Thermodynamics focuses on state functions: $P, V, M, \mathcal{S}, \ldots$

Nature often gives us response functions (derivatives):

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{\text{adiabatic}}$$

$$\chi_T \equiv \left(\frac{\partial M}{\partial H}\right)_T$$

<u>Example</u> Non-ideal gas

Given

- Gas $\rightarrow$ ideal gas for large T & V

- $$\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V - Nb}$$

- $$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{NkT}{(V - Nb)^2} + \frac{2aN^2}{V^3}$$

Find P

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT$$

$$P = \int \left(\frac{\partial P}{\partial T}\right)_V dT + f(V) = \int \left(\frac{Nk}{V - Nb}\right) dT + f(V)$$

$$= \frac{NkT}{(V - Nb)} + f(V)$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{NkT}{(V-Nb)^2} + \underbrace{f'(V)} = -\frac{NkT}{(V-Nb)^2} + \underbrace{\frac{2aN^2}{V^3}}$$

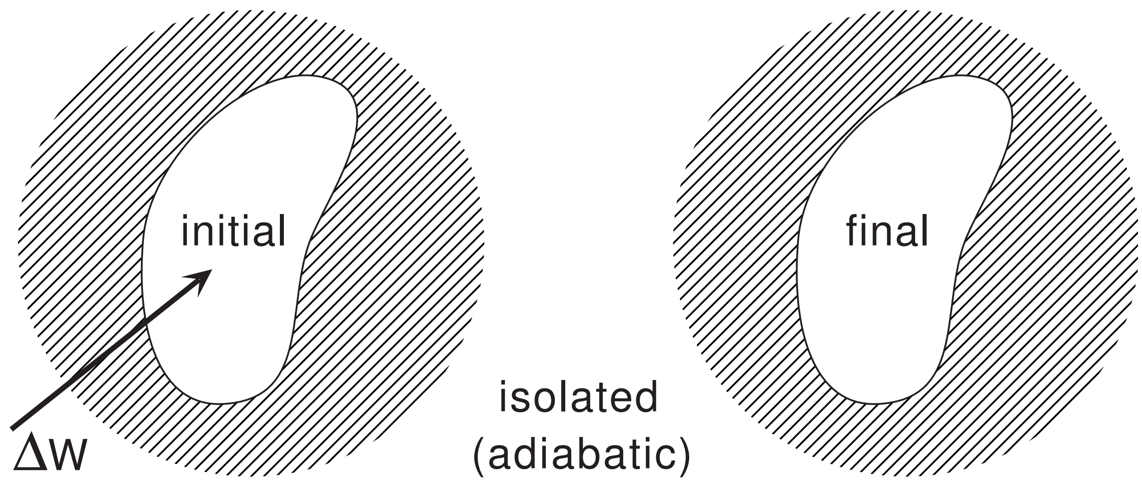
$$f(V) = \int \frac{2aN^2}{V^3}\, dV = -\frac{aN^2}{V^2} + c$$

$$P = \frac{NkT}{(V-Nb)} - \frac{aN^2}{V^2} + c$$

but $c = 0$ since $P \to NkT/V$ as $V \to \infty$

Internal Energy U

Observational fact



Final state is independent of how ΔW is applied.

Final state is independent of which adiabatic path is followed.

$\Rightarrow$ a state function U such that

$$\Delta U = \Delta W_{\text{adiabatic}}$$

$$\begin{aligned} U &= U(\text{independent variables}) \\ &= U(T,V) \text{ or } U(T,P) \text{ or } U(P,V) \text{ for a simple fluid} \end{aligned}$$

Heat

If the path is not adiabatic, $dU \neq đW$

$$đQ \equiv dU - đW$$

$đQ$ is the heat added to the system.

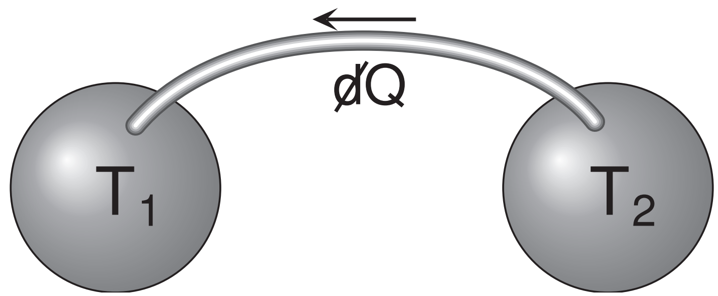
It has all the properties expected of heat.

First Law of Thermodynamics

$$dU = đQ + đW$$

- U is a state function
- Heat is a flow of energy
- Energy is conserved

Ordering of temperatures



When $đW = 0$, heat flows from high T to low T.

Example Hydrostatic System: gas, liquid or simple solid

Variables (with N fixed): P, V, T, U.

Only 2 are independent.

$$C_V \equiv \left(\frac{đQ}{dT}\right)_V \qquad C_P \equiv \left(\frac{đQ}{dT}\right)_P$$

Examine these heat capacities.

$$dU = đQ + đW = đQ - PdV$$

$$đQ = dU + PdV$$

We want $\dfrac{d}{dT}$. We have dV.

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$đQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) dV$$

$$\Rightarrow \frac{đQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) \frac{dV}{dT}$$

$$C_V \equiv \left(\frac{đQ}{dT}\right)_V = \underline{\left(\frac{\partial U}{\partial T}\right)_V}$$

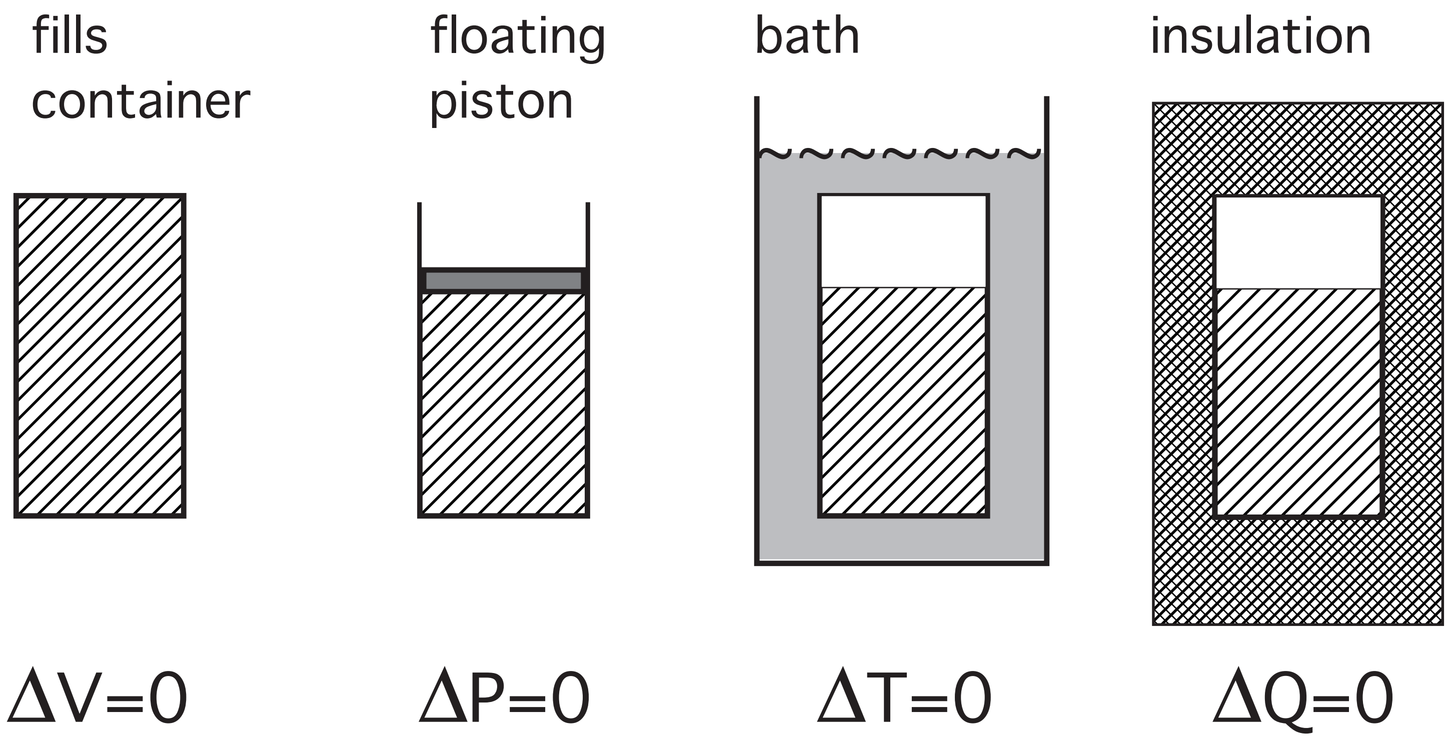
$$C_P \equiv \left(\frac{đQ}{dT}\right)_P = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)\underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{\alpha V}$$

$$\underline{C_P - C_V = \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)\alpha V}$$

The 2^{nd} law will allow us to simplify this further.

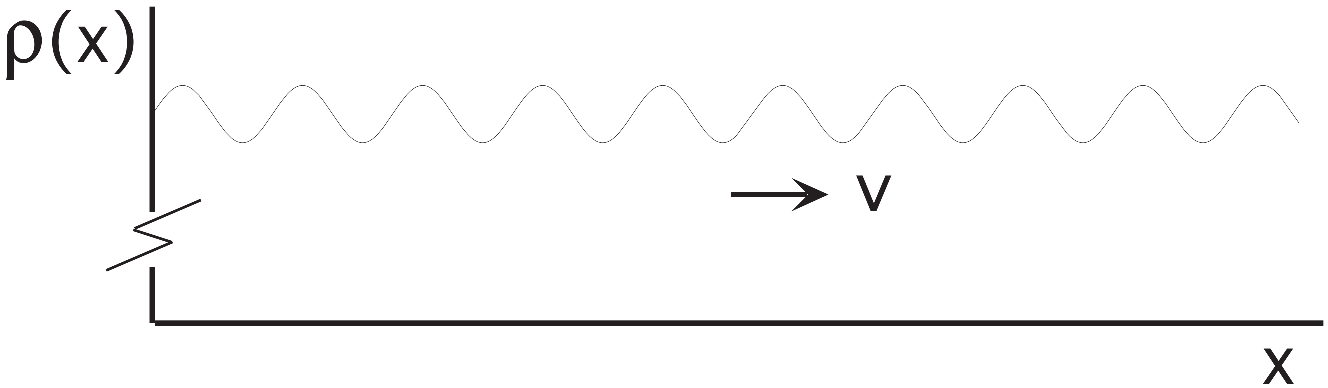
Note that $C_P \neq \left(\frac{\partial U}{\partial T}\right)_P$.

<u>Paths</u> Experimental conditions, not just math



$\Delta Q = 0$ could come from time considerations

Example Sound Wave



too fast for heat to flow out of compressed regions

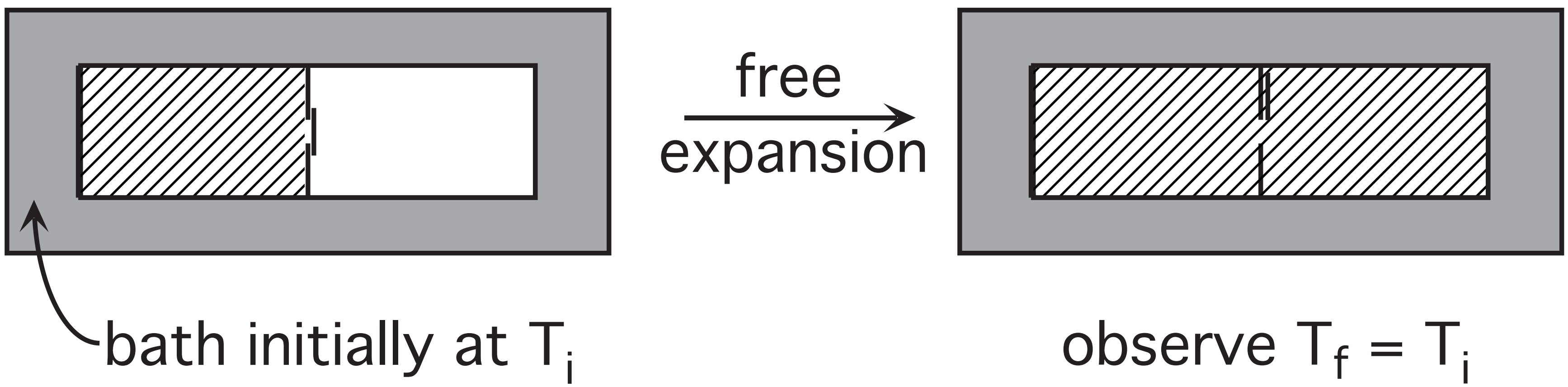
$$v = \sqrt{\frac{1}{\rho \kappa_S}}$$

Example Hydrostatic system: an ideal gas, PV=NkT

New information $\left.\frac{\partial U}{\partial V}\right|_T = 0$,

3 possible sources

- Experiment



No work done so $\Delta W = 0$

$T_f = T_i \Rightarrow \Delta Q = 0$

together $\quad \Rightarrow \quad \underbrace{\Delta U = 0}_{\text{here}} \quad \rightarrow \quad \underbrace{(\partial U/\partial V)_T = 0}_{\text{quasi-static changes}}$

- Physics: no interactions, single particle energies only $\Rightarrow (\partial U/\partial V)_T = 0$
- Thermo: 2^{nd} law + $(PV = NkT) \Rightarrow (\partial U/\partial V)_T = 0$

Consequences

$$dU = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{0} dV$$

$$U = \int_0^T C_V(T')\,dT' + \underbrace{\text{constant}}_{\text{set}=0}$$

In a monatomic gas one observes $C_V = \frac{3}{2}Nk$.

Then the above result gives $U = C_V T = \frac{3}{2}NkT$.

$$C_P - C_V = (\underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{0} + P) \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{\frac{\partial}{\partial T}(NkT/P)_P = Nk/P}$$

$$= Nk \qquad \text{for any ideal gas}$$

Applying this to the monatomic gas one finds

$$C_P = \frac{3}{2}Nk + Nk = \frac{5}{2}Nk$$

$$\gamma \equiv C_P/C_V = \frac{5}{3}$$

Adiabatic Changes $\quad đQ = 0$

Find the equation for the path.

Consider a hydrostatic example.

$$đQ = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \underbrace{\left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)}_{(C_P - C_V)/\alpha V} dV = 0$$

$$\left(\frac{\partial T}{\partial V}\right)_{\Delta Q=0} = -\left(\frac{C_P - C_V)}{C_V}\right)\frac{1}{\alpha V} = -\frac{(\gamma - 1)}{\alpha V}$$

This constraint defines the path.

Apply this relation to an ideal gas.

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\,\frac{\partial}{\partial T}\left(\frac{NkT}{P}\right)_P = \frac{1}{V}\left(\frac{Nk}{P}\right) = \frac{1}{V}\frac{V}{T} = \frac{1}{T}$$

Path

$$\frac{dT}{dV} \;=\; -(\gamma - 1)\frac{T}{V}$$

$$\frac{dT}{T} \;=\; -(\gamma - 1)\frac{dV}{V} \rightarrow \ln\left(\frac{T}{T_0}\right) = -(\gamma - 1)\ln\frac{V}{V_0}$$

$$\left(\frac{T}{T_0}\right) \;=\; \left(\frac{V}{V_0}\right)^{-(\gamma-1)}$$

Adiabatic

$TV^{\gamma-1} = c$

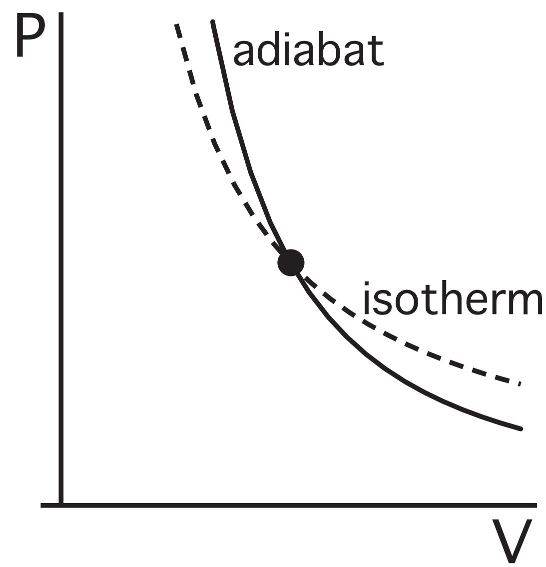
$PV^{\gamma} = c'$

$\gamma = 5/3$

(monatomic)

$P \propto V^{-5/3}$

$$\frac{dP}{dV} = -\frac{5}{3}\frac{P}{V}$$



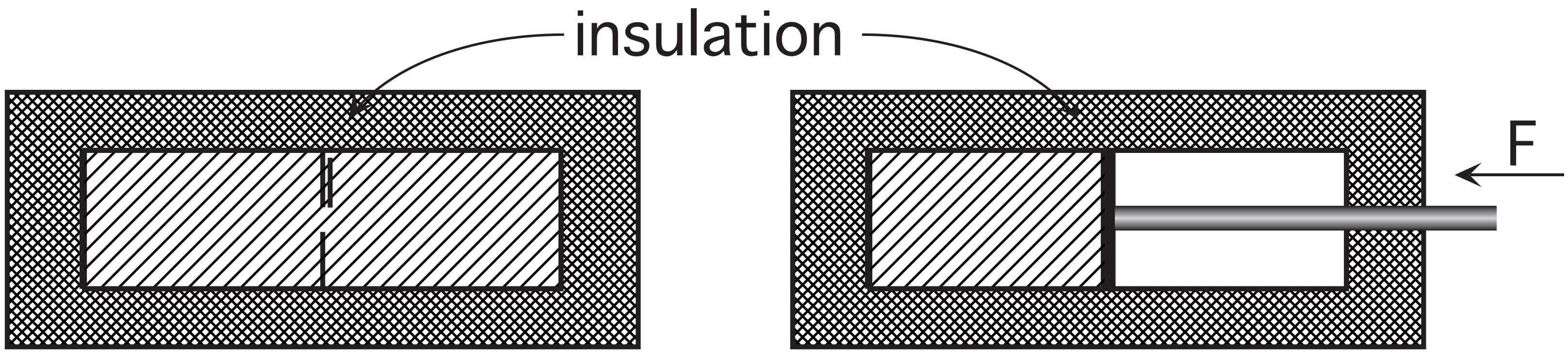
Isothermal

$PV = c''$

$P \propto V^{-1}$

$$\frac{dP}{dV} = -\frac{P}{V}$$

Expansion of an ideal gas



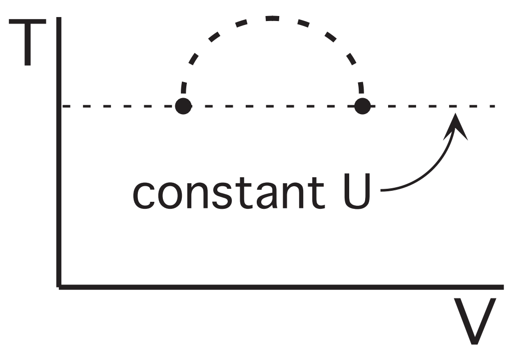
rupture diaphragm

adiabatic $\Delta Q = 0$

not quasistatic

$\Delta W = 0$

$\rightarrow \Delta U = 0$



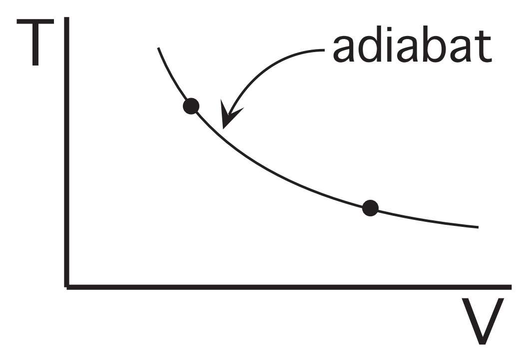
slowly move piston

adiabatic $\Delta Q = 0$

quasistatic

ΔW is negative

$\rightarrow \Delta U =$ is negative



Starting with a few known facts,

1^{st} law, $đW$, and state function math,

one can find

relations between some thermodynamic quantities,

a general expression for dU,

and the adiabatic constraint.

Adding models for the equation of state and the heat capacity allows one to find

the internal energy U

and the adiabatic <u>path</u>.