Physics 418 - A. N. Jordan, Lecture #1 ①

Review of Thermodynamics:

fast variables { Microscopic variables - Detailed description of system - i.e. positions + momenta of all particles in a gas

slow, course-grained variables { Macroscopic Variables - Typically conserved quantities, such as energy that do not change in time. → "Thermodynamic Variables" specify state of Macroscopic system.

Extensive: Value of the coordinate scals with size of system:

V, volume $\qquad$ M, magnetization
U, internal energy $\qquad$ $\mathbb{P}$, polarization
N, # of particles

Intensive: Coordinate is independent of system size.

T, temperature $\qquad$ $\mathbb{E}$, electric field
P, pressure $\qquad$ $\mathbb{B}$, magnetic field
$\rho = N/V$, density $\qquad$ μ, chemical potential

~~Simplest case is a gas: (V, U, N) and (T, P)~~

~~5 variables (odd dimension)~~

~~The variables are "conjugated"~~

~~$V \Longleftrightarrow P$;~~

Review Laws of Thermodynamics - from which it all follows

① First Law: Energy conservation:

The internal energy U should be a state function of the system. Value of U depends only on what the coordinate is now, not what is was in the past.

$$\int_i^f dU = U_f - U_i$$ is independent of path taken by other coordinates.

U is changed by adding energy, or by doing mechanical work on the system.

1st Law

$$\rightarrow dU = \text{đ}Q + \text{đ}W$$

Defined so as to increase energy U.

$\text{đ}Q$ = heat added, $\text{đ}W$ = Work done on system

If a process is quasi-static (always close to an equilibrium state), then at every point, the coordinates are well defined, and $\text{đ}Q$ and $\text{đ}W$ may be expressed in terms of them.

③

Recall equilibrium is characterized by E, V, N alone. and does not change in time.

- Hydrodynamic Systems:

$$\text{đ}W = -P\,dV$$

- Wire / polymer: $\text{đ}W = \mathbb{T}\,dL$, $\mathbb{T}$ = tension, L = length

- Surface dominated system (~~aka~~ i.e. surface tension)

~~σ~~ $\text{đ}W = \alpha\, dA$, $\alpha \longleftrightarrow$

- ~~de.~~ Electro-Magnetic system:

$$\text{đ}W = \int dV \left[\mathbb{E}\cdot d\vec{P} + \mu_0 \vec{\mathbb{B}}\cdot d\vec{M}\right] \quad \text{(MKS)}$$

$\mathbb{E}, \mathbb{B}$ = electric + Magnetic fields

$\mathbb{P}, \mathbf{M}$ = polarization (electric) + Magnetization

$\Rightarrow$ Work determined by specific system

Define properties of walls containing a gas:

- Adiabatic ⟺ thermally isolated, $\text{đ}Q = 0$
- Diathermal ⟺ allows heat transfer, $\text{đ}Q \neq 0$
- Non-rigid ⟷ can change volume, $dV \neq 0$
- Non-permeable ⟷ N can change, $dN \neq 0$

$$dU = \text{đ}Q + \text{đ}W$$

Consider adiabatic, mechanical process, $\text{đ}Q = 0$

$\Rightarrow$ we can now find energy U relative to a reference.

Second Law of Thermodynamics [Carathedory]

In the neighborhood of any equilibrium state of a system, there exists states that cannot be reached by a reversible adiabatic process.

Example: Ideal Gas, $PV = NkT$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad nRT$

k = Boltzmann constant
R = gas constant

(equation of state)

$\text{đ}W = -PdV$

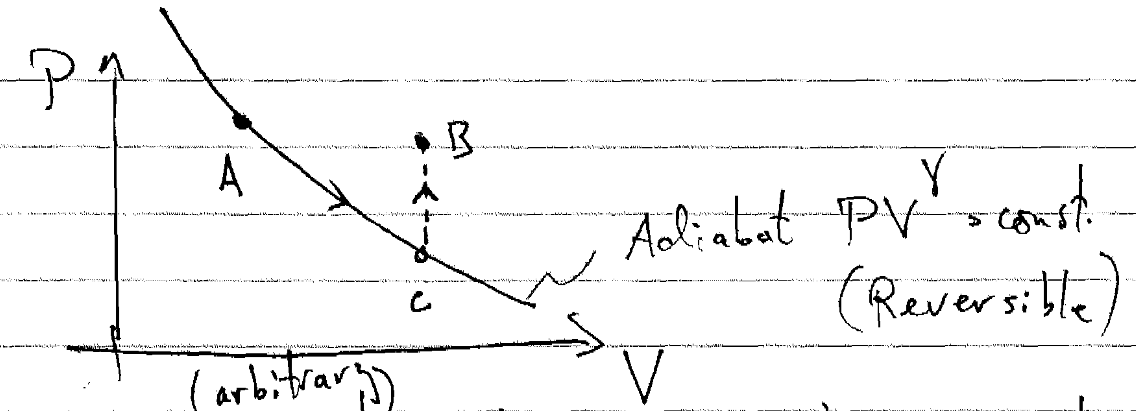
$dU = \cancelto{0}{\text{đ}Q} + \text{đ}W \Rightarrow U_f - U_i = -\int P\,dV$ [reversible
(just change the volume)

(set $U_i = 0$) But T changes!

~~$U = NkT$~~

$U = \frac{3}{2} N k_b T$; PV^{γ} = const. along adiabat

$\gamma = 5/3$ for monoatomic gas



Consider (arbitrary) points A and **B**, there must exist an adiabatic mechanical path from
$A \to B$ <u>or</u> $B \to A$

If only one exists, then the asymmetry implies irreversibility

We can increase P at constant V, adiabatically, by using a mechanical stirrer, this would raise T, increasing P, but when it is (doing work) taken away, T stays the same because heat <u>cannot be</u> lost, $dQ = 0$

∴ From any point in <u>coordinate space</u> (U, V, N, ...) there **exists** a manifold of points that can be reached by reversible adiabatic paths.

[1 constraint]

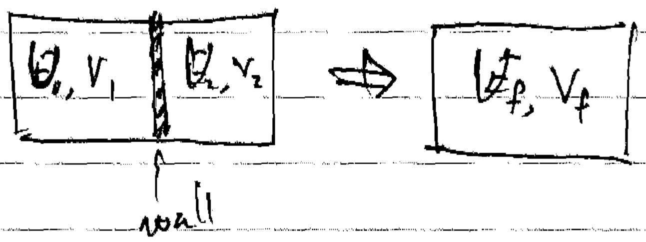
$$f(U, V, N, M, \dots) = \text{constant}$$

→ surface w/ Dimension $D-1$; f defined as entropy

Callen's Postulates:

I: Equilibrium definition

II: Entropy S is maximized when a constraint is removed: (~~S is extensive~~)

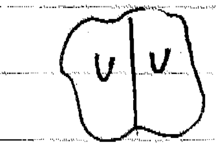


III: Entropy additive over subsystems

$$S = \sum_{\alpha} S_{\alpha}\left(U^{(\alpha)}, V^{(\alpha)}, N^{(\alpha)}\right)$$

$$\Rightarrow S(\lambda U, \lambda V, \lambda N, \dots) = \lambda S(U, V, N)$$

$\Leftrightarrow$ (Extensive function)



and Monotonicly increasing with energy,

$$\left.\frac{\partial S}{\partial U}\right|_{V,N} > 0$$

$S_{tot}(2U, 2V, \dots) = 2S(U,V)$

N.B. This is true only in "thermodynamic limit" $N \to \infty$, $V \to \infty$

because there are generally surface effects

$U = U_1 + U_2 + U_{12}$; E_{12} = interaction energy

$U_1 \sim V_1$, $U_2 \sim V_2$, $U_{12} \sim A$, but $\frac{A}{V} \to 0$ in T.L.

[Fundamental relation, complete information]

Define intensive variables

$s = \frac{S}{N}$, $\quad S(U,V,N) = N s(u,v)$

(entropy representation) $\quad u = \frac{U}{N}$, $v = \frac{V}{N}$

[here $\lambda = N$]

$S(U)$ is monotonically increasing ⇒ 1-1 function

Invert to find $U(S,V,N)$ ⇝ (energy representation)

IV states for which $\left.\frac{\partial U}{\partial S}\right|_{N,V} = 0$

(will eventually be $T=0$)

have $S=0$, zero entropy

(3rd Law of Thermodynamics: Impossible to obtain $T=0$)

Consider total derivative of U:

$$dU = \left.\frac{\partial U}{\partial S}\right|_{V,N} dS + \left.\frac{\partial U}{\partial V}\right|_{S,N} dV + \frac{\partial U}{\partial N} dN$$

$$\begin{tikzcd} \left.\frac{\partial U}{\partial S}\right|_{V,N} \arrow[d] & \left.\frac{\partial U}{\partial V}\right|_{S,N} \arrow[d] & \frac{\partial U}{\partial N} \arrow[d] \\ T\text{, temperature} & -P\text{, pressure} & \mu\text{, chemical potential} \end{tikzcd}$$

(define)

$$\therefore \boxed{dU = TdS - PdV + \mu dN}$$

If we set $dN = 0$, as before

$dU = TdS - PdV$

Recall first Law; $dU = \text{đ}Q + \text{đ}W$

we already identified $\text{đ}W = -PdV$
(consistent)

$\therefore \boxed{\text{đ}Q = TdS}$ is the heat absorbed by the gas.

$$\Rightarrow dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

$$\Rightarrow \left.\frac{\partial S}{\partial U}\right|_{V,N} = \frac{1}{T}, \quad \left.\frac{\partial S}{\partial V}\right|_{U,N} = \frac{P}{T}, \quad \left.\frac{\partial S}{\partial N}\right|_{U,V} = -\frac{\mu}{T}$$

Note, any variable can be the priveledged variable, not just S, or U.

Notice variables come in conjugate pairs,

$$V \Leftrightarrow P, \quad S \Leftrightarrow T, \quad \mu \leftrightarrow N$$

but there is the odd man out, U

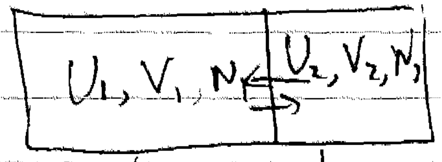
In the entropy representation S is the odd man out, and the conjugate variables are

$$\frac{1}{T} \leftrightarrow U, \quad \frac{P}{T} \leftrightarrow V, \quad -\frac{\mu}{T} \leftrightarrow V$$

The number of thermodynamic coordinates is odd-dimensional.

[More on this later]

Let two systems exchange heat: (diathermal)



$U = U_1 + U_2$ (conservation of energy)

total entropy $\quad S = S_1 + S_2$ (postulate III)

postulate II $\Rightarrow dS = 0 = dS_1 + dS_2$
(Max)

$$dS = \frac{\partial S_1}{\partial U_1}\bigg|_{V_1,N_1} dU_1 + \frac{\partial S_2}{\partial U_2}\bigg|_{V_2,N_2} dU_2 = 0$$

$$\frac{1}{T_1} dU_1 + \frac{1}{T_2} dU_2 = 0 \quad ; \quad U = U_1 + U_2$$

$$dU_1 = -dU_2$$

$$\Rightarrow \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 = 0$$

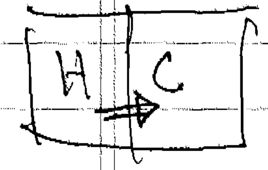
⇒ Thermal Equilibrium (when $dS = 0$)

⇒ $T_1 = T_2$ ⇒ same temp.

(Good)

To approach Equilibrium, $dS \geq 0$

⇒ heat flows from hot to cold



if $T_1 > T_2 \Rightarrow dU_1 < 0$

If we let the wall be porous (and move), ~~same~~ similar argument ⇒

$$T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2$$

in Equilibrium.

Additivity of the entropy ~~[illegible]~~ ⇒

$$\lambda S(U, V, N) = S(\lambda U, \lambda V, \lambda N)$$

$$\lambda U(S, V, N) = U(\lambda S, \lambda V, \lambda N)$$

Differential λU w.r.t. S:

$$\lambda \left.\frac{\partial U}{\partial S}\right|_{V,N} = \left.\frac{\partial U}{\partial(\lambda S)}\right|_{\lambda V, \lambda N} \frac{\partial(\lambda S)}{\partial S}$$

$$\Rightarrow \lambda T(S, V, N) = T(\lambda S, \lambda V, \lambda N) \cdot \lambda$$

$$\text{or } T(S, V, N) = T(\lambda S, \lambda V, \lambda N)$$

sim. w/ P and μ

let $\lambda = \frac{1}{N}$

$$\left.\begin{aligned} \Rightarrow T(S, V, N) &= T(s, v) \\ P(S, V, N) &= P(s, v) \\ \mu(S, V, N) &= \mu(s, v) \end{aligned}\right\} \text{"Equations of state"}$$

If we know all 3, we have complete info.

(Eq. to fundamental relation, via the Euler relation)