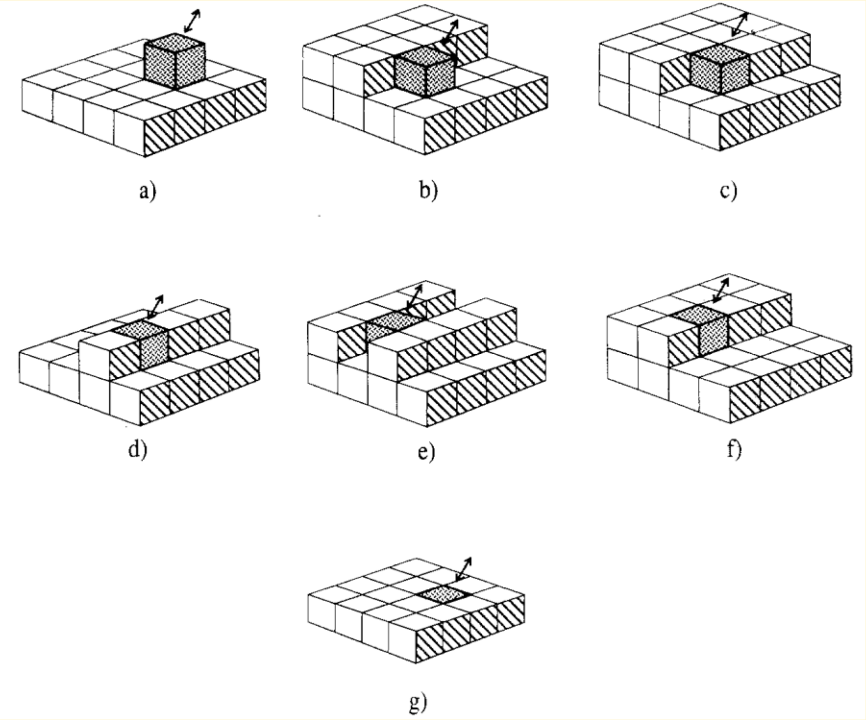
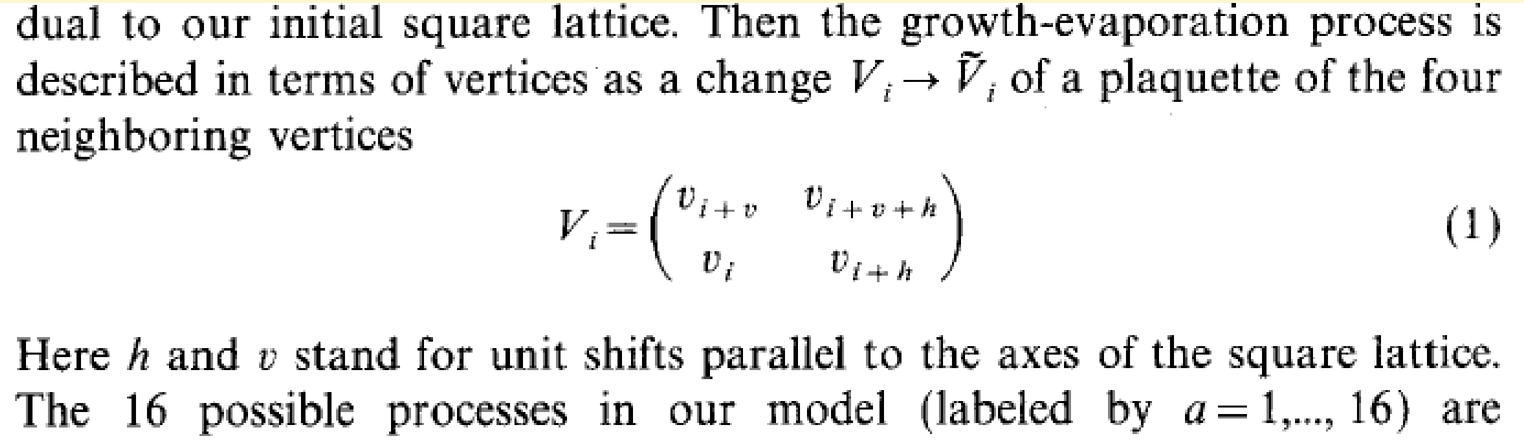
Kinetic BCC growth model



Různé typy procesu kondenzace & evaporace na SC mříži



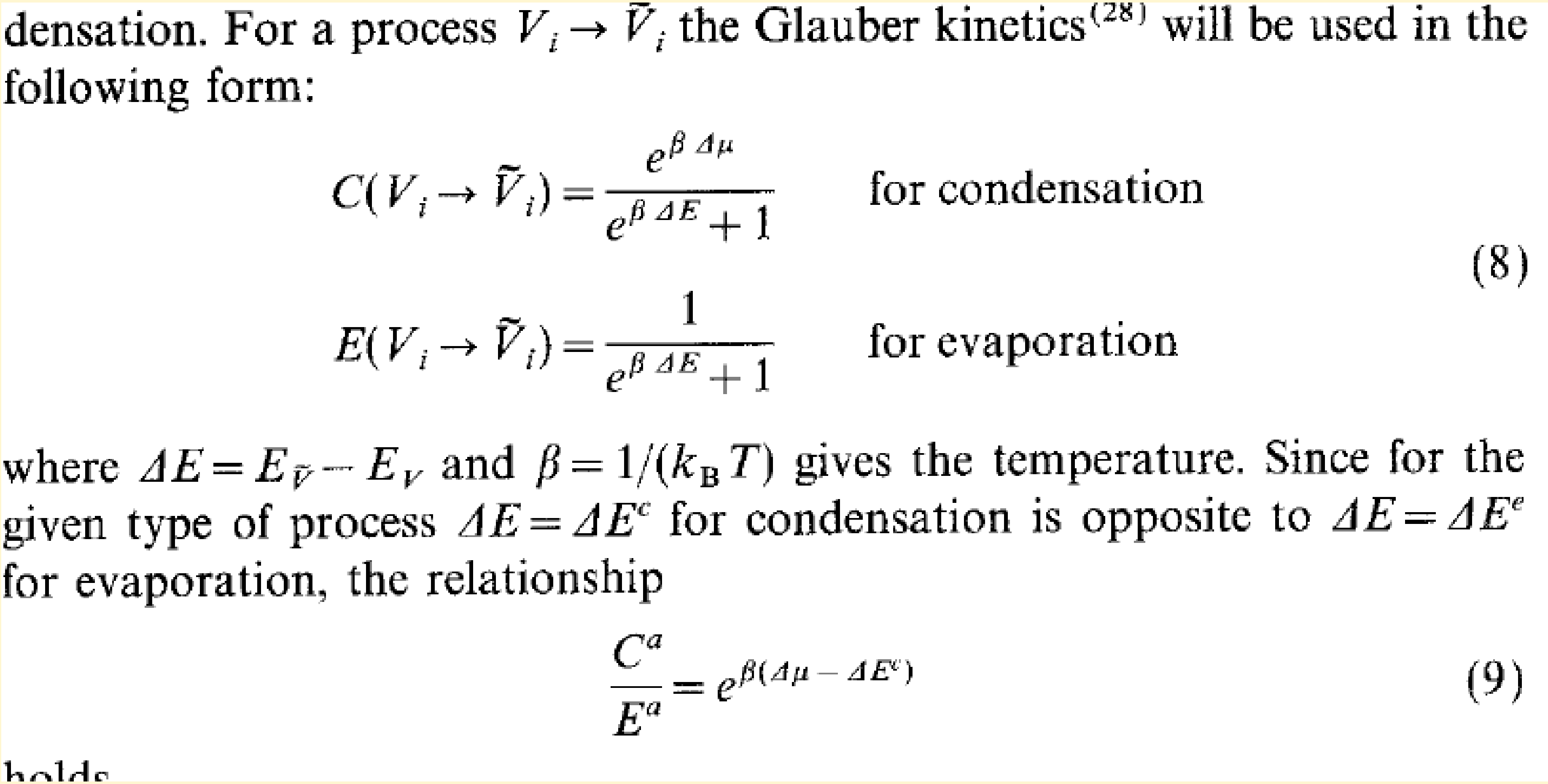
dual to our initial square lattice. Then the growth-evaporation process is described in terms of vertices as a change $V_i \to \tilde{V}_i$ of a plaquette of the four neighboring vertices

$$V_i = \begin{pmatrix} v_{i+v} & v_{i+v+h} \\ v_i & v_{i+h} \end{pmatrix} \qquad (1)$$

Here h and v stand for unit shifts parallel to the axes of the square lattice. The 16 possible processes in our model (labeled by $a = 1, \dots, 16$) are

Kinetic BCC growth model

Pravděpodobnosti kondenzace & vypařování



densation. For a process $V_i \rightarrow \tilde{V}_i$ the Glauber kinetics$^{(28)}$ will be used in the following form:

$$C(V_i \rightarrow \tilde{V}_i) = \frac{e^{\beta\,\Delta\mu}}{e^{\beta\,\Delta E} + 1} \qquad \text{for condensation}$$

$$E(V_i \rightarrow \tilde{V}_i) = \frac{1}{e^{\beta\,\Delta E} + 1} \qquad \text{for evaporation} \tag{8}$$

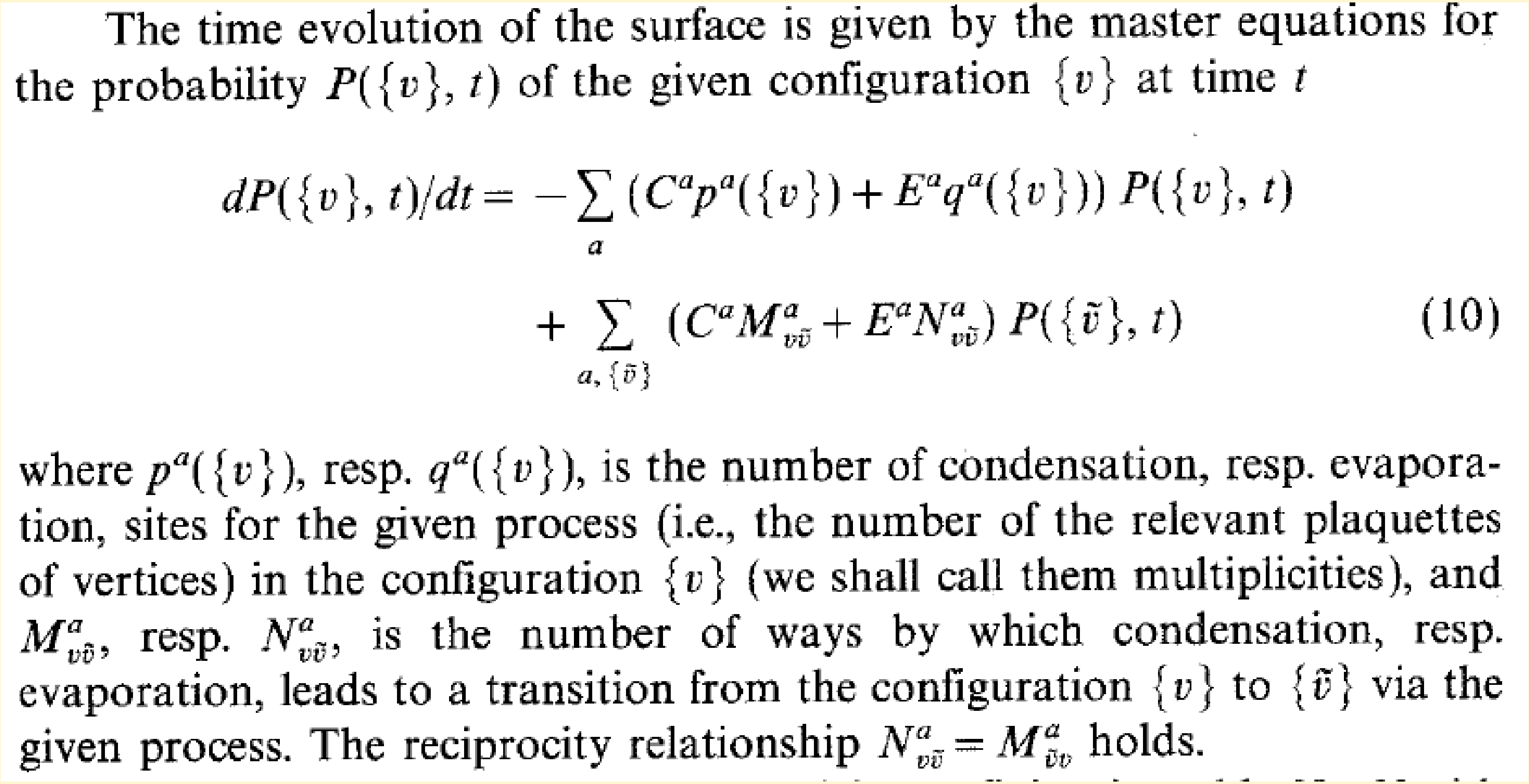
where $\Delta E = E_{\tilde{V}} - E_V$ and $\beta = 1/(k_B T)$ gives the temperature. Since for the given type of process $\Delta E = \Delta E^c$ for condensation is opposite to $\Delta E = \Delta E^e$ for evaporation, the relationship

$$\frac{C^a}{E^a} = e^{\beta(\Delta\mu - \Delta E^c)} \tag{9}$$

holds

Kinetic BCC growth model

Časový vývoj:



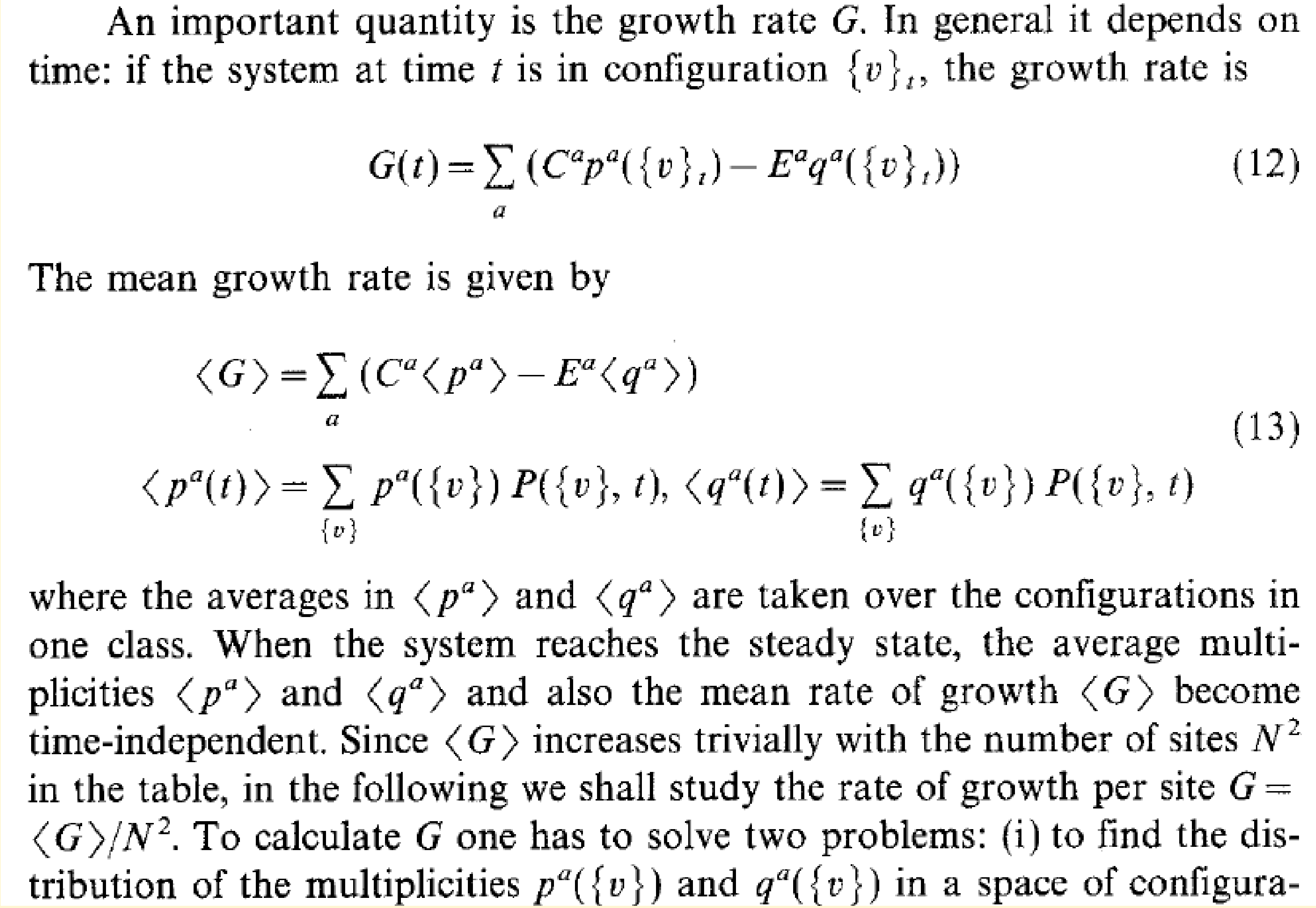
The time evolution of the surface is given by the master equations for the probability $P(\{v\}, t)$ of the given configuration $\{v\}$ at time t

$$dP(\{v\}, t)/dt = -\sum_{a} (C^a p^a(\{v\}) + E^a q^a(\{v\}))\, P(\{v\}, t) + \sum_{a, \{\tilde{v}\}} (C^a M^a_{v\tilde{v}} + E^a N^a_{v\tilde{v}})\, P(\{\tilde{v}\}, t) \qquad (10)$$

where $p^a(\{v\})$, resp. $q^a(\{v\})$, is the number of condensation, resp. evaporation, sites for the given process (i.e., the number of the relevant plaquettes of vertices) in the configuration $\{v\}$ (we shall call them multiplicities), and $M^a_{v\tilde{v}}$, resp. $N^a_{v\tilde{v}}$, is the number of ways by which condensation, resp. evaporation, leads to a transition from the configuration $\{v\}$ to $\{\tilde{v}\}$ via the given process. The reciprocity relationship $N^a_{v\tilde{v}} = M^a_{\tilde{v}v}$ holds.

Kinetic BCC growth model

Výpočet rychlosti růstu:



An important quantity is the growth rate G. In general it depends on time: if the system at time t is in configuration $\{v\}_t$, the growth rate is

$$G(t)=\sum_a \left(C^a p^a(\{v\}_t)-E^a q^a(\{v\}_t)\right) \tag{12}$$

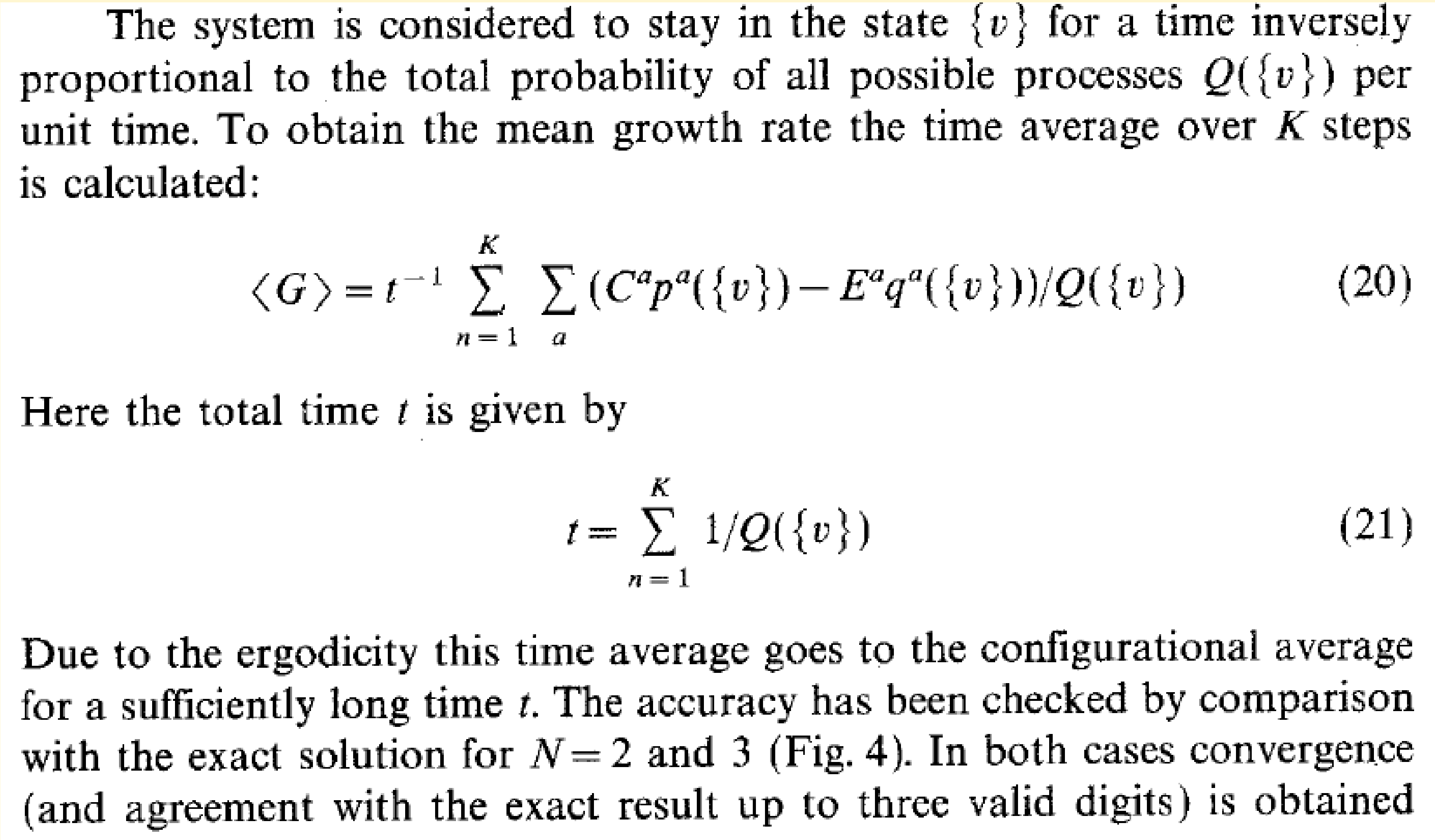
The mean growth rate is given by

$$\begin{aligned} \langle G\rangle &= \sum_a \left(C^a\langle p^a\rangle - E^a\langle q^a\rangle\right) \\ \langle p^a(t)\rangle &= \sum_{\{v\}} p^a(\{v\})\,P(\{v\},t),\ \langle q^a(t)\rangle = \sum_{\{v\}} q^a(\{v\})\,P(\{v\},t) \end{aligned} \tag{13}$$

where the averages in $\langle p^a\rangle$ and $\langle q^a\rangle$ are taken over the configurations in one class. When the system reaches the steady state, the average multiplicities $\langle p^a\rangle$ and $\langle q^a\rangle$ and also the mean rate of growth $\langle G\rangle$ become time-independent. Since $\langle G\rangle$ increases trivially with the number of sites N^2 in the table, in the following we shall study the rate of growth per site $G=\langle G\rangle/N^2$. To calculate G one has to solve two problems: (i) to find the distribution of the multiplicities $p^a(\{v\})$ and $q^a(\{v\})$ in a space of configura-

Kinetic BCC growth model

Kinetické Monte Carlo



The system is considered to stay in the state $\{v\}$ for a time inversely proportional to the total probability of all possible processes $Q(\{v\})$ per unit time. To obtain the mean growth rate the time average over K steps is calculated:

$$\langle G\rangle = t^{-1} \sum_{n=1}^{K} \sum_{a} (C^a p^a(\{v\}) - E^a q^a(\{v\}))/Q(\{v\}) \tag{20}$$

Here the total time t is given by

$$t = \sum_{n=1}^{K} 1/Q(\{v\}) \tag{21}$$

Due to the ergodicity this time average goes to the configurational average for a sufficiently long time t. The accuracy has been checked by comparison with the exact solution for $N=2$ and 3 (Fig. 4). In both cases convergence (and agreement with the exact result up to three valid digits) is obtained

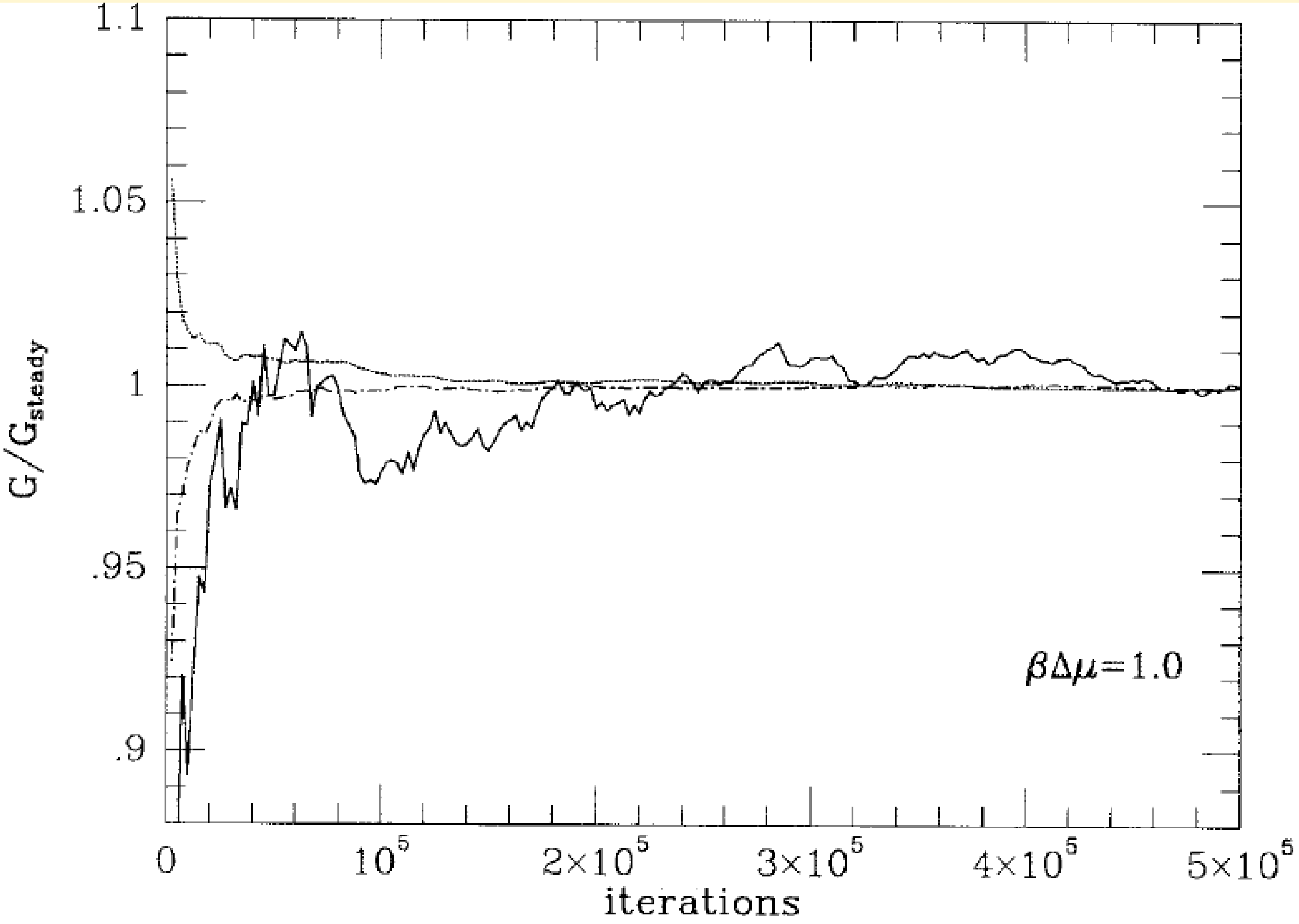


Fig. 5. The evolution of the calculated mean growth rate $\langle G \rangle$ during the simulation for $N = 32$, (001) surface, $\beta \, \Delta\mu = 1$, and three temperatures as in Fig. 4.

already after 10,000 steps. For large N the quantity $\langle G \rangle$, of course, oscillates much longer (see Fig. 5). For $T \geqslant T_R$, $\beta \, \Delta\mu \geqslant 1$, and the size up to $N = 32$ the convergence is obtained after 500,000 steps. The necessary

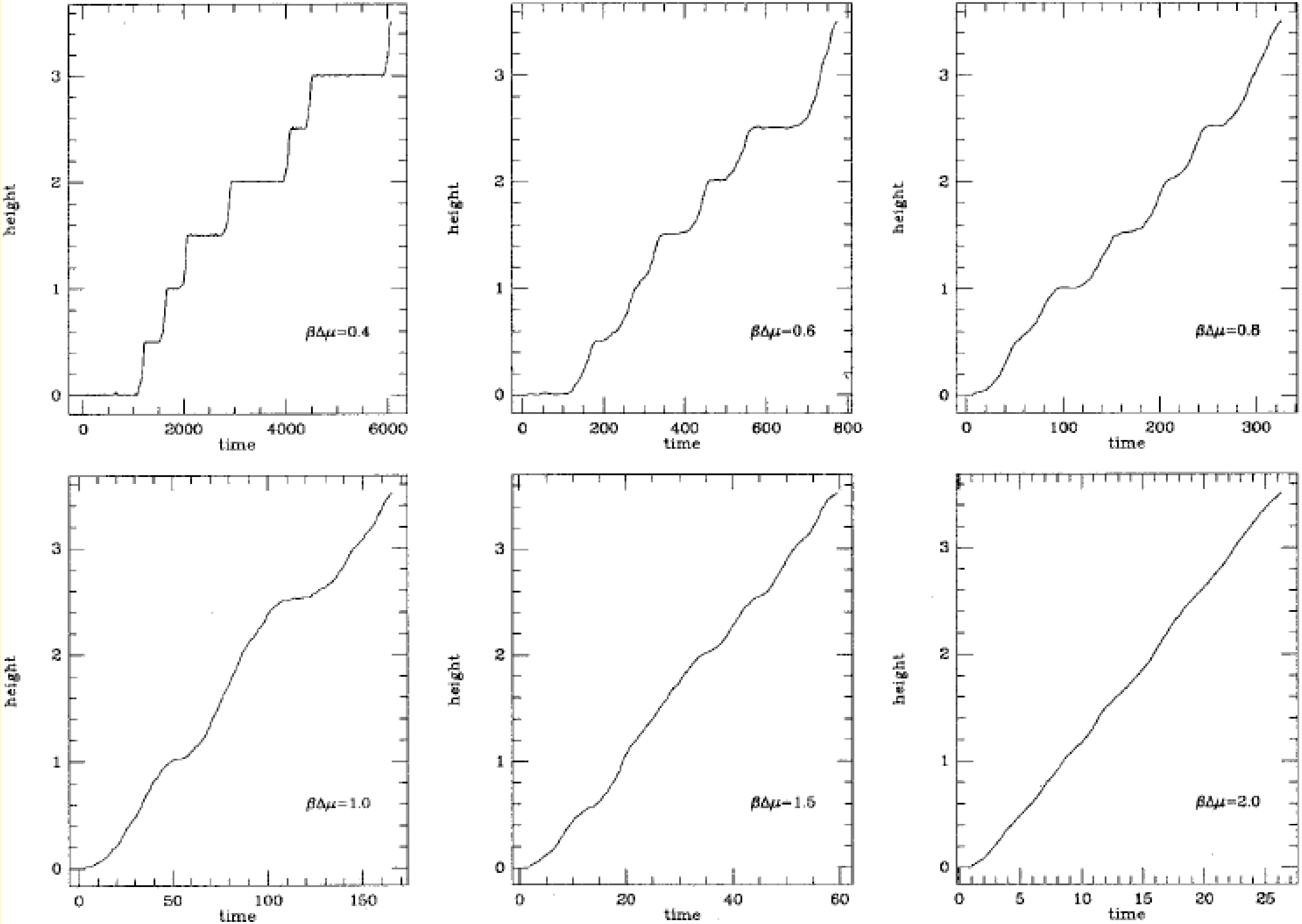


Fig. 10. The time dependence of the average height on (001) surface in units of the bcc spacing *a* for $T/T_R = 0.5$, $N = 32$, and several values of the disequilibrium.

Módy růstu

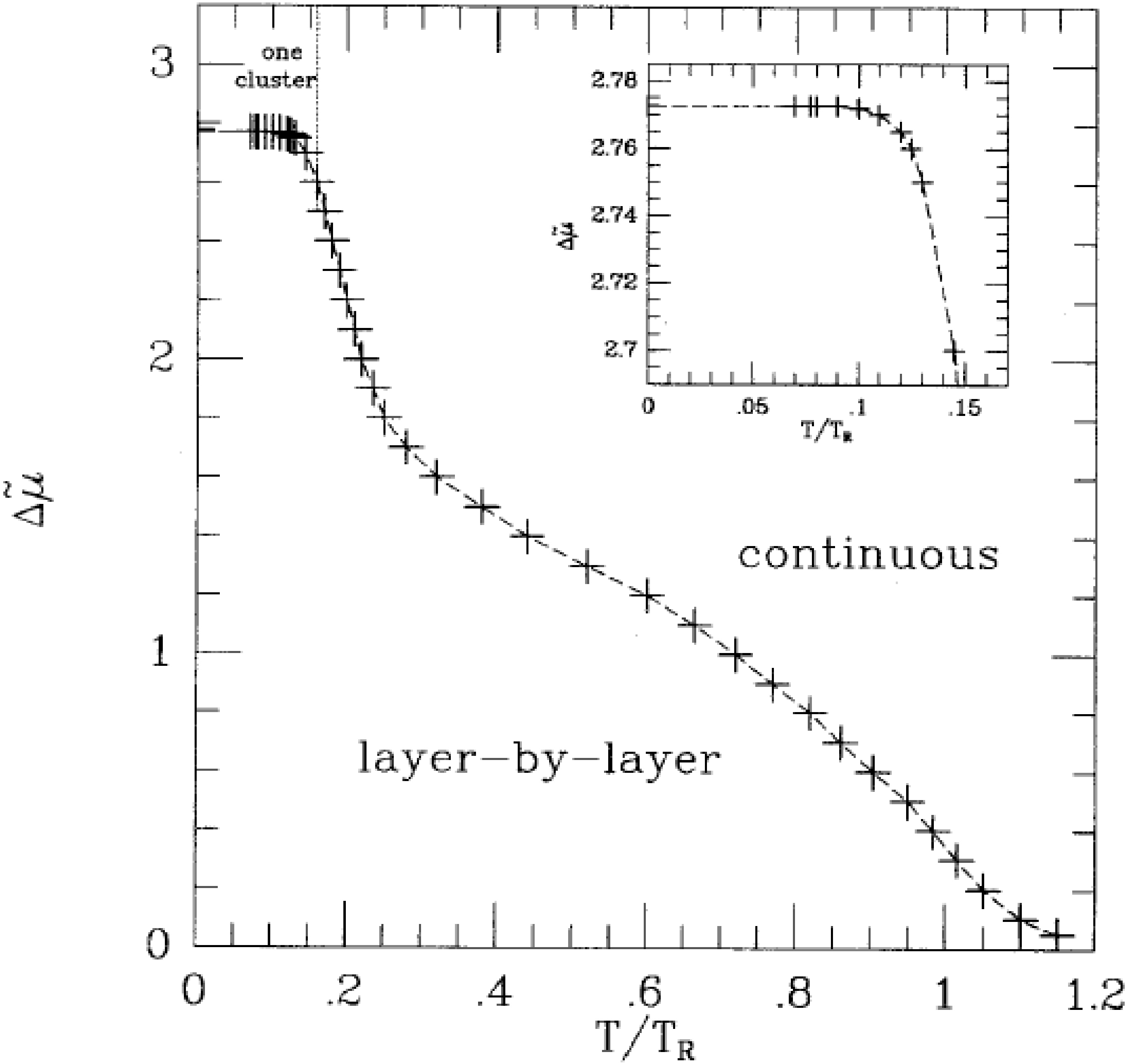
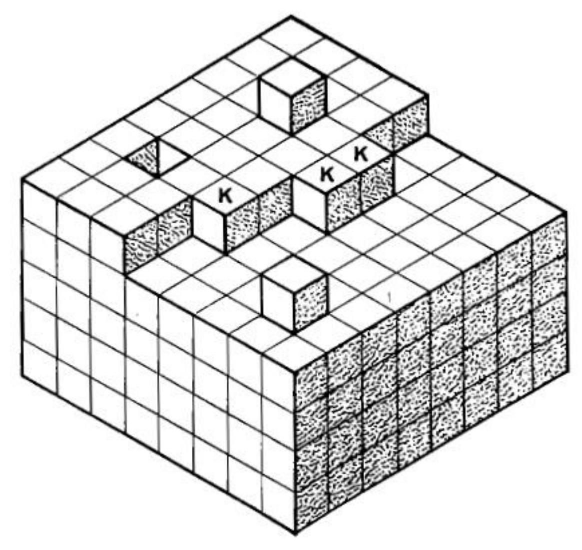


Fig. 11. The regions of different modes of growth in the ($\Delta\tilde{\mu}$, T) plane. The dotted line indicates the region of the one-cluster mode of growth.

Simulace pro materiálově důležitý růst i) růst z páry

Počátky matematického studia a simulací růstu krystalů jsou spojeny s užitím **solid-on-solid** modelu blízko rovnováhy.



Dynamics of crystal growth, JD Weeks, GH Gilmer
Adv. Chem. Phys 40 (489), 157-227, **1979**

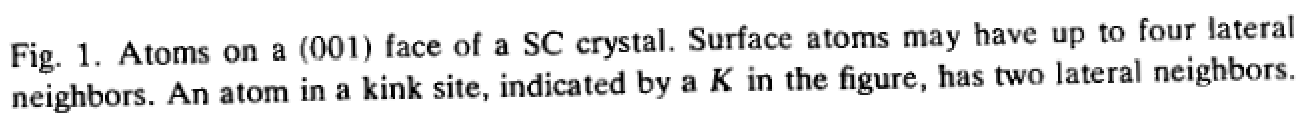
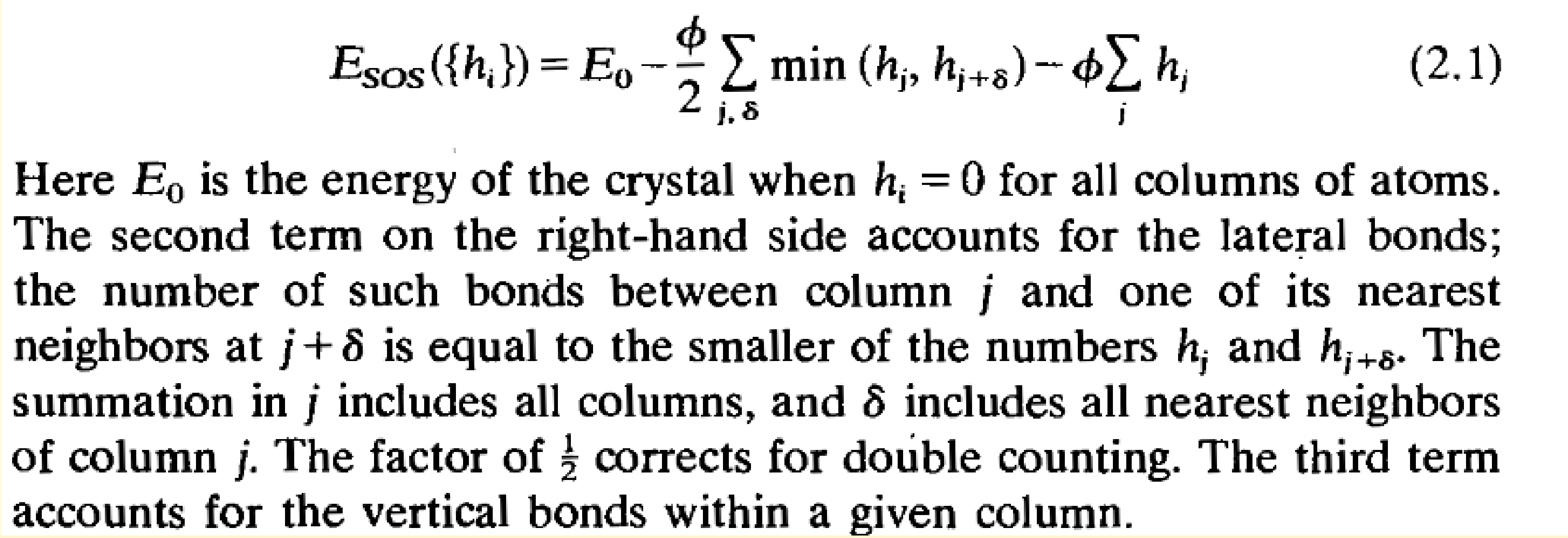


Fig. 1. Atoms on a (001) face of a SC crystal. Surface atoms may have up to four lateral neighbors. An atom in a kink site, indicated by a *K* in the figure, has two lateral neighbors.

Pravidla pro růst v SOS modelu



$$E_{SOS}(\{h_i\}) = E_0 - \frac{\phi}{2}\sum_{j,\delta} \min(h_j, h_{j+\delta}) - \phi\sum_j h_j \tag{2.1}$$

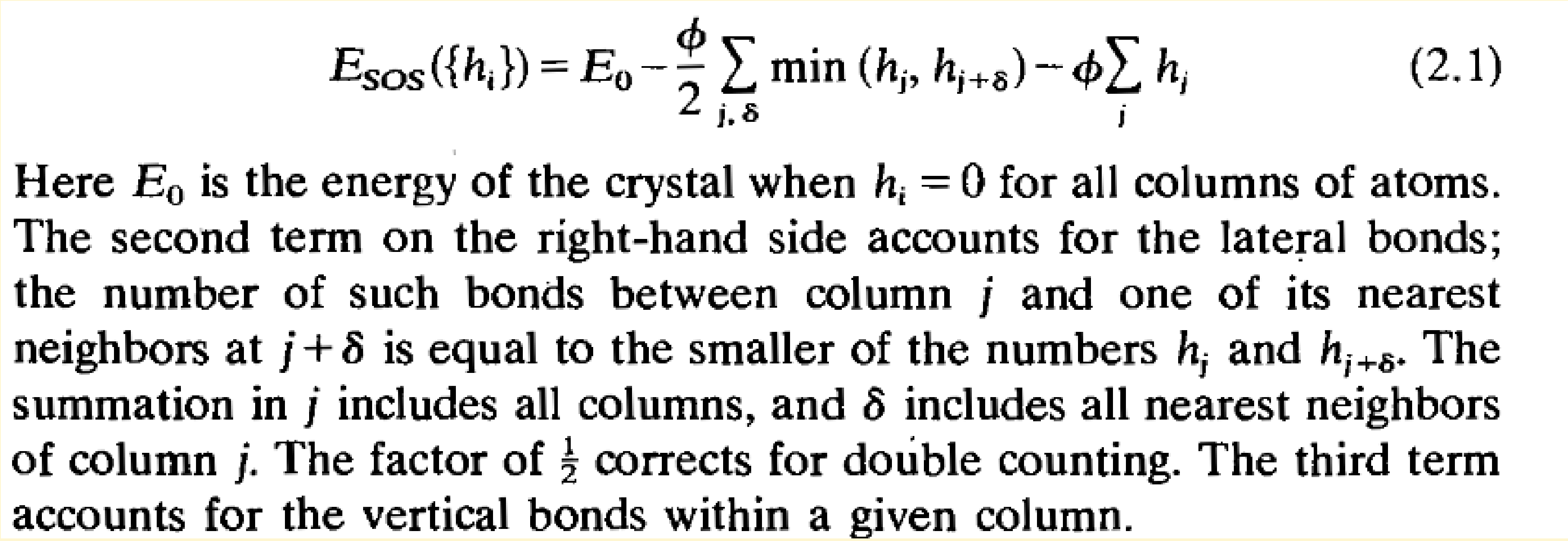
Here E_0 is the energy of the crystal when $h_i = 0$ for all columns of atoms. The second term on the right-hand side accounts for the lateral bonds; the number of such bonds between column j and one of its nearest neighbors at $j+\delta$ is equal to the smaller of the numbers h_j and $h_{j+\delta}$. The summation in j includes all columns, and δ includes all nearest neighbors of column j. The factor of $\frac{1}{2}$ corrects for double counting. The third term accounts for the vertical bonds within a given column.

první člen - základní energie
druhý člen - počet laterálních vazeb sousedů
třetí člen - počet vertikálních vazeb

ϕ - vazbová energie

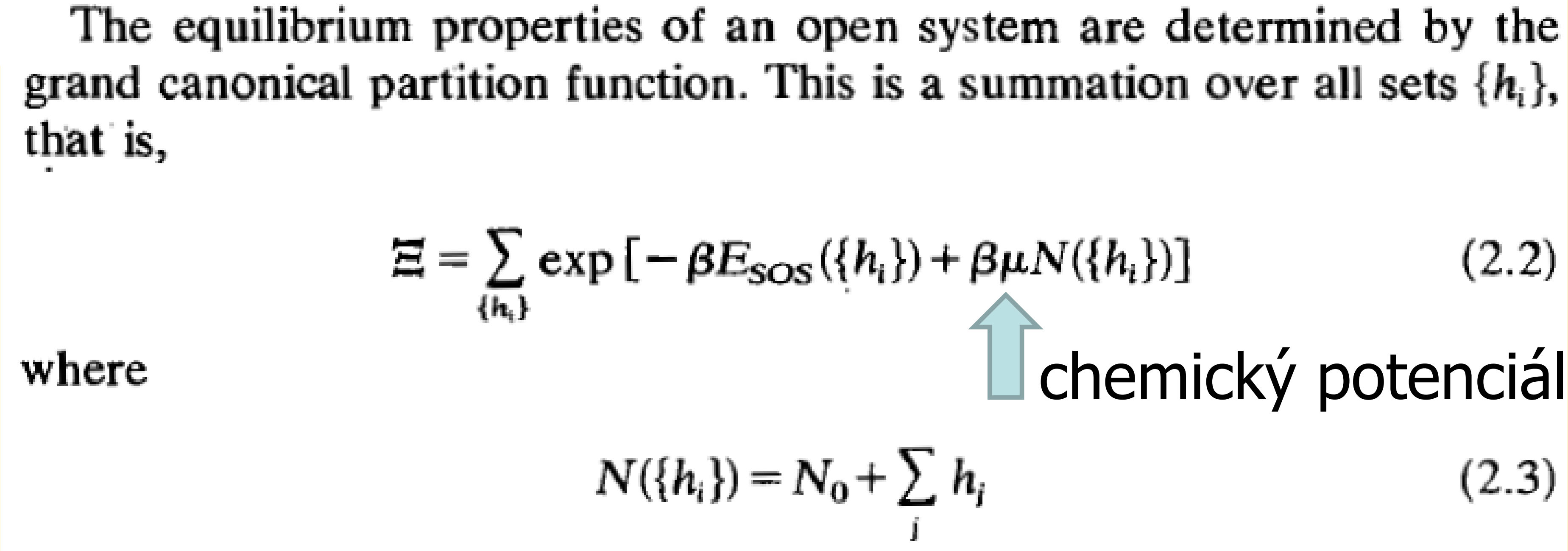
Dynamics of crystal growth, JD Weeks, GH Gilmer
Adv. Chem. Phys 40 (489), 157-227, 1979

Pravidla pro růst v SOS modelu



$$E_{SOS}(\{h_i\}) = E_0 - \frac{\phi}{2}\sum_{j,\delta} \min(h_j, h_{j+\delta}) - \phi\sum_j h_j \qquad (2.1)$$

Here E_0 is the energy of the crystal when $h_i = 0$ for all columns of atoms. The second term on the right-hand side accounts for the lateral bonds; the number of such bonds between column j and one of its nearest neighbors at $j+\delta$ is equal to the smaller of the numbers h_j and $h_{j+\delta}$. The summation in j includes all columns, and δ includes all nearest neighbors of column j. The factor of $\frac{1}{2}$ corrects for double counting. The third term accounts for the vertical bonds within a given column.



The equilibrium properties of an open system are determined by the grand canonical partition function. This is a summation over all sets $\{h_i\}$, that is,

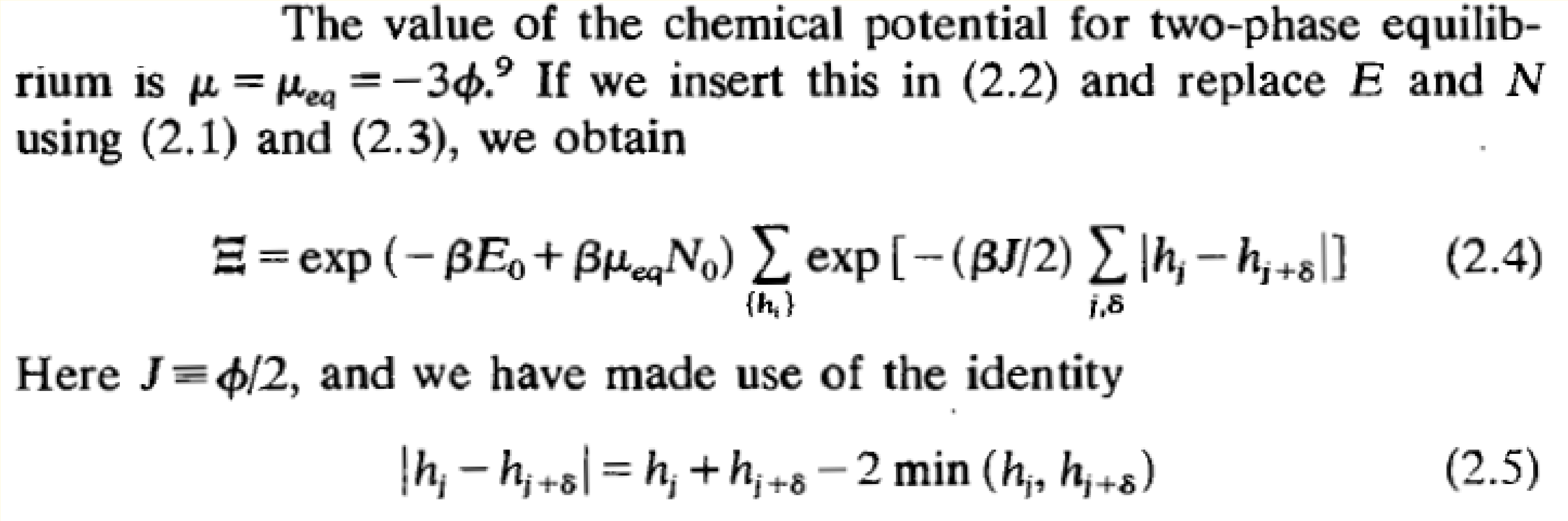
$$\Xi = \sum_{\{h_i\}} \exp[-\beta E_{SOS}(\{h_i\}) + \beta\mu N(\{h_i\})] \qquad (2.2)$$

where

$$N(\{h_i\}) = N_0 + \sum_j h_j \qquad (2.3)$$

chemický potenciál

Pravidla pro růst v SOS modelu



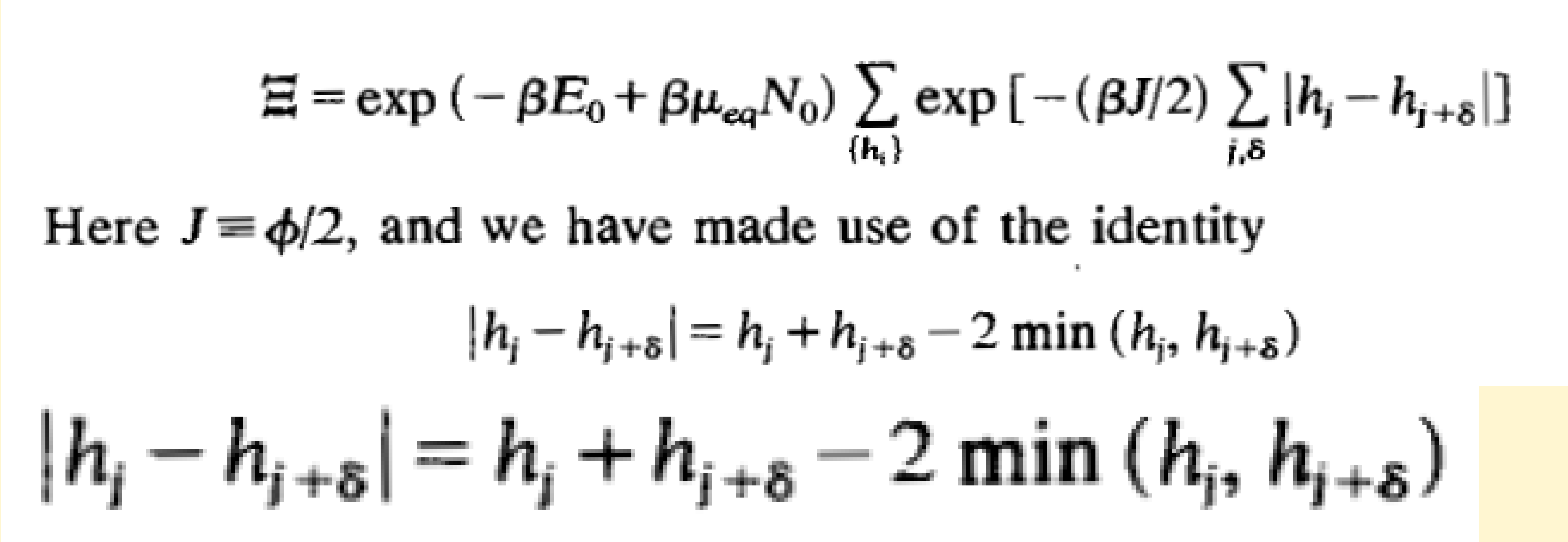
The value of the chemical potential for two-phase equilibrium is $\mu = \mu_{eq} = -3\phi$.[9] If we insert this in (2.2) and replace E and N using (2.1) and (2.3), we obtain

$$\Xi = \exp\left(-\beta E_0 + \beta\mu_{eq} N_0\right) \sum_{\{h_i\}} \exp\left[-(\beta J/2) \sum_{j,\delta} |h_j - h_{j+\delta}|\right] \tag{2.4}$$

Here $J \equiv \phi/2$, and we have made use of the identity

$$|h_j - h_{j+\delta}| = h_j + h_{j+\delta} - 2\min(h_j, h_{j+\delta}) \tag{2.5}$$

Geometrická pravidla pro zmenu energie v SOS modelu

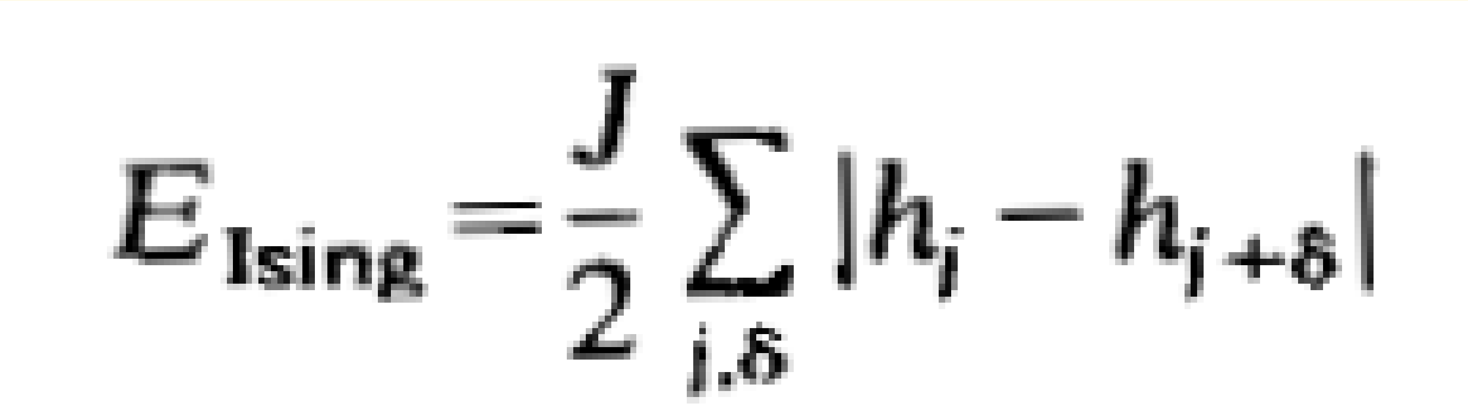


$$\Xi = \exp(-\beta E_0 + \beta\mu_{eq} N_0) \sum_{\{h_i\}} \exp\left[-(\beta J/2) \sum_{j,\delta} |h_j - h_{j+\delta}|\right]$$

Here $J \equiv \phi/2$, and we have made use of the identity

$$|h_j - h_{j+\delta}| = h_j + h_{j+\delta} - 2\min(h_j, h_{j+\delta})$$

$$|h_j - h_{j+\delta}| = h_j + h_{j+\delta} - 2\min(h_j, h_{j+\delta})$$



$$E_{\mathrm{Ising}} = \frac{J}{2} \sum_{j,\delta} |h_j - h_{j+\delta}|$$

Geometrická a dynamická pravidla pro růst v SOS modelu

$$E_{\text{Ising}} = \frac{J}{2} \sum_{j,\delta} |h_j - h_{j+\delta}|$$

Byl užíván model typu kinetický Isingův model.

Pravděpodobnost depozice k^+ je úměrná tlaku páry lze napsat jako:

$$k^+ = k_{eq} \exp(\beta\Delta\mu)$$

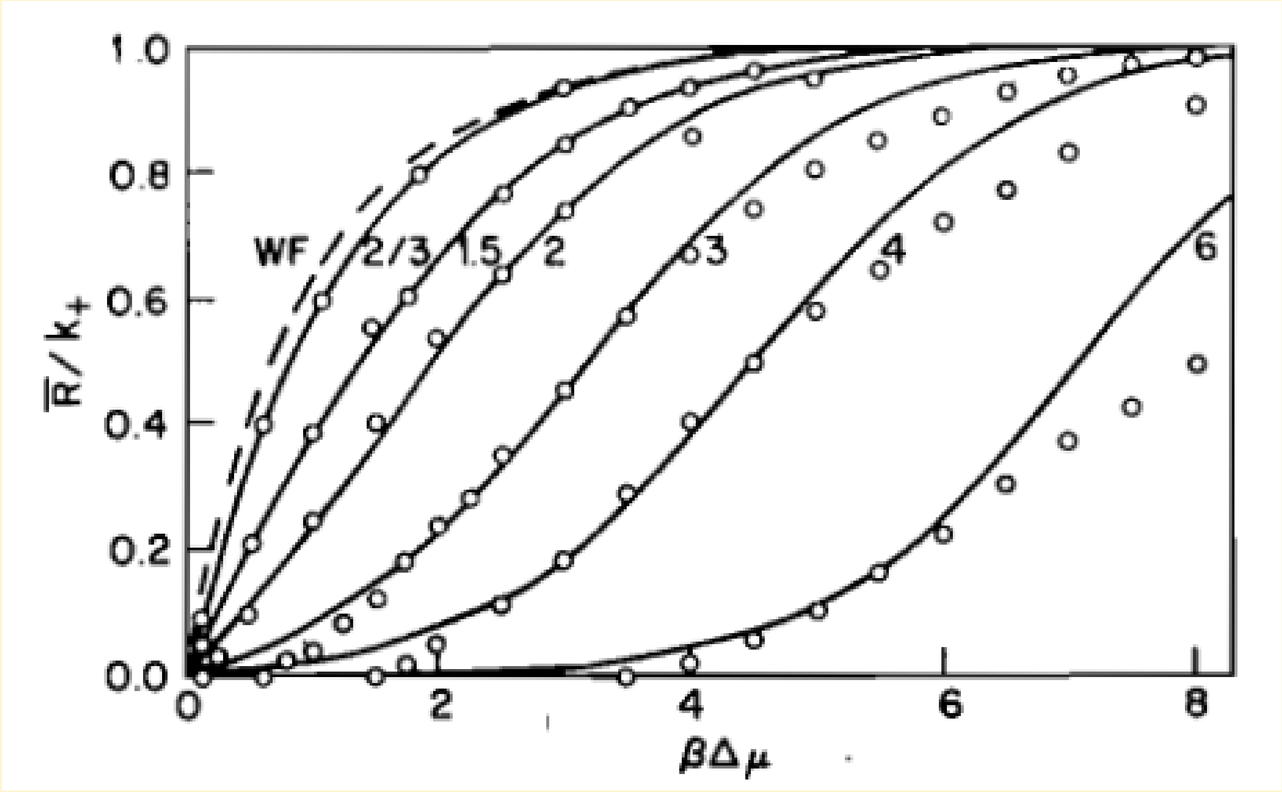
k_{eq} – pravděpodobnost depozice v rovnováze

Dynamics of crystal growth, JD Weeks, GH Gilmer
Adv. Chem. Phys 40 (489), 157-227, 1979

Simulace pro i) růst z páry

Srovnání simulací růstu krystalů užitím solid-on-solid modelu a aproximativných řešení bilančních rovnic. Pro různá $beta.\phi$

$$R_{WF}=k_{eq}\;(\exp(\beta\Delta\mu)-1)$$



Simulace pro materiálově důležitý růst

ii) Epitaxní růst z molekulárních svazků, MBE (molecular beam epitaxy)

Epitaxial growth is the process used to grow a thin crystalline layer on a crystalline surface (substrate). The substrate wafer acts as seed crystal. In this process , crystal is grown below melting point , which uses an evaporation method.

Simulace pro materiálově důležitý růst MBE

teplotně závislý rate $k(\mathrm{T})$ pro jednotlivé procesy má Arrheniovskou formu

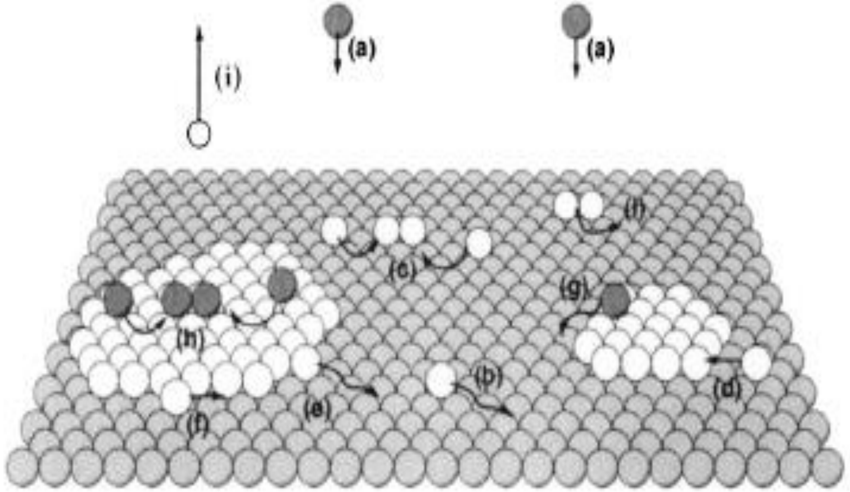
$$k(\mathrm{T})=k_0 \exp(-E_D\,/\,kT)$$

E_D je bariéra pro jednotlivé procesy o kterých se předpokládá, že jsou důležité.

k_0 prefaktor $2kT/h$) nebo pro jednoduchost konstanta 10^{13} s^{-1}

Heteroepitaxial growth

- Important technology for preparation of many novel materials, semiconductors as well as metals.
- There are various elementary processes:
  depozition, diffusion,
  nucleatiom, agregagation
  relaxation, etc.



- They proceed during growth on rather different time and lenth scales.

MULTISCALE MODELI NG IS DESIRABLE

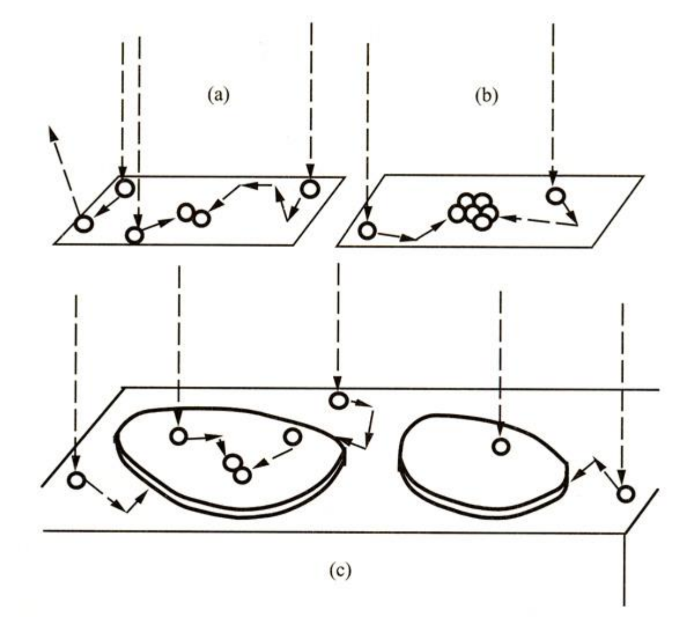
Full treatment is very complex, we restrict here to simple submonolayer growth.

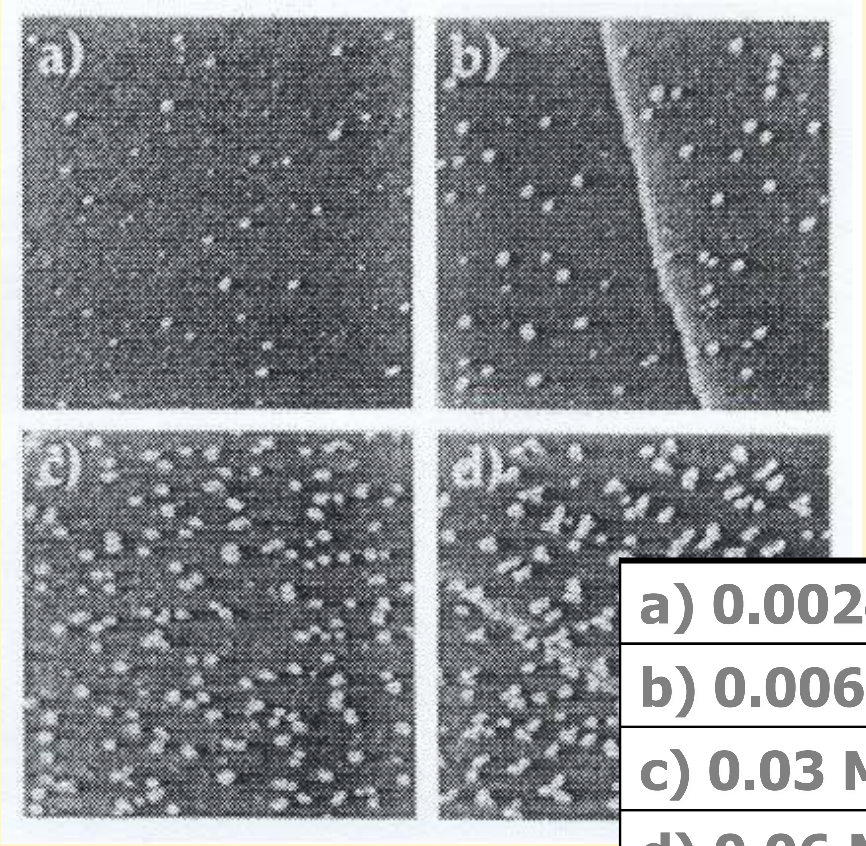
Submonolayer growth

Coverage: $\Theta \leq 1\,\mathrm{ML}$

Observed quantity:

Density of islands N





a) 0.0024 ML
b) 0.006 ML
c) 0.03 ML
d) 0.06 ML

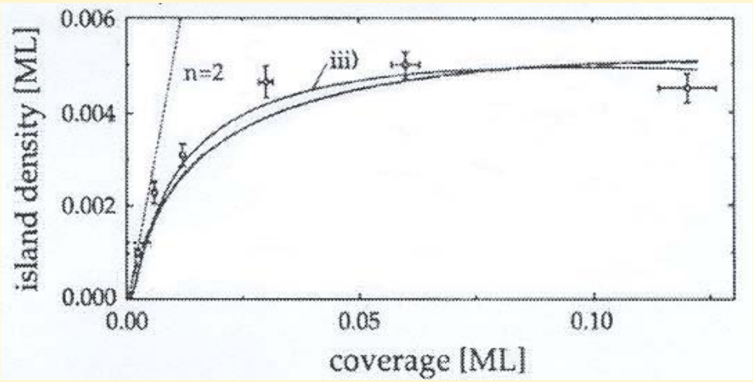
Ag/Pt(111)

H.Brune et al. PRL 73, (1994) 1955

Succession of regimes:

- **nucleation**
- **aggregation**
- **coalescence**

Submonolayer growth, Coverage: $\Theta \leq 1\,\mathrm{ML}$



There is an interval of coverage with saturated island density

We have stationary distribution of island sizes.

Scaling of island densities with coverage is valid.

Importance of submonolayer growth:

(i) the formation of surface features
(ii) measurements of surface diffusion

Studied quantities

N_s –density of islands of size S

coverage

$$\theta = \sum_{s \geq 1} sN_s$$

average island size

$$\langle s \rangle = \left(\sum_{s \geq i} sN_s \right) / N$$

$$N = \sum_{s > i} N_s$$

scaled distribution function

$$p_s(\theta) = sN_s(\theta) / \theta$$

It gives a probability density that

a randomly selected atom is contained in an island of size S.

It is sufficient to calculate function

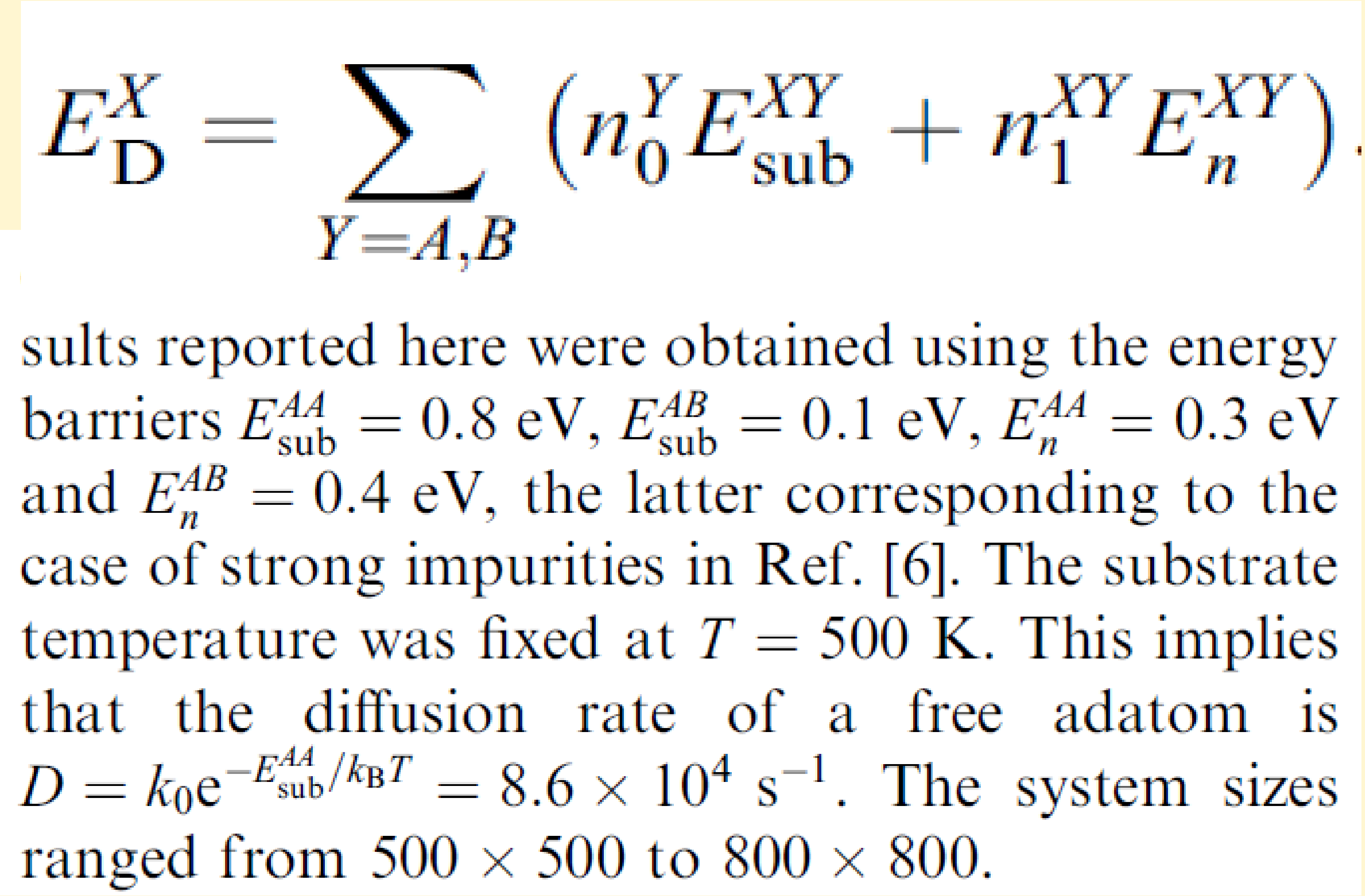
$$g(x) = \langle s \rangle p_s(\theta)$$

here

$$x = {}^{s}\!/\!_{\langle s \rangle}$$

Vliv nečistot na MBE růst - pohyblivé vs. nepohyblivé nečistoty

vzájemné interakce pro dvou složkový adsorbát



$$E_{\mathrm{D}}^{X} = \sum_{Y=A,B} \left(n_0^{Y} E_{\mathrm{sub}}^{XY} + n_1^{XY} E_n^{XY} \right).$$

sults reported here were obtained using the energy barriers $E_{\mathrm{sub}}^{AA} = 0.8$ eV, $E_{\mathrm{sub}}^{AB} = 0.1$ eV, $E_n^{AA} = 0.3$ eV and $E_n^{AB} = 0.4$ eV, the latter corresponding to the case of strong impurities in Ref. [6]. The substrate temperature was fixed at $T = 500$ K. This implies that the diffusion rate of a free adatom is $D = k_0 \mathrm{e}^{-E_{\mathrm{sub}}^{AA}/k_{\mathrm{B}}T} = 8.6 \times 10^4\ \mathrm{s}^{-1}$. The system sizes ranged from 500×500 to 800×800.

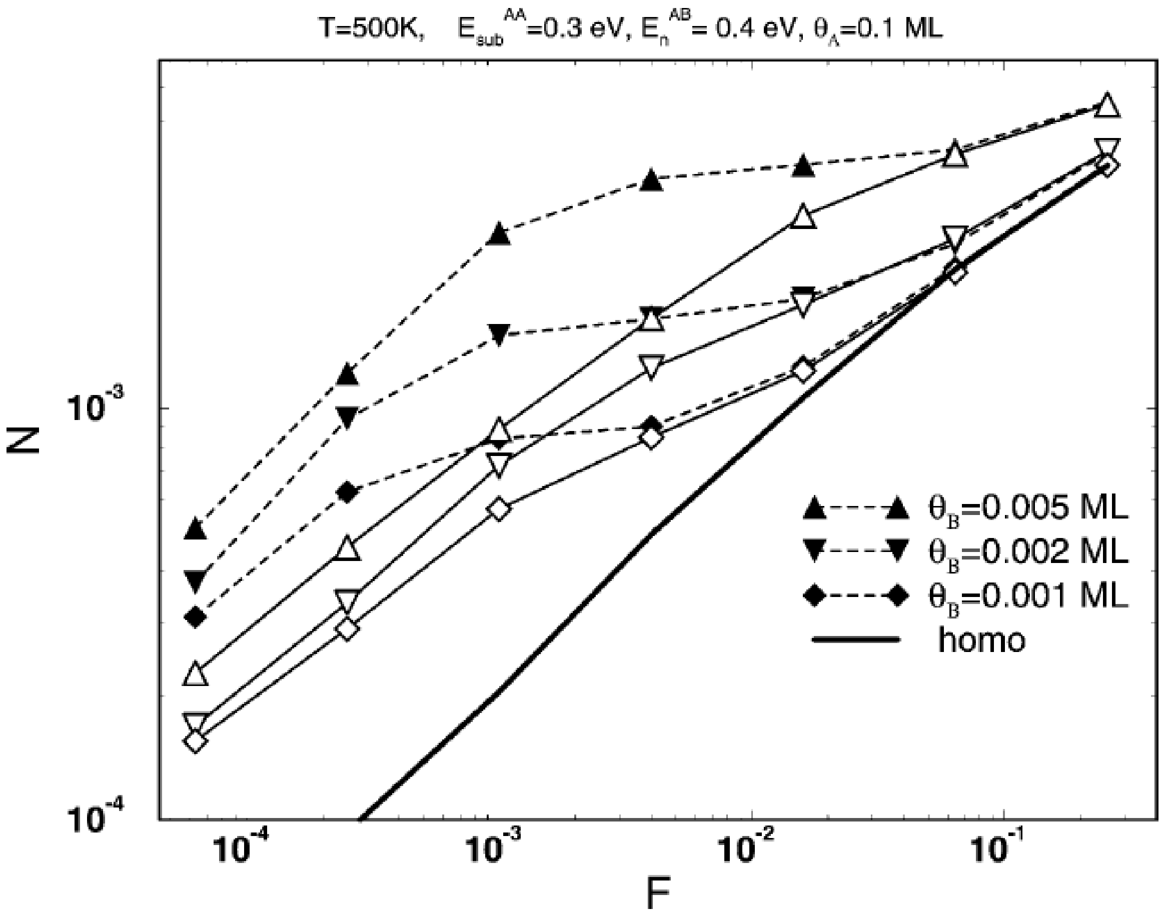


Fig. 1. Averaged island density as a function of flux F for different concentration θ_B of predeposited impurities and different energy barriers: $E_{\text{sub}}^{BA} = E_{\text{ex}} = 1$ eV (△, ▽, ◇), $E_{\text{sub}}^{BA} = E_{\text{ex}} =$ 5 eV (▲, ▼, ◆). The adatom interaction energy $E_n^{AA} = 0.3$ eV and the energy of interaction between impurities and adatoms $E_n^{AB} = 0.4$ eV are fixed, the coverage of adatoms is $\theta_A = 0.1$ ML. The behavior in the absence of impurities (homoepitaxy, $\theta_B = 0$ ML) is shown for comparison.

Pohyblivé vs. nepohyblivé nečistoty

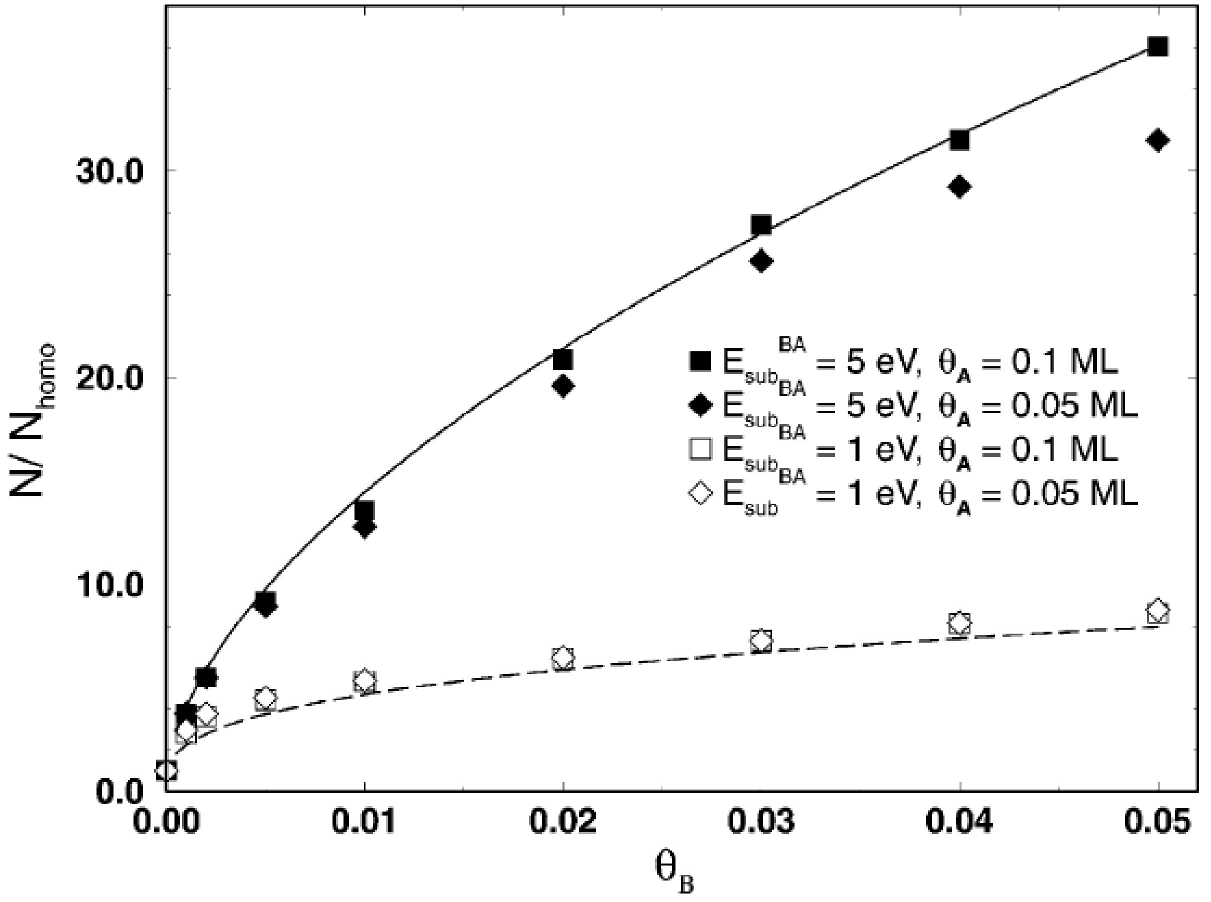
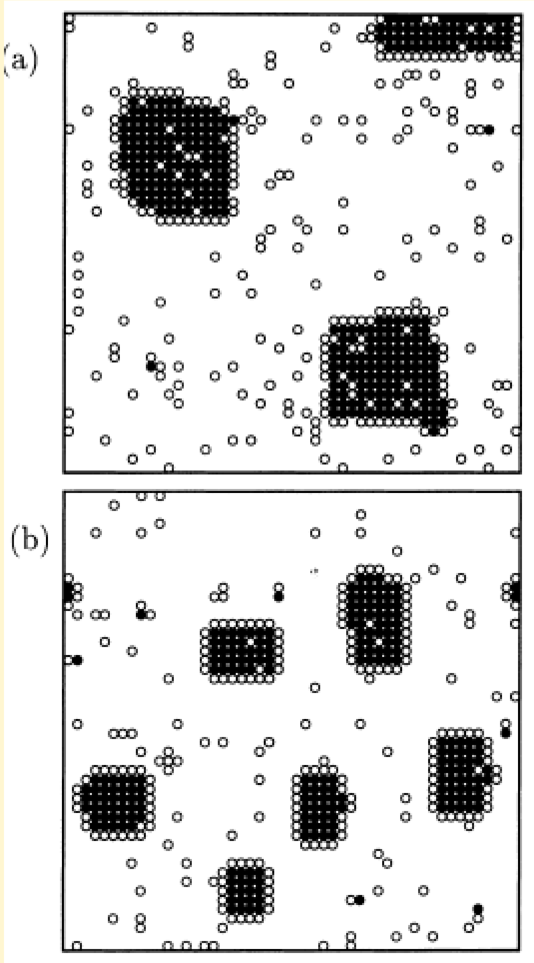
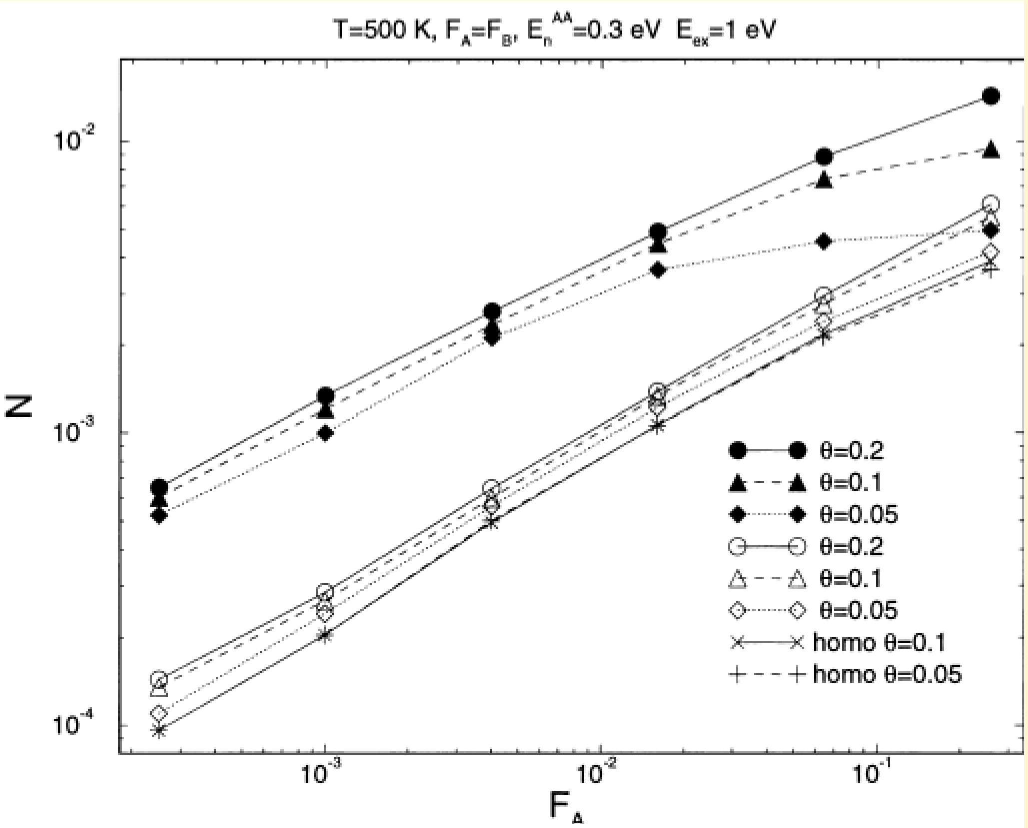


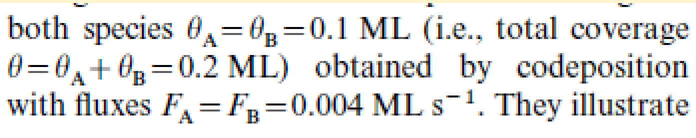
Fig. 3. Relative increase of island density N/N_{homo} as a function of the concentration of predeposited impurities θ_B for mobile, $E_{\text{sub}}^{BA} = 1$ eV (□, ◇) and immobile, $E_{\text{sub}}^{BA} = 5$ eV (■, ◆) impurities and two values of the coverage $\theta_A = 0.05$ ML (◇, ◆) and $\theta_A = 0.1$ ML (□, ■). The flux is fixed to $F = 0.001$ ML/s, the energy barrier for the exchange process is $E_{\text{ex}} = 1$ eV. Lines are fits of the form $[1 + \theta_B \phi]^{\chi}$ with $\phi = e^{E_n^{AB}/k_B T} - 1 \approx 10772$ and $\chi = 0.57$ (- - -), $\chi = 0.33$ (—).

Vliv vzájemné interakce v dvousložkovém adsorbátu při kodepozici : dekorace ostrůvků





$$E_{\mathrm{D}}^{X}=\sum_{Y=A,B}\left(n_0^{Y}E_{\mathrm{sub}}^{XY}+n_1^{XY}E_n^{XY}\right).$$


both species $\theta_{\mathrm{A}}=\theta_{\mathrm{B}}=0.1$ ML (i.e., total coverage $\theta=\theta_{\mathrm{A}}+\theta_{\mathrm{B}}=0.2$ ML) obtained by codeposition with fluxes $F_{\mathrm{A}}=F_{\mathrm{B}}=0.004$ ML s^{-1}. They illustrate

bariera k_{exch}