

Systems at zero temperature. Third law of thermodynamics

A generic system has quantised energy levels

$$\epsilon_0, \epsilon_1, \epsilon_2, \dots$$

Consider very low temperatures  $T \ll \Delta\epsilon = \epsilon_1 - \epsilon_0$

$$E = \epsilon_0$$

$$\text{Then } C_V = \left( \frac{\partial E}{\partial T} \right)_V = \left( \frac{\partial \epsilon_0}{\partial T} \right)_V = 0$$

Previously, we derived also that

$$C_P = C_V - T \frac{\left( \frac{\partial V}{\partial T} \right)_P^2}{\left( \frac{\partial V}{\partial P} \right)_T}$$

Therefore, at  $T=0$  we also have  $C_P=0$

$$\text{So, at } T=0 \quad C_P = C_V = 0$$

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$$\text{Entropy } S = \frac{E}{T} + \ln Z = \frac{\epsilon_0}{T} + \ln e^{-\frac{\epsilon_0}{T}} = 0$$

$$S = 0 - \text{Nernst theorem}$$

$$= \text{3rd law of thermodynamics}$$

(Using the thermodynamic definition we could have said that it's an arbitrary constant)

$$S \rightarrow \text{const}$$

.. .. that

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Then the meaning of the theorem is that this const is independent of other macroscopic parameters

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From this theorem it follows also that

$$\left(\frac{\partial S}{\partial P}\right)_T = 0$$

$$\parallel \leftarrow \text{Maxwell's relation}$$
$$-\left(\frac{\partial V}{\partial T}\right)_P$$

$\Rightarrow$  The thermal expansion coefficient also vanishes,  $\alpha = 0$ , at  $T = 0$

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Note: there may be a violation of the 3rd law if there is a degeneracy of the ground state.

The entropy of  $N$  qubits

$$S = N \ln 2$$