Lecture 2

Last time: introduced state variables:
macro variables describing system
& eqn of state:
relation between state variables

Think of state variables as coordinates (like x).
eqn of state as force law (like $F = G\frac{mm}{r}$)

Analog of Newton's laws = Laws of thermodynamics
But thermo is subtler

Law 0: Three systems A, B, C
Suppose A & B in equilibrium
(in contact, with state variables constant)
And B & C in equilibrium

Then if A is put in contact with C,
will find them in equilibrium as well

Means that thermometers & pressure gauges make sense

Law 1: Energy is conserved

E = total energy in system

E changes if system does mechanical (or E&M) work $đW$
on another system:

$$dE = -đW$$

• Can also change E without doing work,
by adding or removing "heat" $\text{đ}Q$

(Don't worry about what heat is, just describes changing E without doing work.)

Write $\text{đ}Q =$ heat added, so $dE = \text{đ}Q - \text{đ}W$

(can define signs of $\text{đ}W$ & $\text{đ}Q$ as desired, be sure to keep straight!)

• Can also change E by adding or removing particles
"chemical work"

Define chemical potential μ by

$$dE = \text{đ}Q - \text{đ}W + \mu\, dN$$

$\hookrightarrow \sum_j \mu_j\, dN_j$
if multiple species

Can say more about $\text{đ}W$
From classical mechanics + E&M, know
how to calculate work

$$\text{đ}W = P\,dV - J\,dL - \sigma\,dA - V\,\vec{\mathcal{E}}\cdot d\vec{P} - V\,\vec{\mathcal{H}}\cdot d\vec{M}$$

Normally only one used at a time!

Write generically as $\text{đ}W = -Y\,dX$

Y = force $\quad X$ = displacement

$$Y = -P,\ J,\ \sigma,\ \vec{\mathcal{E}},\ \vec{\mathcal{H}}$$

(Pressure tries to increase V; tension tries to decrease L)

$$X = V,\ L,\ A,\ V\vec{P},\ V\vec{M}$$

Usually, V = const for electric or magnetic systems, no big deal

But sign of P is tricky: price for trying to make general theory

End up with $\boxed{dE = đQ + Y\,dX + \mu\,dN}$

Example: ideal gas

For simplicity, assume we know $E = \alpha N k_B T$

$\alpha = \frac{3}{2}$ monatomic
$= \frac{5}{2}$ diatomic
≤ 3 polyatomic

(Can get this from stat mech, or by combining various thermodynamic measurements)

Then $dE = \alpha N k_B\, dT = đQ - P\,dV$

(N fixed)

For insulated container, $đQ = 0$
$\equiv$ adiabatic process (no heat flow)

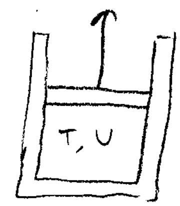
So $\quad \alpha N k_B \, dT = -P\, dU = -\dfrac{N k_B T}{U} dU$

$$\alpha \frac{dT}{T} = -\frac{dU}{U}$$

Integrate: $\quad \alpha \ln T = -\ln V + \text{const}$

$$\ln T^\alpha V = \text{const}$$

or $\quad T^\alpha V = \text{const}$



So if initially have T_0, U_0, then after process get
$$T^\alpha U = T_0^\alpha U_0$$

Describes how T & V change in adiabatic process

If we're interested in pressure, use $U = \dfrac{NkT}{P}$

so $\quad T^\alpha \left(\dfrac{T}{P}\right) = \text{const}$

$$\frac{T^{\alpha+1}}{P} = \text{const}$$

Law 2: Heat flows spontaneously from high to low temperatures, but never the reverse.

Deceptively powerful
Key to applying is <u>Carnot engine</u>

= Reversible thermodynamic process, four stages

Start in state 1: System in contact w/ reservoir at $T = T_h$

Stage 1→2: Absorb heat Q_h from reservoir

Stage 2→3: Adiabatically lower T to T_c

Stage 3→4: Expel heat Q_c into reservoir at T_c

Stage 4→1: Adiabatically heat to T_h

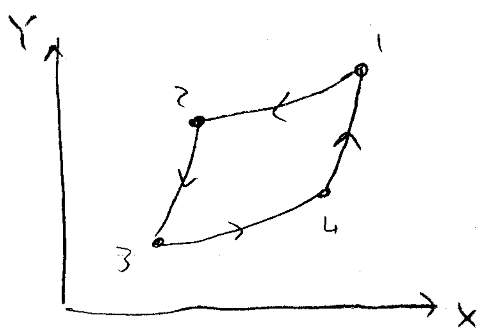
Forms cycle: returns to starting point

1st law says: take up heat Q_h
release heat Q_c

$\Rightarrow$ do work $W = Q_h - Q_c$

If $W > 0$, convert heat to work: very useful

Picture:



$W = \int Y\,dX$
= area enclosed by curve

Define efficiency $\eta = \frac{W}{Q_h}$ $\quad \eta = 1 \Rightarrow$ all heat → work

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

Or, since process is reversible, can also supply work W & move heat from T_c to T_h
$\Rightarrow$ refridgerator

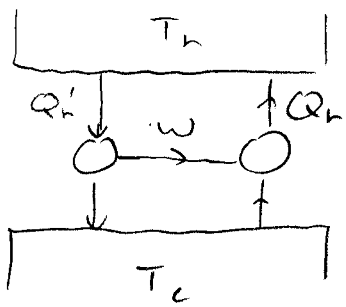
Important result:

No heat engine can be more efficient than a Carnot engine

Suppose one was:

Get work W out for heat input $Q_h' < Q_h$

Then hook new engine up to reversed Carnot engine



Deliver heat Q_h to T_h

Since $Q_h' < Q_h$, net effect is to move heat from T_c to T_h

with no work required

$\Rightarrow$ violates 2^{nd} law!

Conclude that Carnot engine (or any reversible engine) is as efficient as possible

And all Carnot engines with same T_h & T_c have same efficiency.