

## Lecture 3

Last time started discussion of laws of Thermo

1) Energy is conserved

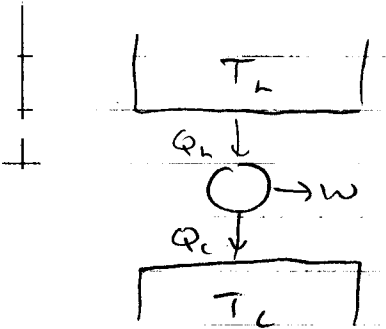
$$dE = \delta Q + Y dx + \mu dN$$

$Y =$  generalized force  $(-P, J, \dots)$

$x =$  " displacement  $(V, L, M)$

2) Heat flows from hot to cold

One consequence: Carnot engine is most efficient possible (because it is reversible)



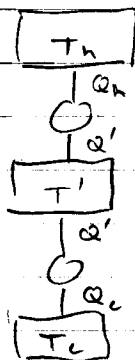
$$\eta = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

So all Carnot engines with same  $T_h + T_c$  have same  $\eta$   
 $\Rightarrow \eta =$  function of  $T_h, T_c$  only

Write  $\frac{Q_c}{Q_h} = f(T_c, T_h)$

Can say more about  $f$ :

Two engines in series



$$\frac{Q'}{Q_h} = f(T', T_h)$$

$$\frac{Q_c}{Q'} = f(T_c, T')$$

Still reversible, so must be equivalent to one engine from  $T_h$  to  $T_c$

$$\frac{Q_c}{Q_h} = f(T_c, T_h) = \frac{Q_c}{Q'} \cdot \frac{Q'}{Q_h} = f(T_c, T') f(T', T_c)$$

Only possible if  $f(T_c, T_h) = \frac{g(T_h)}{g(T_c)}$  for some  $g$

Choice of  $g$  is arbitrary:

Defines Temperature scale

But choice  $g = T$  gives same  $T$  as ideal gas law  
 $\equiv$  Kelvin scale

Then have  $\eta = 1 - \frac{T_c}{T_h}$

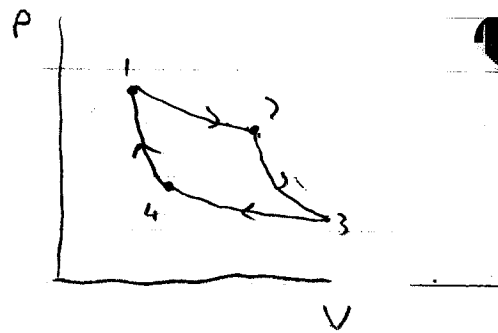
Verify this for ideal gas:

Here  $X = U$

$Y = -P$

$PV = Nk_b T$   
 and  
 $E = \alpha Nk_b T$

Start with compressed,  
 hot gas



Stage 12: Isothermal absorption of heat  $Q_h$

$$dE = dQ - dW = 0 \quad \text{since } E \propto T \quad \text{and } dT = 0$$

$$\text{So } dQ = dW = PdV$$

$$= \frac{Nk_b T_h}{V} dV$$

$$Q_h = \int dQ = \int_{V_1}^{V_2} \frac{Nk_b T_h}{V} dV = Nk_b T_h \ln \frac{V_2}{V_1} = W_{12}$$

Stage 23: Adiabatic expansion

Know from last time that  $T^\alpha V = \text{const}$

$$\text{So } \frac{T_c}{T_h} = \left( \frac{V_2}{V_3} \right)^{1/\alpha}$$

Stage 34: Isothermal compression

Same calculation as stage 12

$$\text{Here } Q_c = \text{heat emitted} = -W_{34} = Nk_b T \ln \frac{V_3}{V_4}$$

Stage 41: Adiabatic compression

$$\text{Like stage 23, get } \frac{T_c}{T_h} = \left( \frac{V_1}{V_4} \right)^{1/\alpha}$$

So efficiency

$$\eta = 1 - \frac{Q_c}{Q_h} = 1 - \frac{Nk_b T_c \ln V_3/V_4}{Nk_b T_h \ln V_2/V_1}$$

From adiabatic stages, see  $\frac{V_2}{V_3} = \frac{V_1}{V_4}$

$$\Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}, \text{ ln's cancel}$$

Leaves  $\eta = 1 - \frac{T_c}{T_h}$ , as claimed. ✓

So second law gives a general way to define temperature scale:

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}$$

or  $\frac{Q_c}{T_c} = \frac{Q_h}{T_h}$

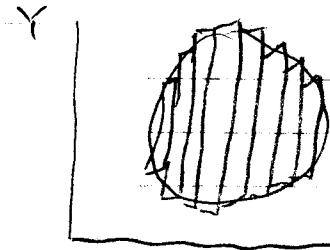
or  $\int_{34} \frac{dQ}{T_c} + \int_{12} \frac{dQ}{T_h} = 0$

if  $dQ \equiv$  heat absorbed by system  
( $-Q_c$ )

But  $dQ = 0$  for 23 + 41. So

$\oint \frac{dQ}{T} = 0$  for Carnot cycle

But note that any reversible cycle can be considered as sum of Carnot cycles:



Means that  $\oint \frac{dQ}{T} = 0$  for any reversible cyclic process

So  $\int_A^B \frac{dQ}{T}$  is independent of path from A to B (as long as path is reversible)

$= S(B) - S(A)$  for some function S

So S is a new state variable  $\equiv$  entropy

Entropy will be very important, but here  
no physical picture.

Because in thermo alone, still don't know  
what "heat" is

Stat mech clarifies that entropy is a particular  
measure of disorder in system.

(Adding heat at high  $T$  creates more disorder)  
than adding heat at low  $T$

Here  $S$  defined for reversible process

But  $S$  is function of state, so for any process,  
get

$$\Delta S = S(\text{final}) - S(\text{initial})$$

Consider an irreversible cyclic process  
 $\Rightarrow$  less efficient than reversible one

$$\text{So } \beta_{\text{irr}} < \beta_{\text{rev}}$$

$$1 - \left(\frac{Q_c}{Q_h}\right)_{\text{irr}} < 1 - \frac{T_c}{T_h}$$

$$\left(\frac{Q_c}{Q_h}\right)_{\text{irr}} > \frac{T_c}{T_h}$$

$$\frac{Q_c}{T_c} > \frac{Q_h}{T_h}$$

$$-\int \frac{dQ}{T_c} > \int \frac{dQ}{T_h}$$

$$\text{So } \oint_{\text{irr}} \frac{dQ}{T} < 0$$

So for a general process, have

$$\int_A^B \frac{dQ_{\text{irr}}}{T} < \int_A^B \frac{dQ_{\text{rev}}}{T} = \Delta S$$

or,  $\frac{dQ}{T} \leq dS$  always

In an isolated system, have  $dQ=0$

So must have  $\Delta S \geq 0$

Conclude: any irreversible process in an isolated system increases entropy,

reversible process keeps  $S = \text{const}$

This is another formulation of 2<sup>nd</sup> Law.

Note that since equilibrium system is stable

$\Rightarrow$  no process occurs spontaneously

$\Rightarrow S$  is already as large as possible

Key connection to stat mech,

As you see, get quite a lot from 2<sup>nd</sup> law, despite its simple nature.

3<sup>rd</sup> law is less exciting:

In limit  $T \rightarrow 0$ ,  $S \rightarrow \text{constant}$ , indep of  $X, Y$ , etc.

Can usually take  $\text{const} = 0$

Main consequence: Can't reversibly cool a system to absolute zero.

Argument is a bit subtle, and not really so critical, refer to text.

Instead, look at relation between entropy and energy

$$\text{Have } dE = dQ + YdX + \mu dN$$

for reversible process,  $dQ = Tds$

So

$$dE = Tds + YdX + \mu dN$$

"Fundamental eqn of thermodynamics"

$$\text{Read off } T = \left(\frac{\partial E}{\partial S}\right)_{X,N} \quad Y = \left(\frac{\partial E}{\partial X}\right)_{S,N} \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,X}$$

Can say more:

Since heat is extensive,  $S$  is extensive

$$\text{write } E = E(S, X, N)$$

all extensive

Then scale system size by  $\lambda$ :

$$E(\lambda S, \lambda X, \lambda N) = \lambda E$$

$$\text{Take } \frac{d}{d\lambda}: \left(\frac{\partial E}{\partial S}\right)_{X,N} S + \left(\frac{\partial E}{\partial X}\right)_{S,N} X + \left(\frac{\partial E}{\partial N}\right)_{S,X} N = E$$

$$\text{or } E = TS + YX + \mu N$$

"Euler's Equation"

Get functional, not just differential, relation

Note that its fine to take differential of this:

$$dE = TdS + SdT + YdX + XdY + \mu dN + Nd\mu$$

$$\text{also} = TdS + YdX + \mu dN$$

Requires

$$SdT + XdY + Nd\mu = 0$$

"Gibbs-Duhem eqn"

→ relationship between variables indep  
of energy or eqn of state

→ consequence of laws of thermo

So for instance,  $S = -X \left( \frac{\partial Y}{\partial T} \right)_{\mu} - N \left( \frac{\partial \mu}{\partial T} \right)_Y$

and other relations

Get even more relations from fact that

$$dE = TdS + YdX + \mu dN \text{ is exact}$$

$$\text{So } \left( \frac{\partial T}{\partial X} \right)_{S,N} = \left( \frac{\partial Y}{\partial S} \right)_{X,N} = \frac{\partial^2 E}{\partial X \partial S}$$

$$\left( \frac{\partial T}{\partial N} \right)_{S,X} = \left( \frac{\partial \mu}{\partial S} \right)_{X,N} = \frac{\partial^2 E}{\partial N \partial S}$$

$$\left( \frac{\partial Y}{\partial N} \right)_{S,X} = \left( \frac{\partial \mu}{\partial X} \right)_{S,N} = \frac{\partial^2 E}{\partial N \partial X}$$

Called Maxwell relations, say more later

Energy  $E$  is example of a thermodynamic potential

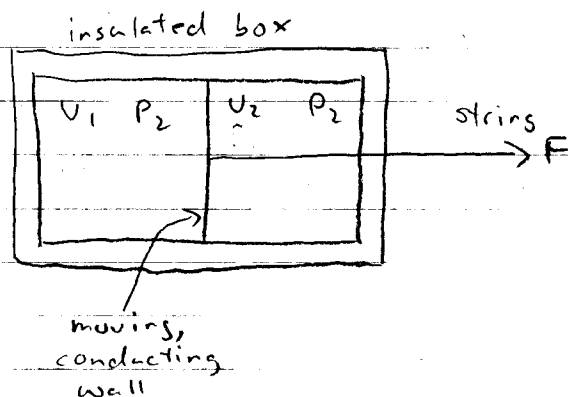
What does that mean?

Consider isolated ( $ds=0$ ) closed ( $dN=0$ ) system  
with fixed volume ( $dV=0$ )

Sounds like  $dE=0$

But can still change  $E$  if system has other  
degrees of freedom

For instance:



Reversibly pull string distance  $\Delta x$   
Do work  $W = \int F dx$  on system

Then  $V$ 's &  $P$ 's change. Could work out,  
but know from 1st law that  $\Delta E = W$

Later on, can move string back and recover  
 $W$  completely

Here acts like potential energy (cf, spring):  
Can reversibly store and release work

Call energy stored this way "free" energy:  
available to do work.

Not all energy is free!

if  $P_1 = P_2$ , no work available  
but  $E \neq 0$

Compare springs: total energy  $\sim mc^2$   
only  $\frac{1}{2} kx^2$  is free

Can also see that equilibrium state has  
minimum  $E$  for given  $S, U, N$

→ Any other state has free energy & can  
change by doing work (perhaps  
irreversibly)

+ So can find equilibrium by minimizing  $E$   
+ (subject to  $S, U, N$  constant)  
+

→ Familiar from mechanics