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

Nature often gives us response functions (derivatives):

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

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

Example 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

$$
\begin{aligned}
dP &= \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT \\
P &= \int \left(\frac{\partial P}{\partial T}\right)_V dT + f(V) = \int \left(\frac{Nk}{V - Nb}\right) \, dT + f(V) \\
&= \frac{NkT}{(V - Nb)} + f(V)
\end{aligned}
$$

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

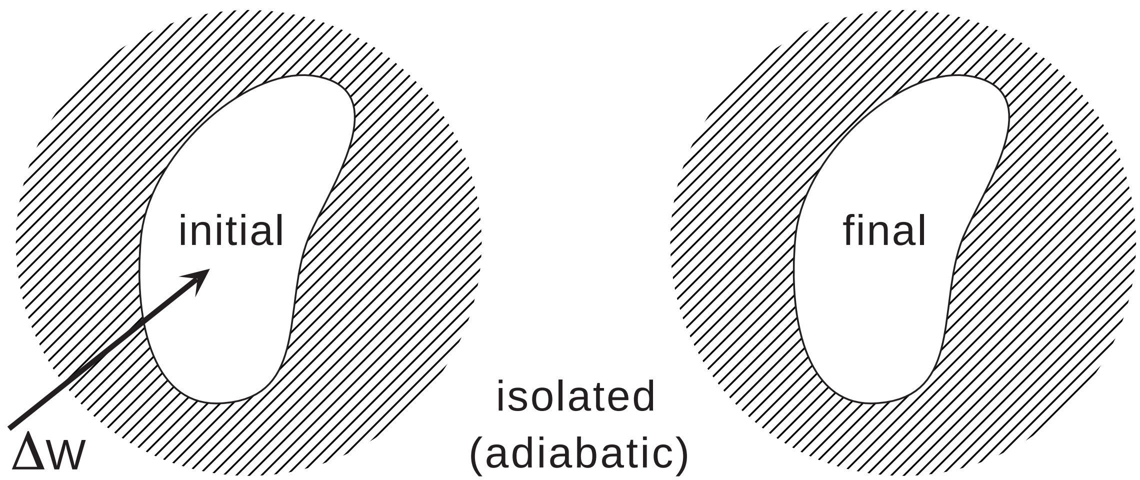
$$f(V) = \int \frac{2aN^2}{V^3}\, dV = -\frac{aN^2}{V^2} + c$$

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

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

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

$$U = U(\text{independent variables})$$

$$= U(T,V) \text{ or } U(T,P) \text{ or } U(P,V) \text{ for a simple fluid}$$

Heat

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

$$đQ \equiv dU - đW$$

$đQ$ is the heat added to the system.

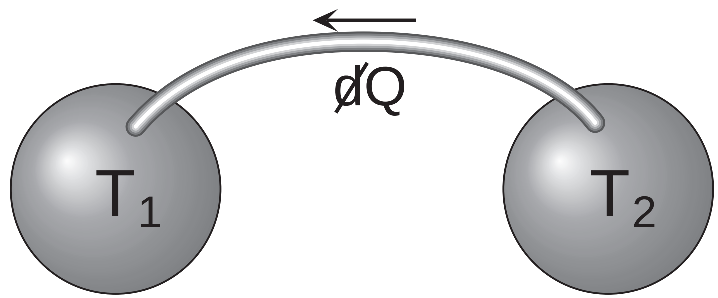
It has all the properties expected of heat.

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