{ affecting each other ∴ they
chg ∴ not in equil; can
we use our postulates?

INTERACTIONS AMONG MACRO STATES:

SPECIFYING MACRO STATE: will need to know if state changed

EXTERNAL PARAMETERS:

SET OF MACRO VARIABLES $X_1 \dots X_n$ THAT SPECIFY MACRO SYSTEM (USUALLY FEW) ⇒ LEVERS I CONTROL

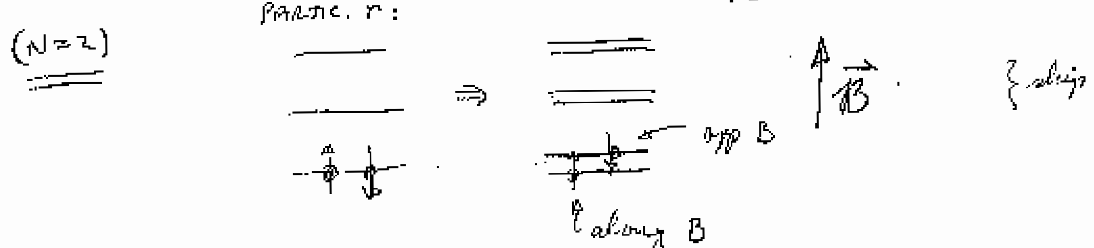
ex: V, $\vec{\mathcal{E}}$, $\vec{B}$, … (magn, elec field)

DETERMINE
- V's PARTICLES MOVE IN
- MOTION OF PARTICLES INSIDE (~CLASSICAL)
- ENERGY LEVELS OF MICRO STATES (QM) + TRANSITION

MICRO STATE r: $\boxed{E_r = E_r(X_1, \dots X_n)}$ IMPLICIT FN OF X_α

ex: BOX: L_x, L_y, L_z ⇒ $E_{\vec{n}} = \hbar^2\left(\left(\frac{n_x\pi}{L_x}\right)^2 + \left(\frac{n_y\pi}{L_y}\right)^2 + \left(\frac{n_z\pi}{L_z}\right)^2\right)$, FOR EACH PARTICLE

TURN ON $\vec{B} = B\hat{z}$ GET ADDITIONAL $\Delta E = \pm\mu B$ FOR EACH



** not nearly a complete charac. of sys. ⇒ $E_r(L_x, L_y, L_z, \vec{B})$

∴ when talk about, invariably have ensemble in mind; it specifies a set

MACROSTATE: ~ SPECIFIED BY X_α + CONSTRAINTS (what's possible) (i.e. OTHER THINGS KNOWN; ex E or N)

ENSEMBLE ~~FOR THIS MACROSTATE~~: INCL ALL MICROSTATES CONSISTENT WITH THESE (MANY STATES)

EXCHANGING E:

Identical, which micro system of the many possible am I talking about?

(I) MICRO DESCRIPTION 2 WAYS:

(1) LEAVE X_α FIXED ⇒ E LEVELS FIXED

⟶ MOVE SYSTEM TO DIFF LEVEL $r \to r'$, $E_r(X_\alpha) \to E_{r'}(X_\alpha)$

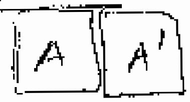
(2) LEAVE IN SAME STATE r, BUT CHANGE X_α'S: $E_r(X_\alpha) \to E_r$

(ex → box: even if stay in ~~box~~ gnd state, if decrease L's, E will incr. smoothly)

(Classical: move to diff. place in U vs. changing U)

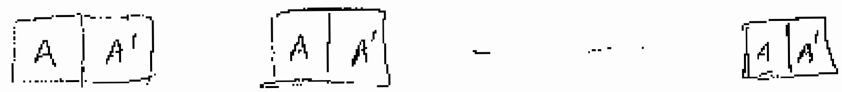
(II) MACRO DESCRIPTION: ALSO TWO WAYS.

(1) THERMAL INTERACTIONS:

SYSTEMS  START EACH IN EQUIL.
PUT IN CONTACT
ISOLATED FROM OUTSIDE

- KEEP x_α, x'_α FIXED → SAME POSSIBLE $E_A, E_{A'}$'s
- WILL EXCHANGE E IN GENERAL { jump or drop to diff. ~~allowed~~ E_a, $E_{a'}$; classical — fast molecules bounce into slower ones, speed up

⇒ "THERMAL INT"

ENS: 

E CONSERVED: $\Delta E_A + \Delta E_{A'} = 0$ FOR EACH (this will be diff

AVE: $\Delta \bar{E}_A + \Delta \bar{E}_{A'} = 0$

HEAT Q ABSORBED BY A: $\boxed{Q \equiv \Delta \bar{E}_A}$

NOTE:
- ONLY DEF'D ON
- MACRO CONCEPT

*(not necessary in micro; summarizes all ΔE's w/o chg we're not keeping track of)

(AVE E ABSORBED BY THERMAL INT.)

⇒ $Q + Q' = 0$ (E CONS)

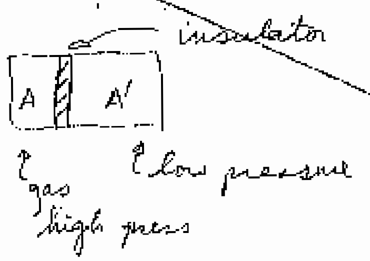
THERMALLY ISOLATED (INSULATED):

≡ CAN'T EXCHANGE E THIS WAY

⇒ STAY IN INDEP. EQUIL. IF x_α, x'_α FIXED

(2) MECHANICAL INTERACTIONS:

INSULATED SYSTEMS CAN EXCH. E BY CHANGING x_α's

ex 

(a) HOLD WALL FIXED ⇒ NOTICE A, A' STAY IN EQUIL, NO E CHG

(b) RELEASE ⇒ WALL MOVES

⇒ L_x's CHANGE

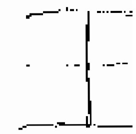
⇒ ALLOWED STATES CHG ... ⇒ E, E' CH

⇒ WILL ALSO GET TRANSITIONS IN GENERAL

skip

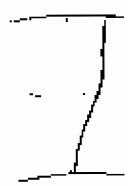
COMMENT (quick)

- Q ONLY DEF'D ON AVE (ie FOR ENSEMBLE)



WHY?

- Used to talk about heat as a kind of continuous fluid, as if it's something could see leave one, go into another; reasonable:
  - can see T drop as leaves,
  - conserved (at least if no work)



- Micro sys:

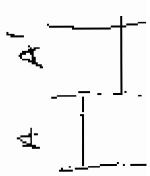
  Think of particles bouncing around;

  Put in "thermal contact"

  Don't see heat

  Do see: ① particles from inside bounce into wall, lose E

  ② particles in wall give E to those in 2ND sys, move faster



  Can describe everything in terms of K & U for indiv particles

  1 w/ direction

  maybe T is prob better than heat

  No need for concept

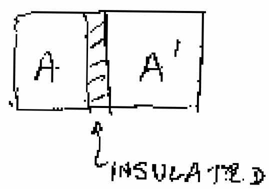
- Macro sys: (≡ ENSEMBLE)
  - diff indiv systems exch. more, less
  - on ave, have smooth flow w/ t of E
  - happens in way I don't see
  - on ave, behaves as a fluid ⇒ convenient summary of lots of individ

{ interested in ways systems can interact, exchg. E

(2) MECHANICAL INTERACTIONS

INSULATED SYS CAN EXCH E BY ΔX_α's :

ex



A: GAS, HIGH PRESSURE p IN EQUIL
A': " LOW "

(a) HOLD FIXED : A, A' STAY IN EQUIL
NO ΔE

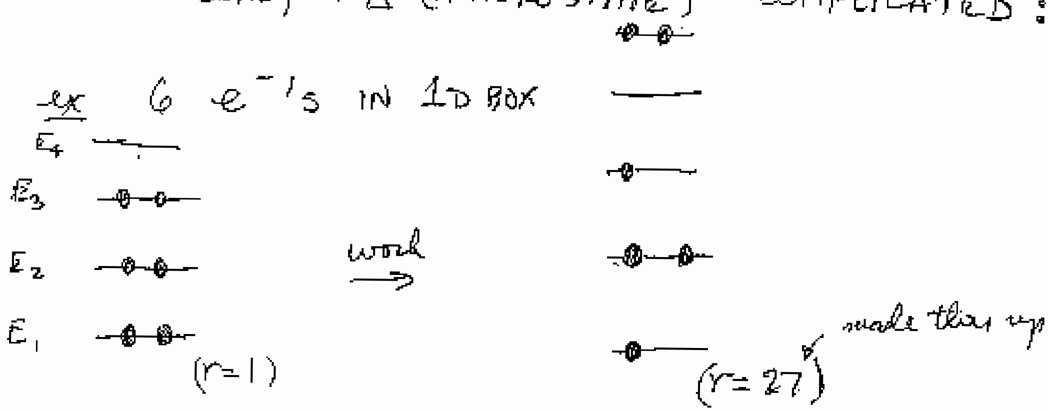
(b) RELEASE :

- WALL MOVES → V, V' CHG
- SYS. A DOES WORK ON A', A' ON A ⇒ ONE GAINS, ONE LOSES E

skip { RECALL $W = \int \vec{F} \cdot d\vec{r}$ }

IN GENERAL, Δ (MICROSTATE) COMPLICATED :

ex 6 e^-'s IN 1D BOX



(i) EXT PARAM L CHGS → E LEVELS CHG

(ii) TRANSITIONS

WORK CAN CAUSE BOTH

(~~this can restrict~~ to (i) if do it ~~slowly enough~~) later

ENS:

NOT IN EQUIL (IN GEN)

ex (CLASSICAL)

RELEASE PISTON QUICKLY:

- NOT ALL STATES EQ. OCCUPIED
- FEEL p WAVES CHG w/ t
- IF WAIT → EQUIL

ENSEMBLE:

- CHG. x_α SAME ON EACH SYS $\alpha = 1, \ldots, n$
- WORK DONE ON EACH CAN VARY   (ex: gas – some systems have many hitting wall as expand, some have few)

MACRO WORK: $(Q=0)$

$$W \equiv \text{AVE WORK DONE \underline{BY} SYSTEM}$$

$$= -\Delta_{x_\alpha} \bar{E}$$

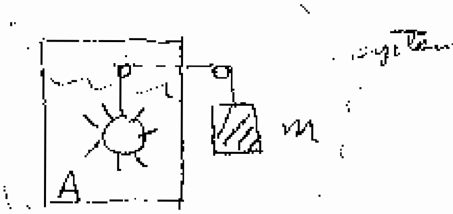
(chg in $\bar{E}$ due to chg in x_α)

E CONS: $W + W' = 0$ (INSULATED)

GENERAL INTERACTIONS: (NOT INSULATED, x_α CHG)

$$\Delta \bar{E} = -W + Q$$

I CAN OFTEN MEAS. W: ex



$W_A = mg\Delta y$

USEFUL TO THINK OF AS DEFN:

HEAT $\boxed{Q \equiv \Delta \bar{E} + W}$

= AVE ΔE NOT DUE TO MACRO WORK

10/11/0?

INFINITESIMALS:

$$\text{đ}Q = d\bar{E} + \text{đ}W$$

$d\bar{E}$ = SMALL $\bar{E}_f - \bar{E}_i$ $\equiv$ DIFFERENTIAL

$\text{đ}Q$, $\text{đ}W$:

- NOT A CHG OR DIFFERENTIAL

(Q, W ARE <u>EXCH.</u> OF E)

~~Q IN SYSTEM~~
~~W " "~~
~~DIFF $Q_f - Q_i$~~
~~" $W_f - W_i$~~

- MEANS SMALL (INFINITESIMAL)

ex $\text{đ}W$ GIVES CLUE CAN TREAT $\vec{F}$ CONST

" $\text{đ}W \approx \vec{F} \cdot d\vec{r}$

$$W = \int_{\vec{r}_1}^{\vec{r}_2} \vec{F} \cdot d\vec{r}$$

skip { Lots of confusion based on this distinction. May go back to idea that Q was a kind of fluid w/ T saying how much and flow of Q really meant some left one container and into other }

<u>Note</u>: đ sometimes called an "inexact differential" → terrible nomenclature; is it the chg in some fn? well, not exactly

3/4/04

want to make connection between work and chgs in params; simple & dir. in class. mechanics; not quite so " " in stat mech

(many x_α's not lengths; 2.21 would like not to convert to a distance everytime want $W = \int \bar{F} \cdot d\bar{r}$)

goal $\Rightarrow$ CONNECTION BETWEEN W & x_α !

RECALL $\quad F_x = -\frac{\partial}{\partial x} U(x) \quad$ (3D $\bar{F} = -\bar{\nabla} U$)

TO SEE:

(IF $\Delta K = 0$)

$$đW_{(\text{BY SYS})} = -dE = -dU = -\frac{\partial U}{\partial x} dx$$ } chging U by chg. x

$$\equiv F_x dx \Rightarrow F_x = -\frac{\partial U}{\partial x}$$

PARAMETER : x (POSITION)

PROBLEM: LIN COORDS NOT ALWAYS MOST CONVENIENT EXT PARAMS

FIX: GENERALIZE :

- SYSTEM IN MICROSTATE r W/ $E_r(x_1 \cdots x_n)$
- IF STAYS IN r, ALL ΔE_r DUE TO ΔX's

$$đW_r = -dE_r = \sum_{\alpha=1}^{n} \left(-\frac{\partial E_r}{\partial x_\alpha}\right) dx_\alpha$$

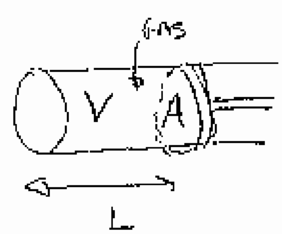
i.e. WORK BY SYS. IN r

GENERALIZED FORCE (in analogy to above)

$$\boxed{X_{\alpha,r} \equiv -\frac{\partial E_r}{\partial x_\alpha}}$$

force related to chg in x_α for sys. in state r

ex PRESSURE :



$A \equiv$ area

KNOW $\quad p = F/A$ ON CYL.

$$đW_r = F_r dL = p_r A dL = p_r dV = -dE_r$$

$$\therefore \boxed{p_r = -\frac{\partial E_r}{\partial V}} = \text{GEN. FORCE ASSOC. w/ } V$$

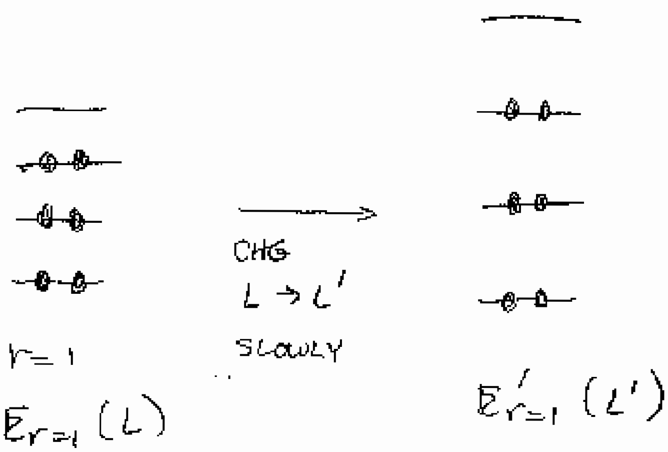
TRUE IN GENERAL (for any chg in V - cf REIF)

PROBLEM: (not too useful yet)

- STATE DOESN'T STAY IN r (IN GEN.): (don't have a direct connection to x_α)

FIX: GO SLOWLY

ex BOX
IF IN STA. ST:



- CHG IN E FROM WORK DUE ONLY TO ΔL
- CAN COMPUTE X AS ABOVE

PROBLEM:

- IN ENS., STATES CHG BY THEMSELVES EVEN IN EQUIL (ie GO FROM $r \to r'$)

QM: transitions
CLASSICAL: particles move

{so on micro state-by-state basis can't make direct connection between ΔX_α and ΔE

FIX:

- WORKS ON AVE: IN EQUIL

(1) NO ΔX_α $\rightarrow$ $P(r)$ CONST, EQUAL

(2) CHANGE X_α QUASI-STATICALLY:

QUASI-STATIC CHG:

- SLOW ENOUGH (cf TO RELAX t) THAT SYS. STAYS IN EQUIL. } what does that mean if I'm chg'ing by defn?

⇒ IF STOP DURING PROCESS, IMMED. IN EQUIL

chgs { - $P(r,t)$ DURING PROCESS, $P(r)$ AS SOON AS STOP

- AT ANY t DURING PROCESS
  - ~~P(r,t)~~ P IS SAME AS FOR ENS. IN EQUIL w/ SAME X_α + CONSTRAINTS.

(means we're not as limited as we thought by equil. regime → we can describe systems which chg, but slowly)

⇒ ~~P(r,t)~~ P DEPENDS ON t ONLY VIA X_α, CONSTRAINTS

⇒ AT EACH t, DESCR. BY EQUIL. ENS

⇒ CAN USE FUND POST. TO COMPUTE AVES. DURING CHG
(at any t, freeze the motion, look at x_α's, same as if sitting there forever: equally likely in any accessible r) [⇐ INSERT]

USEFUL MACRO DEFN:

(for me NOTATION: AVE OVER POSSIBLE r IN ENS. BETTER NOTA. MIGHT BE $\overline{-\frac{\partial E_r}{\partial x_\alpha}}$ or $\langle -\frac{\partial E}{\partial x_\alpha}\rangle_r$)

$$\overline{X}_\alpha \equiv -\overline{\frac{\partial E_r}{\partial x_\alpha}}$$

(ONLY DEP. ON MACRO VARS $(x_\alpha, E, \ldots)$ NOT HOW CHANGE & CONSTR.)

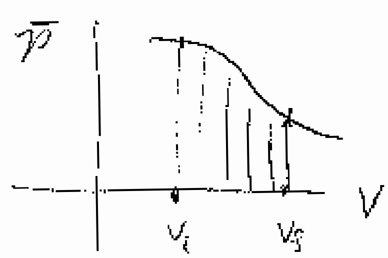
IF $Q=0$ ⇒ $đW = đW_r = \sum_{\alpha=1}^{n} \overline{X}_\alpha \, dx_\alpha$ } all work on ave is due to dx_α
(the # of sys. in each state in stays fixed, so on ave work only dep. on params; it's same as if no state made a transition)

⇒ CAN GET W BY $\int$

ex PRESSURE: (ISOLATED SYS) (GAS)

- $\overline{p}$ ONLY DEP. ON V IF Q-S

- $W_{if} = \int_{V_i}^{V_f} \overline{p}(V)\, dV$



makes sense to plot

*(contrast w/ pulling piston [gas] out quickly; p ↓ ∴ W depends on how fast; very fast → molecules can't keep up → $p=0$)

(INSERT)

MORE DETAIL:

say — DURING ANY TYPE OF CHG, CAN ALWAYS USE ENS. TO MEAS $W = \Delta \bar{E}$ (why not?)

$\Rightarrow$ P CAN ALWAYS BE MEAS'D, BUT CAN DEP. ON HOW CHG. IS MADE IN COMPLICATED WAY

say — WE'D LIKE TO PREDICT W VS ΔX_x (as in mass on spring) AND ESP. TO USE FUND. POST.

CONSIDER (1 PARAM x FOR SIMPLICITY) (ex BOX LENGTH L)

$$\bar{E} = \sum_r \underbrace{P(r, x, t)} E_r(x)$$

COMPLETELY GENERAL FOR NOW

- ALLOW TO DEP. ON PARAM x (so if chg, state in ens could jump around unequally to diff r's)
- COULD DEP. ON t BY ITSELF (as in non-equil. case)

CHG x, CONSIDER RATE CHG IN $\bar{E}$:

$$\frac{d\bar{E}}{dt} = \sum_r \left[\frac{\partial P}{\partial x} \frac{dx}{dt} E_r + \frac{\partial P}{\partial t} E_r + P \frac{dE_r}{dx} \frac{dx}{dt} \right]$$

- VERY COMPLICATED, DEPS. HOW MAKE CHG
- MAY HAVE TO SOLVE AT MICRO LEVEL

Q-S: ALWAYS IN EQUIL; NOTHING CHGS EXCEPT VIA Δx

$$\Rightarrow \frac{\partial P}{\partial t} = 0$$

FUND POST: P CONST

$$\Rightarrow \frac{\partial P}{\partial x} = 0, \quad P \text{ SAME FOR ALL } r$$

THEN

$$\frac{d\bar{E}}{dt} = \underbrace{\left[\sum_r P(r) \frac{dE_r}{dx}\right]}_{\overline{\frac{dE_r}{dx}}} \frac{dx}{dt} \Rightarrow dW = -d\bar{E} = -\overline{\frac{dE_r}{dx}} \cdot dx$$

WHEN IS AN INFINITESIMAL A DIFFERENTIAL ?:

just wordy

INFIN. ≡ SMALL

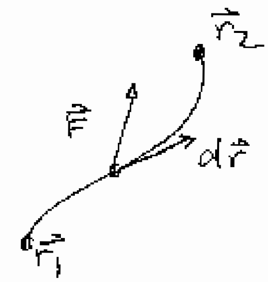
DIFF. ≡ INFIN. WHICH IS CHG IN SOME FN (ie DIFFERENCE)

(MORE SPECIFIC, CAN SAY MORE)

CLASSICAL MECHANICS :

- CAN I DEF. A $\mathcal{U}$ FOR SOME $\vec{F}$?
  (IS $\vec{F}$ CONSERVATIVE ?)

IN GENERAL



$$đW = \vec{F}\cdot d\vec{r}$$

$$W_{1\to 2} = \int_{PATH} \vec{F}\cdot d\vec{r}$$

ALL CAN SAY

SOMETIMES CAN DEFINE $\mathcal{U}(\vec{r})$ (ex GRAV, SPRING)

THEN IF $\boxed{\Delta K = 0}$ (w/ $\vec{F}$, W BY SYS) keep track of work for you

$$W = \int_{PATH} \vec{F}\cdot d\vec{r} = -\left[\mathcal{U}(\vec{r}_2) - \mathcal{U}(\vec{r}_1)\right]$$

OR

$$đW = \vec{F}\cdot d\vec{r} = -d\mathcal{U}$$

⇒ IN <u>THIS</u> CASE $đW$ IS A DIFF'L, NOT JUST INFIN.'L

WHEN DOES THIS WORK? (NPI)
WHEN IS $đW = \vec{F}\cdot d\vec{r}$ A DIFF'L ?

NECESSARY CONDITIONS:

$$(I) \quad W = \int_{PATH} đW = \int_{PATH} \vec{F}\cdot d\vec{r}$$

$$= -\left[\mathcal{U}(\vec{r}_2) - \mathcal{U}(\vec{r}_1)\right]$$

$\mathcal{U}(\vec{r})$ ONLY DEPENDS ON $\vec{r}$ $\therefore$ $\boxed{\int đW = \int \vec{F}\cdot d\vec{r} \text{ ONLY DEPENDS ON ENDPTS, NOT PATH.}}$

⇒ Diff. to test ⇒ must do all possible paths
⇒ look at in more detail to get diff. version:

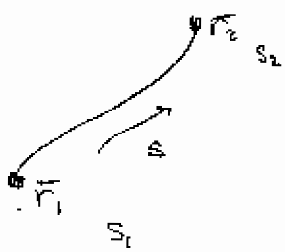
$$\boxed{(II) \quad \oint_{\text{CLOSED PATH}} đW = 0 = -[\mathcal{U}(\vec{r}_1) - \mathcal{U}(\vec{r}_1)]}$$

HOW DOES THIS WORK?

$$đW \overset{\vec{F}\cdot d\vec{r}}{=} \underbrace{F_x(x,y)}_{\text{some fns of } x,\, y}\, dx + F_y(x,y)\, dy \qquad (2d)$$

(add z if want)

$$W_{1\to 2} = \int_{PATH} [F_x\, dx + F_y\, dy]$$



PARAMETRIZE: $\vec{r}(s) = (x(s), y(s))$

$$\int_{s_1}^{s_2} ds \left[F_x(x(s),y(s))\frac{dx}{ds} + F_y(x(s),y(s))\frac{dy}{ds}\right]$$

WILL DEP. ON PATH (ex FRICTION)

BUT IF $\mathcal{U}$ EXISTS; above: $d\mathcal{U} = -đW = -F_x\, dx - F_y\, dy$,

$$\Rightarrow \quad F_x = \frac{-\partial \mathcal{U}(x,y)}{\partial x}, \quad F_y = \frac{-\partial \mathcal{U}(x,y)}{\partial y}$$

(ie if there's a fn $\mathcal{U}$ which satisfies these conditions)

THEN $\quad W_{1\to 2} = -\int_{s_1}^{s_2} ds \left[\frac{\partial U}{\partial x}\frac{dx}{ds} + \frac{\partial U}{\partial y}\frac{dy}{ds} \right]$

$$\underset{\text{(CHAIN RULE)}}{=} - \int_{s_1}^{s_2} ds \, \frac{dU}{ds} = -\left[U(\vec{r}_2) - U(\vec{r}_1)\right]$$

ONLY DEPENDS ON ENDS ✓

⇒ (III) DIFFERENTIAL VERSION:

IF $\quad F_x = \frac{-\partial U(x,y)}{\partial x} \qquad F_y = -\frac{\partial U(x,y)}{\partial y}$ $\left\{ \begin{array}{l} \text{sometimes can just} \\ \text{guess } U \text{ be} \\ \Rightarrow \text{done} \end{array} \right.$

THEN $\quad \frac{\partial F_x}{\partial y} = \frac{-\partial^2 U}{\partial x \partial y} = \frac{\partial F_y}{\partial x}$

$$\Rightarrow \boxed{\frac{\partial F_x}{\partial y} = \frac{\partial F_y}{\partial x}}$$

GENERAL: $\vec{\nabla} \times \vec{F} = 0$ (curl is zero)

most useful: only depends on F, not on knowing U; derivs easier than $\int$

now { THEN:

- F "CONSERVATIVE"
- CAN DEF. $U(\vec{r})$
- $đW = -dU$ A DIFF., NOT JUST AN INFIN. (if $\Delta K = 0$)

THERMO:

IN GENERAL

(2) $đW$, $đQ$ INFIN., NOT DIFF

(REFER TO TRANSFER OF E, NOT CHG IN FN)

just swap steps

(1) CAN DEFINE $\bar{E}$, V, $\bar{p}$, ... FOR MACROSTATE, $\therefore$ $d\bar{E}$, dV, $d\bar{p}$, ... ARE DIFF'S

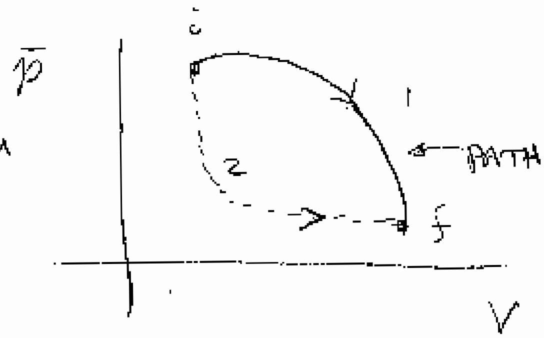
IN GENERAL $đW$ NOT A DIFF'L;

$\Rightarrow$ W_{if} DEPENDS ON PATH

ex

ONLY EXT PARAM IS V

$\Rightarrow \bar{p} \equiv -\dfrac{\partial \bar{E}}{\partial V}$



QUASISTATIC (SO $\bar{p}_V$ ONLY DEP. ON V WELL DEF'D)

EXPANSION

W_{if} = AREA UNDER $\Rightarrow$ DEPENDS ON PATH

(WILL HAVE DIFF Q'S)

BUT

IF THERM. ISOLATED $(Q=0)$

$$W_{if} = -\Delta\bar{E} \quad \text{OR} \quad đW = -d\bar{E}$$

$\therefore$ INDEP. OF PATH { ie no matter what you do; in what sequence – pistons, paddle whee... if get to same final state, add all diff work done → same }

$$\boxed{\begin{array}{l}1^{ST}\ \text{LAW OF THERMO:}\\ \text{FOR ISOLATED SYSTEM, } W_{if} \text{ INDEP OF PATH}\end{array}}$$

$\boxed{\equiv \text{CONS. OF } E}$

(only interesting if > 1 x_α; otherwise there is only 1 path w/ Q = 0) skip

(SO FOR EX. ABOVE, BOTH CAN'T HAVE $Q=0$)

(2) EXT. PARAMS FIXED $\Rightarrow$ $đW = 0$

$$đQ = d\bar{E}$$

$\Rightarrow$ AMT. OF HEAT ABS. INDEP. OF PATH
ONLY DEPENDS ON FINAL & INITIAL SYSTEMS

(3) ALWAYS:

COMBINATION

$$\underbrace{đQ - đW}_{\text{EXACT DIFF.}} = d\bar{E}$$