Recitation 6

Thermodynamic identities &

Legendre transformation

1st law of thermodynamics (conservation of energy)

$$\boxed{dU = \delta Q + \delta W}$$

"heat is a form of energy"

heat exchange — work done on the system

note: beware of sign conventions!
in the convention above:
- all net energy transfer to the system is counted positive
- energy transfer from the system negative

- for reversible processes $\delta Q = T \cdot dS$

$$\Rightarrow \boxed{dU = TdS - pdV} \Rightarrow U(S, V)$$

→ you always have to know what the independent variables are.

→ can obtain thermodynamic relations:
the total differential of $U(S,V)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\Rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T \quad \& \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

- next thing we did in class is to introduce another quantity

"the Helmholtz Free Energy"

→ mathematically speaking this is a

$\boxed{\text{Legendre transformation}}$

and we change the independent variable

→ practical purpose: in experiment it is sometimes easier to control ~~the T parameter~~ than entropy.

<u>Legendre trafo:</u>

suppose you have function of 2 variables

$f(x,y)$

$$\rightarrow df = \left.\frac{\partial f}{\partial x}\right|_y dx + \left.\frac{\partial f}{\partial y}\right|_x dy$$

defining $u = \left.\frac{\partial f}{\partial x}\right|_y$ & $w = \left.\frac{\partial f}{\partial y}\right|_x$

$$\Rightarrow df = u\,dx + w\,dy$$

"$u \Leftrightarrow x$" conjugate variables

- look at the differential

$$d(ux) = du \cdot x + u \cdot dx$$

- subtract this from the original definition:

$$df = u\,dx + w\,dy$$

$$\rightarrow d(f - ux) = w\,dy - x\,du$$

def: $\boxed{g = f - u \cdot x}$ Legendre transformation

$$\Rightarrow dg = w\,dy - x\,du$$

$$\Rightarrow \boxed{g = g(y, u)}$$

x as independent variable for

we have traded $u = \left(\frac{\partial f}{\partial x}\right)_y$

- remark: we could have traded $y \Leftrightarrow w$ to obtain $h(x, w)$ or both to obtain $k(u, w)$

$\Rightarrow$ there are 4 possible versions: $f(x, y)$, $g(u, y)$, $h(x, w)$, $k(u$

- Contact to thermodynamics:
  - can describe the system by 3 independent variables. (e.g. $\cancel{T}$ S, V, N)
  - we call the functions (f, g, h, ℓ)

"thermodynamic potentials"
and there are in principle 8 of them
(neglecting electric, magnetic and other properties of systems)

$U(S,V,N) \to$ "total internal energy"

$H(S,P,N) \to$ the "enthalpy"

$F(T,V,N) \to$ the "Helmholtz free energy"

$G(T,P,N) \to$ the "Gibbs free energy"

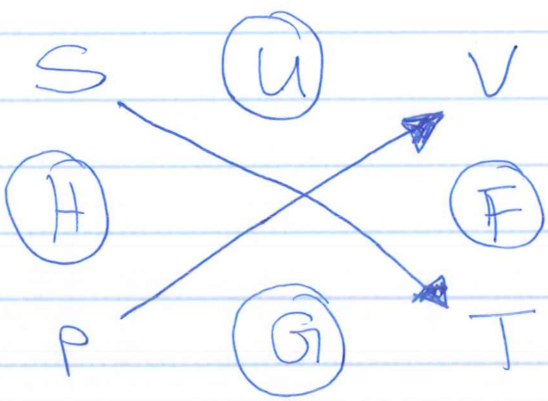
+4 potentials with N traded for the "chemical potential" μ

starting from

$$dU = TdS - pdV + \mu dN$$

can do Legendre transformations to swap $T \leftrightarrow S$
$p \leftrightarrow V$
$\mu \leftrightarrow N$

memorize the Potentials and their dependences:



$$\frac{\partial U}{\partial V} = -p, \quad \frac{\partial U}{\partial S} = T$$

$$\frac{\partial F}{\partial V} = -p, \quad \frac{\partial F}{\partial T} = -S$$

$$\frac{\partial G}{\partial T} = -S, \quad \frac{\partial G}{\partial p} = +V$$

$$\frac{\partial H}{\partial S} = T, \quad \frac{\partial H}{\partial p} = +V$$

Good physicists have studied under very fine teachers.

and $\boxed{dU = TdS - pdV + \mu dN}$

- Example in classical mechanics:

Lagrange formulation $\mathcal{L}(q, \dot{q})$

velocity

$$\Updownarrow$$

Hamiltonian formulation $\mathcal{H}(q, p)$

$$d\mathcal{L} = \frac{\partial \mathcal{L}}{\partial q} dq + \frac{\partial \mathcal{L}}{\partial \dot{q}} d\dot{q}$$

$$p = \frac{\partial \mathcal{L}}{\partial \dot{q}}$$

$$\Rightarrow d(p\dot{q}) = \dot{q}\, dp + p\, d\dot{q}$$

$$\Rightarrow d\big(\underbrace{\mathcal{L} - p\dot{q}}_{\overset{\text{def}}{=} -\mathcal{H}(q,p)}\big) = \left(\frac{\partial \mathcal{L}}{\partial q}\right)_p dq - \dot{q}\, dp$$

$$\Rightarrow \frac{\partial \mathcal{H}}{\partial q} = -\frac{\partial \mathcal{L}}{\partial q} \qquad \frac{\partial \mathcal{H}}{\partial p} = +\dot{q}$$

$$\frac{\partial \mathcal{H}}{\partial q} = -\frac{\partial V}{\partial q} = F = \dot{p}$$

$$\Rightarrow \boxed{\frac{\partial \mathcal{H}}{\partial q} = -\dot{p} \qquad \frac{\partial \mathcal{H}}{\partial p} = \dot{q}}$$

Hamiltonian equations of motion

• Example in classical mechanics:

Lagrangian formulation $\mathcal{L}(q,\dot{q})$

velocity

$\updownarrow$

Hamiltonian formulation $\mathcal{H}(q,p)$

$$d\mathcal{L} = \frac{\partial \mathcal{L}}{\partial q}\,dq + \frac{\partial \mathcal{L}}{\partial \dot{q}}\,d\dot{q}$$

$$\frac{\partial \mathcal{L}}{\partial \dot{q}} = p$$

$$\Rightarrow d(p\dot{q}) = \dot{q}\,dp + p\,d\dot{q}$$

$$\Rightarrow \underbrace{d(\mathcal{L} - p\dot{q})}_{-\mathcal{H}(q,p)} = \frac{\partial \mathcal{L}}{\partial q}\,dq - \dot{q}\,dp$$

$$\Rightarrow \frac{\partial \mathcal{H}}{\partial q} = -\frac{\partial \mathcal{L}}{\partial q} \qquad \frac{\partial \mathcal{H}}{\partial p} = +\dot{q}$$

$$\dot{p} = F = -\frac{\partial V}{\partial q} = \frac{\partial \mathcal{L}}{\partial q}$$

$$\Rightarrow \boxed{\frac{\partial \mathcal{H}}{\partial q} = -\dot{p} \qquad \frac{\partial \mathcal{H}}{\partial p} = \dot{q}}$$

Hamiltonian equations of motion