Boltzmann distribution

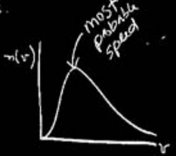
# of molecules per unit volume with energy between E and E + dE

$$n(E) = n_0 e^{-E/k_B T}$$

- Distribution of molecular speeds.

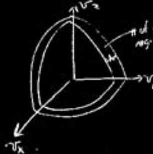
N_v = number of molecules with velocities between v and $v + dv$

$$N(v) = \left[4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2}\right] v^2 e^{-mv^2/2k_B T}$$



n(E) + n(v) have different "shapes"

reason is velocity is a vector -



most probable speed - Speed at which N(v) is maximum

find by setting $\frac{dN(v)}{dv} = 0$

$$\frac{d}{dv}\left[v^2 e^{-mv^2/2kT}\right] = 0$$

$$\Rightarrow v = \sqrt{\frac{2k_BT}{m}}$$

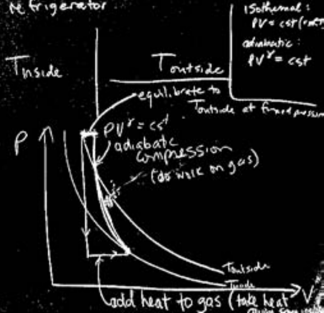
compare to $v_{rms} = \sqrt{\frac{3k_BT}{m}}$

Ch 22 Heat engines + Entropy.

Heat engine → Converts heat into work

refrigerator/air condition → use work to ~~transfer~~ heat from hotter to cooler resevoir

Refrigerator



∴ efficiency of engine.

Q_h = heat absorbed from hot reservoir

Q_c = heat given up to cold reservoir

engine does work Wbg

1st law of thermo: $\Delta E = \Delta Q + \Delta W$

E state variable

so around loop, $\Delta E = 0$, so $\Delta W = -\Delta Q$

So work done by engine

$$W_{eng} = Q_h - Q_c$$

efficiency $\varepsilon = \dfrac{W_{eng}}{Q_h}$

2^{nd} law of thermo

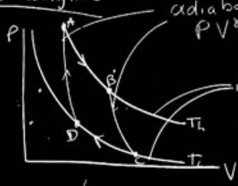
cannot construct an engine with $\varepsilon = 1$

Carnot:

max efficiency $\varepsilon_{max} = 1 - \dfrac{T_C}{T_H}$

Reversible processes - stay arbitrarily close to thermal equilibrium.

Carnot engine



1) A→B add heat
2) B→C adiabatic expansion lowers T
3) C→D isothermal compression expel heat
4) D→A adiabatic compression

net work done =

$W_{AB} + W_{BC} - W_{CD} - W_{DA}$

= area enclosed on P-V plot

Find $\varepsilon = \frac{\text{net work}}{|Q_h|}$

$= 1 - \frac{|Q_c|}{|Q_h|}$

find ΔQ along isotherm:

T same, so $\Delta E = 0$, so $\Delta Q = \Delta W$

so $\Delta Q = \int_{V_A}^{V_B} P\,dV = nR\int_{V_A}^{V_B} \frac{dV}{V} = nRT \ln\left(\frac{V_B}{V_A}\right)$

so $\Delta Q_h = nRT_h \ln(V_B/V_A)$

$\Delta Q_c = nRT_c \ln(V_C/V_D)$

$$e = 1 - \frac{T_c[nR\ln(\frac{V_C}{V_D})]}{T_h[nR\ln(\frac{V_B}{V_A})]} = 1 - \frac{T_c \ln(V_C/V_D)}{T_h \ln(V_B/V_A)}$$

recall B-C is adiabat: $P_B V_B^{\gamma} = P_C V_C^{\gamma}$

use $PV = nRT$:

$T_{hot} V_B^{\gamma-1} = T_C V_C^{\gamma-1}$

similarly

$T_{hot} V_A^{\gamma-1} = T_C V_D^{\gamma-1}$

divide $\Rightarrow \left(\frac{V_B}{V_A}\right) = \left(\frac{V_C}{V_D}\right)$

So $\varepsilon = 1 - \frac{T_c}{T_h}$ Carnot engine

Carnot's theorem

No engine can be more efficient than this

Suppose not – then can build machine that transfers heat

from cold to hot with no work at all!

Entropy

State variables E, T, P. vs transfer W, Q

$dW = P\,dV$

$$dQ = S\,dT$$

def of entropy

postulate: state variable