Principios de analyse 4: Nano/Angstrom-teorico:

Dinamica Molecular (Newton de novo), jogos do azar (Monte Carlo), campos de forca parmetrizados,

modelagem termodinamica

Metodos quanticos- de Schrdinger a Teoria do Funcional da Densidade

Monte Carlo – Do you feel lucky today?


The Casino at Monte Carlo

Ladies and Gentlemen, Place your bets!

A darker (Russian) version:


In statistics and in statistical physics, the Metropolis–Hastings algorithm is a Markov chain Monte Carlo (MCMC) method for obtaining a sequence of random samples from a probability distribution for which direct sampling is difficult. This sequence can be used to approximate the distribution (i.e., to generate a histogram), or to compute an integral (such as an expected value). Metropolis–Hastings and other MCMC algorithms are generally used for sampling from multi-dimensional distributions, especially when the number of dimensions is high.
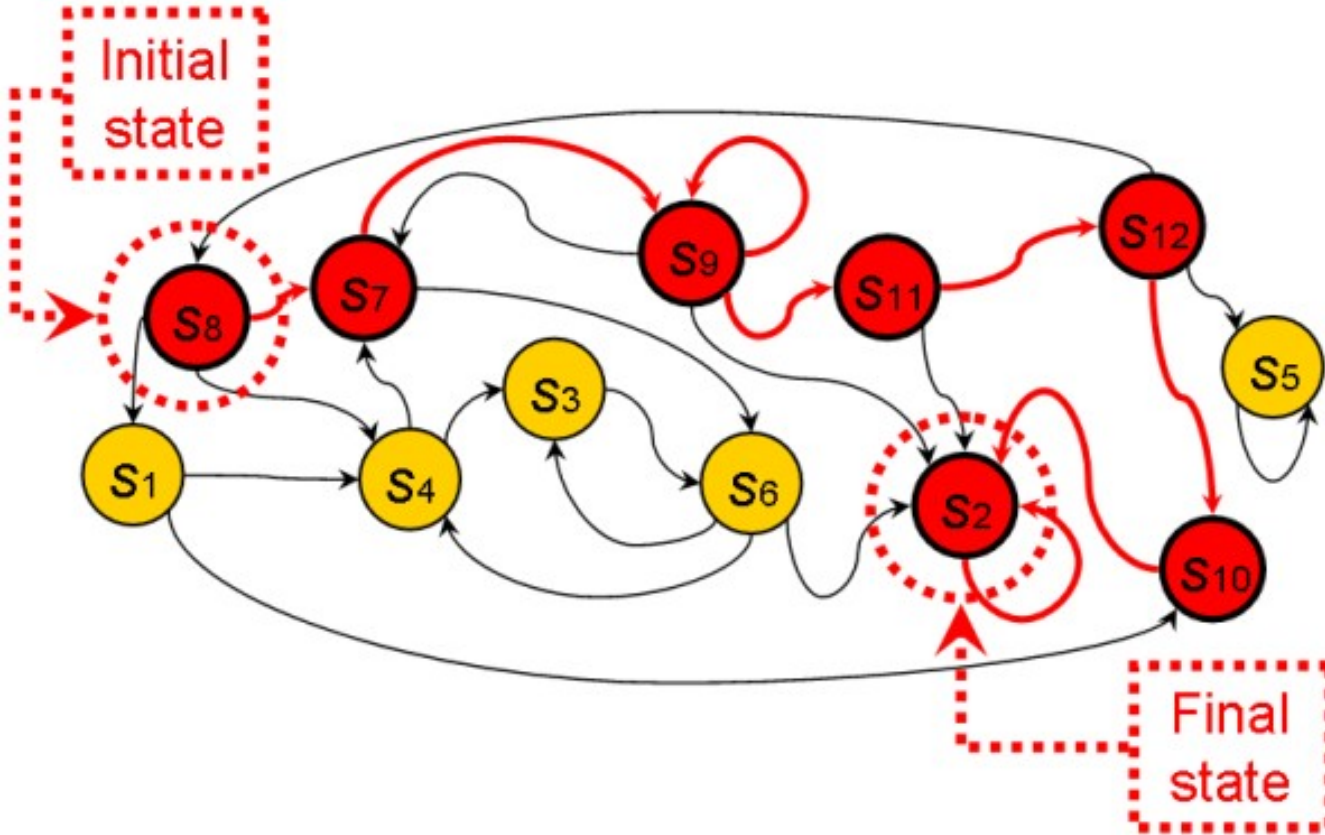
Schematic transition diagram of a Markov chain. Circles denote states and directed arrows indicate possible transitions between states. In this figure, circles and arrows colored in red represent one possible path where the initial state is s8 and the final state is s2. Simple example for MC/MD simulation: each state represents an 'atomic configuration' $\{R_i\}_N$
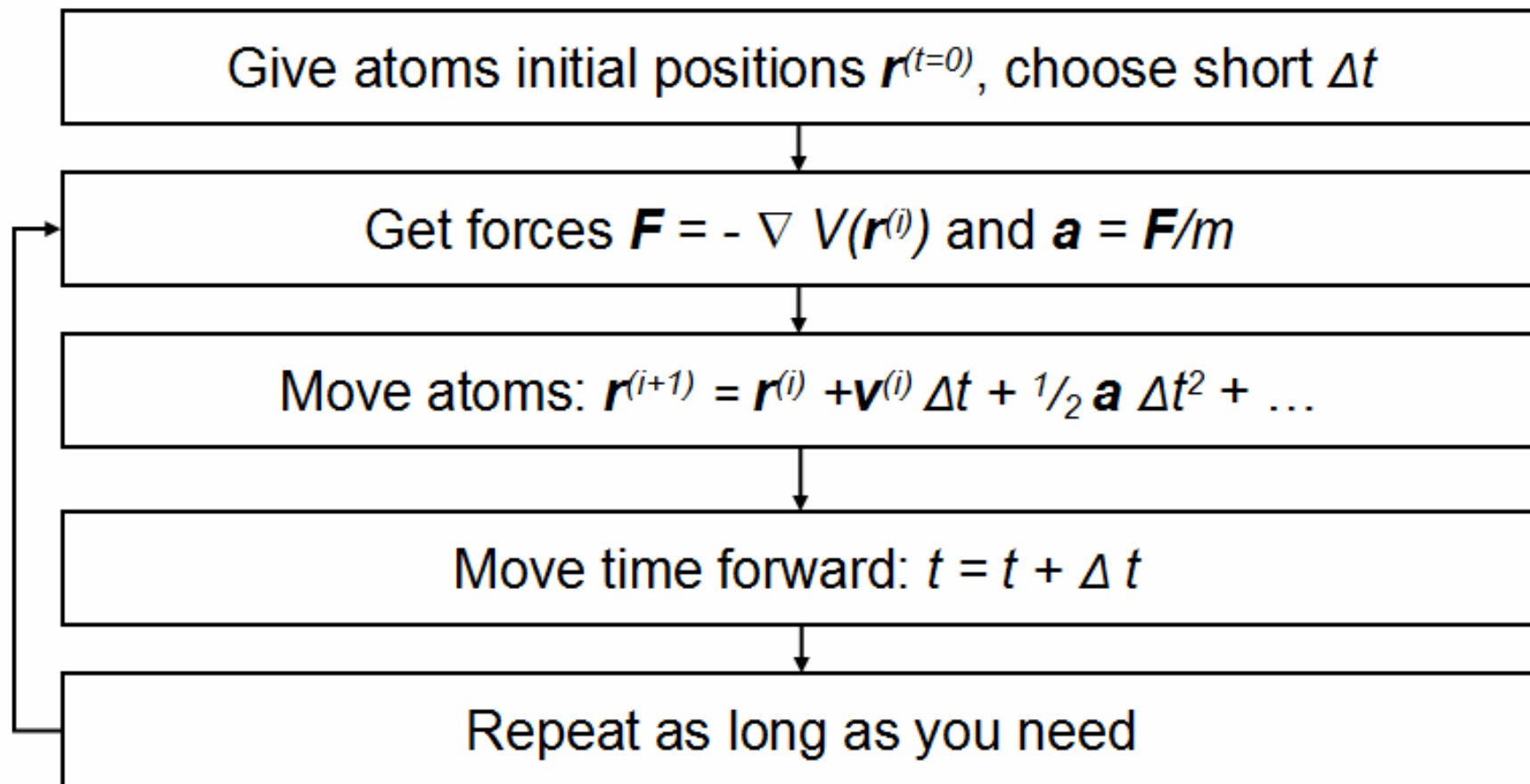
Molecular Dynamics
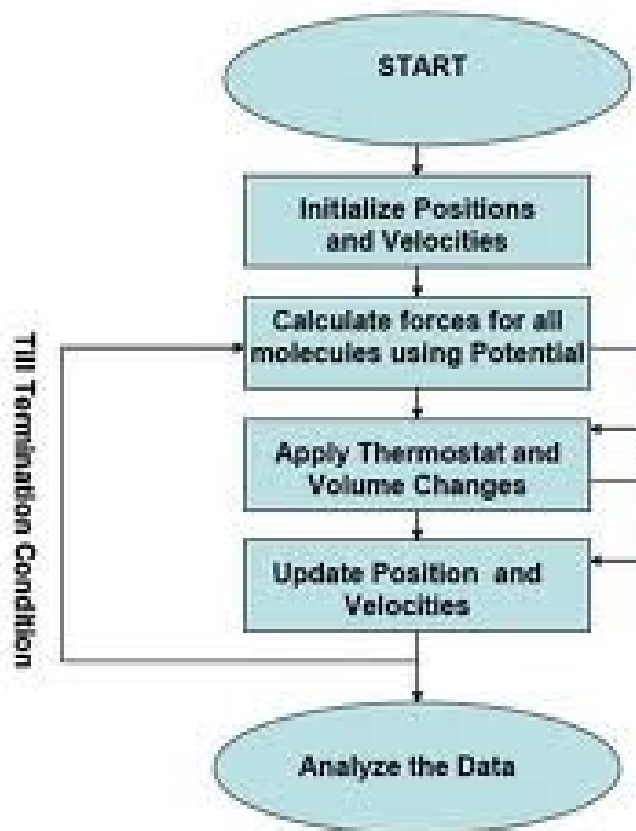
Basic MD workflow
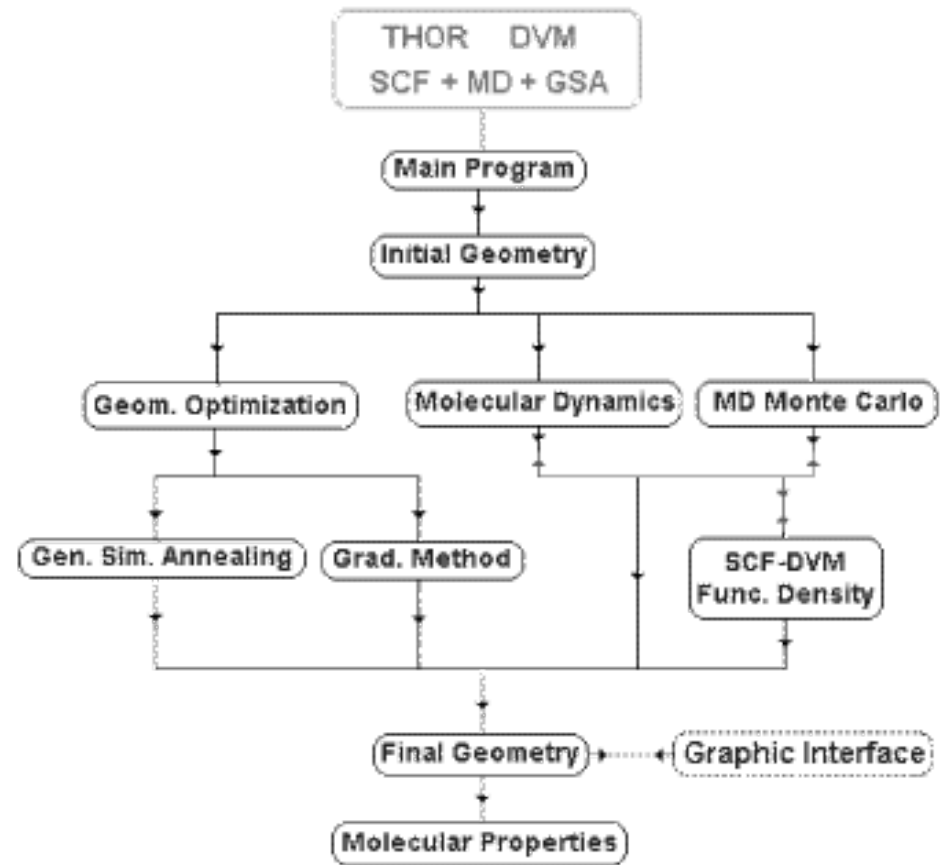
Hybrid work-flow with MD, Monte Carlo
And Density Functional components

A few details...

- For a system of N particles with coordinates X and velocities V, the following pair of first order differential equations (for all 3N degrees of freedom) may be written in Newton's notation as

- $F(X) = -\nabla U(X) = M\, dV/dt$

- $V(t) = -\, dX/dt$

- The potential energy function $U(X)$ of the system is a function of the particle coordinates X. It is referred to simply as the "potential" in physics, or the "force field" in chemistry. The principal problem in MD is <u>not</u> the time-serial solution of the particle trajectories, but is the <u>selection and refinement</u> of the potential function **U**.

The world's dumbest MD algorithm

Give atoms initial positions $r^{(t=0)}$, choose short Δt

Get forces $F = - \nabla V(r^{(i)})$ and $a = F/m$

Move atoms: $r^{(i+1)} = r^{(i)} + v^{(i)} \Delta t + \frac{1}{2} a \Delta t^2 + \ldots$

Move time forward: $t = t + \Delta t$

Repeat as long as you need

If you want to learn how to really program MD, look up:
Verlet algorithm,
Velocity-Verlet,
Leap-Frog

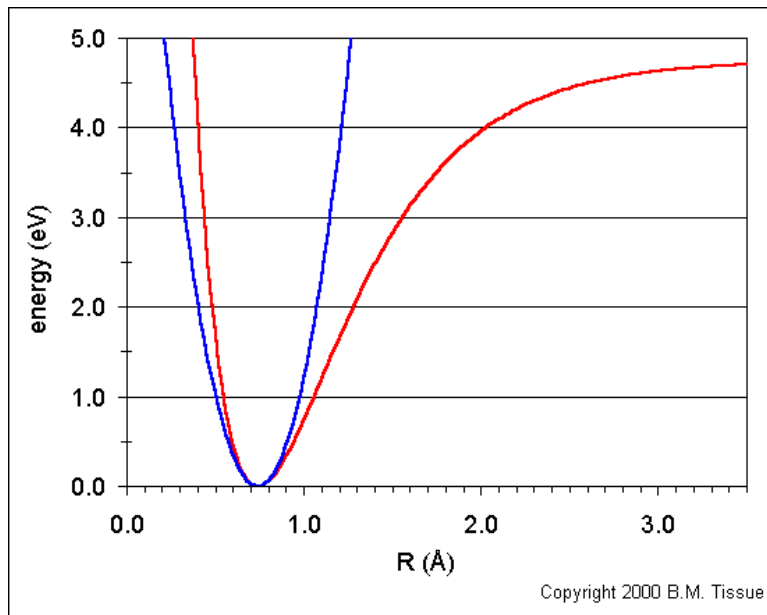$$V_{n+\frac{1}{2}} = V_n + \frac{\Delta t}{2} M^{-1} F_n$$

$$X_{n+1} = X_n + \Delta t V_{n+\frac{1}{2}}$$
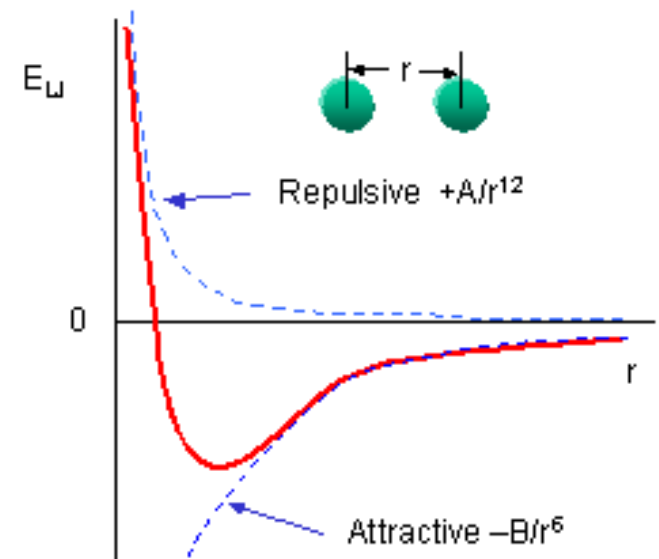
$$F_{n+1} = F(X_{n+1})$$

$$V_{n+1} = V_{n+\frac{1}{2}} + \frac{\Delta t}{2} M^{-1} F_{n+1}$$

A few more details....

$$U(\vec{r}) = \sum U_{\text{bonded}}(\vec{r}) + \sum U_{\text{nonbonded}}(\vec{r}),$$

Compare harmonic (bonded) with Morse (non-bonded) two-body potentials


Van der Waals (6-12) potential is probably most used.

$$U_{\text{angle}} = k_\theta(\theta - \theta_0)^2 + k_{\text{ub}}(r_{ik} - r_{\text{ub}})^2,$$

Angular harmonic interactions depend on the angle Θ (i, j ,k) between three atoms, and a possible (Urey-Bradley) spring connecting r (i,k)
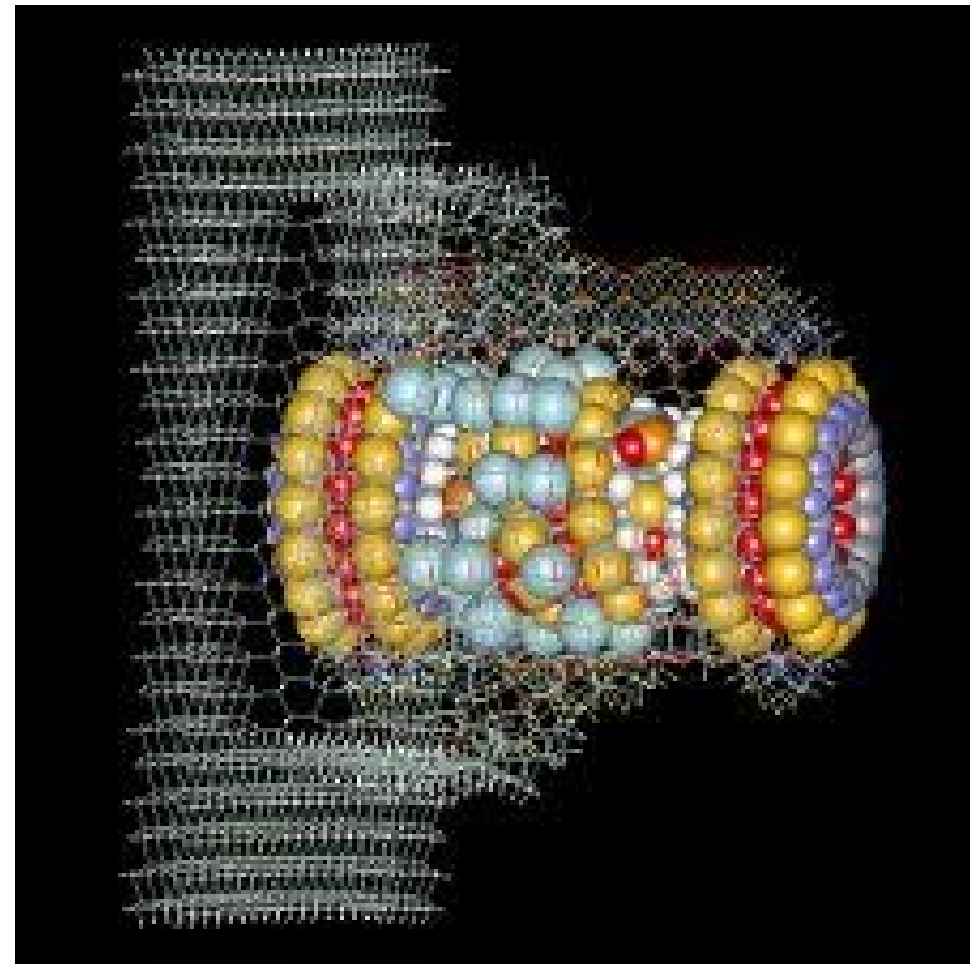
$$U_{\text{tors}} = \begin{cases} k(1 + \cos(n\psi + \phi)) & \text{if } n > 0, \\ k(\psi - \phi)^2 & \text{if } n = 0, \end{cases}$$

Dihedral angular interactions depend upon angle Ψ between planes formed by four atoms: (i,j,k) plane vs (j,k,l) plane
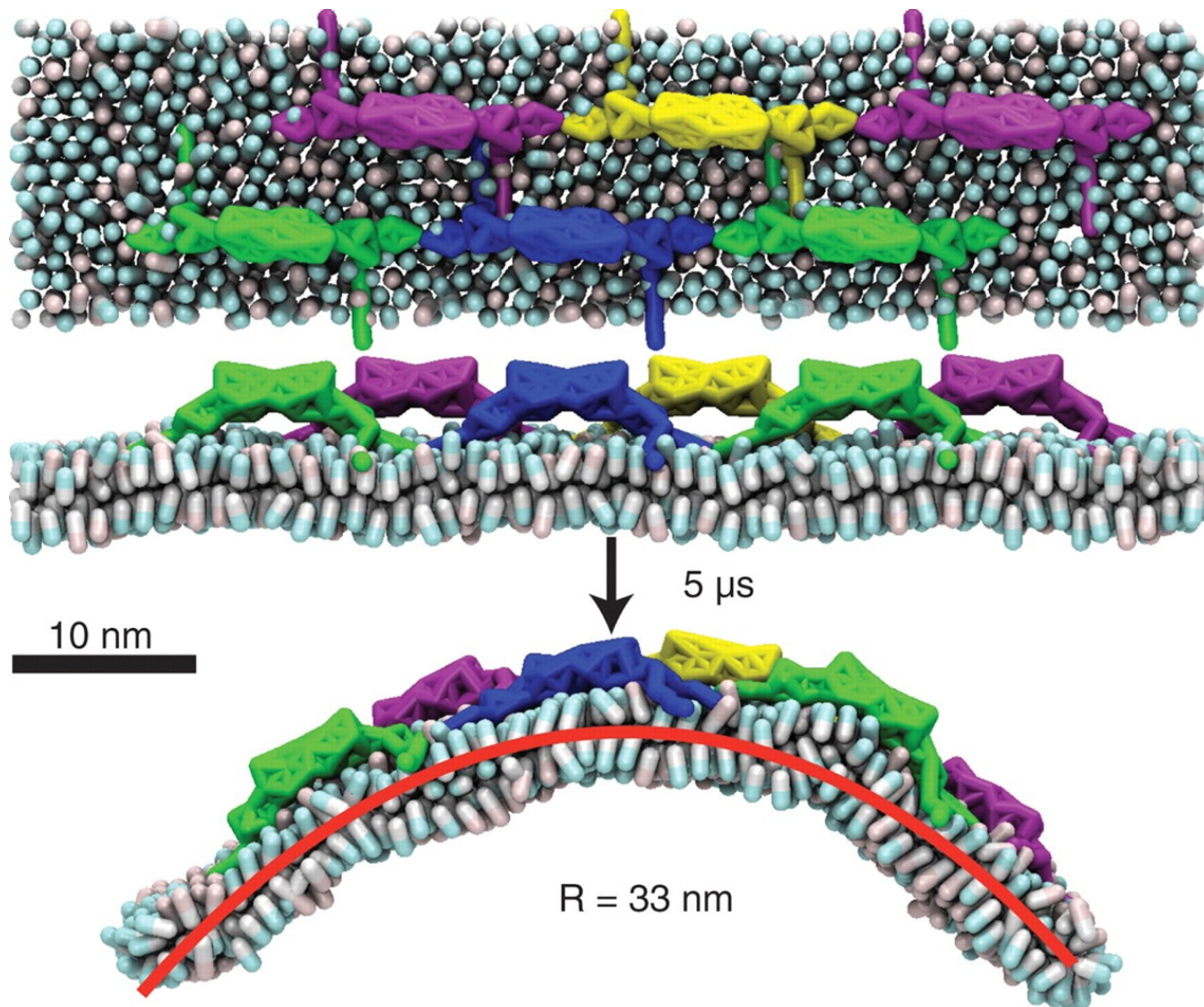
Try this: ice_melting
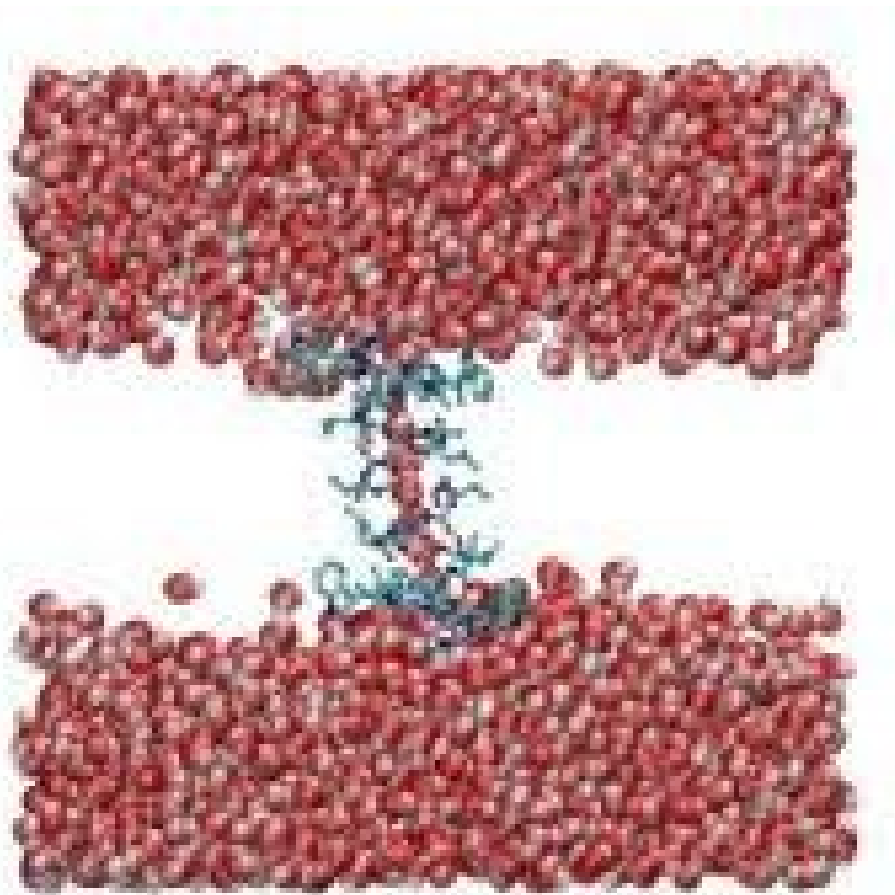
Molecule-interface interactions.

Molecular motor simulation.

MD simulation of cell membrane interactions, using a coarse-grained model of functional groups, simultaneous with individual atoms. This way, systems with millions of atoms can be modeled, representing one kind of multiscaling approach.

10 nm

5 μs

R = 33 nm

Self-assembly of a protein cylinder, starting from a flat template. Snapshots in time sequence from top to bottom. R is the radius of curvature of the membrane induced by the protein-BAR domains.
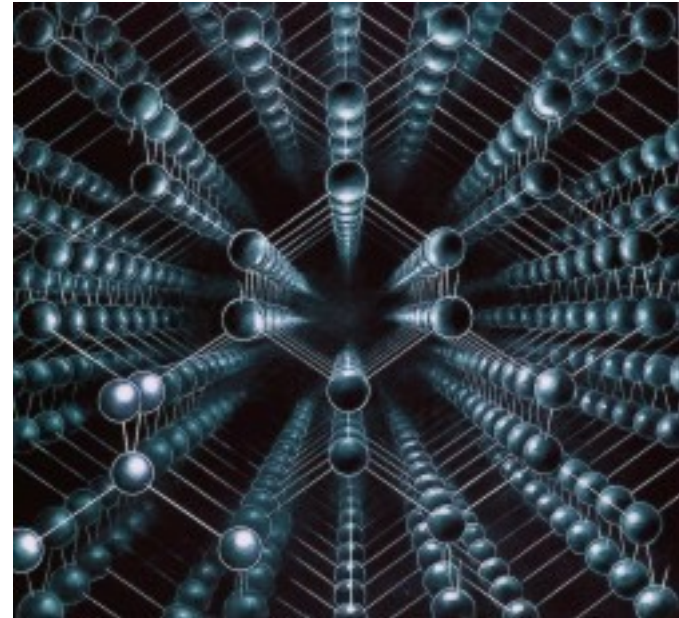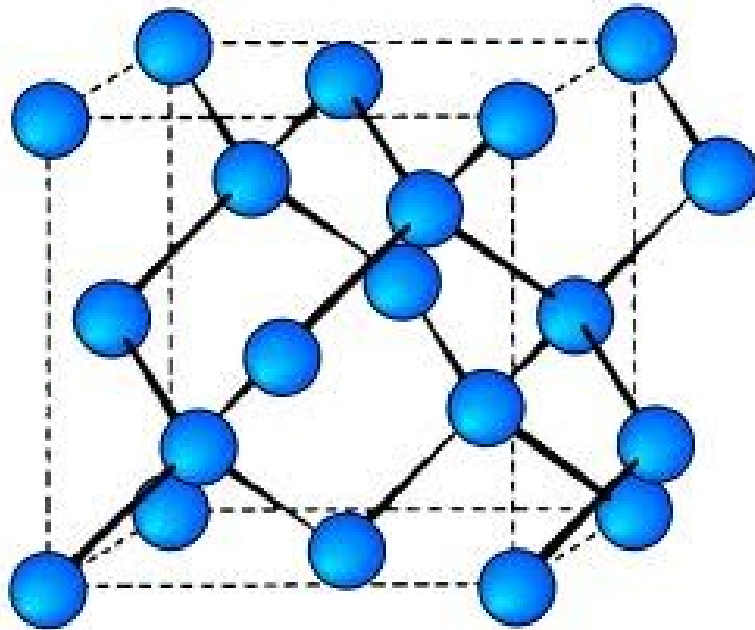
Exemplos e Perspectivos
Historia e evolucao da microeletronica

Silicon dioxide (SiO_2) is the most abundant mineral in the earth's crust. The manufacture of the hyperpure silicon for photovoltaics starts with locating a source of silicon dioxide in the form of silica or sand.
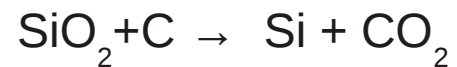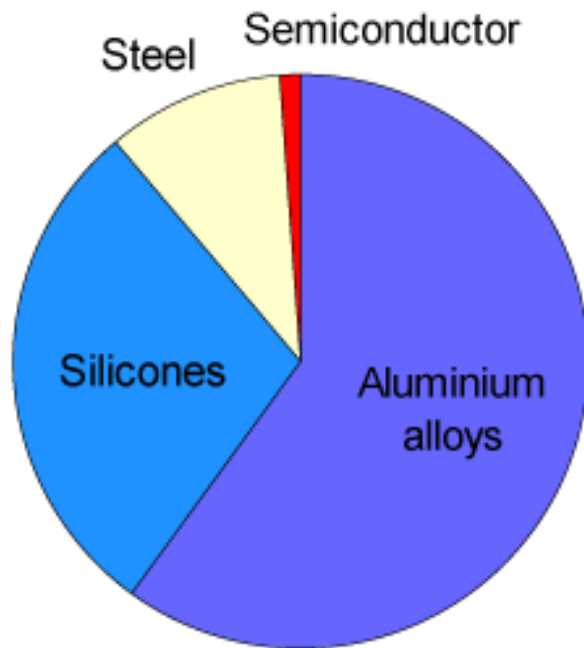
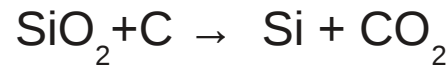# Microelectronics- or the story of silicon

Crystalline form of Si, with *fcc* diamond structure. Every atom has covalent bonds to its four nearest neighbors.

Ideally the silica has low concentrations of iron, aluminium and other metals. The silica is reduced (oxygen removed) through a reaction with carbon in the form of coal, carcoal and heating to 1500-2000 °C in an electrode arc furnace. The resulting silicon is metallugical grade silicon (MG-Si). It is 98% pure and is used extensively in the metallugical industry.

$$SiO_2 + C \rightarrow Si + CO_2$$

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$$SiO_2 + C \rightarrow Si + CO_2$$

Total production ~ 900 000 tonnes/p.a.

| Element	Concentration (ppma)
Al	1200-4000
B	37-45
P	27-30
Ca	590
Cr	50-140
Cu	24-90
Fe	1600-3000
Mn	70-80
Mo	<10
Ni	40-80
Ti	150-200
V	100-200
Zr	30

A small amount of the metallurgical grade silicon is further refined for the semiconductor industry. Powdered MG-Si is reacted with anhydrous HCl at 300 °C in a fluidised bed reactor to form $SiHCl_3$

$$Si + 3HCl \rightarrow SiHCl_3 + H_2$$
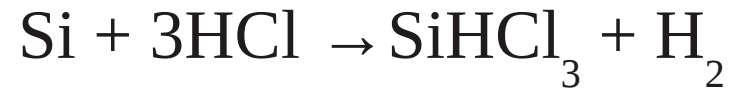
During this reaction impurities such as Fe, Al, and B react to form their halides (e.g. $FeCl_3$, $AlCl_3$, and BCl_3). The $SiHCl_3$ has a low boiling point of 31.8 °C and distillation is used to purify the $SiHCl_3$ from the impurity halides. The resulting $SiHCl_3$ now has electrically active impurities(such as Al, P, B, Fe, Cu or Au) of less than 1 ppba.

Finally, the pure SiHCl$_3$ is reacted with hydrogen at 1100°C for ~200 – 300 hours to produce a very pure form of silicon.
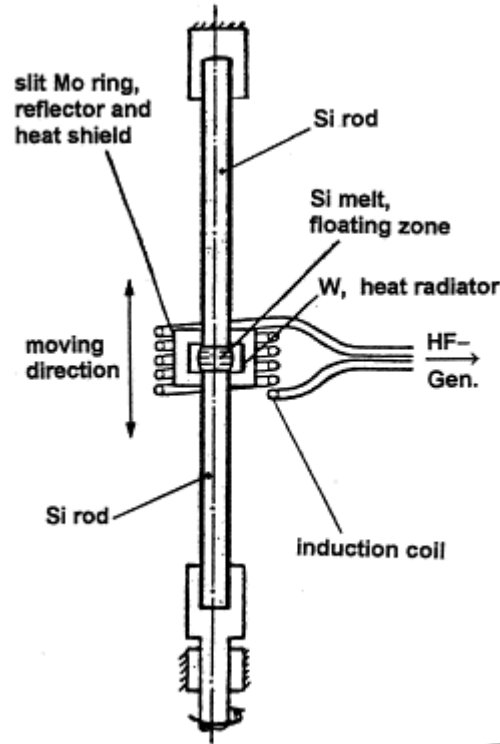
$$SiHCl_3 + H_2 \rightarrow Si + 3HCl$$
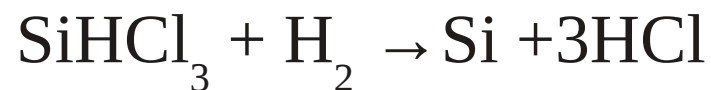
(note that this is just the reverse of the previous reaction)

The reaction takes place inside large vacuum chambers and the silicon is deposited onto thin polysilicon rods (small grain size silicon) to produce high-purity polysilicon rods of diameter 150-200mm. The process was first developed by Siemens in the 60's and is often referred to as the Siemens process.
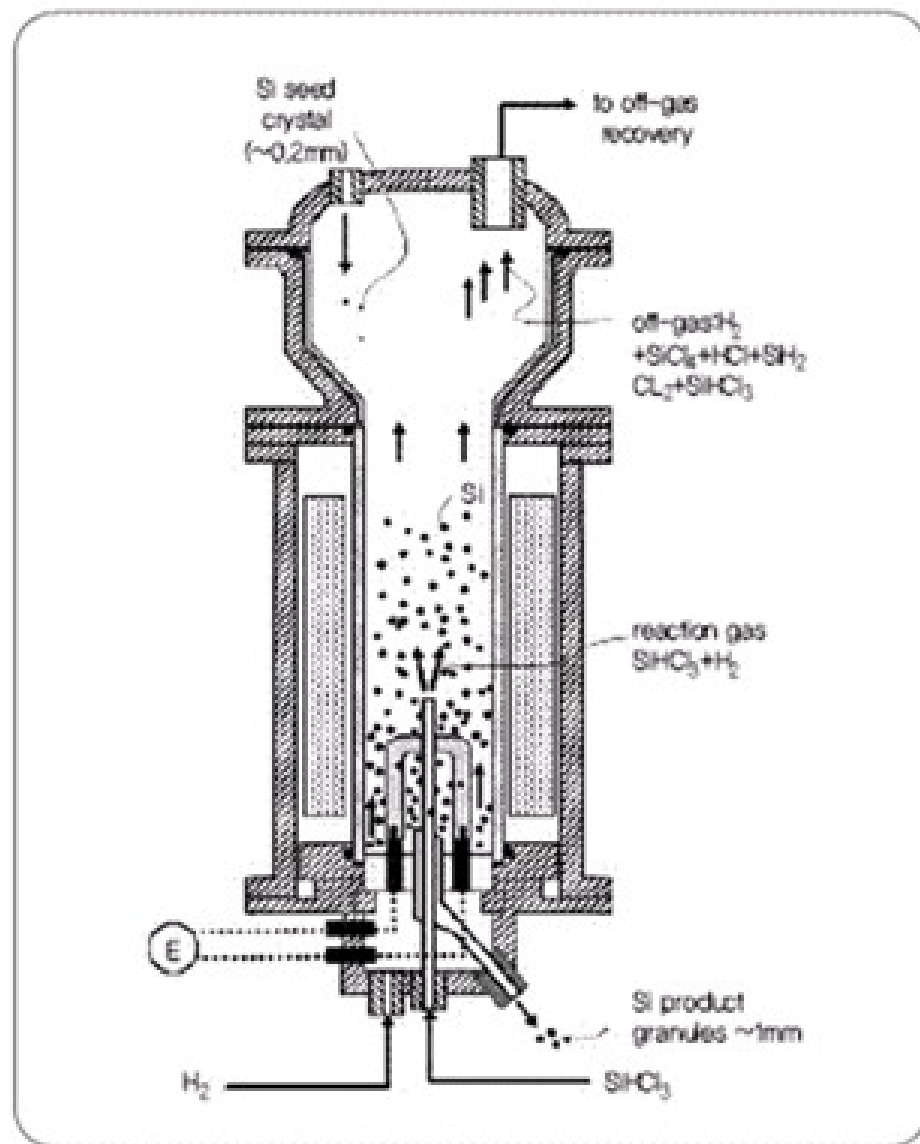
The resulting rods of semiconductor grade silicon are broken up to form the feedstock for the crystallisation process. The production of semiconductor grade silicon requires a lot of energy. Solar cells can tolerate higher levels of impurity than integrated circuit fabrication and there are proposals for alternative processes to create a "solar-grade" silicon.


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slit Mo ring, reflector and heat shield

Si rod

Si melt, floating zone

W, heat radiator

moving direction

HF– Gen.

Si rod

induction coil

Starting from an ultrapure seed, a single crystal ingot is pulled from the melt.

Further purification is gained by passing a floating zone of melted material multiple times along the ingot. The 'dirty' end is sawed off and recycled.

Standard Si wafers (99.9999999% purity==9N) of up to 300mm diameter, thickness 775 μm (450mm in development) are sliced off ingots and processed (microfabrication) to make circuit elements. Orientation is defined by the Miller index with [100] or [111] faces being the most common.
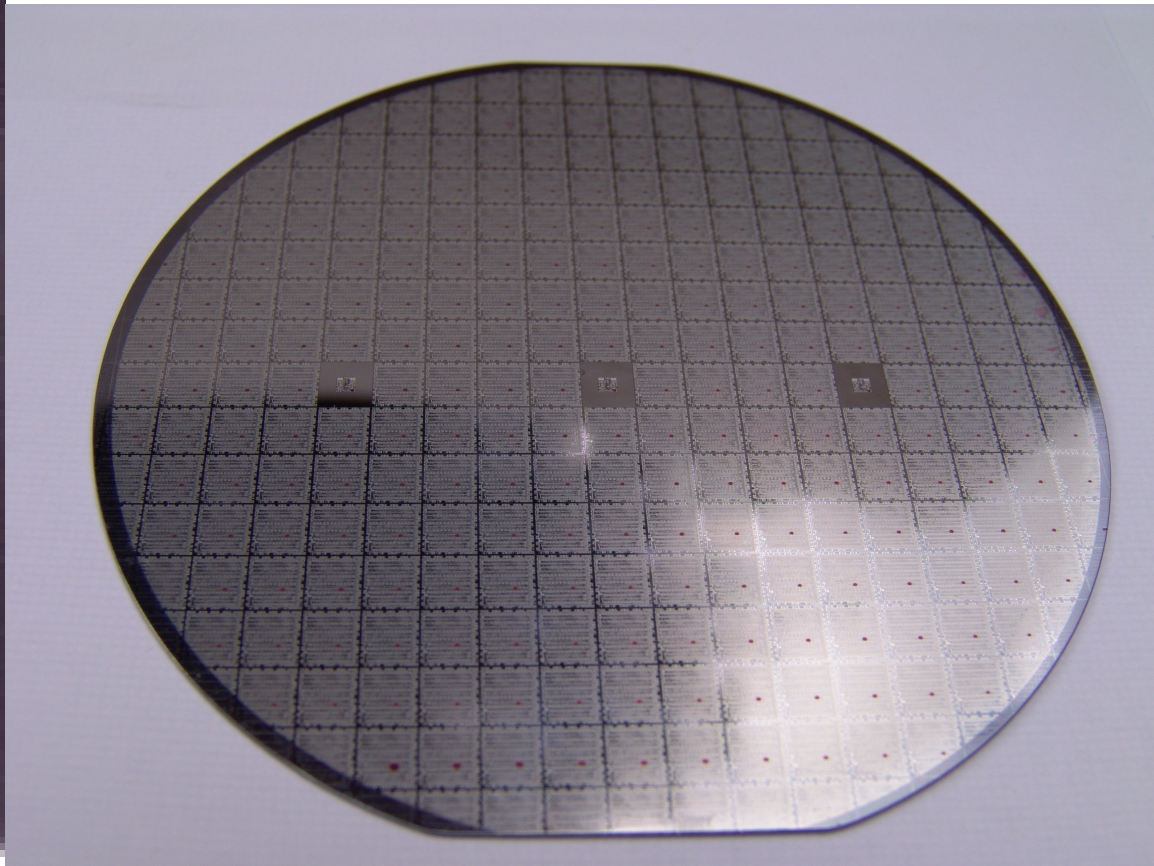
What?!? After all we went through to make ultrapure Si, NOW you want to add dirt!?!?!

- Silicon wafers are generally not 100% pure silicon, but are instead formed with an initial impurity doping concentration between 10^{13} and 10^{16} atoms per cm^3 of boron, phosphorus, arsenic, or antimony which is added to the melt and defines the wafer as either bulk n-type or p-type. However, compared with single-crystal silicon's atomic density of 5×10^{22} atoms per cm3, this still gives a purity greater than 99.9999%. The wafers can also be initially provided with some interstitial oxygen concentration. Carbon and metallic contamination are kept to a minimum. Transition metals, in particular, must be kept below parts per billion concentrations for electronic applications.

# Basic ideas of semiconductor doping
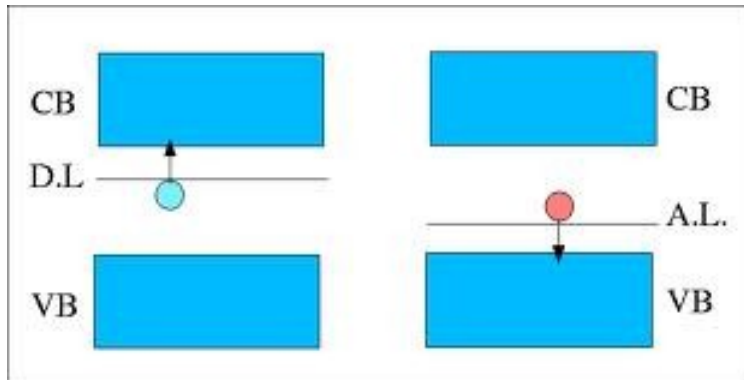
Baby model of donor levels (DL) and acceptor levels (AL) relative to valence band (VB) and conduction band (CB)
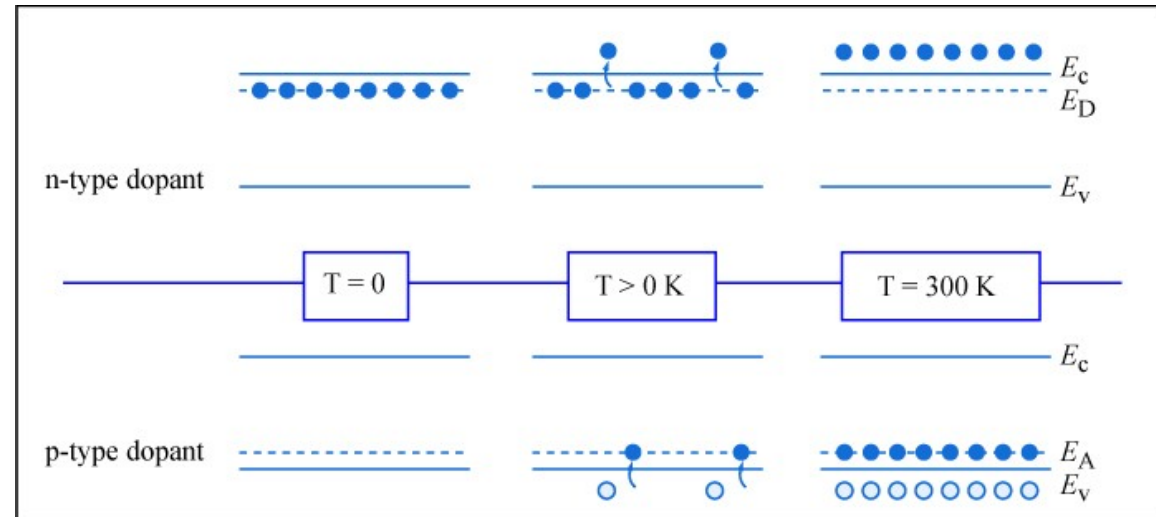
Temperature dependence of band-filling.
•For T>0, electrons leave VB to live in the AL, leaving behind mobile holes (p-type conduction).
• Meanwhile electrons leave the DB to become mobile in the CB (n-type conduction)

# What are the favorite donors/acceptors?
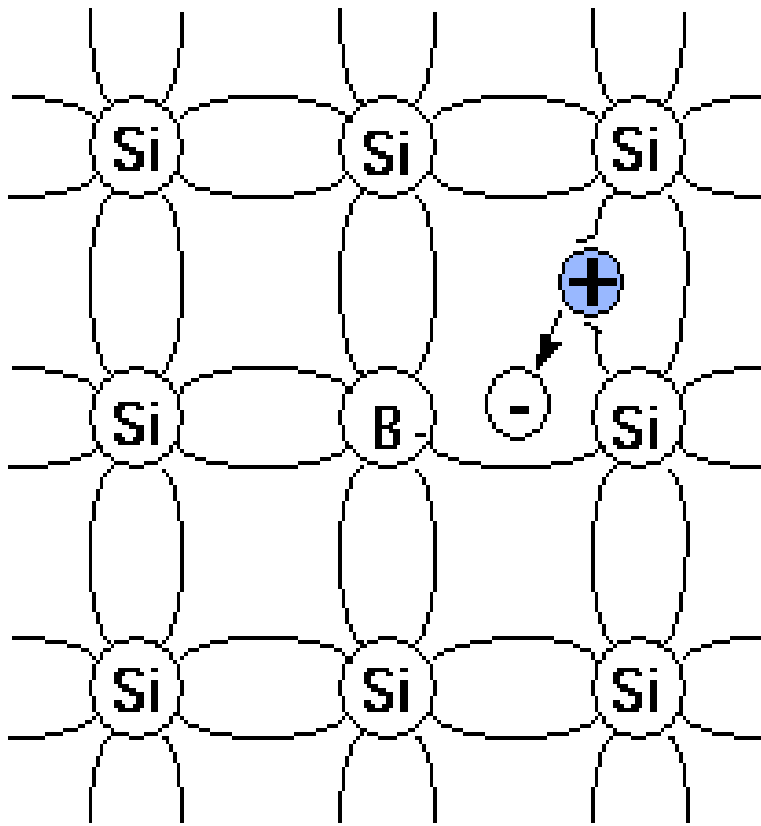
Trivalent atoms like B, Al, In, Ga are eager to accept one electron from tetravalent Si, creating a positive 'hole sea'.
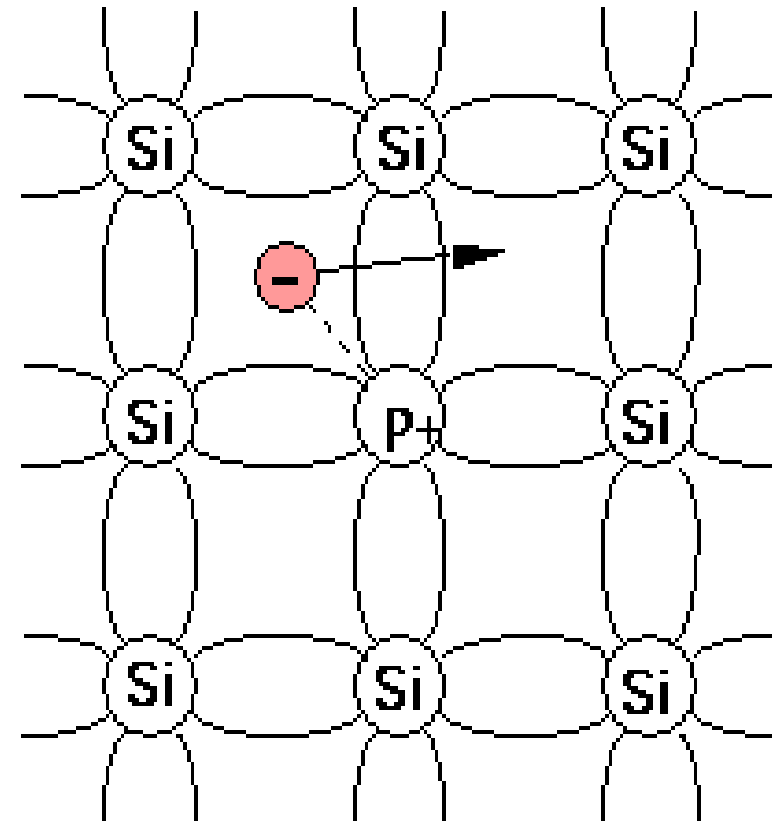
Pentavalent atoms like P, As, Sb, Bi are eager to donate one electron, to the negative 'conduction sea'.

Semiconductors:electronic band structure

Pure Si has a direct band gap of 3.40 eV and an indirect gap of 1.08 eV. It is practically useless as an electronic material, becoming useful only as electron-donating or electron-accepting impurities are deliberately added.
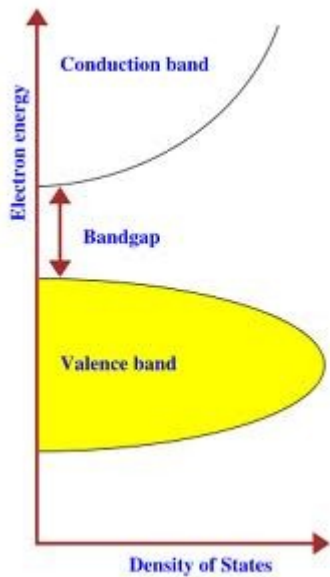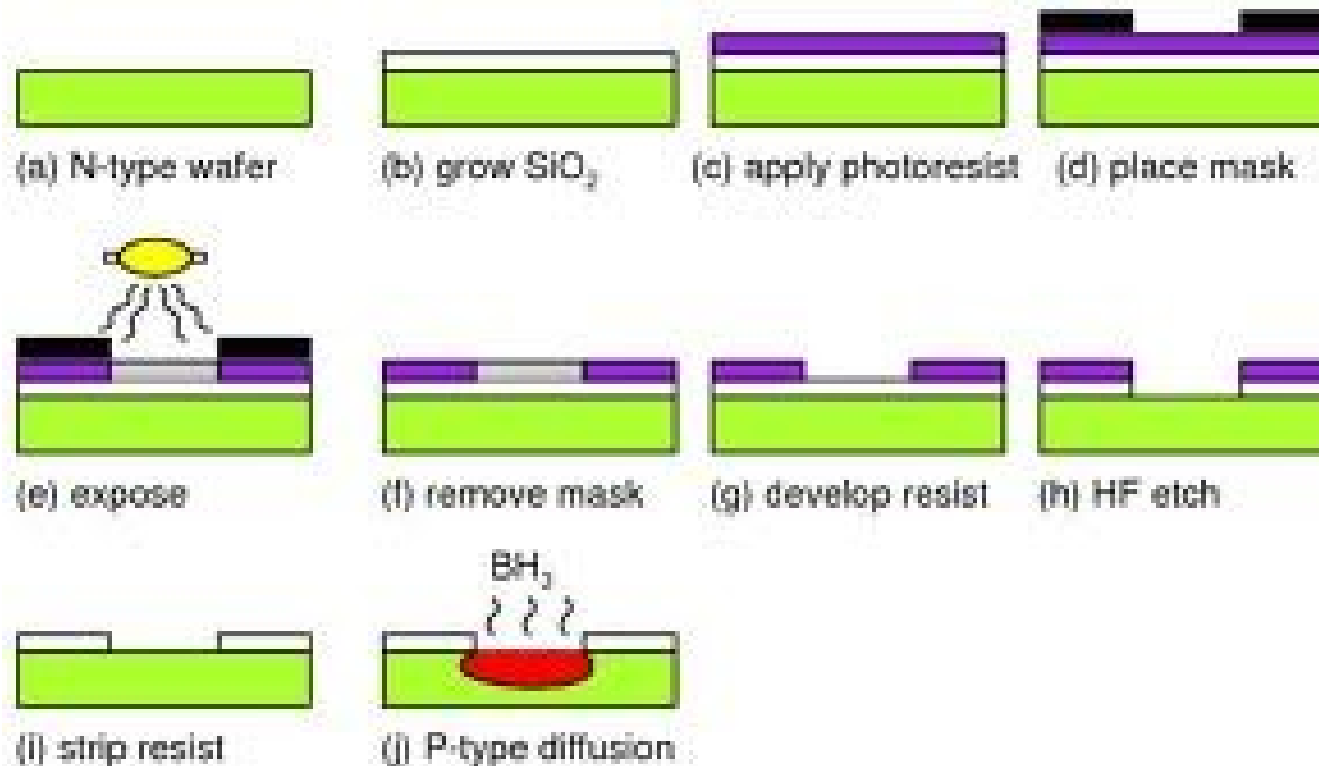

A baby model of semiconductor bands
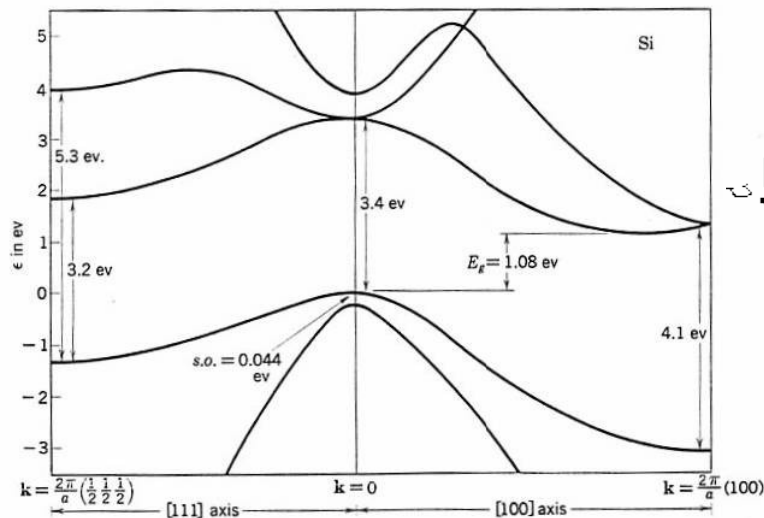
A 2D projection of Si bands along symmetry directions in k-space
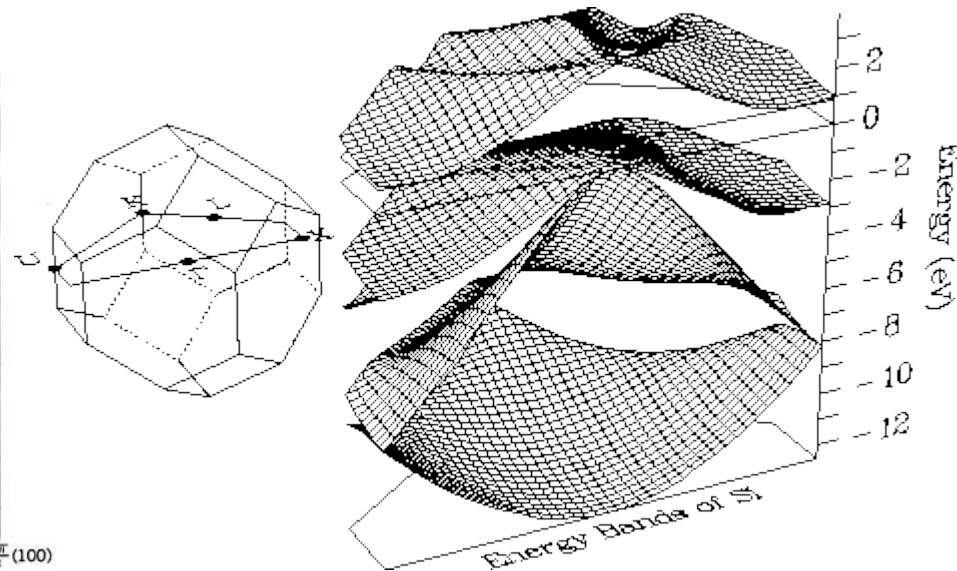
A perspective view of Si bands with a sketch of the *fcc* Brillouin zone

How to grow a p-n junction diode

(a) N-type wafer (b) grow SiO₂ (c) apply photoresist (d) place mask

(e) expose (f) remove mask (g) develop resist (h) HF etch

(i) strip resist (j) P-type diffusion

Attach conductors top and bottom, pronto!

P-n diodes come in all sizes, are manufactured in the billions annually

device package

anode — cathode

anode ▷|— cathode

schematic symbol

Source: TU-Berlin
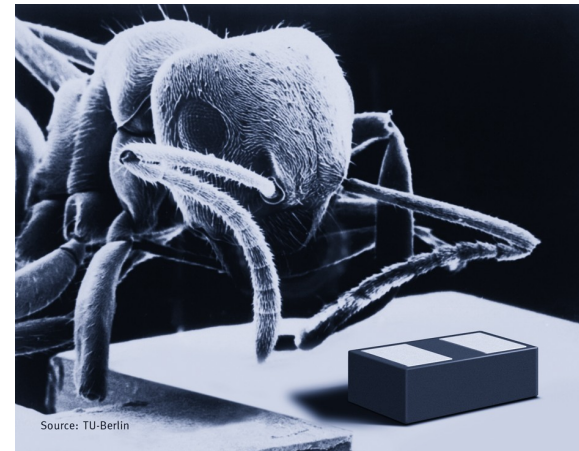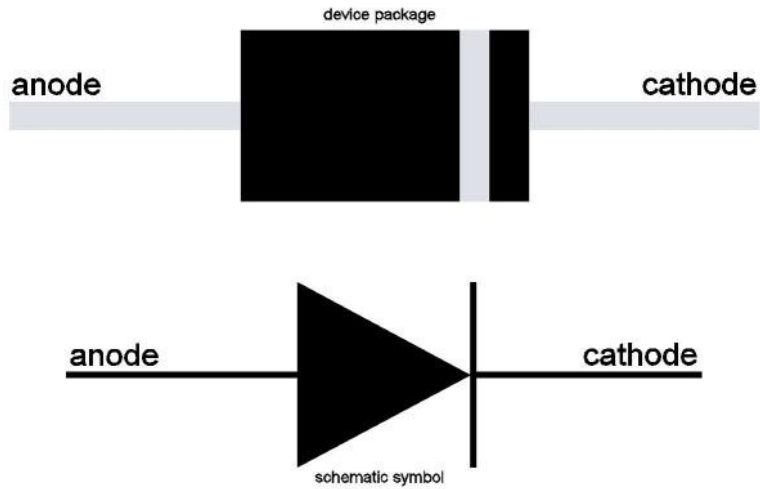
Above: TVS (transient voltage suppression) diode, ok up to 20kV
Below: High current automotive diode

I_D

forward

reverse-bias

forward-bias

V_D

0.7 V

breakdown!

reverse