Thermodynamics

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Physics & Chemistry of Soft Matter

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Acknowledgements

- Hugo Meekes (Nijmegen)
- David Manolopoulos (Oxford)
- Peter Atkins (Oxford)

Content of the course

- Introduction to Thermodynamics and gases
- The First Law of Thermodynamics
- Heat Capacities, Enthalpy and Thermochemistry
- The Second Law of Thermodynamics
- Helmholtz and Gibbs free energies
- Phase Transitions and Chemical Equilibrium
- Electrochemistry
- Ideal solutions, Colligative properties
- Condensation in the Van der Waals Equation of State

Required tools

- Mathematics
  - Integration (by parts), differentiation, total differentials, partial derivatives, ...
  - see Dr Maarten van Pruijssen's lectures
- Pen and paper
- Your brain
- Practise (lots of it)

Lectures, tutor hours and problem classes

- Lectures
  - Mondays 10:30 – 12:15 (LIN 1)
- Tutor hours:
  - Wednesday 8:30 – 9:15
  - Same tutor groups as 1st quarter
- Problem classes
  - Wednesdays 9:30 – 12:15

… this is where you practice, so this is where you learn thermo …

Problems for problem classes (& locations & answers & study guide)

http://www.dullenslab.com/teaching/thermo-1/ and also Brightspace

Literature

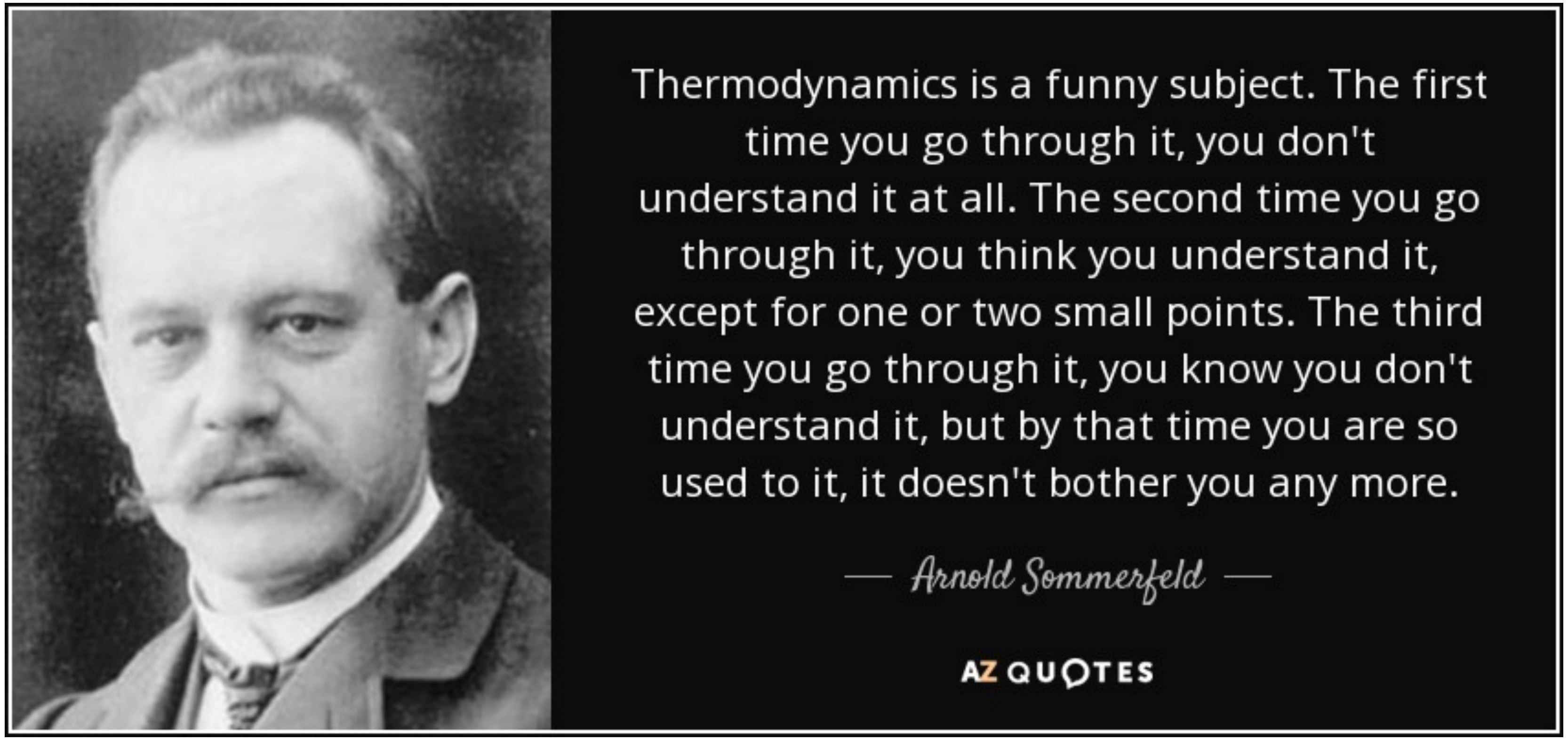
Main textbook:

- Physical Chemistry by Atkins, Oxford University Press, 11^{th} Ed. (2018)

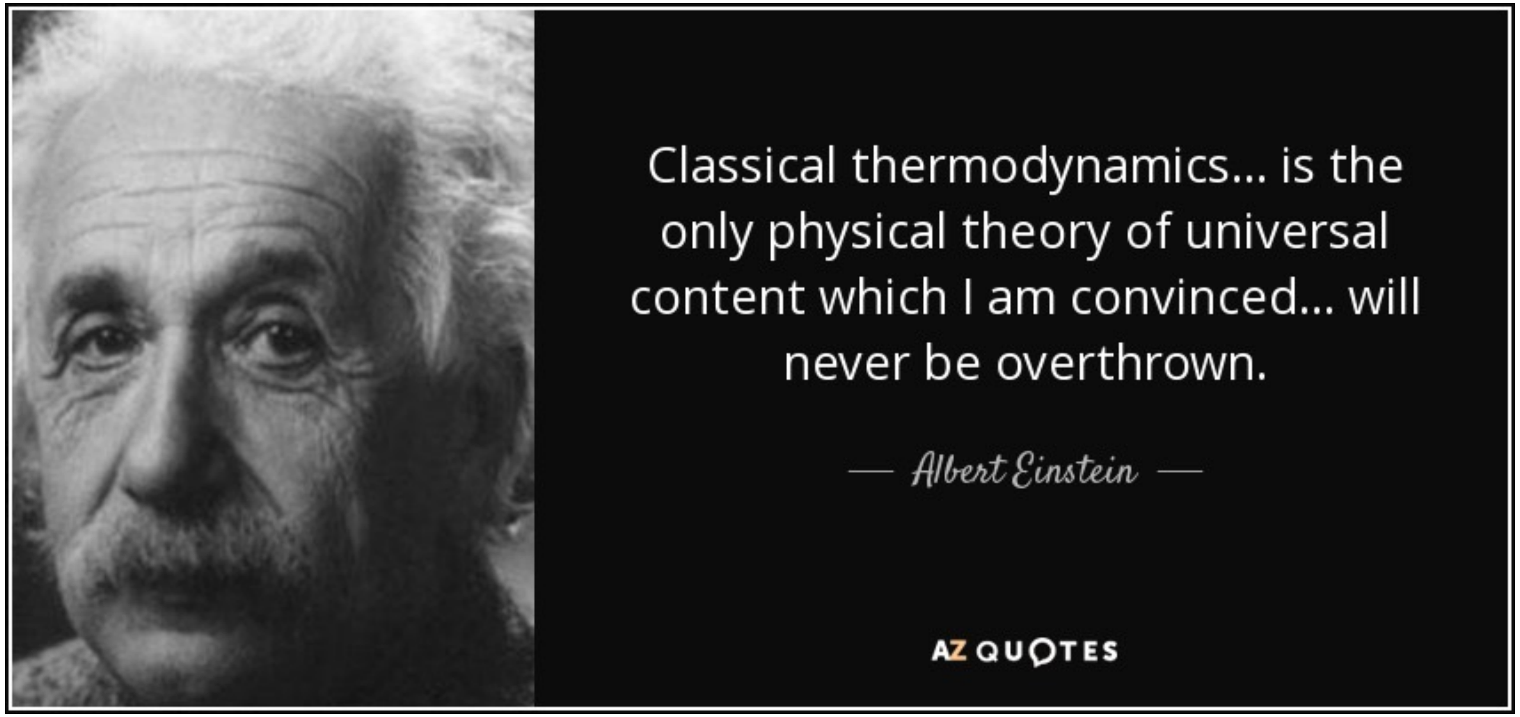
Other (useful) books (that I used):

- Thermodynamics and Chemistry by Devoe, 2^{nd} Ed., Pearson Education, Inc. (2020)
- Concepts in Thermal Physics by Blundell and Blundell, 2^{nd} Ed., OUP (2010)
- Molecular driving forces by Dill & Bromberg, Garland Science, New York (2003)
- Thermodynamics and Statistical Mechanics by Greiner, Springer (1995)
- Molecular Thermodynamics by McQuarrie and Simon, University Science Books (1999)

Now then ... Thermodynamics ...



Now then ... Thermodynamics ...



So here we go ...

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Today’s lecture (1)

- Introduction to Thermodynamics
  - Le Chatelier’s Principle
  - Classical vs Statistical Thermodynamics
  - Equations of State: gases
    - Gases: Perfect gas law, virial equation, Van der Waals Equation of State
- Thermodynamics: concepts
  - Reversible and irreversible processes
  - Extensive and intensive variables
  - Systems and surroundings
  - Heat and work
- The First Law of Thermodynamics
  - Different types of work: expansion (mechanical, chemical, ...)

Le Chatelier's Principle

"A system at equilibrium will respond to a perturbation so as to relieve the effect of the perturbation"

Henry Louis Le Chatelier
(1850 – 1936)

1. Chemical reaction, e.g. Haber process

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Thermodynamics:

- ***calculate*** the yield as function of T and p (lecture 6)
- tells us equilibrium position, but ***nothing*** about the rate

Le Chatelier's Principle

Henry Louis Le Chatelier
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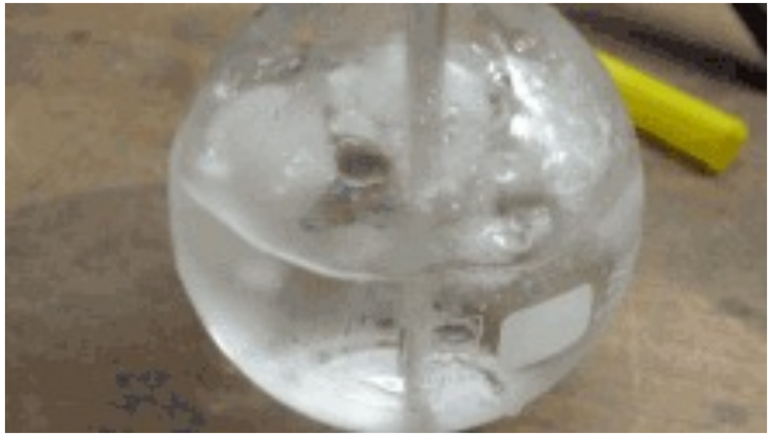
"A system at equilibrium will respond to a perturbation so as to relieve the effect of the perturbation"

2. Phase diagram of water



Thermodynamics:

- ***calculate*** the slope of the ice-water phase boundary (lecture 5)

Le Chatelier's Principle

"A system at equilibrium will respond to a perturbation so as to relieve the effect of the perturbation"

Henry Louis Le Chatelier
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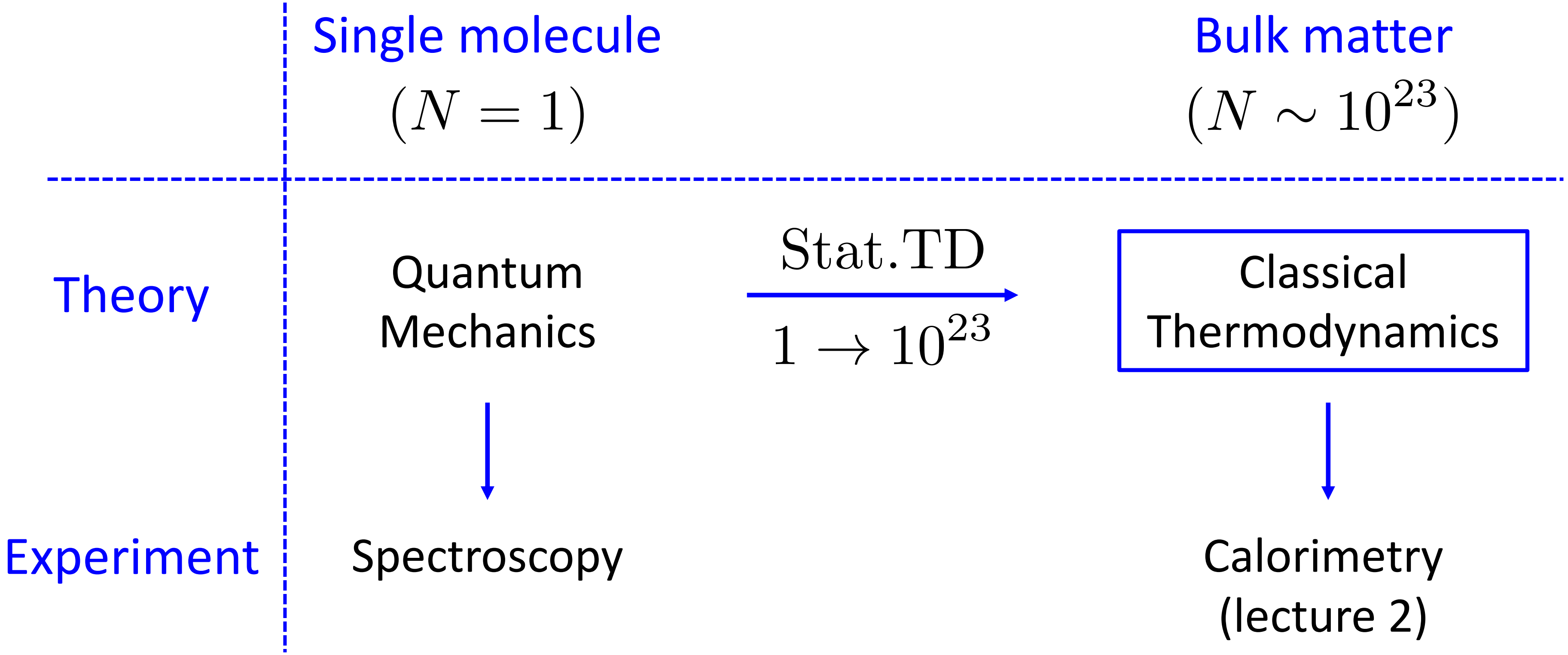
Thermodynamics

- ***Quantifies*** Le Chaterlier's Principle
- Tells us whether a process will run or not
- In which direction it will run (spontaneously)
  - Arrow of Time ... https://youtu.be/uQSoaiubuA0 (lecture 3)

Classical vs Statistical Thermodynamics

- This course: <u>**classical**</u> TD (*independent* of molecular hypothesis)
- Years 2 and 3: statistical TD (based on molecular hypothesis)



State variables and Equations of State

Thermodynamic properties (e.g. heat capacity) vary with:

- Pressure *p*
- Temperature *T*
- Volume *V*
- No. of moles *n*

These ***state variables*** are related for all substances by an

Equation of State:

$$p = p(n, V, T)$$

Perfect gas equation

$$p = \frac{nRT}{V}$$

- Point-like particles
- No interactions
- Holds for any gas as $p \to 0$

Robert Boyle
(1627 – 1691)

$$pV = cst$$

Jacques Charles
(1746 – 1823)

$$\frac{V}{T} = cst$$

Amedeo Avogadro
(1776 – 1856)

$$\frac{V}{n} = cst$$

Real gases

- Perfect gas: no condensation ... (no interactions)
- Deviations from perfect gas (at high *p* and low *T*)
- Different Equation of State required ...

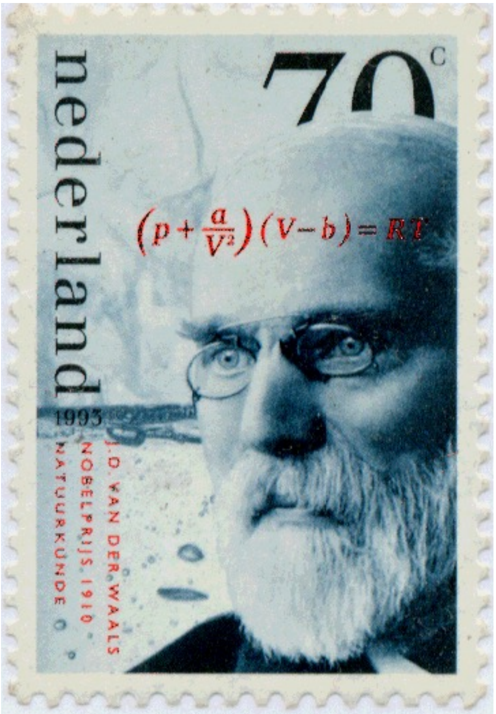
Virial Equation of State:

$$p = \frac{nRT}{V}\left(1 + B(T)\left(\frac{n}{V}\right) + C(T)\left(\frac{n}{V}\right)^2 + ...\right)$$

Virial coefficients:

parametrise intermolecular interactions

Van der Waals Equation of State



Johannes Diderik Van der Waals
(1837 – 1923)

Over de continuïteit van den gas – en vloeistof toestand

PhD-Thesis, Leiden, 1873
The Netherlands

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

Condensation requires *repulsion* and *attraction* (lecture 7)

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- **Thermodynamics: concepts**
  - Reversible and irreversible processes
  - Extensive and intensive variables
  - Systems and surroundings
  - Heat and work
- The First Law of Thermodynamics
  - Different types of work: expansion (mechanical, chemical, ...)

Reversible and irreversible processes

Thermodynamics applies to both
reversible and **irreversible** processes

Direction of process can be reversed by an infinitesimal change of a variable (d*x*)

Very slow process via (quasi-static) 'equilibrium' states

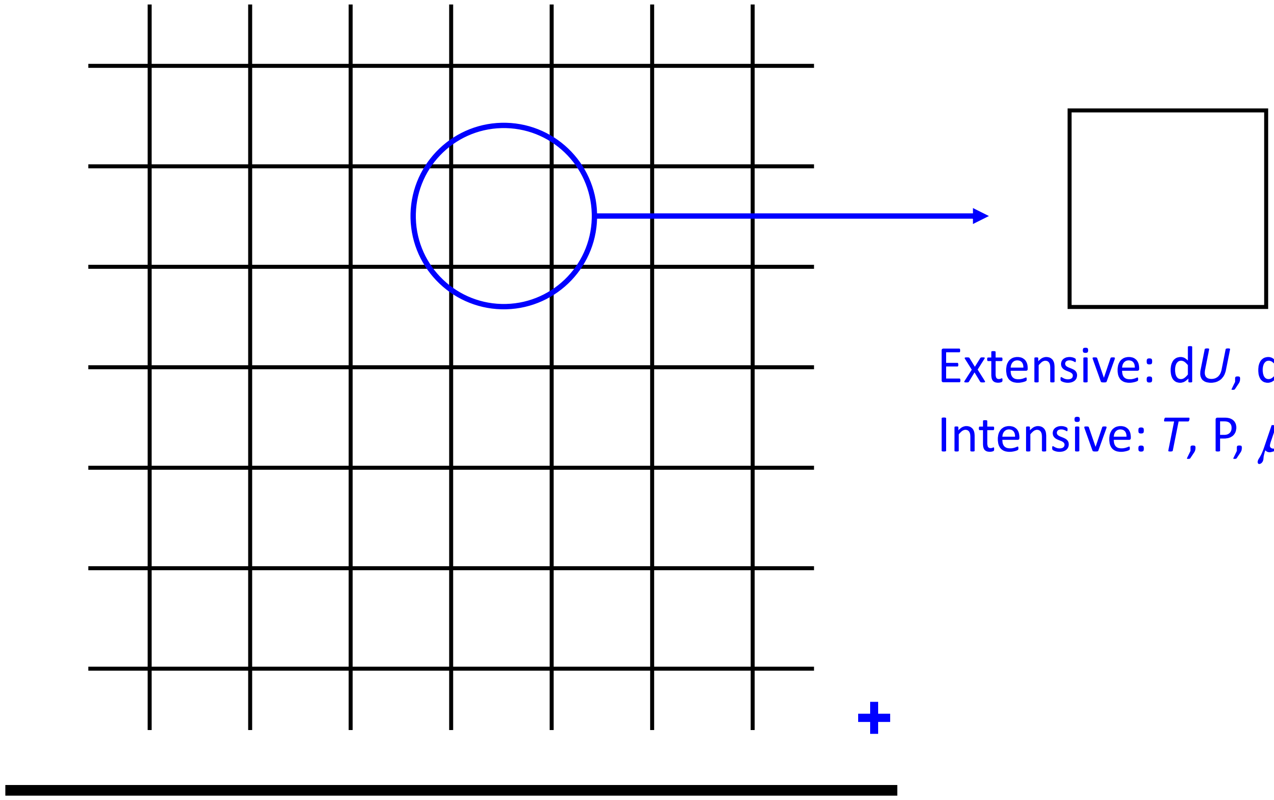
Direction of (spontaneous) process ***cannot*** be reversed

Very fast (spontaneous) process via non-equilibrium states

$$\Delta x = \int_{x_i}^{x_f} \mathrm{dx} = \mathrm{x_f} - \mathrm{x_i}$$

A ***state function*** does not depend on the path,
only on final and initial states

Extensive and intensive variables



Extensive: dU, dV, dn, ...

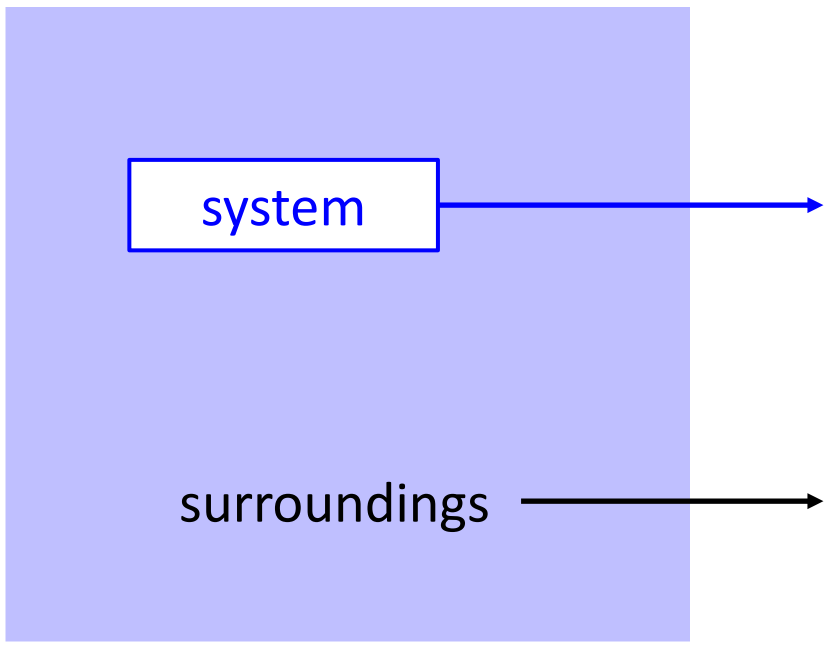
Intensive: T, P, μ, ...

Extensive: U, V, n, ...

Intensive: T, P, μ, ...

Systems and surroundings

Thermodynamics considers energy transactions
between a **system** and its **surroundings**

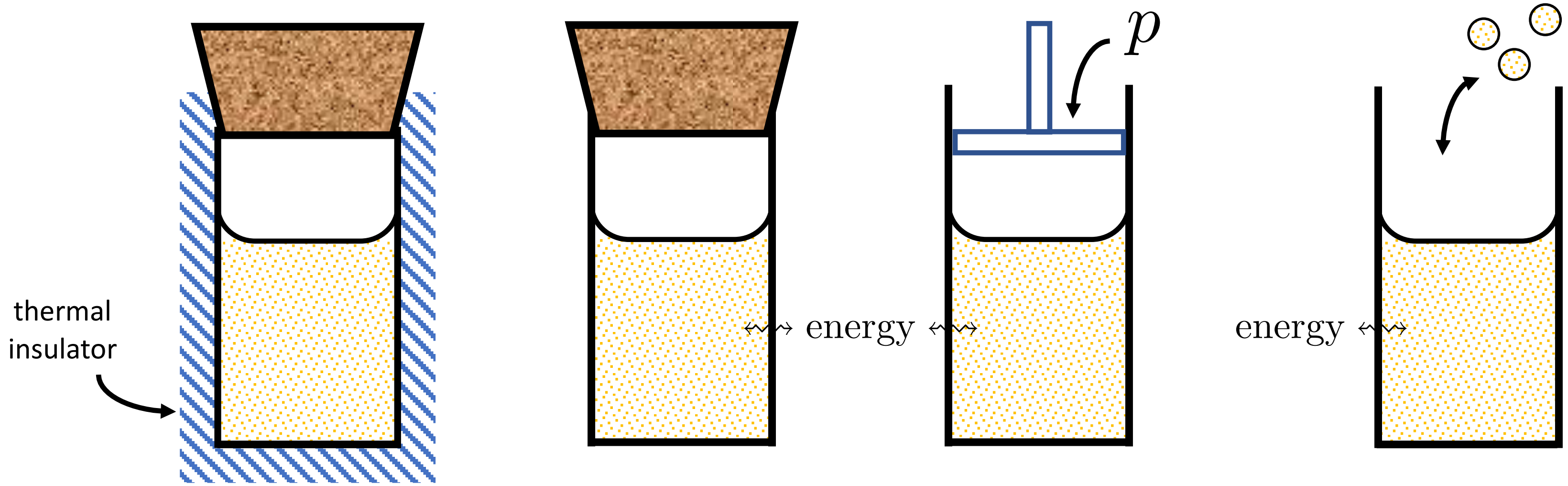


reaction vessel, cell, engine, ...

e.g. a large water bath at temp. T
that is isolated from ***its*** surroundings

$$system + surroundings = \text{“}universe\text{”}$$

Isolated, closed and open systems



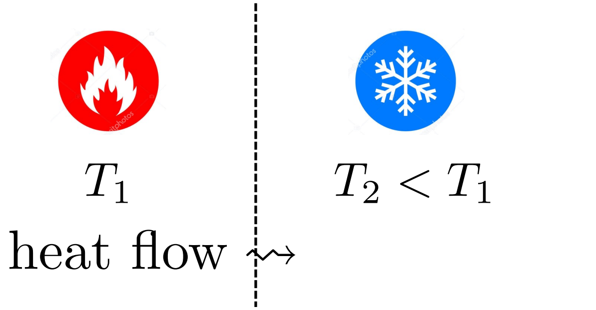
	isolated	closed (constant V)	closed (constant p)	open
energy exchange with surroundings?	×	✓	✓	✓
matter exchange with surroundings?	×	×	×	✓

Heat and work

Closed system can exchange energy with its surroundings as **heat** (q) and **work** (w)

heat

- Flow/transfer of energy down a temperature gradient
- Thermal energy in transit (Blundell and Blundell)
- Statistically distributed energy amongst particles in a system (Greiner)



... it stops when $T_1 = T_2$ ...

Thermal Equilibrium

Zeroth Law of Thermodynamics:

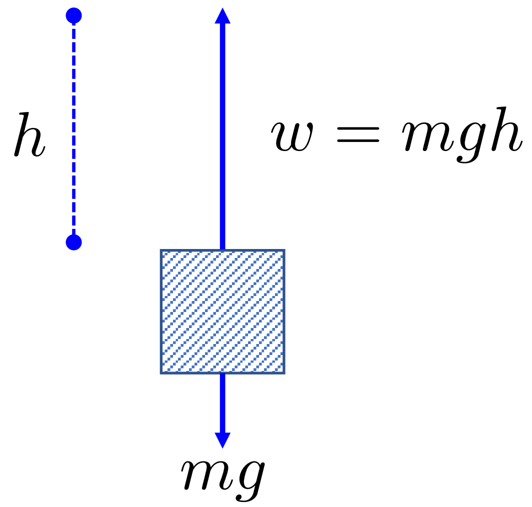
Two systems, each separately in thermal equilibrium with a third, are in equilibrium with each other

Heat and work

Closed system can exchange energy with its surroundings as **heat** (q) and **work** (w)

work

- Is done to achieve motion against an opposing force
  - lifting a weight in the surroundings



Heat and work

Closed system can exchange energy with its surroundings as **heat** (q) and **work** (w)

heat

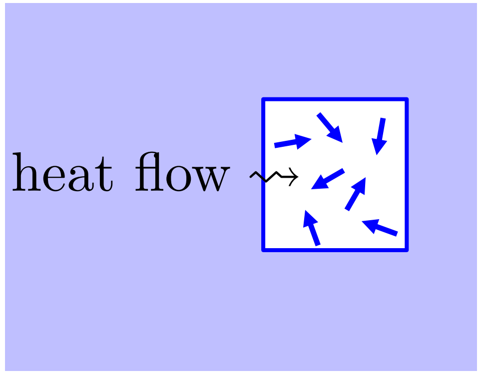
- Flow/transfer of energy down a temperature gradient

work

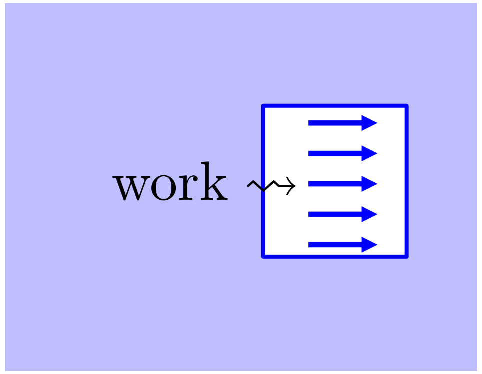
- Is done to achieve motion against an opposing force

molecular interpretation

- Heat leads to random motion



- Work leads to uniform motion



Heat and work

Closed system can exchange energy with its surroundings as **heat** (q) and **work** (w)

By convention:

$w > 0$: work is done ***on*** the system (by surr.)

$w < 0$: work is done ***by*** the system (on surr.)

$q > 0$: heat is transferred ***to*** the system (from surr.)

$q < 0$: heat is transferred ***from*** the system (to surr.)

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- **The First Law of Thermodynamics**
  - Different types of work: expansion (mechanical, chemical, ...)

First Law of Thermodynamics

The internal energy *U* of the system keeps track of these energy transactions:

$$\Delta U = q + w$$

change in internal energy of the system = heat added to the system + work done on the system

1st Law in infinitesimal changes:

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$$

Properties of the internal energy *U*

- *U* is sum of E_{kin} and E_{pot} of molecules $\rightarrow f(V,T)$

For example: Internal energy of perfect gas*

$$U_{\text{pg}} = \frac{3}{2}nRT$$ for n moles of atomic perfect gas

$$= \frac{3}{2}Nk_BT$$ for *N* molecules of atomic perfect gas

U_{pg} only depends on the temperature

* Not derived here

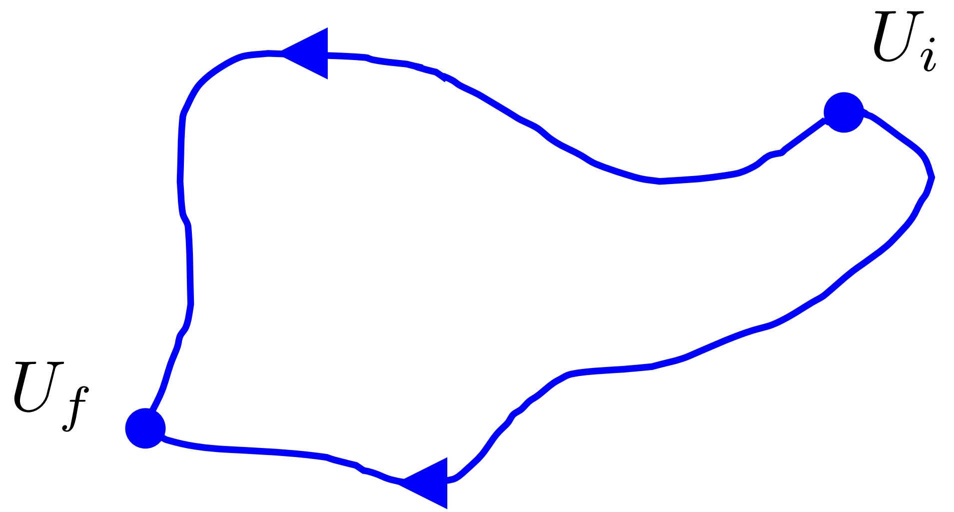
Properties of the internal energy *U*

- *U* is sum of E_{kin} and E_{pot} of molecules $\rightarrow f(V,T)$

- *U* is a state function
  - Independent of the path
  - Total (exact) differential

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

see Dr Maarten van Pruijssen's lectures & lecture 4



- Note that: *q* and *w* are ***NOT*** state functions
  - Dependent upon the path

Different types of work

- Expansion work
- Chemical work
- Many others:
  - Electric work
  - Surface work
  - ...

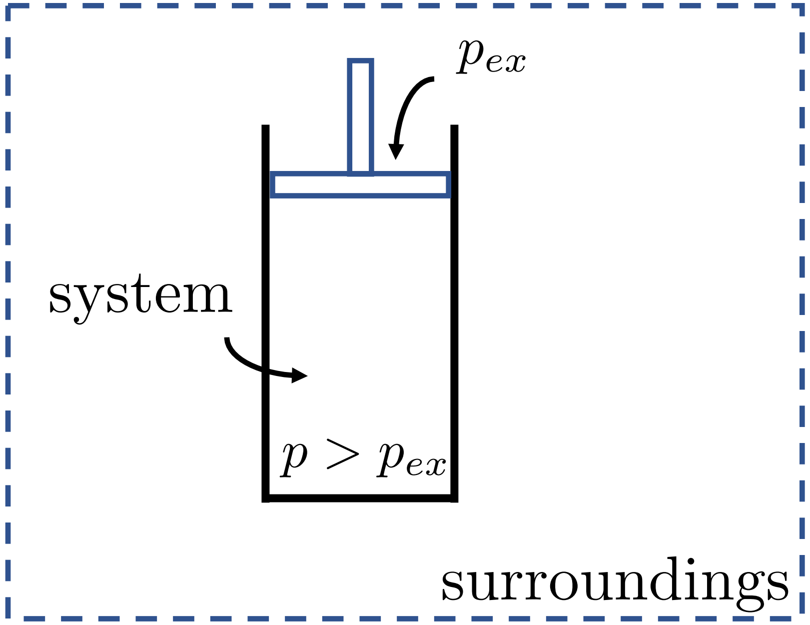
Expansion work

- *Constant external pressure (irreversible)*
- *Reversible isothermal (dT=0) expansion*

$$p = p_{ex} \xrightarrow{\text{in general}} p_1 = p_2$$

Mechanical Equilibrium

- *w is not a state function*
- *Reversible processes achieve maximum work*

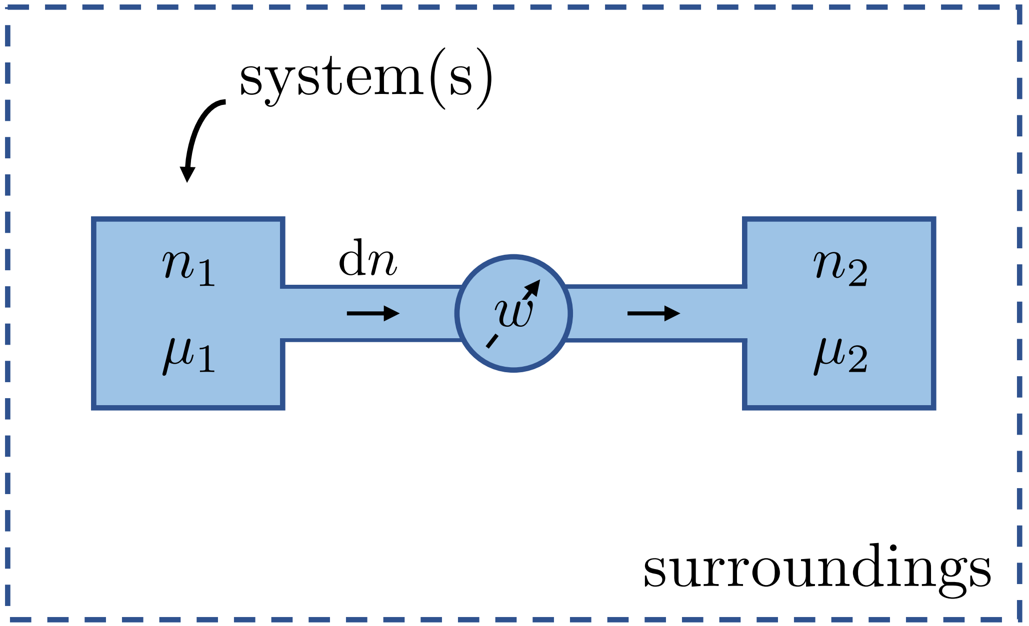


$$đw = -p_{\mathrm{ex}} \mathrm{d}V$$

$$w = -\int p_{\mathrm{ex}} \mathrm{d}V$$

Chemical work

- μ: chemical potential [J mol^{-1}]
- μ: work required to add one mole (to a system)



$$\mu_1 = \mu_2$$

Chemical Equilibrium

$$đw = \mu \mathrm{d}n$$

Different types of work

- Expansion work $\mathrm{d}w = -p_{\mathrm{ex}}\mathrm{d}V$
- Chemical work $= \mu\mathrm{d}n$
- Many others:
  - Electric work $= \phi\mathrm{d}Q$
  - Surface work $= \gamma\mathrm{d}\sigma$
  - ...

Into thermodynamic machinery
... via the 1st Law ...

$$\mathrm{d}U = \mathrm{d}q + \boxed{\mathrm{d}w}$$

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- ✓ Introduction to Thermodynamics and gases
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- **Heat Capacities, Enthalpy and Thermochemistry** ⟶ **Next Monday, lecture 2**
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