Theory of Adsorption

"Accumulation at the solid –vapor interface of atoms or molecules coming from the vapor"

Physical adsorption

Adsorption is defined as the concentration of gas molecules at the surface of a solid material.

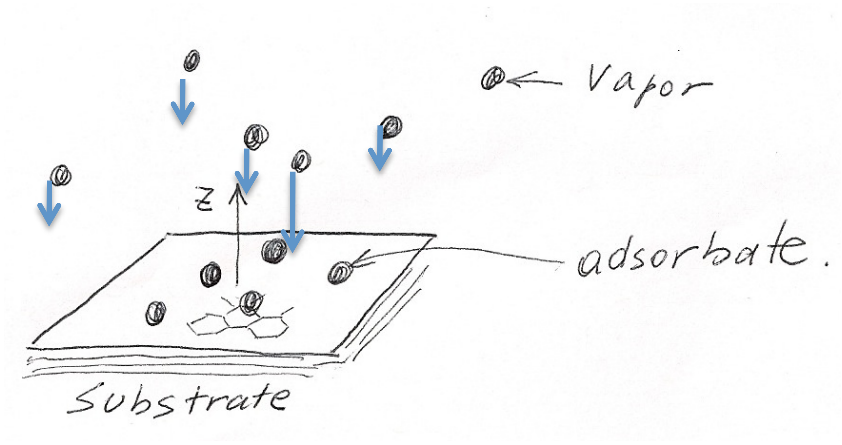
The adsorbed gas is called adsorbate and the solid where adsorption takes place is known as the adsorbent or substrate.

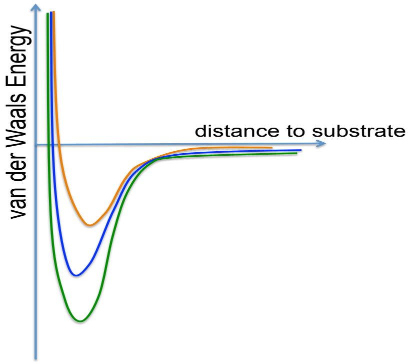
Adsorption is a physical phenomenon (usually called physisorption) that occurs at any environmental condition (pressure and temperature) but only at very low temperature it becomes measurable.

Physical adsorption

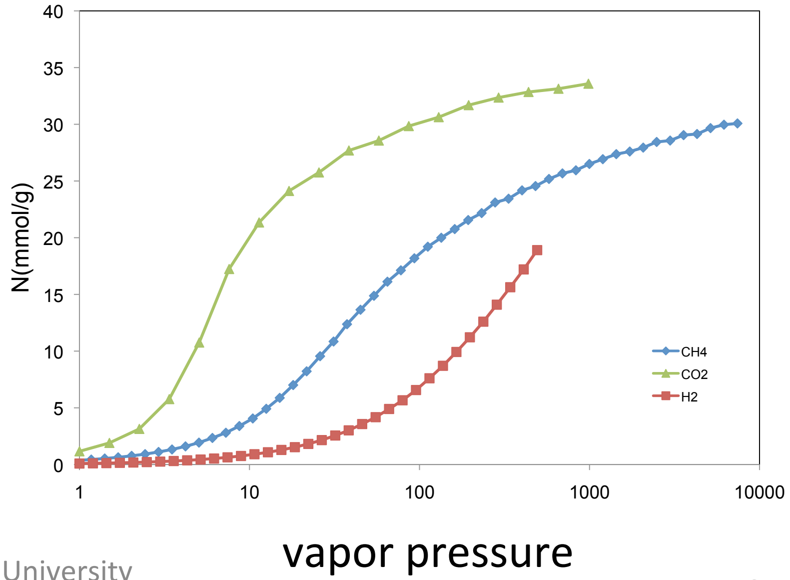
Adsorption takes place because of the presence of an intrinsic surface energy.

- When a material is exposed to a gas, an attractive force acts between the exposed surface of the solid and the gas molecules: physical or Van der Waals adsorption
- in contrast to the stronger chemical attractions associated with chemisorption.
- Due to the weak bonds involved between gas molecules and the surface (less than 15 kJ/mole or 0.16 eV/atom), adsorption is a reversible phenomenon.



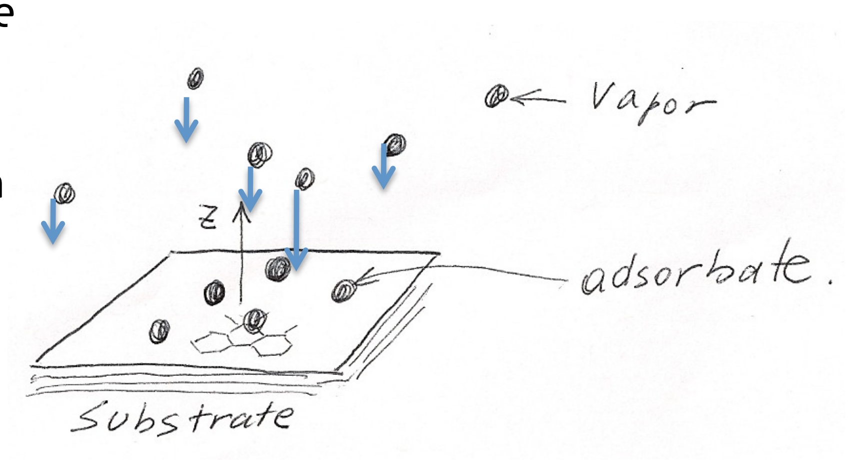


Adsorption isotherm:



Physical adsorption

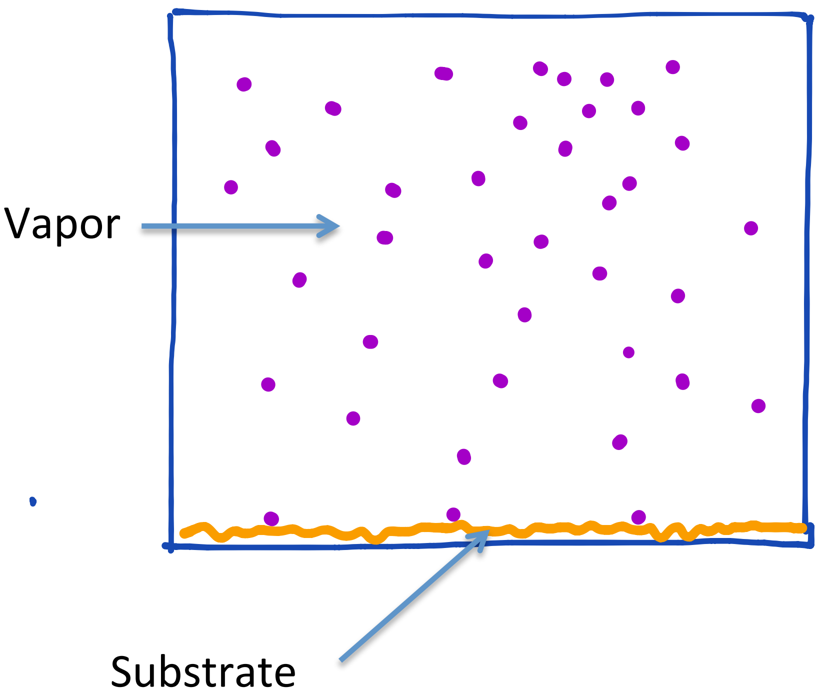
- A surface is exposed to a vapor held at pressure P and temperature T.
- A film forms on the surface, in equilibrium with the vapor.
- The coverage depends on P, T and the interaction potential.
- For low P (but not low T), a monolayer forms



DESORPTION is easy: heat it up!

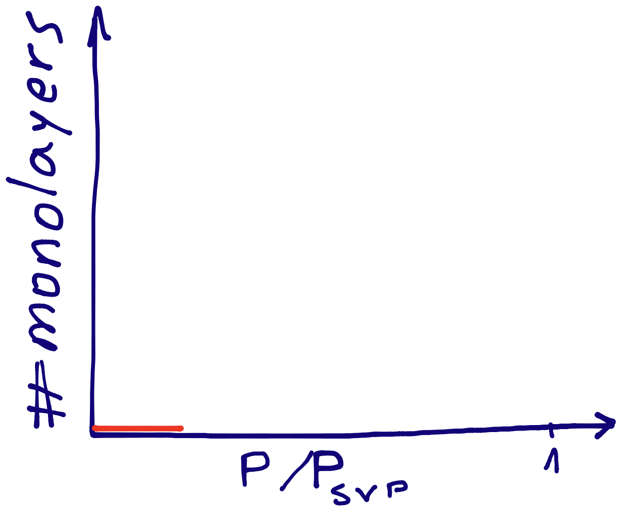
Silvina Gatica, Howard University
sgatica@howard.edu

Physical adsorption



Vapor

Substrate



Low P: zero monolayers

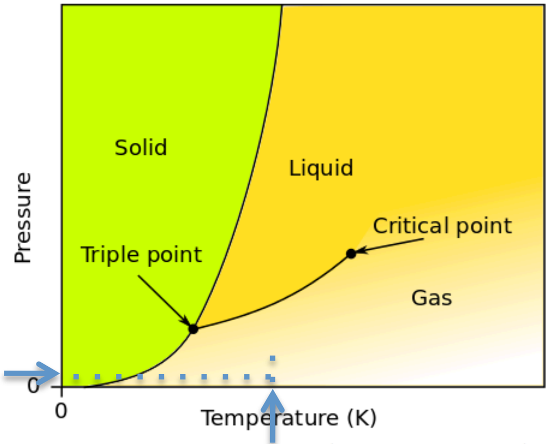
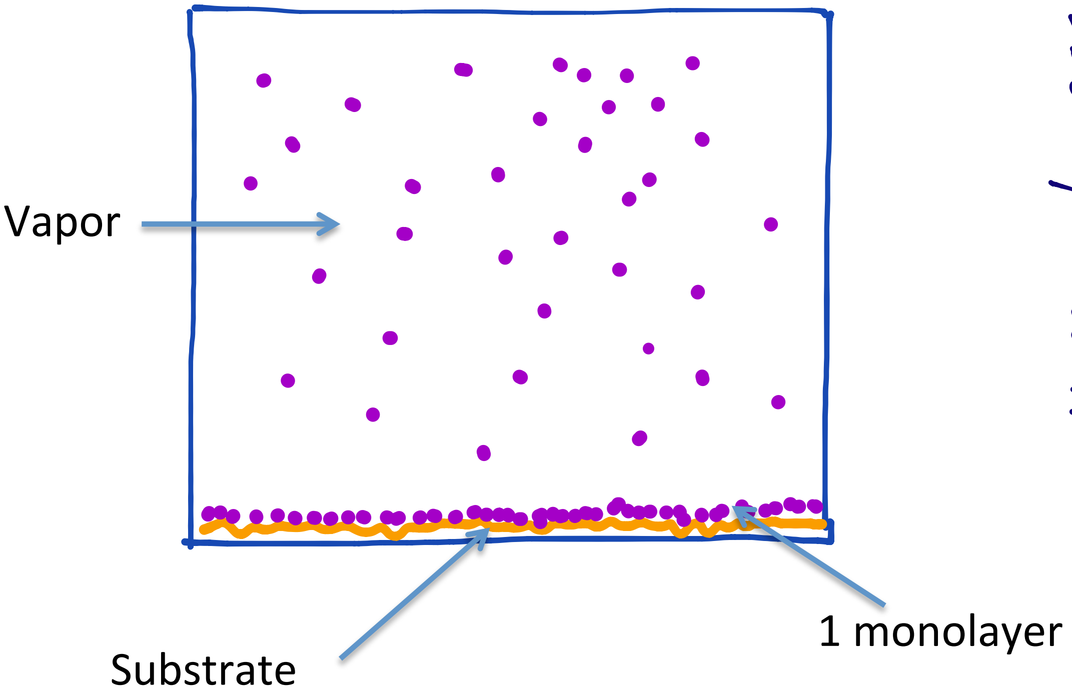


Figure 2 : A typical phase diagram (water, air, oxygen, etc.)

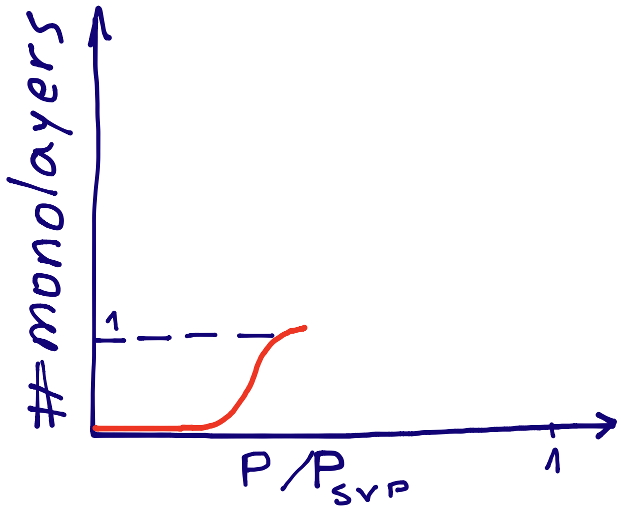
Physical adsorption



Vapor

Substrate

1 monolayer



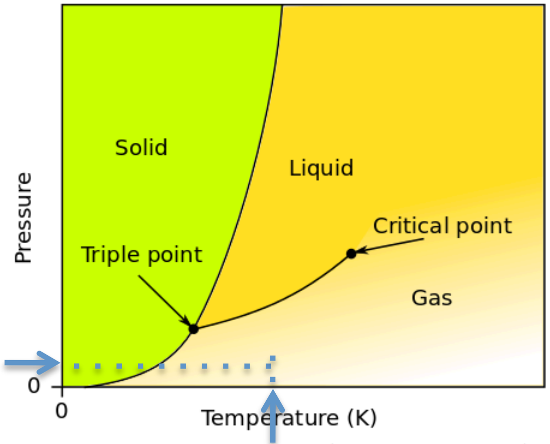
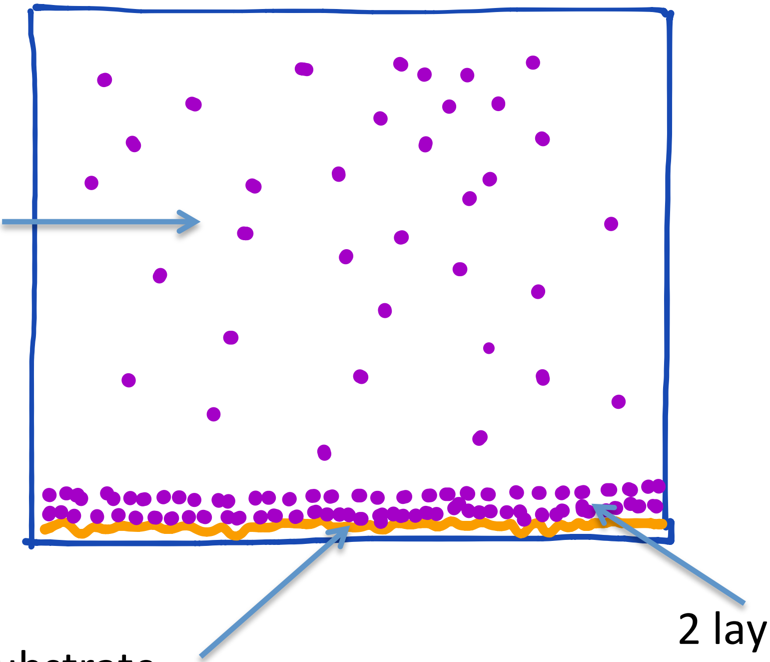


Figure 2 : A typical phase diagram (water, air, oxygen, etc.)

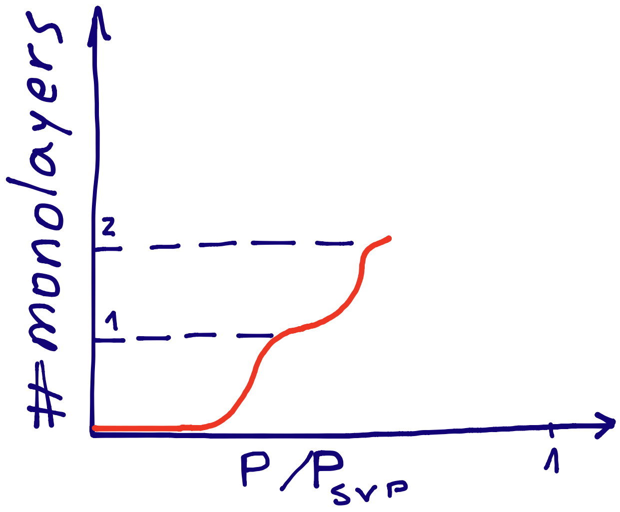
Physical adsorption



Vapor

Substrate

2 layers



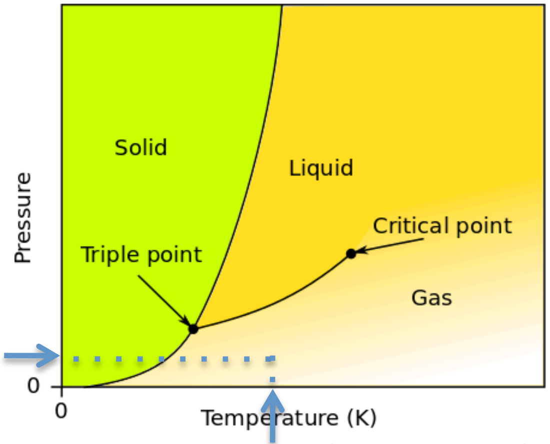
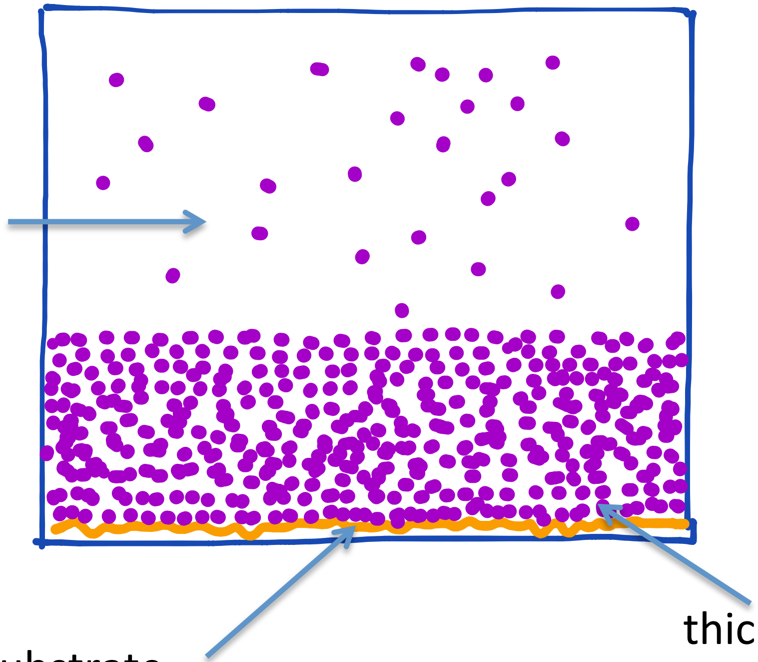


Figure 2 : A typical phase diagram (water, air, oxygen, etc.)

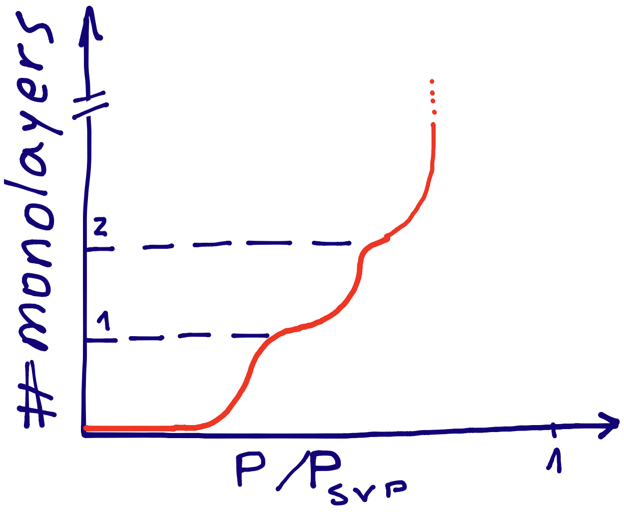
Physical adsorption



Vapor

Substrate

thick film (wetting) at $P<P_{svp}$



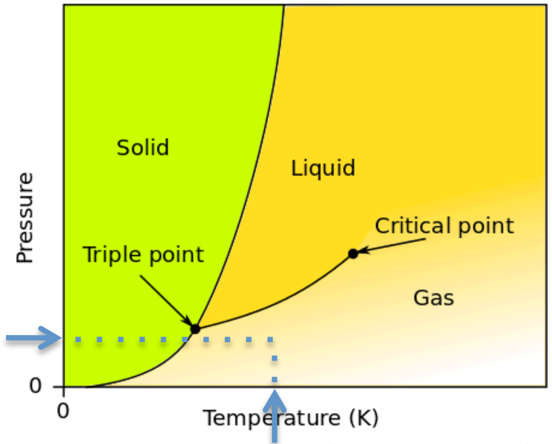


Figure 2 : A typical phase diagram (water, air, oxygen, etc.)

Adsorption is defined as the concentration of gas molecules near the surface of a solid material.

The adsorbed gas is called adsorbate and the solid where adsorption takes place is known as the adsorbent or substrate.

Adsorption is a physical phenomenon (usually called physisorption) that occurs at any environmental condition (pressure and temperature) but only at low temperature it becomes measurable.

Thus physisorption experiments are performed at low temperature, usually at the boiling temperature of liquid nitrogen at atmospheric pressure. (77K)

Adsorption takes place because of the presence of an intrinsic surface energy. When a material is exposed to a gas, an attractive force acts between the exposed surface of the solid and the gas molecules. The result of these forces is characterized as physical (or Van der Waals) adsorption, in contrast to the stronger chemical attractions associated with chemisorption.

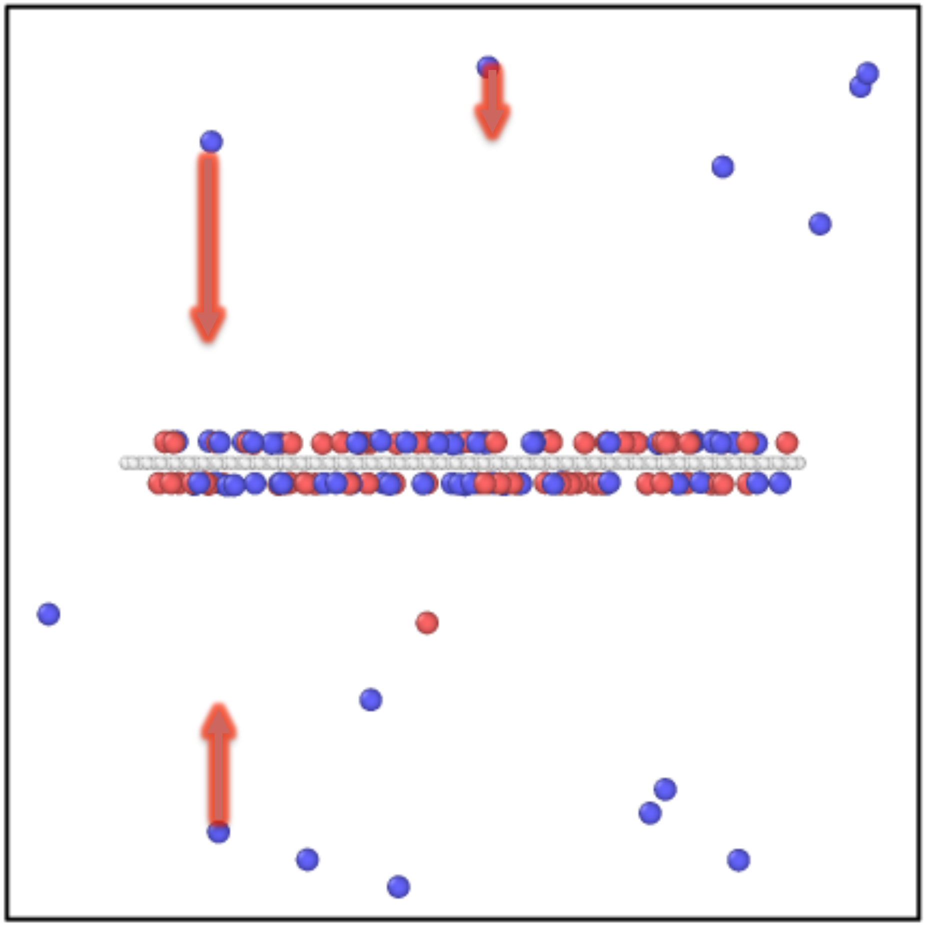
Due to the weak bonds involved between gas molecules and the surface (less than 15 KJ/mole), adsorption is a reversible phenomenon.

Filling a monolayer enables the measurement of the surface area of the material

vdW Force

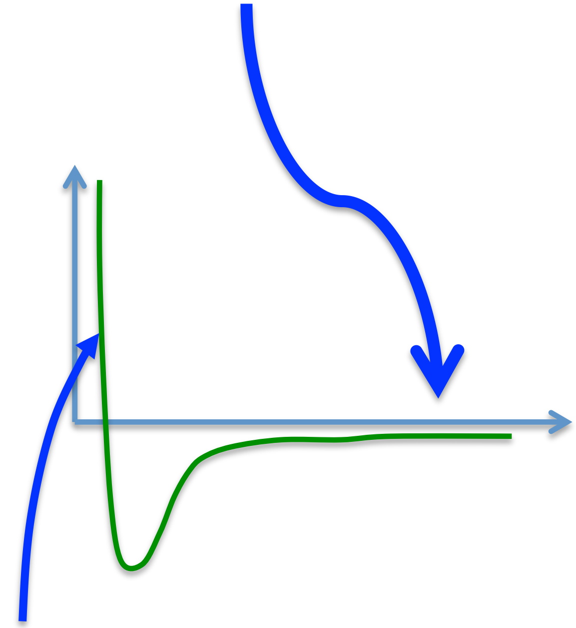
electrostatic forces:

dipolar
quadrupolar

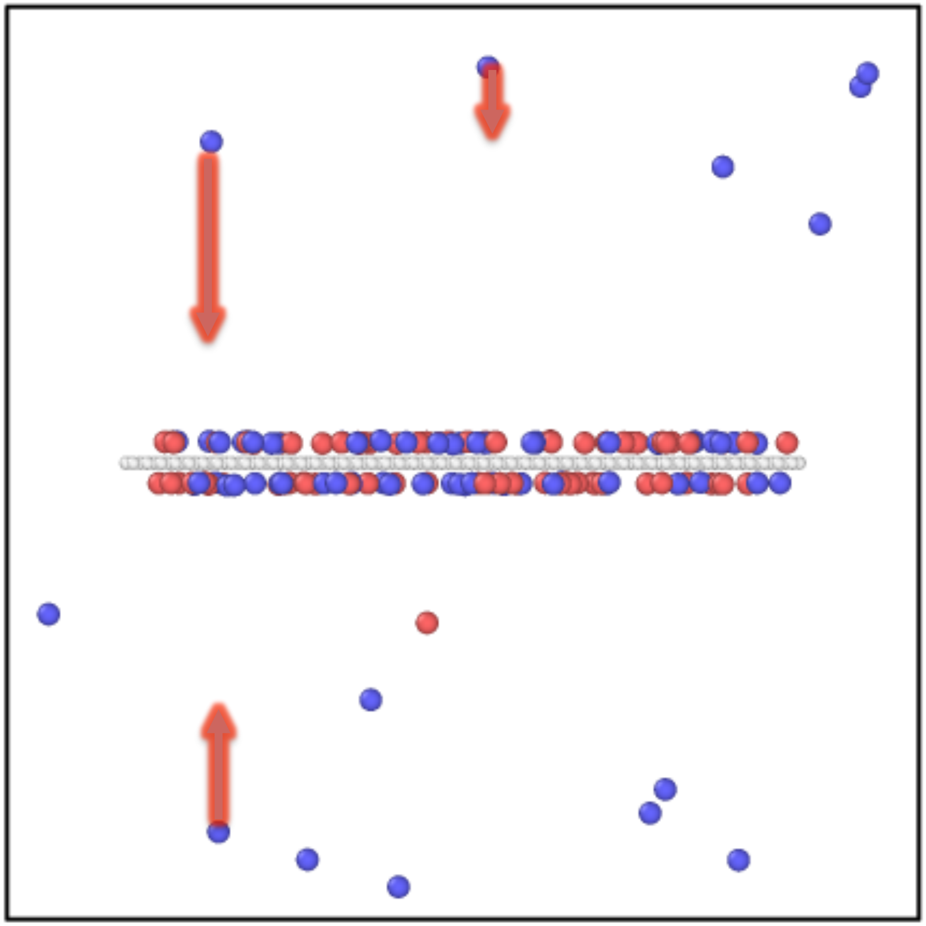


atom-atom vdW energy

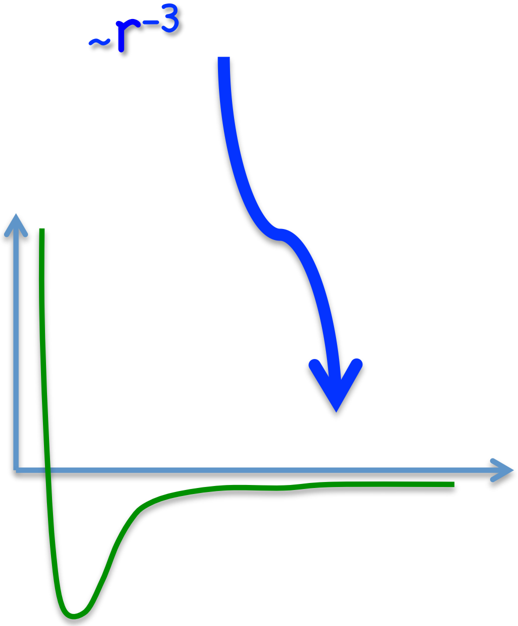
$\sim r^{-6}$

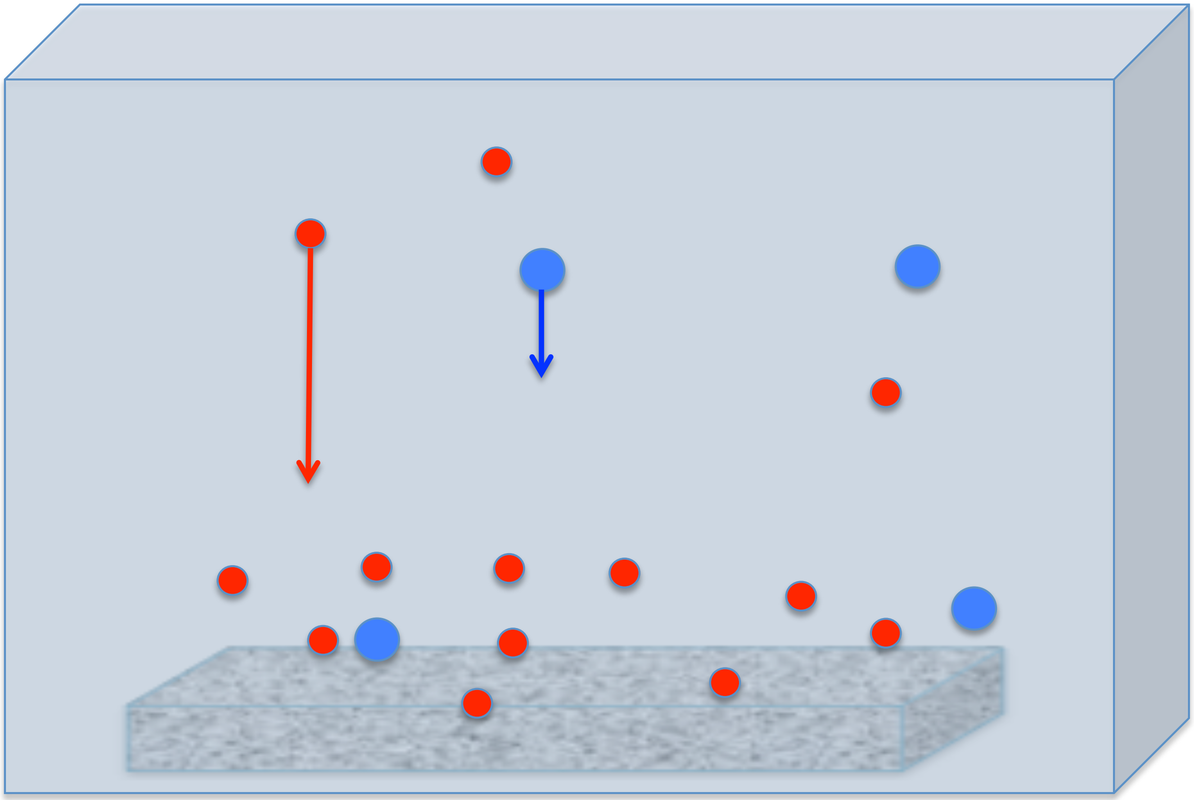


repulsion e-

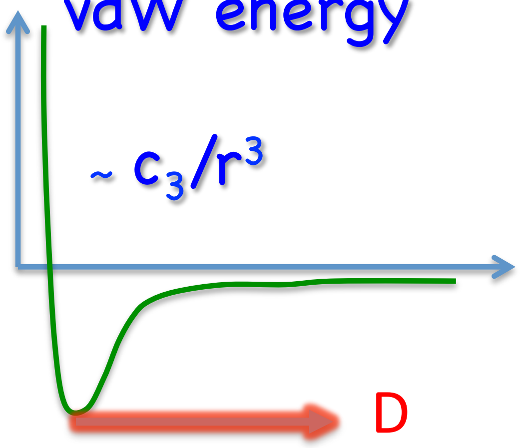


atom-substrate
vdW energy

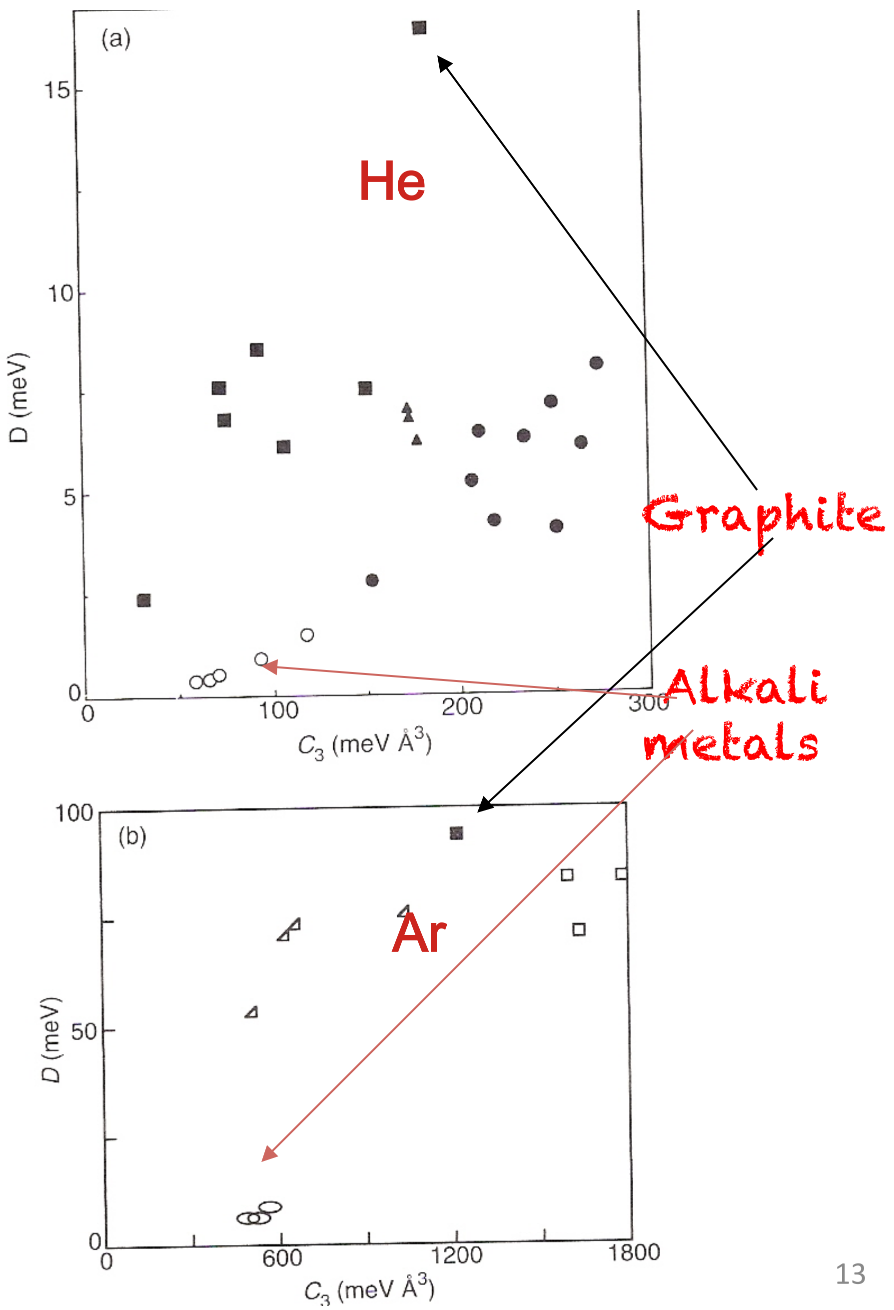




atom-substrate vdW energy



Note that graphite provides the largest attraction and alkali metals the smallest attraction



Physical Interactions

3 relevant interactions to Adsorption:

- Atom-atom
- Atom-surface
- 3 body effects (the proximity of the surface modifies the atom-atom interaction)

- Theoretical characterization of the interactions involves knowledge of the electron densities, or wave functions and their response to external fields. (Solve the many-body Schrödinger equation)

- These long-range attractive interactions, called "dispersion forces" arise from purely quantum mechanics through the coupled (zero-point) motion of the electrons.

> "In the structure of matter there can be no fundamental distinction between chemical and physical forces: it has been customary to call a force chemical when it is more familiar with the chemists and physical the physicist discovers an explanation for it"
>
> *I. Langmuir*, 1950

Most important quantity for adsorption: BINDING ENERGY (energy release when an atom sticks on to the surface)

Physical adsorption (physisorption): small binding energies, van der Waals forces, no mixing orbitals. (~ 0.1 eV)

Chemisorption: strong binding energy, a bond is formed.

Intermolecular forces & Interaction energies

The distinction between physical or chemical interactions is already present in interatomic interactions

2 H atoms for a H2 molecule: chemical bond

2 He atoms interact very weakly: No chemical bond

Both situations are based on the SAME Coulomb e-e, e-nucleus forces!

In any case, the EXACT calculation of the energy means solving the equation of **Schrödinger** for the Hamiltonian:

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} - \sum_{i=1}^{N} \left[\frac{e^2 Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \frac{e^2 Z_B}{|\mathbf{r}_i - \mathbf{R}_B|} \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{e^2 Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}$$

The calculation is a formidable task! → We must use approximations and models

van der Waals force

At large interatomic separations, (but not too large) the AB coulomb term is a perturbation to the isolated atomic Hamiltonians

The energy has origin in:

Correlations between electronic motions in atoms A,B

Attractive force: Dispersion or van der Waals force (London theory)

$$V_{vdW}(R) = -\frac{C_6}{R^6}$$

$$C_6 = \frac{3\hbar}{\pi}\int_0^\infty du\, \alpha_a(iu)\alpha_b(iu)$$

dynamic polarizabilities

If the atoms have permanent or induced dipole, quadrupole etc, the electrostatic interactions between multipole moments are added to the vdW force.

At all distances: Semiempirical construction

$$V(R) = V_{rep}(R) + V_{att}(R)$$

$$-f_N(\alpha R)\frac{C_6}{R^6}$$

Model:
Damped dispersion force

$$f_N(x) = 1 - e^{-x}\sum_{n=0}^{N}\frac{x^n}{n!}$$

wavefunctions overlap $V_0\, e^{-\alpha R}$

Parameters: N, α

Lennard-Jones Model (LJ)

$$\phi^{\mathrm{LJ}}(r) = 4\varepsilon_{\mathrm{fc}}\left[\left(\frac{\sigma_{\mathrm{fc}}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{fc}}}{r}\right)^{6}\right]$$

parameters: σ, ε

This model represents well "spherical" atoms or molecules (He, Ne, Kr, Ar, CH_4)

Non-spherical molecules: Universal Force Field (UFF)

$$E = E_{\mathrm{R}} + E_{\theta} + E_{\phi} + E_{\omega} + E_{\mathrm{vdw}} + E_{\mathrm{el}}$$

inversion

bond stretch

angle bend

torsion

LJ

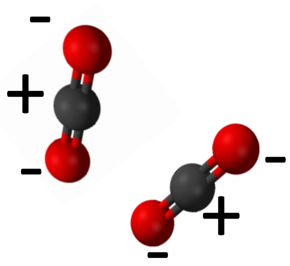
electrostatic

$$E_{\mathrm{R}} = \tfrac{1}{2}k_{\mathrm{IJ}}(r - r_{\mathrm{IJ}})^2$$

$$E_{\gamma} = K\sum_{n=0}^{m} C_n \cos n\gamma$$

Three point model

$$E_{ij} = \frac{q_i q_j}{r} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$



For molecules with non-zero quadrupole moment (CO_2, H_2…)

Basic: Lennard Jones (LJ) potential

$$U_{\mathrm{aa}}(r) = 4\varepsilon_{\mathrm{aa}}\left[(\sigma_{\mathrm{aa}}/r)^{12} - (\sigma_{\mathrm{aa}}/r)^{6}\right]$$

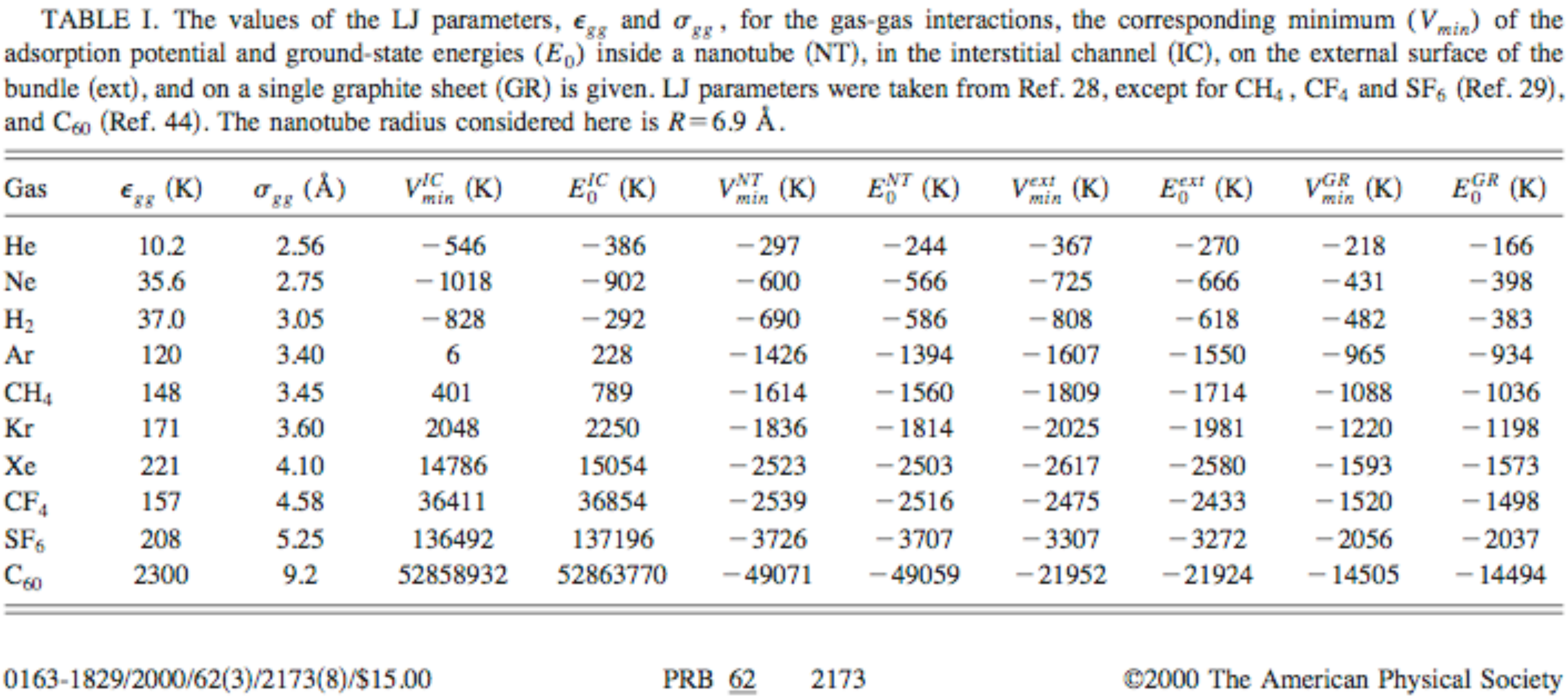


TABLE I. The values of the LJ parameters, ϵ_{gg} and σ_{gg}, for the gas-gas interactions, the corresponding minimum (V_{min}) of the adsorption potential and ground-state energies (E_0) inside a nanotube (NT), in the interstitial channel (IC), on the external surface of the bundle (ext), and on a single graphite sheet (GR) is given. LJ parameters were taken from Ref. 28, except for CH_4, CF_4 and SF_6 (Ref. 29), and C_{60} (Ref. 44). The nanotube radius considered here is $R=6.9$ Å.

Gas	ϵ_{gg} (K)	σ_{gg} (Å)	V_{min}^{IC} (K)	E_0^{IC} (K)	V_{min}^{NT} (K)	E_0^{NT} (K)	V_{min}^{ext} (K)	E_0^{ext} (K)	V_{min}^{GR} (K)	E_0^{GR} (K)
He	10.2	2.56	−546	−386	−297	−244	−367	−270	−218	−166
Ne	35.6	2.75	−1018	−902	−600	−566	−725	−666	−431	−398
H_2	37.0	3.05	−828	−292	−690	−586	−808	−618	−482	−383
Ar	120	3.40	6	228	−1426	−1394	−1607	−1550	−965	−934
CH_4	148	3.45	401	789	−1614	−1560	−1809	−1714	−1088	−1036
Kr	171	3.60	2048	2250	−1836	−1814	−2025	−1981	−1220	−1198
Xe	221	4.10	14786	15054	−2523	−2503	−2617	−2580	−1593	−1573
CF_4	157	4.58	36411	36854	−2539	−2516	−2475	−2433	−1520	−1498
SF_6	208	5.25	136492	137196	−3726	−3707	−3307	−3272	−2056	−2037
C_{60}	2300	9.2	52858932	52863770	−49071	−49059	−21952	−21924	−14505	−14494

0163-1829/2000/62(3)/2173(8)/$15.00 PRB 62 2173

Adsorbate-surface interaction

Usually the adsorbate-substrate interaction is much weaker than within the substrate

The atoms in the substrate can be assumed to be at the equilibrium positions pre-adsorption

If the energy wave function and E are found, the interaction energy V(R) is:

$$V(\mathbf{R}) = E(\mathbf{R}) - E_0^a - E_0^s$$

At large separations, V is analogous to vdW

At short distances, the wavefunctions overlap there is short term repulsion
For a metallic surface, there is a change in the electron density, so it requires a more accurate description, for example using DFT

vdW interaction for atom-substrate:

Extension of the London theory:

Case of one atom interacting with a semi-infinite solid:

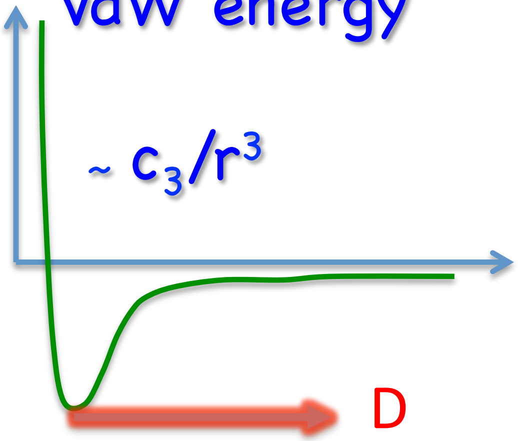
$$V_{vdW}(Z) \simeq -C_3/Z^3 \qquad C_3 = \frac{\hbar}{4\pi}\int_0^\infty d\omega \, \frac{[\epsilon(\imath\omega) - 1]}{[\epsilon(\imath\omega) + 1]}\alpha(\imath\omega)$$

ε = dielectric function of the substrate

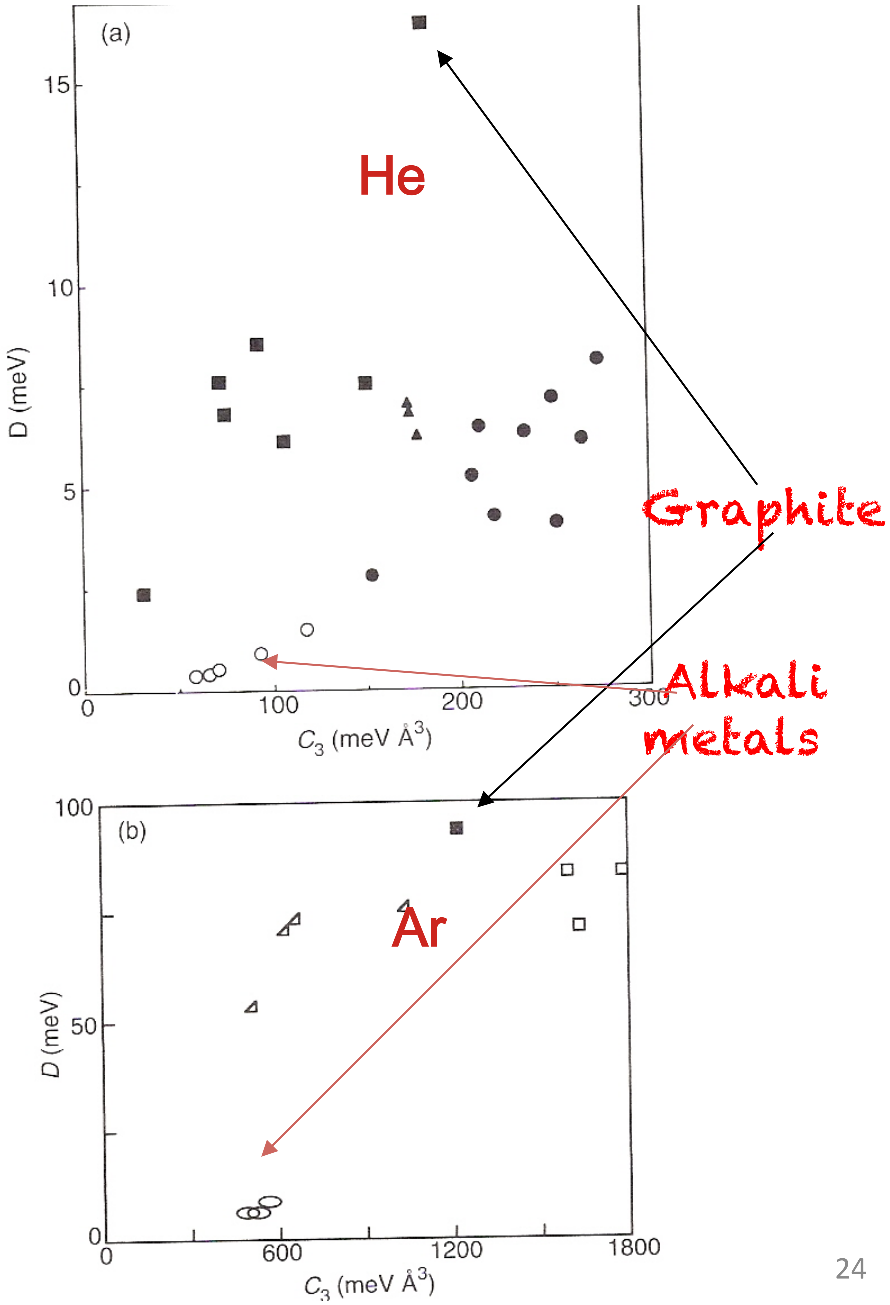
including short range repulsion:

$$V(z) = \frac{4C_3^{\,3}}{27D^2z^9} - \frac{C_3}{z^3}$$

atom-substrate vdW energy



$$V(z) = \frac{4C_3^{\,3}}{27D^2z^9} - \frac{C_3}{z^3}$$



Semiempirical methods

Sum of pairwise interaction: $$V(\{\mathbf{R}_\alpha\}) = \sum_{\alpha, j_\beta} \phi_{\alpha,\beta}(\mathbf{R}_\alpha - \mathbf{R}_{j_\beta})$$

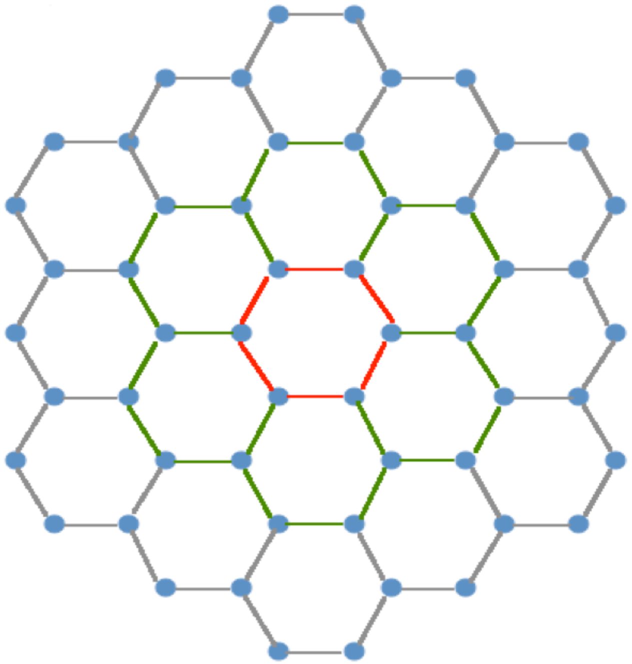
with for example LJ → $$\phi^{\mathrm{LJ}}(r) = 4\varepsilon_{\mathrm{fc}}\left[\left(\frac{\sigma_{\mathrm{fc}}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{fc}}}{r}\right)^{6}\right]$$

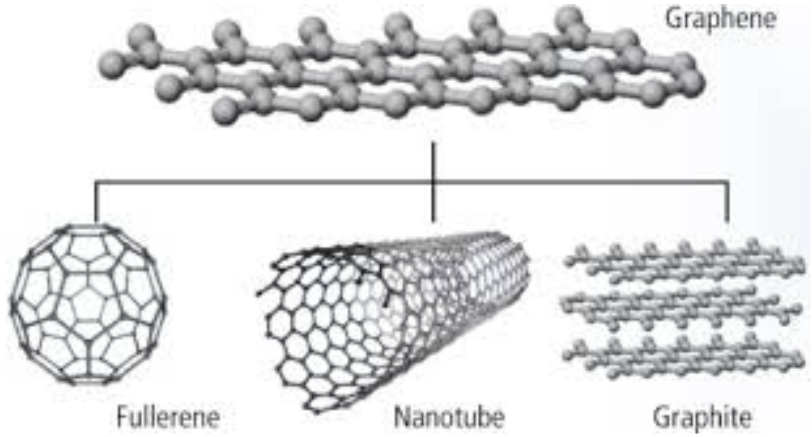
The parameters for the mixed interaction are fit from known properties or using combining rules:

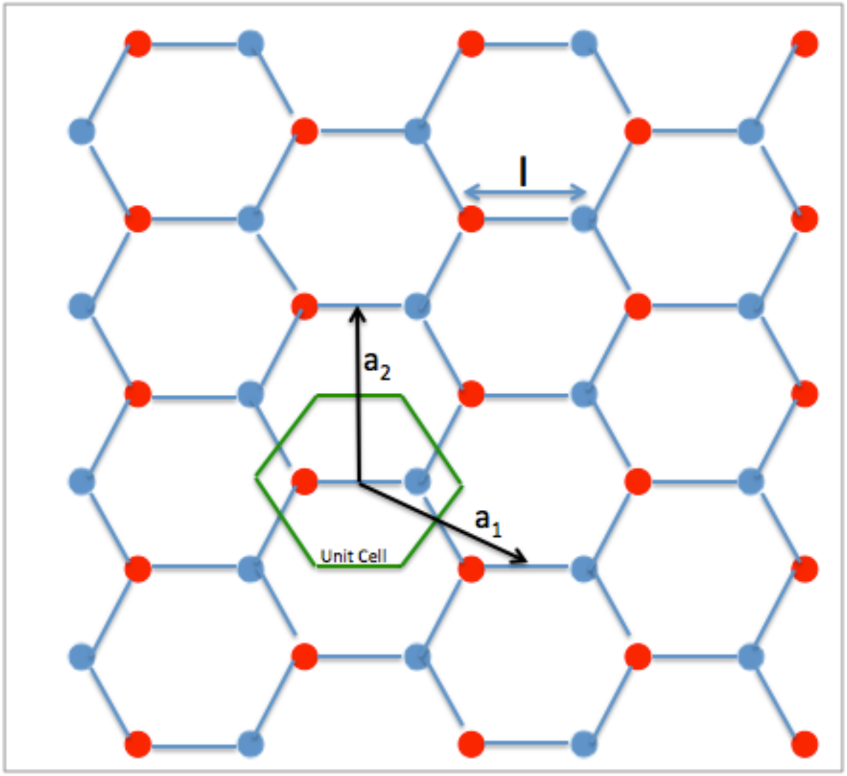
$$\begin{aligned} \epsilon_{XY} &= \sqrt{\epsilon_{XX}\epsilon_{YY}} \\ \sigma_{XY} &= \frac{1}{2}(\sigma_{XX} + \sigma_{YY}) \end{aligned}$$

Electrostatic contributions may be added (dipoles, quadrupoles)

Graphene







$$R = na_1 + ma_2$$

$$a_1 = \frac{3l}{2}\left(\vec{x} - \frac{\sqrt{3}}{3}\vec{y}\right) \text{ and } a_2 = \sqrt{3}l\,\vec{y}$$

Graphene

The spatial arrangement of graphitic crystallites determines the pore structure, i.e., the pore morphology and topology.

all simple models of porous carbons are based on stacks of graphene sheets representing the pore walls.

discrete as well as mean-field models of single graphene sheets or stacks of them are available.

Discrete model of a graphene

placing (model) carbon atoms on a −2D hexagonal lattice with lattice constant (carbon–carbon bond length) $l = 0.1415$ nm

Carbon atoms as well as the adsorbate molecules are often modeled by the LJ 12-6 potential,

$$\phi^{\mathrm{LJ}}(r) = 4\varepsilon_{\mathrm{fc}}\left[\left(\frac{\sigma_{\mathrm{fc}}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{fc}}}{r}\right)^{6}\right]$$

distance between atoms
or molecules

$$\sum_i \phi^{\mathrm{LJ}}\left(r_{ij}\right)$$

where $\varepsilon_{\mathrm{fc}}$ and σ_{fc} are the fluid–carbon energy and distance parameters,

Continuous model of graphene

If we can disregard the atomistic nature of the graphene sheet, the sheet is sufficiently characterized by an areal carbon density.

A mean-field model is obtained by replacing the sum over individual carbon atoms by an integral of the LJ potential over the area of the graphene sheet.

If the sheet is assumed to be infinite in lateral dimensions one obtains the well-known Steele (10-4) potential

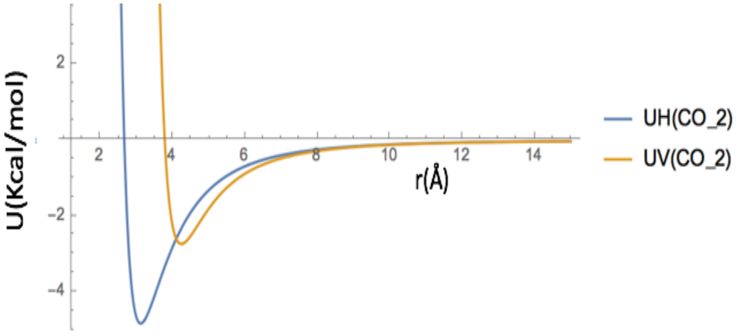
$$U(z) = 2\pi\varepsilon_{fc}\rho_S d\sigma_{fc}^2 \left[\frac{2}{5}\left(\frac{\sigma_{fc}}{z}\right)^{10} - \left(\frac{\sigma_{fc}}{z}\right)^{4}\right]$$

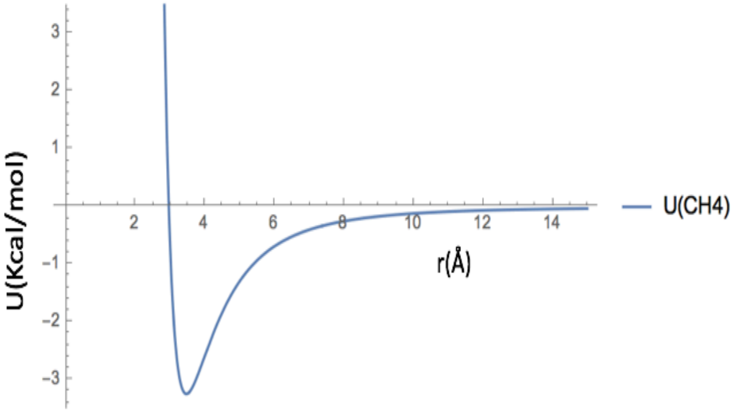
$\rho_S d$ is the areal number density of carbon atoms in the graphene layer.

$$\rho_S = 2.0/\left(dl^2\sqrt{3}(3/2)\right) \approx 114\,\mathrm{nm}^{-3}$$

Graphite

$$U_{Steel}(z) = 2\pi\epsilon\rho\sigma^2\Delta\left[\frac{2}{5}\left(\frac{\sigma}{z}\right)^{10} - \left(\frac{\sigma}{z}\right)^4 - \left(\frac{\sigma^4}{3\Delta\left(z+0.61\Delta\right)^3}\right)\right]$$





Simple model of adsorption: Henry's Law

The adsorbed layer is in thermodynamic equilibrium with the vapor:

- $\mu_a=\mu_v$
- $T_a=T_v$

For low coverage (N), a low density 2D film is in equilibrium with a low density 3D vapor (except at very low temperature)

In this regime, for N~P→ Henry's Law

$$P=k_H(T)\ N/A$$

Henry's constant:
depends on the
adsorption potential

(small N/A)

Langmuir theory

Adsorption on identical sites of a surface lattice, with site energy –eps
Adsorbate-adsorbate interactions are omitted
Multilayers are ignored

$$\theta = \frac{KP_A}{1 + KP_A}$$

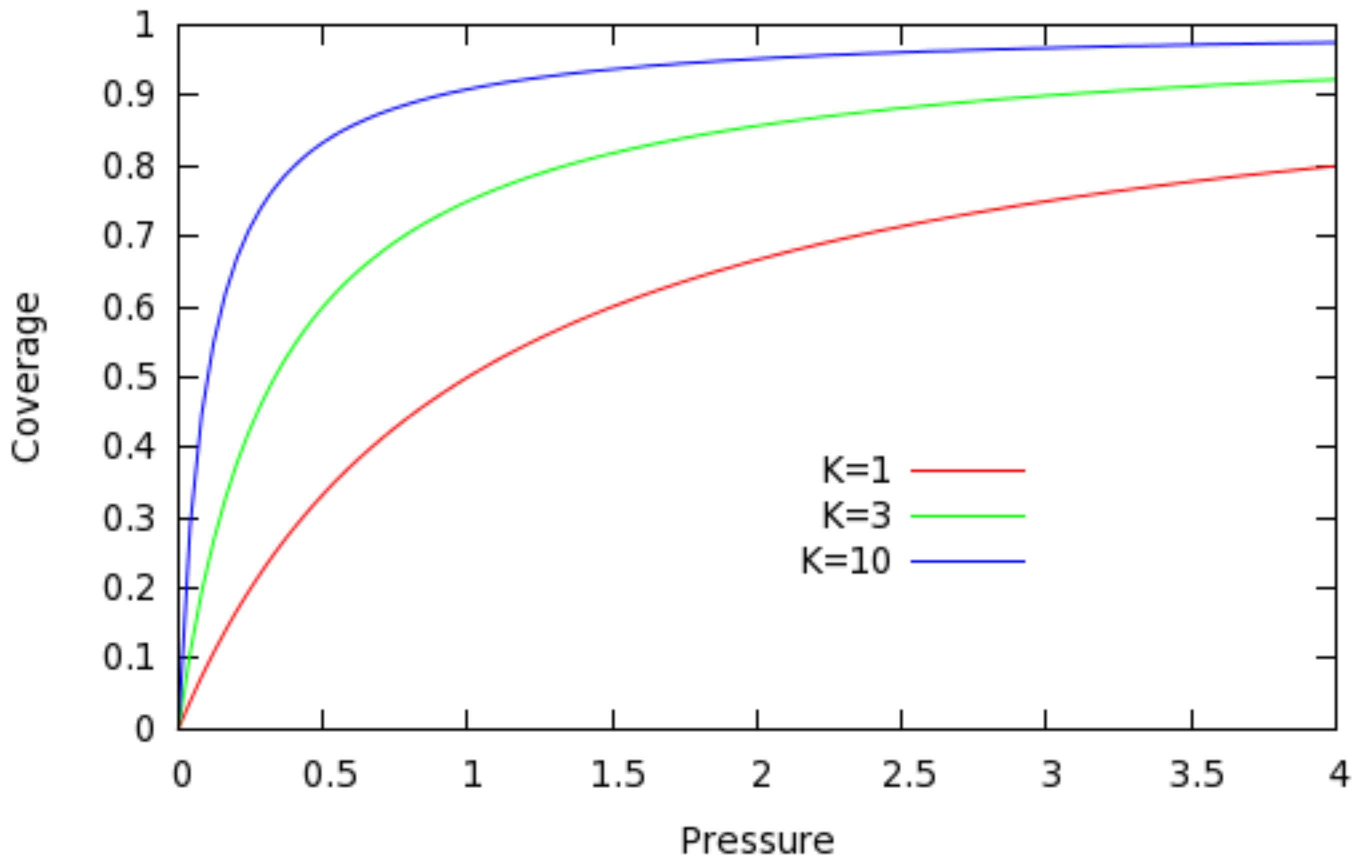
fraction of sites occupied

K~exp[beta eps]

eps=|BE|, energy of sites

Alternative model: Brunauer, Emmett, Teller (BET) include multilayers but ignores lateral interactions

The Langmuir isotherm is only accurate under conditions where the underlying assumptions are accurate: low pressures (so that molecules don't try and adsorb on top of each other), and strong adsorbents (so that intermolecular interactions in the adsorbed layer can safely be neglected.)



- At high *K* the surface is strongly adsorbent, and the adsorbing gas forms a nearly complete monolayer at low pressures.
- At low *K*, much higher gas pressures are required for the same coverage.
- In all cases, at sufficiently low coverage, the isotherm is linear. This is called the Henry's Law region, because it is analogous to Henry's Law for gases dissolved in solution.