# MATH327: StatMech and Thermo

Tuesday, 3 March 2026

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**Something to consider**

Since $PV = NT$ and $\langle E \rangle = \frac{3}{2} NT$ for ideal gases,

energy must flow as these control parameters vary.

How can we relate this to everyday concepts of heat and work?

<u>Recap</u>

Dist'able vs. indist'able ideal gases

Mixing and irreverible

Control parameters → equation of state (ideal gas law)

<u>Today</u>

Work and heat

Thermodynamic processes → therm. cycles

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

<u>Work</u> done by force $\vec{F}$

displacing object by $d\vec{r}$

changing energy by $dE$

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

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

Example: Object falling due to gravity $\vec{F} = (0, 0, -mg)$

Starts at rest $E_0 = 0$ at height $h$

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

$$\frac{\cancel{m} v_f^2}{2} = \cancel{m} gh \qquad v_f = -\sqrt{2gh}\,\hat{z}$$

~~N~~ For $N \gg 1$ work is $\Delta\langle E\rangle$ due to force that changes $V$

Example: Piston

~~Force~~ 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

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

Even if entropy changes, $W = -P\,dV$ is general

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

$\frac{NT}{V}$ from ideal gas law

$W > 0$ is work done <u>on gas</u> by surroundings raising $\langle E\rangle$

$W < 0$ is work done <u>by gas</u> on surroundings lowering $\langle E\rangle$

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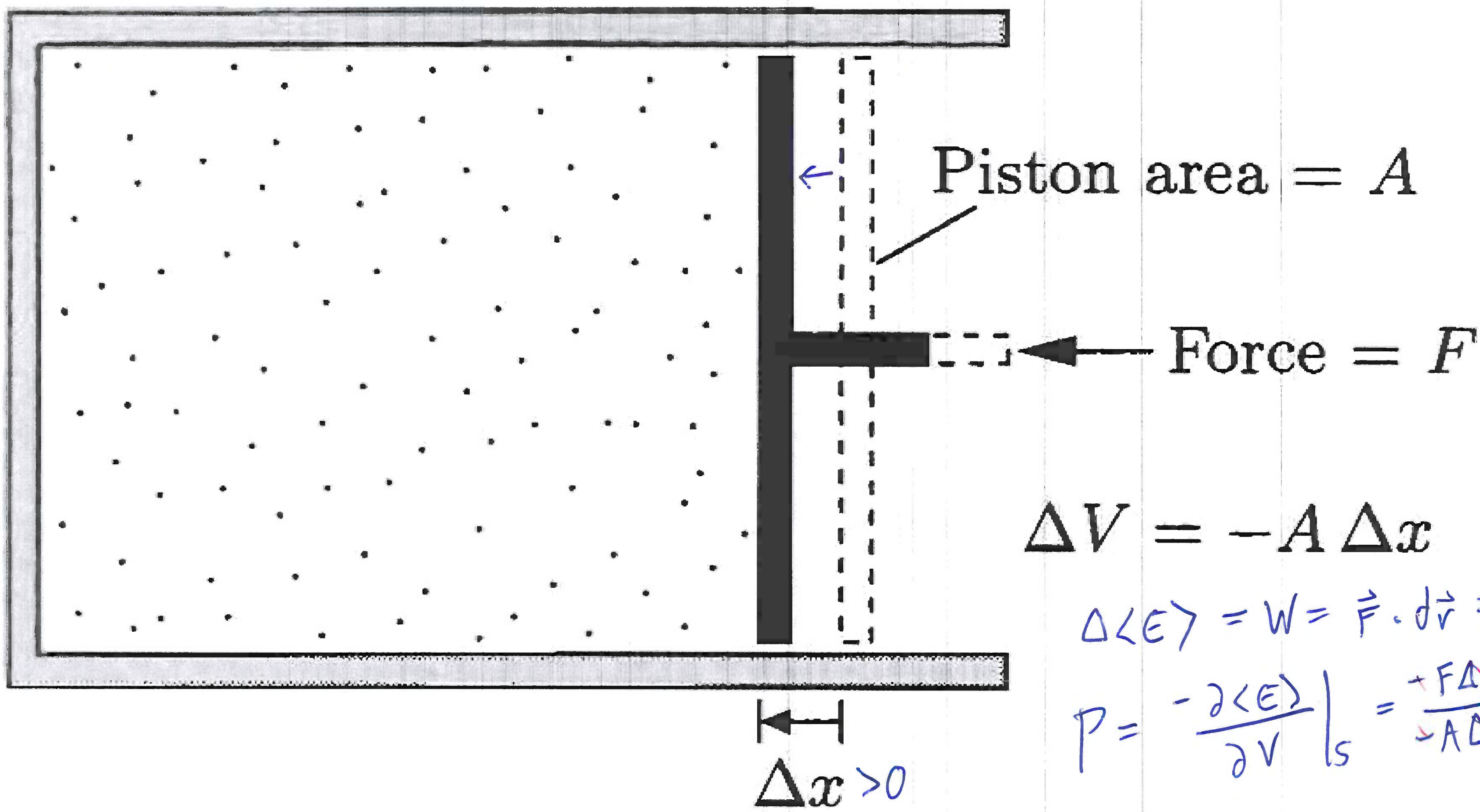
Can change $\langle E\rangle = \frac{3}{2} NT$ with constant volume

$W = 0$

$d\langle E\rangle = \frac{3}{2} N\,dT \neq 0$




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

$$\Delta\langle E\rangle = W = \vec{F}\cdot d\vec{r} = F\Delta x$$

$$P = -\frac{\partial\langle E\rangle}{\partial V}\bigg|_S = \frac{+F\cancel{\Delta x}}{-A\cancel{\Delta x}} = \frac{F}{A} > 0$$

Entropy must change

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

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$$\boxed{dS = \frac{3}{2} N \frac{dT}{T} = \frac{d\langle E \rangle}{T} \neq 0}$$

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

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

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

assuming $S(T)$ invertible

Assume entropy not created or destroyed

Like energy, $dS \neq 0$ flows between system and surroundings

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

Adiabatic + reversibility $\rightarrow$ isentropic $dS = 0$

Fast — no time for heat flow

Other extreme: isothermal process changes $\langle E \rangle$ with fixed $T$

Slow — all possible heat to/~~flow~~ from reservoir

Real processes in between - usually closer to adiabatic

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

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

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

$-P$

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

Generalized first law: Any change in internal energy

matched by $\begin{cases} \text{heat flow to/from surroundings} \\ \text{work done on/by surroundings} \end{cases}$