Lecture 18: Entropy and Statistical Mechanics

Connecting Thermo to Stat Mech

Calculating W

Formula for W

$$S = k_B \ln W$$

$$W = \frac{A!}{\prod_i a_i!} \text{ (A is total particles)}$$

$$A = \sum_i a_i \text{ (sum over microstates)}$$

$$(4,4,4,4,4) \to 1$$

$$(16,1,1,1,1) \to \binom{5}{1} = 5$$

$$(16,4,0,0,0) \to 5 \times 4 = 20$$

$$(9,9,1,1,0) \to \binom{5}{2} \times \binom{3}{1} = 30$$

$$(4,4,4,4,4) \to \frac{5!}{5!} = 1$$

$$(16,1,1,1,1) \to \frac{5!}{1! \cdot 4!} = 5$$

$$(16,4,0,0,0) \to \frac{5!}{1! \cdot 1! \cdot 3!} = 20$$

$$(9,9,1,1,0) \to \frac{5!}{2! \cdot 2! \cdot 1!} = 30$$

Derivation of Entropy from Q

Stat Mech: $q \to Q \to$ properties, Thermo: A copies, divide by A

$$W = \frac{A!}{\prod_i a_i!} \qquad A = \sum_i a_i$$

$$S_{\text{ensemble}} = k_B \ln W = k_B \ln \frac{A!}{\prod_i a_i!}$$

Using Stirling's approximation, $\ln n! \approx n \ln n - n$:

$$\begin{aligned} S_{\text{ensemble}} &\approx k_B(A \ln A - A) - k_B \sum_i (a_i \ln a_i - a_i) \\ &= k_B A \ln A - k_B A - k_B \sum_i a_i \ln a_i + k_B \sum_i a_i \\ &= k_B A \ln A - k_B \sum_i a_i \ln a_i \end{aligned}$$

Derivation of Entropy from Q

$$= k_B A \ln A - k_B \sum_i a_i \ln a_i$$

Substitute using probabilities $p_i = a_i/A$, so $a_i = p_i A$:

$$\begin{aligned} S_{\text{ensemble}} &= k_B A \ln A - k_B \sum_i p_i A \ln(p_i A) \\ &= k_B A \ln A - k_B \sum_i p_i A(\ln p_i + \ln A) \\ &= k_B A \ln A - k_B \sum_i p_i A \ln p_i - k_B \sum_i p_i A \ln A \\ &= -k_B A \sum_i p_i \ln p_i \end{aligned}$$

Dividing by A gives the entropy per system:

$$\boxed{S_{\text{system}} = -k_B \sum_i p_i \ln p_i}$$

Derivation of Entropy from Q

For a canonical ensemble with $p_i = \frac{e^{-\beta E_i}}{Q}$:

$$S = -k_B \sum_i \frac{e^{-\beta E_i}}{Q} \ln\left(\frac{e^{-\beta E_i}}{Q}\right)$$

$$= -k_B \sum_i \frac{e^{-\beta E_i}}{Q} (-\beta E_i - \ln Q)$$

$$= k_B \beta \sum_i \frac{e^{-\beta E_i}}{Q} E_i + k_B \ln Q \sum_i \frac{e^{-\beta E_i}}{Q}$$

Recognize definitions: $U = E = \sum_i p_i E_i$ and $\sum_i p_i = 1$:

$$\boxed{S = \frac{U}{T} + k_B \ln Q}$$

Derivation of Differential Entropy

$$
\begin{aligned}
S &= -k_B \sum_i p_i \ln p_i \\
dS &= -k_B \sum_i d(p_i \ln p_i) \\
&= -k_B \sum_i \left[(\ln p_i)\, dp_i + p_i\, d(\ln p_i)\right] && \text{(Product rule)} \\
&= -k_B \sum_i \left[(\ln p_i)\, dp_i + p_i \left(\frac{1}{p_i} dp_i\right)\right] \\
&= -k_B \sum_i \ln p_i\, dp_i - k_B \sum_i dp_i && \text{(Pull out the derivative)} \\
&= -k_B \sum_i \ln p_i\, dp_i - k_B\, \cancel{d\left(\sum_i p_i\right)} && \text{(Derivative of constant is 0)} \\
dS &= -k_B \sum_i \ln p_i\, dp_i
\end{aligned}
$$

Derivation of Differential Entropy

$$\begin{aligned}
p_i &= \frac{e^{-\beta E_i}}{Q} \\
\ln p_i &= -\beta E_i - \ln Q \\
\sum_i \ln p_i \, dp_i &= \sum_i (-\beta E_i - \ln Q) \, dp_i \\
&= -\beta \sum_i E_i \, dp_i - \ln Q \cancel{\left(\sum_i dp_i \right)} \\
&= -\beta \, dU
\end{aligned}$$

$dw = 0$ since work would change the energy levels E_i (volume change):

$$= -\frac{dq_{rev}}{k_B T}$$

$$\boxed{dS = \frac{dq_{\text{rev}}}{T}}$$

Major Takeaways

Key Equations

Boltzmann demonstrated that statistical mechanics and thermodynamics are consistent with each other

$$S = k_B \ln W$$

$$S = \frac{U}{T} + k_B \ln Q$$

$$S = -k_B \sum_i p_i \ln p_i$$

$$dS = \frac{dq_{\text{rev}}}{T}$$

Considering low temperature limit of S

$$S = \frac{U}{T} + k_B \ln Q$$

As $T \to 0$, only ground state is populated:

$$Q \xrightarrow{T \to 0} \Omega_0 \, e^{-E_0/k_B T}$$

$$\begin{aligned} S_0 &= \frac{U}{T} + k_B \ln\left(\Omega_0 \, e^{-E_0/k_B T}\right) \\ &= \frac{E_0}{T} + k_B \ln \Omega_0 + k_B \ln e^{-E_0/k_B T} \\ &= \frac{E_0}{T} + k_B \ln \Omega_0 - \frac{E_0}{T} \\ &= k_B \ln \Omega_0 \end{aligned}$$

Boltzmann Residual Entropy

Entropy S as $T \to 0$

$$S_0 = k_B \ln \Omega_0$$

- $\Omega_0 = 1,\ S_0 = 0 \to$ consistent with the Third Law
- $\Omega_0 > 1,\ S_0 > 0 \to$ system has disorder at $T = 0$