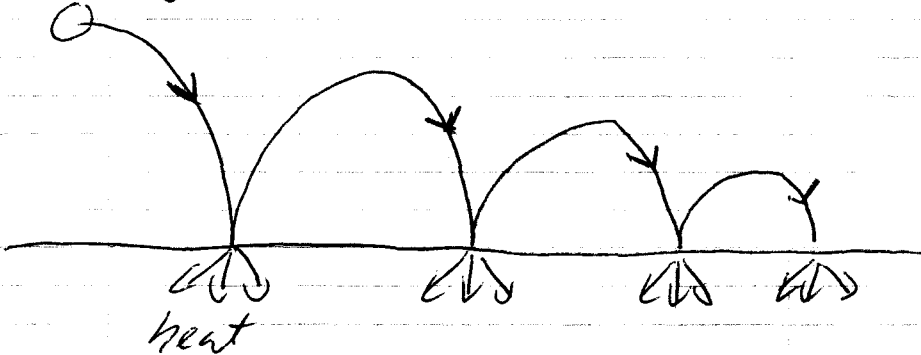# 1.5. Entropy

bouncing ball:

heat

no heat flow back into the ball!

⇒ spontaneous change:

the direction of change that leads to more disorderly
disposal of the total energy of the isolated system!

⇒ less information

⇒ more possible states or configurations

⇒ selfassembly is not possible in an isolated system!

Entropy S

The entropy of an isolated system in the
course of a spontaneous change:
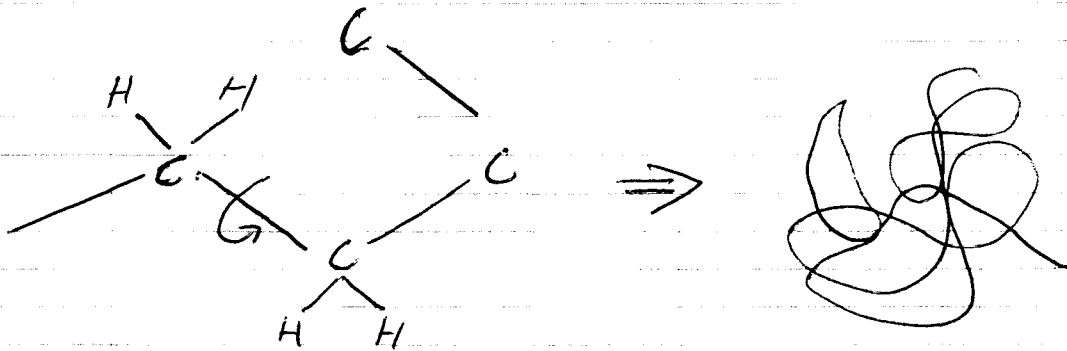
$$\Delta S_{tot} > 0$$

Molecular interpretation

1) The molecules in a system at high temperature are highly disorganized. A small additional transfer of energy will result in a relatively small additional disorder. In contrast, the molecules in a system at low temperature have access to fewer energy states and the same quantity of heat will have a pronounced effect.
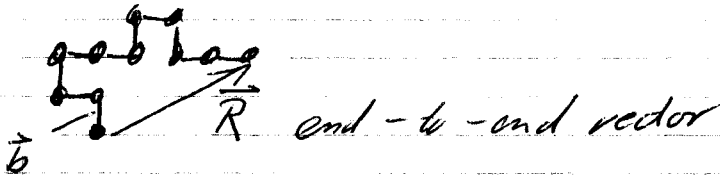
$$\boxed{dq_{rev} = T\, dS}$$

2) Entropy of a flexible polymer chain
(Doi, Introduction to Polymer Physics)

⟹ polymer chain performs a random walk since bending costs no energy!

N monomer = N random steps

$\vec{R}$ end-to-end vector

probability distribution of polymer end being at $\vec{R}$:

$$P(\vec{R}, N) = \frac{1}{Z} \sum_{i=1}^{Z} P(\vec{R} - b_i, N-1)$$

possible directions
for last polymer segment
in 3 dimensions; $Z = 6$

$N \gg 1$, $|\vec{R}| \gg |b|$:

$$P(\vec{R} - \vec{b}_i, N-1) = P(\vec{R}, N) - \frac{\partial P}{\partial N} - \sum \frac{\partial P}{\partial R_\alpha} b_{i\alpha} + \sum \frac{1}{2} \frac{\partial^2 P}{\partial R_\alpha \partial R_\beta} b_{i\alpha} b_{i\beta}$$

$$\frac{1}{Z} \sum_{i=1}^{Z} b_{i\alpha} = 0$$

$$\frac{1}{Z} \sum_{i=1}^{Z} b_{i\alpha} b_{i\beta} = \frac{\delta_{\alpha\beta} b^2}{3}$$

$$\Rightarrow \frac{\partial P}{\partial N} = \frac{b^2}{6} \frac{\partial^2 P}{\partial R^2} \qquad R=0 \text{ for } N=0$$

$$\Rightarrow P(\vec{R}, N) - \left(\frac{3}{2\pi N b^2}\right)^{3/2} e^{-\frac{3\vec{R}^2}{2N b^2}}$$

not normalized

Gaussian distribution
as predicted by
central limit theorem

$\Rightarrow$ number of possibilities to achieve an end-to-end distance $|\vec{R}|$:

$$W(R) \sim \underset{\uparrow}{z^N} R^2 \cdot P(\vec{R}, N) \overset{\text{Kugeloberfläche}}{=} z^N R^2 \left(\frac{3}{2\pi N b^2}\right)^{3/2} e^{-\frac{3N^2}{2Nb^2}}$$

overall number of configurations
the polymer chain can assume

$\Rightarrow$ entropy of the polymer chain with an end-to-end distance R:

$$S_{chain} = -k_B \ln W(R) \Rightarrow \text{thermal energy stored:}$$
$$-k_B T \ln W(R)$$

$\Rightarrow$ total energy of the polymer:

$$A_{chain} = -k_B T \ln W(R) + \text{constant} =$$
$$= \frac{3 k_B t}{2 N b^2} R^2 + \text{constant}$$

$\Rightarrow$ tension pulling on the ends is

$$\boxed{f = -\frac{\partial A_{chain}}{\partial R} = \frac{3 k_0 t}{N B^2} R}$$

$\Rightarrow$ Entropic force!

Entropy of phase transitions:

at the transition temperature (reversible) : $\Delta_{trs} S = \dfrac{\Delta_{trs} H}{T_{trs}}$

freezing, condensing $\Rightarrow$ exothermic $\Rightarrow$ $\Delta_{trs} H < 0$

$\Rightarrow$ $\Delta_{trs} S < 0$

$\Leftrightarrow$ system becomes more

ordered

melting, vaporizing $\Rightarrow$ endothermic $\Rightarrow$ $\Delta_{trs} H > 0$

$\Rightarrow$ $\Delta S > 0$

$\Leftrightarrow$ system becomes
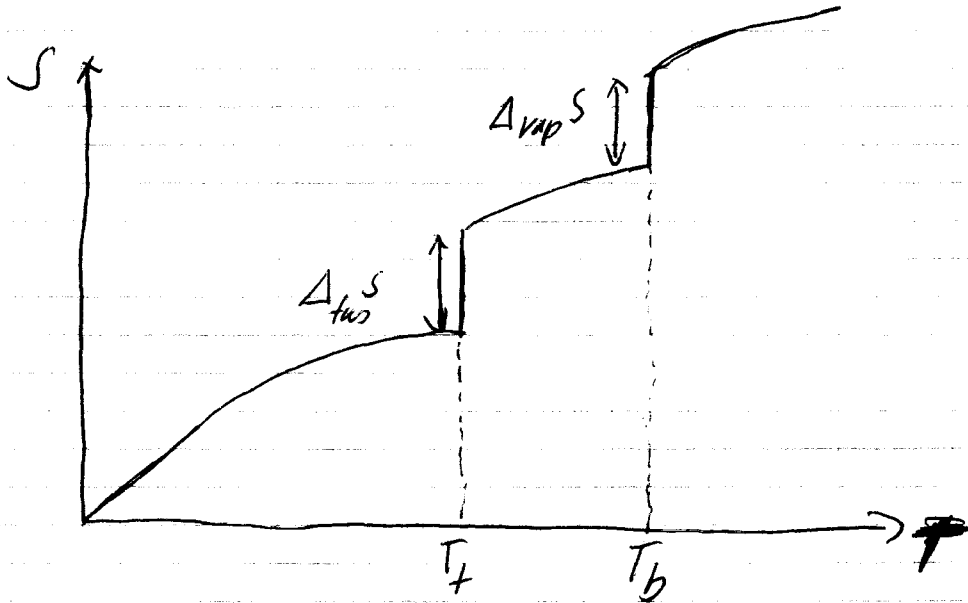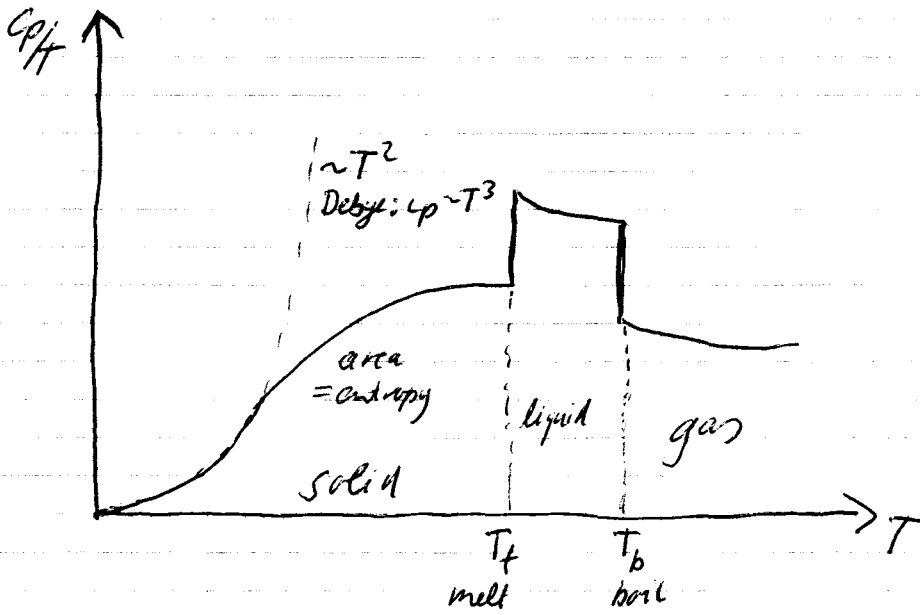
more disordered

$\Rightarrow$ Trouton's rule:

A wide range of liquids give approximately
the same standard entropy of vaporization

$\approx 85 \dfrac{J}{K\,mol}$

$\Leftrightarrow$ comparable amount of disorder is generated
when any liquid evaporates and becomes a gas

(water has a large entropy of vaporization
arising from hydrogen bonding)

Calorimetry and the measurement of entropy:

$\sim T^2$
Debye: $c_p \sim T^3$

area = entropy

solid

liquid

gas

T_f melt

T_b boil

$\Delta_{vap} S$

$\Delta_{fus} S$

T_f

T_b

$$S(T) = \underset{=0}{S_0} + \int_0^{T_f} \frac{c_p(\text{solid})}{T} dT + \frac{\Delta_{fus} H}{T_f} + \int_{T_f}^{T_b} \frac{c_p(\text{liquid})}{T} dT$$

$$+ \frac{\Delta_{vap} H}{T_b} + \int_{T_b}^{T} \frac{c_p(\text{gas})}{T} dT$$

1.6. Cohesive forces:

$V + dV:$ $\quad U' = U + \dfrac{\partial U}{\partial V}\Big|_T \, dV$

$T + dT:$ $\quad U' = U + \dfrac{\partial U}{\partial T}\Big|_V \, dT$

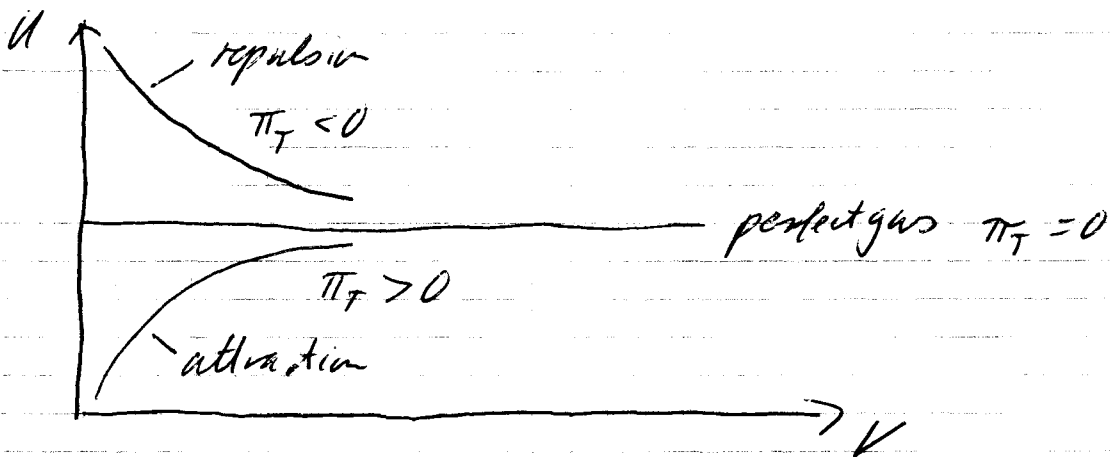$$U' = U + \frac{\partial U}{\partial V}\Big|_T \, dV + \frac{\partial U}{\partial T}\Big|_V \, dT$$

$$dU = \frac{\partial U}{\partial V}\Big|_T \, dV + \frac{\partial U}{\partial T}\Big|_V \, dT$$

$$= \frac{\partial U}{\partial V}\Big|_T \, dV + c_V \, dT$$

$$= \pi_T \quad \text{internal pressure}$$

$$dU = \pi_T \, dV + c_V \, dT$$

U — repulsiv — $\pi_T < 0$

perfect gas $\pi_T = 0$
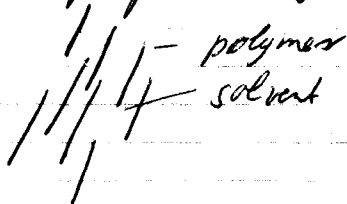
$\pi_T > 0$ — attraction

V

2. Physical Transformations
of pure substances

2.1. Phase Diagrams

A phase of a substance is a form of matter
that is uniform throughout in chemical composition
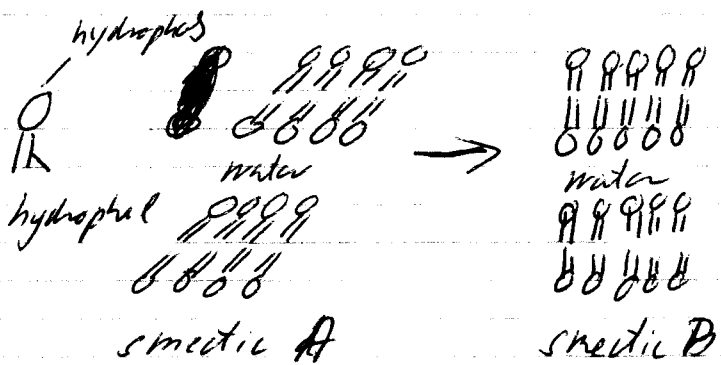and physical state (various solid phases, liquid, gas)

BUT: Liquid Crystals

- rigid polymer (e.g. microtubule)

polymer
solvent

$\Rightarrow$ nematic phase

- lipids $\Rightarrow$ cell membranes

hydrophob

hydrophil

water

smectic A

water

smectic B

- chiral polymer (e.g. DNA)

cholesteric phase

$\Rightarrow$ Landau's definition of a phase:

    phases can be distinguished by
    their degree of order
    $\Rightarrow$ introduces concept of order parameter!

    (Note: gas and liquid the same phase?)

<u>phase transitions</u>:   spontaneous change of
                one phase into another phase

    transitions can be infinitely slow
        $\Rightarrow$ metastable states $\Rightarrow$ glasses

    • sand :

        perfect : hexagonal order
        real : jamming prevents perfect orders
            $\Rightarrow$ much less neighbors

    • diamonds are metastable $\Rightarrow$ ground state ~~graphit~~
                          graphite!

vapour pressure : pressure where

liquid and vapour are at equilibrium

sublimation vapour pressure : vapour ⟷ solid

boiling point, boiling temperature T_b : free vaporization

throughout the liquid

critical fluid, critical temperature T_c, critical pressure p_c :
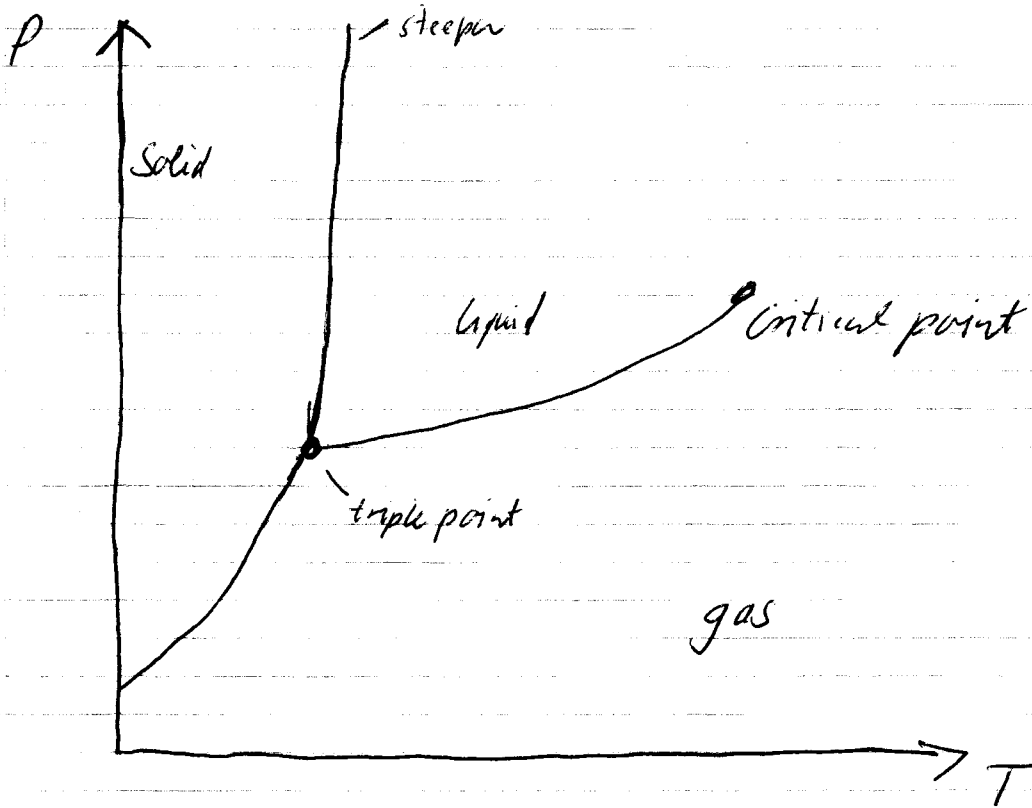
liquid and gas phase are

indistinguishable !

melting = freezing temperature
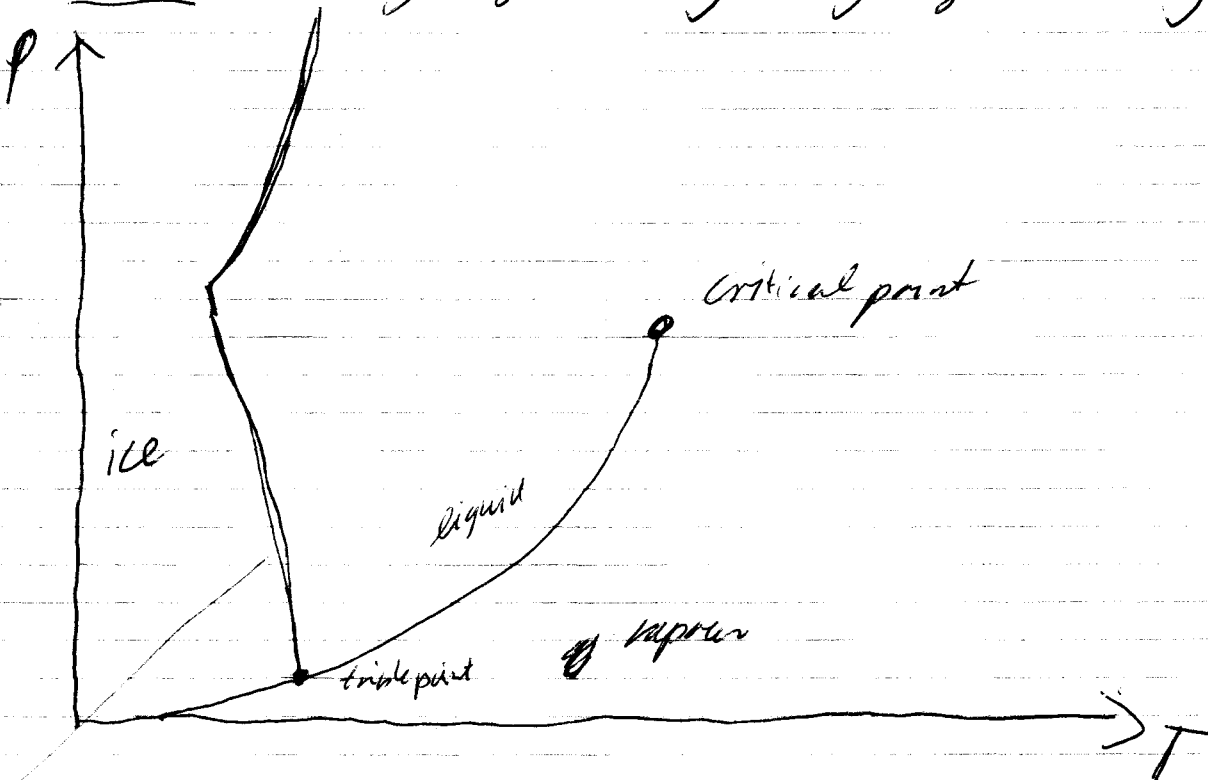
triple point : three phase boundaries meet

typical phase diagrams

1. CO_2 characteristic of most substances

steeper

p

Solid

Liquid   critical point

triple point

gas

T

2. water   hydrogen bonding!

p

ice

critical point

liquid

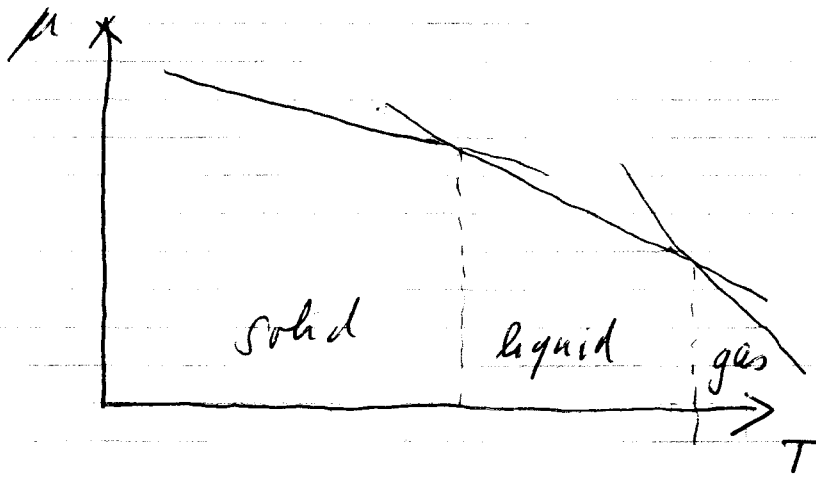triple point   vapour

T

Ice has larger volume than water

• At equilibrium the chemical potential of a substance is the same throughout a sample regardless of how many phases are present

Proof: $\mu_1 > \mu_2$ amount dn transferred from $1 \to 2$

$$\Rightarrow dG = (\mu_2 - \mu_1) dn < 0$$

spontaneous reaction

• $S(gas) > S(fluid) > S(solid)$

$$\left. \frac{\partial \mu}{\partial T} \right|_p = -S$$

• $\left. \frac{\partial \mu}{\partial p} \right|_T = V$ $V(liquid) > V(solid)$

— pressure increases μ more in a liquid than in a solid

— most substances melt at a higher temperature when subject to pressure