

Lecture Notes: Intro to Thermodynamics

①

thermodynamics - theory of matter in the aggregate - consequence of underlying symmetries of nature

- thermodynamics makes use of state variables (pressure, temperature, etc.)

- statistical physics: microscopic foundations of thermodynamics

- at microscopic level \Rightarrow many states available
 \rightarrow determine macroscopic behavior from how these states are sampled

- many-body systems continually pass between the many microscopic states available to them
symmetries/conservation laws \Rightarrow give thermodynamic variables

- complexity \rightarrow entropy \Rightarrow entropy is the quantity which ~~quant~~ is associated with complexity

Thermodynamics

③

- observation: matter in the aggregate can exist in macroscopic states \Rightarrow stable / reproducible
 - stable \rightarrow do not change in time
 - reproducible \rightarrow same state if thermodynamic variables are the same
(for example for an ideal gas $P, V \rightarrow T$ for a particular P, V always same T)
- thermodynamics: accurate in temperature range $10^{-9} \text{ K} \leftrightarrow 10^6 \text{ K}$
- four laws:
 - \Rightarrow 0th law: two bodies in equilibrium with a third body are also in equilibrium with each other
 - 1st law: Energy is conserved
 - 2nd law: heat flows spontaneously from high temperature to low temperature.
 - 3rd law: It is not possible to reach absolute zero in a finite number of reversible steps.

- equilibrium state: specified in terms of state (3) variables

state variables: can be extensive or intensive

extensive \rightarrow change when size of system is changed

intensive \Rightarrow independent of system size

- pairs of intensive - extensive variables will occur together in expression for energy/work

\rightarrow intensive variable is generalized force

\rightarrow extensive variable is generalized displacement

examples: P , pressure - force

V , volume - displacement

$P \leftrightarrow V$
 $\vec{B} \leftrightarrow \vec{M}$
 $\vec{E} \leftrightarrow \vec{D}$
 $J \leftrightarrow L$
 $\sigma \leftrightarrow \epsilon$

} express work done on system by external agent

- unique pair of extensive \leftrightarrow intensive \Rightarrow entropy/temperature
 S T

- related to heat change in a system

- one remaining pair of interest: $\mu \leftrightarrow N$
chemical potential μ / number of particles N

μ, μ changes with composition of system (4)

in general $\Rightarrow \mu_i, \mu_i \quad i=1, \dots, m$
each component

Other thermodynamic variables:

- response functions: heat capacity C

susceptibilities: magnetic χ

- thermodynamic potentials:

- internal energy, enthalpy, Helmholtz,
Gibbs, grand potential

- Some variables are state variables

- if we change the state of system from
A to B \Rightarrow change in state variable

is simply $U(B) - U(A)$

and is independent of the path

\rightarrow such variables can be described in terms
of exact differentials

walls are very important in thermodynamics

① isolated system: no heat exchange / no exchange
of matter with surrounding medium

② closed system: exchanges energy but not matter

③ open system: can exchange both matter and energy ⑤

thermodynamics depends crucially on the existence of such forms of isolation

Energy Conservation (1st law)

U - internal energy - energy stored in system

changes dU occur because work is done on system, heat is absorbed by the system or the chemical composition is altered

$$dU = dQ - dW + \sum_{j=1}^v \mu_j dN_j$$

$dU \rightarrow$ exact differential / state function

$dQ, dW \rightarrow$ not exact differentials

\rightarrow path dependent

$$dW = p dV - J dL - \sigma dA - \vec{E} \cdot d\vec{P} - \vec{F} \cdot d\vec{M} - q de$$

work \rightarrow generalised forces / displacements

Entropy (2nd law)

(6)

- entropy \Rightarrow results from second law
extensive variable S conjugate to
temperature T
- will develop idea through example of
Carnot engine

Carnot engine (Carnot cycle)

- heat engines: if heat is allowed to flow from
hot to cold, part of heat can be turned
into work
- Carnot's observation: heat flow from hot
to cold can also occur without doing
work
 \Downarrow
try to understand efficiency of heat engines
most efficient heat engines \Rightarrow reversible steps

Carnot engine

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runs between hot and cold reservoirs
 T_h T_c

4 steps:

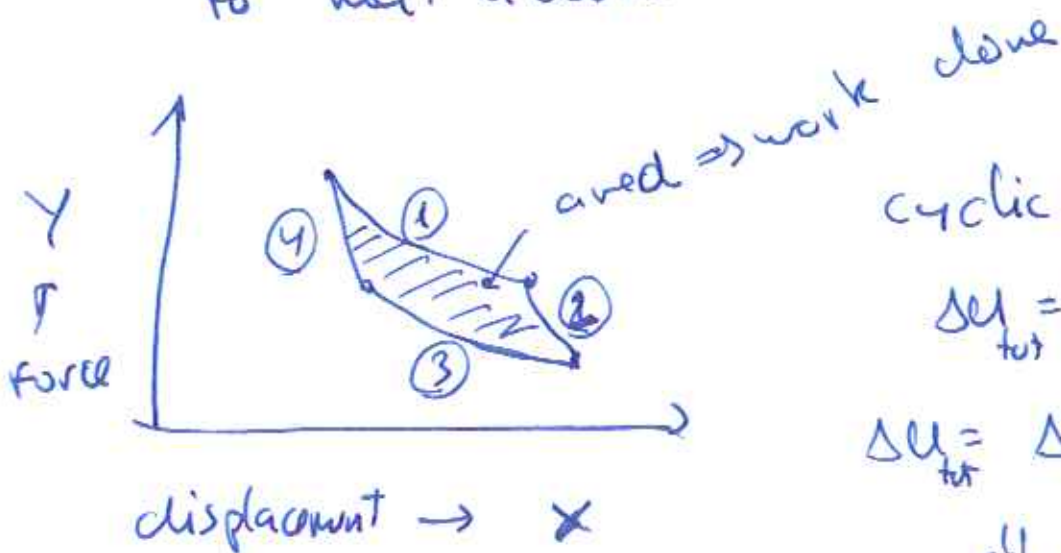
(1) isothermal heat absorption from hot reservoir
(T_h)

(2) adiabatic cooling $T_h \rightarrow T_c$

(3) isothermal heat ~~absorption~~ expulsion to cold reservoir (T_c)

(4) back to original state T_h adiabatically

efficiency η of engine: ratio of work done to heat absorbed (step 1)



cyclic process

$$\Delta U_{tot} = 0$$

$$\Delta U_{tot} = \Delta Q_{tot} - \Delta W_{tot} = 0$$

\Downarrow

$$\Delta Q_{tot} = \Delta W_{tot}$$

ΔQ_{tot} - net heat absorbed

$$\Delta Q_{tot} = \Delta Q_{abs} - \Delta Q'_{exp} = \Delta W_{tot}$$

$\Delta Q'_{exp}$ - heat expelled in step (3)

ΔQ_{abs} - heat absorbed in step (1)

efficiency η :
$$\eta = \frac{\Delta W_{tot}}{\Delta Q_{abs}} = 1 - \frac{\Delta Q_{exp}}{\Delta Q_{abs}}$$

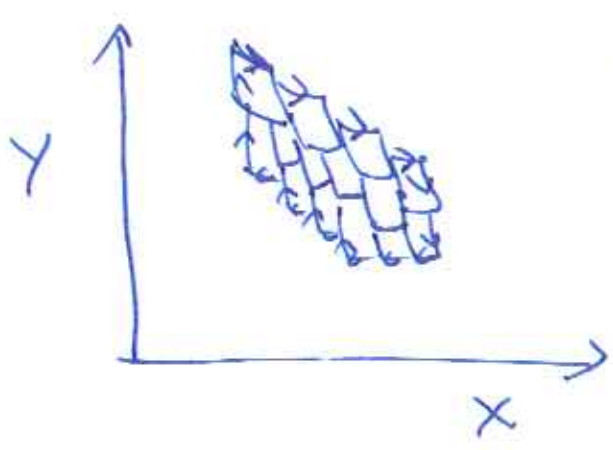
- 100% efficiency \Rightarrow convert all ΔQ_{abs} to work
- one can use Carnot cycle to set temperature scale (Lord Kelvin)

$$\frac{\Delta Q_{exp}}{\Delta Q_{abs}} = \frac{T_c}{T_h} \Rightarrow \frac{\Delta Q_{abs}}{T_h} - \frac{\Delta Q_{exp}}{T_c} = 0$$

$\Delta Q'_{exp}$ - heat expelled $\rightarrow \Delta Q_{exp} = -\Delta Q'_{exp}$

$$\frac{\Delta Q_{abs}}{T_h} + \frac{\Delta Q_{exp}}{T_c} = 0$$

- can couple Carnot cycles to each other



\rightarrow using infinitesimal Carnot cycles one can construct any cyclic path in x-y space

→ one can define a new state variable ⑨

$$\frac{dQ}{T} \Rightarrow \oint \frac{dQ}{T} = 0$$

for a state variable $\oint dU = U(T) - U(T) = 0$

$$dS = \frac{dQ}{T} \Rightarrow \text{entropy}$$

if there are irreversible processes:

$$\text{consider } \frac{\Delta Q_{\text{abs}}}{T_{\text{h}}} - \frac{\Delta Q'_{\text{exp}}}{T_{\text{c}}} = 0$$

more heat will be expelled $\Rightarrow \Delta Q'_{\text{exp}}$ will increase

$$\Rightarrow \frac{\Delta Q_{\text{abs}}}{T_{\text{h}}} - \frac{\Delta Q'_{\text{exp}}}{T_{\text{c}}} < 0$$

$$\Rightarrow \text{in this case } \oint \frac{dQ}{T} < 0$$

and $\frac{dQ}{T}$ is not an exact differential

emphasis: entropy S is an equilibrium property,

it is a state variable $\oint dS = 0$

for irreversible processes $\frac{dQ}{T} < dS$ (10)

hence not all entropy contributions are included

$$\Rightarrow dS = \frac{dQ}{T} + \sum_i dS_i \Rightarrow \sum_i dS_i \geq 0$$

$\sum_i dS_i$ - spontaneous processes (irreversible processes) produce entropy (could be dissipation due to friction, etc.)

isolated system: $dQ = 0$

$$dS \geq \sum_i dS_i \geq 0$$

entropy change is always positive

entropy always increases (or remains

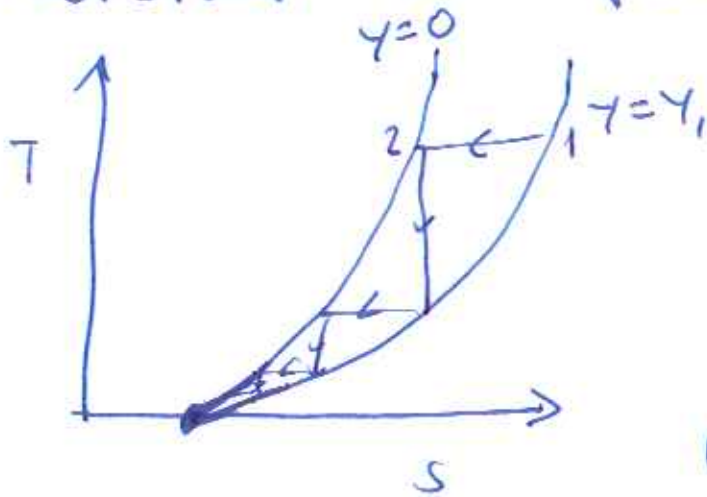
constant) in a spontaneous process

Third law

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- it is impossible to reach absolute zero in a finite number of reversible steps

- consider S-T plane



- generalized force

$$Y = 0 \quad Y = Y_1$$

for exact differentials it holds that

$$\left(\frac{\partial T}{\partial Y}\right)_{S,N} = - \left(\frac{\partial T}{\partial S}\right)_{Y,N} \left(\frac{\partial S}{\partial Y}\right)_{T,N}$$

* thermodynamic stability: $C_{Y,N} = \left(\frac{\partial S}{\partial T}\right)_Y \geq 0$

* if T decreases as Y increases adiabatically then S must increase as Y increases isothermally

we can repeat these steps \Rightarrow absolute zero will not be reached

~~Other~~

other consequence: at $T \rightarrow 0K$ certain derivatives of entropy are zero

$$S(Y, T, N) \Rightarrow dS = \left(\frac{\partial S}{\partial Y}\right)_{T,N} dY$$

$$dS = 0 \text{ by 2nd law}$$

$$\Rightarrow \left(\frac{\partial S}{\partial Y}\right)_{T,N} = 0 \quad \text{if } dN=0$$