Lecture 3. Fundamental Equations of Thermodynamics.

1. The basic task of (equilibrium state) statistical mechanics.
   Defining a multi-state system
   \[
   \begin{array}{cccc}
   1 & 2 & 3 & \cdots \\
p_1 & p_2 & p_3 & \cdots \\
\end{array}
   \]

   Degrees of freedom: \( \{ p_i \} \)
   Constraints: \( \sum_i p_i = 1 \) (the weakest possible constraint)
   Extremum: \( S = k \ln N = -k \sum_i p_i \ln p_i \)

   Solving for equilibrium: \( \frac{\partial S}{\partial p_i} = 0 \) subject to \( \sum_i p_i = 1 \)
   Equilibrium state: \( p_1 = p_2 = \cdots = p \)

2. More thermodynamic constraints?
   Considering particles in a big box.
   \[
   S = -Nk \sum_i p_i \ln p_i;
   \]
   \[
   N: \text{particle number}
   \]
   \[
   V: \text{Volume - the number of accessible positional states.}
   \]
   \[
   U: \text{Internal energy} = \frac{1}{4} \sum_i \epsilon p_i = \langle \epsilon \rangle \text{ for one particle.}
   \]

3. Fundamental Thermodynamic Equations.
   Given \( U, V, N \) constraints, we can solve for \( \{ p_i \} \) that gives the equilibrium state \( S \).
   Therefore,
   \[
   S = S(U, V, N)
   \]
   is the fundamental thermodynamic equation for entropy.
   Historically, the fundamental equation was about energy.
   \[
   U = U(S, V, N)
   \]
   In total differential form,
   \[
   dU = \left( \frac{\partial U}{\partial S} \right)_{V,N} dS + \left( \frac{\partial U}{\partial V} \right)_{S,N} dV + \left( \frac{\partial U}{\partial N} \right)_{S,V} dN
   \]
   \[
   dU = \left( \frac{\partial U}{\partial S} \right)_{V,N} dS - p dV + \mu dN \Rightarrow \text{the definition of } T, p, \mu
   \]
   Similarly
   \[
   dS = \left( \frac{\partial S}{\partial U} \right)_{V,N} dU + \left( \frac{\partial S}{\partial V} \right)_{U,N} dV + \left( \frac{\partial S}{\partial N} \right)_{U,V} dN
   \]
   \[
   = \left( \frac{1}{T} \right) dU + \left( \frac{p}{T} \right) dV - \left( \frac{\mu}{T} \right) dN
   \]
4. Deriving thermodynamic properties using fundamental equations.

**Ideal gas: non-interacting particles.**

Considering only position multiplicity:

- Volume = V, Volume element = dS, \( M = V/S \)
- \( S = N k l n M = N k l n (V/S) \)
- Given \( \frac{P}{T} = (\frac{\partial S}{\partial V})_{u,N} \)

\[
\frac{P}{T} = \frac{1}{V} N k l n \frac{V}{S} = N k \frac{V}{V} \Rightarrow P V = N k T
\]

5. \( \frac{V}{T}, \frac{P}{V} \) and \( \frac{-M}{T} \) are driving forces for energy exchange.

\[
dS_{AB} = dS_A + dS_B = \frac{dU_A}{T_A} + \frac{dU_B}{T_B} = (\frac{1}{T_A} - \frac{1}{T_B}) dU_A
\]

\[
dU_A + dU_B = 0
\]

When only heat exchange allowed: \( dS_{AB} = 0 \Rightarrow T_A = T_B \)

**Spontaneous process:**

\[
dS_{AB} > 0. \Rightarrow \frac{1}{T_A} > \frac{1}{T_B} \text{ if } dU_A > 0 (A \text{ absorbs heat})
\]

\[
T_A < T_B \text{ (only when } T_A = T_B > 0)\]

Therefore, \( \frac{1}{T} \) is the driving force for heat exchange.