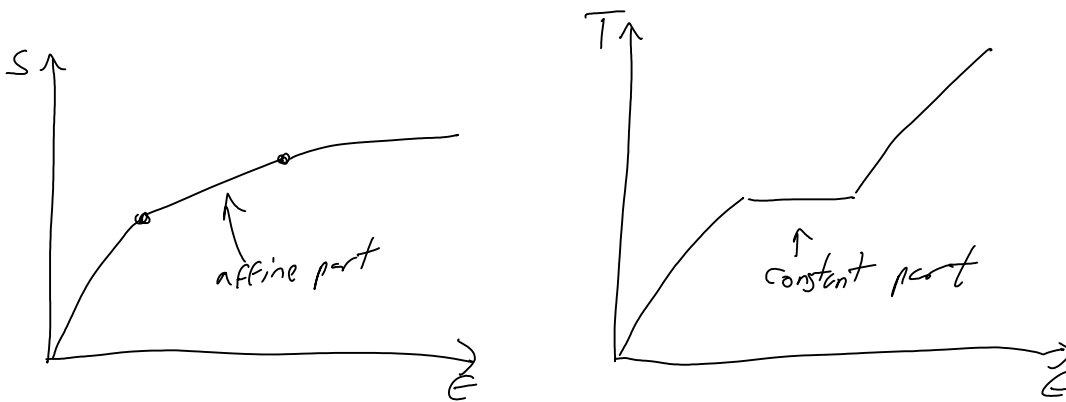


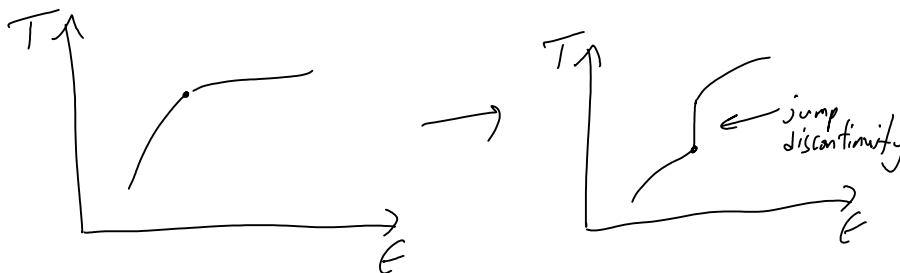
Question How do such phase transitions manifest themselves in thermodynamic functions?

Assume v is held fixed



$$\frac{\partial S}{\partial E} = \frac{1}{T} \Rightarrow \left(\text{affine pieces of the } S/E \text{ graph} \right) \Leftrightarrow \left(\text{constant pieces of the } T/E \text{ graph} \right)$$

What are points of non-diffiability of $E \rightarrow S(E)$



Does not seem to happen.

Hypothesis: $(E, v) \mapsto S$ is everywhere differentiable,
 $\Rightarrow p, T$ are cont. functions of (E, v) .

Helmholtz free energy: $F = E - TS$ or $F = E - TS$
 or, with $\beta = \frac{1}{T}$, $-\beta F = -\beta E + S$

or, with $\beta = \frac{1}{T}$, $-\beta F = -\beta E + S$

⋮

Proposition Let $u(t)$ be a convex function on $(a, b) \subset (0, \infty) \Rightarrow s \mapsto s \cdot u(1/s)$ is also convex. Equivalently, $t \mapsto t u(t)$ convex $\Rightarrow s \mapsto u(\frac{1}{s})$ convex

More generally, if $u(t, \vec{x})$ is convex on a convex domain in $(0, \infty) \times \mathbb{R}^n$, then

$(s, \vec{y}) \mapsto s u(\frac{t}{s}, \frac{\vec{x}}{s})$ is convex with a convex domain of definition.

Equivalently, $(t, \vec{x}) \mapsto t \cdot u(t, \vec{x})$ convex $\Rightarrow (s, \vec{y}) \mapsto u(s^{-1}, \vec{y})$ is convex.

pf

Follows from " $(t, \vec{x}) \mapsto (\frac{t}{t}, \frac{\vec{x}}{t})$ carries lines into lines".

Let $u(\xi)$ be a convex function of one variable set (Legendre transform)

$$\hat{u}(\eta) = \sup_{\xi} \{ \xi \eta - u(\xi) \} \quad \text{is again convex}$$

then $u \mapsto \hat{u}$ is an involution.

(ξ^*, η^*) is a "conjugate pair" if

$$\xi \mapsto (\xi \eta^* - u(\xi)) \text{ takes its supremum at } \xi^*$$

(morally, if $u(\xi^*) = \eta^*$)

$$\Leftrightarrow \hat{u}(\eta^*) = \xi^* \eta^* - u(\xi^*)$$

$$\Leftrightarrow \xi^* \eta^* - u(\xi^*) - \hat{u}(\eta^*) = 0$$

Fact: u is differentiable at ξ^* iff \hat{u} is strictly convex at η^* .

... Can be generalized to $\xi \in V$, $\eta \in V^*$ when V is a v.s. & V^* its dual.

$\beta F \Leftrightarrow$ the Legendre transform of S .

Phase transitions \Leftrightarrow non-strict concavity of S

\Leftrightarrow non-differentiability of F .