MATH327: Statistical Physics

Friday, 8 March 2024

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Something to consider

We can describe the air in this room, and the air in the hall, as ideal gases governed by the canonical ensemble.

What should we expect to happen if we open or close the door that separates them?

Classical ideal gases, canonical ensemble

Partition functions for continuous energies

$$Z_D = Z_1^N = \left(\frac{V}{\lambda_{th}^3}\right)^N$$

$$\lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{mT}}$$

$$Z_I = \frac{1}{N!} Z_D = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N$$

Derive $\langle E\rangle_D = \langle E\rangle_I = \frac{3}{2}NT$

doesn't depend on information

(unlike spin system)

Entropies differ

$$\left.\begin{aligned} S_D &= \frac{3}{2}N + N\log\left(\frac{V}{\lambda_{th}^3}\right) \\ S_I &= \frac{5}{2}N + N\log\left(\frac{V}{N\lambda_{th}^3}\right) \end{aligned}\right\} \text{ which is larger?}$$

$S = -\sum_i p_i \log p_i$

$S_I - S_D = N - N\log N = -\log(N!) < 0$

$S_I < S_D$ — extra info from dist'ability

Entropies depend on $\frac{V}{\lambda_{th}^3}$ — "occupied volume" for particle $\left(\frac{2\pi\hbar^2}{mT}\right)^{3/2}$

Classical regime $\frac{V}{\lambda_{th}^3} \gg 1$ assumed above

(negative entropies if $\frac{V}{\lambda_{th}^3} \ll 1$ sign of breakdown / violated assumptions)

Mixing

$$\Omega_A \otimes \Omega_B \longrightarrow \Omega_C \longrightarrow \Omega_A' \otimes \Omega_B'$$

$$S_A + S_B \longrightarrow S_C \longrightarrow S_A' + S_B'$$

Check $S_A + S_B \leq S_C \leq S_A' + S_B'$

Indist'able case

$$\boxed{\begin{aligned} S_A + S_B &= 2S_I(N,V,T) = 5N + 2N\log\left(\frac{V}{N\lambda_{th}^3}\right) \\ S_C &= S_I(2N, 2V, T) = 5N + 2N\log\left(\frac{2V}{2N\lambda_{th}^3}\right) \\ &= S_A + S_B \end{aligned}}$$

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consistent w/ second law ✓

Re-separate ~~the~~ system

Need to sum over all possible particle divisions
$\{\nu, 2N-\nu\}$

Each $Z_\nu = Z_I(\nu, V, T) \otimes Z_I(2N-\nu, V, T)$

$$= \frac{1}{\nu!\,(2N-\nu)!}\left(\frac{V}{\cancel{\nu}\lambda_{th}^3}\right)^{\nu}\left(\frac{V}{\cancel{(2N-\nu)}\lambda_{th}^3}\right)^{2N-\nu}$$

sorry for the mix-up fixed post-lecture!

$$Z' = \sum_{\nu=0}^{2N} Z_\nu = \left(\frac{V}{\lambda_{th}^3}\right)^{2N} \sum_\nu \frac{1}{\nu!\,(2N-\nu)!}$$

Entropy $S' = \frac{\partial}{\partial T}(T \log Z')$

$$= 2N\frac{\partial}{\partial T}\left(T\log\left(\frac{V}{\lambda_{th}^3}\right)\right) + \log\left(\sum_\nu\left[\frac{1}{\nu!\,(2N-\nu)!}\right]\right)$$

complicated!

Simplify - Gibbs approximation

$N \gg 1 \rightarrow$ almost all entropy from even division

$$N_A' = N_B' = N$$

$$S' \approx 2S_I(N, V, T) = S_A + S_B = S_C$$

No change in entropy - <u>reversible</u> process

For dist'able particles

$$\Delta S_{mix} = S_C - (S_A + S_B) = 2N\log 2 > 0$$

$S' \approx 2S_D(N, V, T) < S_C$ would violate second law

"Gibbs paradox"

Explanation

Dist'ability $\rightarrow$ more info. than N_A', N_B'

Many more micro-states with different labels in addition to $\Omega_A \otimes \Omega_B$

$\rightarrow$ Larger entropy $S_A' + S_B' > S_A + S_B$

Complicated calculation confirm $S_A' + S_B' \geq S_c$

Simpler case for tutorial

For dist'able particles, practically impossible to return to original system

Irreversible process that increase entropy

$$Z_D, Z_I \propto \left(\frac{V}{\lambda_{th}^3}\right)^N \propto (V T^{3/2})^N$$

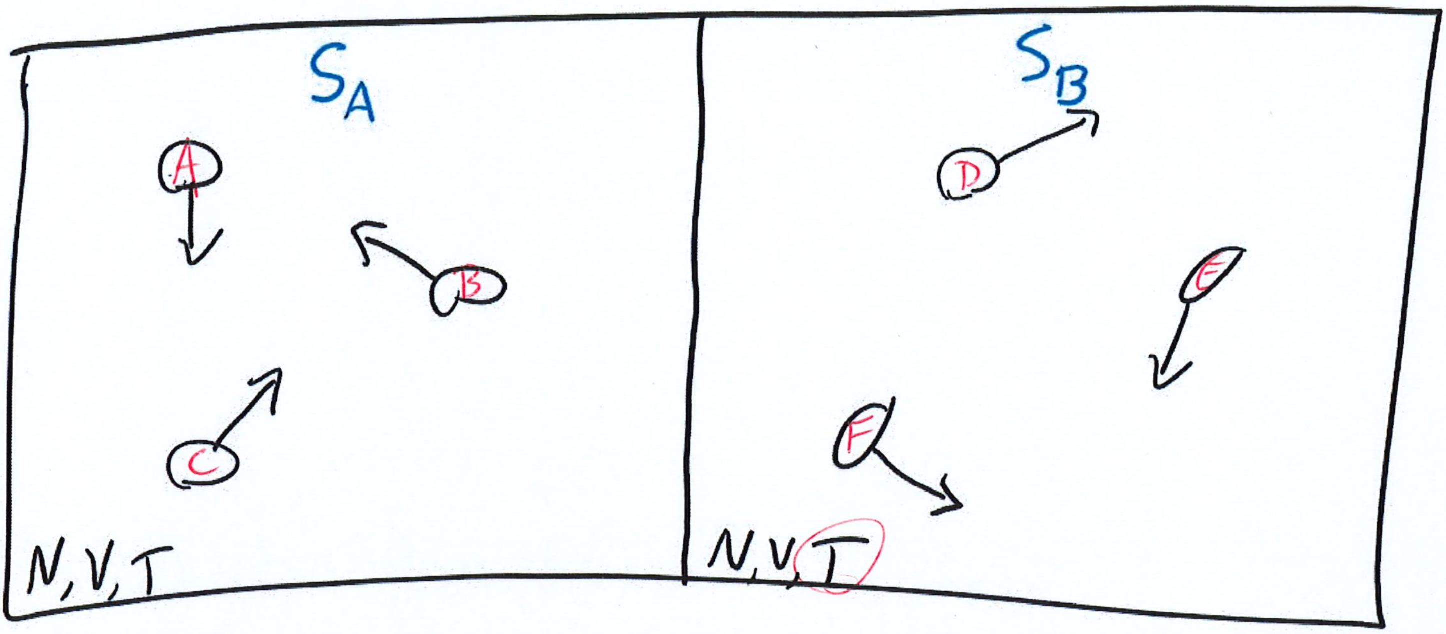
V and T are control parameters (similar to H in spin systems)

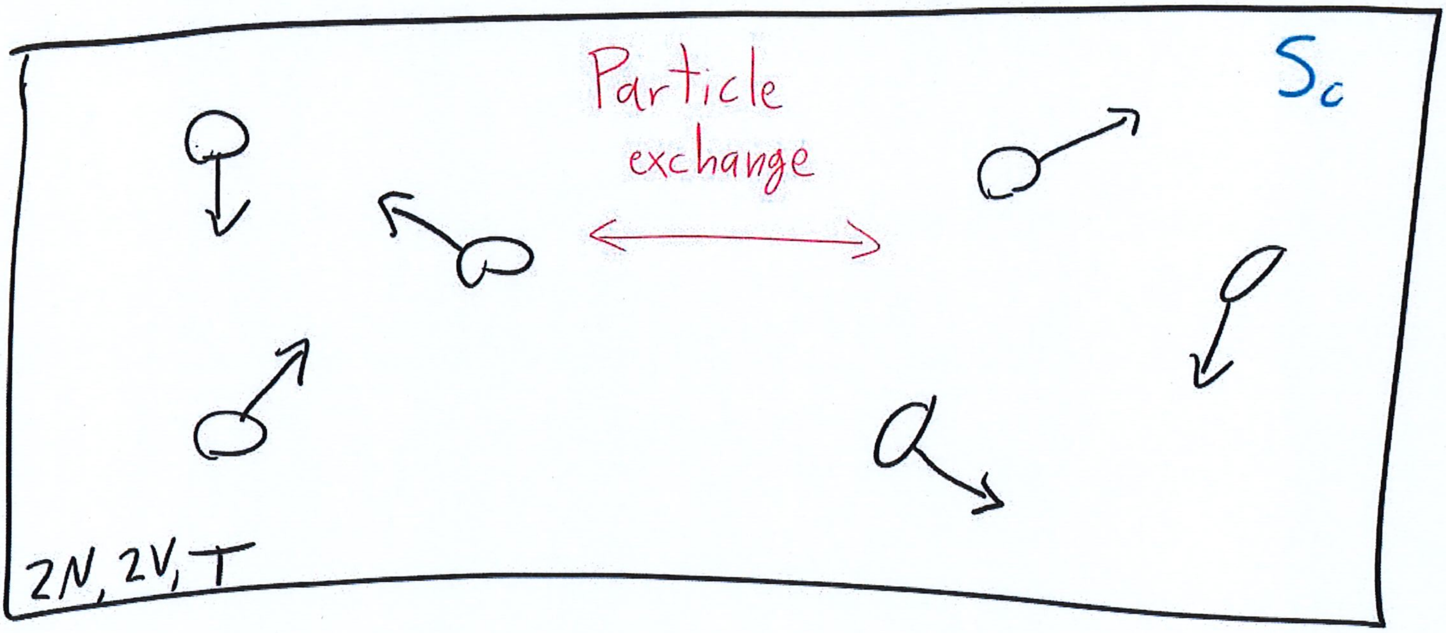
In principle control experimentally measure respondse to change

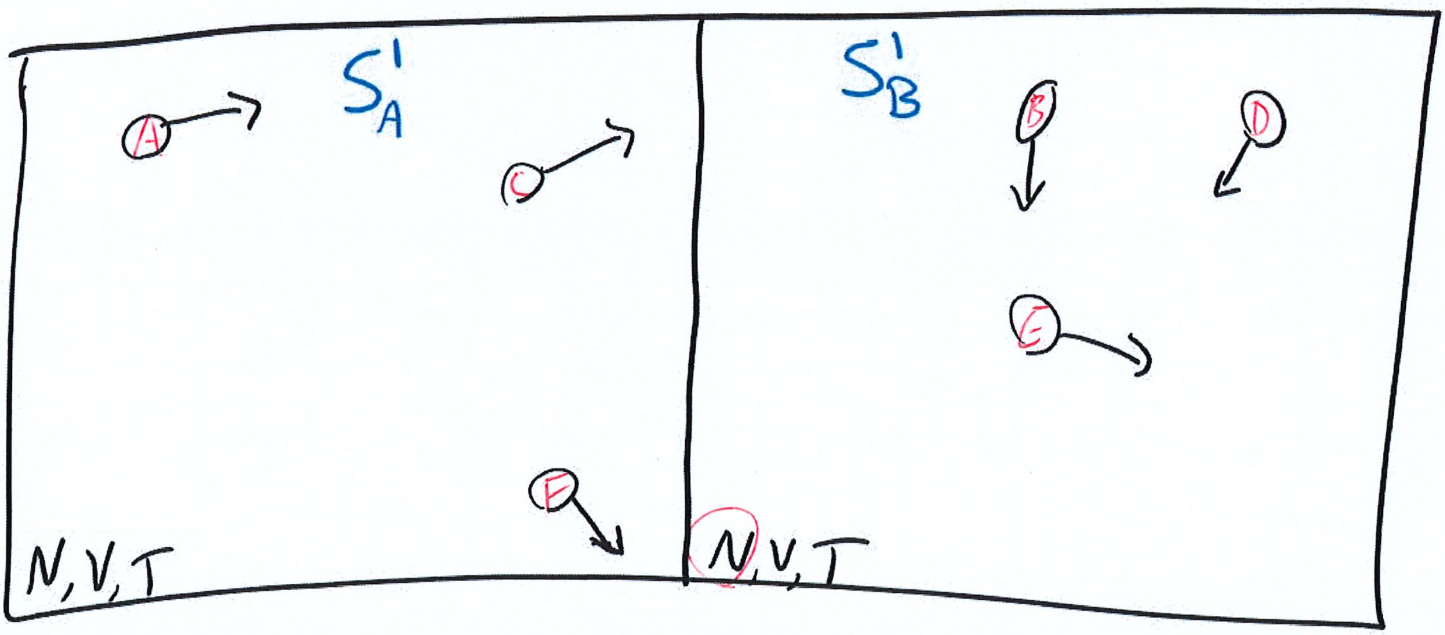
(Canonically changing T by connecting system to different reservoir $T_i \rightarrow T_f$)

Vary one at a time

$$C_V = \left.\frac{\partial \langle E \rangle}{\partial T}\right|_V \qquad \frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N$$


S_A
A
B
C
N, V, T
S_B
D
E
F
N, V, T


Particle exchange
S_c
2N, 2V, T


S'_A
A
C
F
N, V, T
S'_B
B
D
E
N, V, T

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

change volume with fixed entropy
(isentropic)

Ideal gas S_D, S_I depend on $\frac{V}{\lambda_{th}^3} \propto V T^{3/2}$

Constant entropy $\rightarrow V T^{3/2} = c^{3/2}$

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

$$\langle E \rangle = \frac{3}{2} N T = \frac{3c}{2} \frac{N}{V^{2/3}}$$

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$$\boxed{P = -\frac{3c}{2} N \left(-\frac{2}{3} \frac{V^{-2/3}}{V} \right) = \frac{N}{V} \left(c V^{-2/3} \right) = \frac{NT}{V}}$$

$PV = NT$ is ideal gas law

Equation of state (EoS)

thermodynamic macro-state

EoS are relations among macroscopic properties

P, V, T, internal energy, density

Historically empirical observations, followed by math'ical explanations

Robert Boyle, 1660s

change pressure with fixed T & N

Find $PV = $ const. "Boyle's law"

Fix N & P

$\frac{V}{T} = \text{const.}$

"Charles's law"
1787

Fix N & V

$\frac{P}{T} = \text{const.}$

"Gay-Lussac's law"
1802

fix P & T

$\frac{V}{N} = \text{const.}$

"Avogadro law"
1820

Combined into ideal gas law in 1830s

Derived from statistical physics in 1850s

Mutual reinforcement of scientific progress
& Industrial Revolution
including engines

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

Work done by force $\vec{F}(\vec{r})$
displacing object by $d\vec{r}$
changing energy by dE

Infinitesimal $W = dE = \vec{F} \cdot d\vec{r}$

$W = \Delta E = E_f - E_0 = \int_{r_0}^{r_f} \vec{F} \cdot d\vec{r}$ (line integral)

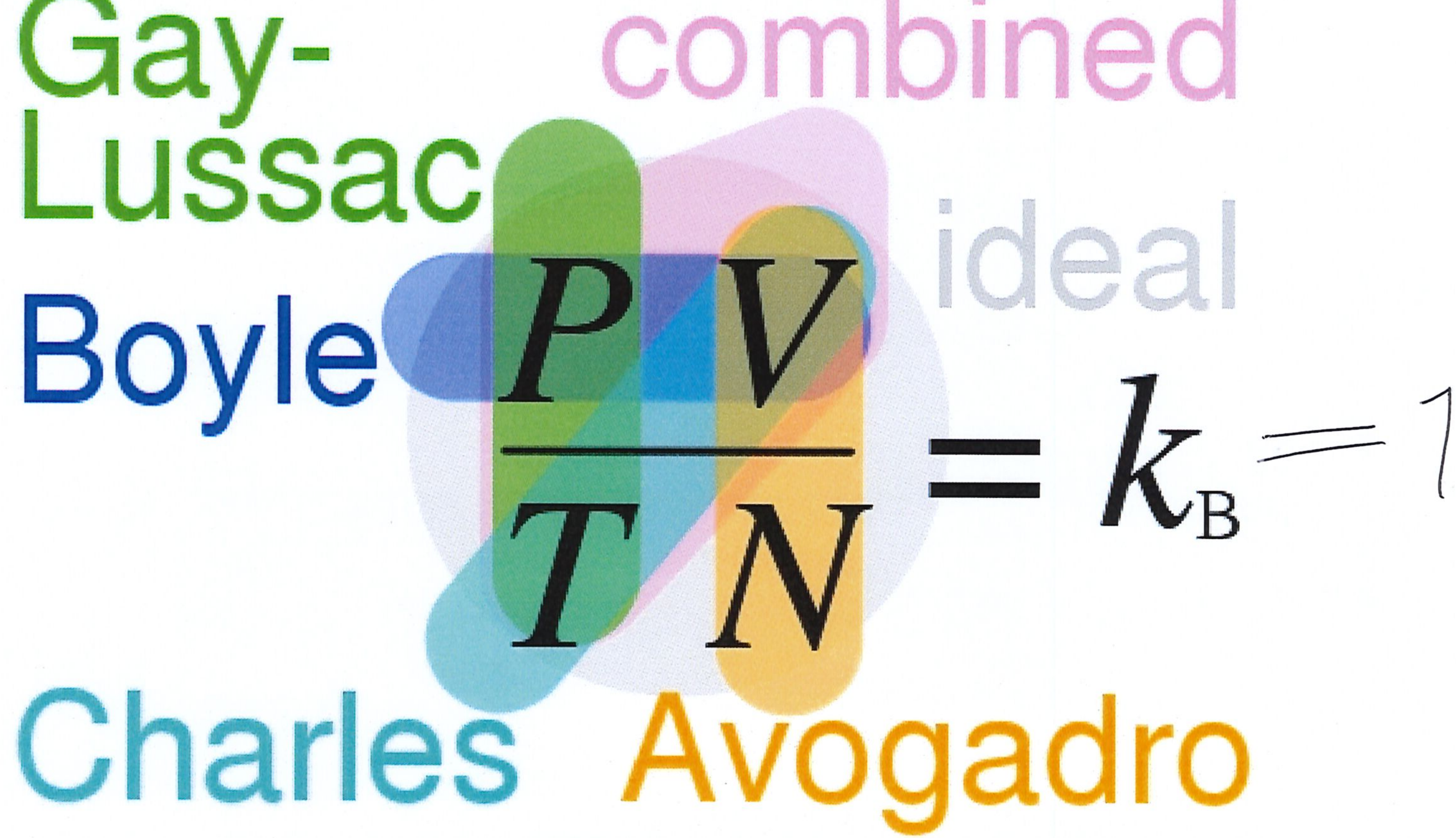
Example: Object falling due to gravity

$\vec{F} = (0, 0, -mg)$

Start at rest, $E_0 = 0$ at height h

Final $E_f = W = \int \vec{F} \cdot d\vec{r} = -mg \int_h^0 dz = mgh > 0$

$\frac{p_z^2}{2m} = mgh \rightarrow p_z = -m\sqrt{2gh}$



commons.wikimedia.org/wiki/File:Ideal_gas_law_relationships.svg

$N \gg 1$: Work is change in internal energy
due to force that changes volume

Example : Piston
→ Pressure is force per unit area
on surface of container holding gas

Assuming constant entropy, $\Delta\langle E\rangle = -P\Delta V = W$
$\langle E\rangle$ can also change by changing entropy
$\therefore \Delta\langle E\rangle = W + \underline{\text{more}}$

General: $W = -P\,dV$ (infinitesimal)

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

ideal gas law gives $P(V) = \frac{NT}{V}$

$W > 0$ work done on gas by surroundings
raising $\langle E\rangle$

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

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

change T with constant V
$W=0$

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

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

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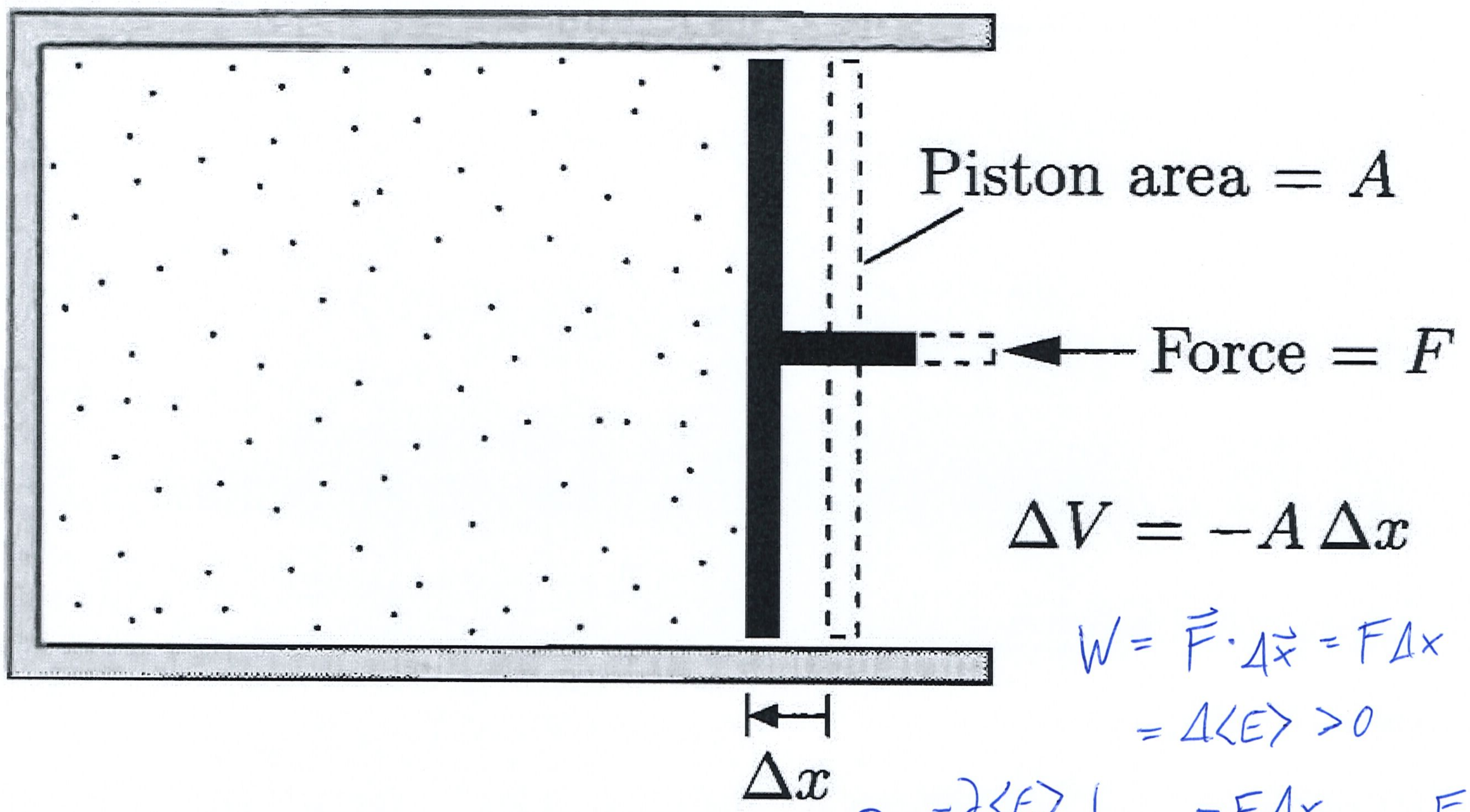
$\boxed{dS = \frac{3}{2}N\frac{dT}{T} = \frac{d\langle E\rangle}{T}} \rightarrow d\langle E\rangle = T\,dS = \underset{\text{heat}}{Q}$



$$W = \vec{F} \cdot \Delta\vec{x} = F\Delta x$$
$$= \Delta\langle E\rangle > 0$$

$$p = \left.\frac{-\partial\langle E\rangle}{\partial V}\right|_S = \frac{-F\Delta x}{-A\Delta x} = \frac{F}{A} > 0$$