

# Statistical Physics

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## The Microcanonical Ensemble

This represents the possible states of an **isolated system** whose total **energy** is exactly specified.

**Number of states.**  $\Omega(E)$  = number of states with energy  $E$ ; have  $p(n) = \begin{cases} \frac{1}{\Omega(E)} & \text{if energy} = E(|n\rangle) \\ 0 & \text{otherwise} \end{cases}$

**Entropy.**  $S(E) = k_b \log \Omega(E)$  (additive)

**Temperature.**  $\frac{1}{T} = \frac{\partial S}{\partial E}$

**Heat capacity.**  $C = \frac{\partial E}{\partial T}$  and  $\Delta S = \int_{T_1}^{T_2} \frac{C(T)}{T} dT$

**Pressure.**  $p = T \left( \frac{\partial S}{\partial V} \right)_E$

**First Law of Thermodynamics.**  $dE = TdS - pdV$

**Heat capacity (in terms of  $S$ ).**  $C_V = T \left( \frac{\partial S}{\partial T} \right)_V$  and  $C_p = T \left( \frac{\partial S}{\partial T} \right)_p$

## The Canonical Ensemble

This represents the possible states of a system in thermal equilibrium with a **heat reservoir** at **fixed temperature**.

**Approximation for  $\Omega(E_{\text{tot}})$ .**  $\Omega(E_{\text{tot}}) \approx e^{S_R(E_{\text{tot}})/k_B} \sum_n e^{-E_n/k_B T}$

**Boltzmann distribution for CE.**  $p(n) = \frac{e^{-E_n/k_B T}}{\sum_m e^{-E_m/k_B T}}$

**Partition function.**  $Z = \sum_n e^{-\beta E_n} \implies p(n) = \frac{e^{-\beta E_n}}{Z}$  where  $\beta = 1/k_B T$

**Energy statistics for CE.**  $\langle E \rangle = -\frac{\partial}{\partial \beta} \log Z$ ,  $\Delta E^2 = -\frac{\partial}{\partial \beta} \langle E \rangle = k_B T^2 C_V$

**CE entropy.**  $S = -k_B \sum_n p(n) \log p(n)$  and  $S = k_B \frac{\partial}{\partial T} (T \log Z)$

**Free energy.**  $F = E - TS$ ,  $F = -k_B T \log Z$  (most likely  $E$  minimises  $F$ )