

Cluster growth on surfaces

组员：顾高臣 王晓静 徐丽 张雪
盛倩 孔俊丽 陈国富

INTRODUCTION

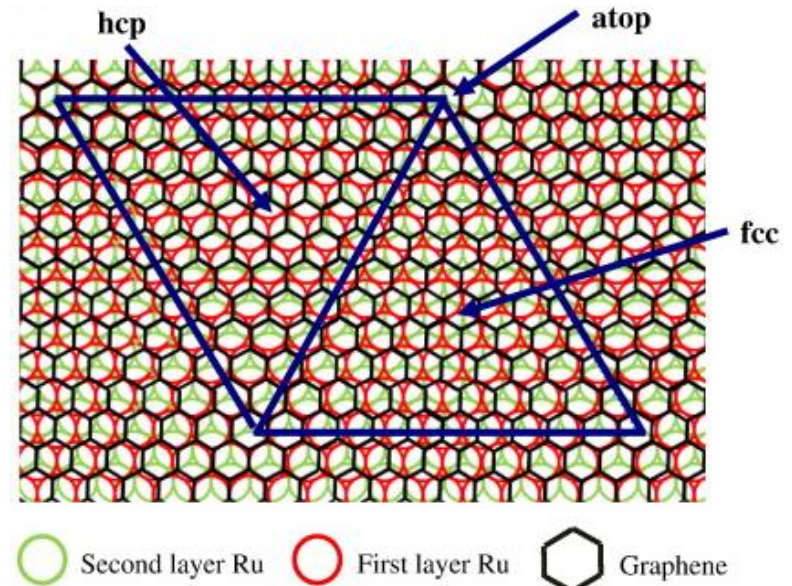
A widely applied method for design of materials with nanoscale dimensions

- deposit atoms or molecule on a solid substrate
- Adsorbed atoms diffuse along the surface, nucleate, and form aggregates, interplay leads to a rich variety of self-organized growth
- The physical properties differ distinctly from the bulk phases

STM and AFM to uncover microscopic detail

Motivation: many of the basic questions in the field of surface growth appear

- self-organized growth of nanoalloys
- epitaxial growth of colloids
- growth of graphene on metal substrates
- growth of metallic nanoparticles on graphene



Elementary Processes and Rate Equations

- Advanced computer simulation techniques
- Basic assumptions: ideal surfaces
- Types of atomic moves
- Factors influencing the nucleation and growth of islands
- Measurement of island densities----Rate equations

表面上原子运动种类和岛的形成

在薄膜生长中原子扩散是一个极为重要的动力学过程，原子的表面扩散可以大致总结为如下的各种表现：

- (1) 原子沉积到基底上。
- (2) 单个原子在基底表面上的扩散。
- (3) 扩散原子与另外一个扩散原子相遇形核。
- (4) 扩散原子被基底上已存在的岛所俘获。
- (5) 岛边缘的原子有一定几率脱离岛。
- (6) 岛边缘的原子与岛保持键合并沿着岛边扩散
- (7) 直接沉积在岛上的原子扩散后再落到基底上
- (8) 沉积原子在岛上形核。
- (9) 两个（**dimer**）或多个原子组成的原子团的集体扩散运动。

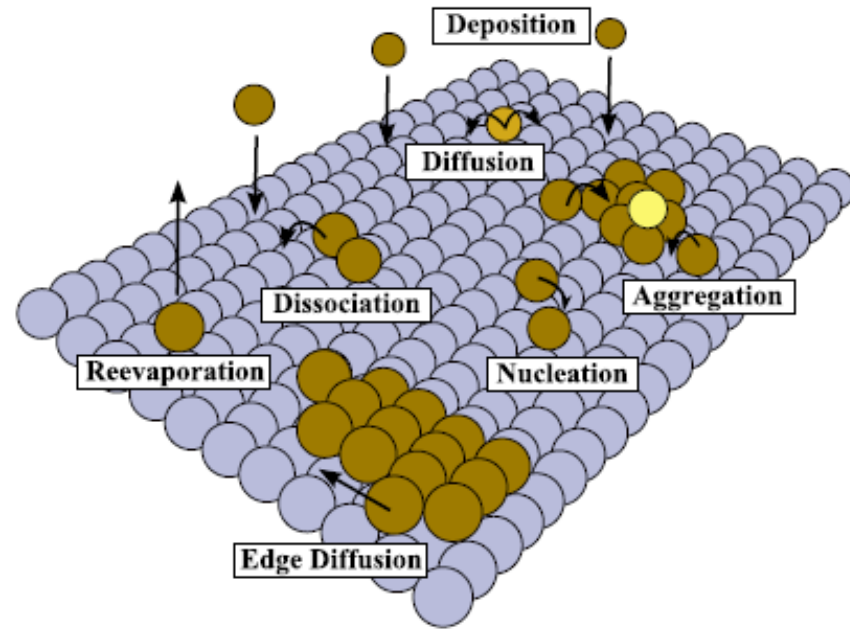


FIG. 1 (color online). Illustration of (a) elementary moves during growth after deposition onto a surface.

Basic assumptions: ideal surfaces

- Disregard all complicating factors arising at real surfaces.
e.g. surface steps, impurities, anisotropies, or reconstruction
- a sequence of a large number of moves eventually leads to a high degree of self-organization and to complex terminal structures.

- reevaporation can be ignored and diffusion is active.
- Thermal energies $k_B T$ are significantly lower than the binding energy E_B between two adatoms.
- $k_B T \ll E_B$ ensures that only a few atoms are required to form a stable island.

Factors influencing the nucleation and growth of islands:

- F: the flux of atoms' deposition onto the surface
- D: thermally activated diffusion coefficient of adatoms along the surface

$$D \simeq D_{\infty} \exp(-U/k_{\text{B}}T).$$

U: diffusion barrier. $D_{\infty} = va^2$, v: attempt frequency and a: the lattice constant of the substrate

The mean time for a atom to hit a unit cell is $1/Fa^2$ and the mean time for the atom to leave the cell by diffusion is a^2/D . The ratio $\tau = D/Fa^4$ control the growth kinetics.

Rate equations (RE):

- the infinite set of equations:

$$\frac{dn}{dt} = F - 2D\sigma_1 n^2 - Dn \sum_{s=2}^{\infty} \sigma_s n_s + 2K_2 n_2 + \sum_{s=3}^{\infty} K_s n_s, \quad (2a)$$

$$\frac{dn_s}{dt} = D\sigma_{s-1} n n_{s-1} - D\sigma_s n n_s + K_{s+1} n_{s+1} - K_s n_s, \quad (2b)$$

$s = 2, 3, \dots$

Neglect: reevaporation of atoms, direct impingement of arriving atoms onto clusters, coalescence of clusters, or dissociation of clusters into subclusters. $n_s(T)$: densities of islands

composed of s atoms. Monomers' density: $n_1(T) = n(T)$. σ_s : 包含 s 个原子的团簇对外来原子的捕获数 $\sigma_s D n n_s$: 扩散的单个原子与包含 s 个原子的团簇的触碰几率 K_s : 单个原子从包含 s 个原子的团簇中脱离出来的几率

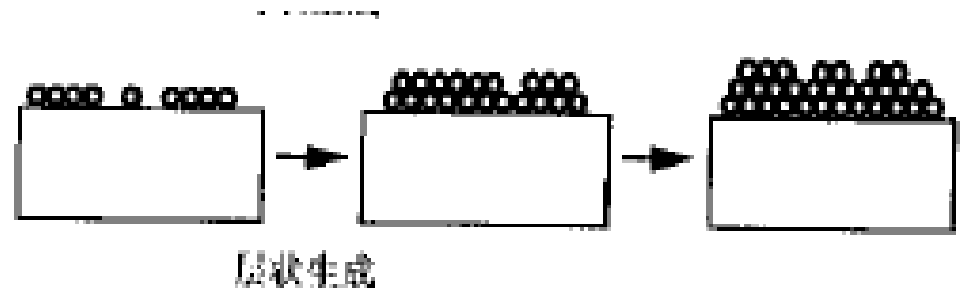
Islands with $s \geq 2$ are considered to be immobile.

Three growth modes

- Frank-van der Merwe(LBL) 层状生长
- Volmer-Weber 岛状生长
- Stranski-Krastanov 混合生长

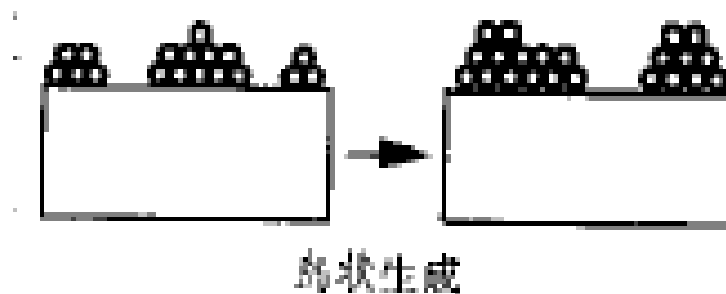
层状生长模式

- 当被沉积物质与衬底之间浸润性很好时，被沉积物质的原子便倾向于与衬底原子成键结合，因此，薄膜从形核阶段开始即采取二维扩展模式



岛状生长模式

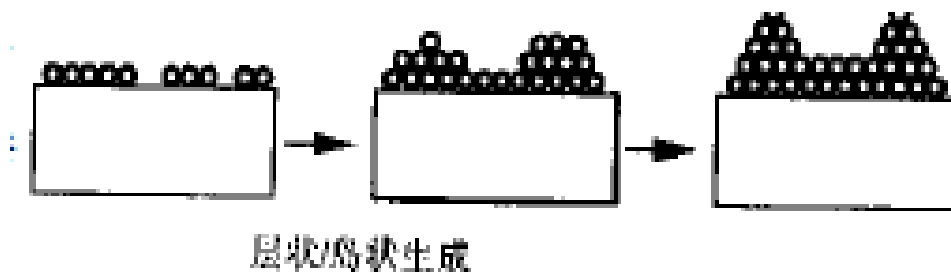
- 该种模式下，被沉积物质的原子或分子倾向于与自身相互键合起来，它们与衬底原子之间浸润性不好，因此避免与衬底原子键合，从而形成许多岛，造成表面粗糙。



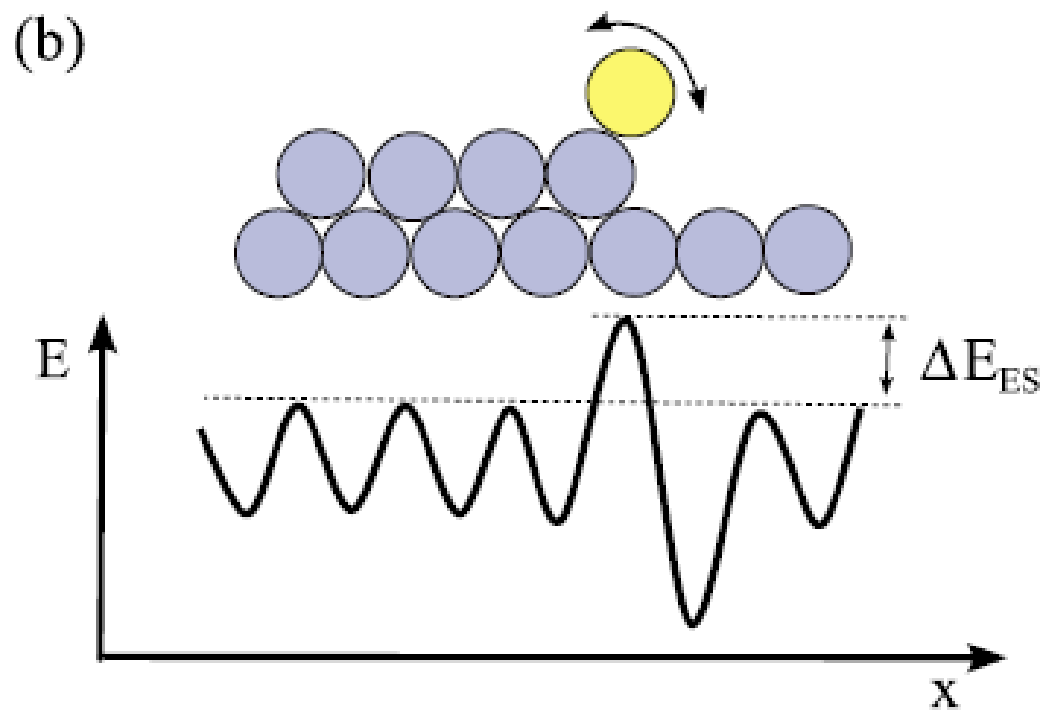
在原子不断沉积的过程中三维岛台阶宽度的演化：较宽台阶的宽度逐渐变窄，而较窄台阶的宽度逐渐变宽。到一定程度之后，台阶宽度就会演化到相等。一旦台阶宽度相等，对于相等的台阶上的原子的层间扩散几率也就变得一样了。因此，台阶宽度会在一定时间内保持相等并不变，岛的斜率也保持不变。只有当受到边界影响之后才会失去了这一平衡。

混合生长模式

- 在最开始一两个原子层厚度时采用层状生长，之后转为岛状生长。



在原子尺度上，产生平滑均匀的薄膜意味着层状生长或者二维生长，相反则是三维生长。这些是热力学和动力学共同作用的结果。



原子跨越边界，扩散到下一层需要克服的边界势垒示意图

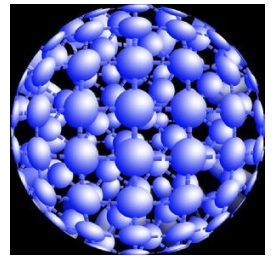
原子需要克服一个边界势垒 ΔE_{ES} 才能穿越岛边界扩散到下一层，假如 ΔE_{ES} 足够大，沉积到岛上的原子无法克服边界势垒而扩散到下一层，因此沉积原子便容易在已形成的岛上形核生长，这样，下一层生长尚未结束，沉积原子便在岛上形核产生新的岛，形成山包状结构，导致表面粗糙。

临界岛尺寸*i*

在形核过程中存在着一个数值，当一个生长岛所包含的原子数大于这个数值时，则该岛是稳定的；而当此岛所包含的原子数量小于或等于该数值时，该岛是不稳定的。

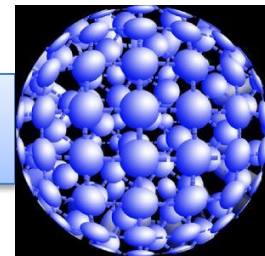
对不同的材料，它们对应的原子临界岛尺寸通常是不同的；而且，对同一种沉积原子当实验条件不同时，例如改变衬底温度或沉积速率，它的临界岛尺寸也会不一样。

How Many Islands Form



SURFACE PHYSICS

- Island densities of one-component adsorbates
- Island densities of binary alloys



➤ Island densities of one-component adsorbates

根据速率方程，单体密度满足

$$\frac{dn}{dt} = F - 2D\sigma_1 n^2 - Dn \sum_{s=2}^{\infty} \sigma_s n_s + 2K_2 n_2 + \sum_{s=3}^{\infty} K_s n_s \quad (2a)$$

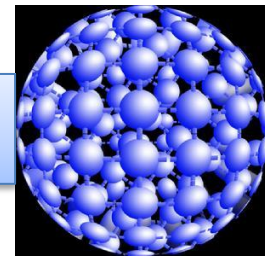
由s个原子组成的岛密度满足

$$\frac{dn_s}{dt} = D\sigma_{s-1} n n_{s-1} - D\sigma_s n n_s + K_{s+1} n_{s+1} - K_s n_s \quad (2b)$$

为了预测稳定岛的密度 $N = \sum_{s=i+1}^{\infty} n_s$ ，方程 (2) 中 σ_s 应该换成平均捕获数 $\bar{\sigma}$ 。

$$\bar{\sigma} = \frac{1}{N} \sum_{s=i+1}^{\infty} \sigma_s n_s \quad (3)$$

Zinsmeister, 1966; Venables, 1973);
Venables, Spiller, and Hanbucken, 1984;
Brune, 1998; Venables, 2000).



➤ Island densities of one-component adsorbates

假设尺寸为 $2 \leq s \leq i$ 的不稳定岛是拟稳态的，在这个状态里衰落和聚集近似平衡。对于一个单体原子，从 s 个原子的团簇中分离，必须要克服能量势垒：团簇对该原子的束缚能 ($E_{s-1} - E_s$) 和扩散势垒 ($K_s = \mu_s D \exp[-(E_{s-1} - E_s)/k_B T]$)。那么沃尔顿公式可以写成：

$$n_s = b_s \exp\left(\frac{E_s}{k_B T}\right) n^s \quad (4)$$

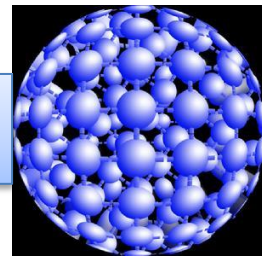
其中， $b_s = \prod_{j=1}^{s-1} \sigma_j / \mu_{j+1}$

将方程 (3)、(4) 带入速率方程 (2) 中，得到：

$$\frac{dn}{dt} = F - (1 + \delta_{i,1}) \sigma_i D n n_i - \bar{\sigma} D n N \quad (5a)$$

$$\frac{dN}{dt} = \sigma_i D n n_i \quad (5b)$$

方程(5b)表明，稳定岛的密度 $N(t)$ 随着晶核形成过程而增加。



SURFACE PHYSICS

➤ Island densities of one-component adsorbates

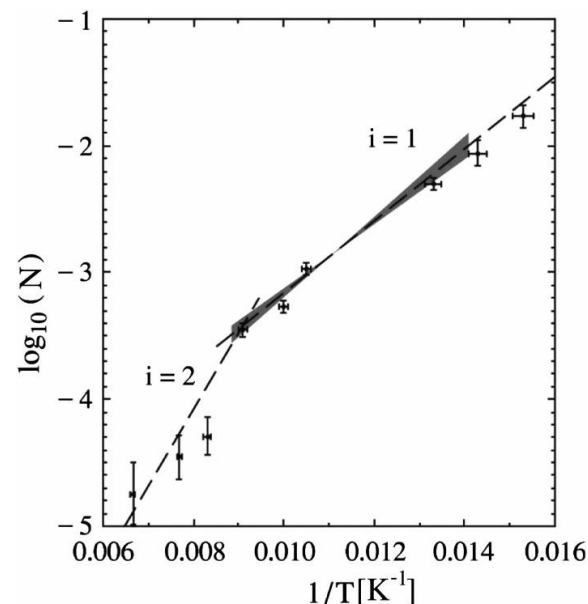
实验值 Γ 非常大，一般在 $(10^5, 10^{11})$ ，这意味着，当 $\Gamma \rightarrow \infty$ 时，方程式(5)有个渐进解：

$$N(\Gamma, \Theta) \sim \left[\frac{(i+2)\sigma_i b_i}{\bar{\sigma}^{i+1}} \Theta \right]^{1/(i+2)} e^{E_i/(i+2)k_B T} \Gamma^{-i/(i+2)} \quad (6a)$$

$$n(\Gamma, \Theta) \sim \frac{1}{\bar{\sigma} \Gamma N(\Gamma, \Theta)} \quad (6b)$$

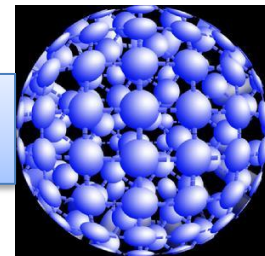
把 N 当作 F 和 T 的函数来测量有助于我们获得岛的临界尺寸、扩散系数和束缚能。图中是在铅(111)上银原子岛的密度阿列纽斯曲线。曲线的斜率代表了原子的激活能 $(iU + E_i)/(i+2)$ 。

在低温区， $i=1$ 时，扩散势垒 $U = 0.168 \pm 0.005 eV$ ；在高温区， $i=2$ 时，斜率表示二聚物的成键能 $E_2 = 0.15 \pm 0.02 eV$ 。



Brune, 1998

Brune, 1999



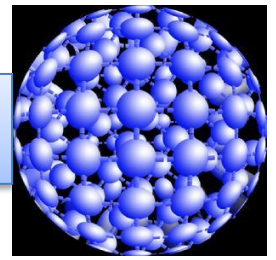
➤ Island densities of binary alloys

对于二元合金，其生长动力学由它们的混合比和表面扩散系数等参数控制，这些参数随着原子种类的不同有很大的差异。而不同种类的原子在表面上的束缚能也不一样，这将导致不同成核路径间的竞争。

对于两种组分A、B，设其单体密度分别为 n_A 、 n_B ，形成二聚物的密度是 n_{AB} ，其速率方程满足

$$\frac{dn_{AB}}{dt} = (D_A + D_B)\sigma_1 n_A n_B - \left(\sum_B D_B n_B \right) \sigma_2 n_{AB} - K_{AB} n_{AB}$$

其中， $D_A + D_B$ 是A和B单体的相对扩散系数； $K_{AB} = K_{BA}$ 是二聚物的分离速率。



➤ Island densities of binary alloys

➤ 如果二聚物是稳定的($i=1$), 那么

$$N \cong \left(\frac{3\sigma_1\Theta}{\bar{\sigma}^2}\right)^{1/3} \Gamma_{eff}^{-1/3},$$

其中, $\Gamma_{eff} = D_{eff}/F$, $D_{eff} = D_A D_B / (x_A D_B + x_B D_A)$ 描述两种组分不同的扩散系数和摩尔分数对体系的影响。显然, 较低扩散系数的原子控制了 N 对温度的关系。

➤ 如果二聚物是不稳定的($i=2$), 那么需要寻找更普适性的沃尔顿方程去用吸附原子密度表示二聚物的密度。由二聚物的形成与分离近平衡得:

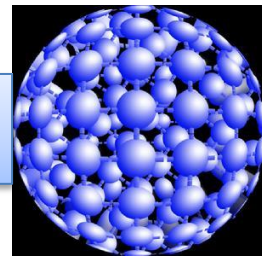
$$\sigma_1 D_\alpha n_\alpha^2 \cong K_{\alpha\alpha} n_{\alpha\alpha}, \quad \alpha = A, B; \quad \sigma_1 = (D_A + D_B) n_A n_B \cong K_{AB} n_{AB}$$

其中, $K_{\alpha\beta} = \mu_{\alpha\beta} D_{\alpha\beta} \exp(-E_{\alpha\beta}/k_B T)$

对应扩散系数 $D_{\alpha\alpha} = D_\alpha$, $D_{AB} = (D_A + D_B)/2$

由于二聚物的束缚能 $E_{\alpha\beta} \geq 0$, 这种情况下, 二聚物岛的密度可以表示为:

$$N \cong \left(\frac{4\sigma_1\sigma_2\Theta}{\bar{\sigma}^3}\right)^{1/4} \left[\sum_{\alpha,\beta} \mu_{\alpha\beta}^{-1} e^{E_{\alpha\beta}/k_B T} \frac{F_\alpha F_\beta}{D_\alpha D_\beta} \right]^{1/4}$$



➤ Island densities of binary alloys

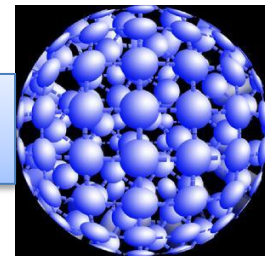
- 如果二聚物的组分有不同的稳定性，那么情况就更复杂了。例如，只有BB型的二聚物是不稳定的($K_{AA} = K_{AB} = 0, K_{BB} > 0$)，或者只形成AA型二聚物是稳定的($K_{AB}, K_{BB} > 0, K_{AA} = 0$)。对于这两种以及其他类似的情况，我们可以借助方程式(10), (11)对二聚物密度对院子密度的关系式进行因式分解来获得一个关于 N 的近速率方程。

$$\frac{dN}{d\Theta} = \frac{b}{N^2} + \frac{c}{N^3} \quad (13)$$

方程式右边的现行叠加表示二聚物成核($dN/d\Theta \sim N^{-2}$)和三聚物成核($dN/d\Theta \sim N^{-3}$)两种路径。

该方程的完整是：

$$N = \left(\frac{c}{b}\right)\psi\left(b^4 \frac{\Theta}{c^3}\right) \quad (14)$$



SURFACE PHYSICS

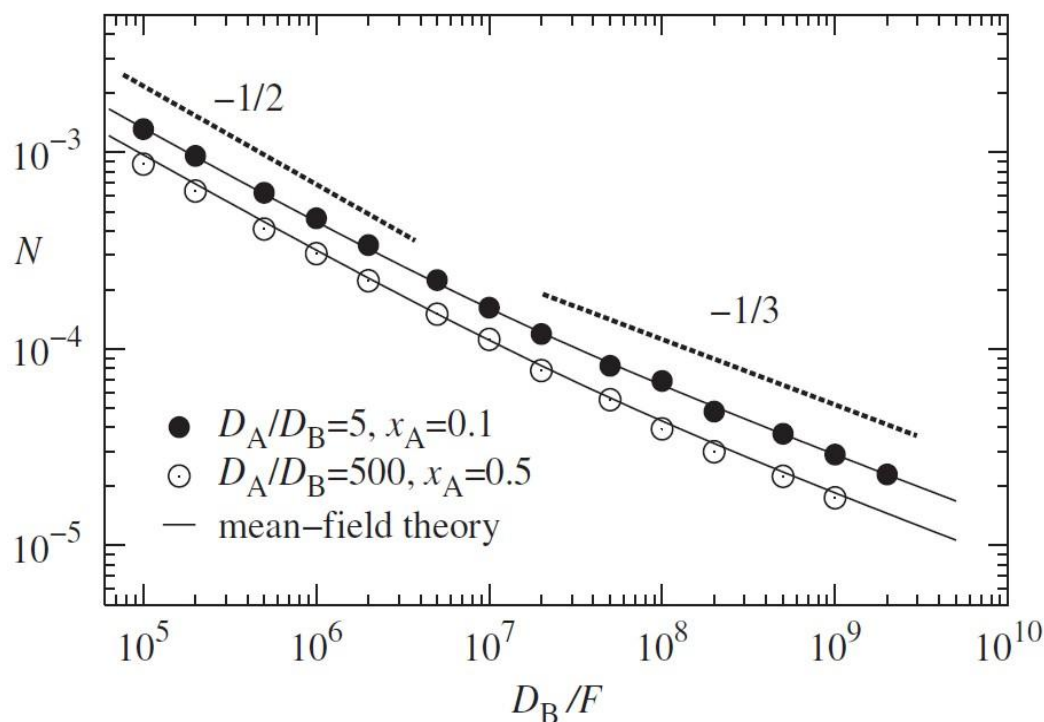
➤ Island densities of binary alloys

在上述情形中，如果稳定的二聚物只是AA型的，那么

$$b \propto F_A/D_A, \quad c \propto \frac{F_A F_B}{D_A D_B} + \left(\frac{F_B}{D_B}\right)^2,$$

这和经过AB，BB两种路径形成三聚物是一致的。

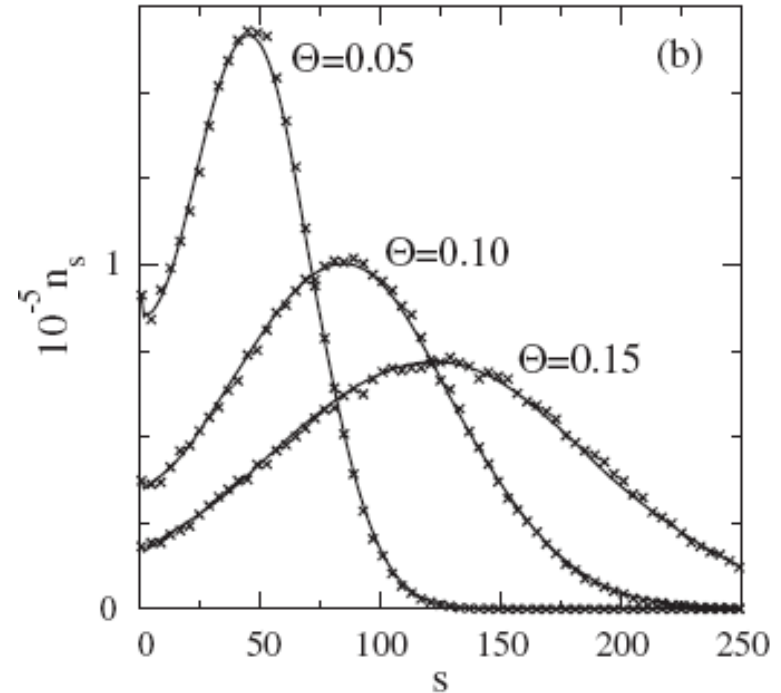
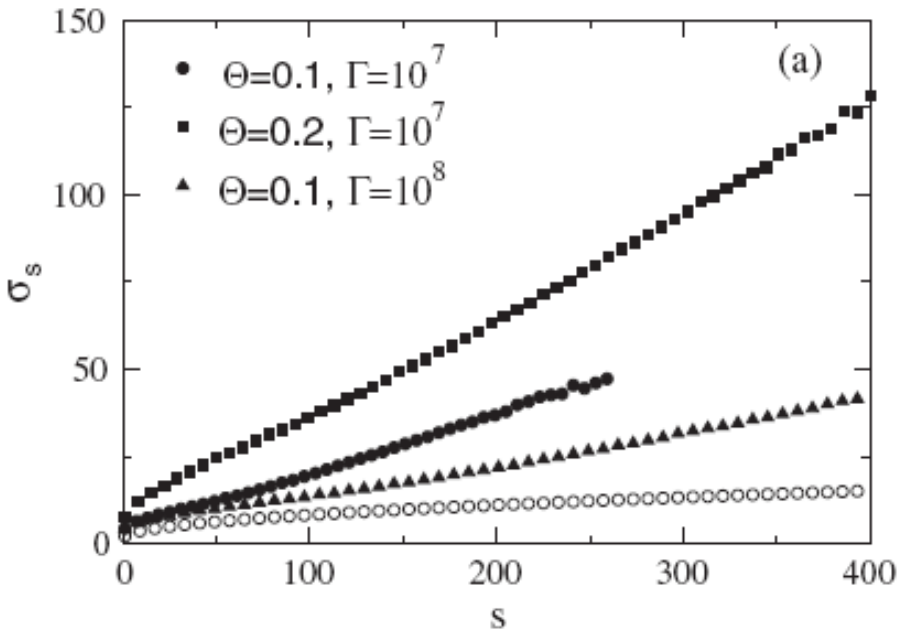
由此可以断定，二聚物的路径是控制B快速扩散和 x_A 大；三聚物则是B慢扩散而 x_B 大。两者之间光滑的转换在右图中很好的呈现。图中 N 对 D_B/F 函数关系的前提是假设AA二聚物是稳定的，且AB、BB二聚物的束缚能为0。



Simulated number densities N of stable islands

什么是岛尺寸分布？

岛的尺寸分布是指不同尺寸的原子岛在基底表面的分布状况，从岛尺寸分布(ISD) $n_s(\Theta, \Gamma)$ ，可以获得关于亚单原子层生长动力学生长的更多的详细的信息。



(a) 俘获数目 (b) 在 (100) 表面的hit-and-stick凝聚的生长动力学的KMC模拟的岛尺寸分布。(a) 中的空心圆曲线是自洽理论在 $\Theta = 0.1$ and $\Gamma = 10^7$ 时的理论预测。(b) 中的实线是把模拟的 $\sigma_s(\Theta, \Gamma)$ 输入时的速率方程的解。

Since the refined RE with those simulated Θ -dependent σ_s were shown to be suitable for predicting the ISD, the challenge is to find an accurate description of the functional form of the $\sigma_s(\Theta, \Gamma)$.

Difficulty: $\sigma_s(\Theta, \Gamma)$ is sensitive to the island morphologies and probably also to details of the growth kinetics.

For improving theories for the ISD, it was argued that correlation effects between island sizes and capture areas need to be taken into account.

It is difficult to find a theoretical description of the details in $\sigma_s(\Theta, \Gamma)$, a simpler approach to the ISD becomes possible when assuming that the dependence of $n_s(\Theta, \Gamma)$ on Θ and Γ is mediated by the mean island size $\bar{s}(\Theta, \Gamma)$.

In this case the ISD should obey the following scaling form:

$$n_s(\Theta, \Gamma) = \frac{\Theta}{\bar{s}^2(\Theta, \Gamma)} f\left(\frac{s}{\bar{s}(\Theta, \Gamma)}\right).$$

here the scaling function $f(x)$ must fulfill the normalization and first moment conditions:

$$\int_0^{\infty} f(x) dx = \int_0^{\infty} x f(x) dx = 1$$

because $\sum_s n_s \simeq N \simeq \Theta / \bar{s}$ and $\sum_s s n_s = \Theta$ Vicsek and Family(1984)

An explicit expression for $f(x)$ suggested by Amar and Family in 1995:

$$f(x) = C_i x^i \exp(-i a_i x^{1/a_i})$$

The dependence of the function on i allow one to determine the size of the critical nucleus from measurements of the ISD.

A semiempirical form for the distribution of capture-zone areas A suggested by Pimpineli and Einstein in 2007:

$$P_\beta = c_\beta a^\beta \exp(-d_\beta a^2)$$

where $a = A/\bar{A}$ is the capture zone rescaled with respect to the mean \bar{A} and $\beta = i + 2$.

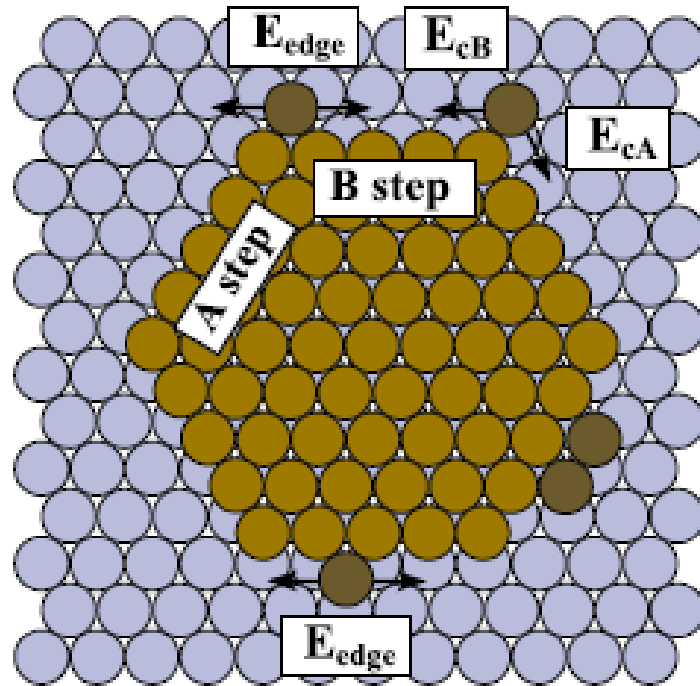
这两种理论公式都可以用于确定临界岛尺寸，俘获区域标度最近被用来确定有机薄膜生长中的临界岛尺寸：在云母石（001）面基底上沉积聚六苯（6P）的实验中，这两个公式在 $i=3$ 时给出了很有说服力的证据。

What determines outer shape and inner structure of island?

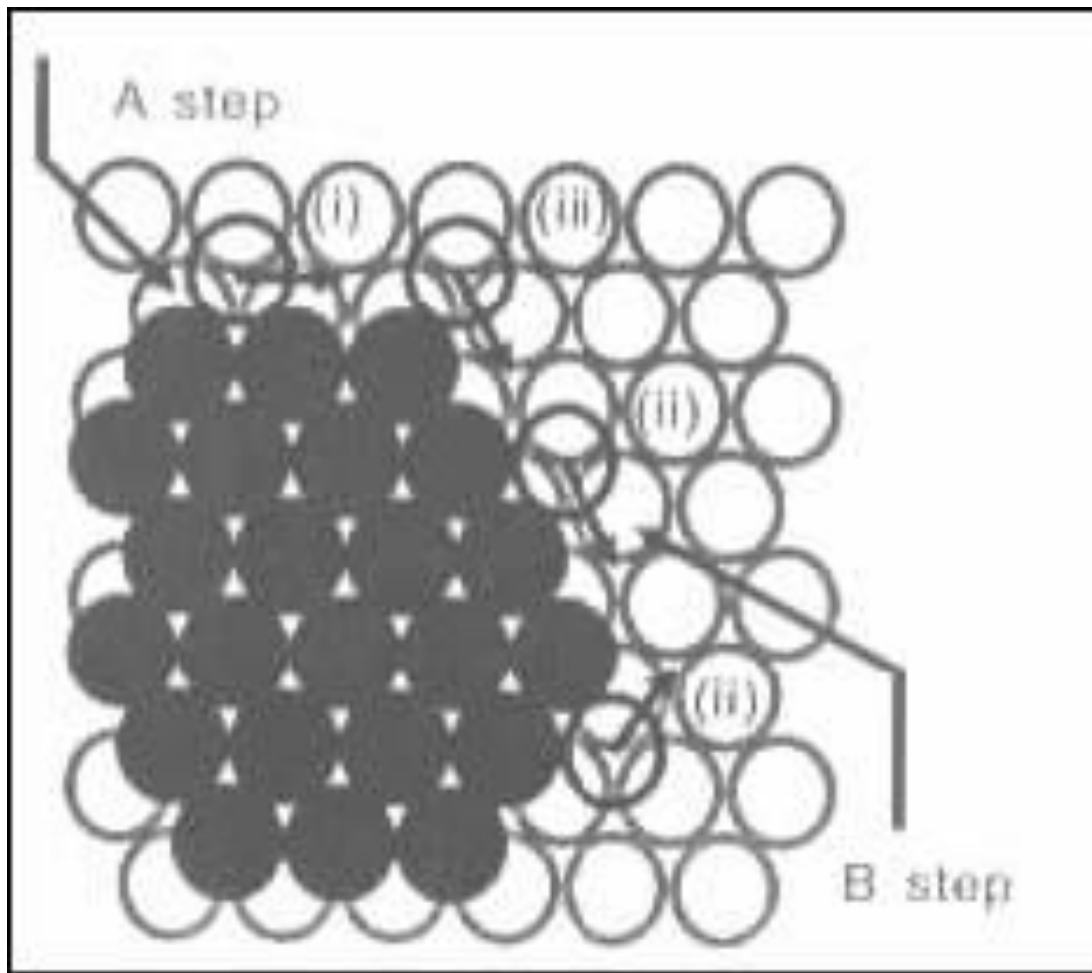
- 在热力学平衡时，对于一个给定的团簇大小，团簇形貌由最小晶面自由能控制；
- 在非平衡条件下，团簇形貌由原子、分子在团簇表面或其附近的运动控制。
- 当吸附到团簇表面时，吸附原子可能遭遇许多不同环境，像镜面(facets)、边(edges)、结(kinks)、棱角(corners)等与基础跳跃能量有关的改变，这导致大量外部形貌和内构的排列。

Eg: Island shapes on (111) surfaces

(111) 表面二维群岛形貌在许多金属外延系统中研究，像广泛知道的 Pt/Pt(111)、 Ag/Pt(111)、 Al/Al(111)、 Ag/Ag(111)、 Au/Pt(111)，它们都是岛的结构由非平衡动力学控制的例子。



Sketch of atomic movements and energy barriers involved in diffusion processes along and between island edges of A and B type on a (111) surface.



A类台阶：台阶上每个原子与下层原子的最近邻原子数为1也叫（100）台阶。

B类台阶：与下层原子所形成的小面为（111）面，与下层原子最近邻原子数为2.

Differences between the two steps in the diffusion properties originate primarily from three sources:

- (i) Stronger binding of adatoms to, say, A steps. Attaching adatoms then have a tendency to enrich at A steps.
- (ii) Same binding energy, but faster diffusion of adatoms along A, caused by a lower energy barrier. This leads to a faster nucleation of new atomic rows at A steps.
- (iii) Asymmetric corner diffusion, which means that a onefold coordinated adatom at a corner site goes preferentially to, say, A steps. Also this effect leads to an enrichment of atoms at A steps.

Conclusion

Cluster growth on surfaces:

connect fundamental studies of non-equilibrium phenomena with the development of nanomaterials of practical use

The rate equation approach

It can provide an accurate framework and predict the island size distribution (ISD) for the analysis of future experiments on the submonolayer kinetics driven by codeposition of two or more atomic species.

Some challenges in this area

- to clarify how far concepts based on single atom surface kinetics remain valid
- require modification : larger sizes, potential nonspherical shapes, and internal degrees of freedom of the molecules.
- understanding of mechanisms underlying organic surface growth: begin
 - ① particular relevance : explain which type of island morphologies develop and how they can be controlled.
 - ② Organic molecules exhibit often only weak interactions with the substrate.
- standard theories of cluster growth in monocomponent atomic systems still imply basic

THANK YOU!