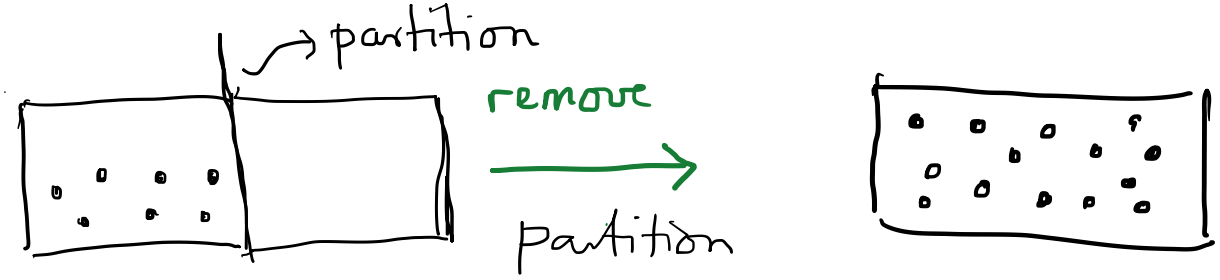
Quasistatic Transformations

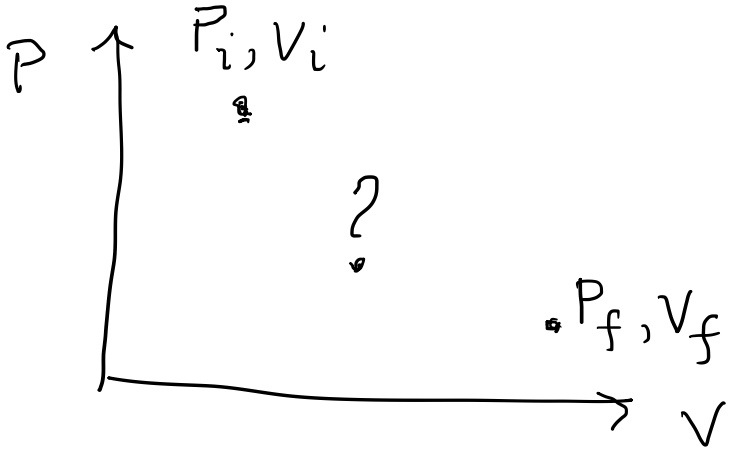
- A thermodynamic system in perfect equilibrium is boring
- We are interested in consequences of changes of equilibrium states.
- Not every transformation can be studied within the framework of thermodynamics

For example, free expansion of a gas ..



Initial state P_i, V_i, T_i

Final state P_F, V_f, T_f

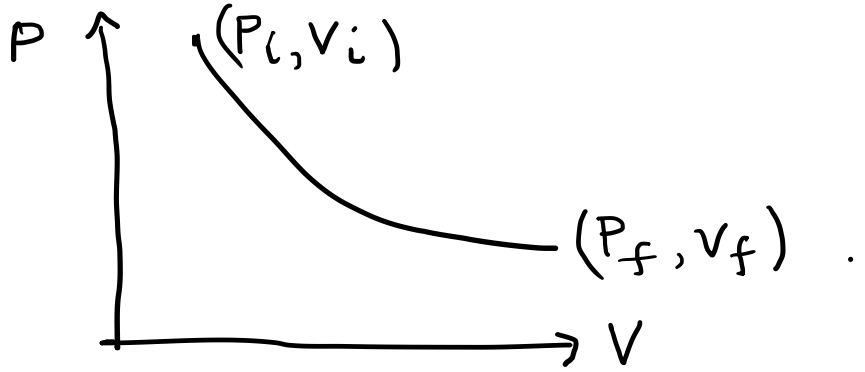


Alternative scenario ..

P_i, V_i
initial

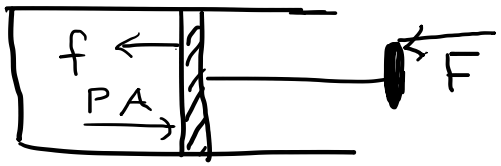
P_f, V_f
final

Quasi static transformation: Every state differs infinitesimally from an equilibrium state.



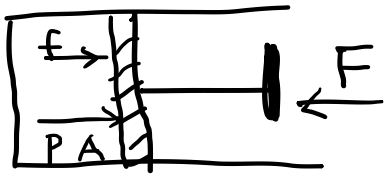
Reversible and Irreversible transformations

A quasistatic transformation from state A to state B is said to be **reversible** if the transformation can be carried out in the reverse direction without introducing any other changes in the system or surroundings.



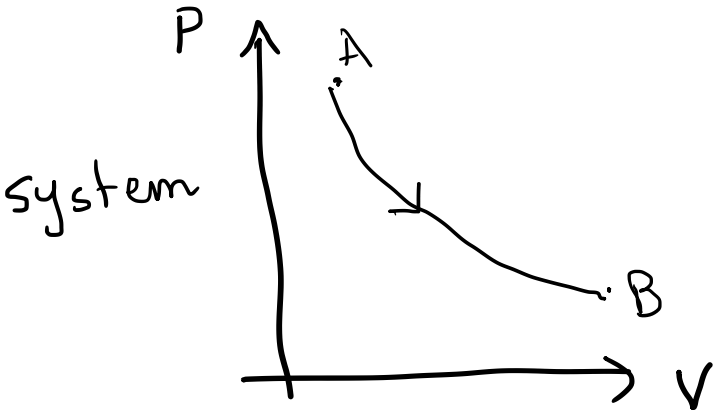
expansion

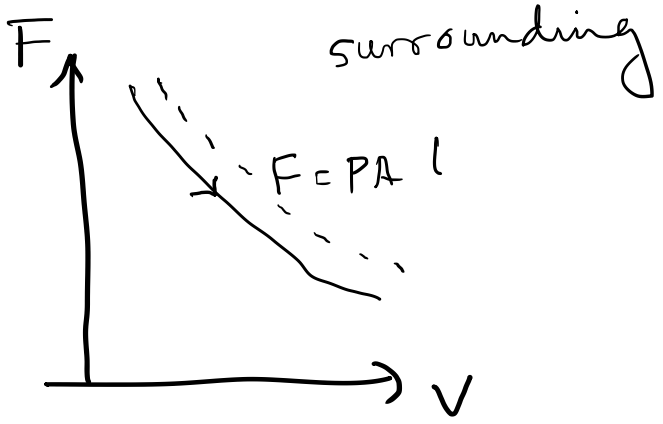
$F = PA - f$



compression

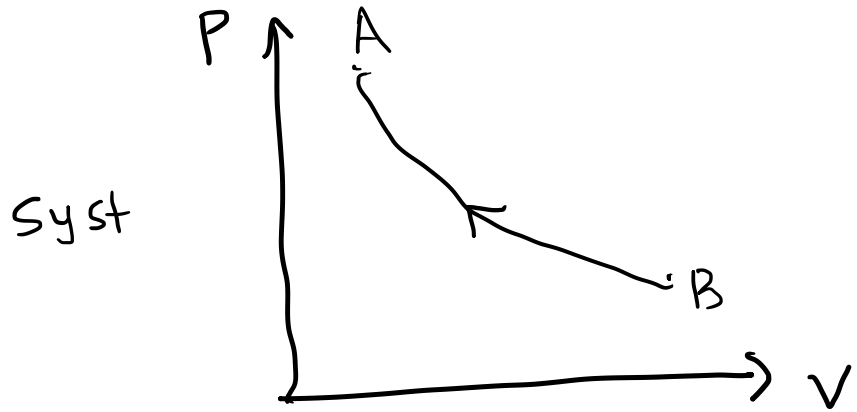
$F = PA + f$

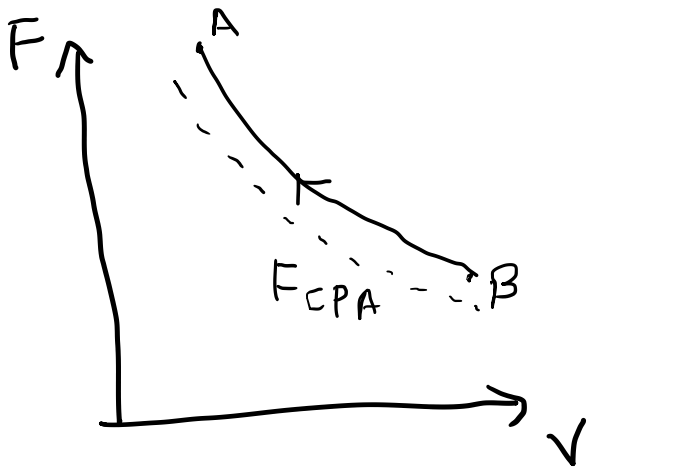




$F = PA - f$

expansion





surrounding

$F = PA + f$

compression

eliminate friction ⟶ reversible

Mathematical Interlude: Infinitesimals and differentials; exact and inexact differentials

2d plane x, y , dx, dy

multiply dx by # $\longrightarrow$ another infinitesimal

$2xy^3\,dx$, $3x^2y^3\,dy$

In general will have a form

$$dF = A(x,y)\,dx + B(x,y)\,dy \qquad (1)$$

Differentials

Consider fn. $G(x,y)$

$$dG = \left(\frac{\partial G}{\partial x}\right)_y dx + \left(\frac{\partial G}{\partial y}\right)_x dy$$

e.g. $G = x^2 y^3$

$$dG = \underbrace{2x\,y^3\,dx}_{A(x,y)} + \underbrace{3x^2 y^2\,dy}_{B(x,y)}$$

→ exact differential.

Infinitesimals that are not exact

$$dF = 2xy^2dx + 3x^2y^3dy$$

Q: Is there a corresponding $F(x,y)$?

If F were a fn:

$$\left(\frac{\partial F}{\partial x}\right)_y = 2xy^2 \quad \text{—①} \qquad ; \qquad \left(\frac{\partial F}{\partial y}\right)_x = 3x^2y^3 \quad \text{—②}$$

Integrate ①, $F(x,y) = x^2y^2 + c(y)$

Integrate ② $F(x,y) = \frac{3}{4}x^2y^4 + k(x)$

cannot find $c(y)$, $k(x)$

to match $F(x,y)$

$F(x,y)$ does not exist

dF is an inexact differential