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 = \( F = \frac{\partial U}{\partial x} \))

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 or pressure gauges make sense

Law 1: Energy is conserved

\[ E = \text{total energy in system} \]

\( E \) changes if system does mechanical (or heat) work \( \Delta W \)
on another system:

\[ dE = -\Delta W \]
* Can also change $E$ without doing work, by adding or removing "heat" $dQ$

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

Write $dQ = \text{heat added}$, so $dE = dQ - dW$

(can define signs of $dW$ and $dQ$ as desired, be sure to keep straight!)

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

Define chemical potential $\mu$ by

$$dE = dQ - dW + \mu dN$$

$$\sum \mu_i dN_i$$

If multiple species

Can say more about $dW$
From classical mechanics + E&M, know how to calculate work

$$dW = PdV - JdL - \sigma dA - V \sum \frac{\partial f}{\partial \rho} d\rho - V \frac{\partial f}{\partial m} dm$$

Normally only one used at a time!

Write generically as $dW = -YdX$
Y = force    X = displacement

Y = (-\(P\), J, \(\tau\), \(\varepsilon\), \(\Omega\))

X = \(U\), L, A, \((\sqrt{P})\), \(\sqrt{M}\)

(Pressure tries to increase \(U\); tension tries to decrease \(L\))

Usually \(U = \text{const}\) for electric or magnetic systems; no big deal

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

End up with \(dE = dQ + YdX + \mu dN\)

Example: ideal gas

For simplicity, assume we know \(E = \alpha Nk_b T\)

\[\alpha = \begin{cases} \frac{3}{2} & \text{monatomic} \\ \frac{5}{2} & \text{diatomic} \\ \frac{3}{2} & \text{polyatomic} \end{cases}\]

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

Then \(dE = \alpha Nk_b dT = dQ - PdV\) \(\text{ (N fixed)}\)

For insulated container, \(dQ = 0\)
\(\equiv\) adiabatic process (no heat flow)
So \( \alpha N k_B \frac{dT}{dT} = -p \frac{dU}{dT} = -\frac{Nk_B T}{U} \frac{dU}{dT} \)
\[ \alpha \frac{dT}{T} = -\frac{dU}{U} \]

Integrate:
\[ \alpha \ln T = -\ln U + \text{const} \]
\[ \ln T^\alpha U = \text{const} \]

or
\[ T^\alpha U = \text{const} \]

So if initially have \( T_0, U_0 \), then after process get
\[ T^\alpha U = T_0^\alpha U_0 \]

Describes how \( T \propto U \) change in adiabatic process

If we're interested in pressure, use \( U = \frac{Nk_B T}{p} \)

so
\[ T^\alpha \left( \frac{T}{p} \right) = \text{const} \]
\[ \frac{T^\alpha}{p} = \text{const} \]

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

Deceptively powerful
Key to applying is Carnot engine

= Reversible thermodynamic process, four stages

Start in state \( L \): 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 \( Q_c \)

\[ \Rightarrow \text{ do work } W = Q_h - Q_c \]

If \( W > 0 \), convert heat to work: very useful

Picture:

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

\[ \eta = 1 - \frac{Q_c}{Q_h} \]

Or, since process is reversible, can also supply work \( W \) & move heat from \( T_c \) to \( T_h \)

\( \Rightarrow \) refrigerator
Important result:
No heat engine can be more efficient than a Carnot engine.

Suppose one does:
Get work \( W \) out for heat input \( Q_{h'} < Q_{h} \)

Then hook new engine up to reverse Carnot engine.

\[ \begin{array}{c}
\text{Th} \\
\downarrow \\
Q_{h'} \\
\downarrow \\
W \\
\uparrow \\
Q_{h} \\
\downarrow \\
T_{c}
\end{array} \]

Deliver heat \( Q_{h} \) to \( Th \)

Since \( Q_{h'} < Q_{h} \),
net effect is

to move heat from \( T_{c} \) to \( Th \)

with no work required

\( \Rightarrow \) violates 2nd law!

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

And all Carnot engines with same \( Th \) \( \neq \) \( T_{c} \)
have same efficiency.