Sharif University of Technology
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Advanced Thermodynamics

Lecture 7

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Extreme Principles

- Postulate #2 $\longrightarrow$
  - fundamental equation can be written with the energy or entropy as the dependent quantities (in terms of U or S), respectively.

$$S = S(U,\ V,\ N_1,\ldots,\ N_r) \quad or \quad U = U(S,\ V,\ N_1,\ldots,\ N_r)$$

- Postulate #3 $\longrightarrow$
  - S is continuous, differentiable, homogeneous, and first-order.

$$S = S = \sum S_i \quad and \quad S(aU,\ aV,\ aN_i) = a\ S(U,\ V,\ N_i)$$

  - S is increase monotonically W.R.T. U, $\left(\partial S/\partial U\right)_{V,\ N_1,\ldots,\ N_r} > 0$
- Postulate #4 $\longrightarrow$

$$\left(\partial S/\partial U\right)_{V,\ N_1,\ldots,\ N_r} = 0 \qquad (S = 0 \quad at \quad T = 0^o\ K)$$

Extreme Principles …

- Equilibrium condition $\longrightarrow$ $dS=0$, Stability condition $\longrightarrow$ $dS<0$
- **Entropy Maximum Principle:** The equilibrium value of any unconstrained internal parameter is such as to maximize the entropy for the given value of the total internal energy.
- **Energy Minimum Principle:** The equilibrium value of any unconstrained internal parameter is such as to minimize the energy for the given value of the total entropy.
- These two principles are shown to be equivalent.
- Interchangeability of the roles of energy and entropy suggests the first reformulation of the thermodynamic formalism.

Legendre Transformations

- The extensive parameters are mathematically independent variables in both the energy and entropy representations.
- The intensive parameters are more easily-measured and, therefore, it is more convenient to be considered as independent variables.
- The Legendre Transformations make it possible.
- The problem is that an equation is given, $Y = Y(X_0, X_1, \ldots, X_t)$

  It is desired to find a method whereby the derivatives $P_k \equiv \dfrac{\partial Y}{\partial X_k}$ may be considered as independent variables without sacrificing any of mathematical content of the given equation.

- Consider a simple case where the fundamental relation is a function of only a single independent variable, $Y = Y(X)$
- It is desired to consider *P*, $P = \partial Y / \partial X$ as an independent variable.
- Knowledge of *Y* as a function of the slope, *P*, would not lead to reconstruct the curve as a function of *X*, due to an undetermined integration constant.
- The practicable solution considers a relation as $y = y(P)$, where *P* is the slope of the line and y is its intercept along the *Y*-axis.
- This relation is completely equivalent to the given fundamental relation and it may be considered a fundamental relation as well.

Legendre Transformation

$Y = Y(X)$	$y = y(P)$
$P = \dfrac{dY}{dX}$	$-X = \dfrac{dy}{dP}$
$y = -PX + Y$	$Y = XP + y$
Elimination of X and Y yields	Elimination of P and y yields
$y = y(P)$	$Y = Y(X)$

- $Y = Y(X)$ is a fundamental relation in Y-representation.
- $y = y(P)$ is a fundamental relation in y-representation.
- The generalization of the Legendre Transformation to functions of more than a single independent variable is straightforward. It may be applied for a (t+2)-dimensional hyper-surface $Y = Y(X_0, X_1, \ldots, X_t)$