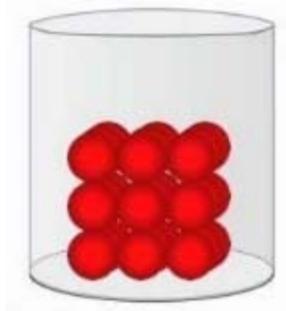


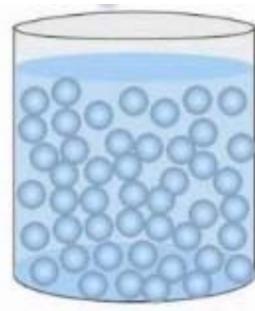
Gases, liquids, liquid crystals and solids

Erika Balog



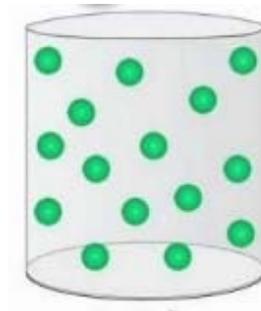
Solid (crystals)

long-range order
rigid
fixed shape
fixed volume



Liquid

short-range order
not rigid
no fixed shape
fixed volume



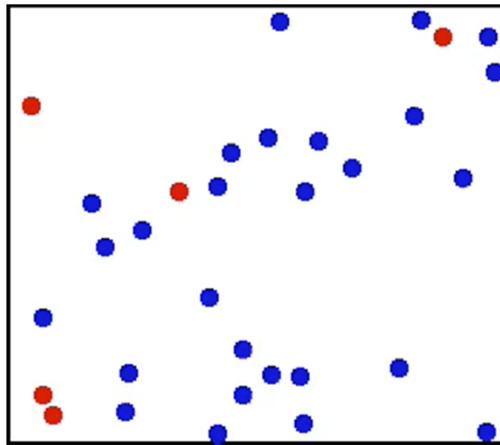
Gas

no order
not rigid
no fixed shape
no fixed volume

Gases

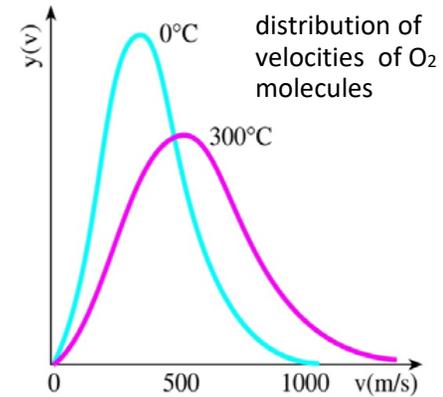
The ideal gas

- Composed of a **large** number (Avogadro number) of particles with identical masses.
- Particles are **point-like**, their volume is **negligible**.
- There is **no interaction** between the particles.
- They collide **elastically** with each other and with the wall of the container (sum of energies is constant).
- Particle motion follows the laws of classical (Newtonian) mechanics.



The ideal gas

Maxwell velocity distribution



Average energy of a particle:

Equipartition theorem: in a system of thermal equilibrium ($T=\text{const}$) the total energy is distributed in such a way that an average of $\frac{1}{2} k_B T$ energy corresponds to each degree of freedom.

- translational motion: 3 degrees of freedom:

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

Upon increasing temperature:

- the average of the absolute value of molecular velocities increases
- the width of the distribution increases

Internal energy of a system containing N particles:

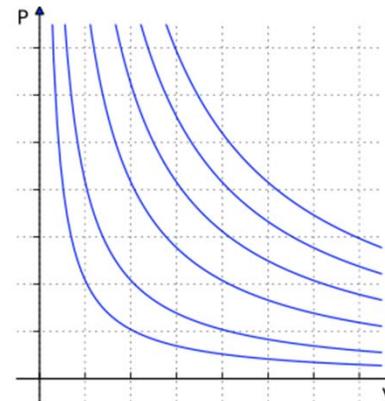
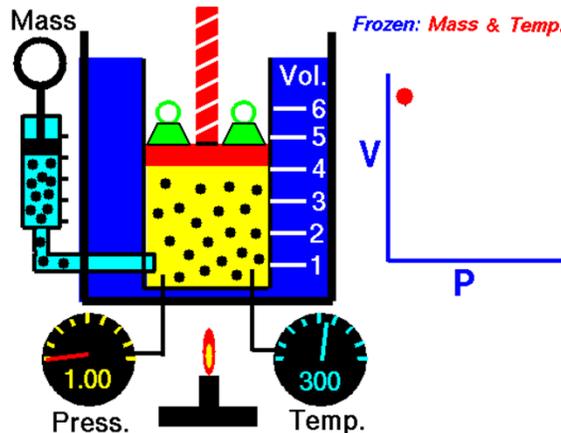
$$E_{\text{internal}} = \frac{3}{2} N k_B T$$

Universal gas law (state equation) - relationship between the parameters characterizing the state of the gas (pressure, volume, temperature and number of particles):

$$pV = Nk_B T$$

- P = pressure (Pa)
- V = volume (m^3)
- R = gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$)
- T = absolute temperature (K)
- N = number of particles
- k_B = Boltzmann's constant

Pressure-volume isotherms:



The real gas

- Particles are **not point-like**, their volume (b) is not negligible.

Consequence: the volume available for motion is:

$$V - Nb$$

N = particle number

with no interaction between the particles, the pressure would be:

$$p = \frac{Nk_B T}{V - Nb}$$

$$(pV = Nk_B T)$$

- **Interactions** (a) arise between the particles.

Consequence: pressure becomes reduced

$$p = \frac{Nk_B T}{V - Nb} - an^2$$

n = number of particles in unit volume (N/V)

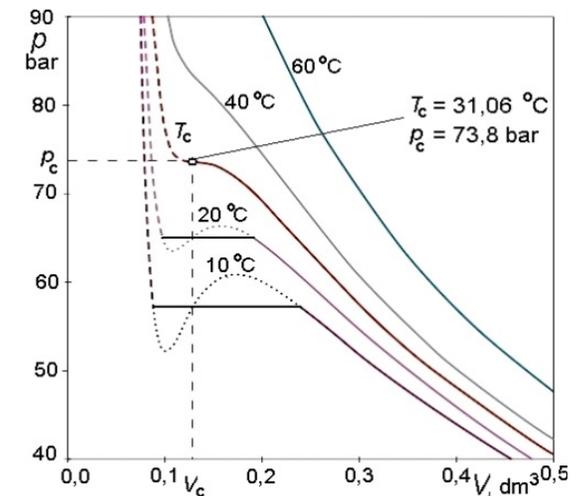
- Van der Waals state equation:

$$\left(p + a \frac{N^2}{V^2} \right) (V - Nb) = Nk_B T$$

Van der Waals isotherms:

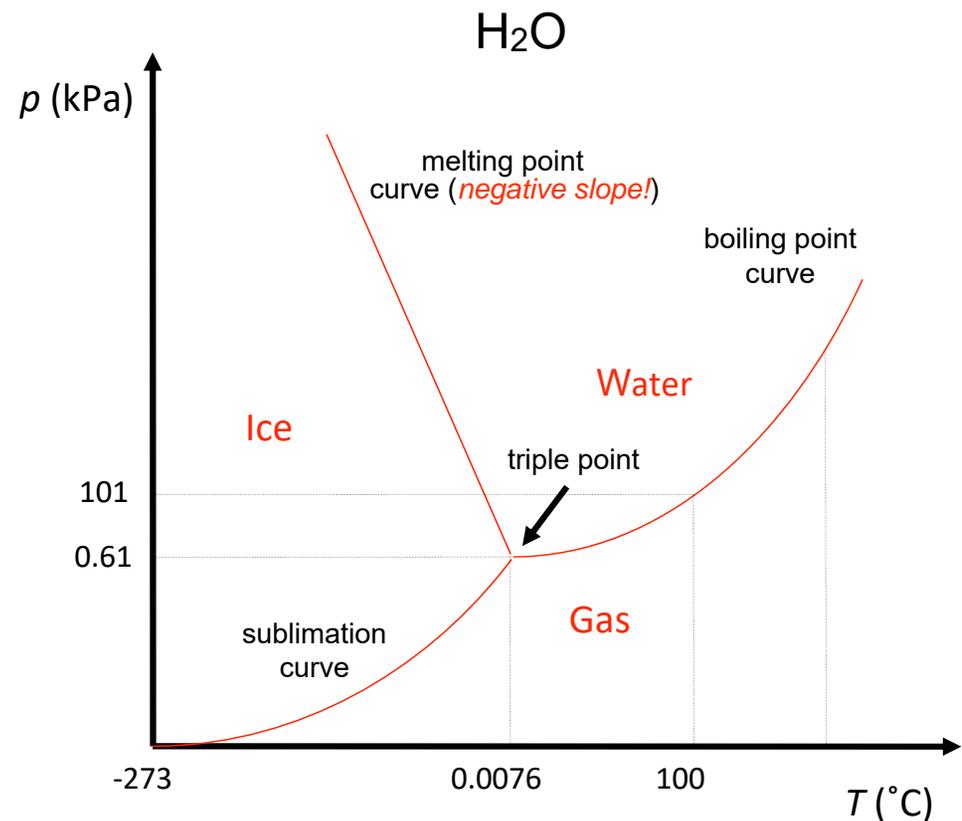
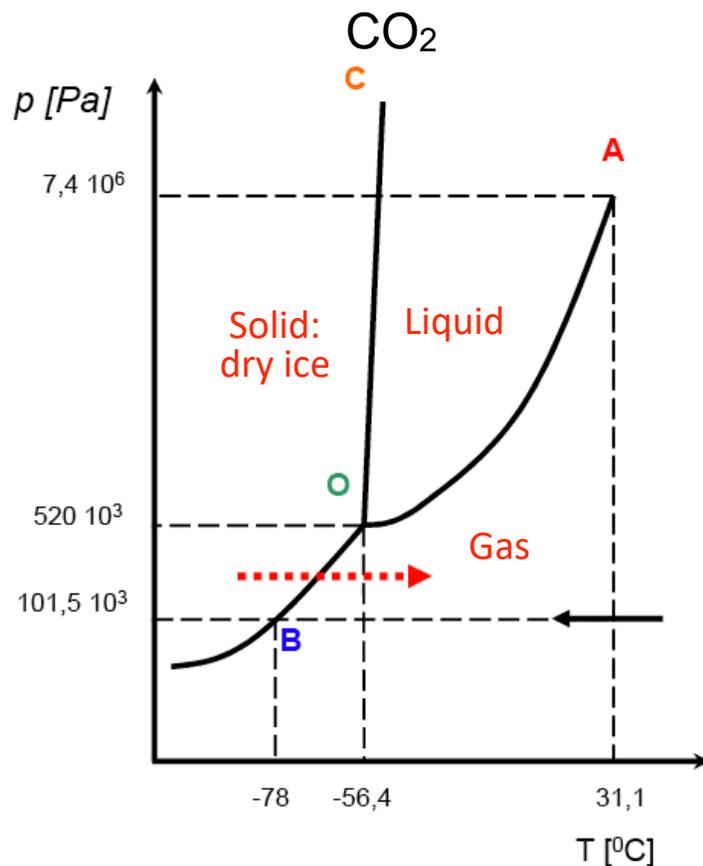
- below a critical temperature (T_c), at a critical pressure (p_c) phase transition occurs (e.g., condensation)

Pressure-volume diagram of CO₂



Phase, phase transition

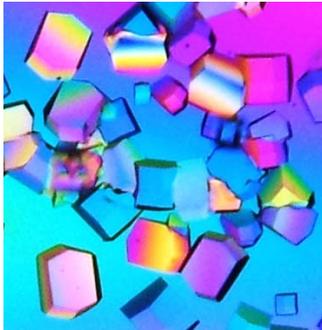
- Phases: regions of the material with identical chemical, but different physical properties
- Phase diagram: plot displaying the nature of phases as a function of thermodynamic variables (pressure, temperature)
- Phase curve: two phases are in equilibrium
- Area between phase curves: a single phase is present
- Intersection of phase curves: triple point



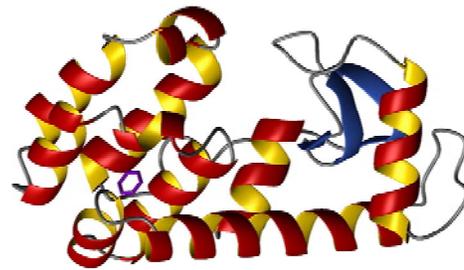
Solids

A. Crystalline materials

- Periodic long-range order
- Lattice - elementary cell (in nature 14 different, “Bravais-lattices”)
- According to the nature of interactions (bonds) of the structural elements:
 - covalent bond: atomic lattice (Si)
 - ionic bond: ionic lattice (NaCl)
 - metallic bond: metal lattice (positive ions)
 - secondary bonds: molecular lattice (molecules eg. lysozyme)



Lysozyme protein crystals in polarized light (anisotropy)



Lysozyme protein molecule

B. Amorphous materials

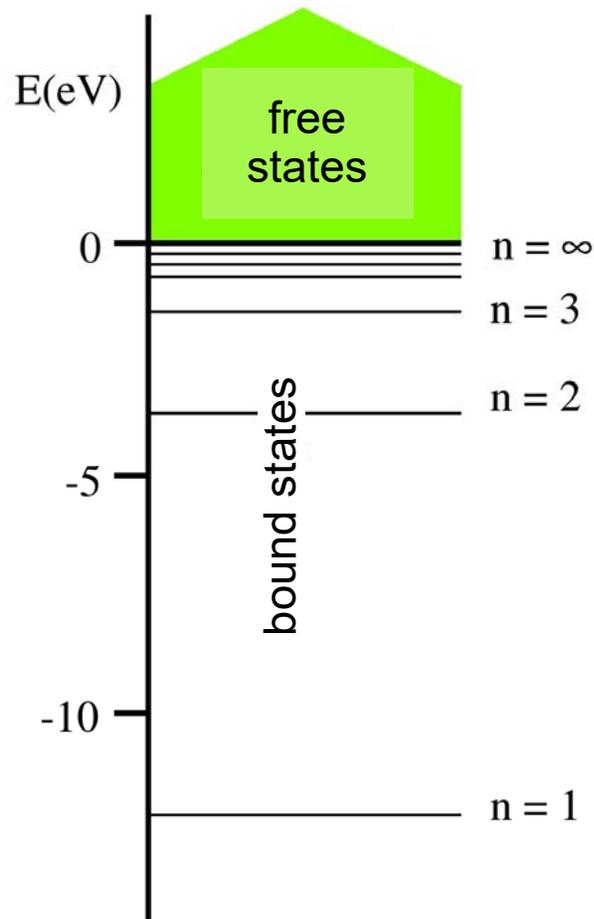
glass-like, viscous “fluids”

Bravais-lattices			
$\beta \neq 90^\circ$ $a \neq c$ 	$\beta \neq 90^\circ$ $a \neq c$ 		
$a \neq b \neq c$ 	$a \neq b \neq c$ 	$a \neq b \neq c$ 	$a \neq b \neq c$
$a \neq c$ 		$a \neq c$ 	
$\alpha \neq 90^\circ$ 			
$\gamma = 120^\circ$ 			

Energy levels in crystals

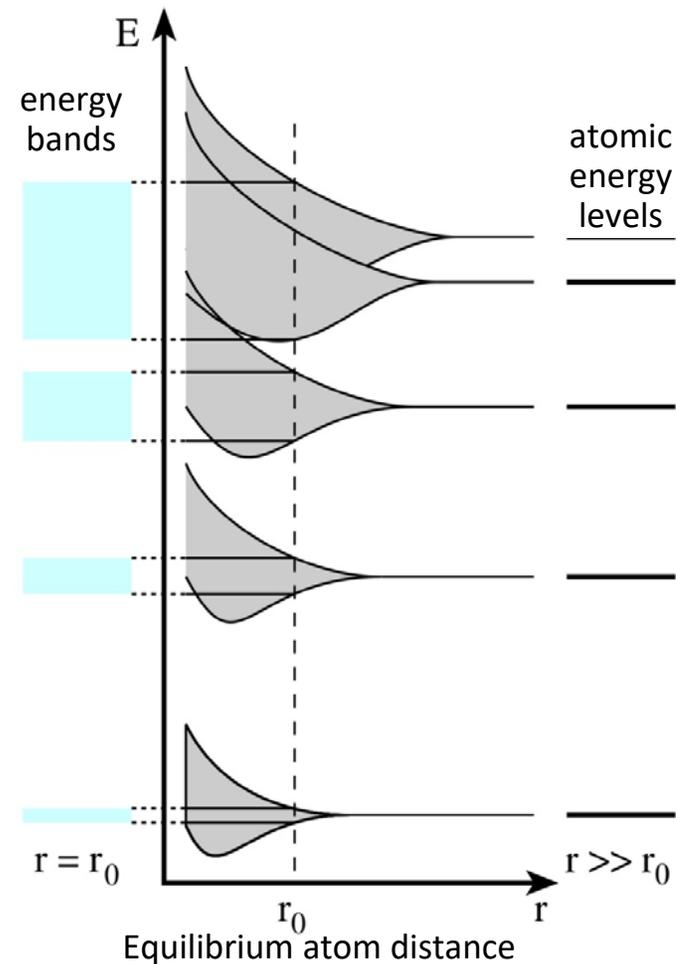
Isolated hydrogen atom

- No interaction with other atoms
- Discrete (quantized) energy levels
- Pauli's principle: there can not be two electrons bound to the same atom with all 4 quantum numbers being identical

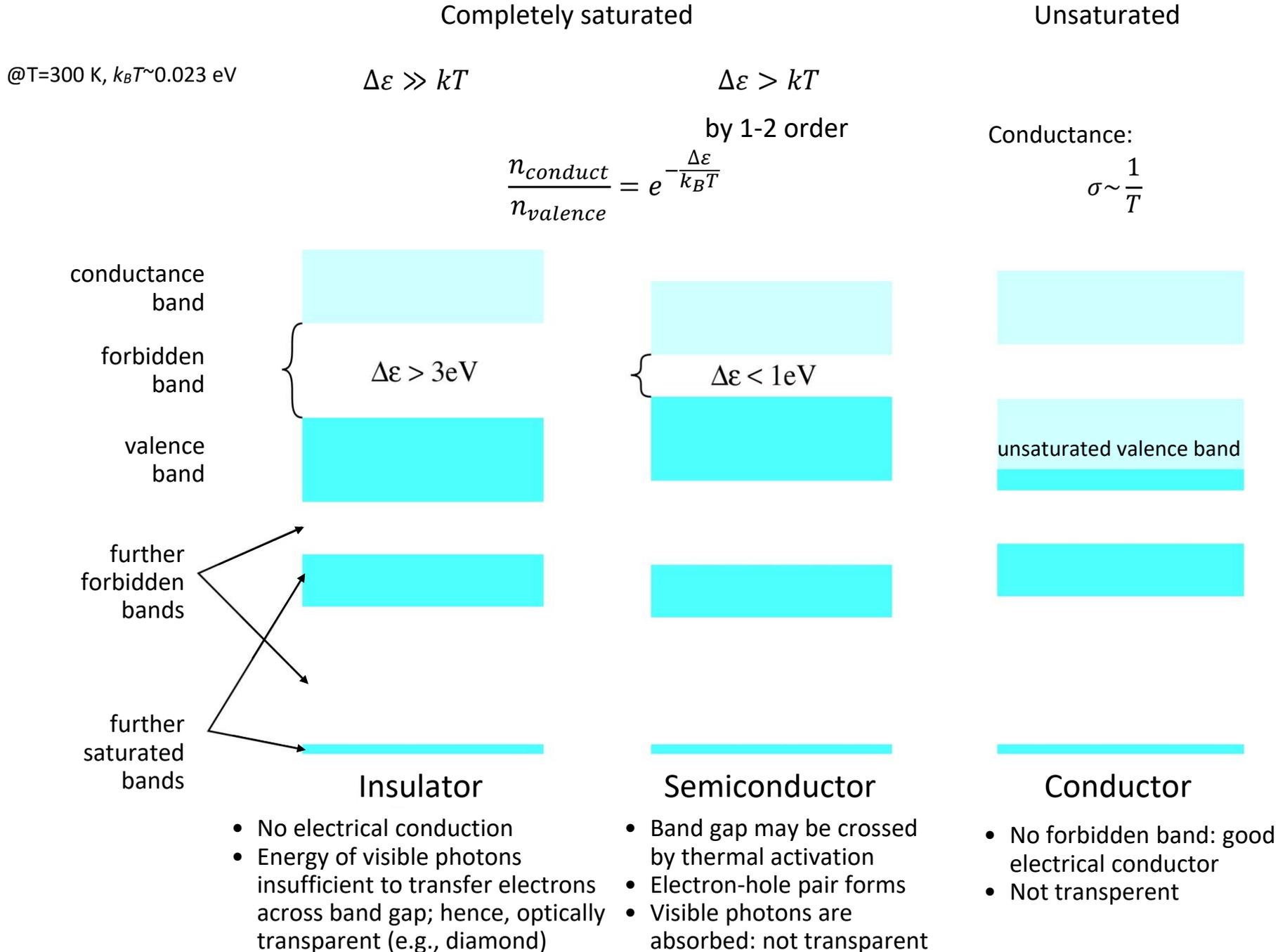


Crystal

- Atoms interact
- consequence of Pauli's principle: in order to avoid identical quantum states the discrete atomic energy levels of interacting atoms split, forming:
- Nearby levels merge into **energy bands**



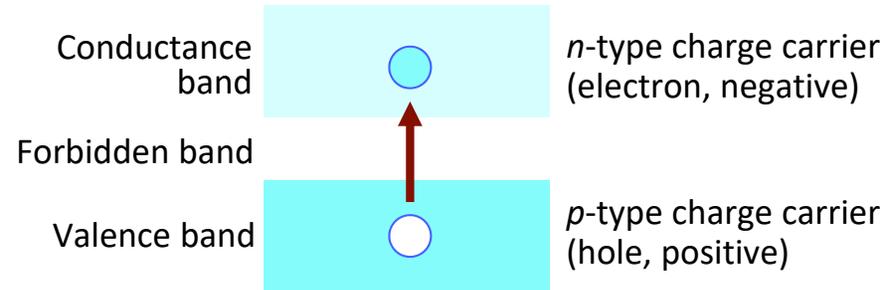
Solids with different band structure



Semiconductors

A. Pure semiconductors

- Two types of charge carriers (n , p):



- Electrical conductance is temperature-dependent:
$$\sigma = konst \cdot e^{-\frac{\Delta\varepsilon}{2k_B T}}$$
- Width of forbidden band ($\Delta\varepsilon$) < 1 eV
- Crossing of forbidden band may be evoked by the absorption of visible light (1.5-3 eV):
- Forbidden band may be crossed by thermal activation
$$hf_{vis} > \Delta\varepsilon$$
- Optically not transparent

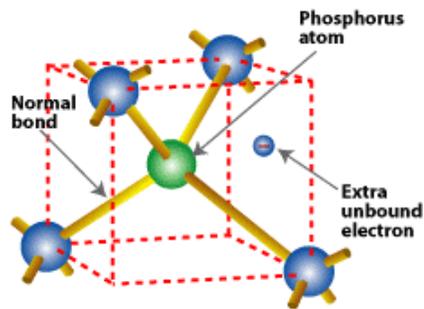
Semiconductors

B. Doped semiconductors

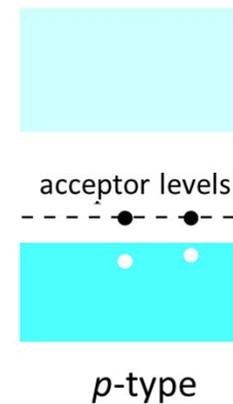
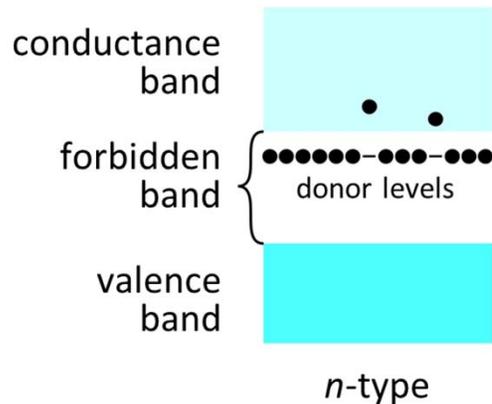
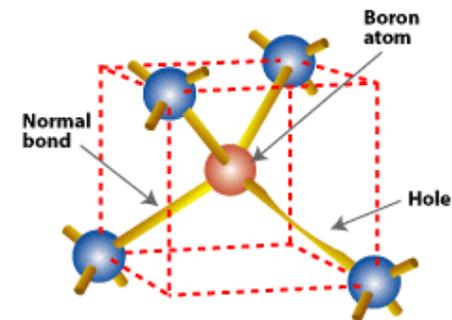
Dopant: - small number of foreign atoms in between the host atoms of the lattice:
 - provides a new e^- state that narrows the forbidden band

$$\frac{N_{host}}{N_{dopant}} \approx 10^6$$

n-type semiconductor (*e*-donor): 5-valence dopant (P, As, Bi) in a 4-valence host (Si, Ge)

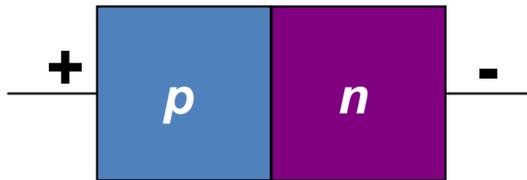


p-type semiconductor (*e*-acceptor): 3-valence dopant (Al, Ga, In, B) in a 4-valence host (Si, Ge)



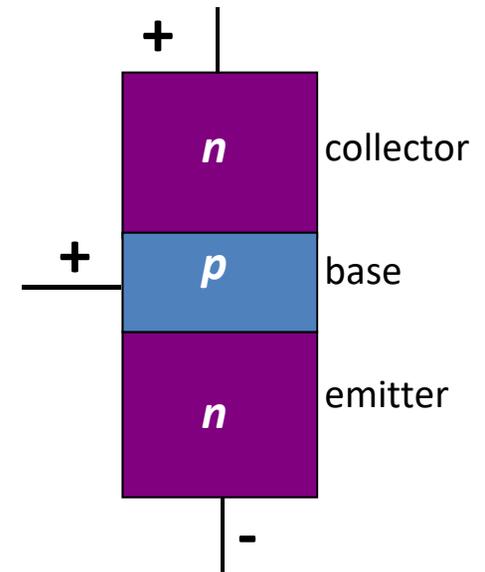
Semiconductor diode and transistor

- microelectronic devices constructed by adjoining doped, *p*- and *n*-type semiconductors



Diode

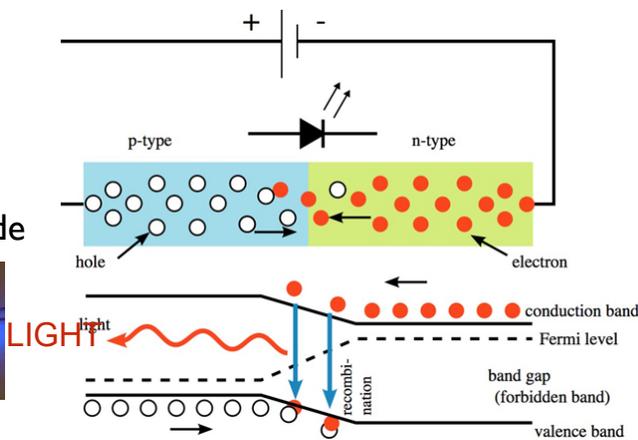
- asymmetric conductance
- electrical voltage → light emission, LED
- illumination → voltage → CCD pixel



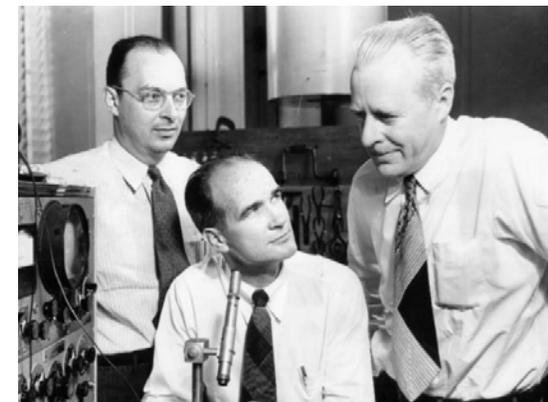
Transistor

- amplifier
- elements of digital memory
- counters, multivibrators

LED:
Light Emitting Diode



Isamu Akasaki, Shuji Nakamura, Hiroshi Amano, Nobel-prize 2014



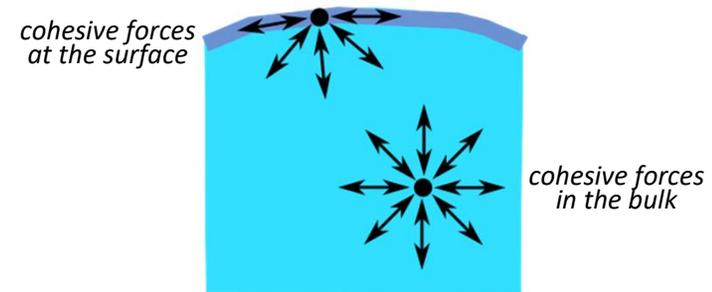
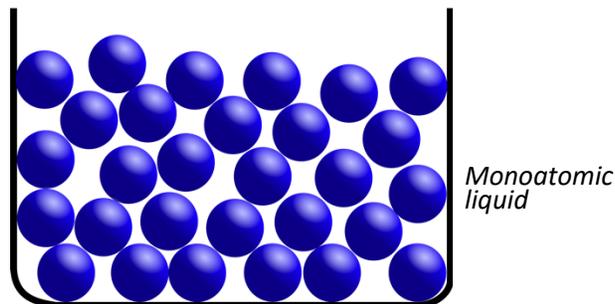
John Bardeen, William Shockley, Walter Brattain, Nobel-prize 1956

Liquids

- Incompressible: retains nearly constant volume independent of pressure.
- Density similar to that of the solid (“condensed matter”).
- Flows: displays fluid behavior (as gases and plasma); conforms to the shape of the container; internal friction (“viscosity”, η) decreases with temperature:

$$\eta \sim e^{-\frac{E}{k_B T}}$$

Viscosity decreases with increase in the relative concentration of vacancies.

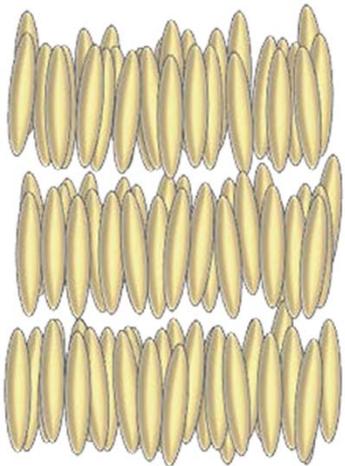


- Microscopically: composed of particles (atoms, molecules) held together by short-range cohesive forces (no long-range order)

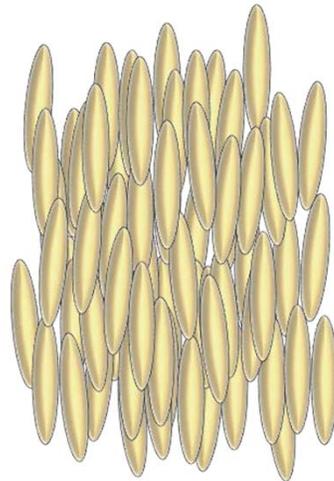
- Imbalance of cohesive forces (between bulk *versus* surface) results in surface tension (tendency to contract into spherical shape)

Liquid crystals

- Display both liquidlike and solidlike behavior: flow (weak intermolecular interactions), long-range order.
- Molecules are not spherically symmetric: calamitic (rod-like), discotic (disc-like)
- Order type: translational, rotational



Smectic phase (orientational and translational order)



Nematic phase (only orientational order, but no translational order)



Cholesteric phase (nematic order in different planes; special case: twisted nematic phase - pitch affects color)



Discotic phase (disc-shaped molecules, translational order)

Liquid crystals

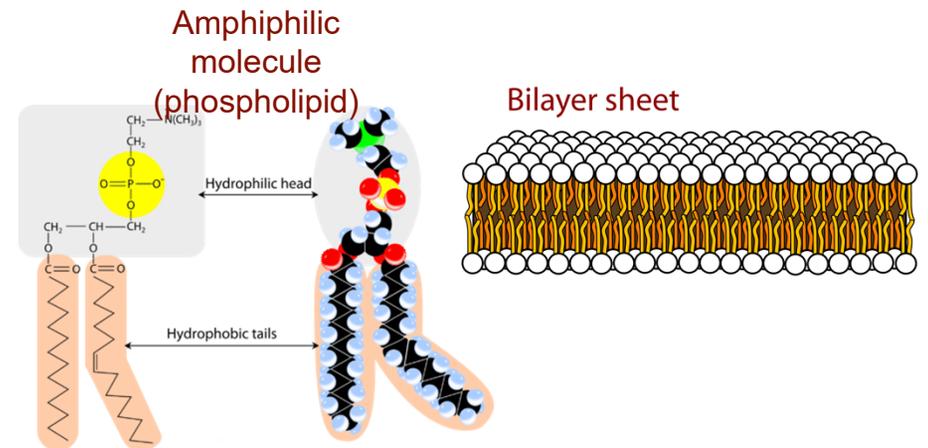
Thermotropic

(order depends on temperature)

- Color changes with temperature (thermo-optical properties) – cholesteric liq. cryst; application: contact thermography
- If molecules are electrical dipoles, polarization, transmittance changes with electrical field (electro-optical properties) – nematic liq. cryst; application: LCD displays, etc.

Lyotropic

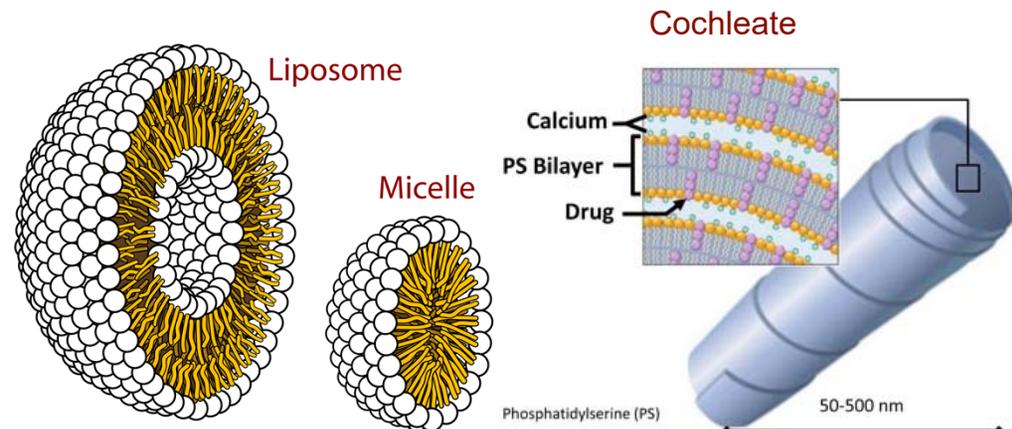
(order depends on concentration of the components)



Contact thermography

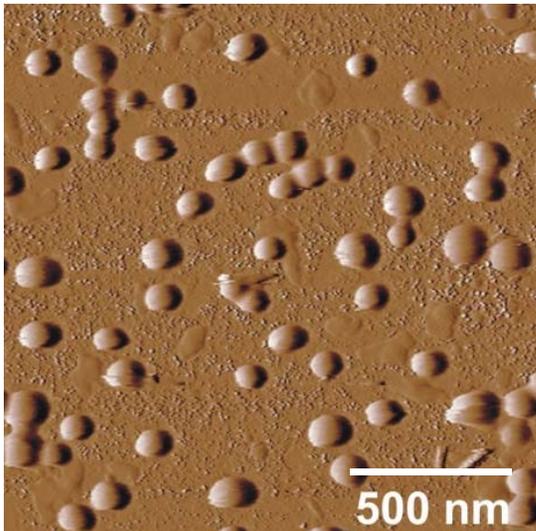


LCD display

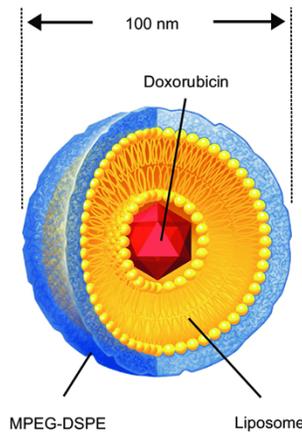


Liposome applications

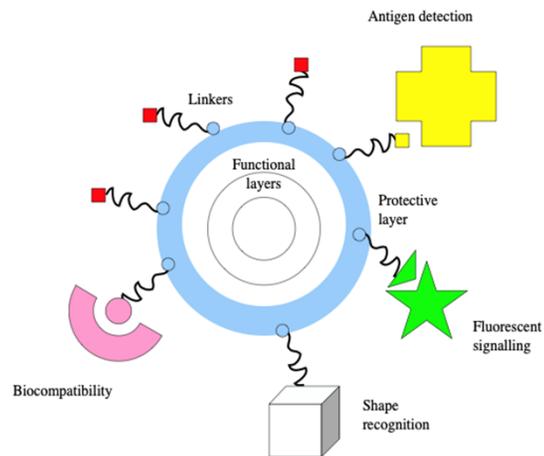
AFM image of liposomes on substrate surface



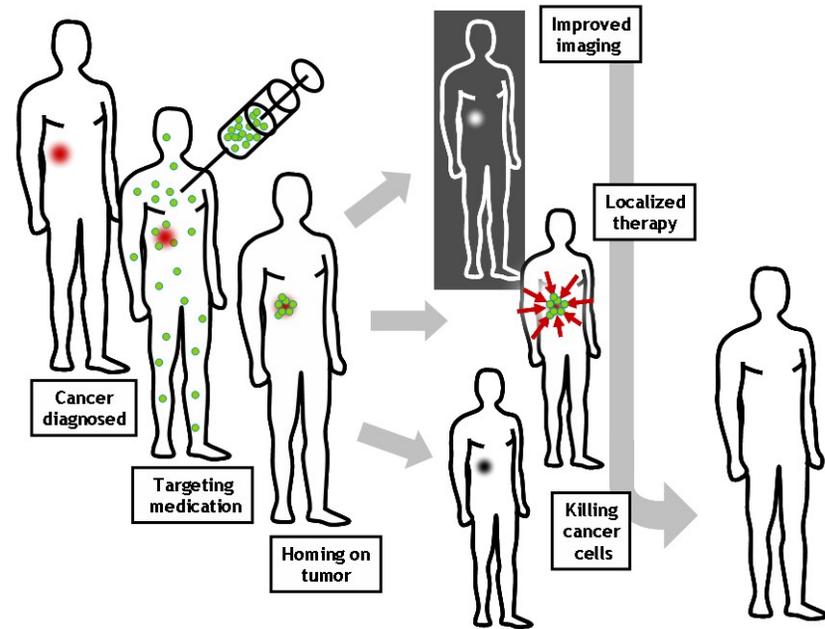
Liposome as carrier of toxic drug



“Intelligent” liposome



Teranostics (therapy + diagnostics)



Feedback

