

Tue 7 Mar

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Mixing entropy - more in tutorial

Pressure $P = - \frac{\partial \langle E \rangle}{\partial V} \Big|_S$ connected to mechanical work

$$P = \frac{-F \Delta x}{-A \Delta x} = \frac{F}{A} = \frac{-W}{\Delta V}$$

$$\underline{W = \Delta \langle E \rangle = F \Delta x = -P \Delta V} \quad (\text{assumed } \underline{\text{constant entropy}})$$

\searrow $\langle E \rangle$ can also change due to changing entropy

$$\Delta \langle E \rangle = W + \underline{\text{more}}$$

$W = -P dV$ holds whether or not entropy changes

\hookrightarrow infinitesimal generalizes to $W = - \int_{V_0}^{V_F} P dV$

Ideal gas law: $P(V) = \frac{NT}{V}$

$W > 0$ is work done on gas by surroundings (raises energy)

$W < 0$ is work done by gas, reduces $\langle E \rangle$

How can $\langle E \rangle$ change without work?

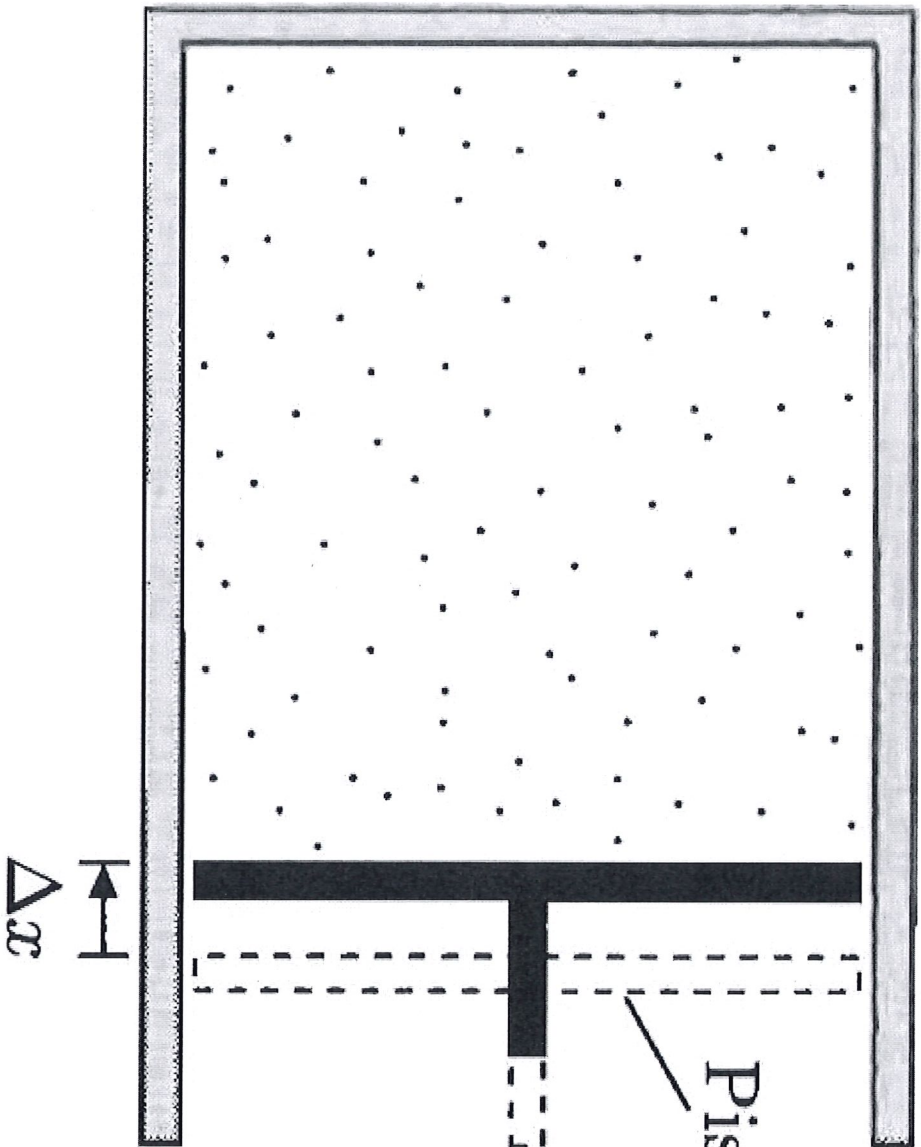
Keep V constant $\rightarrow W = 0$

Change temperature dT

$$\langle E \rangle = \frac{3}{2} NT \rightarrow d\langle E \rangle = \frac{3}{2} N dT$$

Canonical ensemble demands fixed T

We considering different canonical systems in equilibrium with different thermal reservoir $\rightarrow T_i, T_f$



Piston area = A

Force = F

$$\Delta V = -A \Delta x$$

$$W = F \Delta x = \Delta E$$

Δx

$$d\langle E \rangle = \frac{3}{2} N dT$$

↳ Expect change in entropy

$$S = N \log(\lambda_{th}^{-3}) + T\text{-indep.}$$

$$\lambda_{th} \propto \frac{1}{\sqrt{T}}$$

$$= N \log(T^{3/2}) + T\text{-indep.}$$

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$$dS = d\left(\frac{3}{2} N \log T\right) = \frac{3}{2} N \frac{dT}{T} = \frac{d\langle E \rangle}{T}$$

$$\rightarrow d\langle E \rangle = T dS$$

This change in internal energy with constant V, N

is the heat $Q = T dS$

$$\rightarrow Q = \int_{S_0}^{S_f} T(S) dS$$

↳ assuming $S(T)$ invertible

With no work $d\langle E \rangle = Q = \int T dS$

Energy and entropy not being created or destroyed

Instead (reversibly) flowing back & forth

between system & surroundings

I s e n t r o p i c processes $dS = 0$

More generally, no heat transfer, $Q = 0$

→ adiabatic process

Adiabatic & reversible = isentropic

In practice, adiabatic processes must be fast

no time for heat exchange

Other extreme of slow processes ← all possible heat exchange

Keeps temperature fixed to T of reservoir

↳ isothermal

Real processes in between extremes - usually closer to adiabatic

Putting things together

Invert $S(T, V) \rightarrow T(S, V)$

Fixing N

$$\langle E \rangle(T, V) \rightarrow \langle E \rangle(S, V)$$

Taylor expand change in energy

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_V$$

$$\langle E \rangle(S, V) \approx \langle E \rangle(S_0, V_0) + (S - S_0) \left. \frac{\partial \langle E \rangle}{\partial S} \right|_V + (V - V_0) \left. \frac{\partial \langle E \rangle}{\partial V} \right|_S + \dots$$

$$d\langle E \rangle = dS(T) + dV(-P) = TdS - PdV = Q + W$$

Generalized first law

Any change in system's internal energy matched by heat exchange w/ surroundings or work done (or both)

Other key ideal gases equations

$$\langle E \rangle = \frac{3}{2} NT$$

$$S \propto VT^{3/2} \quad (\text{constant})$$

$$EoS \quad (\text{ideal gas law}) \quad PV = NT$$

Sequence of processes that returns to initial macro-state $(P, V, T, \langle E \rangle)$

~~Thermodynamic cycle~~

Thermodynamic cycle can be repeated to do work, transfer heat, etc. (engine) (refrigerator)

Fixing $N \rightarrow$ all info contained in pressure and volume

$$T = \frac{PV}{N}$$

$$\langle E \rangle = \frac{3}{2} NT = \frac{3}{2} PV$$

$$S \propto V \left(\frac{PV}{N} \right)^{3/2}$$

Useful tool: Represent macro-state as a point in pressure-volume plane

*PV diagram

State ~ point

Process ~ line

Cycle ~ closed path

