Laws of thermodynamics & thermal properties of matter

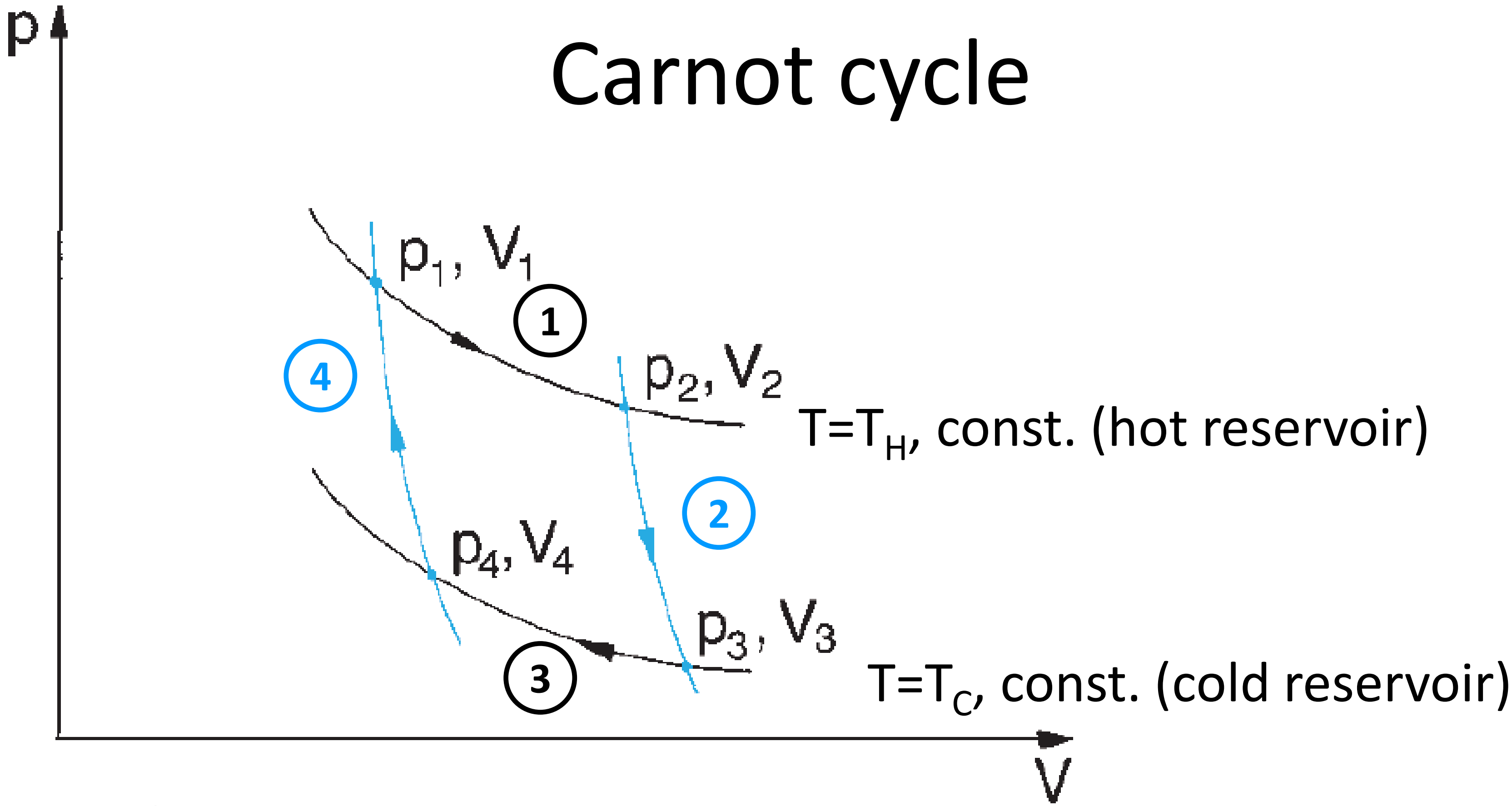
phase transitions and phase diagrams

diffusion, osmosis

Introduction to Physics I

For Biologists, Geoscientists, & Pharmaceutical Scientists

Reversible heat-work transformation
Carnot cycle



1. quasi-static, isothermal absorption of heat from a hot reservoir
2. quasi-static, adiabatic expansion to a lower temperature
3. quasi-static, isothermal release of heat to a cold reservoir
4. quasi-static, adiabatic compression back to the original state

Trautwein, Tipler

2^{nd} law of thermodynamics

A process whose only net result is to absorb heat from a cold reservoir and release the same amount of heat to a hot reservoir is impossible.

Clausius statement

It is impossible for a heat engine working in a cycle to produce only the effect of absorbing heat from a single reservoir and performing an equivalent amount of work.

Heat-Engine statement

Tipler

Laws of thermodynamics

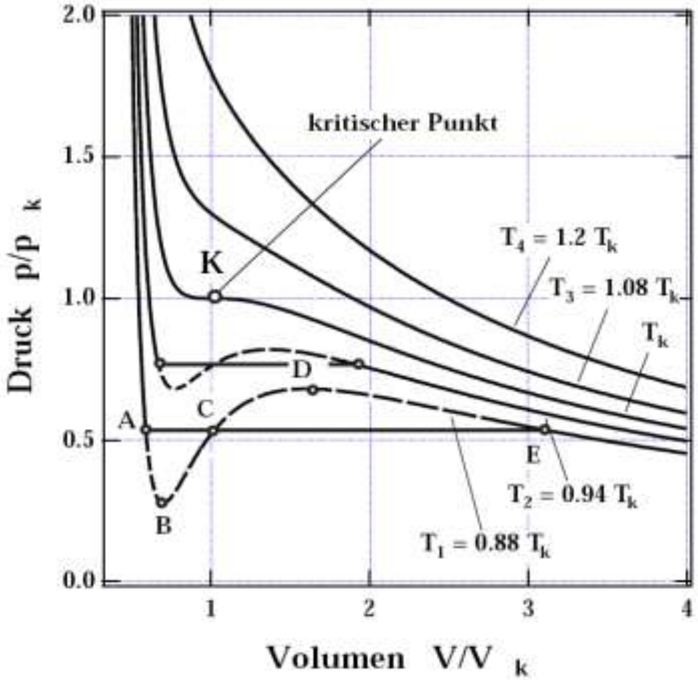
The laws of Thermodynamics

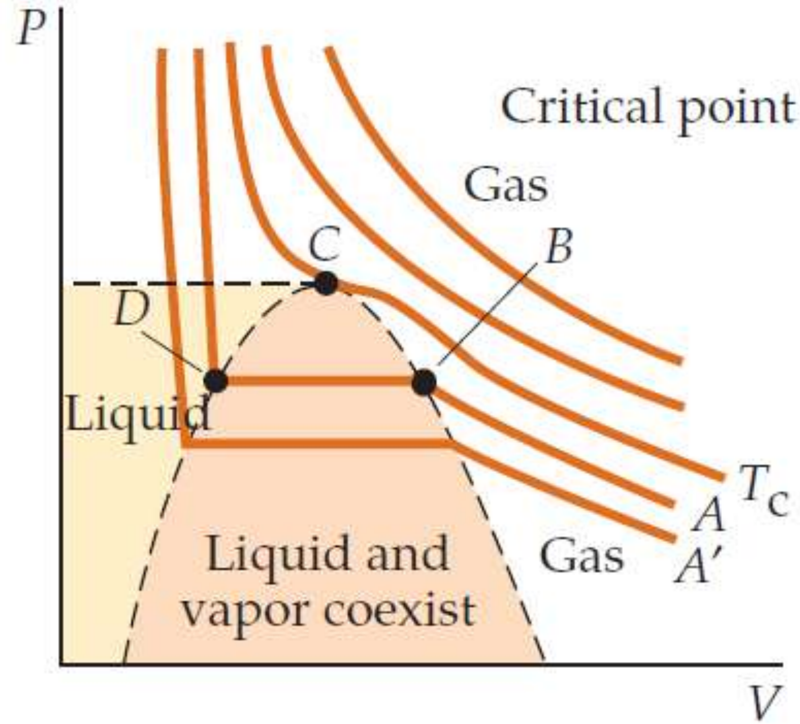
1: You can't win, you can only break even.

2: You can only break even at T=0.

3: You can't reach T=0....

real gas law: van der Waals





$$\left(P + \frac{an^2}{V^2}\right)(V - bn) = nRT$$

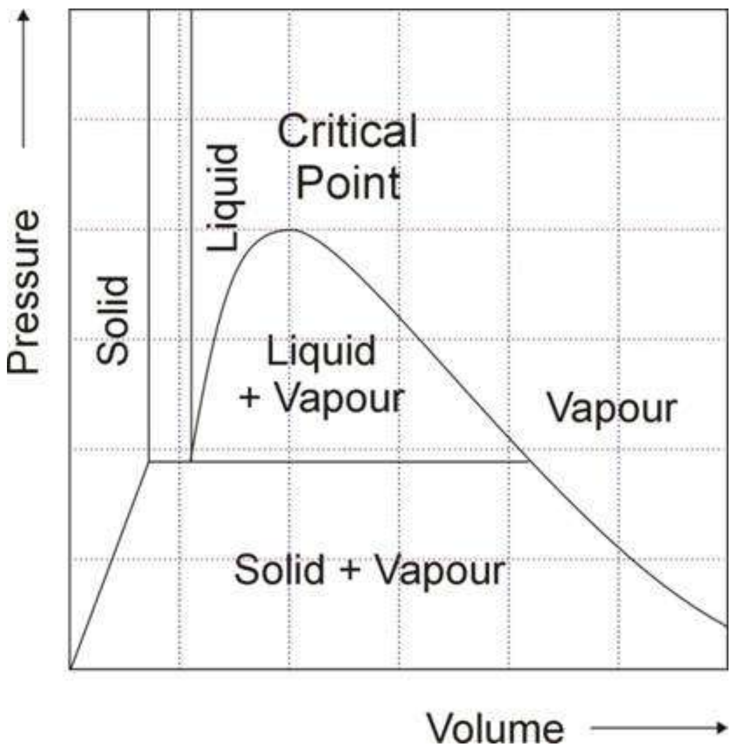
Van der Waals equation of state

FIGURE 20-5 Isotherms on the *PV* diagram for a substance. For temperatures above the critical temperature T_c, the substance remains a gas at all pressures. Except for the region where the liquid and vapor coexist, these curves are described quite well by the van der Waals equation. The pressure for the horizontal portions of the curves in the shaded region is the vapor pressure, which is the pressure at which the vapor and liquid are in equilibrium. In the region shaded yellow, to the left of the region shaded pink, the substance is a liquid and is nearly incompressible.

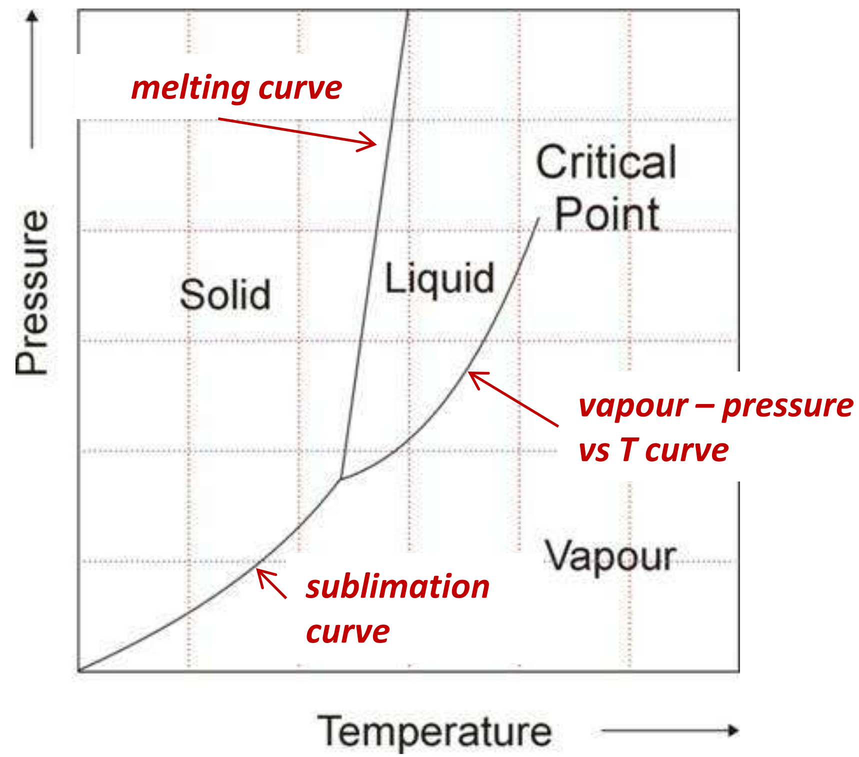
Tipler

PV & PT phase diagrams

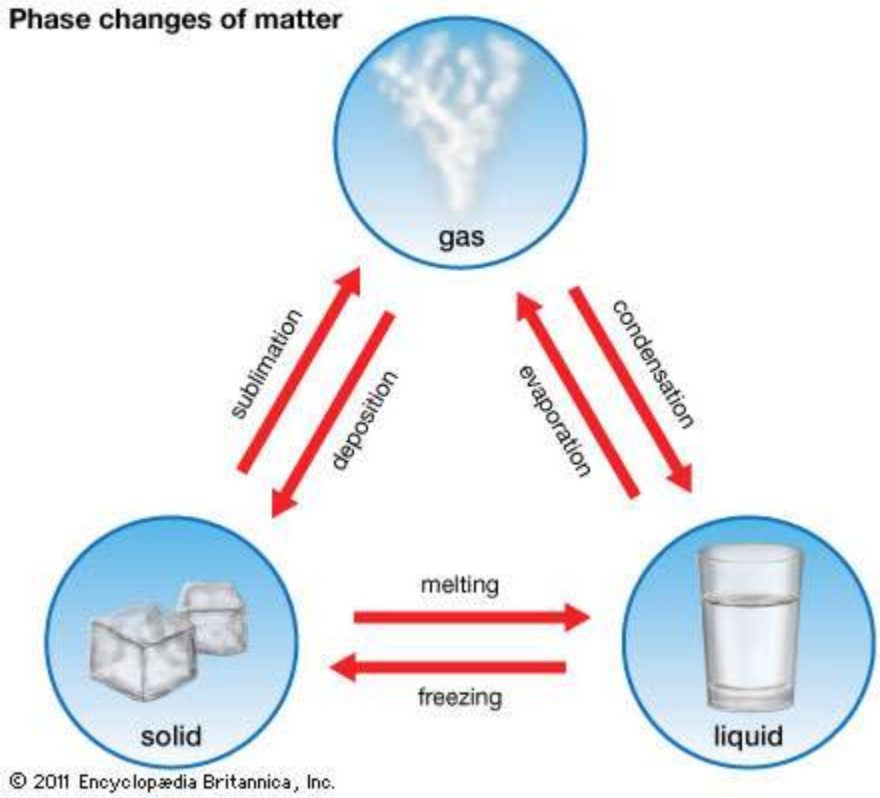
extended PV diagram



PT diagram



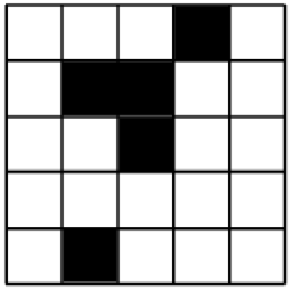
phase transitions



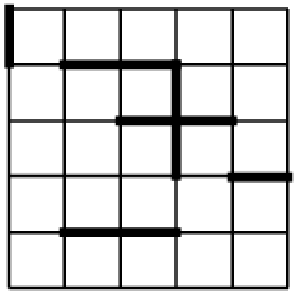
phase transitions…
a general class of phenomenon

For instance, **percolation**: phenomenon of a liquid passing through a porous material.

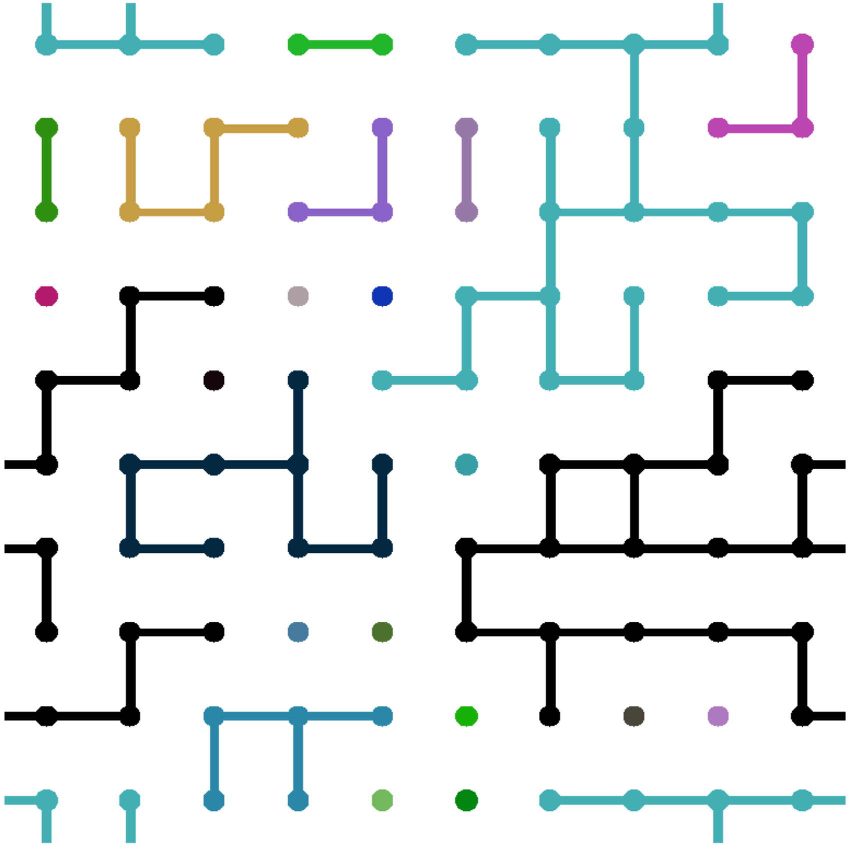
Below a certain critical porosity, the material would be unable to allow the liquid to pass - phase transition.



site percolation



bond percolation

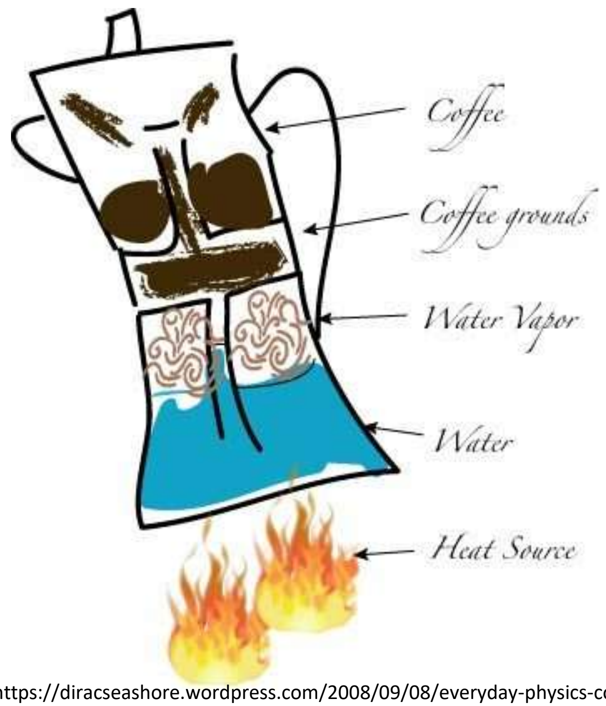


MIT, mathworld.wolfram

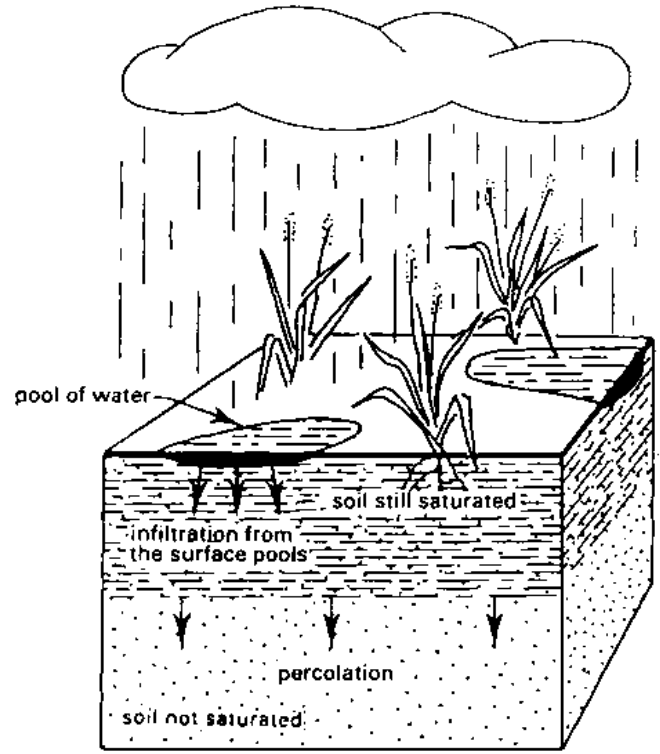
phase transitions… more

For instance, **percolation**: phenomenon of a liquid passing through a porous material.

Below a certain critical porosity, the material would be unable to allow the liquid to pass - phase transition.



https://diracseashore.wordpress.com/2008/09/08/everyday-physics-coffee/

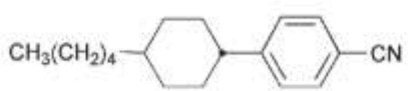


phase transitions… more

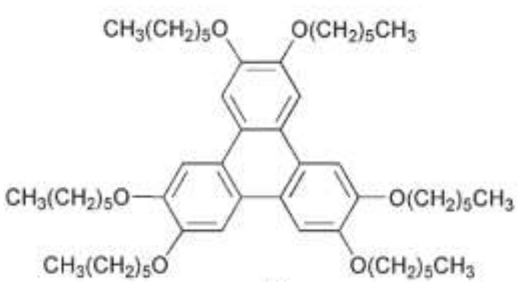
The **boiling of a liquid to a gas** exhibits a **decrease in order** as the molecules are no longer bound and are only weakly interacting

The **freezing of a liquid to a solid** exhibits **an increase in order** as the atoms occupy locations on a regular crystal lattice

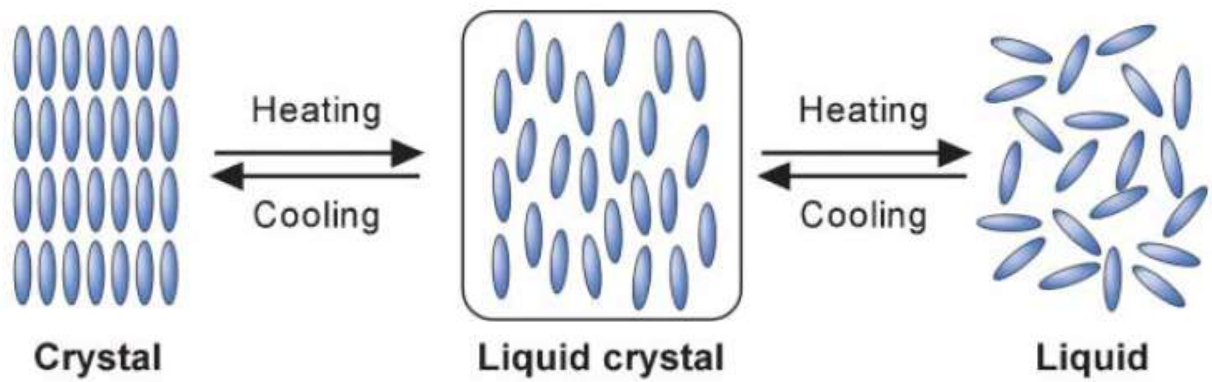
The **alignment of liquid crystals** shows **an increase in directional order** (although not necessarily spatial order) as the long liquid crystal molecules align and point in the same direction



9



10



Kato et al., Chem. Soc. Rev. 2017

phase transitions… more

The **boiling of a liquid to a gas** exhibits a **decrease in order** as the molecules are no longer bound and are only weakly interacting

The **freezing of a liquid to a solid** exhibits **an increase in order** as the atoms occupy locations on a regular crystal lattice

The **alignment of liquid crystals** shows **an increase in directional order** (although not necessarily spatial order) as the long liquid crystal molecules align and point in the same direction

The **appearance of a permanent magnetic moment** in a ferromagnet is an example of **an increase in order** as the individual magnetic spins point together in the same direction (Curie temperature)

The **segregation of block copolymers** in a polymer melt demonstrates **an increase in order** as the individual monomer chains separate and aggregate

The format
wavefuncti

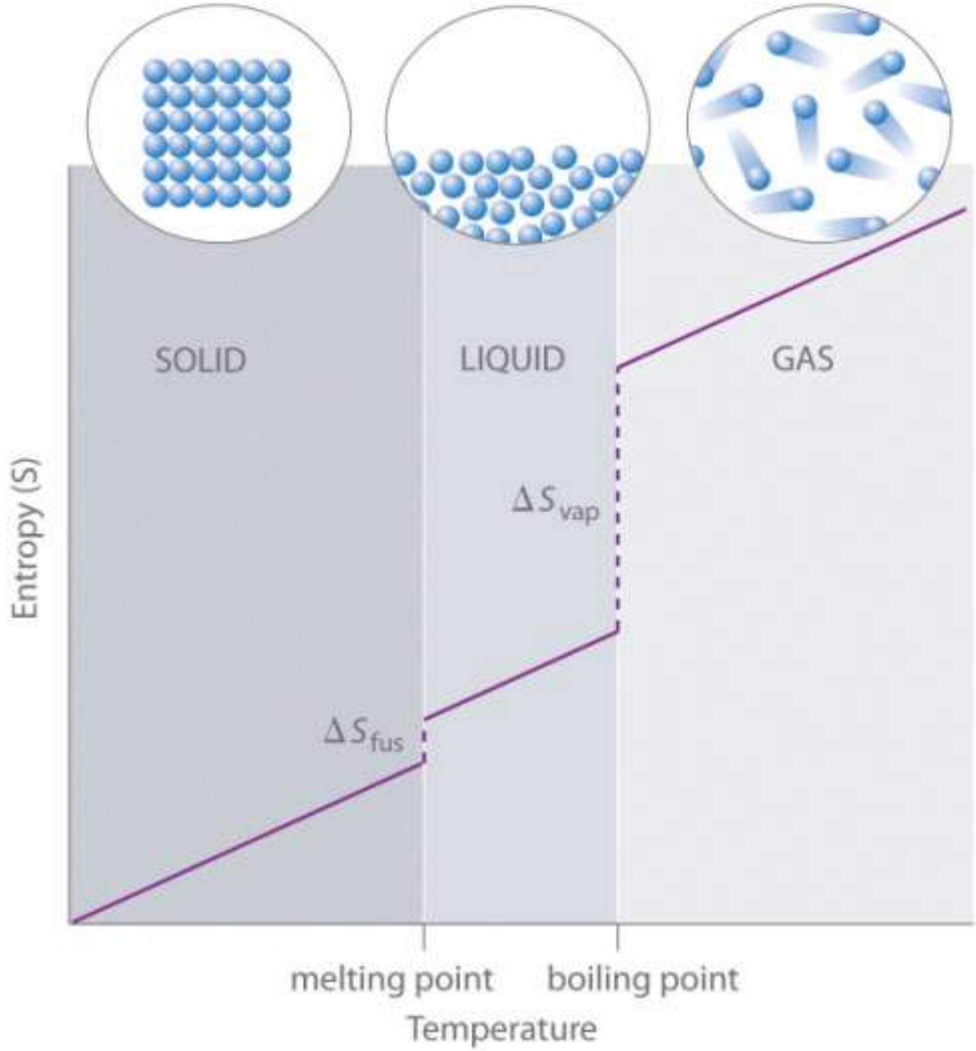
Supercond rently

Phase transitions occur in a variety of materials & systems

Phase transition ⇔ change in constituents' order (order parameter)

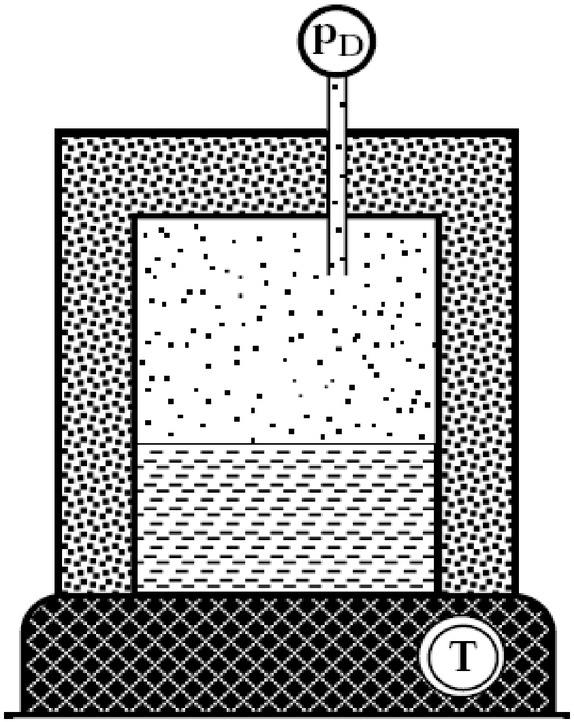
Different phases ⇔ variety of properties, technological applications

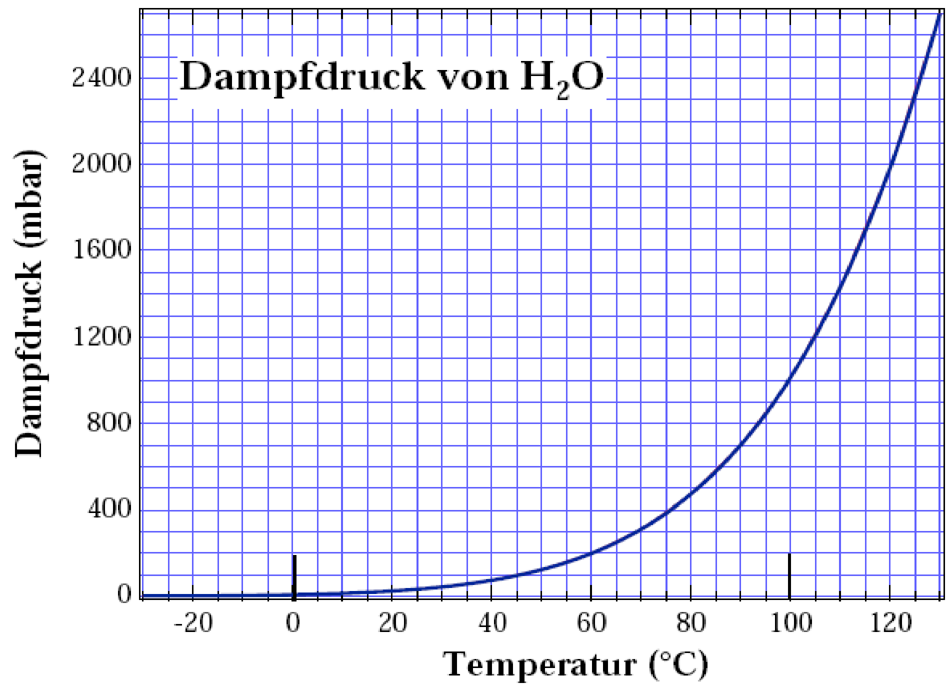
entropy during phase transitions



chem.libretexts.org

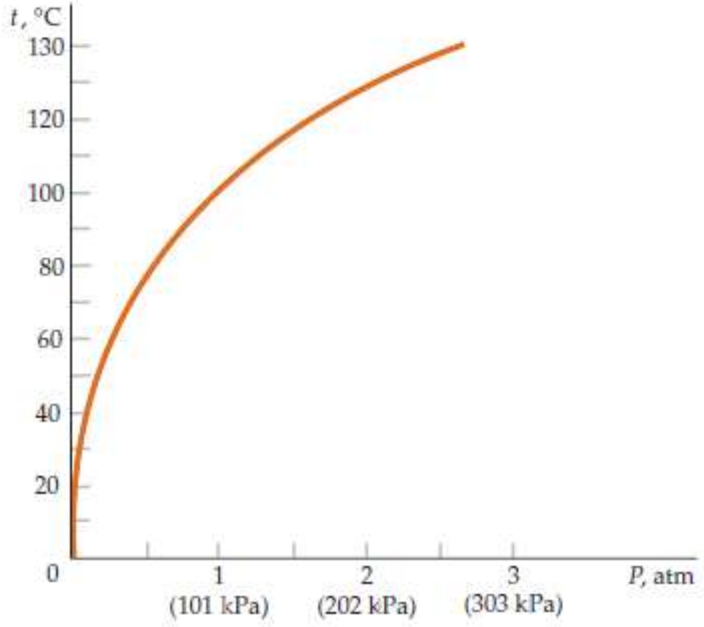
vapor pressure

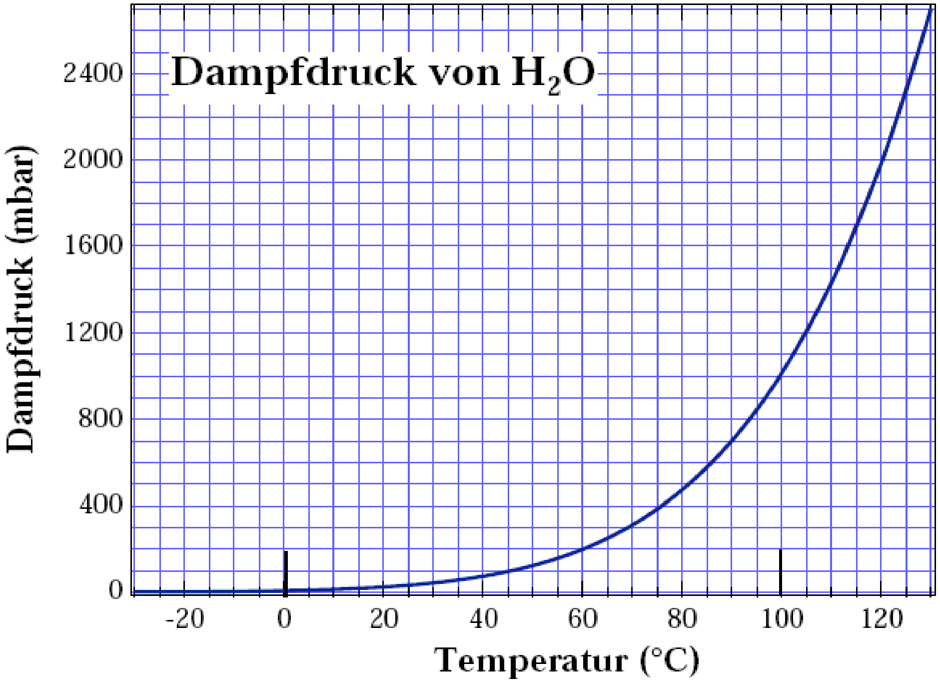




vapor pressure

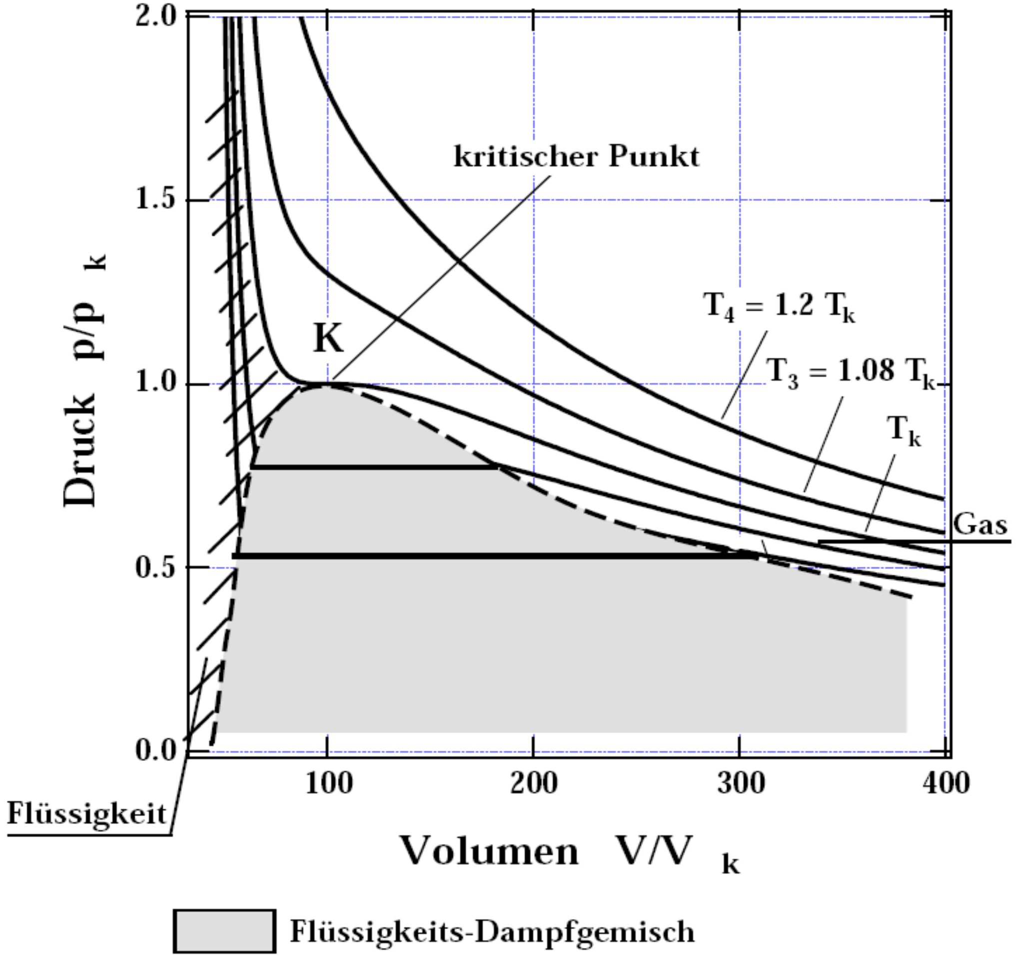
Boiling point of water vs pressure



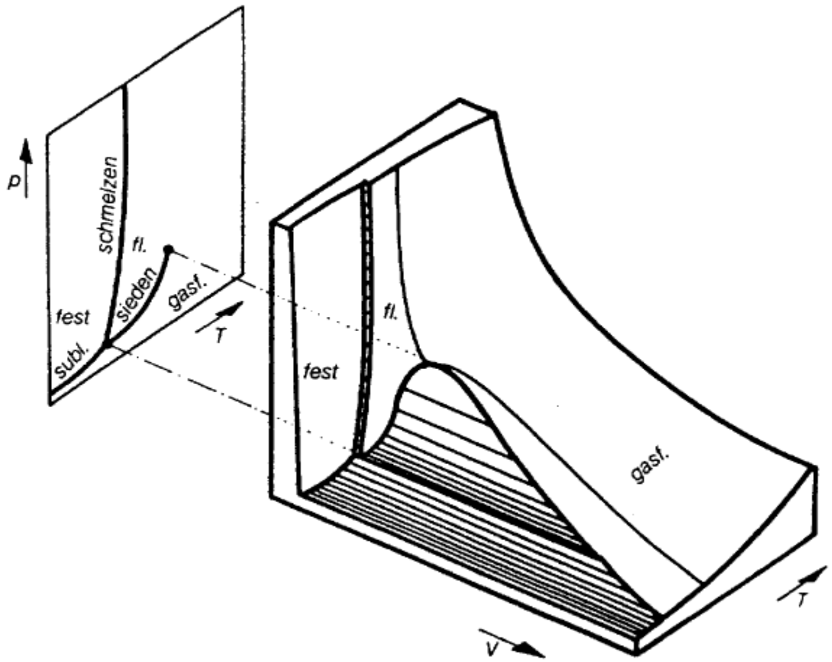


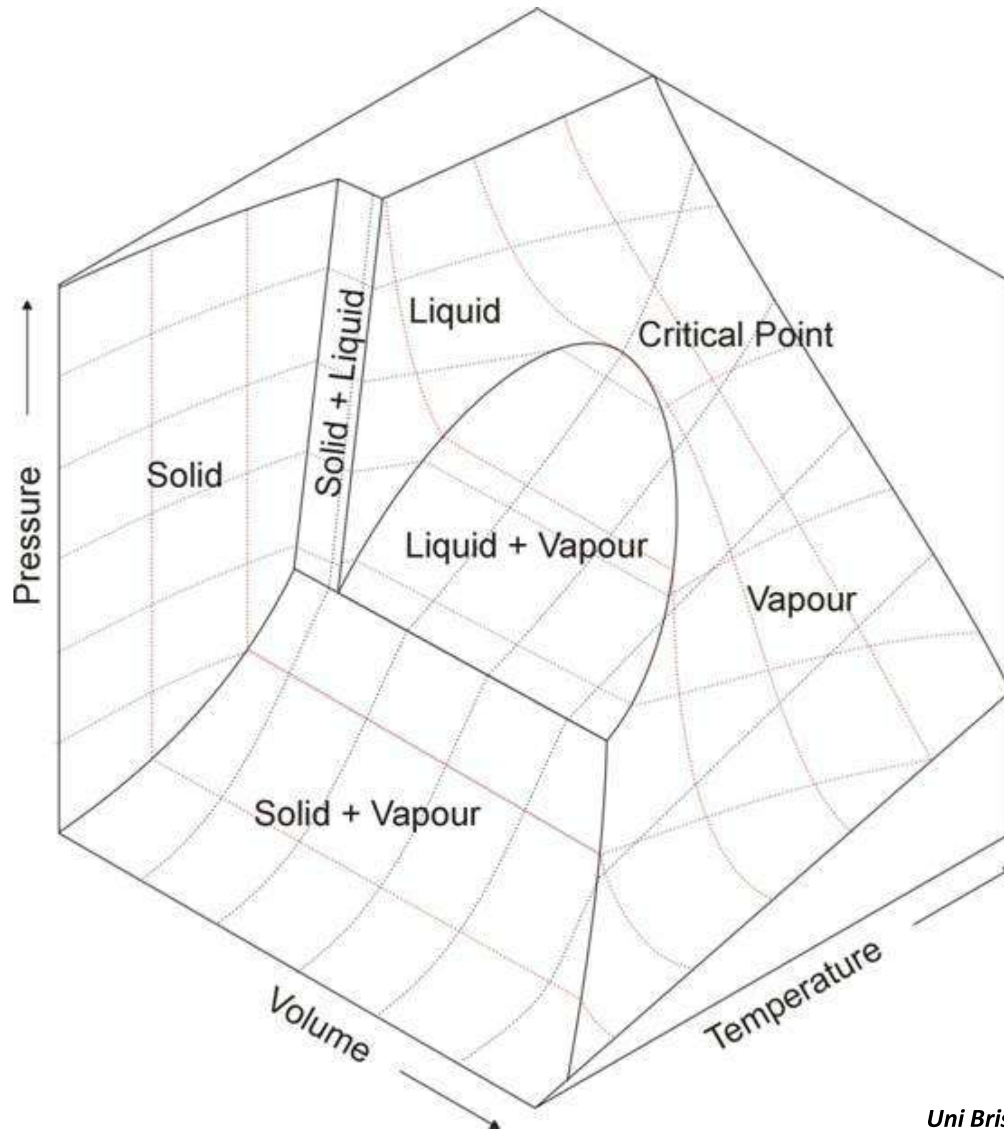
Tipler

PV diagram


2.0
1.5
1.0
0.5
0.0
100
200
300
400
kritischer Punkt
K
T4 = 1.2 Tk
T3 = 1.08 Tk
Tk
Gas
Flüssigkeit
Druck p/p k
Volumen V/V k
Flüssigkeits-Dampfgemisch

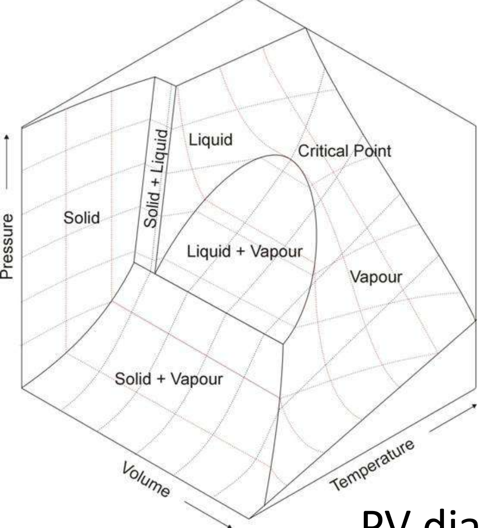
PVT phase diagram

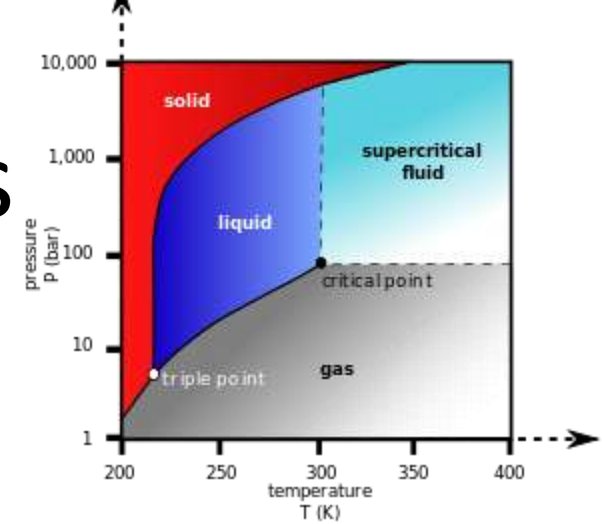




Uni Bristol

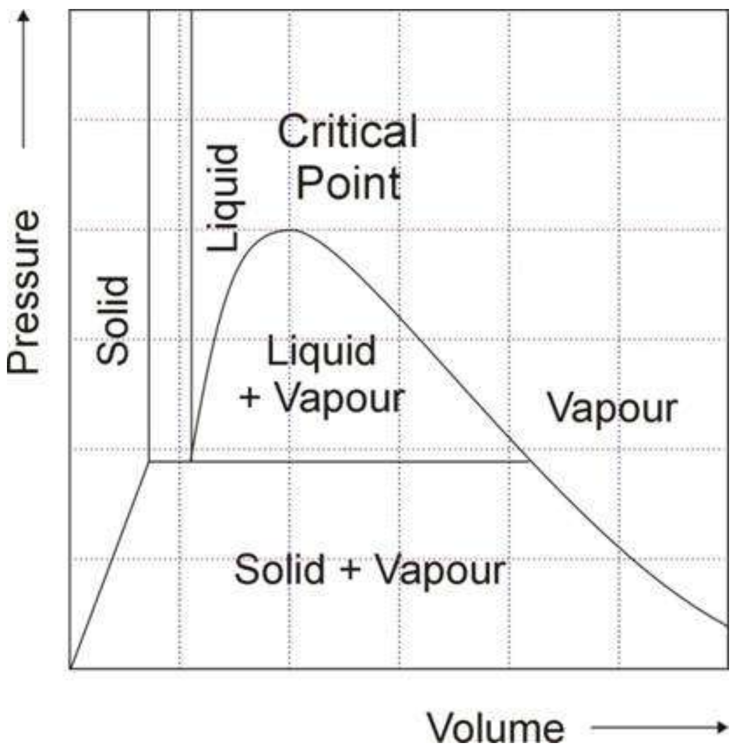
phase diagrams

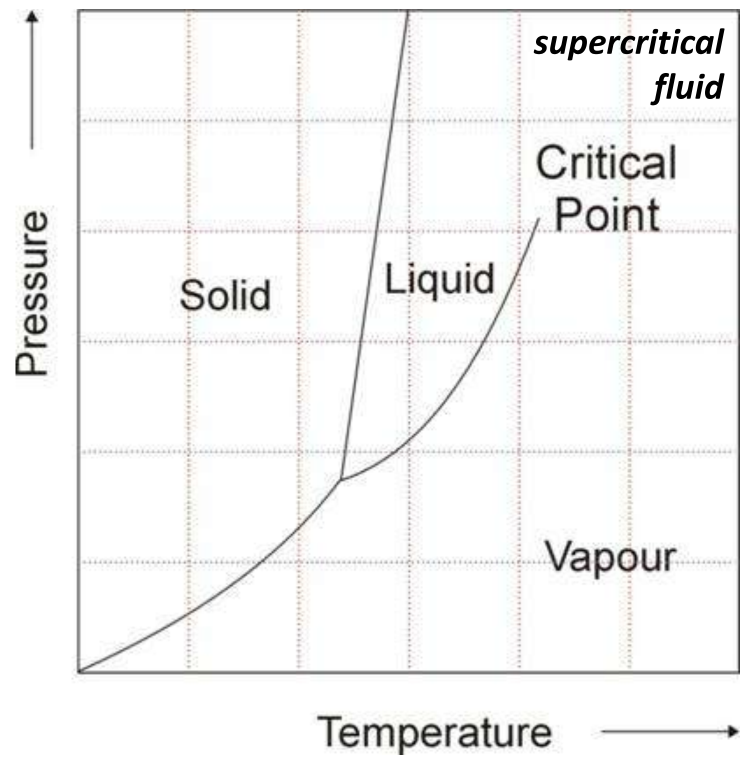




PV diagram

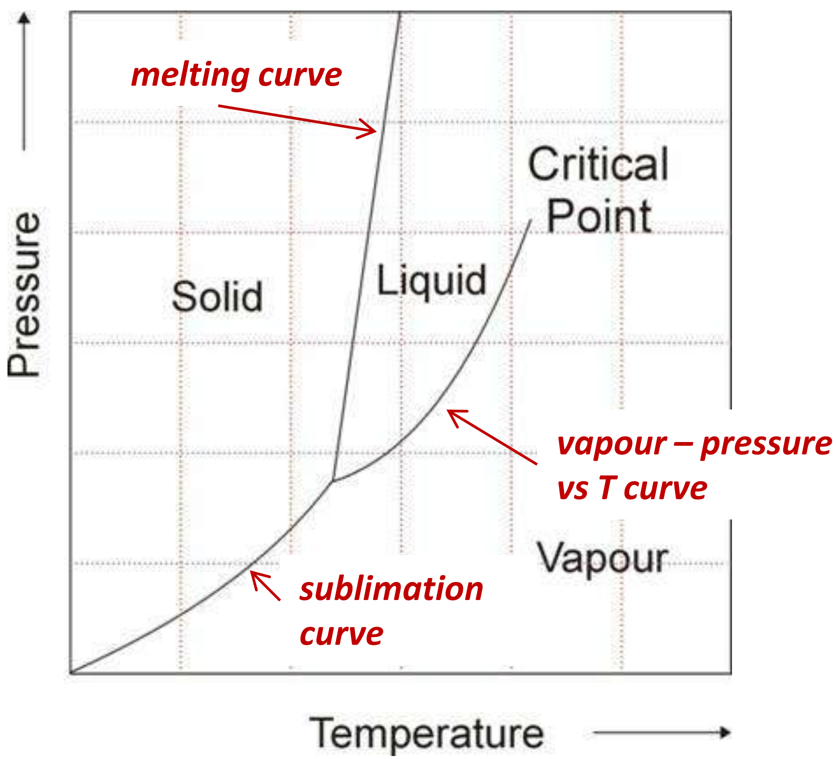
PT diagram



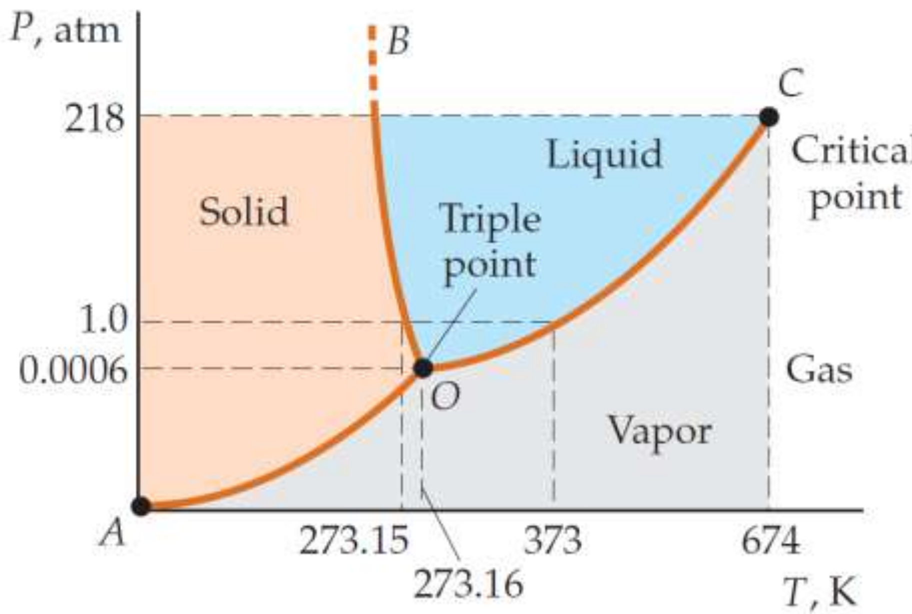


Uni Bristol

PT phase diagrams



water



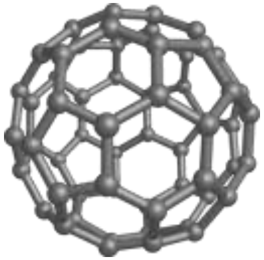
NB: The pressure and temperature scales are not linear but are compressed to show the points of interest.

scale of things: down to the nanometer

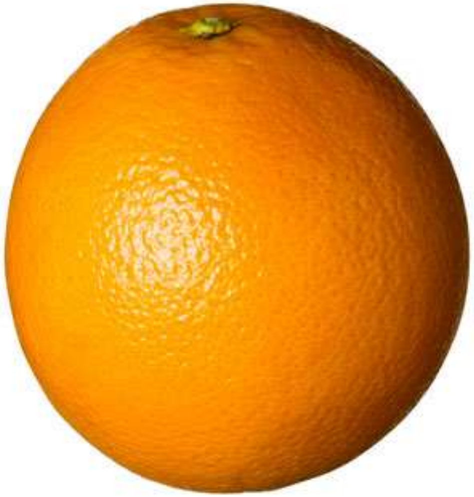
10 cm

x 10^8

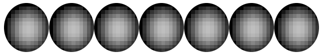
C60



x 10^8



1 nm

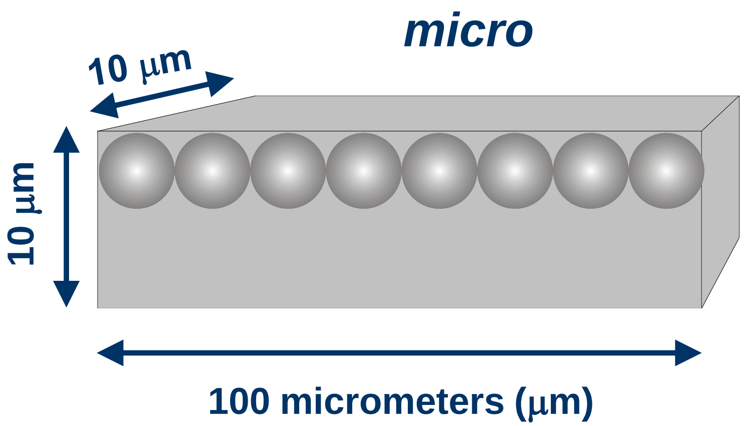


7 Carbon atoms

surface vs bulk

Atome and der Oberfläche oder tief in Festkörper sind nicht "egal"

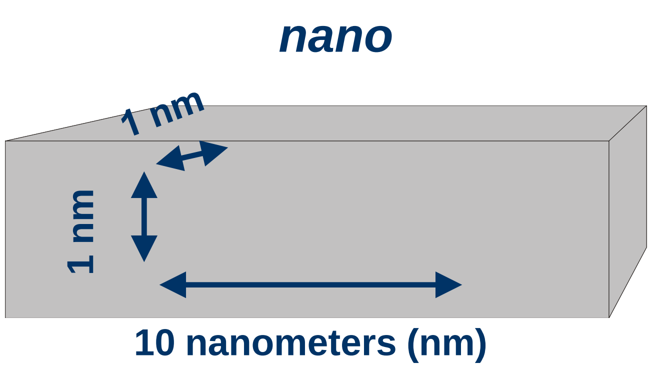
Oberfläche/Volumen



$$R = \frac{nb.\ surface\ atoms}{total\ nb.\ atoms}$$

1 atom ~ (0.1nm)x(0.1nm)x(0.1nm)

R (micro) ≈ 0.004 %



***R (nano)* ≈ 40% !**

⇨ ***important surface effects***

e.g.: lower melting temperature, higher chemical reactivity

example: melting temperature of nanoparticles

Au nanoparticles

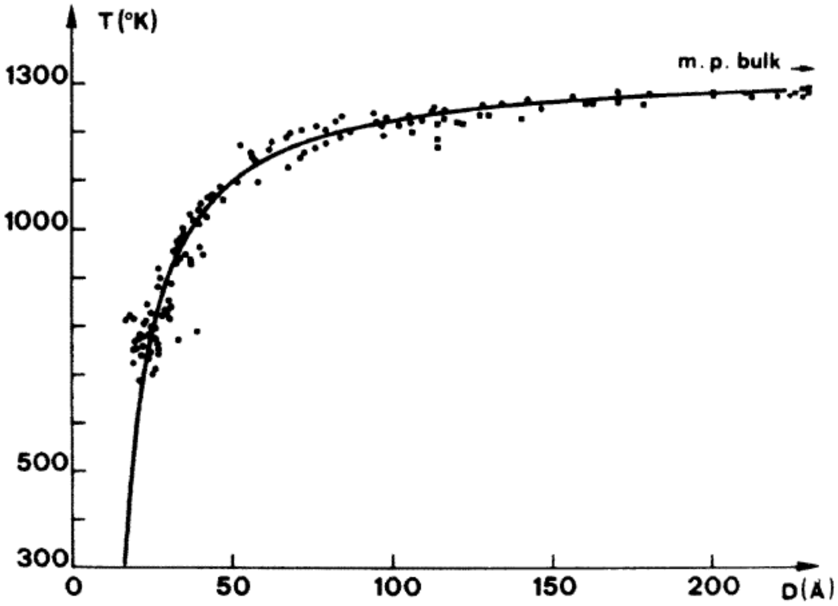
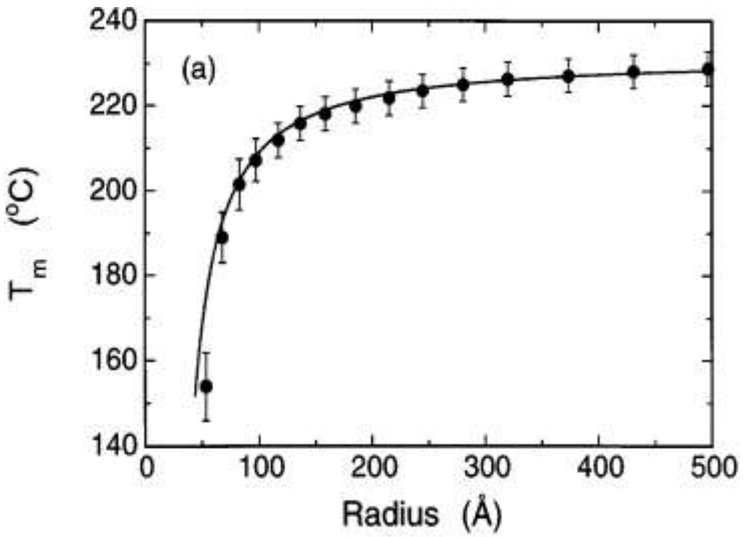


FIG. 5. Experimental and theoretical values of the melting-point temperature of gold particles: circles, present work; squares, Sambles (Ref. 28); the solid line results from a least-squares fit to the second-order relations of the first model, Eq. (13), using all the experimental data of the present work and an estimated value of the Debye-Waller factor.

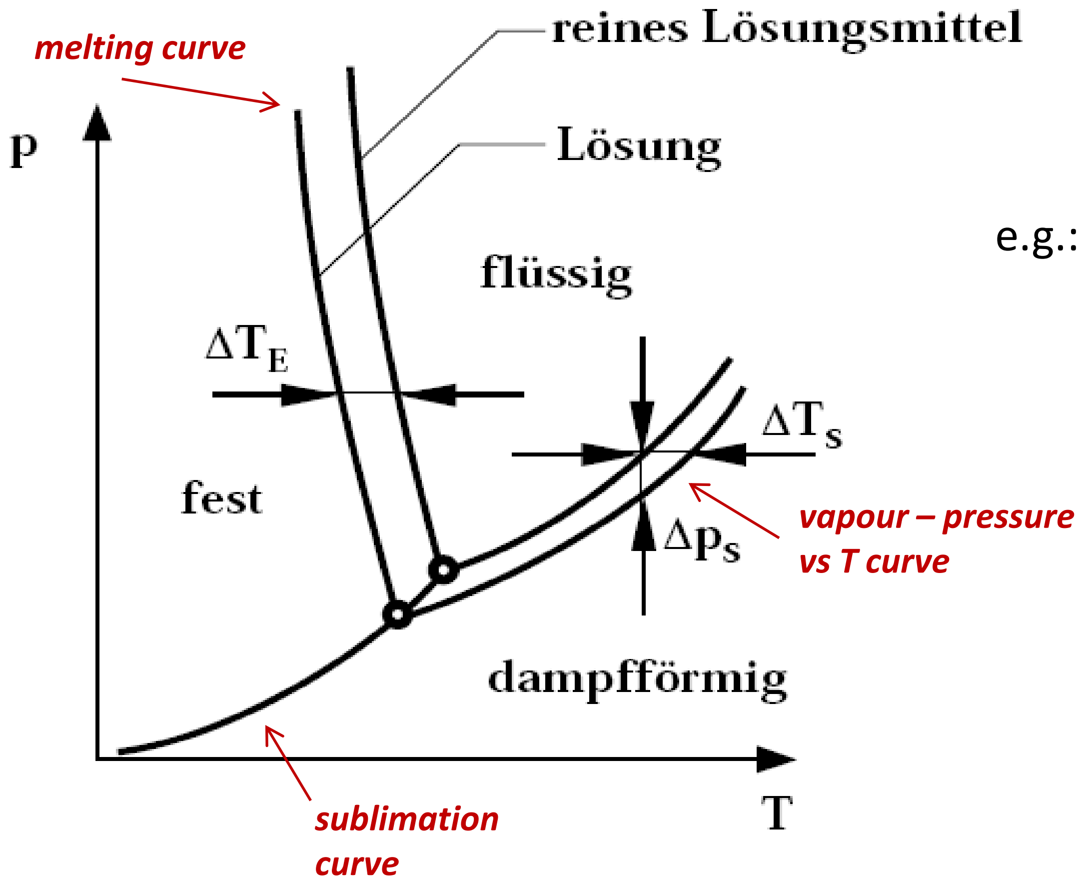
Buffat et al., Phys. A (1976)

Sn nanoparticles



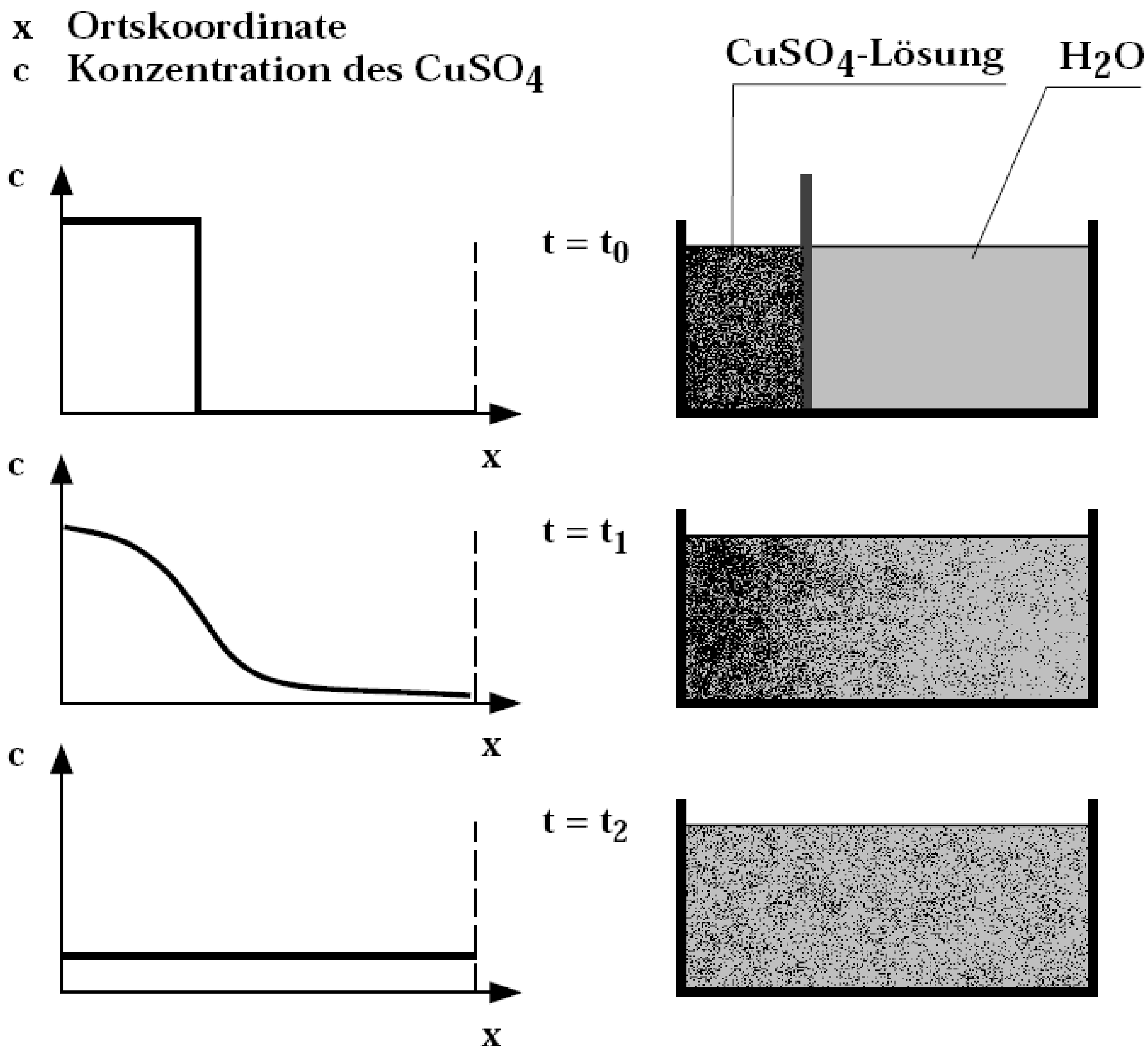
Lai et al., Phys. Rev. Lett. (1996)

phase diagram: mixing substances

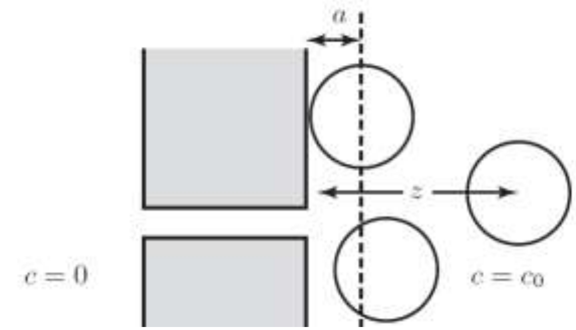


e.g.: salt in water

diffusion

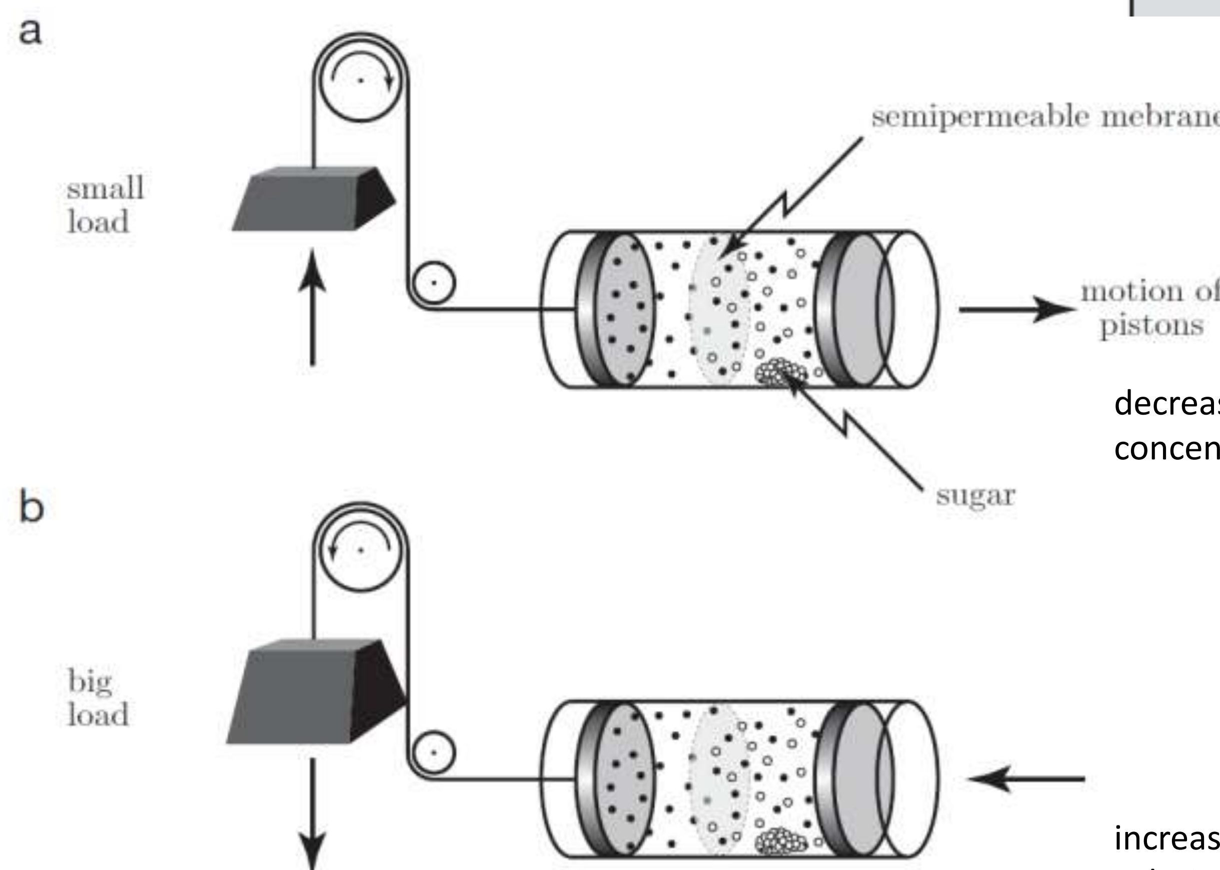

x Ortskoordinate
c Konzentration des $CuSO_4$
$CuSO_4$-Lösung
H_2O
c
x
$t = t_0$
c
x
$t = t_1$
c
x
$t = t_2$

osmosis



osmotic flow

reverse osmosis

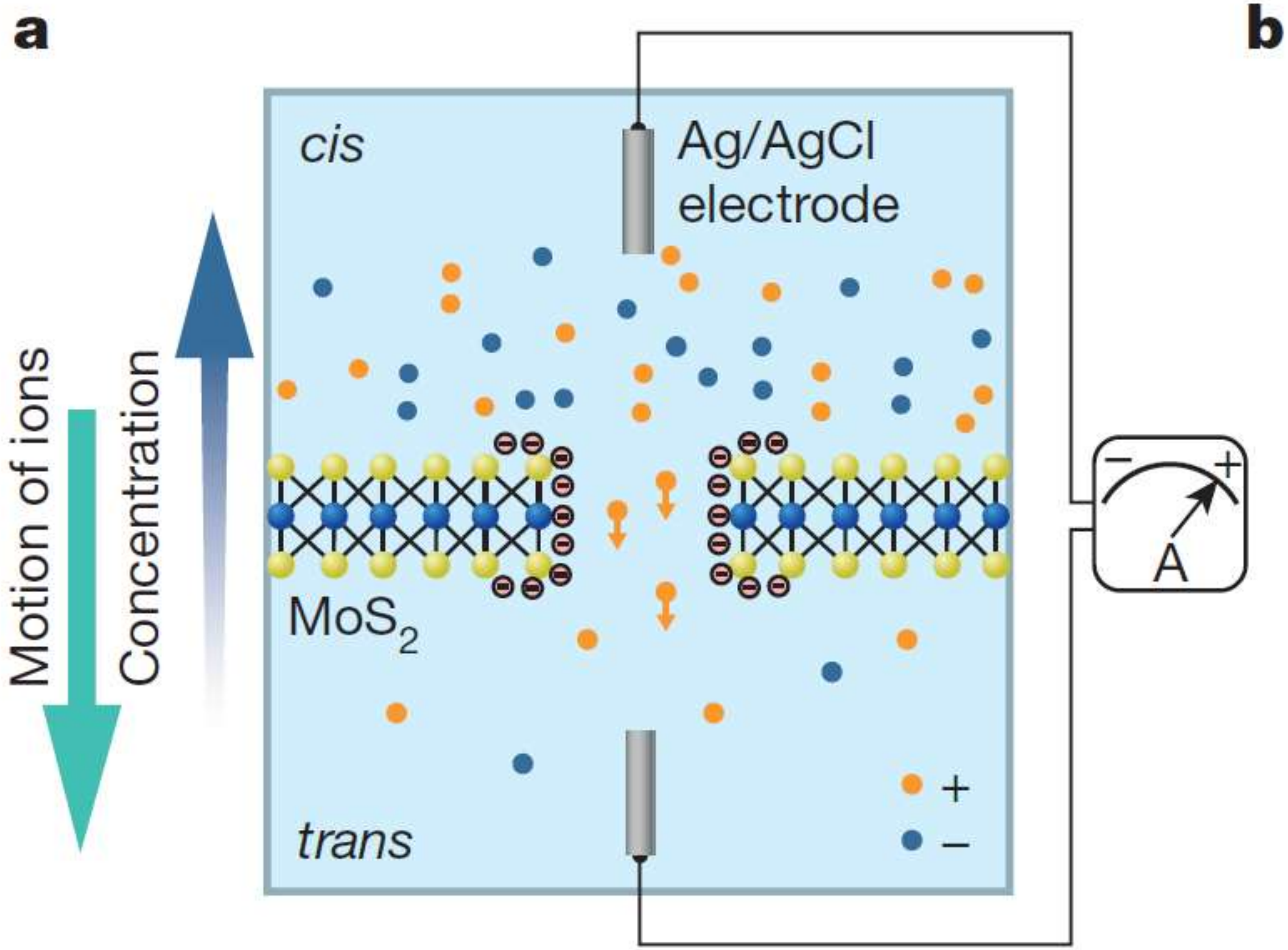


decrease of sugar concentration

increase of sugar solution & heat generation

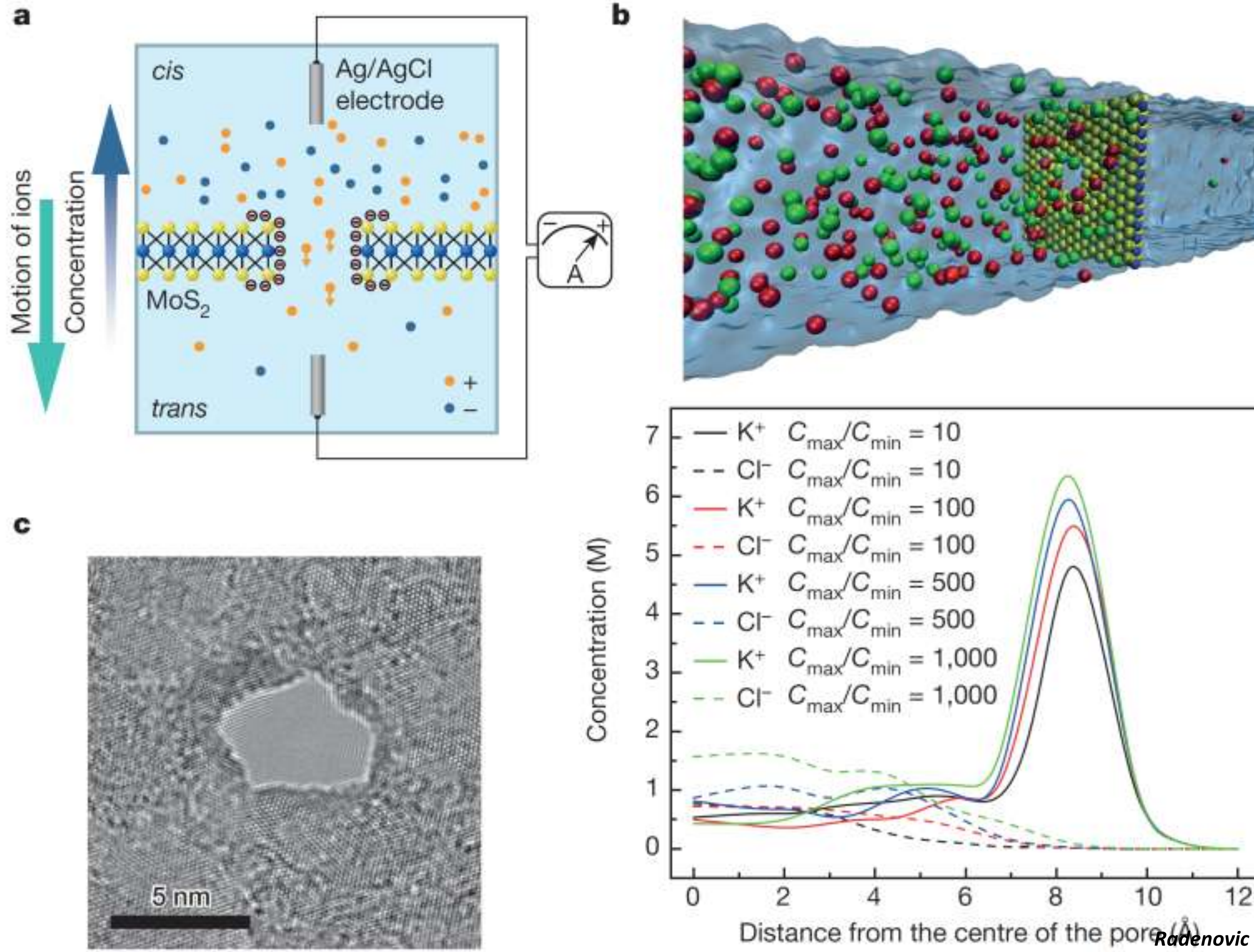
Biological physics, P. Nelson

osmosis: electrical power generation



Radenovic et al., Nature (2016)

osmosis: electrical power generation



Radenovic et al., Nature (2016)

Merry Christmas
and
a happy new year!

Merry Christmas
and
a happy new year!

Is the 2^{nd} law of thermodynamics ("law of increasing entropy") driving the origin and evolution of life ?

see the article by Natalie Wolchover, Scientific American, Jan. 28, 2014