\[ \Omega = \Omega(E, V, N \ldots) \equiv \text{Volume of the accessible region of phase space.} \]
4. Entropy

\[ S(E, V, N) \equiv k \ln \Omega(E, V, N) \]
\[ \approx k \ln \Phi(E, V, N) \quad \text{Differ only by } \ln N \]
\[ \approx k \ln \omega(E, V, N) \]

• It is a state function.
• It is extensive.
• It is a logarithmic measure of the microscopic degeneracy associated with a macroscopic (that is, thermodynamic) state of the system.
• \( k \) is Boltzmann’s constant, units of energy per \( ^0K \).
5. Statistical Mechanical Definition of Temperature

Find the most probable $E_1$

\[ \equiv E_1^* \]

- **Total** is microcanonical
- $\phi W_{1\rightarrow 2} = 0$
- Interaction between 1 & 2 is so small that $\Omega$ can be separated
\[ p(E_1) = \frac{\Omega'}{\Omega} = \frac{\Omega_1(E_1) \Omega_2(E - E_1)}{\Omega(E)} \]

\[ \ln p(E_1) = \ln \Omega_1(E_1) + \ln \Omega_2(E - E_1) - \ln \Omega(E) \]

\[ = \frac{1}{k} \left( S_1(E_1) + S_2(E - E_1) - S(E) \right) \]

\[ \frac{\partial}{\partial E_1} \ln p(E_1) = \frac{1}{k} \left( \left( \frac{\partial S_1}{\partial E_1} \right)_{\phi W_1=0} - \left( \frac{\partial S_2}{\partial E_1} \right)_{\phi W_2=0} \right) = 0 \]
The condition for determining $E_1^*$ is

$$\left( \frac{\partial S_1}{\partial E_1} \right)_{\phi W_1=0} = \left( \frac{\partial S_2}{\partial E_2} \right)_{\phi W_2=0}$$

But this also specifies the equilibrium condition. Thus

$$\left( \frac{\partial S}{\partial E} \right)_{\phi W=0} = f(T) \equiv \frac{1}{T} \quad \text{(in equilibrium)}$$
6. Two Fundamental Inequalities

What if $E_1 \neq E_1^*$?

$\mathbb{I} \rightarrow \mathbb{I}^*$ as equilibrium is established.

$$p(E_1) \leq p(E_1^*)$$

$$\Omega_1(E_1)\Omega_2(E - E_1) \leq \Omega_1(E_1^*)\Omega_2(E - E_1^*)$$

$$1 \leq \frac{\Omega_1(E_1^*)}{\Omega_1(E_1)} \cdot \frac{\Omega_2(E - E_1^*)}{\Omega_2(E - E_1)}$$
\[
0 \leq \frac{S_1(E_1^*) - S_1(E_1)}{\Delta S_1} + \frac{S_2(E - E_1^*) - S_2(E - E_1)}{\Delta S_2}
\]

\[
\Rightarrow \quad \Delta S = \Delta S_1 + \Delta S_2 \quad \text{increases}
\]

\[
\Delta S \geq 0
\]

The total entropy of an isolated system always increases or, at equilibrium, remains constant.
Now assume $\exists \gg \mathbb{1}^* \Rightarrow T_2 \equiv T_{\text{bath}}$ does not change.

$$dS_2 = \frac{dE_2}{T_2} = \frac{\phi Q_2}{T_2} = -\frac{\phi Q_1}{T_{\text{bath}}}$$

$$dS = dS_1 + dS_2 = dS_1 - \frac{\phi Q_1}{T_{\text{bath}}} \geq 0$$

$$\Rightarrow \bullet \quad dS_1 \geq \frac{\phi Q_1}{T_{\text{bath}}}$$

In particular, for systems in equilibrium with a bath
$$dS = \phi Q / T.$$
Example Ideal Monatomic Gas

\[ \Phi \approx V^N \left( \frac{4\pi emE}{3N} \right)^{3N/2} = \left\{ V \left( \frac{4\pi emE}{3N} \right)^{3/2} \right\}^N \]

\[ \rightarrow S(E, N, V) = kN \ln \left\{ V \left( \frac{4\pi emE}{3N} \right)^{3/2} \right\} \]

\[ \Omega \approx \left( \frac{3N \Delta}{2 \ E} \right) V^N \left( \frac{4\pi emE}{3N} \right)^{3N/2} \]

\[ \rightarrow S(E, N, V) = kN \ln \left\{ V \left( \frac{4\pi emE}{3N} \right)^{3/2} \right\} - \ln \left( \frac{2}{3 \ \Delta \ N} \right) \]
The Energy Relation

\[
\frac{1}{T} \equiv \left( \frac{\partial S}{\partial E} \right)_{N,V} = \frac{Nk}{\{\} \ 2 \ E} \{\} = \frac{(3/2)Nk}{E}
\]

\[
\Rightarrow \ E = (3/2)NkT
\]

Here \( U = E \) so \( C_V = \left( \frac{\partial U}{\partial T} \right)_V = (3/2)Nk \).
The Adiabatic Condition

\[ \Delta Q = 0 \Rightarrow \Delta S = 0 \] for a quasistatic process.

\[ S(E, N, V) = kN \ln \left\{ V \left( \frac{4\pi e m E}{3N} \right)^{3/2} \right\} \]

Use the energy relation to eliminate \( E \).

\[ S(E, N, V) = kN \ln \left\{ V \left( \frac{4\pi e m ((3/2)NkT)^{3/2}}{3N} \right) \right\} \]

\[ \Delta S|_{\Delta N=0} \Rightarrow VT^{3/2} = \text{constant} \]
Microcanonical:  $E$ fixed + equal a priori probabilities

⇒ microscopic probability densities [S.M.]

Together with the definition of entropy

⇒ temperature scale and $2^{ND}$ law inequalities [Thermodynamics]
\[ \Delta S \geq 0 \]
\[ dS_1 \geq \frac{dQ_1}{T} \]
\[ \begin{cases} \Delta S \geq 0 \\ dS_1 \geq \frac{dQ_1}{T} \end{cases} \]

Quasi-static means arbitrarily close to equilibrium.

- Necessary for work differentials to apply
- Required for \( = \) in above \( 2^{ND} \) law relations