3. The Surface Chemical Bond

3.1 Adsorbate Structures

Many atoms and molecules form *ordered* adsorbate layers (adlayers) on a low index surface at certain temperatures

Commensurate - well-defined relationship to substrate structure

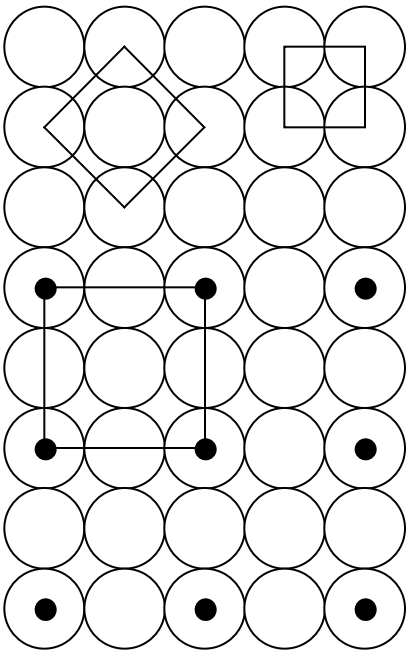
Incommensurate - adsorbate structure independent of substrate

3.1.1 Woods Notation

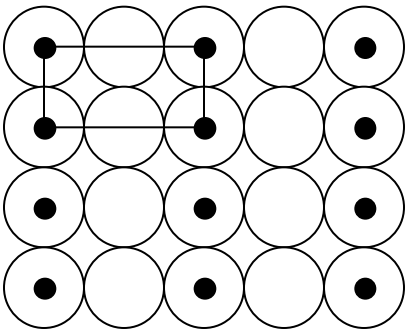
Ordered adlayer defined in terms of relationship to surface net (primitive plane lattice):

Relative size

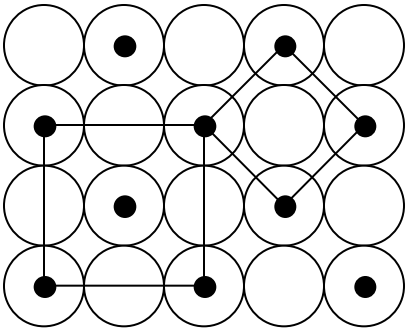
Rotation (anticlockwise)



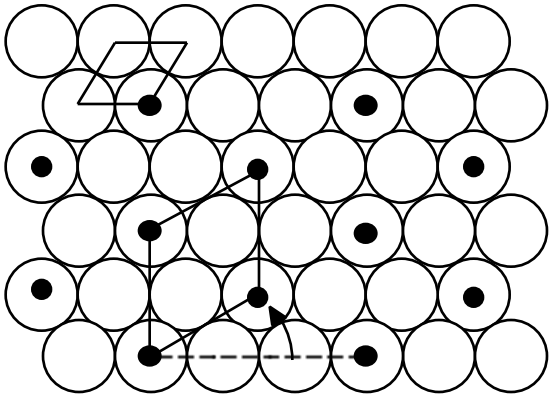
FCC-(100)-p(2x2)
or
FCC(100)-(2x2)



FCC-(100)-(2x1)



FCC-(100)-c(2x2)
or
FCC(100)-(√2x√2)R45



FCC-(111)-(√3x√3)R30

3.1.2 Matrix Notation

A more general (but less intuitive) way of defining any adsorbate structure is to use *matrices* and *surface vectors*

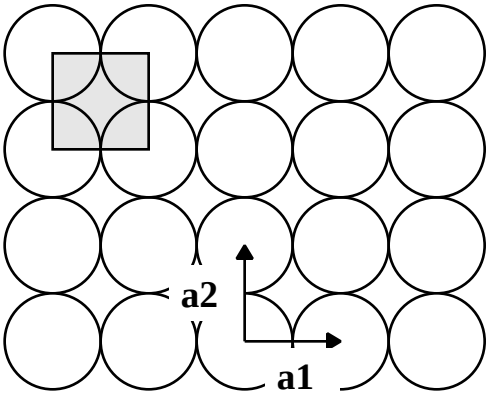
$$\overbrace{\begin{pmatrix}\mathbf{b1}\\ \mathbf{b2}\end{pmatrix}}^{\text{adlayer}} = \overbrace{\begin{pmatrix} n_{a11} & a_{a21} \\ n_{bl2} & n_{b22}\end{pmatrix}}^{\text{matrix}} \overbrace{\begin{pmatrix}\mathbf{a1}\\ \mathbf{a2}\end{pmatrix}}^{\text{substrate}}$$

In principle, can choose any two vectors for **a1** and **a2**. In practice, use conventional surface net.

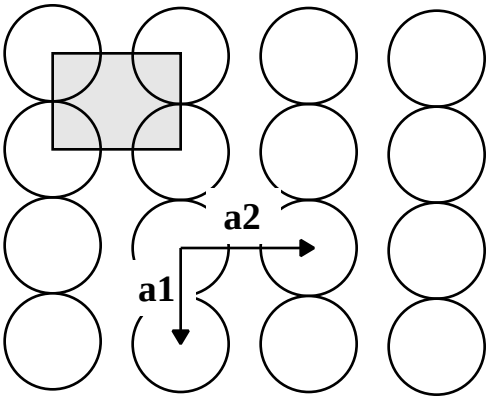
Rules for defining unique surface vectors **a1**, **a2**, **b1**, **b2**:

1. Choose $\mathbf{a1} \rightarrow \mathbf{a2}$ in anticlockwise manner
2. Choose $|\mathbf{a2}| \geq |\mathbf{a1}|$

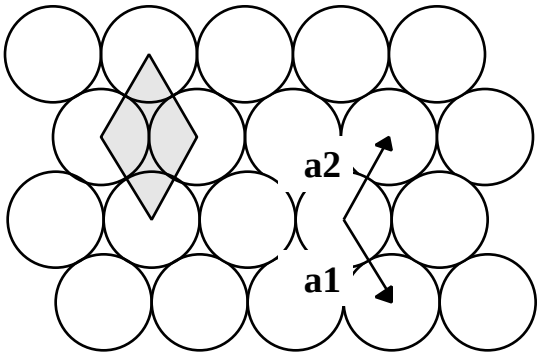
Unit Cell Vector Conventions:
(i) Assign **a1** and **a2** anticlockwise
(ii) **a2**>**a1**



For FCC(100)
|**a1**|=|**a2**|
Perpendicular



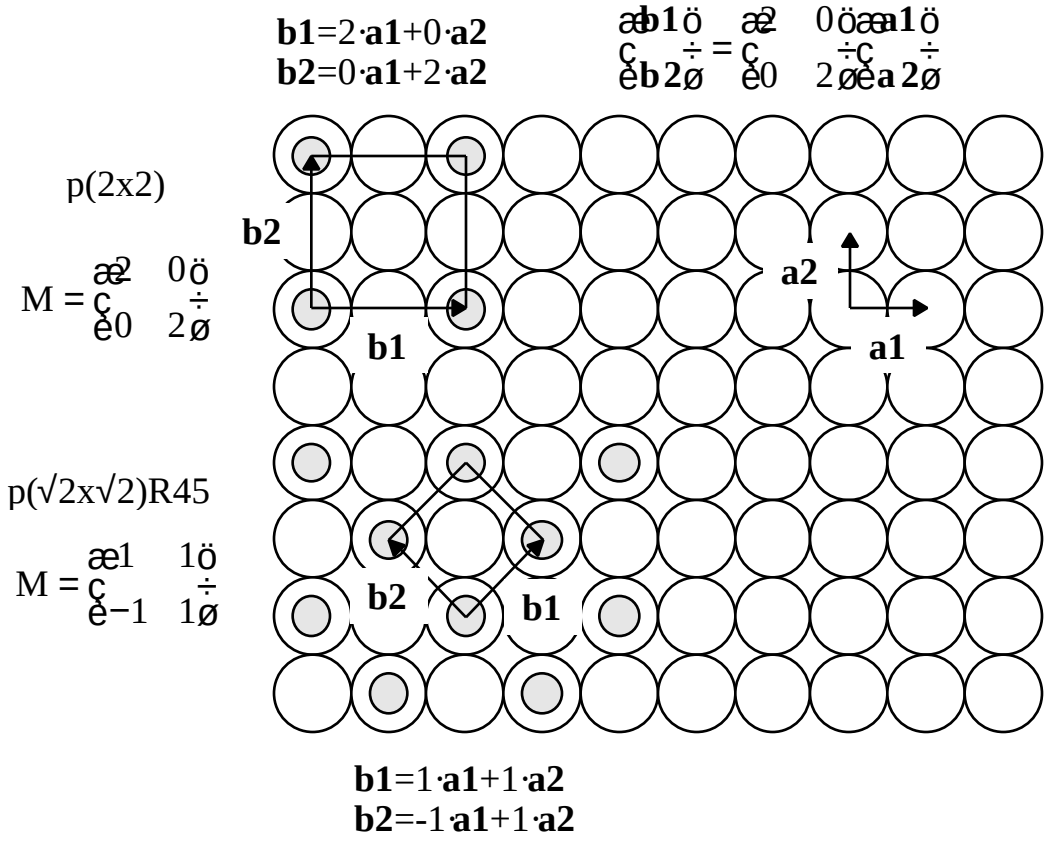
For FCC(110)
|**a1**|<|**a2**|
Perpendicular



For FCC(111)
|**a1**|=|**a2**|
Non-Perpendicular

Matrix?

FCC(100)

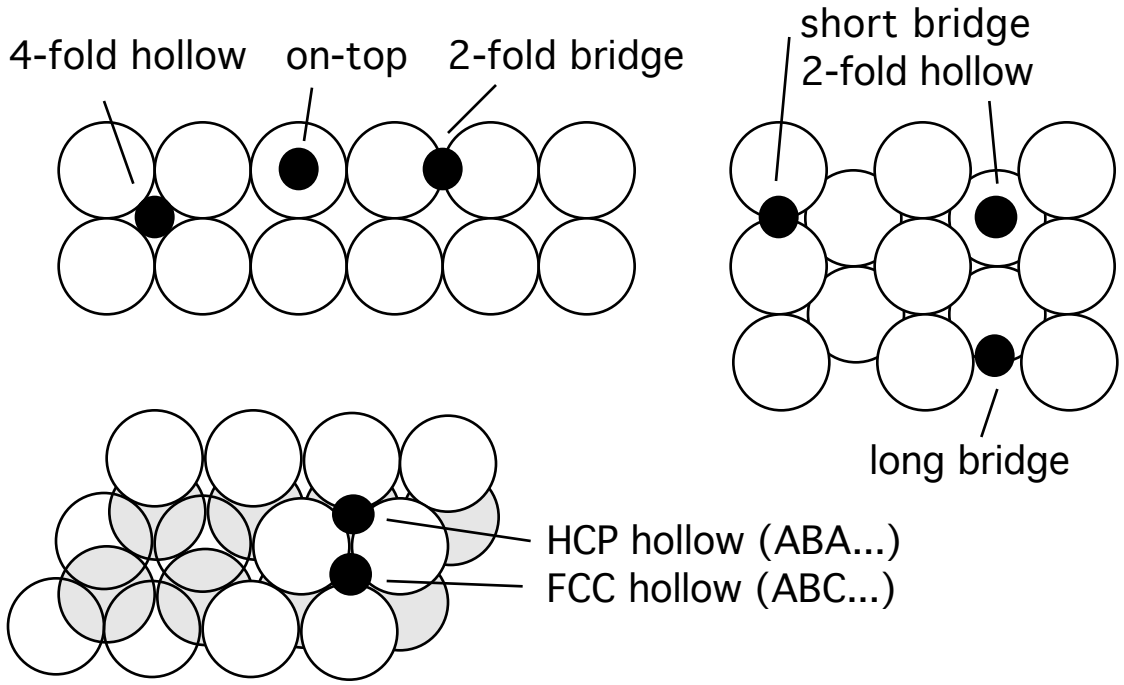


How do I write full notations?

$$\underbrace{\text{Ni}}_{\text{substrate}}\ \underbrace{(110)}_{\text{plane}}\ \underbrace{\underbrace{c}_{\text{centered}}\ \underbrace{(2x2)}_{\text{mesh ratio}}}_{\text{Woods notation}}\ -\ \underbrace{\text{O}}_{\text{adsorbate}}$$

$$\underbrace{\text{Pt}}_{\text{substrate}}\ \underbrace{(100)}_{\text{plane}}\ \underbrace{\underbrace{(2\sqrt{2}x\sqrt{2})R45}_{\text{mesh ratio}}}_{\text{Woods notation}}\ -\ \underbrace{\text{O}}_{\text{adsorbate}}\ \equiv\ \underbrace{\text{Pt}}_{\text{substrate}}\ \underbrace{(100)}_{\text{plane}}\ \underbrace{\overbrace{\begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix}}^{M=}}_{\text{Matrix notation}}\ -\ \underbrace{\text{O}}_{\text{adsorbate}}$$

3.1.3 Adsorption Sites



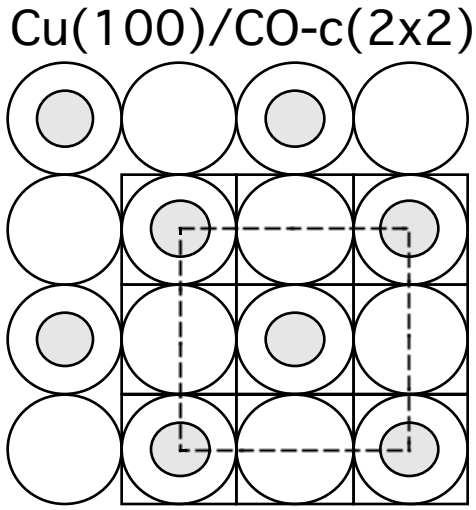
Neither Woods nor Matrix notation tell us anything about where adsorbate is!

Depends on nature of bonding to surface

- non-directional bonds may → highest symmetry hollow sites
- directional bonds may → low symmetry bridge or on-top sites

3.1.4 Coverage

Example: If saturation coverage of CO on Cu(100) at 85 K formed a c(2x2) monolayer



Molecular coverage θ of a surface can be stated:

(a) fraction of saturated monolayer (e.g. CO/Cu(100) Θ_{sat} = 1.0 ML)

(b) absolute number of adsorbates per unit area (e.g. CO/Cu(100) Θ_{sat} = 7.69×10^{14} cm^{-2})

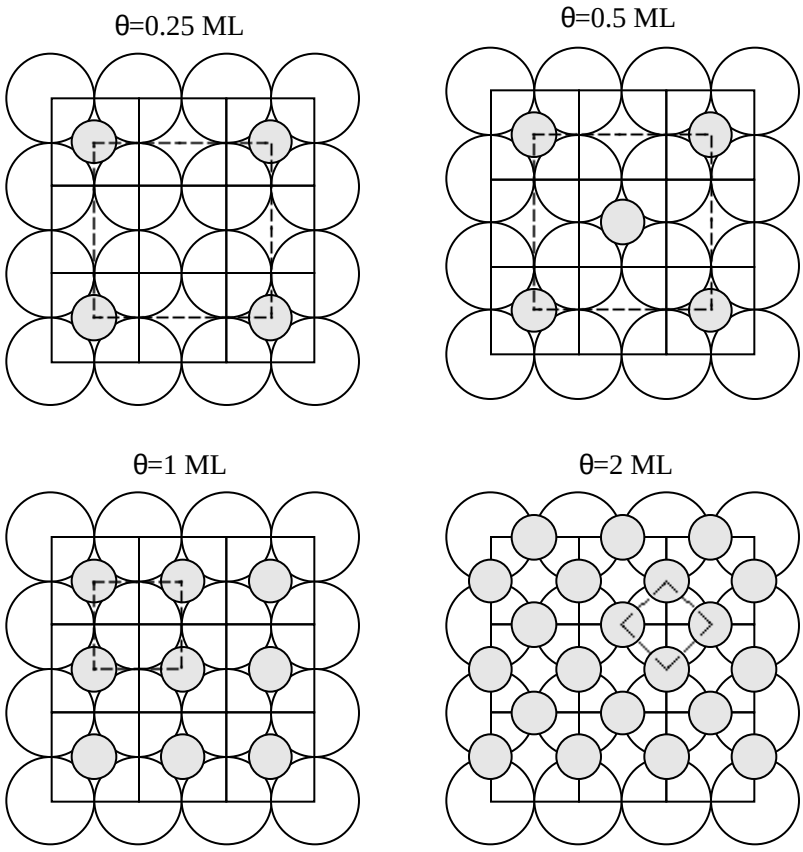
Monolayer can refer to number of adsorbates

(a) per primitive surface unit cell

$$CO/Cu(100)\ \Theta_{sat} = \frac{\#\ \text{adsorbates}}{\text{primitive unit mesh}} = \frac{2}{4} = 0.5\ \text{ML}$$

(b) per surface atom (*not* the same as the primitive unit cell if the surface is not elemental or a 1:1 compound for example)

$$CO/Cu(100)\ \Theta_{sat} = \frac{\#\ \text{adsorbates}}{\text{surface atom}} = \frac{1 + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4}}{4} = 0.5\ \text{ML}$$



p(2x2) Θ=0.25 ML c(2 x 2) Θ = 0.5 ML

p(1 x 1) Θ = 1.0 ML p(√2/2 x √2/2)R45 Θ = 2.0 ML

3.2 Adsorption and Ordered Adlayers

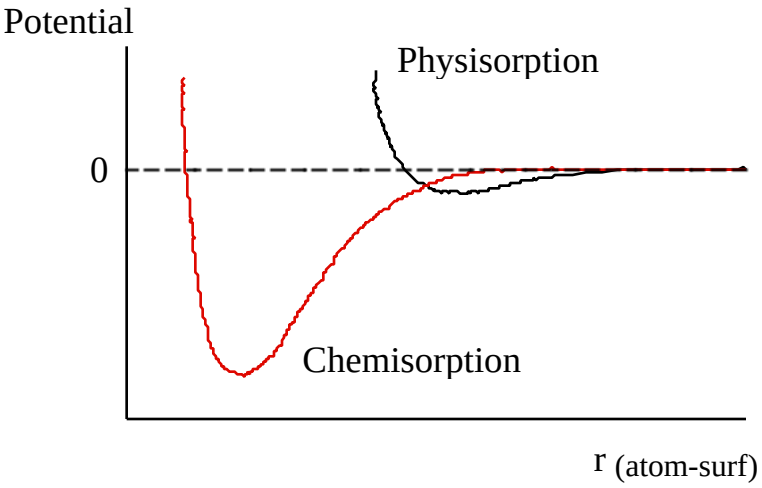
Order is result of:

(a) Adsorbate-substrate interactions (vdW, ionic, metallic, covalent)

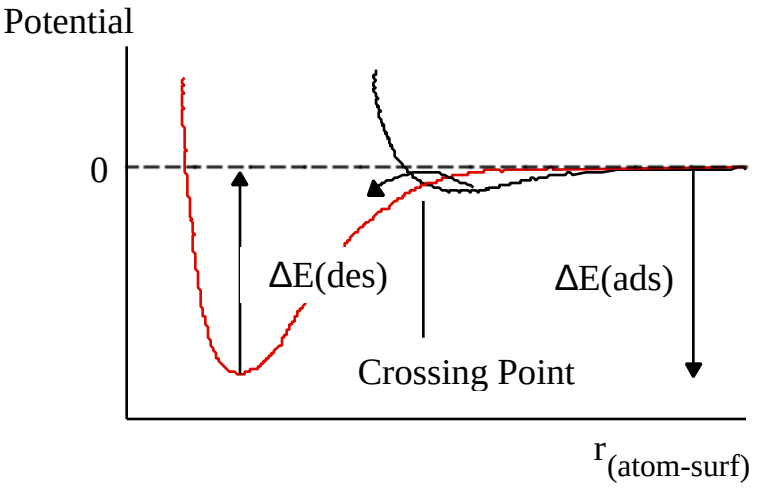
(b) Adsorbate-adsorbate interactions (attractive or repulsive)

(c) Surface diffusion

3.2.1 Adsorbate-Substrate Interactions (Chemisorption and Physisorption)



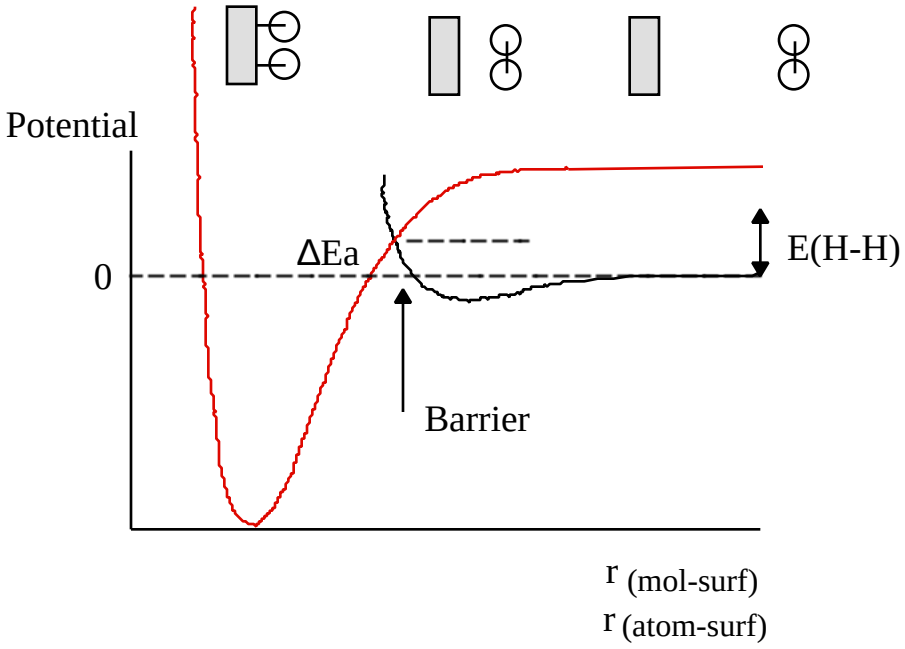
Physical Adsorption
(Physiorption)
- no barrier (not activated)
- fast
- vdW/dipole interactions
- weak (<0.4 eV)
- always atomic/molecular
- reversible
- surface symmetry insensitive
- may form multilayers
- surface T < condensation T



Chemical Adsorption
(Chemisorption)
- may have barrier
- variable uptake kinetics
- covalent/metallic/ionic
- strong (>0.4 eV)
- may be dissociative
- often irreversible
- surface symmetry specific
- limited to monolayer
- wide range surface T

If non-dissociative molecular adsorption, sensitive to
- initial orientation of molecule
- changes in internal bonding
- point of approach (adsorption site)

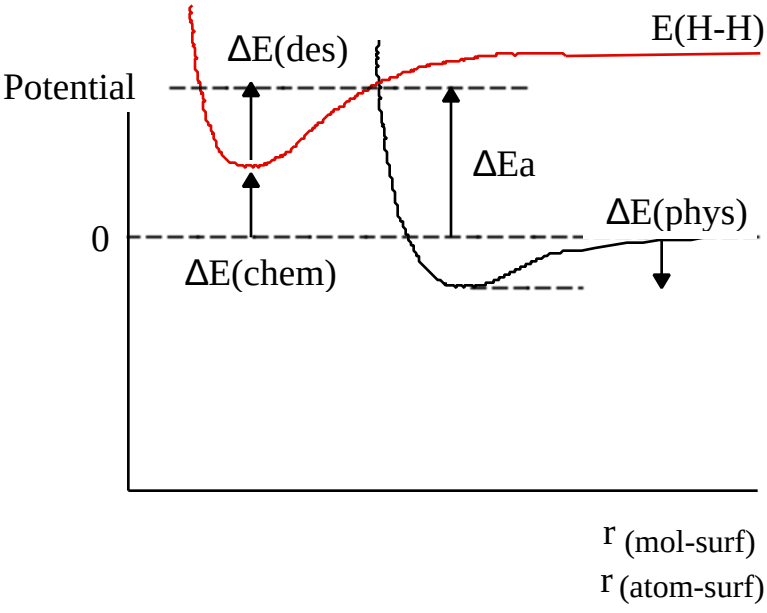
Often chemisorption is activated and may be dissociative:



Direct chemisorption usually not observed
- transient physisorption
-"precursor mediated adsorption"

Barrier height affects
- adsorption klinetics
- lifetime of transient
- desorption kinetics

Not all physisorption leads to chemisorption:



If activated (dissociative or non-dissociative) adsorption
- ΔE(des) not equal to ΔE(ads)

H_2 physisorbs on Au(111) - chemisorption is exothermic

H atoms chemisorb on Au(111), but desorb as H_2

3.2.2 Adsorbate-Adsorbate Interactions

Interactions may be

- electrostatic (vdW, permanent/induced dipoles, quadrupoles, hydrogen bonding)

- metallic

- covalent (rare)

For *physisorption*, adsorbate-adsorbate interactions similar to adsorbate-substrate

Choice of surface site less important

"Directionality" of bonding may influence structure

Attractive interaction - islanding in incommensurate close packed structure

Repulsive interactions - non-close-packed arrays or lattice gas

For *chemisorption*, adsorbate-adsorbate interactions weaker than adsorbate-substrate

Structure dominated by surface site

Commensurate close-packed or non-close-packed structures

As Θ increases, steric repulsion between adsorbates competes with ΔH_{ads} and reach saturation coverage. Consequences?

(a) No further coverage increase

(b) Phase change/adsorbate reorientation

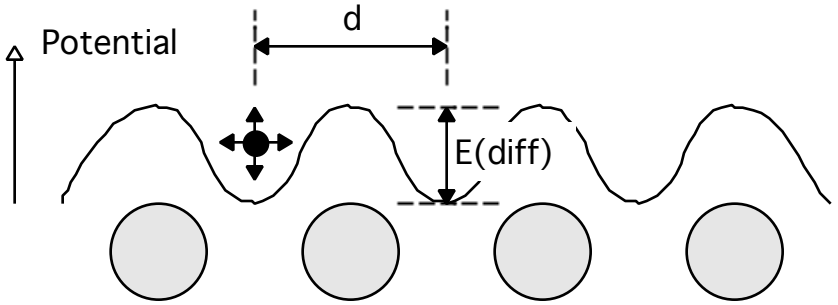
(c) Substrate reconstruction

(d) Compound/alloy formation

(e) Condensation of physisorbed monolayers on top

3.2.3 Surface Diffusion

Ordered monolayers can only form if surface diffusion is high



Adsorbates vibrate in potential well with frequency ν_0. Frequency of site-to-site hopping in one direction, ν, is

$$\nu = \frac{1}{z}\,\nu_0 \exp\left(\frac{-E(diff)}{kT}\right)$$

where z is the number of possible neighboring wells. In terms of diffusion coefficient D ($cm^2 \cdot s^{-1}$)

$$D = D_0 \exp\left(\frac{-E(diff)}{kT}\right) \qquad \text{where } D_0 = \frac{\nu_0\, d^2}{2\, z}$$

Typically, $\nu_0 \sim 10^{13}$ s^{-1} and E(diff) 100-300 $kJ \cdot mol^{-1}$ for self-diffusion

Material	E(diff) ($kJ \cdot mol^{-1}$)	D_0 ($cm^2 \cdot s^{-1}$)
Ni	158.8	300
Pt	110-125	4×10^{-3}
Rh	173.5	4×10^{-2}
Re	217.4	1.0
W	284-326	0.85
Cu	171-192	650
Au	146-176	0.37
Mo	217-234	0.8

Some general observations:

(1) In general, high ΔH_{ads} produces high E(diff).

$$\Omega = \frac{E(diff)}{\Delta H_{ads}} \qquad \text{Corrugation Ratio}$$

For metals/metals $\Omega \sim 0.13$, for non-metals/metals $\Omega \sim 0.23$

(see Seebauer and Allen, Prog. Surf. Sci. 49 (1995) 265)

(2) D and E(diff) often vary with Θ - ordered layers formed when D is high

(3) Adatoms may self-diffuse by exchange with surface

(4) Vacancies diffuse by successive atom filling

(5) Adatoms may hop multiple d spacing in single event

(6) D higher along natural troughs in surface - FCC(110)

Material	D_0 ($cm^2 \cdot s^{-1}$)
Ag / Cu(110)	2.8
Ag / Cu(110)||	7.3
CO / Pt(110)	7×10^{-4}
CO / Pt(110)||	5×10^{-3}

(7) D often higher for close-packed surfaces - FCC(111) > FCC(100)

(8) D higher along steps than up/down them

Material	D_0 ($cm^2 \cdot s^{-1}$)
W / W(211)	4.2×10^{-9}
W / W(211)||	7.7×10^{-3}
H / W(211)	1×10^{-5}
H / W(211)||	2×10^{-4}