# CHM 421/621
# Statistical Mechanics

## Lecture 18 Alternative Formulations

# Introduction and Review

**Lecture Plan**

**Review of Thermodynamics**

Basic Formalism

Conditions of Equilibrium

Equilibrium Relations

Legendre Transformed Representations

Stability of Thermodynamic Systems

# Alternative formulations

**Minimum energy principle**

The equilibrium value of any unconstrained internal parameter is such as to minimise the energy for the given value of the total entropy.

$$P = \left(\frac{\partial U}{\partial X}\right)_S = -T\left(\frac{\partial S}{\partial X}\right)_U = 0$$

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S > 0$$

The properties of thee fundamental equation, i.e., t*he single-valuedness of U w.r.t. S and* $\left(\frac{\partial S}{\partial U}\right)_X > 0$ ensure that this can happen.

# Legendre Transformations

**Motivation**

In both *S* and *U* representations the extensive variables are the independent variables meaning that they can be experimentally controlled.

This is in contrast to the usual situation where intensive variables like temperature and pressure are controlled.

Can we recast the formalism with intensive parameters are independent variables?

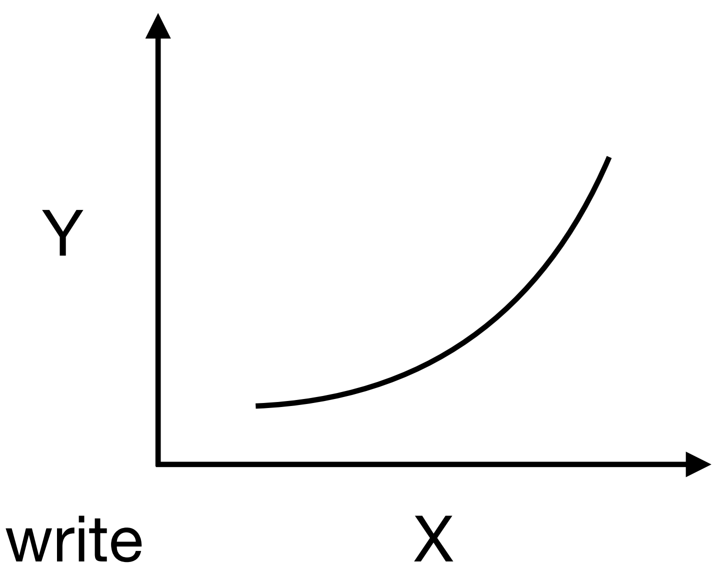
# Legendre Transformations

**Geometric approach** :

Consider a function *Y* of a single variable *X*.

$$Y \equiv Y(X)$$

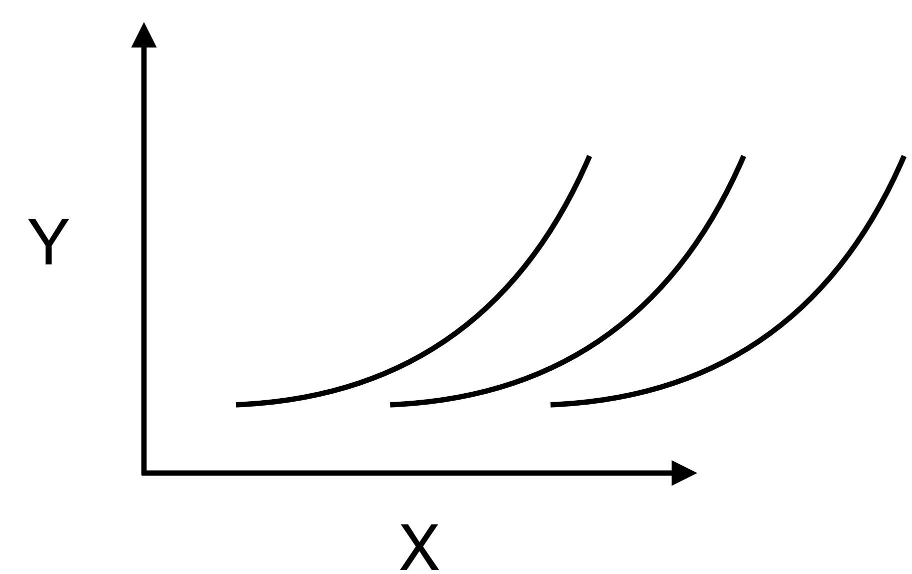
Slope is $$P \equiv \frac{\partial Y}{\partial X}$$




We could eliminate *X* from these two relations and write

$$Y \equiv Y(P)$$

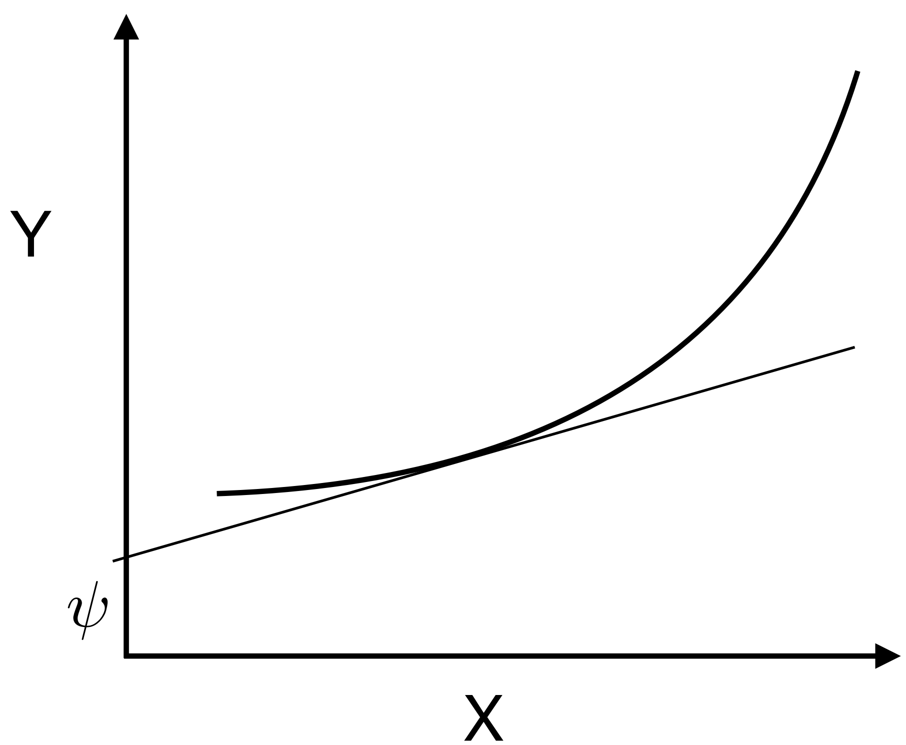
But, we might not be able to get unique definition of *Y* in terms of *X* from this



# Legendre Transformations

**Geometric approach** :

We can, however, get the lost information back if we also knew the intercepts along with the slopes.




Think of a curve as the envelope of a family of tangents given by

$$\psi \equiv \psi(P)$$

Slope-intercept ( $\psi$ ) representation of the function.

Completely equivalent to the original (*Y*) representation.

$$P = \frac{Y - \psi}{X - 0} \quad \text{or} \quad \boxed{\psi = Y - PX}$$

Legendre Transformation

# Legendre Transformations

**Geometric approach** :

Note that $-X = \frac{d\psi}{dP}$ while $P = \frac{dY}{dX}$

So *X* and *P* are conjugate in this sense. It is easily verified that the transformed representation can give back the *Y*-representation uniquely.

Generalizing to the multi-variable case we have that given

$$Y = Y(X_0, X_1, X_2, ..., X_t)$$

$$P_k = \frac{\partial Y}{\partial X_k}$$

We can equivalently represent the dependence through

$$\psi = Y - \sum_k P_k X_k$$

# Legendre Transformations

**Partial Transform** :

Suppose we only want to transform with respect to one variable we can.

$$Y[P_0] = Y - P_0 X_0$$

An infinitesimal change can then be written as

$$dY[P_0] = -X_0 dP_0 + \sum_{i=1,t} P_i dX_i$$

**Inverse transform** :

Note that,

$$X_0 = -\frac{\partial Y[P_0]}{\partial P_0}$$

Thus, we also have

$$Y(X_0) = Y[P] + X_0 P_0$$

# Legendre Transformations

**Example :**

$$y = Ae^{Bx}$$

$$p = \frac{dy}{dx} = ABe^{Bx}$$

$$x = \frac{1}{B}\ln(p/AB)$$

$$Y = y - px = \frac{p}{B}\left(1 - \ln\left(\frac{p}{AB}\right)\right)$$

# Legendre Transformations

**Thermodynamic Potentials** :

Starting from the energetic fundamental relation we can derive various potentials depending on the extensive parameter(s) we want to eliminate

$$U = U(S, V, N_1, N_2, ...)$$

$$U[T] = A(T, V, N_1, N_2, ...) \quad = U - TS$$ Helmholtz Free Energy (Potential) — Also denoted as *F*

$$U[P] = H(P, S, N_1, N_2, ...) = U + PV$$ Enthalpy

$$U[T, P] = G(P, S, N_1, N_2, ...) = U + PV - TS$$ Gibbs Free Energy

$$U[T, \mu_i] = \Omega(\mu, S, N_1, N_2, ...) = U - TS - \mu_i N_i$$ Grand-canonical potential

$$U[T, P, \mu_1, \mu_2, ...] = U - TS + PV - \sum_i \mu_i N_i = \; 0$$ Why?

# Legendre Transformations

**Thermodynamic Potentials** : Enthalpy

All the potentials are extensive and homogenous. So Euler formulae can be derived for each of them.

Since $H \equiv H(P, S, N)$

$$dH = \left(\frac{\partial H}{\partial P}\right)_{S,N} dP + \left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial N}\right)_{P,S} dN$$

But from the Legendre Transform definition, we also have

$$\begin{aligned} dH &= dU + PdV + Vdp \\ &= TdS - PdV + \mu dN + PdV + VdP \\ &= TdS + VdP + \mu dN \end{aligned}$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S,N}$$

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N}$$

$$\mu = \left(\frac{\partial H}{\partial N}\right)_{P,S}$$

# Legendre Transformations

**Thermodynamic Potentials** : Helmholtz Free Energy

Similarly,

Since $A \equiv A(T, V, N)$

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,N} dT + \left(\frac{\partial A}{\partial V}\right)_{T,N} dV + \left(\frac{\partial A}{\partial N}\right)_{T,V} dN$$

Using the Legendre Transform definition, we can show that

$$dA = -SdT + PdV + \mu dN \quad \Longrightarrow$$

$$-S = \left(\frac{\partial A}{\partial T}\right)_{V,N}$$

$$-P = \left(\frac{\partial A}{\partial V}\right)_{T,N}$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

# Legendre Transformations

**Thermodynamic Potentials** : Gibbs Free Energy

Similarly, $G \equiv G(T, P, N)$

$$\Longrightarrow \quad \boxed{\begin{aligned} -S &= \left(\frac{\partial G}{\partial T}\right)_{P,N} \\ V &= \left(\frac{\partial G}{\partial P}\right)_{T,N} \\ \mu &= \left(\frac{\partial G}{\partial N}\right)_{T,P} \end{aligned}}$$

Easy to derive the Maxwell's relations from here. Will feature in the assignments.