



Atomic and molecular interactions; applications

Tamás Bozó
18 October 2012

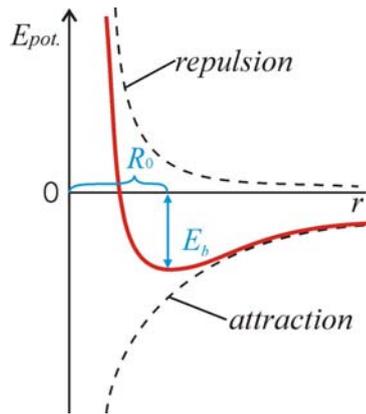
Atomic interactions

Noble gases: found in their atomic form in nature (*He, Ne, Ar, Kr, Xe, Rn*)

Other elements: form molecules held together by chemical bonds. (*e.g. H₂, HCl, H₂O, ...*) Each atom has a (more or less) fixed position in the molecule.

Atomic interactions

Bringing two atoms (ions/molecules/...) close to each other attractive and repulsive forces emerge between them resulting in a net potential energy function with an energy minimum at a certain distance:



$$E_{\text{pot}} = E_{\text{attraction}} + E_{\text{repulsion}}$$

E_{pot} : potential energy of the system
 $E_{\text{attraction}}$: E contribution of attractive forces
 $E_{\text{repulsion}}$: E contribution of repulsive forces
 r : distance of atoms
 E_b : binding energy
 R_0 : binding distance

Bond Types

Classification systems:

- Intra/intermolecular bonds
- According to the strength of bonds:
 - Strong/weak
 - Primary (covalent, metallic, ionic)
 - Secondary (dispersion, dipole-dipole, hydrogen)
- Other Bond types...



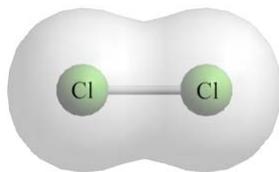
I. Covalent bond

- Atoms are held together by electrons of common orbitals, called molecular orbitals.
- Valence electrons interact the most.
- Single, double or triple bond depending on the number of shared electrons.
- Some electrostatic component may be present (see later), but not predominant.
- Strong interaction: $E_k > 1 \text{ eV}$
- ($1 \text{ eV} = 1,6 \cdot 10^{-19} \text{ J} = 96 \text{ kJ/mol} \sim 100 \text{ kJ/mol}$)

I. Covalent bond

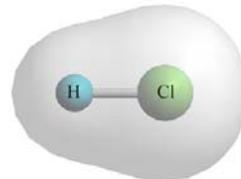
Apolar (nonpolar or homeopolar) bond

Center of (+) és (-) charges of the molecule coincides
 Binding electron(s) shared equally
 „purely covalent”
 E.g. H_2 , Cl_2 , O_2 , ...



Polar (heteropolar) bond

Centers of (+) and (-) charges do not coincide
 Electric dipole is formed
 Electron cloud is polarized
 Electrostatic contribution appears
 E.g.: HCl , HF , H_2O , ...

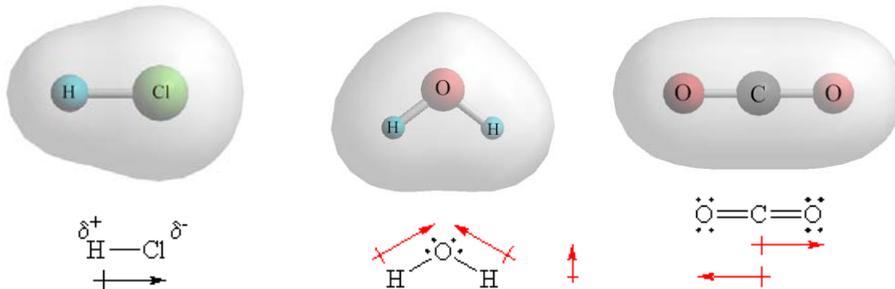


I. Covalent bond

Electric dipole moment: measure of the separation of positive and negative electric charges.

$$\mathbf{p} = Q\mathbf{d}$$

p: electric dipole moment
 Q: charge (positive and negative)
 d: distance of separation
 [D, debye] ($1D = 3,34 \cdot 10^{-30} \text{ Cm}$)



I./b Metallic bond

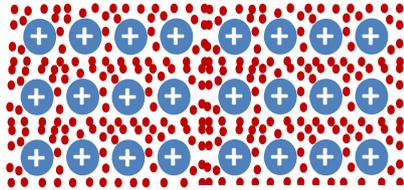
- Atoms are held together by common electrons (delocalized orbital)
- Valence electrons form continuous electron band
- Strong interaction: $E_k > 1 \text{ eV}$
- Multi atomic systems

Periodic Table of the Elements

1	2																	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000
---	---	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	---	---	---	---	---	---	---	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	------

■ hydrogen
 ■ alkali metals
 ■ alkali earth metals
 ■ transition metals
 ■ poor metals
 □ nonmetals
 ■ noble gases
 ■ rare earth metals

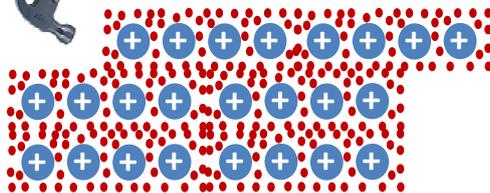
I./b Metallic bond



Metallic lattice: positively charged metal ions in a crystall lattice surrounded by a cloud of delocalized electrons.



I./b Metallic bond



Physical properties:

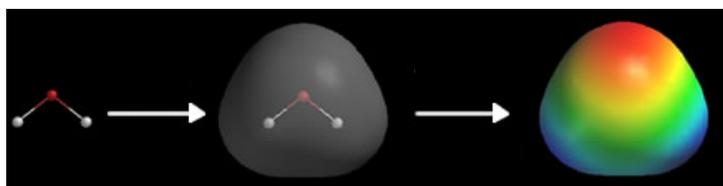
Metals are:

- Non transparent
- Ductile (shapeable)
- Good electric conductors
- etc.

II. Bond types involving electrostatic interactions

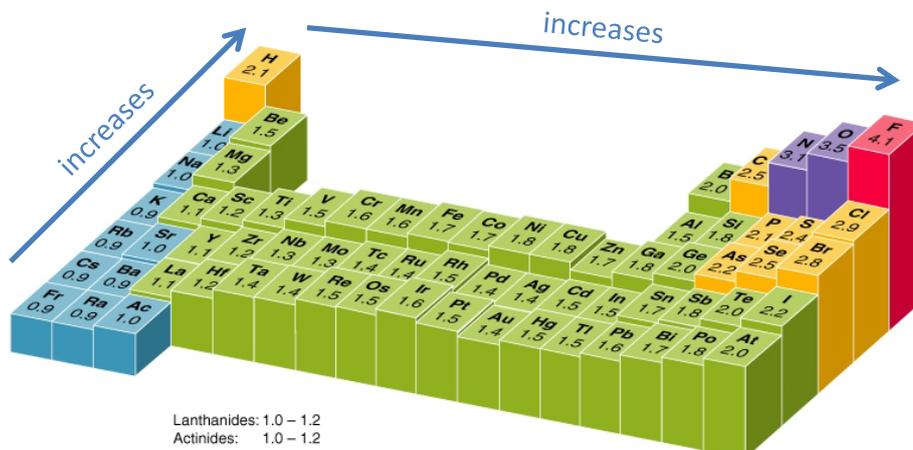
Electronegativity

- is a chemical property that describes the tendency of an atom or a functional group to attract electrons towards itself.
- The higher the associated electronegativity number, the more an element or compound attracts electrons towards it.
- Approximately proportional to the sum of ionization energy and electron affinity.
- Calculated with different methods (*Pauling, Mulliken, Sanderson...*)



II. Bond types involving electrostatic interactions

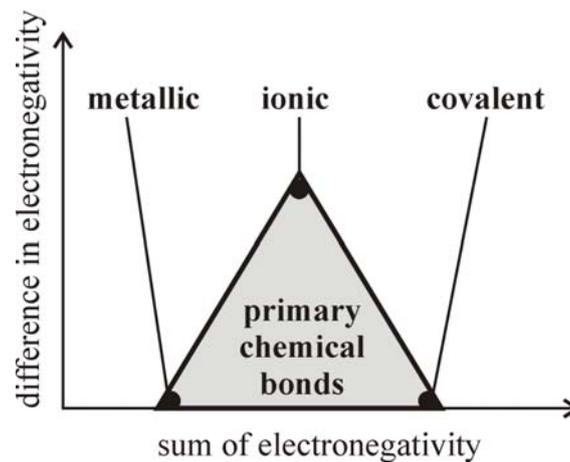
Electronegativity according to L. Pauling (dimensionless units)



II. Bond types involving electrostatic interactions

Classic bonds classified according to electronegativity:

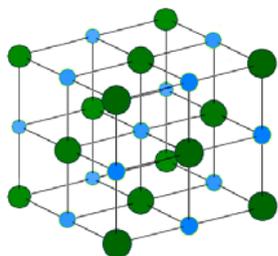
$< 0,6$ (apolar covalent) $0,6 - 2,1$ (polar covalent) $2,1 <$ (ionic)



II./a Ionic bond

- Atoms are held together by Coulombic forces between (+) és (-) point charges
- „Limiting case of heteropolar bonds”
- Formed between atoms of significantly different electronegativity (e.g.: NaCl , $\Delta EN = 3 - 0,9 = 2,1$)
- Can form between two atoms, but usually multi-atom systems.
- Long range interaction - attraction is inversely proportional to the distance (decreases slowly with it).
- Electrostatic interaction can be largely affected by other charged components (eg. *dissociation in water!*)
- Strong interaction ($E_b > 1 \text{ eV}$)

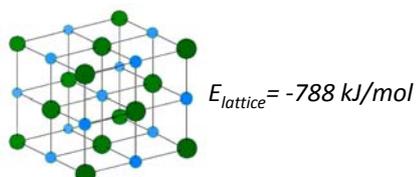
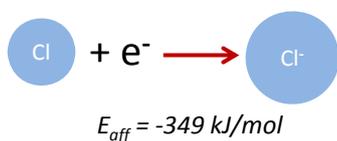
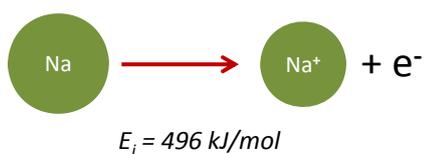
II./a Ionic bond



Ionic crystals: stoichiometric ratio of positive and negative ions are structured into a periodic crystalline structure. (e.g.:NaCl)



II./a Ionic bond



Ionization energy: is the energy *required* to remove electrons from gaseous atoms or ions.

Electron affinity: amount of energy *released* when an electron is added to a neutral atom or molecule to form a negative ion (measured in the gaseous state).

Lattice energy: measure of the strength of bonds in an ionic compound. Energy *required* to completely *separate* one mole of a solid ionic compound into gaseous ionic constituents.

II./b Dipole-dipole interaction

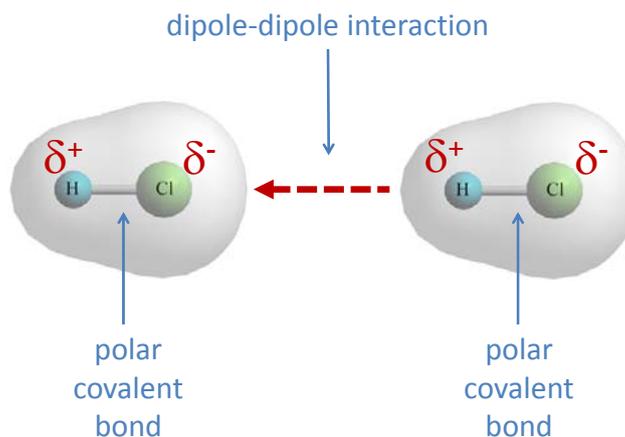
- Constant charge distribution is present in a (given part of a) molecule
- Partially (+) and (-) segments are held together by electrostatic interactions (Coulombic forces)
- Intra/intermolecular interaction.
- Weak interaction ($E_b = 0,003-0,02$ eV)
- Energy of attracting interaction between dipoles:

$$E_{\text{attraction}} = p E$$

p: dipole momentum
E: electric field strength generated by the surrounding partners

($E_{\text{repulsion}}$: stems from the repulsion of the participant's electron cloud)

II./b Dipole-dipole interaction

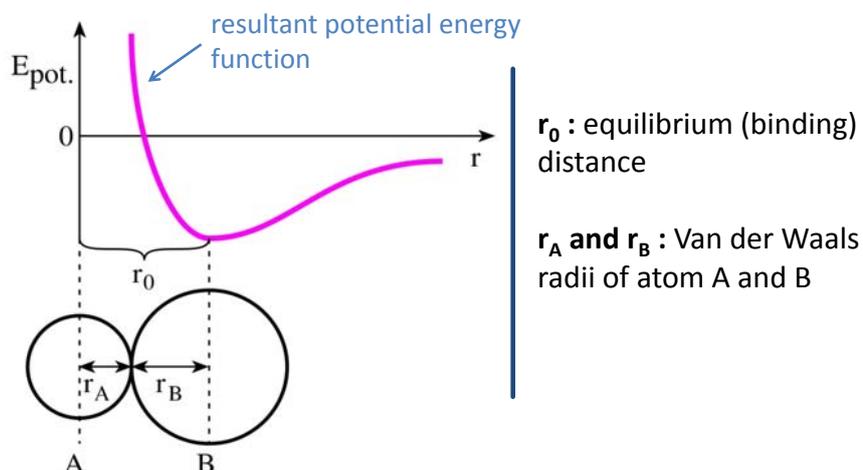


III. Van der Waals-interactions

- Sum of attractive and repulsive interactions between two apolar atoms, molecules or apolar molecular parts.
- The **attractive contribution** (also called *London-*, or *dispersion force*) is a result of temporarily created dipoles that can induce the polarization of other apolar molecule or molecular part.
- Intermolecular or intramolecular interaction.
- Important biological role: formation of organic structures.
- Weak connection ($E_b \sim 0,02 \text{ eV}$)
- [according to other classifications Van der Waals interactions involve all types of weak electrostatic connections (permanent dipole-permanent dipole; permanent dipole-induced dipole, induced dipole-induced-dipole)]

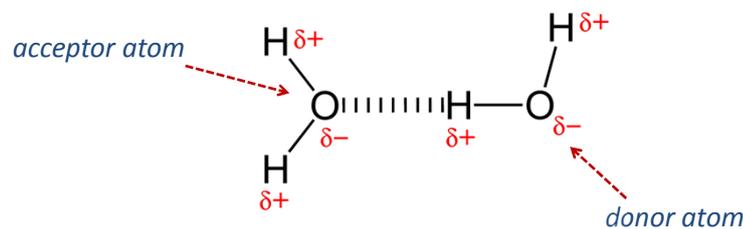
III. Van der Waals-interactions

Equilibrium distance of a Van der Waals interaction can be considered as one definition of atomic size.



IV. Hydrogen bond

- Two atoms of high electronegativity are held together with a Hydrogen-bridge.
- Primarily between **F, N, O** atoms (pillar atoms).
- Intermolecular/intramolecular interaction
- Typical bond distance: 0,23 – 0,35 nm
- Well defined structure.
- Important role in structural biology and biochemical reactions.
- Medium strong interaction (typical $E_b = 0,2$ eV)

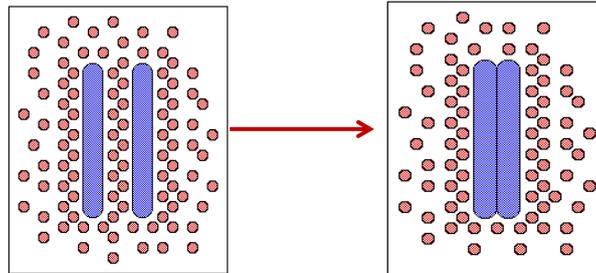


V. Hidrophobic interaction

- Appear in aqueous systems (like biological environments!)
- Apolar, hydrophobic molecules tend to aggregate (form bonds with each other) in aqueous environment in order to exclude the polar water molecules and minimize their surface area exposed to water.
- Intra/intermolecular interaction
- It has mostly entropic origin (*see later at Thermodynamics*) through reduction of highly structured water cage around the apolar surfaces. (*see Organisation of Water later*)
- Important role in structural biology and biochemical reactions.
- Weak interaction.



V. Hydrophobic interaction



Scanning Probe Microscopy (SPM)

Family of instruments used for studying surface properties of various materials.

How do they work?

Etimology and function:

Microscopy: a method being able to form image of small objects.

How small? Size of resolvable objects spans from few pm-s to several μm -s.

They are not „scope“-s in the classic sense of the word: They do not „see“ the object, they „touch“ it.

Scanning Probe Microscopy (SPM)

Probe:

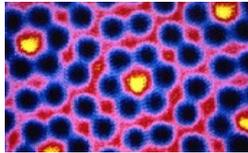
- A tiny, specifically designed component particularly sensitive to *atomic interactions*.
- The probe is brought very close to the sample surface.
- The sensed interactions can be correlated with the distance between the probe and the sample.
- Various interactions can be observed depending on the design of the probe.
- SPM methods are named after the type of atomic interaction sensed by a certain probe.

Scanning Probe Microscopy (SPM)

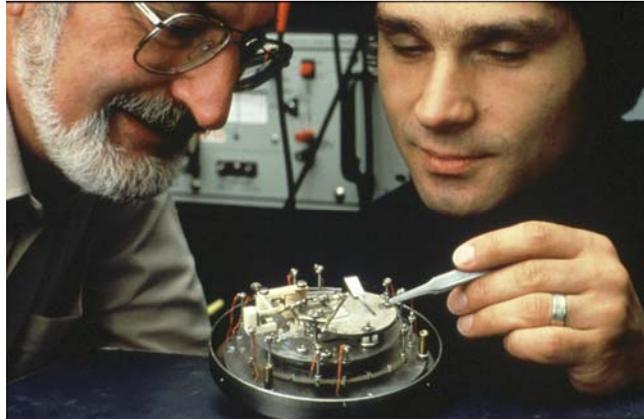
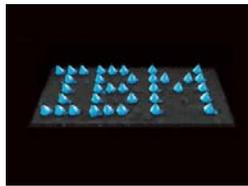
Scanning:

- A scanner controls the precise *position* (X; Y) of the probe and its *distance* (Z) from the surface to be imaged.
- The probe can be moved with pm sensitivity in X; Y; Z directions.
- The surface of region of interest (ROI) is scanned point by point during a measurement.
- (The material that enables such precise positioning is *piezoelectric ceramic*. If voltage is applied on it, the ceramic changes its geometry.)

Scanning Tunneling Microscope (STM) 1981

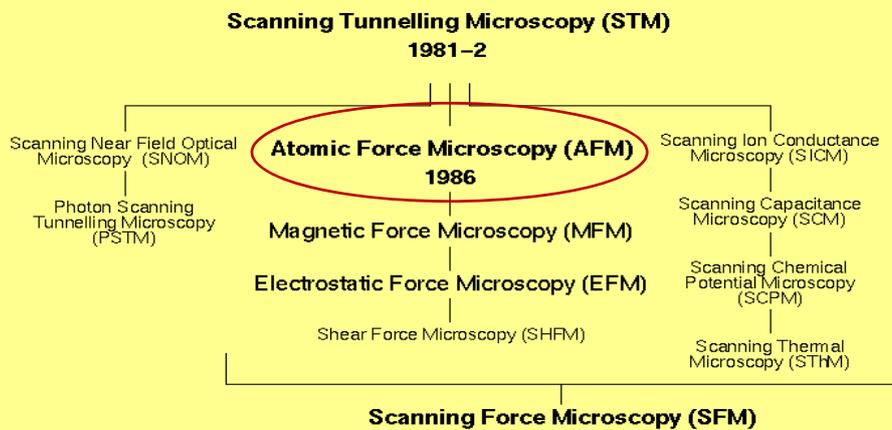


Atoms in a silicon chip



Heinrich ROHRER and Gerd BINNING
Nobel prize: 1986

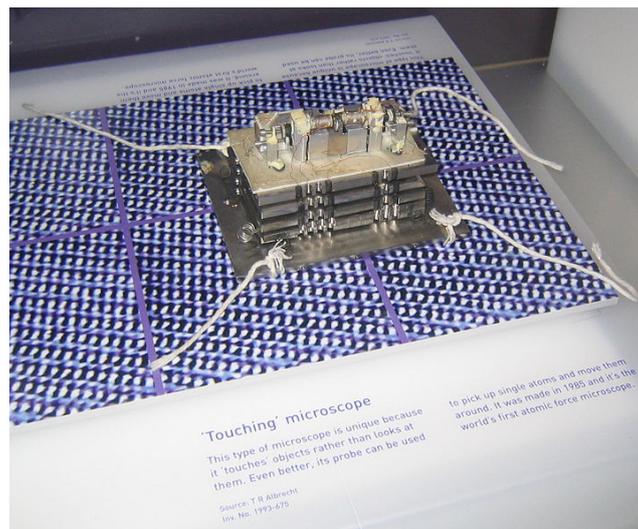
Scanning Probe Microscopy "Family Tree" (SPM)



Atomic Force Microscopy (AFM)

- The probe is a tiny, sharp tip, usually few μm -s tall, and only few nm-s in diameter at the apex.
- The tip is located at the free end of a cantilever that is usually 100-500 μm long.
- Topographic image is collected with ~ 10 pm vertical and somewhat worse horizontal resolution.
- Any surfaces (conductors, insulators and semiconductors) can be imaged.
- Works in air and in fluid environment as well.
- Usually does not require fixation or staining of the sample.
- Biological samples can be examined in their native state and physiological environment.

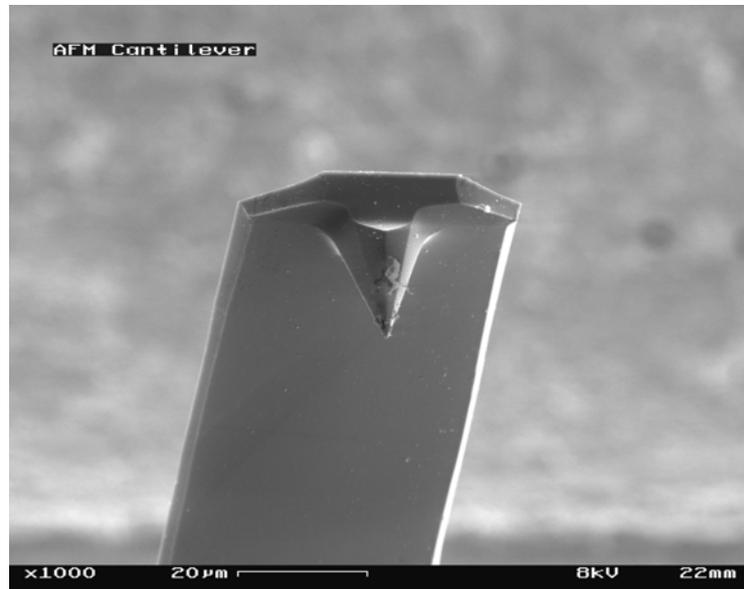
Atomic Force Microscopy



The first one. 1986.

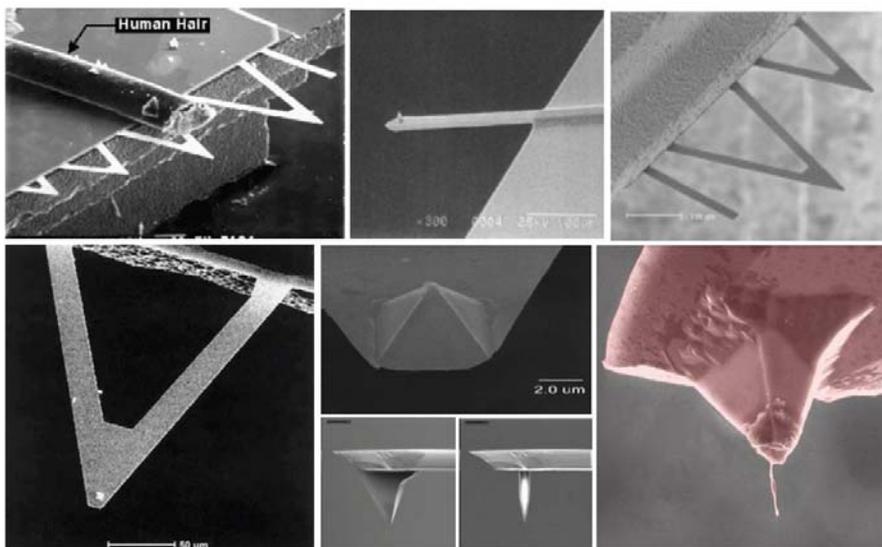
Atomic Force Microscopy

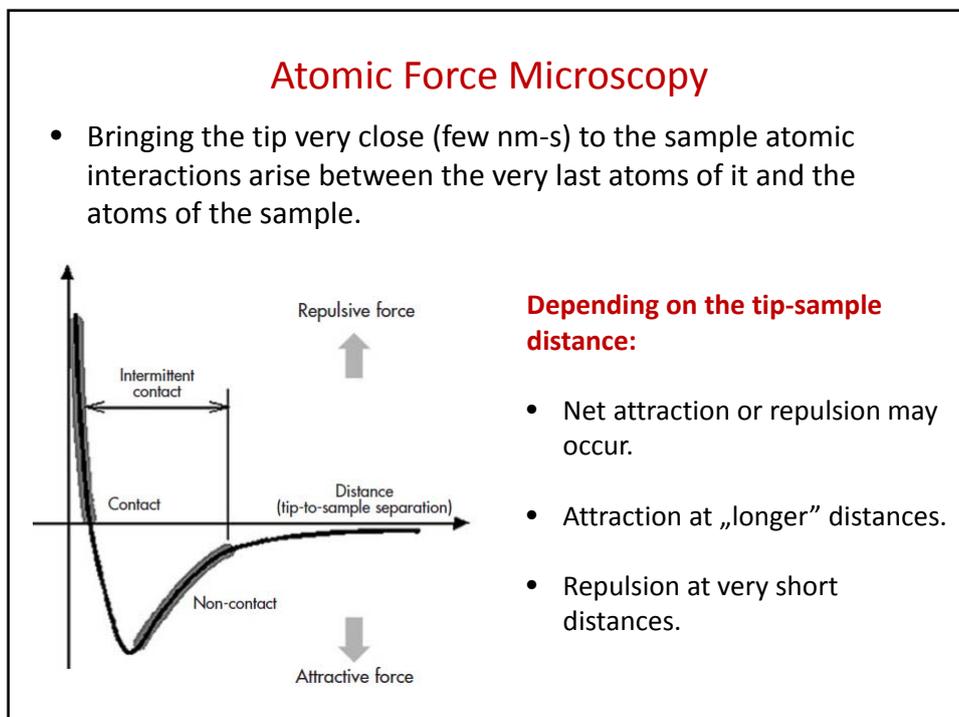
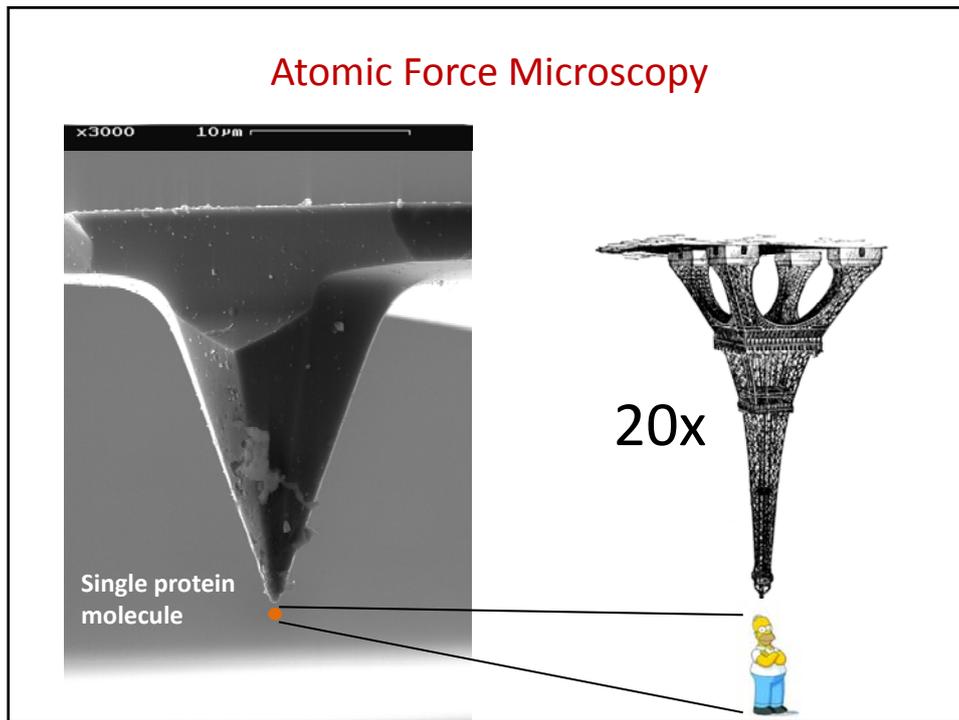
Tip at the end of a cantilever



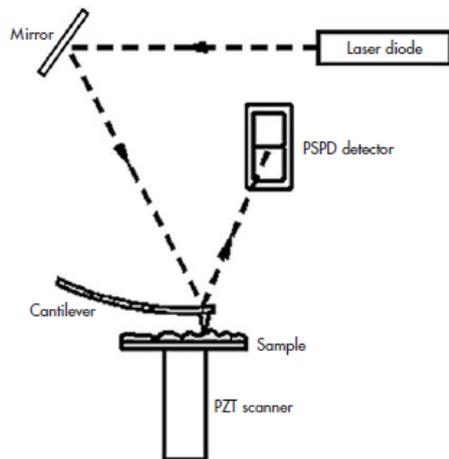
Atomic Force Microscopy

Different types of AFM cantilevers.





Atomic Force Microscopy

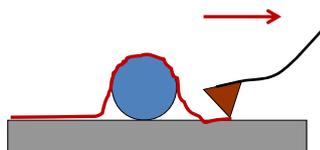


- Attractive and repulsive effects cause the cantilever to bend.
- Deflection of the cantilever is detected by an optical system.
- A laser beam is pointed at the very end of the cantilever, and reflected back to be sensed by a position-sensitive photodetector (PSD).
- Thus vertical deflection of the cantilever is amplified and can be detected with sub-Å sensitivity..

Atomic Force Microscopy

Contact mode:

- The tip is in perpetual contact with the sample surface.
- The deflection of the cantilever, i.e. the force exerted on the sample by the tip is held constant.
- A Z feedback system is utilized to maintain the deflection at a constant value (setpoint) by lifting or lowering the cantilever.
- Topography data (i.e.: height) in each X;Y point is calculated from these Z movements



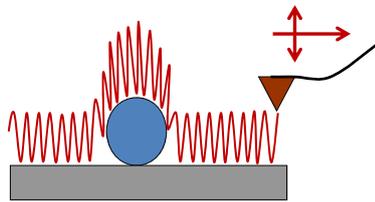
Disadvantage:

- Lateral forces exerted by the scanning tip may damage softer samples.

Atomic Force Microscopy

Oscillating mode: (Tapping mode, Non-contact mode)

- Cantilever is oscillated close to its resonant frequency.
- The tip taps the surface gently
- The amplitude of cantilever oscillation changes with surface topography.
- A Z feedback system is utilized to maintain the amplitude at a constant value (setpoint) by lifting or lowering the oscillating cantilever.
- Topography data (i.e.: height) in each X;Y point is calculated from these Z movements



Advantage:

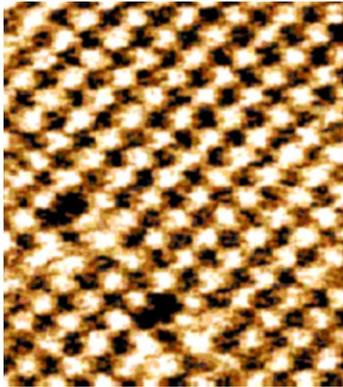
- Virtually eliminated lateral forces.
- Allows more gentle imaging.
- Applicable for soft samples.

Atomic Force Microscopy

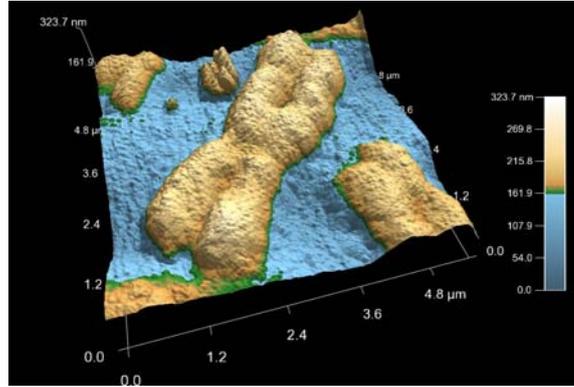
DME - Danish Micro Engineering A/S
DME Nanotechnologie GmbH
<http://www.dme-spm.com>

Manufacturer of Scanning Probe Microscopes
since 1989

Atomic Force Microscopy Images

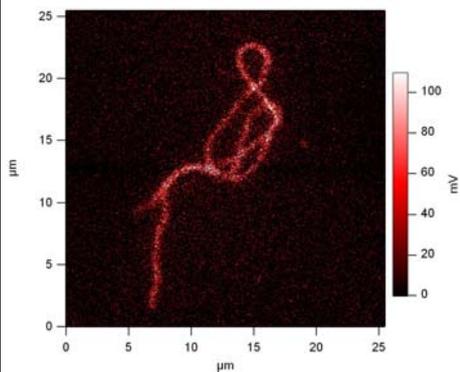


NaCl crystal surface

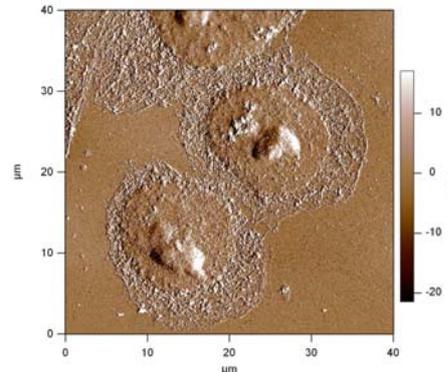


Human metaphase chromosomes

Atomic Force Microscopy Images



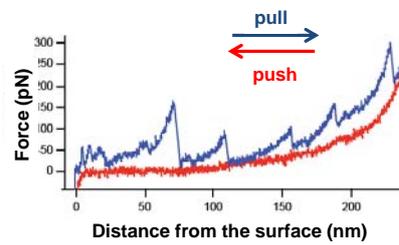
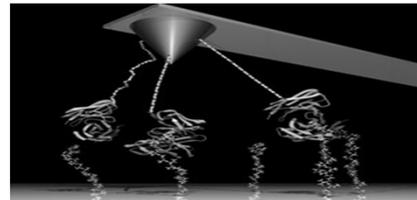
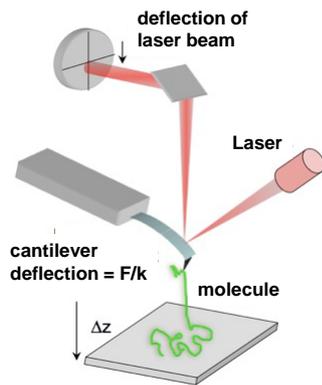
„The thinker“
a single actin polimer



HeLa cells on glass

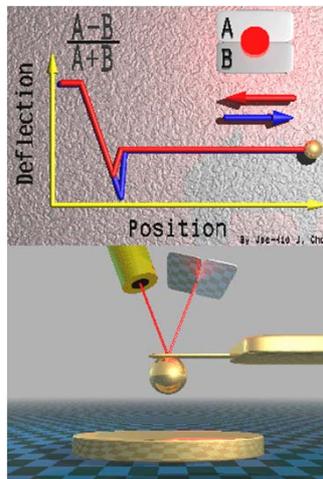
Atomic Force Microscopy

Force spectroscopy: Force-distance traces registered upon push-pull cycles of the AFM tip (movement in Z direction)
 ~10 pN sensitivity

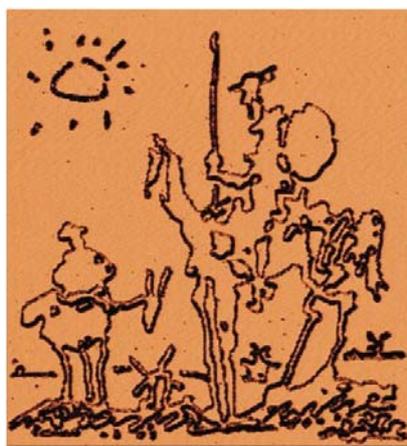


Atomic Force Microscopy

Force spectroscopy:



Thank you for your attention!



Pablo Picasso: "Don Quixote"
polikarbonát felszínbe rajzolva

1 μ m