**FUNDAMENTAL EQUATION**

From Postulate I, we know that we can write

\[ U = U(S, V, N_1, \ldots, N_n) \]  
Energy Equation

or \[ S = S(U, V, N_1, \ldots, N_n) \]  
Entropy Equation

Why? \( U \) and \( S \) can always be varied independently.

Both equations deserve to be called "fundamental" -

- They relate quantities appearing in 1st and 2nd Law
- Involve only extensive properties (no external constr.)

First order in mass

\[ (T, P) \ on \ system \]

Differential form of Fundam. Equation (F.E)

In energy representation

\[ dU = TdS - PdV + \sum \mu_i \, dN_i \]

Derivatives of F.E

\[
\begin{align*}
\left( \frac{\partial U}{\partial S} \right)_{V, N_1, \ldots, N_n} &= T \\
\left( \frac{\partial U}{\partial S} \right)_{S, N_1, \ldots, N_n} &= -P \\
\left( \frac{\partial U}{\partial N_j} \right)_{S, V, N_1, \ldots, N_{i, j}} &= \mu_j
\end{align*}
\]

Intensive Variables

(0th - order in mass)

this means all \( i \) except \( j \)

Euler's theorem (App. C in T+m) states that:

\[
\delta(g(a, b, kx, ky)) = k^2 \delta(9, 10, x, y) = 3
\]
\[ h_F(a_1, b, x, y) = x \left( \frac{\partial h}{\partial a_1} \right)_{a_1, b, x, y} + y \left( \frac{\partial h}{\partial y} \right)_{a_1, b, x, y} \]

Applying Euler's theorem, for \( h = 1 \) (extensive variables)

Integrated form of

\[ U = TS - PV + \sum_i \mu_i N_i \]

\( U \) is still a function of \( S, V, N_1, \ldots, N_n \) and

\[ T = T(S, V, N_1, \ldots, N_n) \quad \mu_i = \mu_i(S, V, N_1, \ldots, N_n) \]

Digression: Intensive properties are only functions of \( n+1 \) independently variable intensive props:

\[ b = \phi(c_1, c_2, \ldots, c_{n+1}, N) \] according to Postulate 1

\[ b = \phi(c_1, c_2, \ldots, c_{n+1}, N) \]

Euler: Integrate using \( \theta = \phi \)

\[ \phi = \left( \frac{\partial b}{\partial N} \right) c_1, c_2, \ldots, c_{n+1} \rightarrow \left( \frac{\partial b}{\partial N} \right) c_1, c_2, \ldots, c_{n+1} = \phi \]

For example, \( \mu = \mu(T, P) \) for a pure component

\[ U: \text{extensive} \quad U: \text{intensive} \]

\[ \left( \frac{\partial U}{\partial N} \right)_S, V = \mu \quad \left( \frac{\partial U}{\partial N} \right)_S, V = \phi \]

\[ \left( \frac{\partial U}{\partial N} \right)_S, V = \phi \quad \left( \frac{\partial U}{\partial N} \right)_S, V = \left( \frac{\partial (N\mu)}{\partial N} \right) \]

\[ U + N \left( \frac{\partial U}{\partial N} \right)_S, V = \mu \]

Since \( U \neq h \), \( \left( \frac{\partial U}{\partial N} \right)_S, V \neq \phi \)
Now, reconsider the expressions

\[ u = u (s, v, n_1, \ldots, n_n) \] \[ T = T (s, v, n_1, \ldots, n_n) \] \[ P = P (s, v, n_1, \ldots, n_n) \]

Often, we would like to work with variables other than \( s, v, \ldots, n_n \). Why don't we just eliminate \( s \) by solving \([2]\) and substituting in \([1]\) to get

\[ u = u (T, v, n_1, \ldots, n_n) \] \[ u = u (S, V, N_1, \ldots, N_n) \]

When going from \( u (s, v, n_1, \ldots, n_n) \) to \( u (T, v, n_1, \ldots, n_n) \), we lose information!

**Explanation**

\[ y(x) = x^2 + 5 \]

\[ \frac{dy}{dx} = 2 = 2x \Rightarrow x = \frac{3}{2} \]

\[ y(3) = \frac{3^2}{4} + 5 \]

\[ y(x) = (x+3)^2 + 5 \]

\[ \frac{dy}{dx} = 2(x+3) \Rightarrow y(3) = \frac{3^2}{4} + 5 \]

\( A \) and \( B \) are not equivalent for \( y(x) \), even though \( y(3) \) is the same in both cases!

To go from \([1]\) \( u = u (s, v, n_1, \ldots, n_n) \) to \([4]\) \( u = u (T, v, n_1, \ldots, n_n) \), we need

\[ T = \left( \frac{\partial u}{\partial S} \right) v, n_1, \ldots, n_n = \delta (s, v, n_1, \ldots, n_n) \Rightarrow \]

\[ S = \delta^{-1} (T, v, n_1, \ldots, n_n) \]

but to go back from \([4]\) to \([1]\) we need to integrate a Partial Differential Equation, which introduces arbitrary constants.
Solution: \textbf{Legendre Transforms}

Basis function: \[ y^{(0)}(x_1, x_2, \ldots, x_n) \]
\[ \frac{dy^{(0)}}{dx} = \frac{\partial y^{(0)}}{\partial x_1} + \frac{\partial y^{(0)}}{\partial x_2} + \ldots + \frac{\partial y^{(0)}}{\partial x_n} \]

First Transform:
\[ y^{(1)}(3_1, x_2, \ldots, x_n) = y^{(0)} - 3_1 x_1 \]
\[ \frac{dy^{(1)}}{dx} = -x_1 \frac{\partial y^{(0)}}{\partial x_1} + \frac{\partial y^{(0)}}{\partial x_2} + \ldots + \frac{\partial y^{(0)}}{\partial x_n} \]

Or, in a neat table:
\[
\begin{array}{ccc}
  y^{(0)} & y^{(1)} \\
  x_1 & \beta_1 & 3_1 & -x_1 \\
  x_2 & \beta_2 & x_2 & 3_2 \\
  \vdots & \vdots & \vdots & \vdots \\
  x_n & \beta_n & x_n & 3_n \\
\end{array}
\]

Reverse transform:
\[ y^{(0)} = y^{(1)} + 3_1 x_1 \]

Example: 1D (0 component system - impossible)

\[ y^{(0)}(x) = x^2 + 5 \]
\[ \frac{dy^{(0)}}{dx} = 2x \]

\[ y^{(1)}(\beta) = \frac{\beta^2}{4} + 5 - \frac{3^2}{2} = -\frac{\beta^2}{4} + 5 \]

revers transform
\[ \frac{dy^{(1)}}{d\beta} = -x = -\frac{3}{2} \Rightarrow y^{(0)}(x) = y^{(1)}(\beta) + x\beta = -x^2 + 5 + 2x^2 = x^2 + 5 \]

\[ y^{(0)} = \sin(x) + x^2/9 \]
\[ \frac{dy^{(0)}}{dx} = 3 = \cos(x) + \frac{2x}{9} \]

No analytical solution possible, invert numerically.
\[ y(q) = \sin(\alpha) + \frac{x^2}{q} \]