Statistical Physics

Understanding the behavior of macroscopic objects

$\sim 10^{23}$ particles

$\Rightarrow$ use statistics

(actually just mean (average) and fluctuations)

Microscopic physics is time-reversible

$$-\vec{\nabla} V(x) = F = m\,\frac{d^2x}{dt^2}$$

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \xrightarrow{t \to -t} i\hbar \frac{\partial \psi^*}{\partial t} = H\psi^*$$

Macroscopic physics is irreversible

Not easy to formulate theoretically

Various types of problems

- irreversibility
- transport (kinetic theory) } time dependent
- equilibrium (easier solutions) } time independent
- exotic phenomena
  - chaos
  - emergence

Thermodynamics: An empirical theory. Successful. Try to "derive" it.

Laws

0th Law: Existence of temperature (and thermometers)

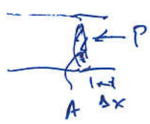
$T_A = T_B$, $T_B = T_C \Rightarrow T_A = T_C$

"Temperature is transitive"

1st Law: Conservation of energy

$$dU = dQ - dW$$

$$dW = P\,dV$$



For a mechanical system $\Delta W = (PA) \cdot \Delta x = P\Delta V$

Magnetic system $dW = -H\,dM$

(P & H are "fields"
V and M are "extensive variables")

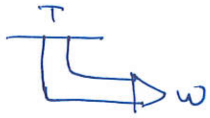
proportional to the amount of material you have

2nd Law: Irreversibility

3rd Law: Simplicity of low temperature

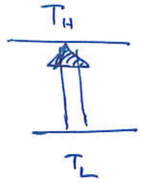
The second law

Kelvin statement



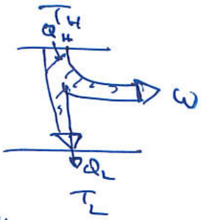
"perfect engine" is not possible

Claussius statement



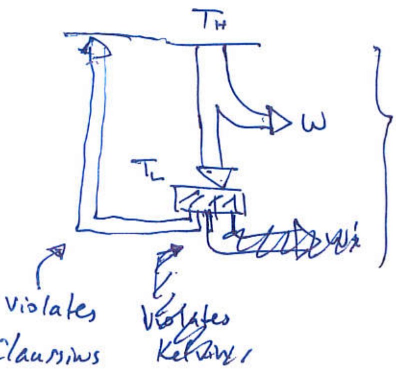
"perfect refrigerator" is not possible

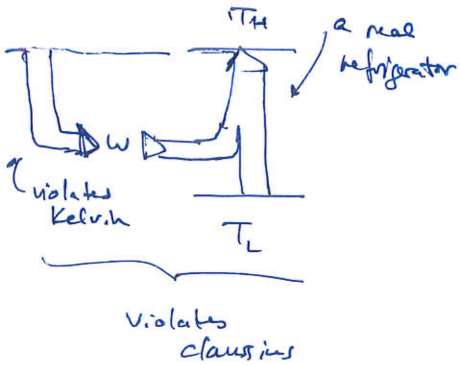
possible system



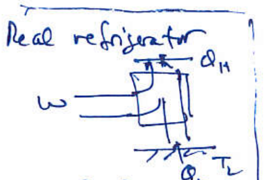
"Engine"

"Refrigerator" if reversed

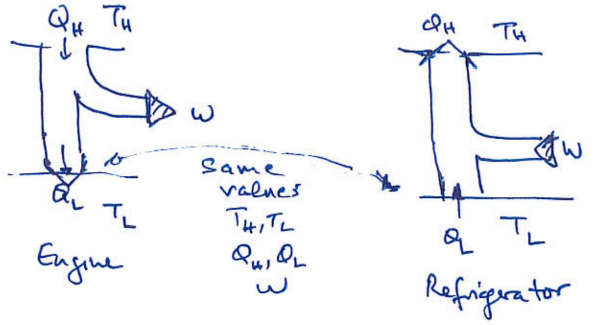




A reversible engine: one that will reverse Q_H, Q_L, W



$\frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} > \eta_e$



Efficiency: $\eta = \frac{W}{Q_H}$

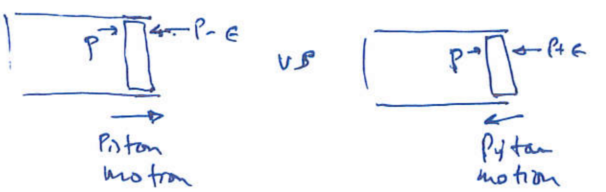
$= \frac{Q_H - Q_L}{Q_H}$

$= 1 - \frac{Q_L}{Q_H}$

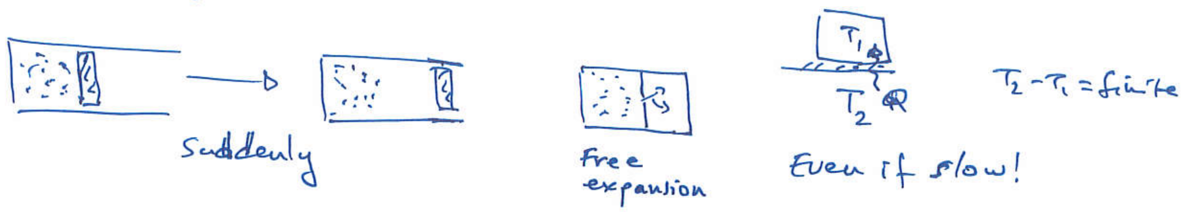
Is such an engine possible?

If you use only "reversible changes".

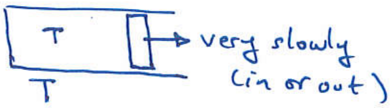
Reversible change is one whose direction may be changed by an infinitesimal change in its surroundings.

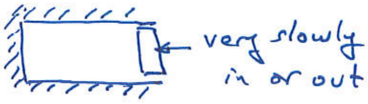


Irreversible changes



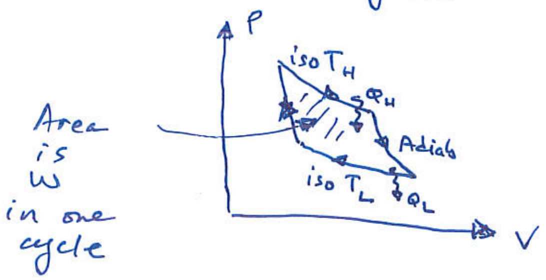
Various types of reversible changes (mechanical system)

Isothermal: 

Adiabatic 

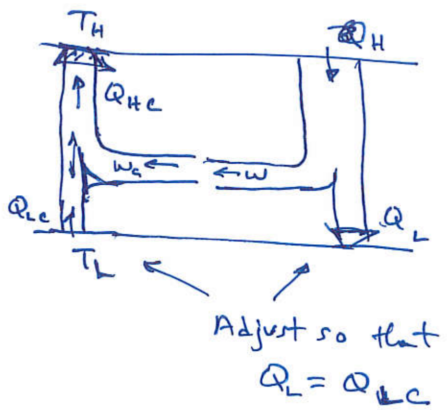
Work is done by the system as it moves out
" " " on " " " " " in

The Carnot cycle



All changes reversible
$\Rightarrow$ reversible engine/refrigerator

Thm: No engine may have an efficiency larger than a Carnot engine.
(For same T_H, T_L)



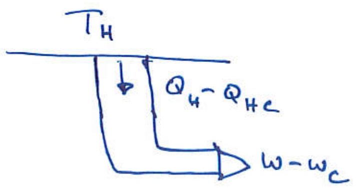
Claim:

$$\eta_C = 1 - \frac{Q_{LC}}{Q_{HC}} < 1 - \frac{Q_L}{Q_H}$$

$$\frac{Q_{LC}}{Q_{HC}} > \frac{Q_L}{Q_H} \qquad Q_H > Q_{HC} \text{ if } Q_L = Q_{LC}$$

i.e. $W > W_C$

|||

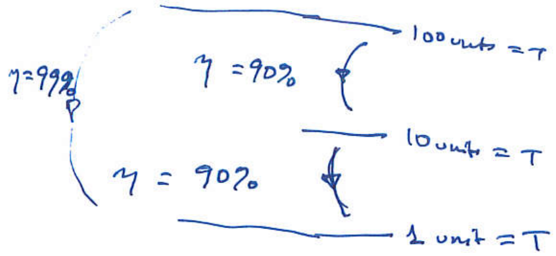


Violates Kelvin!

$\Rightarrow$ All reversible engines have the same efficiency for a certain T_H, T_L
$\Rightarrow$ All realistic " " lower efficiency " " " " "

For any T_H, T_L pair, there is a certain value for the efficiency. We will use this fact to define a temperature scale:

For each T_H, T_L pair, set



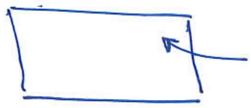
$$1 - \frac{Q_{LC}}{Q_{HC}} = 1 - \frac{T_L}{T_H}$$

or

$$\frac{Q_{LC}}{Q_{HC}} = \frac{T_L}{T_H}$$

→ Page 4.5

The ideal gas



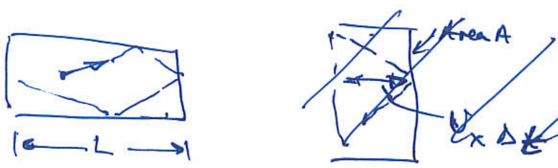
N particles of mass m inside volume V

Internal energy U

$$\frac{1}{N} \sum_{i=1}^{N} \frac{1}{2} m \left(v_{xi}^2 + v_{yi}^2 + v_{zi}^2 \right) = U \frac{1}{N}$$

$$\frac{1}{2} m \cdot 3 \langle v_x^2 \rangle = U/N \qquad \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{3} \frac{U}{N}$$

Near the wall



$\frac{N}{V} v_x \Delta t \cdot A$ ~~atoms to collide with~~

particle i with v_{xi} hits the wall with interval $\frac{2L}{v_{xi}} = \Delta t$

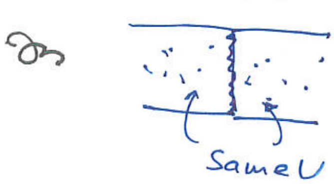
$\frac{\text{momentum transfer to the wall}}{\text{interval}}$: $\frac{2 v_{xi} m}{2L / v_{xi}}$

Total force: $\sum_i m \frac{v_{xi}^2}{L}$

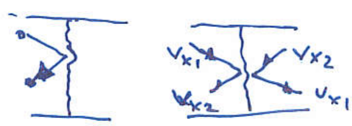
Pressure: $\frac{m}{V} \sum_i v_{xi}^2 = \frac{N}{V} m \langle v_x^2 \rangle = \frac{2}{3} U \frac{1}{V} = P$

$$\boxed{PV = \frac{2}{3} U}$$

Energy transfer at boundary



Assume boundary is elastic, reflects on way hits, otherwise 2 particle collisions



x-velocities interchanged
no effect if same U on both sides → Same U ⇒ same T

$U = U(T)$

$$\eta_C \geq \eta$$

$$1 - \frac{Q_{LC}}{Q_{HC}} \geq 1 - \frac{Q_L}{Q_H}$$

$$-\frac{T_L}{T_H} \geq -\frac{Q_L}{Q_L}$$

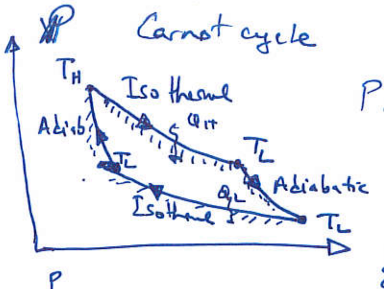
$$\frac{Q_L}{Q_H} \geq \frac{T_L}{T_H}$$

$$\cancel{\frac{T_H}{Q_H} \leq \frac{T_L}{Q_L}} \qquad \frac{Q_L}{T_L} \geq \frac{Q_H}{T_H}$$

$$\cancel{\frac{T_H}{Q_H} - \frac{T_L}{Q_L} \geq 0} \qquad \frac{Q_H}{T_H} - \frac{Q_L}{T_L} \leq 0$$

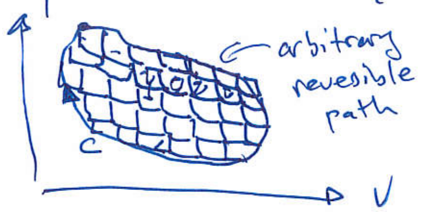
Take heat coming in as positive, heat going out as negative

$$\sum_i \frac{Q_i}{T_i} \leq 0$$



PdV → work done

$$\oint \frac{dQ}{T} \leq 0$$



$$\oint_{rev} \left[\frac{dQ}{T}\right]_{rev} = 0$$

$$\oint P\,dV = \sum_i \oint_{C_i} P\,dV$$

define $\left[\frac{dQ}{T}\right]_{rev} = dS$

dS is a perfect differential

S is an extensive property of the system

ΔS between two states may be found by calculating $\Delta S = \int_A^B \left[\frac{dQ}{T}\right]_{rev}$

An absolute value may be assigned by choosing $\underbrace{S(T=0)=0}_{\text{third Law}}$

(For systems with non-degenerate ground states only!)

A reversible heat transfer:

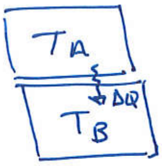
$\Delta S_1 = -\frac{\Delta Q}{T_A}$

$\Delta S_2 = +\frac{\Delta Q}{T_A - \epsilon}$

$\Big\}\ \Delta S = 0 + \underbrace{O(\epsilon)}_{\text{irreversibility factor} \to 0}$

An irreversible heat transfer

$T_A > T_B$

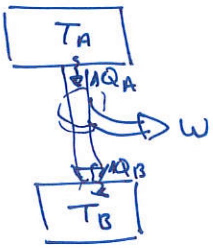


$\Delta S_1 = -\frac{\Delta Q}{T_A}$

$\Delta S_2 = +\frac{\Delta Q}{T_B}$

$\Big\}\ \Delta S = \Delta Q\left(\frac{1}{T_B} - \frac{1}{T_A}\right) > 0$

Transfer the heat using an engine



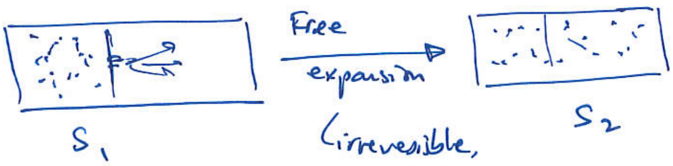
After one cycle, the engine is in its original state $\Rightarrow \Delta S_{engine} = 0$

$\Delta S_A = -\frac{\Delta Q_A}{T_A}$

$\Delta S_B = +\frac{\Delta Q_B}{T_B}$

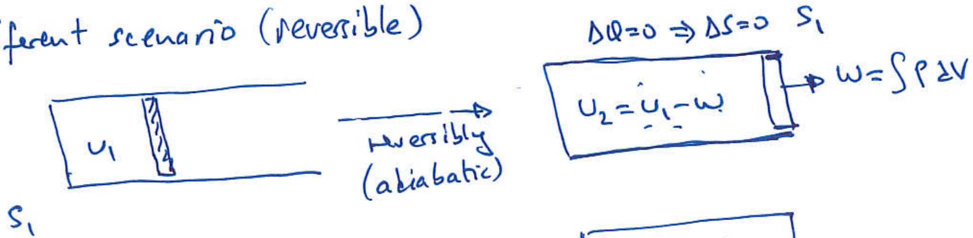
$\Big\}\ \Delta S = \underbrace{\frac{\Delta Q_B}{T_B} - \frac{\Delta Q_A}{T_A}}_{\text{opposite of engine relation}} \geq 0$

Another example

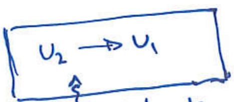


(irreversible, $\Delta S \neq \int \frac{dQ}{T} = 0$

Different scenario (reversible)



$$\boxed{\begin{gathered} U_2 = U_1\left(\frac{V_1}{V_2}\right)^{2/3} \\ \frac{U_2}{U_1}\left(\frac{V_2}{V_1}\right)^{2/3} = 1 \\ S_{\text{ideal gas}} \approx N k_B \ln\left(\frac{V T^{3/2}}{N}\, e\right) \Rightarrow \Delta S = 0 \end{gathered}}$$



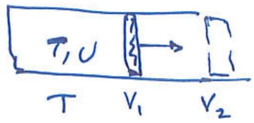
$S_1 \to S_2 : S_2 > S_1$

Total $\Delta S = 0$

ΔS of gas $= -\Delta S$ of heat source

TD5

Ideal Gas <u>isothermal expansion</u>



U constant $\Rightarrow \Delta Q = W$

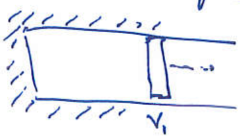
$$PV = \frac{2}{3} U$$

$$P = \frac{2}{3}\frac{U}{V}$$

$$W = \int_{V_1}^{V_2} P\,dV = \frac{2}{3} U \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= \frac{2}{3} U \ln \frac{V_2}{V_1} = \Delta Q$$

<u>Adiabatic expansion</u>



$dQ = 0$

$dU = -P\,dV$

$\frac{dU}{dV} = -P$

$$U = U_1 - \int_{V_1}^{V} P\,dV$$

$$\frac{dU}{dV} = -P = -\frac{2}{3}\frac{U}{V}$$

$$\frac{dU}{U} = -\frac{2}{3}\frac{dV}{V}$$

$$\ln U = -\frac{2}{3}\ln V + c$$

$$U = V^{-2/3} c$$

$U = U_1$ when $V = V_1$ $\Rightarrow$ $U_1 = V_1^{-2/3} c \Rightarrow c = U_1 V_1^{2/3}$

$$\Rightarrow U(V) = U_1 \left(\frac{V_1}{V}\right)^{2/3} \qquad \Delta U = -W$$

"Our" Carnot cycle: start with $U_1, V_1 \xrightarrow{\text{iso } T_H} U_1 V_2$ with $V_2 = 2V_1$

	ΔQ	W	U
$U_1, V_1 \xrightarrow{\text{Iso} T_1} U_1, V_2$	$\frac{2}{3} U_1 \ln 2$	$\frac{2}{3} U_1 \ln 2$	U_1
$U_1 V_2 \xrightarrow{\text{Adiab}} U_3, V_3$	0	$U_1 \cancel{\left(1 - \left(\frac{1}{2}\right)^{2/3}\right)}$	$U_1 \left(\frac{1}{2}\right)^{2/3}$
$U_3 V_3 \xrightarrow{\text{Iso } T_3} U_3, V_2$	$-\frac{2}{3}\left[U_1 \left(\frac{1}{2}\right)^{2/3}\right]$	$-\frac{2}{3}\left[U_1 \left(\frac{1}{2}\right)^{2/3}\right]$	$U_1 \left(\frac{1}{2}\right)^{2/3}$
$U_3, V_2 \xrightarrow{\text{Adiab}} U_?, V_1$	0	$-\left[\cancel{U_1} - U_1 \left(\frac{1}{2}\right)^{2/3}\right]$	$\underbrace{\left[U_1 \left(\frac{1}{2}\right)^{2/3}\right]\left(\frac{2}{1}\right)^{2/3}}_{U_1}$

+

cycle

$Q_H = \frac{2}{3} U_1 \ln 2$

$Q_L = \frac{2}{3} U_1 \left(\frac{1}{2}\right)^{2/3}$

$\frac{2}{3} U_1 \left(\ln 2 - \left(\frac{1}{2}\right)^{2/3}\right)$

$$\frac{T_H}{T_L} = \frac{Q_H}{Q_L} = \frac{\ln 2}{\left(\frac{4}{2}\right)^{2/3}} = \frac{U_1}{U_3}$$

$\Rightarrow$ Internal Energy for an ideal gas is proportional to the temperature.

We need a reference to fix the scale:

The triple point of H_2O $= 273.16\ K$ $= 0.01\,°C$

$\Rightarrow$ $°C \Leftrightarrow K - 273.15$

Thermometers: Expansion (Hg, Alcohol, bimetallic, etc)
Thermocouple
Radiation

} Material properties

With that definition, one has

$$U_{\text{ideal gas}} = \frac{2}{3} k_B T N = \frac{2}{3} \frac{N}{N_A} (N_A k_B) T = \frac{2}{3} n R T$$

$k_B = 1.381 \times 10^{-23}\ J/K$

# of moles

ideal gas constant $8.31\ J/K\text{-mole}$

"Eqn. of state" : $PV = N k_B T = n R T$

Entropy of the ideal gas

Too Early

Start with T_1, $U_1 = \frac{2}{3} k_B T_1$

$\boxed{U_1 = \frac{2}{3} k_B T_1}$

Add energy (heat) at a constant rate

$$U = U_1 + \alpha t = \frac{2}{3} k_B T \Rightarrow T = \frac{3}{2} \frac{U_1 + \alpha t}{k_B}$$

$$\frac{dU}{dt} = \frac{dQ}{dt} = \alpha$$

$S(T=0) \neq 0$ for ideal gas, because its ground state is degenerate.

$$\cancel{\frac{dQ}{T} = \alpha dt \cdot \frac{k_B}{\frac{3}{2}\alpha t} = \frac{2}{3} k_B \frac{dt}{t}}$$

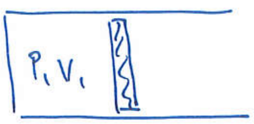
$$\cancel{\int_0^{S_1} dS = \frac{2}{3} k_B \ln t \Big|_0^{t_1}}$$

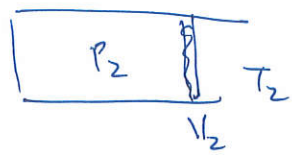
$$\frac{dQ}{T} = \frac{\alpha\, dt}{\frac{3}{2}(\underbrace{U_1 + \alpha t}_{x})/k_B} = \frac{2}{3} k_B \int \frac{dx}{x} = \frac{2}{3} k_B \ln x \Big| = \Delta S$$

$$\Delta S = \frac{2}{3} k_B \ln \frac{U_2}{U_1} \quad \text{for fixed volume}$$

TD7

Free expansion of the ideal gas





$P_1 V_1 = N k_B T_1$

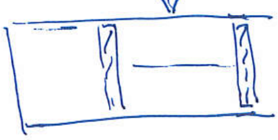
$U_1 = \frac{3}{2} N k_B T_1$

$P_1 V_1 = \frac{3}{2} U$

$U_2 = U_1$

$T_2 = T_1$

$P_2 V_2 = P_1 V_1$



Expand isothermally

U is constant

$\Delta Q = W$

$P = \frac{3}{2}\frac{U}{V}$

$$W = \frac{3}{2} U \int \frac{dV}{V}$$

$$= \frac{3}{2} U \ln \frac{V_2}{V_1}$$

$$= \Delta Q$$

$$\Delta S = \frac{\Delta Q}{T} = \frac{3}{2} \frac{U}{T} \ln \frac{V_2}{V_1}$$

$$= \frac{3}{2} N k_B \ln \frac{V_2}{V_1}$$

First Law + Second Law

$$dQ = dU + P\,dV = T\,dS \quad \text{(rev)}$$

$$dU = T\,dS - P\,dV$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \qquad \left(\frac{\partial U}{\partial S}\right)_V = T$$

TD 8

A "thermodynamic potential"

Helmholtz free Energy

$$A = U - TS$$

$$dA = dU - SdT - TdS$$

$$= dQ - PdV - SdT - TdS$$

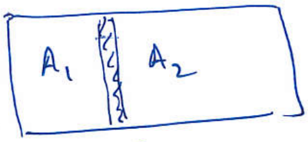
$$dA + PdV + SdT = dQ - TdS \le 0$$

$$dA \le -PdV - SdT$$

$$\underbrace{\left.\frac{\partial A}{\partial V}\right)_T = -P}_{\text{Eqn. of state}} \qquad \left.\frac{\partial A}{\partial T}\right)_V = -S$$

If $dW = 0$, $dT = 0$ A is ~~a~~ decreasing function minimum at equilibrium.

E.g.



T

(isothermal)

$$A = A_1(V_1, T) + A_2(V_2, T) \qquad V_2 = V - V_1$$

$$\frac{\partial A}{\partial V_1} = \frac{\partial A_1}{\partial V_1} - \frac{\partial A_2}{\partial V_2} = 0 \text{ equil} \qquad \frac{\partial}{\partial V_1} = -\frac{\partial}{\partial V_2}$$

$$-P_1 + P_2 = 0 \Rightarrow P_1 = P_2 \text{ at equil}$$