Thermal and Statistical Physics

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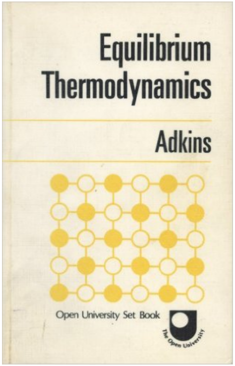
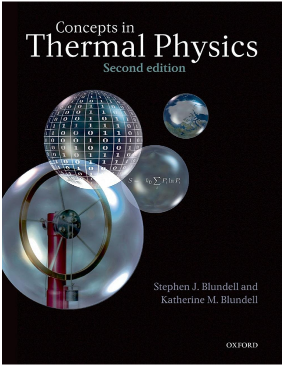
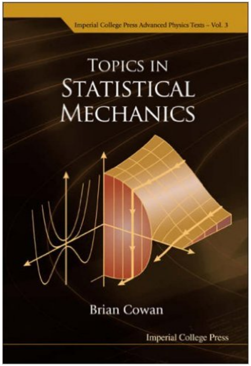
Overview of the course

1. Thermodynamics
   - Introduction
   - Availability and potentials
   - Equilibrium thermodynamics
2. Statistical Mechanics
   - Basic notions
   - Classical statistical mechanics
   - Grand canonical ensemble
   - Fermi gas
   - Bose gas and Bose condensation
3. Interacting systems
   - Real gases and liquids
   - Phase transitions and Landau theory
4. Stochastic physics
   - Fluctuations
   - Brownian motion

Some book recommendations







Other books for background reading:
Bowley & Sanchez, Landau & Lifshitz Vol. 5, Mazo.

The laws of thermodynamics

If two systems are separately in thermal equilibrium with a third, then they must also be in thermal equilibrium with each other.

Energy is conserved when heat is taken into account.

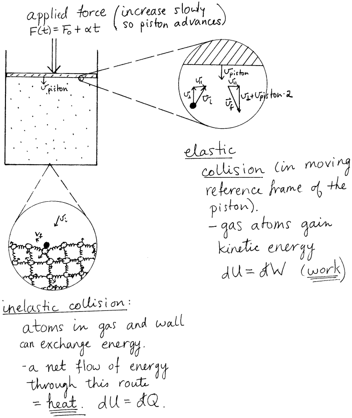
Heat does not flow from a colder to a hotter body. [Clausius]
or
You can't cool an object to below the temperature of its surroundings, and extract work in the process. [Kelvin]
or
The total entropy of the close system cannot decrease....

Internal energy

- **Mechanical energy** (kinetic, potential) accounts for contributions to the overall energy, which are attributed to a few macroscopic degrees of freedom.
- **Internal energy** takes care of contributions to the overall energy, which cannot be attributed to a few macroscopic degrees of freedom.
- We think of the internal energy as residing with **internal,** microscopic degrees of freedom.
- This introduces the difficulty that we can put this energy in – but we do not have enough information about internal degrees of freedom to be able to extract all of it again.
- Once energy is sunk in microscopic motion within the system, it is difficult to get it out again. But that is what a steam engine does, so it is not impossible. Thermodynamics lets us calculate this.

Heat

- Energy can flow into the microscopic degrees of freedom (d.o.f.) of a system out of (i) macroscopic d.o.f. of the environment, or (ii) microscopic d.o.f. of the environment.
- Work: **macroscopic(environment) $\rightarrow$ microscopic(system)**
- Heat: **microscopic(environment) $\rightarrow$ microscopic(system)**



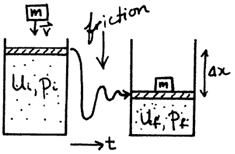
Thermodynamic variables

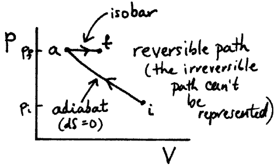
- Systems are characterised by **thermodynamic variables**.
- These occur in conjugate pairs of **thermodynamic force** (p, f, B, T) and **thermodynamic displacement** (V, ℓ, M, S).
- It is easier to think of thermodynamic (or generalised) forces as **intensive:** independent of the size of the system.
- Similarly, it is easier to regard thermodynamic (or generalised) displacements as **extensive:** proportional to the size of the system.
- The Legendre transformation switches between the 'force' and 'displacement' in the conjugate pair.
- The product of a pair of conjugate variables contributes to an extensive **thermodynamic potential** and has dimensions of energy.

Functions of state

We can find the magnitude of the change in a function of state in going between two equilibrium states, **even if the path taken was irreversible,**

by choosing *any* convenient *reversible* path between the initial and final states and integrating along it.



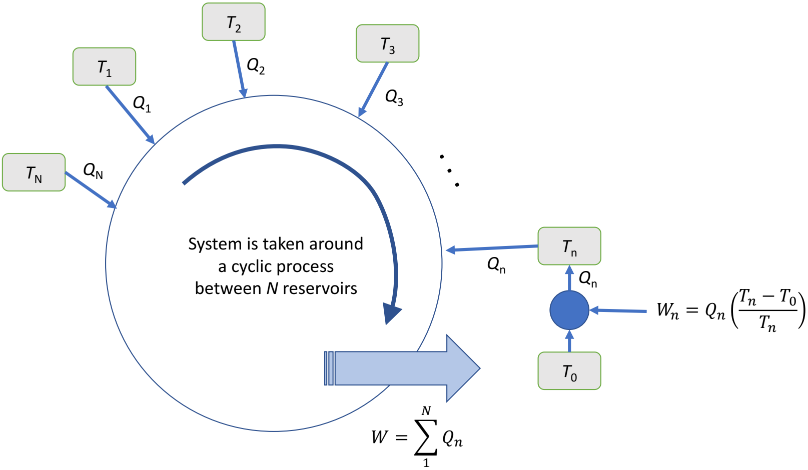


$$U_f = U_i + \frac{1}{2}mv^2 + mg\Delta x$$

$$S_f = \int_a^f \left(\frac{\partial S}{\partial V}\right)_p dV + S_i$$

$$p_f = p_i + \frac{mg}{\text{area}}$$

Cyclic process between N reservoirs, towards a definition of entropy



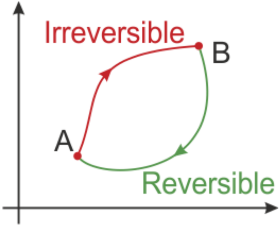
$\oint dQ/T \leq 0$ in general

$$\int_A^B dQ_{rev}/T \geq \int_A^B dQ_{irrev}/T$$

for process on right

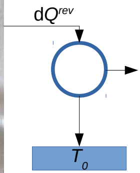
Define $dQ_{rev}/T = dS$

If no heat is exchanged, $dS \geq 0$



irreversible process

reversible process



Lecture 1: here!

0^{th} Law: $A = B$ and $B = C$, then $C = A$..

1^{st} Law: Energy = Work + Heat

2^{nd} Law: → Kelvin

→ Clausius

→ Entropy ...

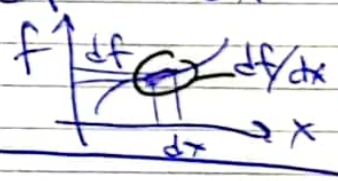
3^{d} Law: Entropy → 0 (constant)

as $T\,°K \to 0$

Thermodynamic Variables

$f = f(x)$

$df \Leftarrow dx$



"Energy" (x, y)

★ $\boxed{\dfrac{\partial\, \text{"Energy"}}{\partial x} = \text{"force"}}$

conjugate to "x"

observable, measurable as well

Conjugate pairs: (f, x) (P, V) (T, S)

T.D. variables are "extensive" ?

T.D. forces are "intensive" ?

Legendre tranform:

$f(x)$: $df = y \cdot dx$

construct $g = f - y \cdot x$

see: $dg = df - d(y \cdot x)$

$= \cancel{y\,dx} - \cancel{y\,dx} - x\,dy$

$dg = -x \cdot dy$

i.e. $\boxed{g = g(y)}$

$U(V)$: $dU = (-P) \cdot dV + \ldots$

$H(P) = U + PV$

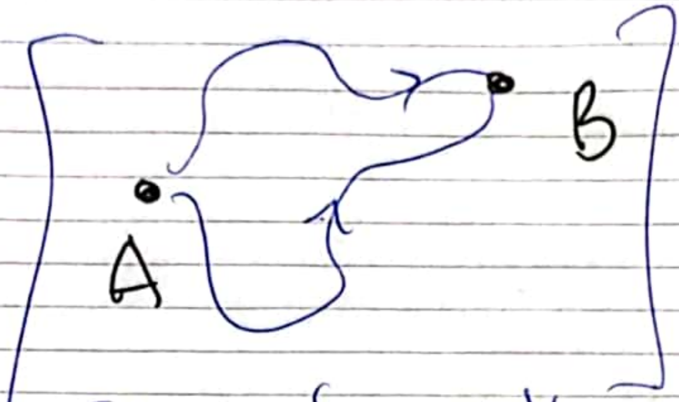
$dH = V\,dP$ etc.

Product of $\underbrace{\text{"force"} \cdot d\,\text{"variable"}}_{d\,\text{"energy"}}$.

$$\boxed{\frac{d\,\text{"Energy"}}{d\,\text{"x"}} = -\text{"force"}}$$

(generalise

"Functions of State" (def.)

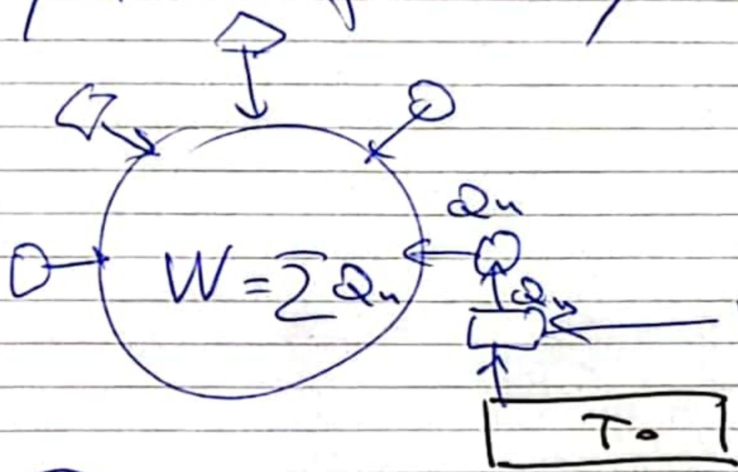


space of variables

$X(A) - X(B)$ same

$\oint X(a)\, da = 0$

Cycle of many heat pumps



$W_n = Q_n \left(\frac{T_n - T_0}{T_n} \right)$

$\downarrow$

out $W = \sum Q_n$

in $\sum_n W_n = \sum_n Q_n - T_0 \sum \frac{Q_n}{T_n}$

$\boxed{W - \sum W_n \leq 0}$

reversible when $= 0$ ...

$$T_0 \sum_n \frac{Q_n}{T_n} \leq 0$$

define $dS = \frac{dQ}{T}$: $\boxed{\int \frac{dQ}{T} \leq 0}$ $\int dS = 0$ in reversibl