

Tue 12 Mar

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## Recap

Mixing and reversibility

Pressure  $P = \left. \frac{-\partial \langle E \rangle}{\partial V} \right|_S$

Ideal gas law  $PV = NT$  (equation of state)

Relate pressure to work done by force  
changing volume

→ change internal energy  $\langle E \rangle$

$$W = -P dV \rightarrow -\int_{V_0}^{V_F} P(V) dV$$

Can also change  $\langle E \rangle = \frac{3}{2} NT$  with constant volume  
( $W=0$ )

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

Entropy =  $\frac{3}{2} N \log T + T$ -indep.

$$\boxed{dS = \frac{3}{2} N \left( \frac{dT}{T} \right) = \frac{d\langle E \rangle}{T}} \quad \text{page 70}$$

Heat is change in  $\langle E \rangle$  with constant  $V$

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

$$\Delta \langle E \rangle = Q = \int_{S_0}^{S_F} T(S) dS$$

(assuming  $S(T)$  invertible)

Energy flowing between system and surroundings  
(not created or destroyed) similar for entropy

Adiabatic process changes  $\langle E \rangle$  with  $Q=0$

Adiabatic + reversible = isentropic  $dS=0$   
↳ assume

Fast - no time for heat flow

Other extreme: isothermal processes change  $\langle E \rangle$   
with fixed  $T$

Slow - all possible heat flow to/from reservoir

Real processes in between - usually closer to adiabatic

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

Taylor expand  $\langle E \rangle(S, V) = \langle E \rangle(S_0, V_0) + (S - S_0) \frac{\partial \langle E \rangle}{\partial S} \Big|_V + (V - V_0) \frac{\partial \langle E \rangle}{\partial V} \Big|_S + \dots$   
↳  $\frac{1}{T} = \frac{\partial S}{\partial E}$   
↳  $P$

$$d\langle E \rangle = dS \left( \frac{1}{T} \right)^{-1} + dV(-P)$$
$$= T dS - P dV = Q + W$$

Generalized First law

Any change in internal energy matched  
by heat flow to/from surroundings  
and work done on/by surroundings

Other key ideal gas equation

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

~~Boltzmann~~

S function of  $VT^{3/2}$

$$PV = NT \quad (EoS)$$

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

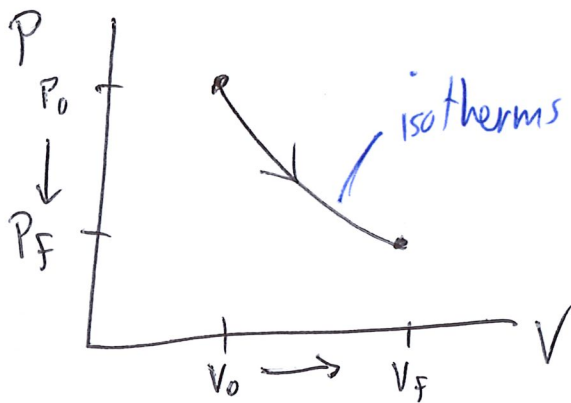
→ Thermodynamic cycle can be repeated  
to do work, transfer heat

### PV ~~Phase~~ diagrams

$N$  Fixed →  $P$  and  $V$  specify macro-state

$$T = \frac{PV}{N} \quad \langle E \rangle = \frac{3}{2} PV$$

$$S \text{ func. of } V \left( \frac{PV}{N} \right)^{3/2}$$



Macro-state ↔ point  
processes ↔ line  
cycles ↔ closed paths

Example: Isothermal expansion (slow)

$$\text{Fixed } T = \frac{P_0 V_0}{N} = \frac{P_F V_F}{N}$$

$$P_F = \left( \frac{V_0}{V_F} \right) P_0 < P_0$$

$$\Delta P = \left[ \left( \frac{V_0}{V_F} \right) - 1 \right] P_0 < 0$$

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$$W = - \int_{V_0}^{V_F} P(V) dV < 0 \rightarrow \text{decreasing } \langle E \rangle = T$$

Need heat to come in to keep  $T = \frac{\langle E \rangle}{\frac{3}{2} N}$  fixed

What happens if two isotherms cross?

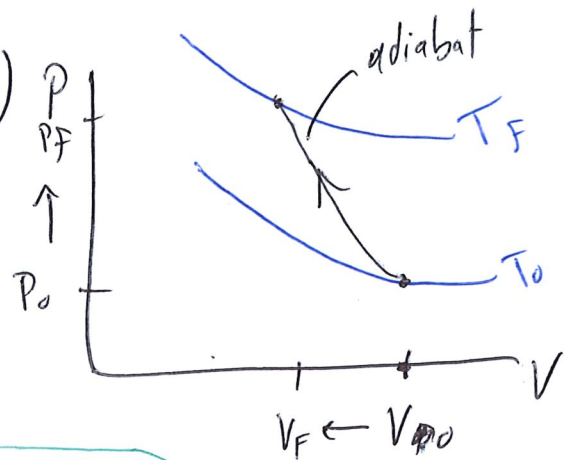
$$\text{Same } \frac{PV}{N} = T \rightarrow \text{same isotherm}$$

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Different isotherms  $T_i \neq T_j$  never cross

Example: Adiabatic compression (fast)

$Q=0 \rightarrow$  temperature changes  
connect two isotherms



$$\text{Constant entropy: } V_0 T_0^{3/2} = V_F T_F^{3/2}$$

$$T_F = \left(\frac{V_0}{V_F}\right)^{2/3} T_0 > T_0$$

$$\Delta T \left[ \left(\frac{V_0}{V_F}\right)^{2/3} - 1 \right] \frac{P_0 V_0}{N} > 0$$

$$V_0^{2/3} \left(\frac{P_0 V_0}{N}\right) = V_F^{2/3} \left(\frac{P_F V_F}{N}\right)$$

$$P_F = \left(\frac{V_0}{V_F}\right)^{5/3} P_0 > P_0$$

$$\Delta P \left[ \left(\frac{V_0}{V_F}\right)^{5/3} - 1 \right] P_0 > 0$$

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