics from the canonical ensemble

**Pressure:** let us show that the pressure is $\boxed{P = -\frac{\partial F(N,V,T)}{\partial V}}$.




$$H = H_{bulk} + \sum_{i=1}^{N} V_w(x_i - L) + \text{other walls}$$

The force exerted by the wall on the particle is $F_w = -\sum_{i=1}^{N} \partial_{x_i} V_w(x_i - L)$

The pressure is the average force per unit area exerted on the wall $\Rightarrow$ $P = \frac{1}{A} \left\langle \sum_{i=1}^{N} \partial_{x_i} V_w(x_i - L) \right\rangle$ by Newton's 3rd law.

### Let us now compute $-\frac{\partial F}{\partial V}$

$V = L \times A \Rightarrow -\frac{\partial F}{\partial V} = -\frac{1}{A}\frac{\partial F}{\partial L}$ if $A$ is kept fixed.

$$-\frac{\partial F}{\partial V} = \frac{k_B T}{A}\frac{\partial \ln Z}{\partial L} = \frac{k_B T}{A Z N! h^{3N}} \frac{\partial}{\partial L} \int d\Gamma \, e^{-\beta\left[H_{bulk} + H_{\substack{other\\walls}}\right] - \beta \sum_{i=1}^{N} V_w(x_i - L)}$$

$$= \frac{1}{A Z N! h^{3N}} \int d\Gamma \sum_{i=1}^{N} V_w'(x_i - L)\, e^{-\beta H_{total}}$$

$$= \frac{1}{A} \left\langle \sum_{i=1}^{N} \partial_{x_i} V_w(x_i - L) \right\rangle = P$$