Kardar, 1.10

The Third Law

Low-temperature experiments indicate that as $T \to 0$, $\Delta S(\vec{x}, T) = \int \frac{đQ_{rev}}{T} \to 0$ for any set of coordinates $\vec{x}$.

This suggests Nernst's statement of the Third Law:

The entropy of all systems at zero absolute temperature is a universal constant that can be taken to be zero, i.e.

$$\lim_{T \to 0} S(\vec{x}, T) = 0$$

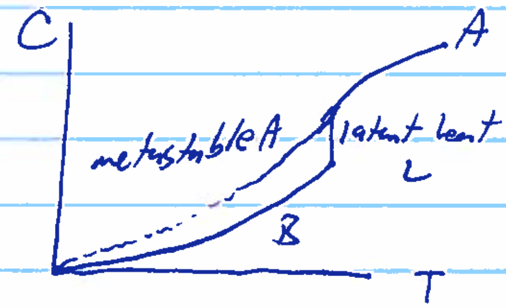
Some materials can exist in various metastable states, such as allotropes with similar crystalline structures.

As a phase A is cooled it might transition to phase B at a temperature T^*, releasing latent heat L.

Cooling rapidly can avoid the transitions with phase A remaining in metastable equilibrium.
Entropy of the two phases are related to their specific heat
$C = \frac{đQ}{dT}$; $S = \int \frac{đQ}{T} = \int dT \frac{C}{T}$:

$$S(T^* + \epsilon) = S_A(0) + \int_0^{T^*} dT' \frac{C_A(T')}{T'} = S_B(0) + \int_0^{T^*} dT' \frac{C_B(T')}{T'} + \frac{L}{T^*}$$

Measurement of heat capacities of such phases verifies $S_A(0) = S_B(0) = 0$.



Consequences of the Third Law

1. $\lim_{T\to 0} \left.\frac{\partial S}{\partial X}\right|_T = 0 \quad \forall$ coordinates X.

2. $S(T,x) - S(0,x) = \int_0^T dT' \, \frac{C_x(T')}{T'}$

   The integral would diverge as $T' \to 0$ unless

   $$\boxed{\lim_{T\to 0} C_x(T) = 0.}$$

3. Thermal expansivities also vanish as $T \to 0$.

   $$d(E - TS - Jx) = -S\,dT - x\,dJ$$

   Maxwell relation: $\left.\frac{\partial S}{\partial J}\right|_T = \left.\frac{\partial x}{\partial T}\right|_J$

   Expansivity $\alpha_J = \frac{1}{x}\left.\frac{\partial x}{\partial T}\right|_J = \frac{1}{x}\left.\frac{\partial S}{\partial J}\right|_T \xrightarrow[T\to 0]{} 0$