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

Nature often gives us response functions (derivatives):

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

$$
\chi_T \equiv \left( \frac{\partial M}{\partial H} \right)_T
$$
Example Non-ideal gas

Given

- Gas → 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 $P$
\[ dP = \left( \frac{\partial P}{\partial V} \right)_T \, dV + \left( \frac{\partial P}{\partial T} \right)_V \, dT \]

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

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

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

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

but \( c = 0 \) since \( P \to NkT/V \) as \( V \to \infty \)
Internal Energy $U$

Observational fact

Final state is independent of how $\Delta W$ is applied. Final state is independent of which adiabatic path is followed.

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⇒ a state function $U$ such that

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

$U = U$(independent variables)

$=$ $U(T, V)$ or $U(T, P)$ or $U(P, V)$ for a simple fluid
Heat

If the path is not adiabatic, \( dU \neq dW \)

\[ \delta Q \equiv dU - dW \]

\( \delta Q \) is the heat added to the system.

It has all the properties expected of heat.
First Law of Thermodynamics

\[ dU = \delta Q + \delta W \]

- \( U \) is a state function
- Heat is a flow of energy
- Energy is conserved
Ordering of temperatures

When $\dot{W} = 0$, 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.

\[
C_V \equiv \left( \frac{\Delta Q}{dT} \right)_V \quad C_P \equiv \left( \frac{\Delta Q}{dT} \right)_P
\]

Examine these heat capacities.
\[ dU = dQ + dW = dQ - PdV \]

\[ dQ = dU + PdV \]

We want \( \frac{d}{dT} \). We have \( dV \).

\[ dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \]
\[ \dot{Q} = \left( \frac{\partial U}{\partial T} \right)_V \, dT + \left( \left( \frac{\partial U}{\partial V} \right)_T + P \right) \, dV \]

\[ \Rightarrow \frac{\dot{Q}}{dT} = \left( \frac{\partial U}{\partial T} \right)_V + \left( \left( \frac{\partial U}{\partial V} \right)_T + P \right) \frac{dV}{dT} \]

\[ C_V \equiv \left( \frac{\dot{Q}}{dT} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V \]
\[ C_P \equiv \left( \frac{dQ}{dT} \right)_P = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T + P \left( \frac{\partial V}{\partial T} \right)_P \]

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

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

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