

Low Dimensional Systems and Nanostructures

Ion Errea

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1. Length scales and low dimensional systems
2. Electronic states in confined systems and low dimensions
3. Response properties of the electron system in reduced dimensions

1. Length scales and low dimensional systems

Outline

1.1 Nano, meso, and macro scales

1.2 Dimensionality

- Chemical bonding approach
- Physical length scales approach
 - De Broglie length, Fermi wave-length
 - Mean free path

1.3 Transport regimes

1.4 Examples of low-dimensional systems

- 2D: transition metal dichalcogenides, semiconducting chalcogenides, layered halogen compounds, graphene, FeSe
- 1D: polymers, inorganic chains, nanotubes, metallic wires, nanowires on surface
- 0D: fullerenes, quantum dots, atomic clusters, synthetic nanocrystals

1. Length scales and low dimensional systems

Outline

1.5 Fabrication and characterization techniques

- Nanolithography
- Atomic Force Microscopy (AFM)
- Scanning Tunneling Microscope (STM)
- Molecular Beam Epitaxy (MBE)

1.6 Exercise

1. Length scales and low dimensional systems

1.1 Nano, meso, and macro scales

Macro scale

- The scale of our everyday life
- The properties of materials are defined by physical bulk properties:
 - Color
 - Density
 - Stiffness
 - Sound velocity
 - Bending rigidity
 - ...
- Classical mechanics are enough

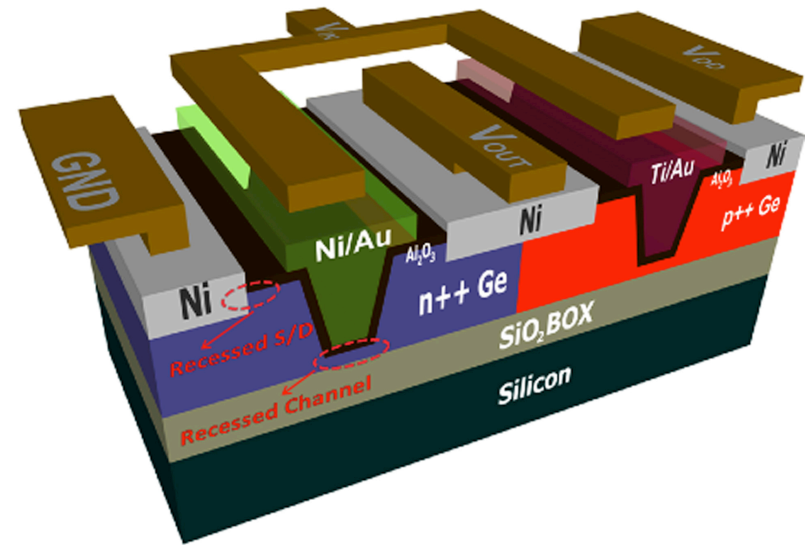


1. Length scales and low dimensional systems

1.1 Nano, meso, and macro scales

Meso scale

- The scale in between the bulk and the atomic limits
- Mesoscopic physics study the properties of small condensed objects
- Bulk properties of materials may be used and classical mechanics may be used
- Quantum mechanical effects appear and may be important

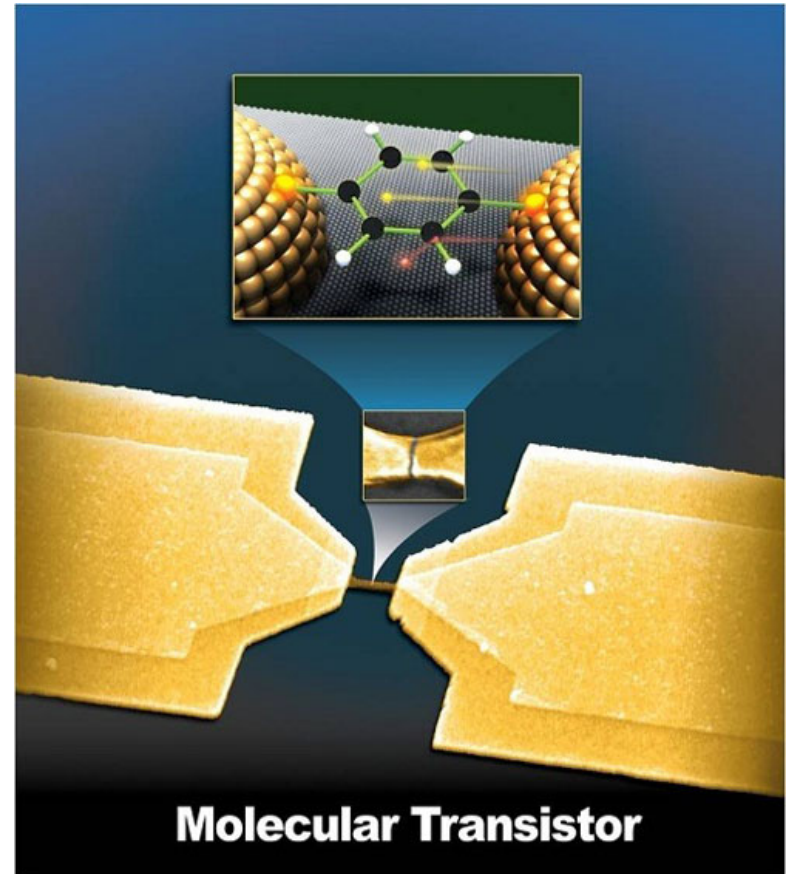


1. Length scales and low dimensional systems

1.1 Nano, meso, and macro scales

Nano scale

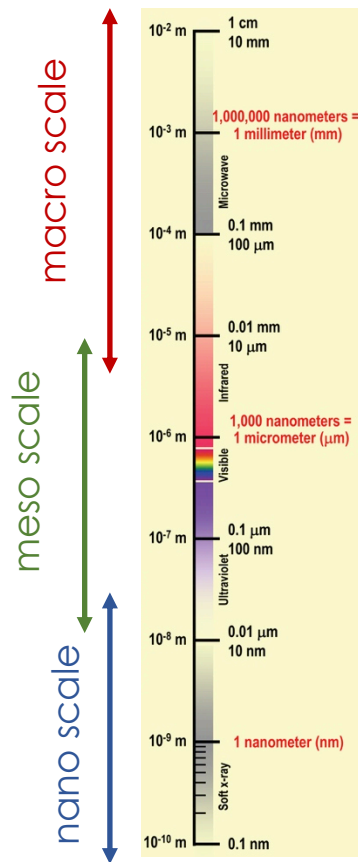
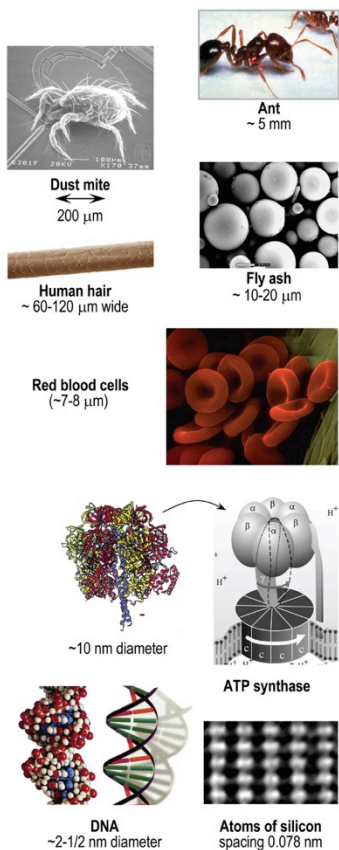
- The scale of the atomic limit
- Bulk properties make no sense
- The quantum nature of the electrons is crucial
- Quantum mechanical description



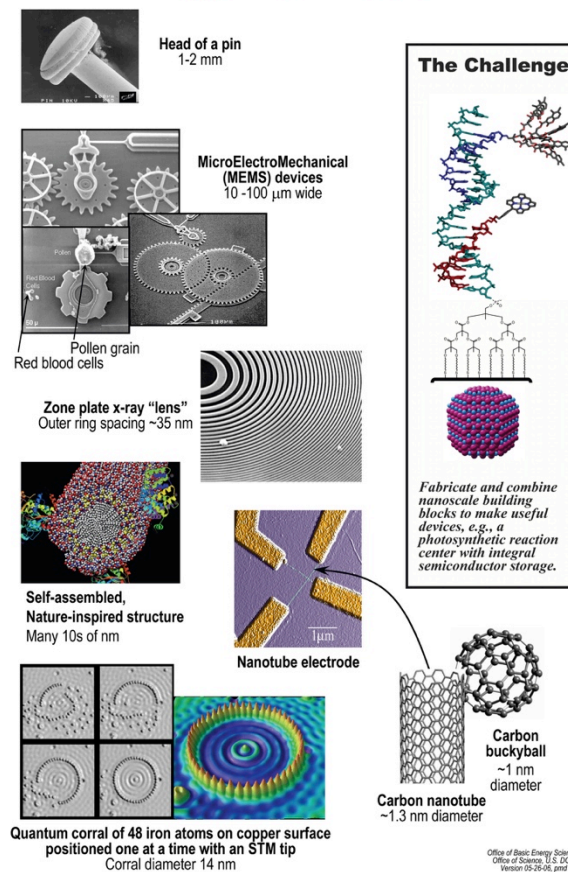
1. Length scales and low dimensional systems

1.1 Nano, meso, and macro scales

Natural things



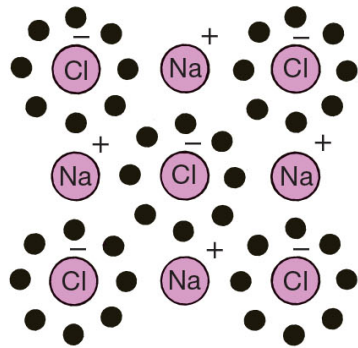
Man-made things



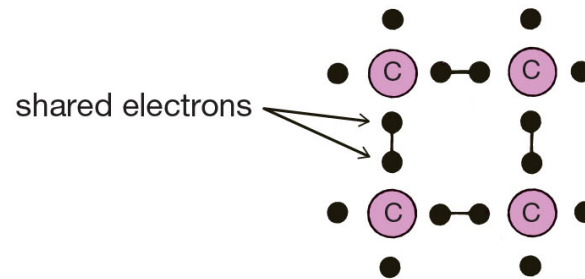
1. Length scales and low dimensional systems

1.2 Dimensionality

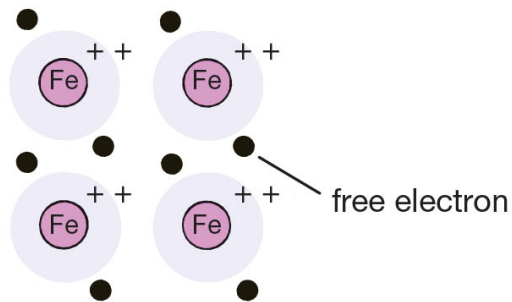
Chemical bonding approach



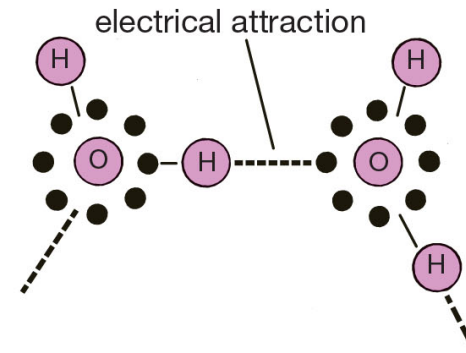
ionic bonding
electron transferred from Na to Cl



covalent bonding
atoms share electrons



metallic bonding
ions surrounded by free electrons



molecular bonding
weak electrical attraction binds molecules

1. Length scales and low dimensional systems

1.2 Dimensionality

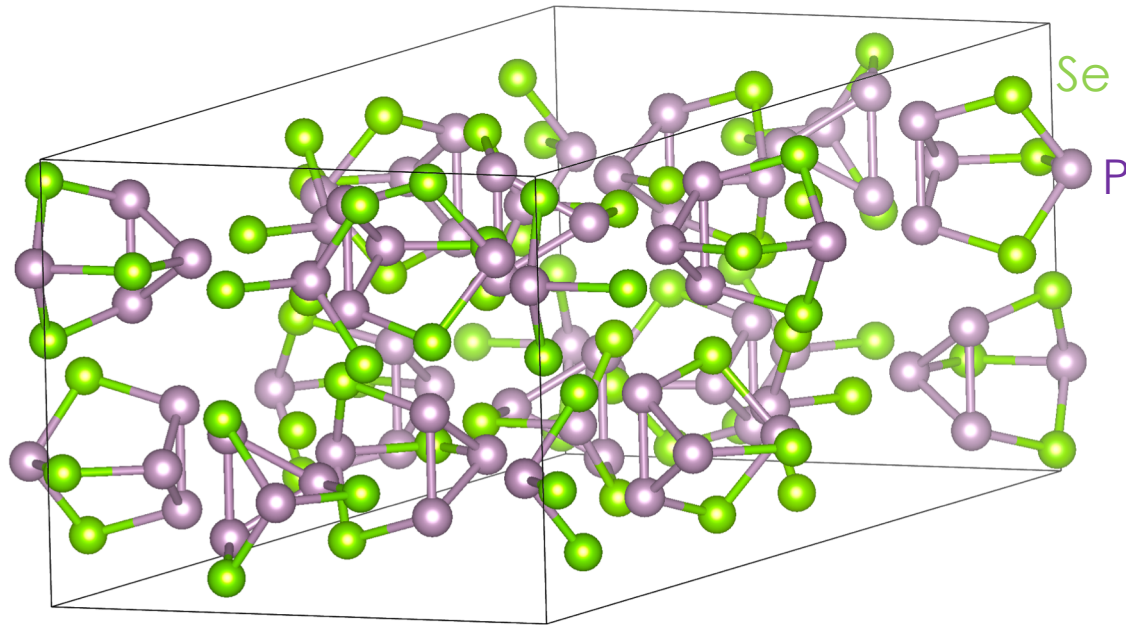
Chemical bonding approach

- In a given compound there might be units strongly bonded by covalent bonds
- These units interact among themselves by weak forces, e.g. hydrogen bonds, Van der Waals forces.
- Depending on the dimension of the unit: 0D, 1D, 2D, 3D systems

1. Length scales and low dimensional systems

1.2 Dimensionality

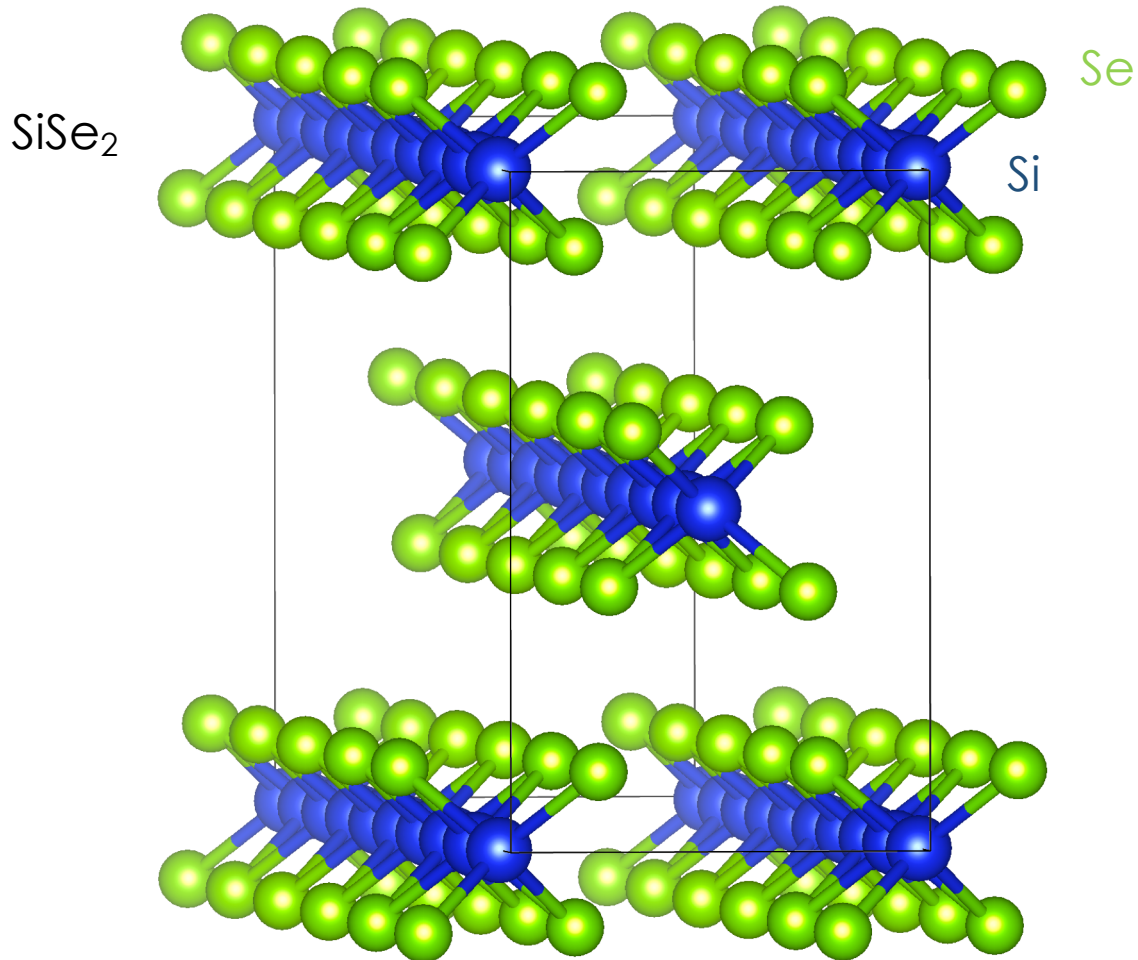
Chemical bonding approach: 0D



1. Length scales and low dimensional systems

1.2 Dimensionality

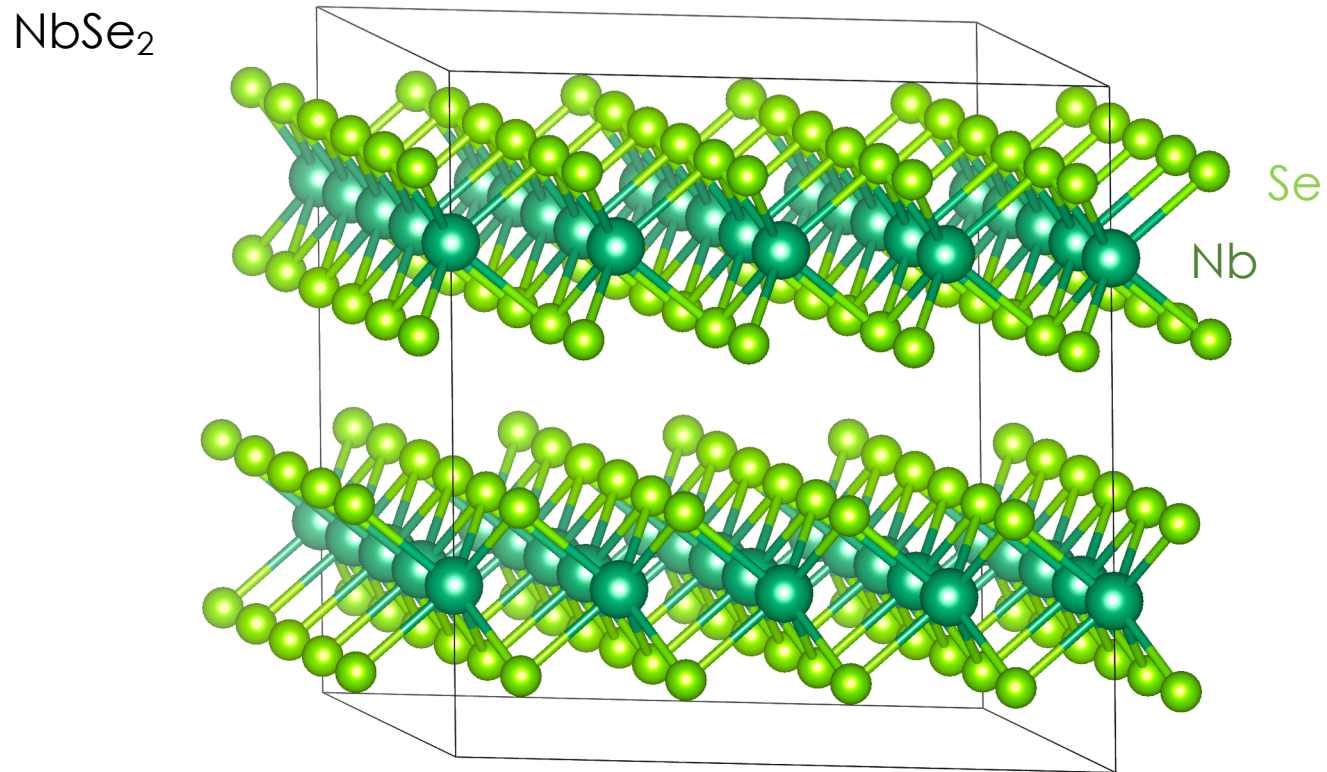
Chemical bonding approach: 1D



1. Length scales and low dimensional systems

1.2 Dimensionality

Chemical bonding approach: 2D

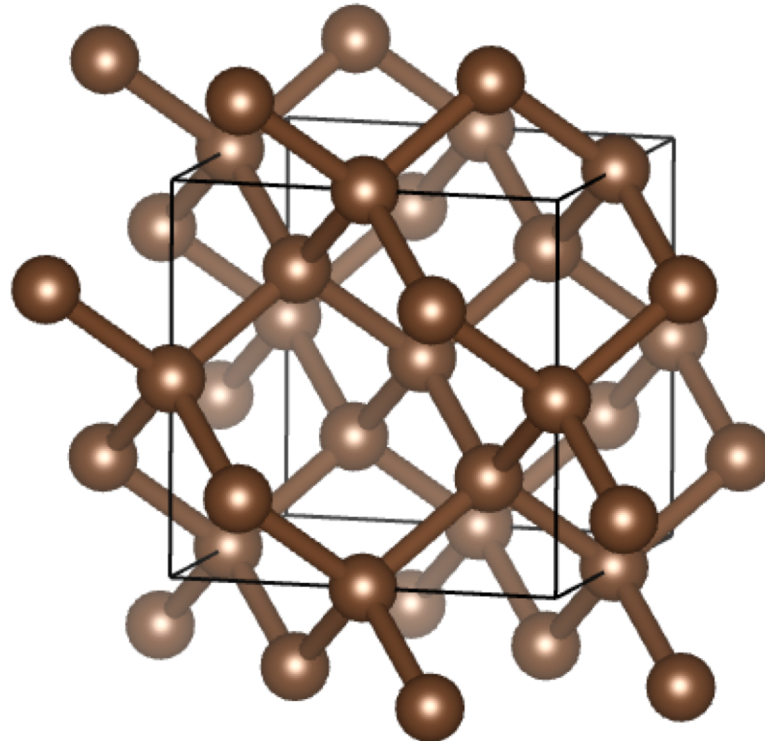


1. Length scales and low dimensional systems

1.2 Dimensionality

Chemical bonding approach: 3D

Diamond



C

1. Length scales and low dimensional systems

1.2 Dimensionality

Van der Waals forces

- Intermolecular forces, or forces between strongly bonded covalent units
 - **Debye forces:** Dipole-dipole interactions
 - **Hydrogen bonds:** Dipole-dipole interactions with hydrogen
 - **London dispersion forces:** Instantaneous dipole-induced dipole interactions in non-polar materials
 - Dipole-induced dipole interactions

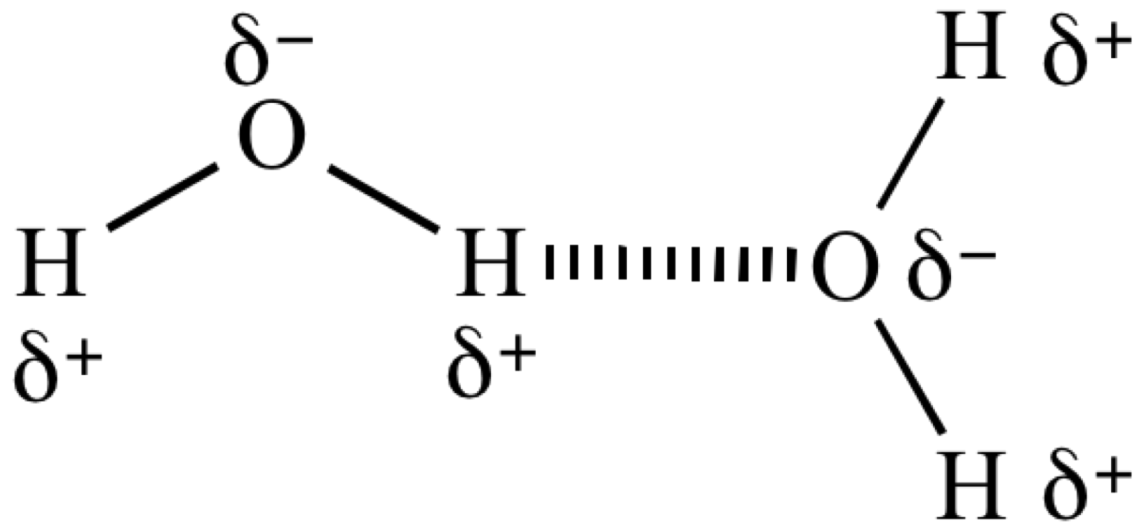
1. Length scales and low dimensional systems

1.2 Dimensionality

Van der Waals forces

- **Debye forces (hydrogen bonds):**
Dipole-dipole interactions

$$F \sim r^{-3}$$



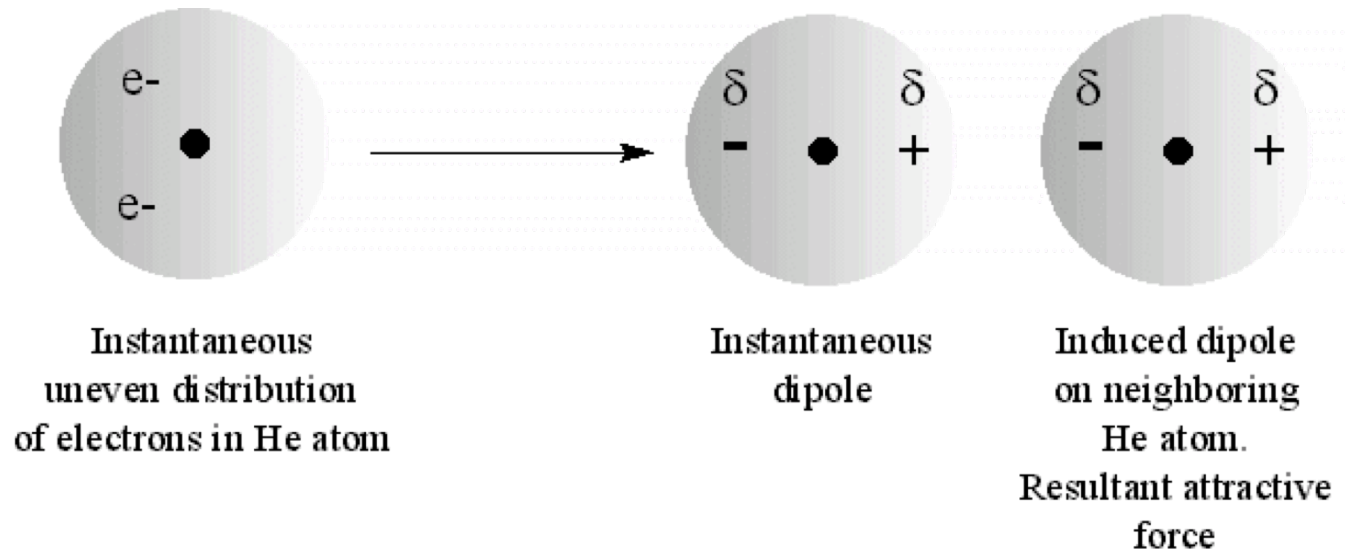
1. Length scales and low dimensional systems

1.2 Dimensionality

Van der Waals forces

- **London dispersion forces:**
Instantaneous dipole-induced dipole interactions in non-polar materials

$$F \sim r^{-6}$$



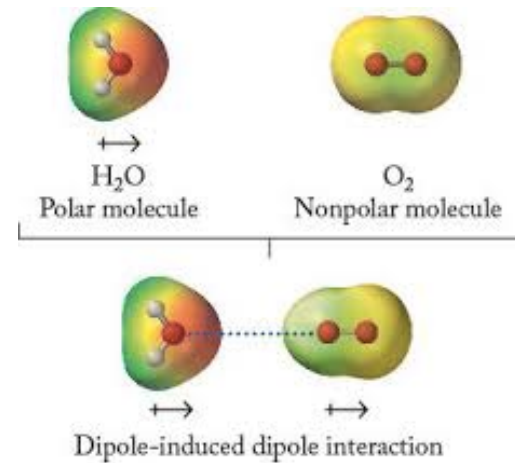
1. Length scales and low dimensional systems

1.2 Dimensionality

Van der Waals forces

- Dipole-induced dipole interactions

$$F \sim r^{-6}$$

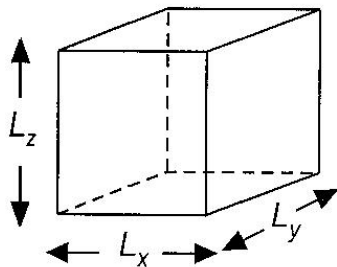


1. Length scales and low dimensional systems

1.2 Dimensionality

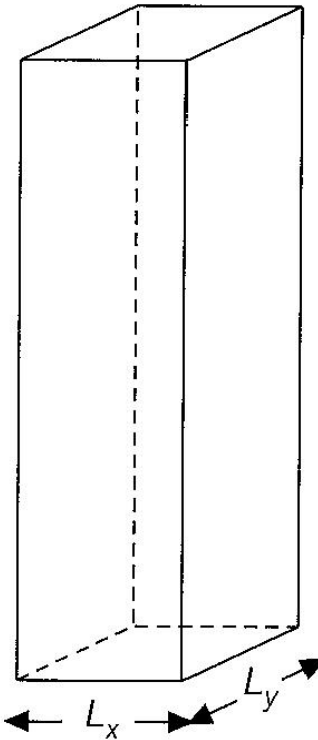
Physical length scales approach

- Based on size dependence of a physical property, e.g. electronic or phonon transport
- Reduced dimension if the dimension of the sample is smaller than a characteristic length L_0



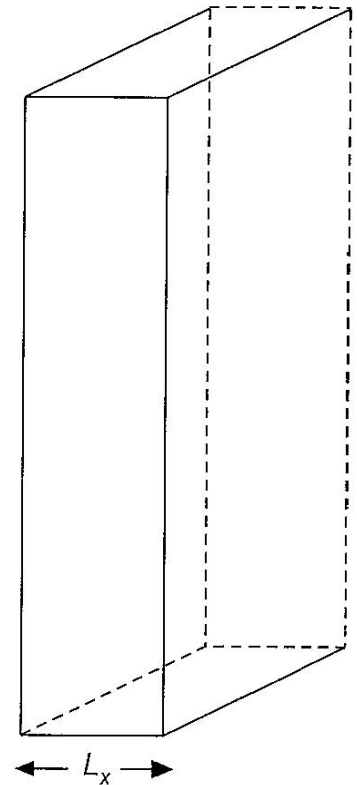
$$L_x, L_y, L_z < L_0$$

0D: Quantum dot



$$L_x, L_y < L_0$$

1D: Quantum wire



$$L_x < L_0$$

2D: Quantum well

1. Length scales and low dimensional systems

1.2 Dimensionality

Physical length scales approach:

- **De Broglie wavelength:**

The (wave)length at which a particle with momentum p shows wave-like (quantum mechanical) behavior

$$\lambda = h/p$$

$$\omega = ck$$

- **Fermi wavelength:**

The (wave)length at which an electron in a metal with energy E_F (Fermi energy) shows wave-like (quantum mechanical) behavior

$$\lambda_F = \sqrt{\frac{h^2}{2mE_F}}$$

$$v_F = \frac{h}{\lambda_F m}$$

1. Length scales and low dimensional systems

1.2 Dimensionality

Physical length scales approach:

Element	E_F (eV)	v_F (10^6 m/s)	λ_F (Å)
Li	4.74	1.29	5.65
Be	7.08	1.28	5.69
K	2.12	0.86	8.47
Pb	9.47	1.83	3.98

1. Length scales and low dimensional systems

1.2 Dimensionality

Physical length scales approach:

- **Mean free path:** L_m

The average distance an electron travels before it experiences a scattering process that changes its initial momentum

- **Elastic scattering:**

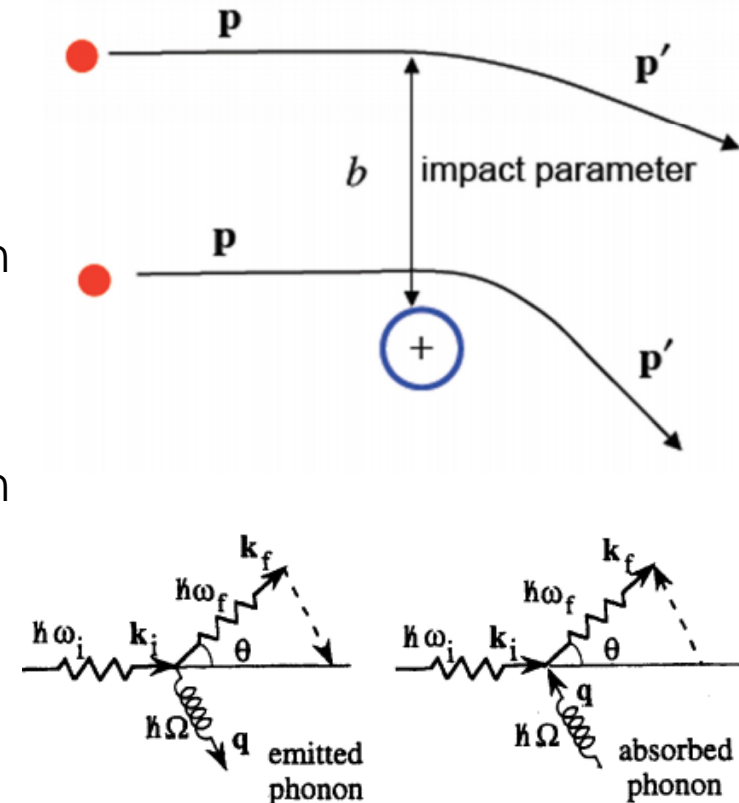
- When the energy of the electron is conserved
- Impurity scattering mainly

- **Inelastic scattering:**

- When the energy of the electron is not conserved
- Electron-electron and electron-phonon scattering mainly

It is related to the relaxation time τ , for a material with carrier velocity v .

$$L_m = v\tau$$



1. Length scales and low dimensional systems

1.2 Dimensionality

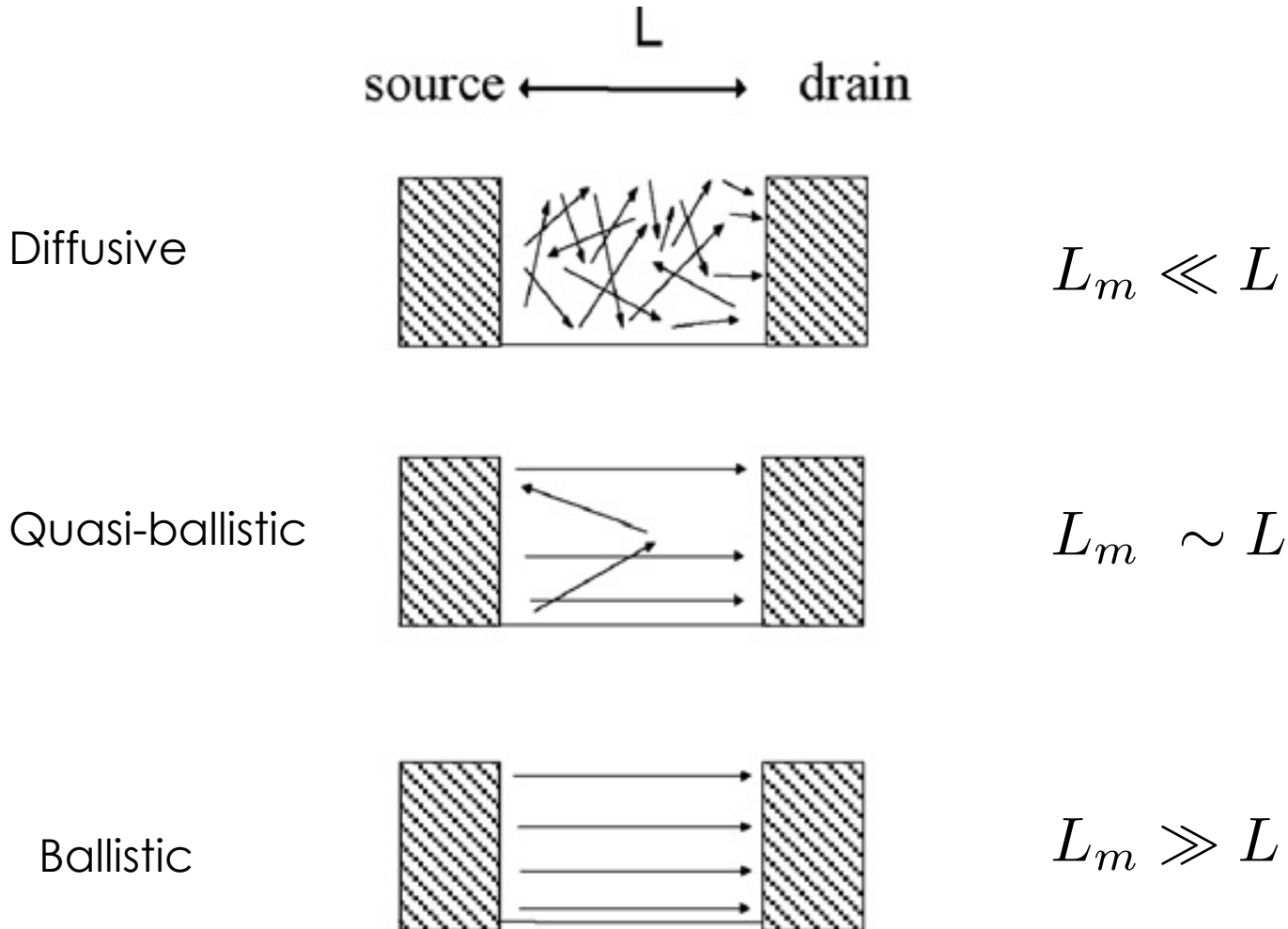
Physical length scales approach:

1 mm	Mean free path in the quantum Hall regime
100 μm	Mean free path / Phase-relaxation length in high mobility semiconductors at $T < 4$ K
10 μm	
1 μm	Commercial semiconductor devices (1990)
100 nm	
10 nm	de Broglie wavelength in semiconductors Mean free path in polycrystalline metal films
1 nm	
1 \AA	de Broglie wavelength in metals Distance between atoms

1. Length scales and low dimensional systems

1.3 Transport regimes

Transport through a constriction:



1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

2D: Transition metal dichalcogenides (TMDs)

MX_2
M = Transition-metal
X = Chalcogen

The periodic table is shown with the following elements highlighted:

- Transition metals (blue bracket):** Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Hf, Ta, W, Re, Ir, Pt.
- Chalcogens (orange arrow):** S, Se, Te.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

Transition metal

Chalcogen

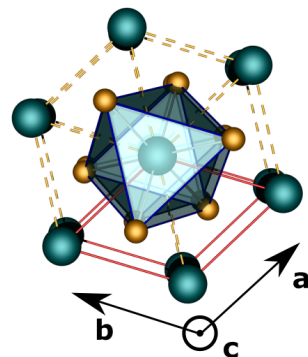
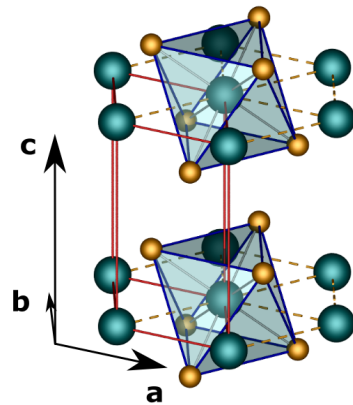
1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

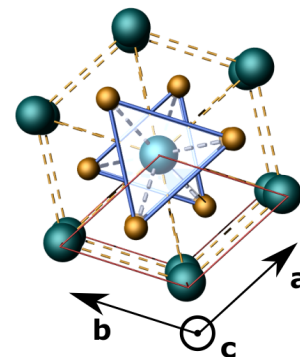
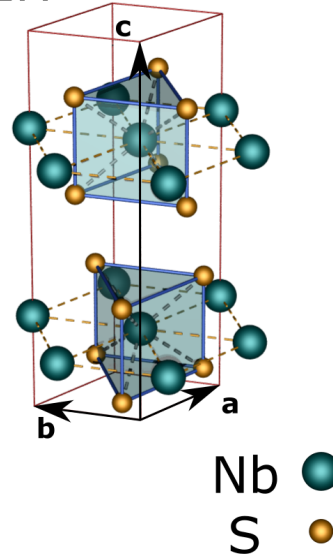
2D: Transition metal dichalcogenides (TMDs)

Crystal structures

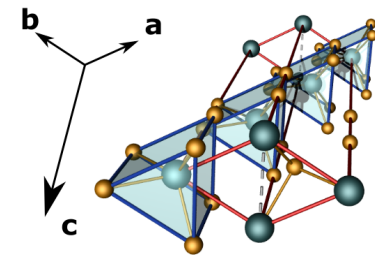
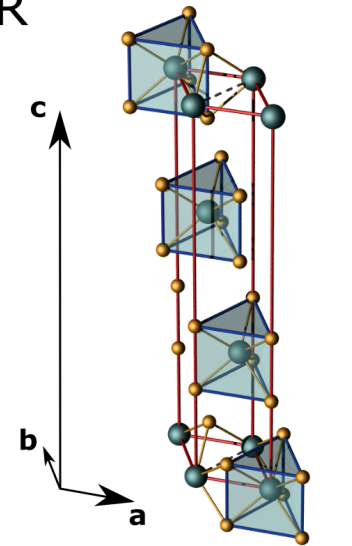
1T



2H



3R

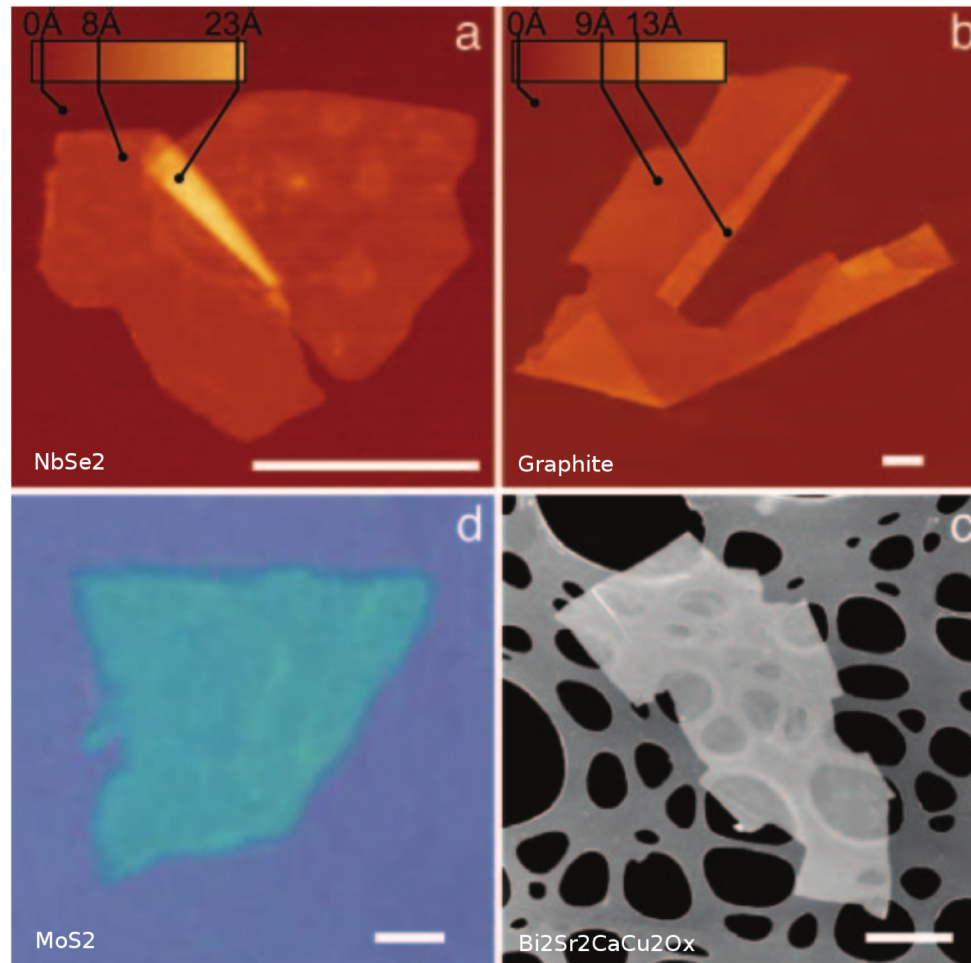


1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

2D: Transition metal dichalcogenides (TMDs)

Exist in the 2D limit

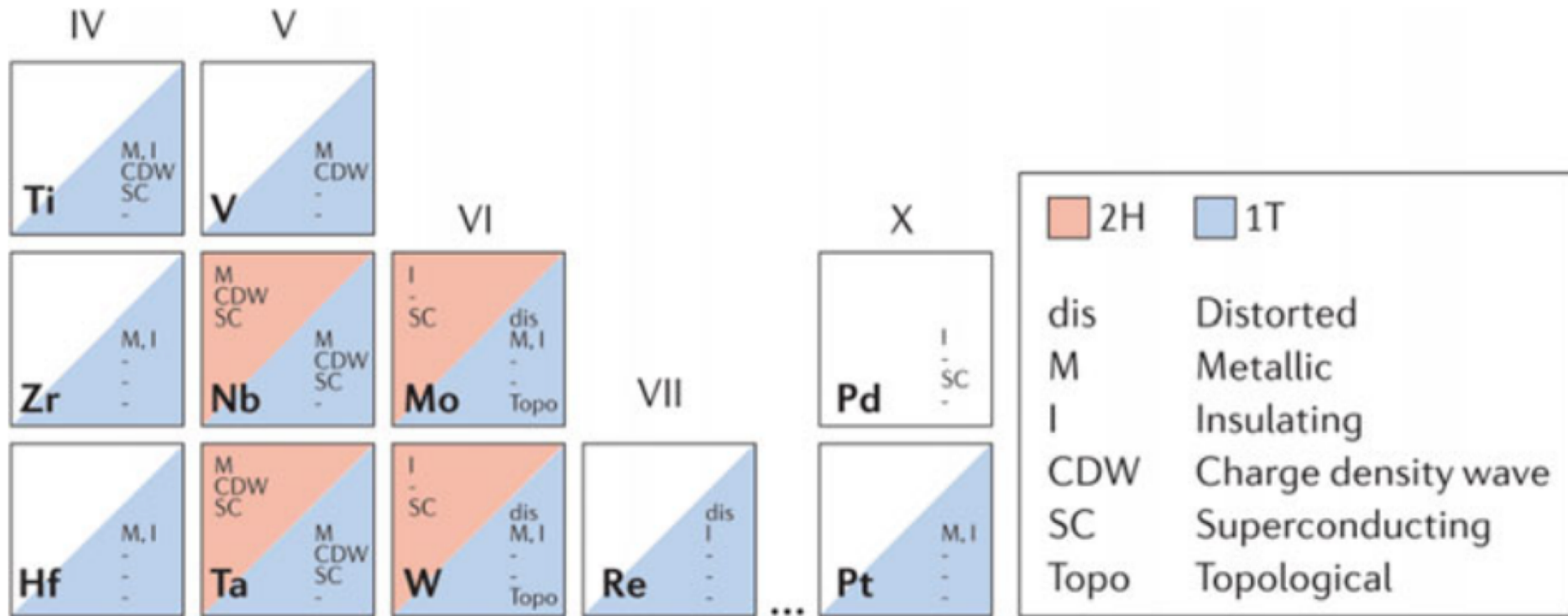


1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

2D: Transition metal dichalcogenides (TMDs)

Properties of TMDs

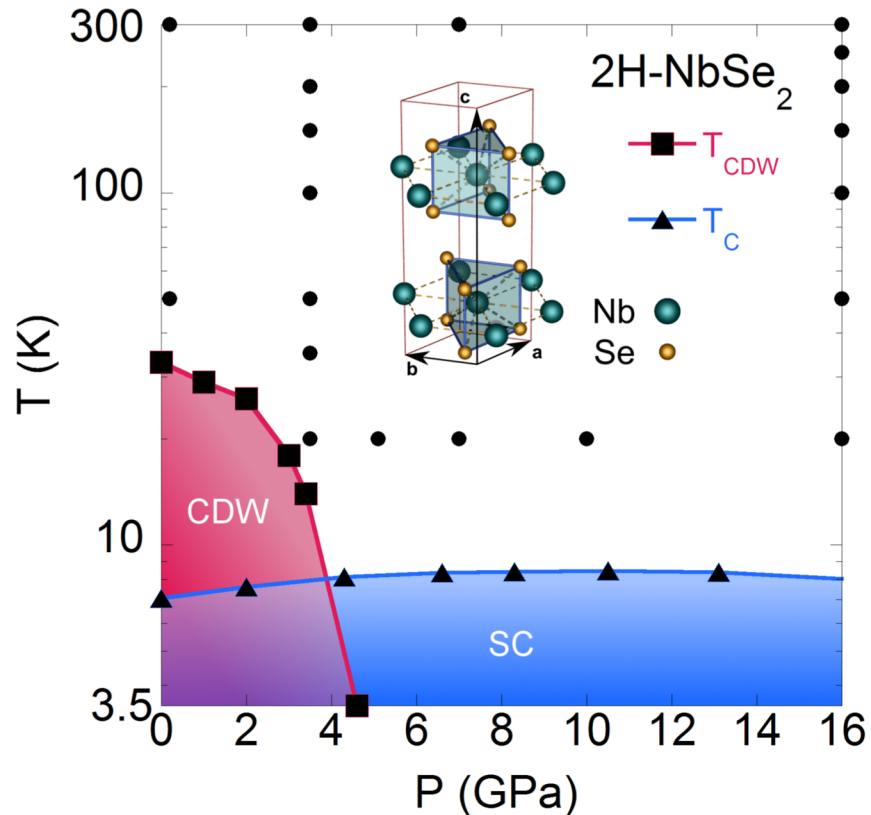


1. Length scales and low dimensional systems

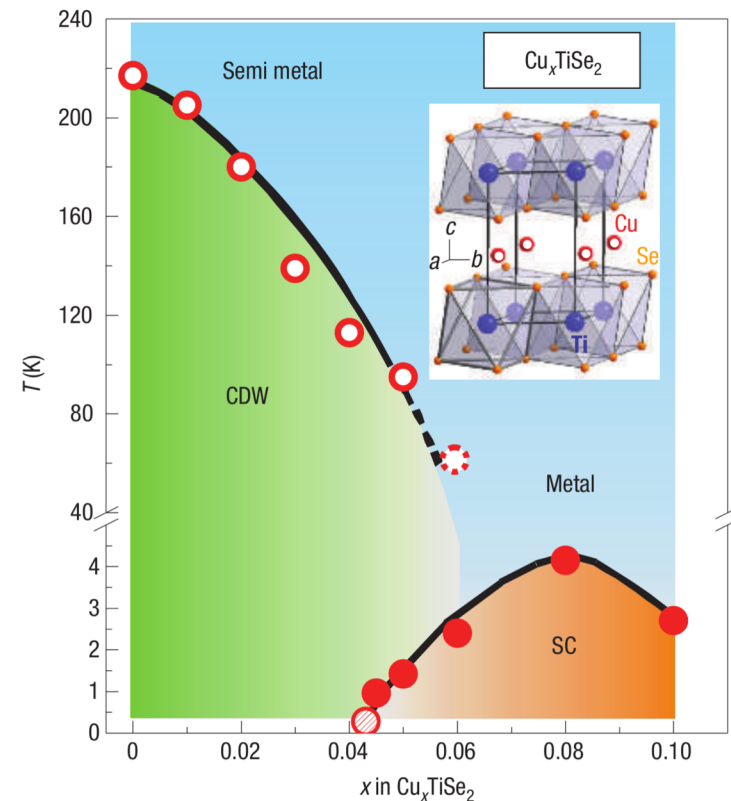
1.4 Examples of low-dimensional systems

2D: Transition metal dichalcogenides (TMDs)

Metallic TMDs phase diagrams with charge-density waves (CDWs) and superconductivity (SC)



Leroux *et al.*, PRB (2015)



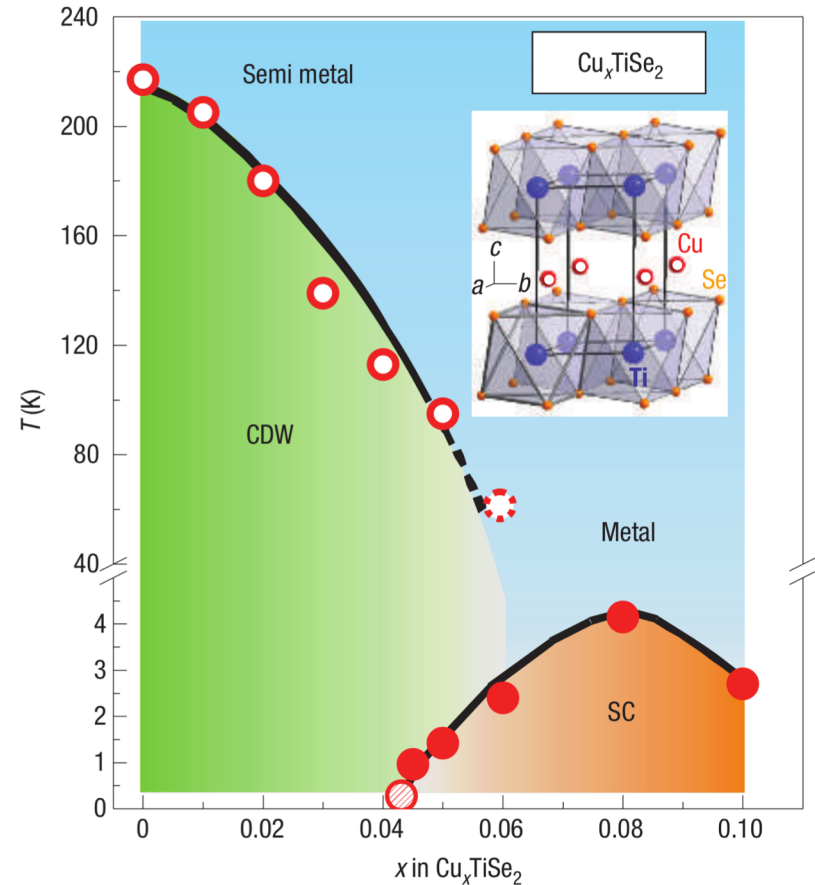
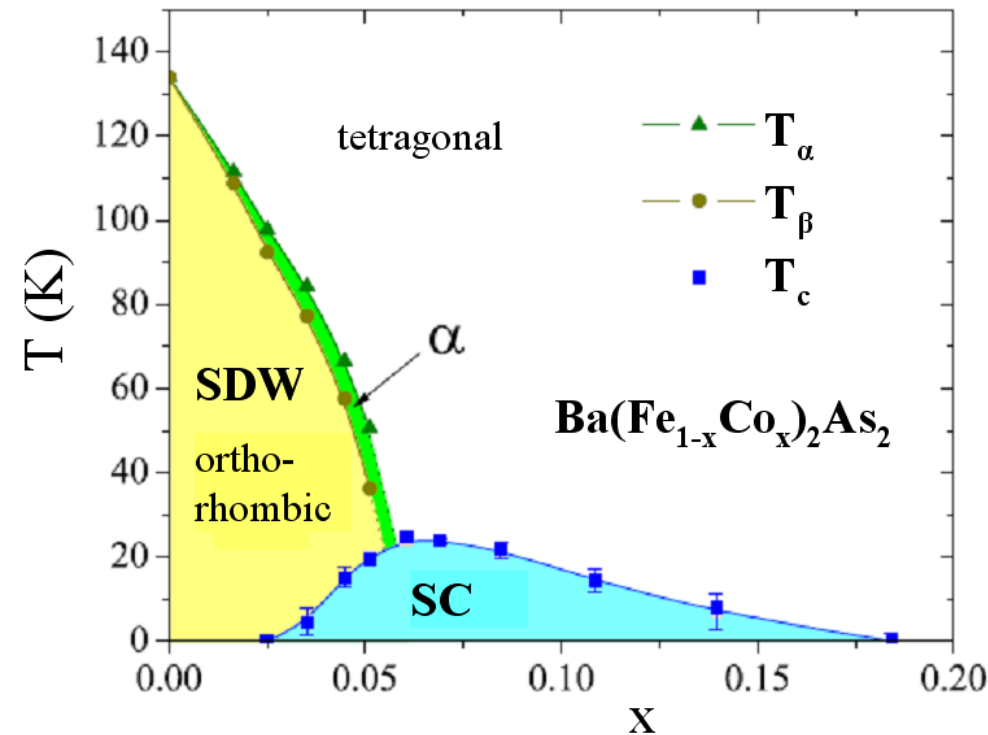
Morosan *et al.*, Nat. Phys. (2006)

1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

2D: Transition metal dichalcogenides (TMDs)

Similar phase diagram to the high-temperature superconductors

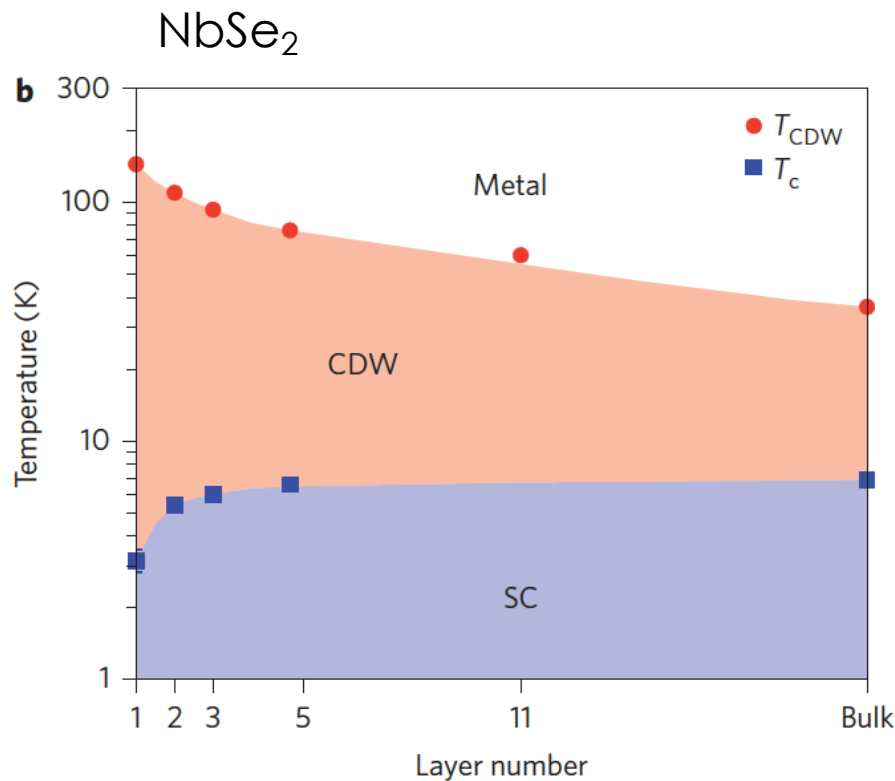


1. Length scales and low dimensional systems

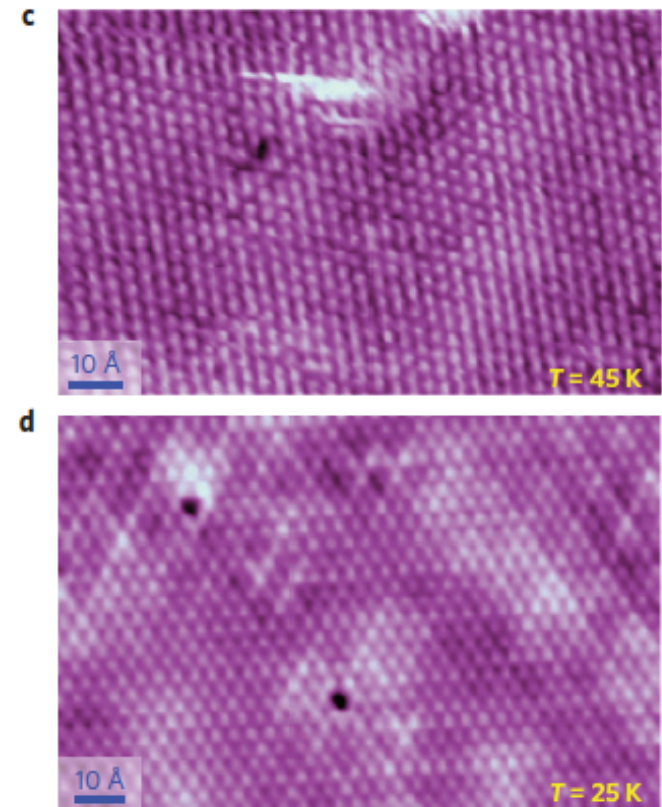
1.4 Examples of low-dimensional systems

2D: Transition metal dichalcogenides (TMDs)

Contradicting results about the CDW temperature in the 2D limit



Xi *et al.*, Nat. Nanotech. (2015)

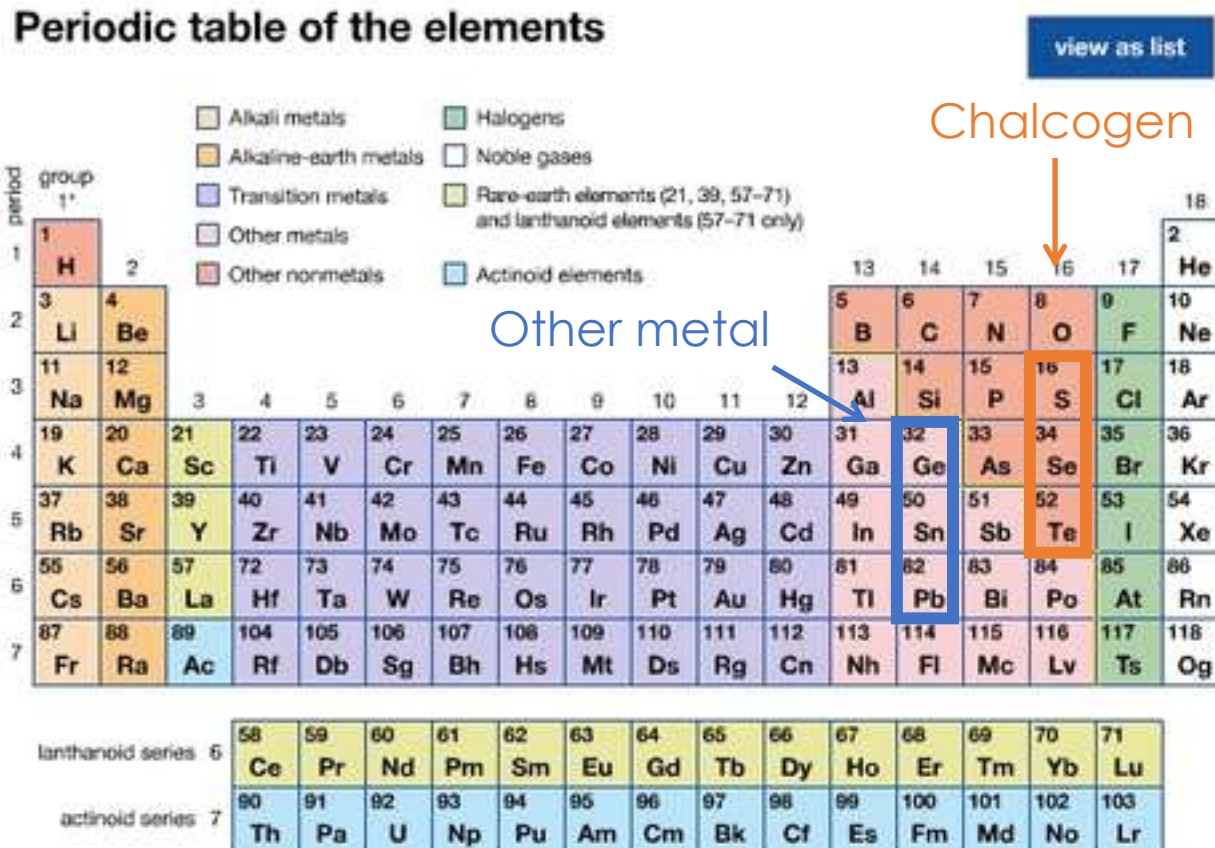


Ugeda *et al.*, Nat. Phys. (2015)

1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

2D: Semiconducting chalcogenides



*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

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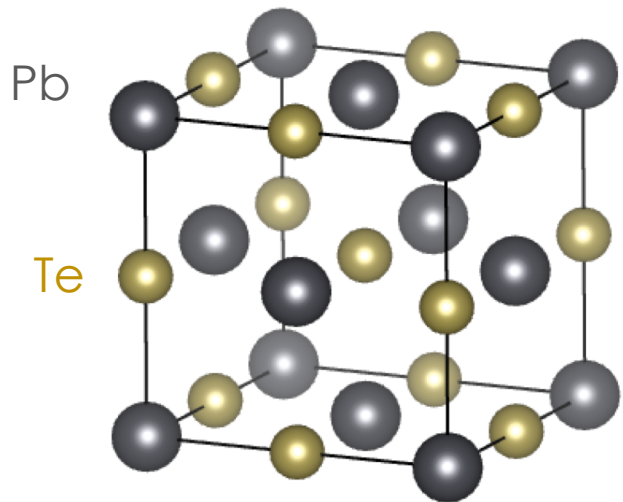
1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

2D: Semiconducting chalcogenides

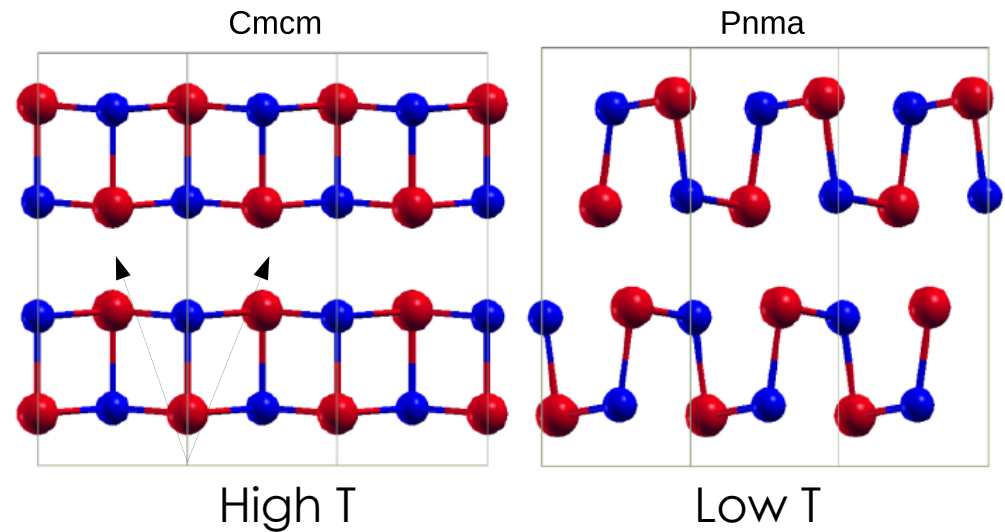
Crystal structures and phase diagrams

PbTe



Rock-salt structure

SnSe



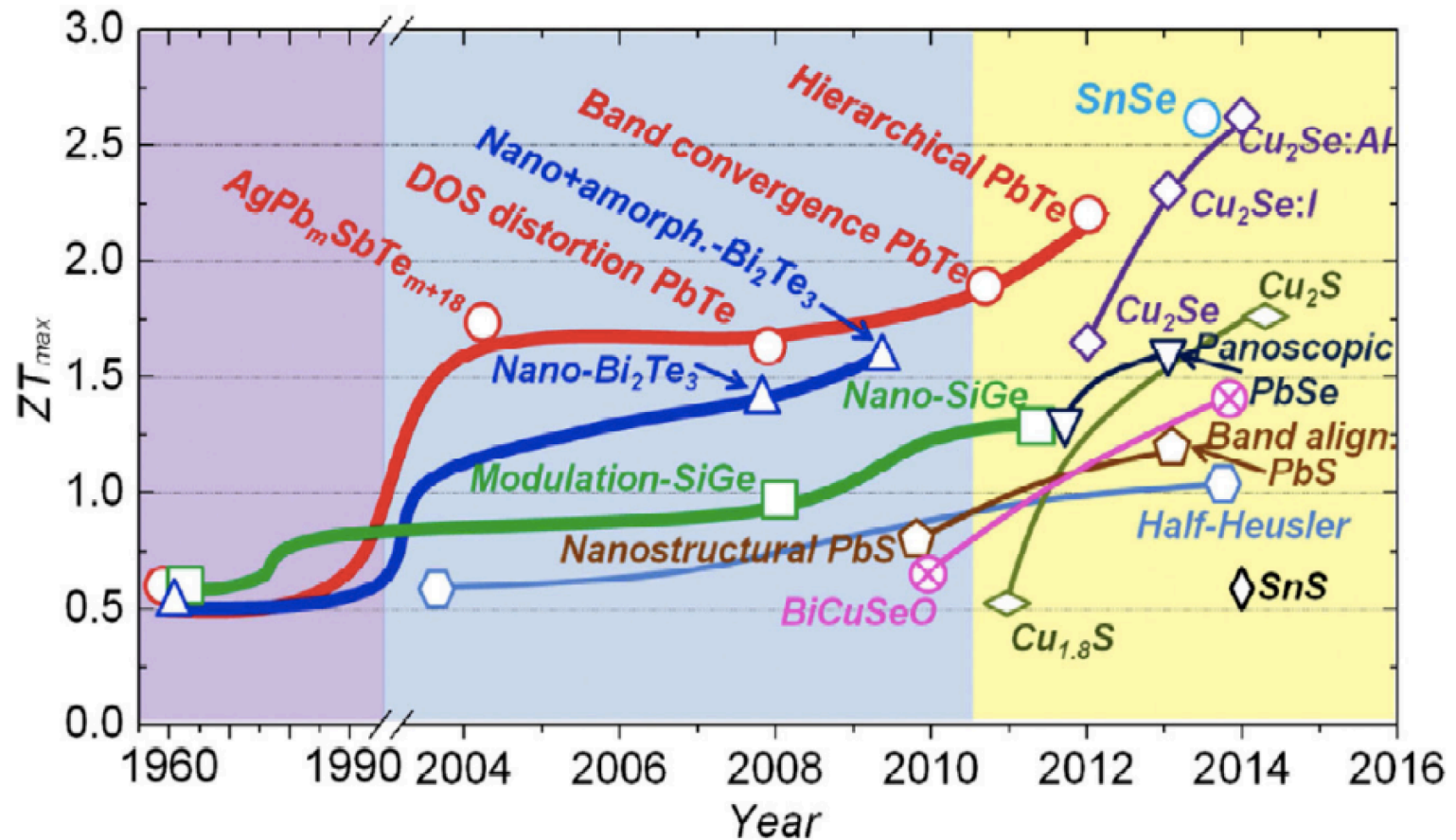
Distortions of rock-salt structure

1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

2D: Semiconducting chalcogenides

Very good thermoelectric materials



1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

2D: Semiconducting chalcogenides

Synthesized in the 2D limit and possible ferroelectricity

REPORTS

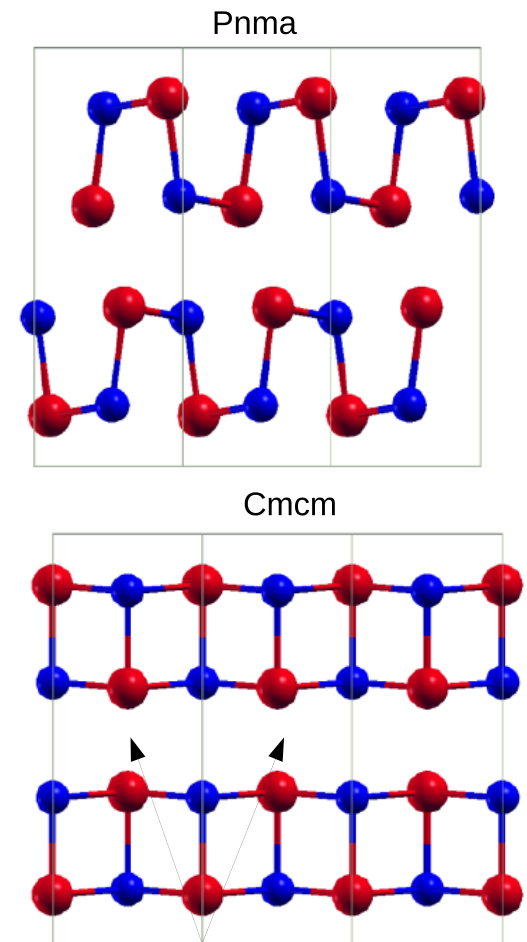
FERROELECTRICITY

Discovery of robust in-plane ferroelectricity in atomic-thick SnTe

Kai Chang,^{1,2*} Junwei Liu,^{3,1,2*} Haicheng Lin,^{1,2} Na Wang,^{1,2} Kun Zhao,^{1,2}
Anmin Zhang,⁴ Feng Jin,⁴ Yong Zhong,^{1,2} Xiaopeng Hu,^{1,2} Wenhui Duan,^{1,2}
Qingming Zhang,^{4,5} Liang Fu,³ Qi-Kun Xue,^{1,2} Xi Chen,^{1,2} Shuai-Hua Ji^{1,2,6}†

Stable ferroelectricity with high transition temperature in nanostructures is needed for miniaturizing ferroelectric devices. Here, we report the discovery of the stable in-plane spontaneous polarization in atomic-thick tin telluride (SnTe), down to a 1-unit cell (UC) limit. The ferroelectric transition temperature T_c of 1-UC SnTe film is greatly enhanced from the bulk value of 98 kelvin and reaches as high as 270 kelvin. Moreover, 2- to 4-UC SnTe films show robust ferroelectricity at room temperature. The interplay between semiconducting properties and ferroelectricity in this two-dimensional material may enable a wide range of applications in nonvolatile high-density memories, nanosensors, and electronics.

Science (2016)



1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

2D: Graphene

A. Geim

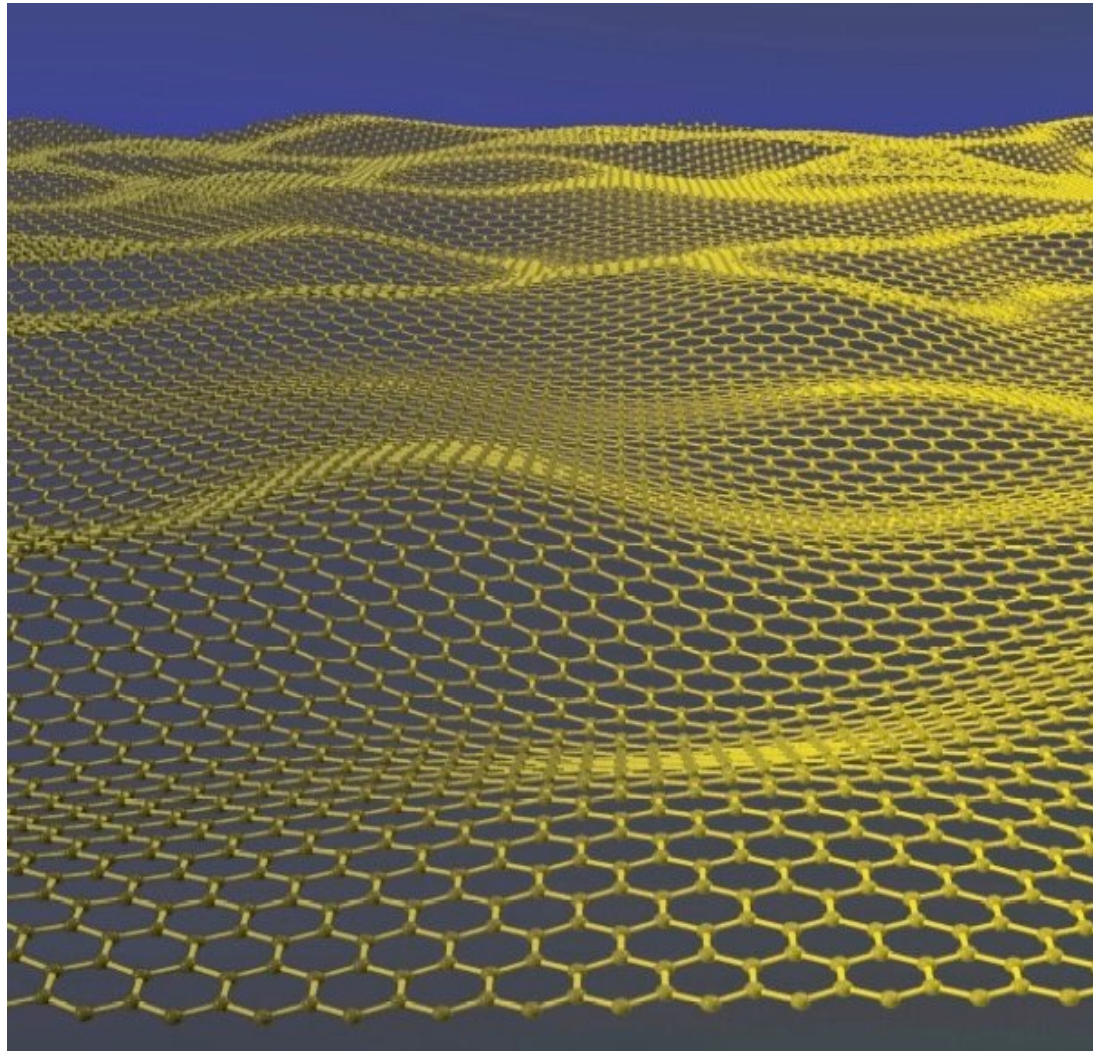


K. Novoselov



Nobel Prize Physics 2010

“for groundbreaking experiments regarding the two-dimensional material graphene ”

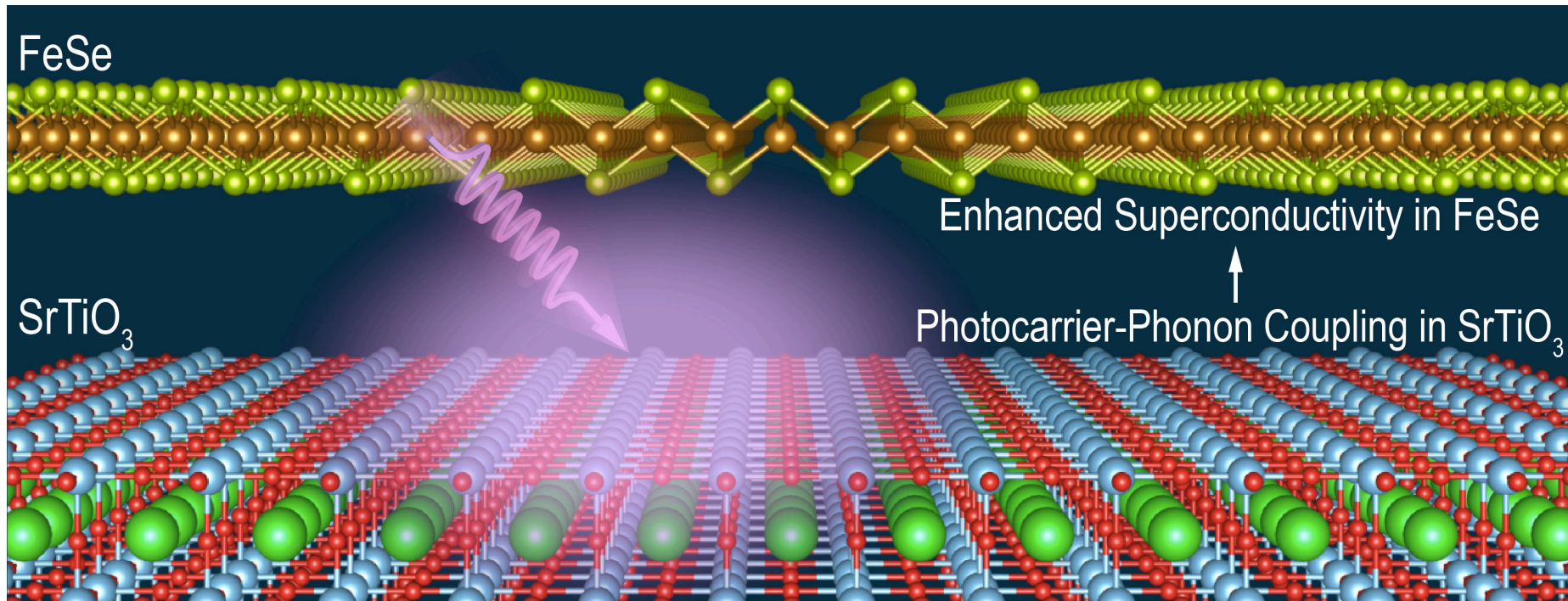


1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

2D: FeSe

- Superconductivity in bulk FeSe at 9K
- On monolayer on top of SrTiO₃ at 65-109K

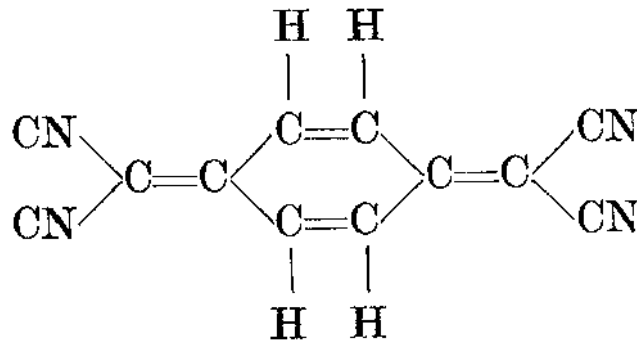


1. Length scales and low dimensional systems

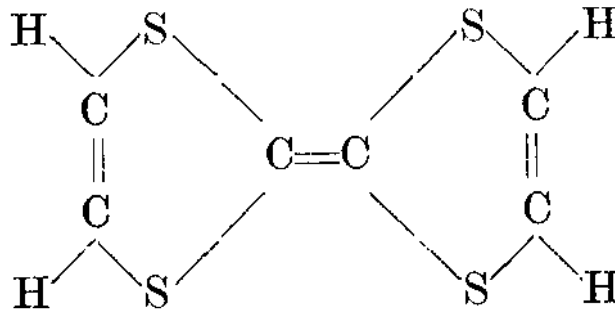
1.4 Examples of low-dimensional systems

1D: Polymers and organic molecules

TCNQ molecule



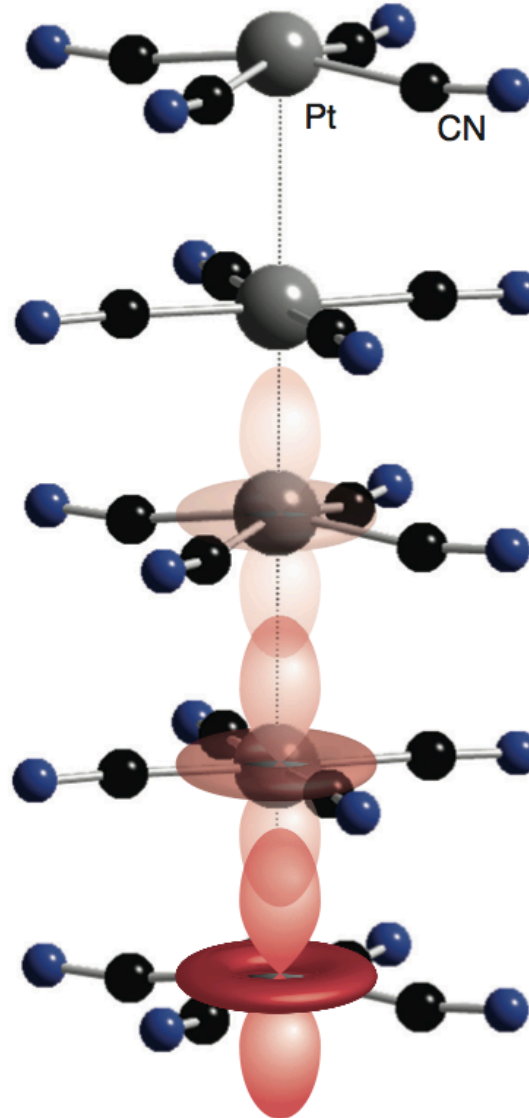
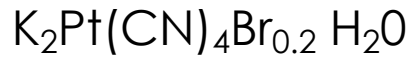
TTF molecule



1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

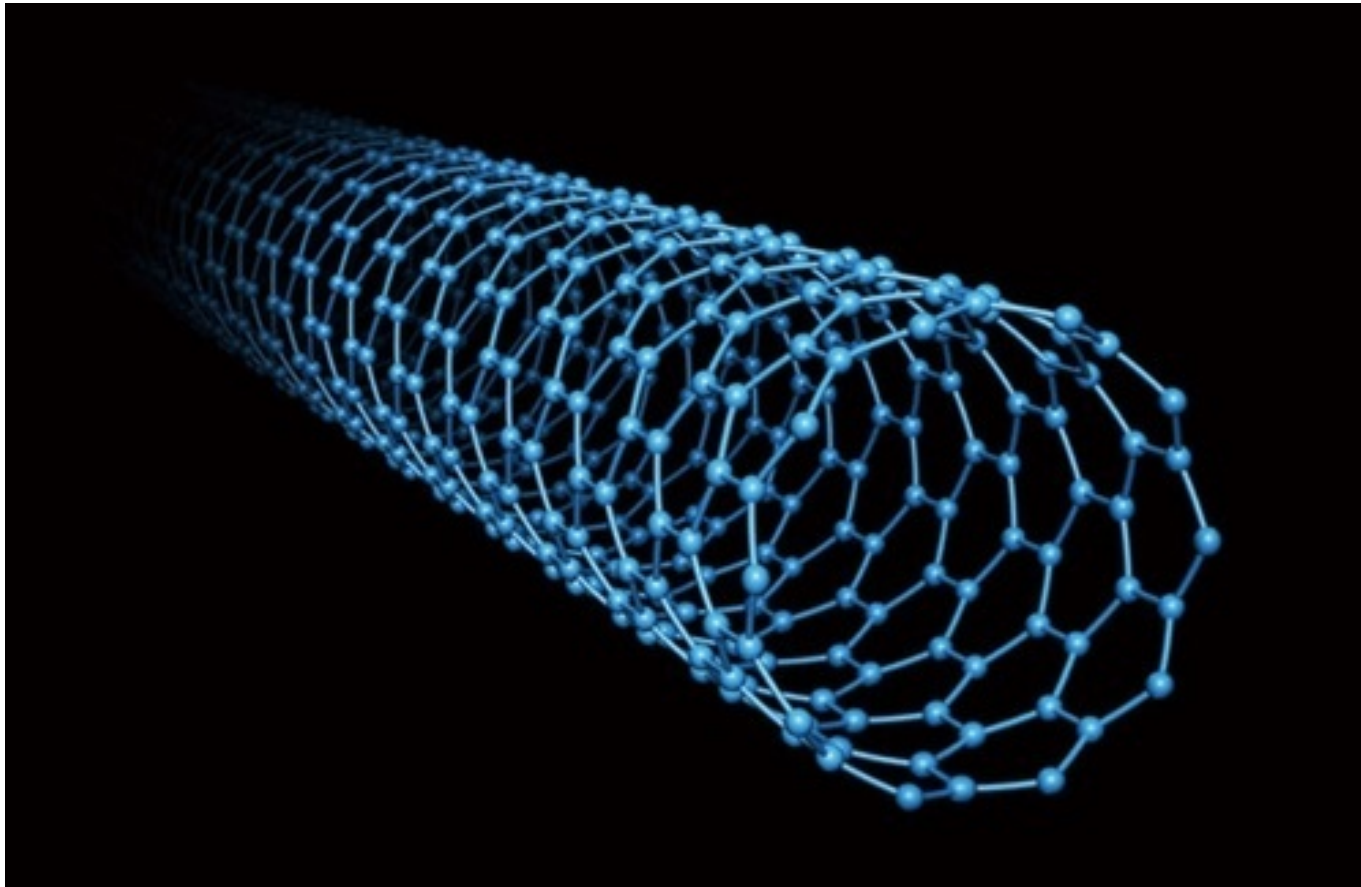
1D: Inorganic chains



1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

1D: Carbon nanotubes

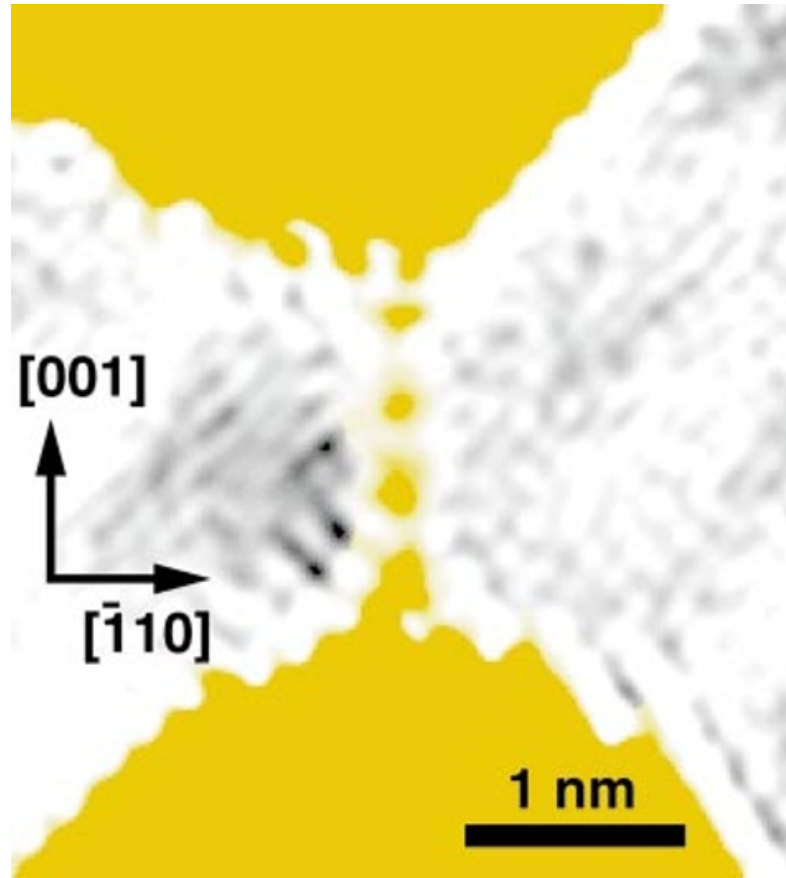


1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

1D: Metallic wires

Gold wires
produced with STM



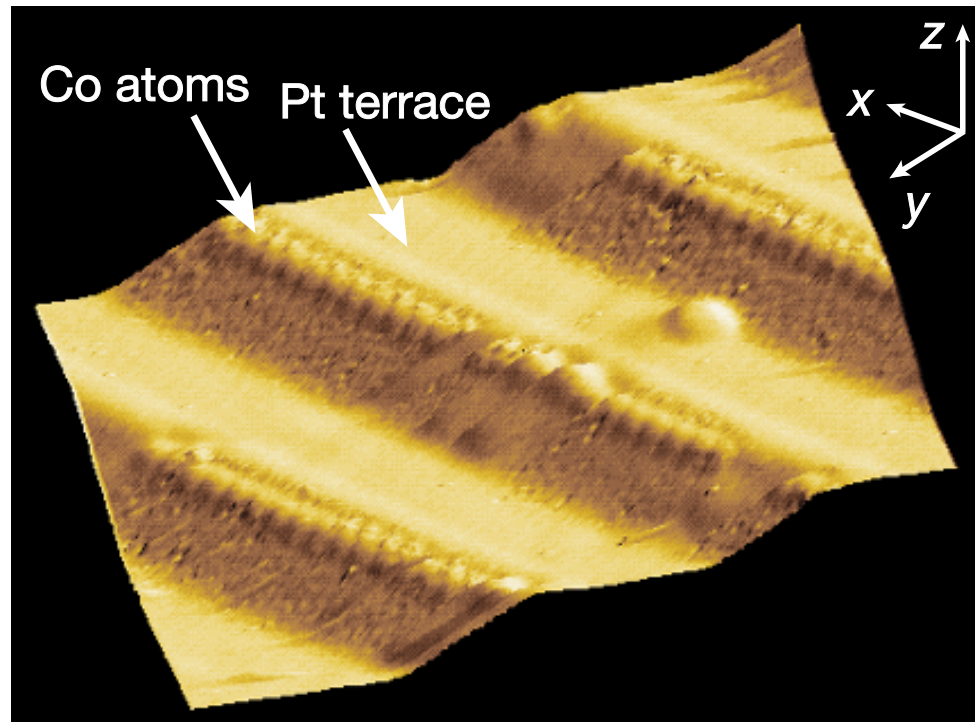
Ohnishi *et al.*, Nature (1998)

1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

1D: Nanowires on surfaces

Ferromagnetic
one-dimensional
monatomic metal
chains



Gambardella *et al.*, Nature (2002)

1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

1D: Overview of some properties

Table 6.3-1. Quasi-one-dimensional materials (SC: superconductor)

Tr: room temperature

GIC: graphite intercalation compound

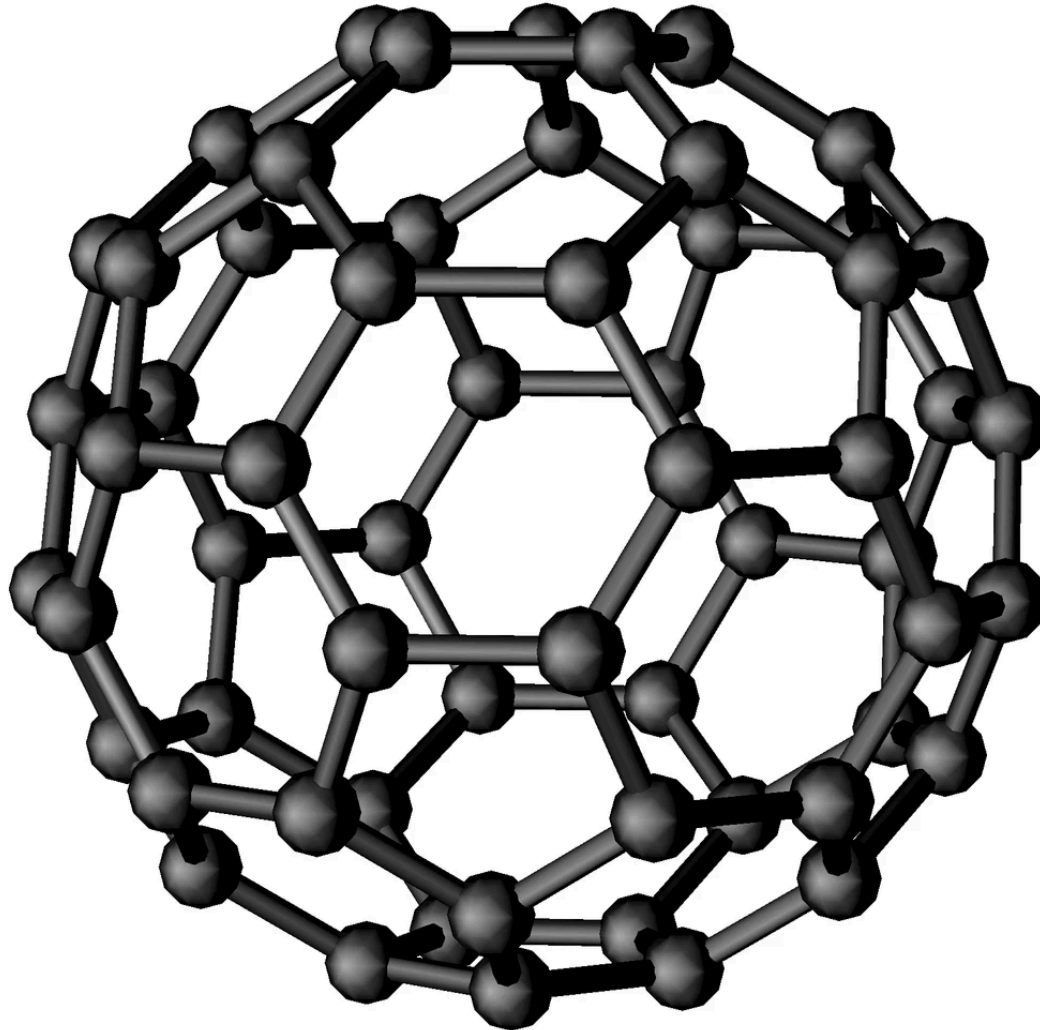
compound	peculiarity
1) TTF-TCNQ (TMTSF) ₂ ClO ₄ (TMTSF) ₂ PF ₆	Peierls transition $T_c = 1.3$ K SC $T_c = 0.9$ K SC (under pressure)
2) KCP K ₂ Pt(CN) ₄ Br _{0.2} · H ₂ O	Peierls transition
3) Hg _{2.86} AsF ₆	SC
4) (SN) _x (SNBr _{0.4}) _x	$T_c = 0.33$ K $T_c = 0.35$ K 3D-SC
5) (CH) _x · SbF ₅	Peierls transition
6) (=C=) _x (-C=C-) _x	α-Carbyne β-Carbyne
7) TaS ₃ NbSe ₃	Peierls transition
8) graphite GIC (SbF ₅) GIC (AsF ₅) GIC (C ₈ K)	semi-metal two-dimensional $T_c = 0.2$ K SC
9) copper aluminium	metal metal three-dimensional

1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

0D: Fullerenes

C_{60}

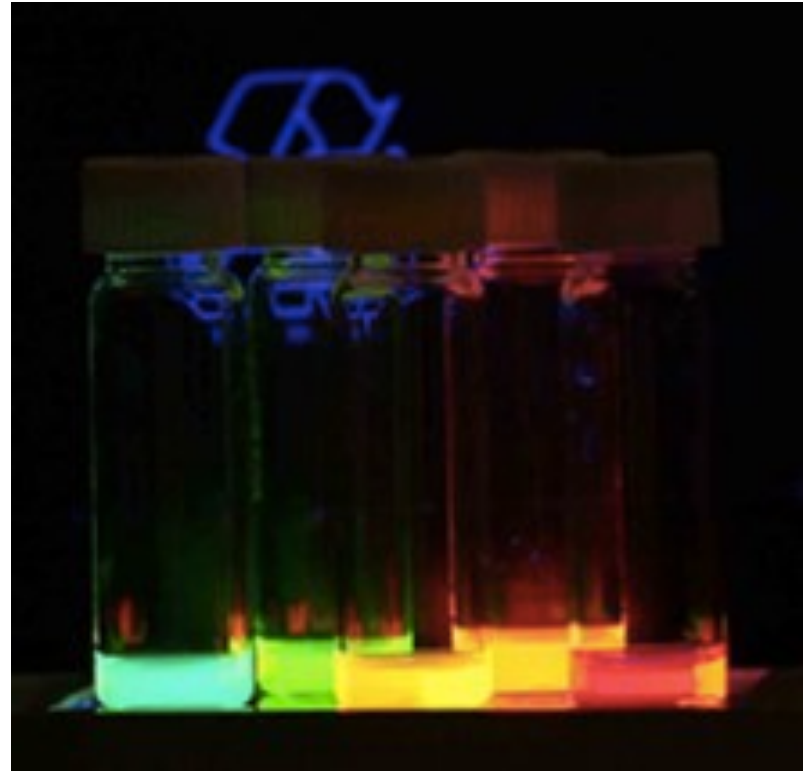


1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

0D: Quantum dots

- Semiconducting particles of few nanometers
- Also called artificial atoms
- Size dependent properties



1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

0D: Atomic clusters

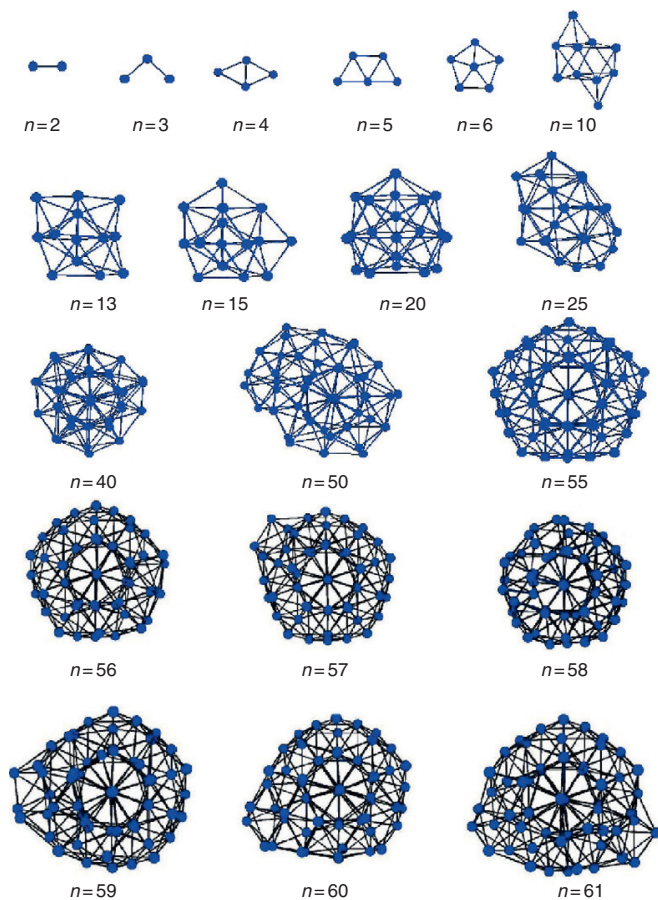
- Clusters can be formed when a hot plume of atoms or molecules in a gas are cooled by collision with rare-gas atoms much as droplets of water are formed when hot steam cools and condenses

1. Length scales and low dimensional systems

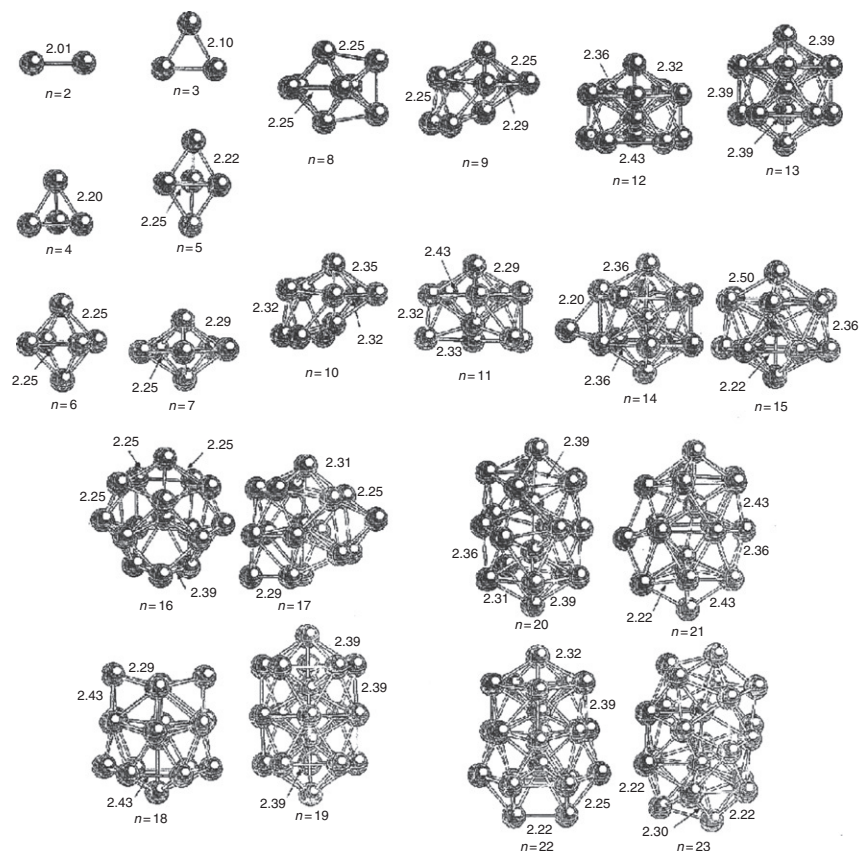
1.4 Examples of low-dimensional systems

0D: Atomic clusters

Na clusters



Ni clusters

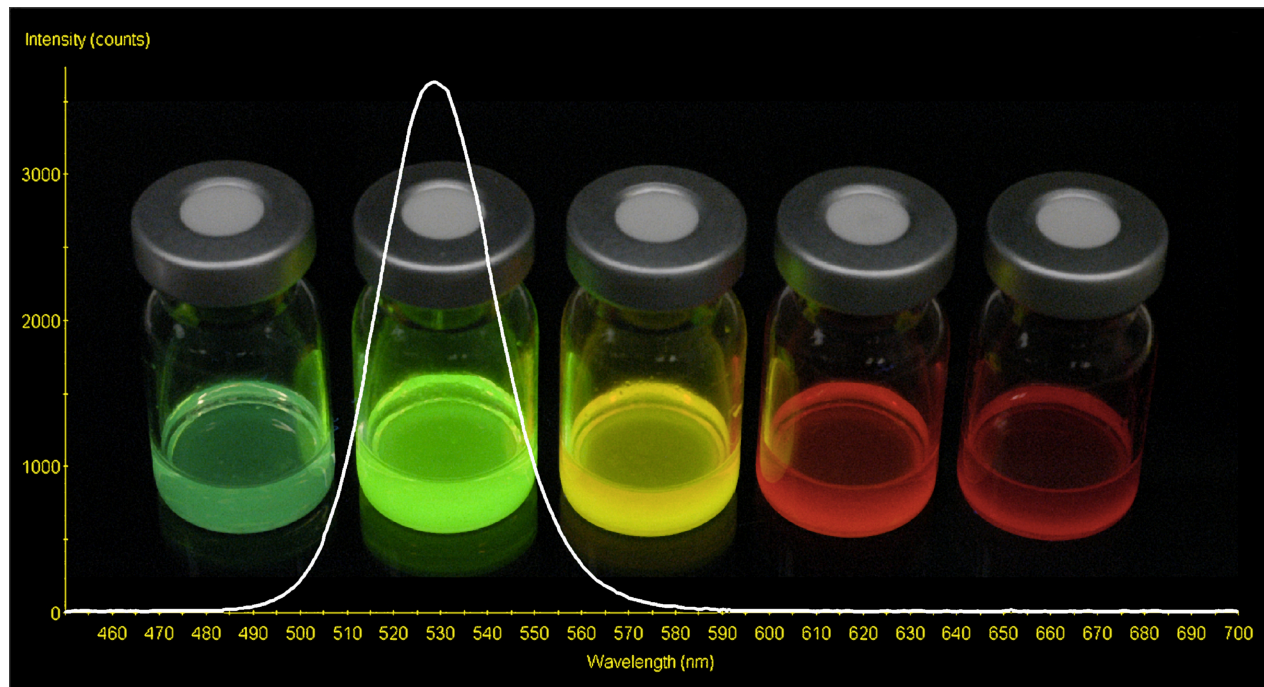


1. Length scales and low dimensional systems

1.4 Examples of low-dimensional systems

0D: Synthetic nanocrystals

- Chemical synthesis of nanoparticles of CdS, CdSe, CuCl
- Size control (from few nm to 200 nm)



1. Length scales and low dimensional systems

1.5 Fabrication and characterization techniques

Nanolitography

- Techniques for etching, writing, printing at the nanoscale
 - Optical lithography
 - Electron-beam lithography
 - Scanning probe lithography
 - Nanoimprint lithography

1. Length scales and low dimensional systems

1.5 Fabrication and characterization techniques

Nanolitography



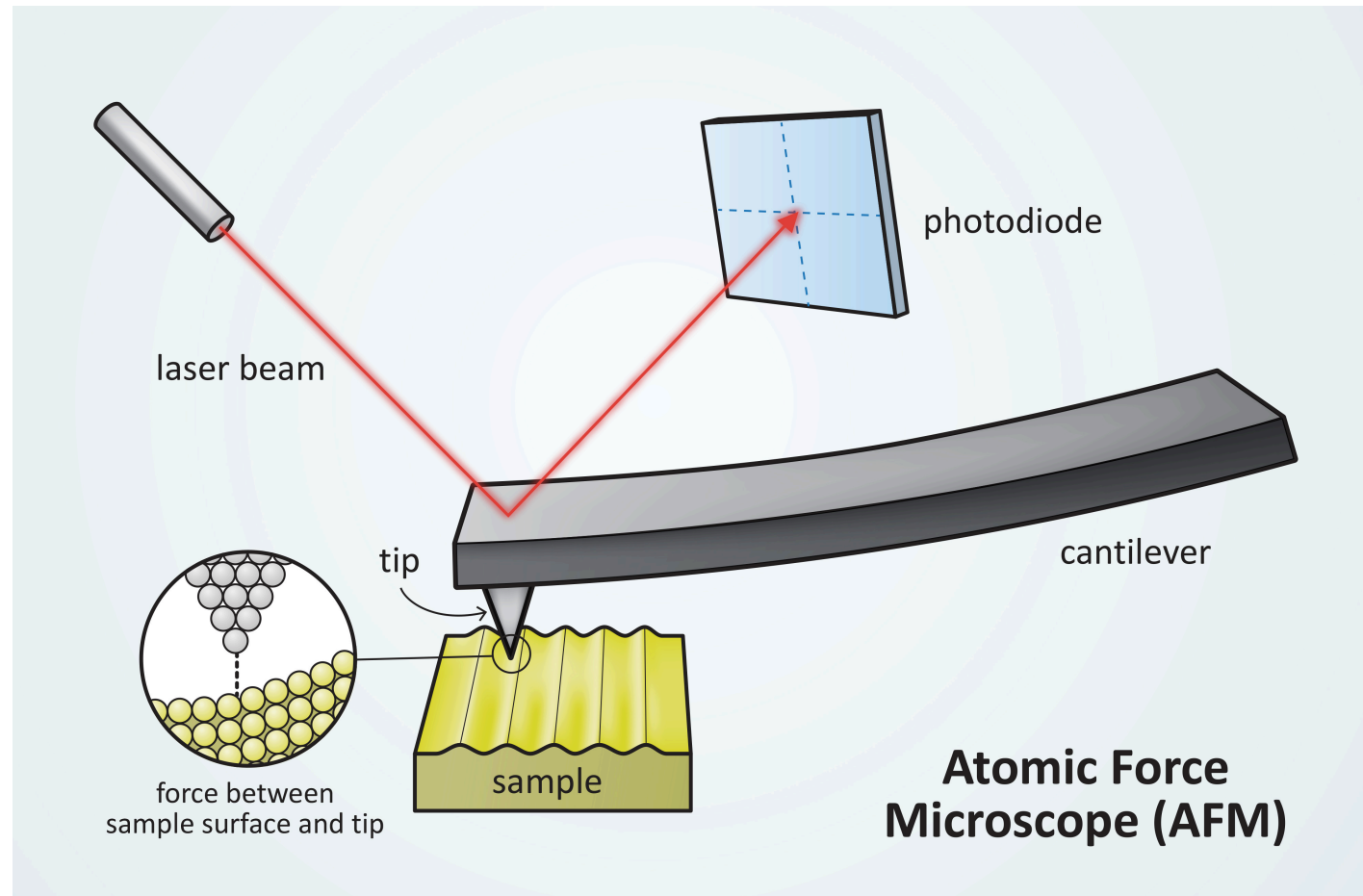
https://www.youtube.com/watch?time_continue=189&v=PWV9pvdRBNY&feature=emb_logo

1. Length scales and low dimensional systems

1.5 Fabrication and characterization techniques

Atomic Force Microscopy (AFM)

- Detects the fluctuations of the tip induced by the forces of the sample
- Can be used for lithography

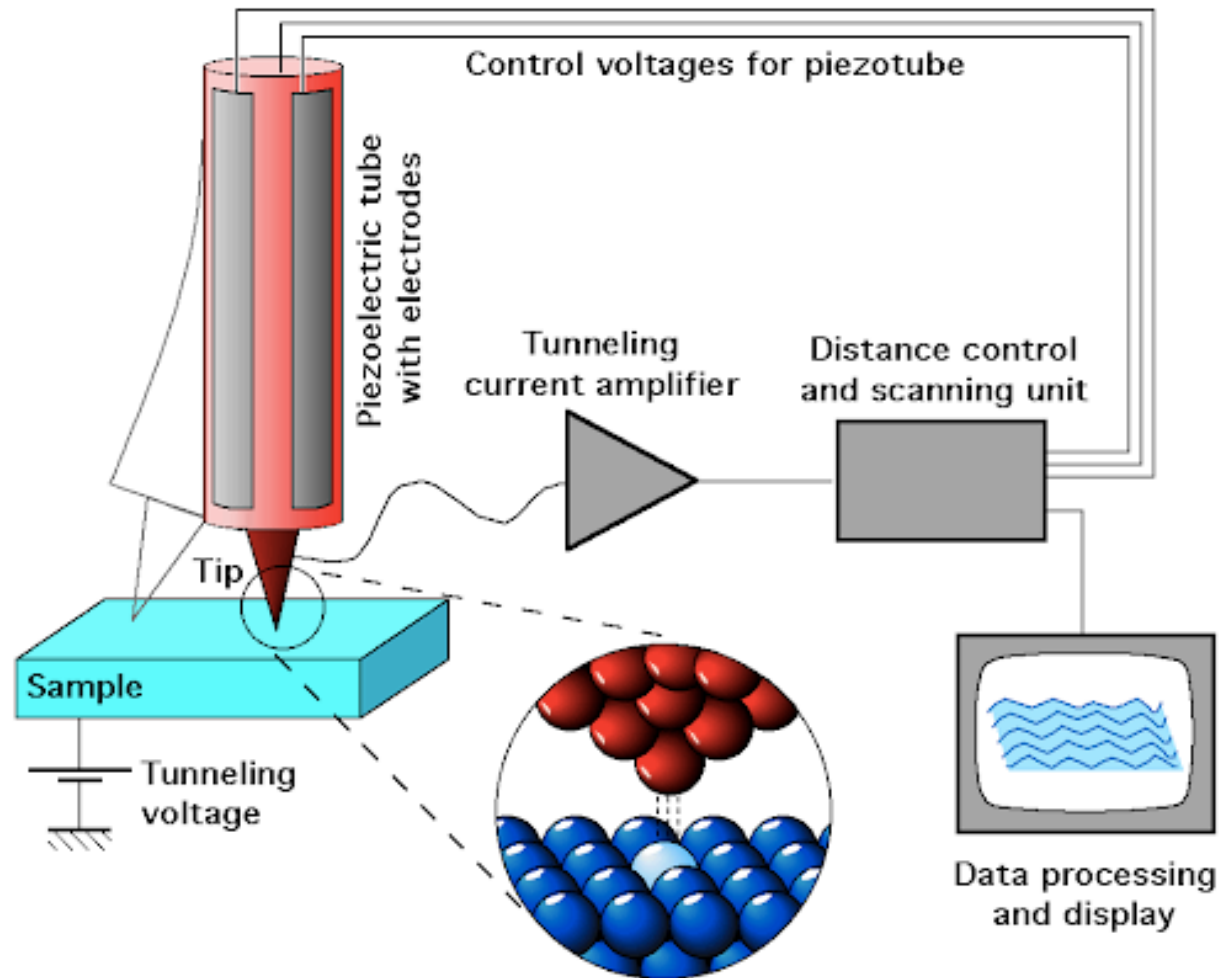


1. Length scales and low dimensional systems

1.5 Fabrication and characterization techniques

Scanning Tunneling Microscope (STM)

- Controls the current tunneled from the sample to the atomic tip.
- Can be used to image and manipulate individual atoms.
- Atomic resolution.

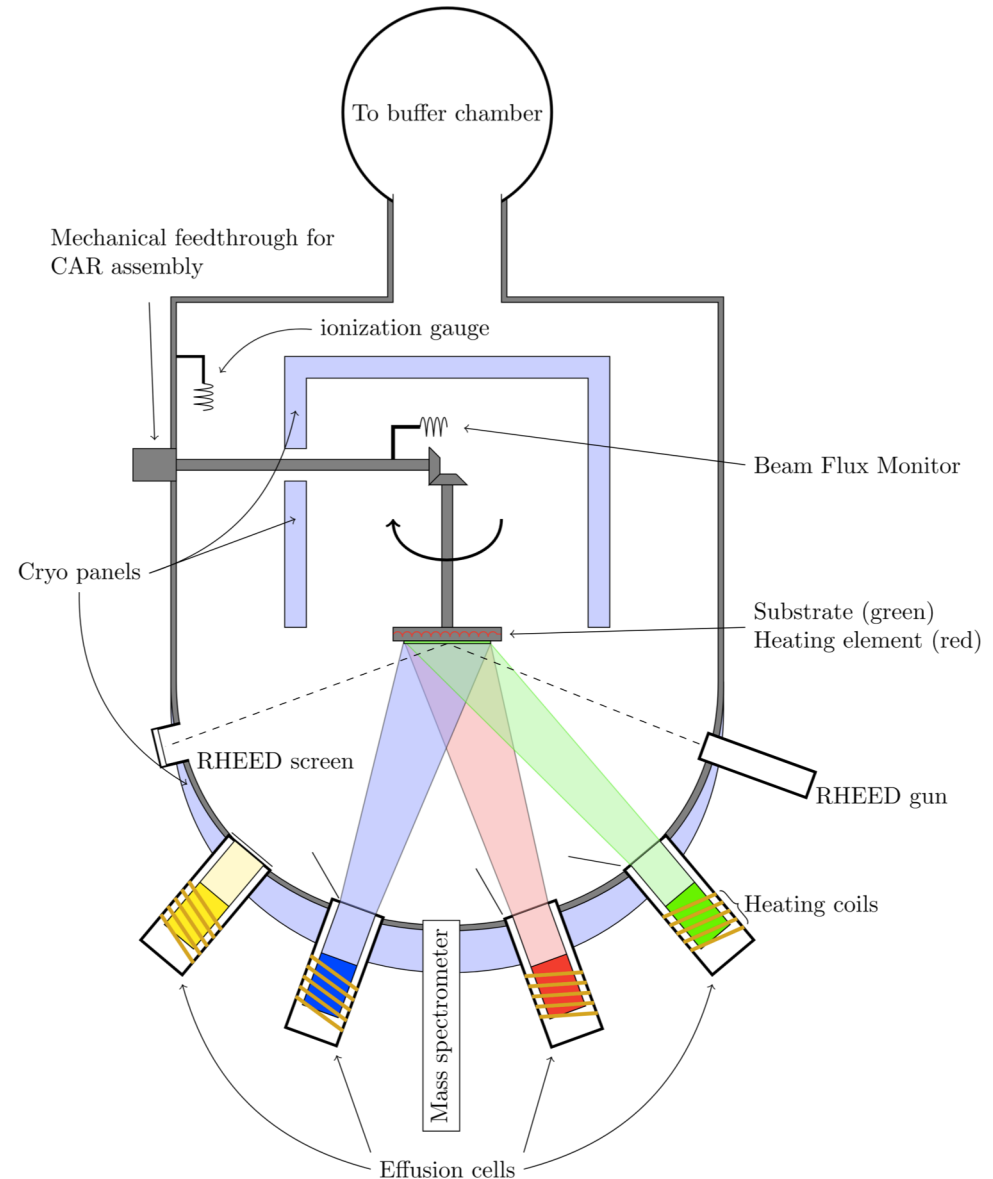


1. Length scales and low dimensional systems

1.5 Fabrication and characterization techniques

Molecular Beam Epitaxy (MBE)

- In ultra-high-vacuum conditions molecules or atoms are deposited on surfaces.
- Monolayer, bilayers, etc. can be created
- The samples are later characterized by STM or AFM.



1. Length scales and low dimensional systems

1.6 Exercise

Perform a literature search and find a material that can be synthesized in low dimensions and or in its bulk form it has low-dimensional features.

- Which are the features in its electronic properties that make it behave as a low-dimensional material?
- Is there any other particular property that makes it behave as a low-dimensional system?