Fluctuations of Steps in Equilibrium

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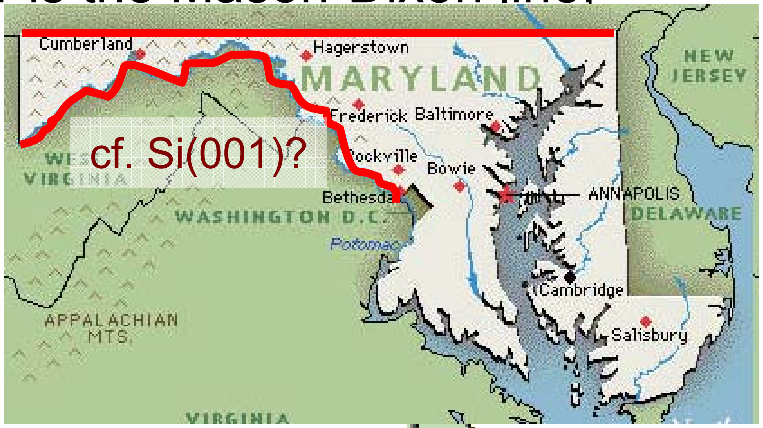
- Steps on vicinal surfaces as meandering fermions in (1+1)D...¿interactions?
- Steps as Brownian strings; seeking signatures of mass transport modes
- Langevin and heuristic analysis
- Islands as circular steps
- Novel applications
- Open questions

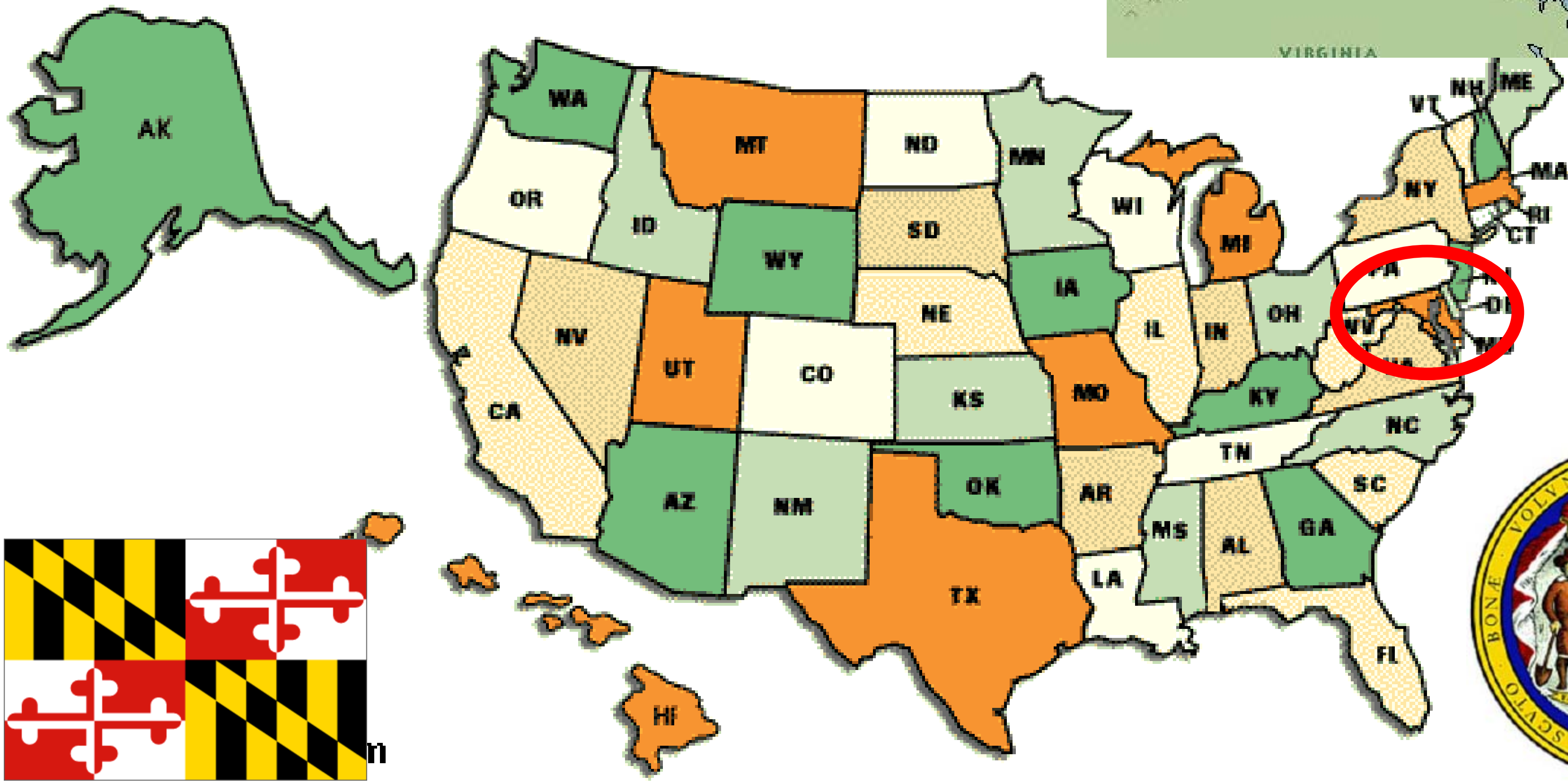
Note the overhangs.

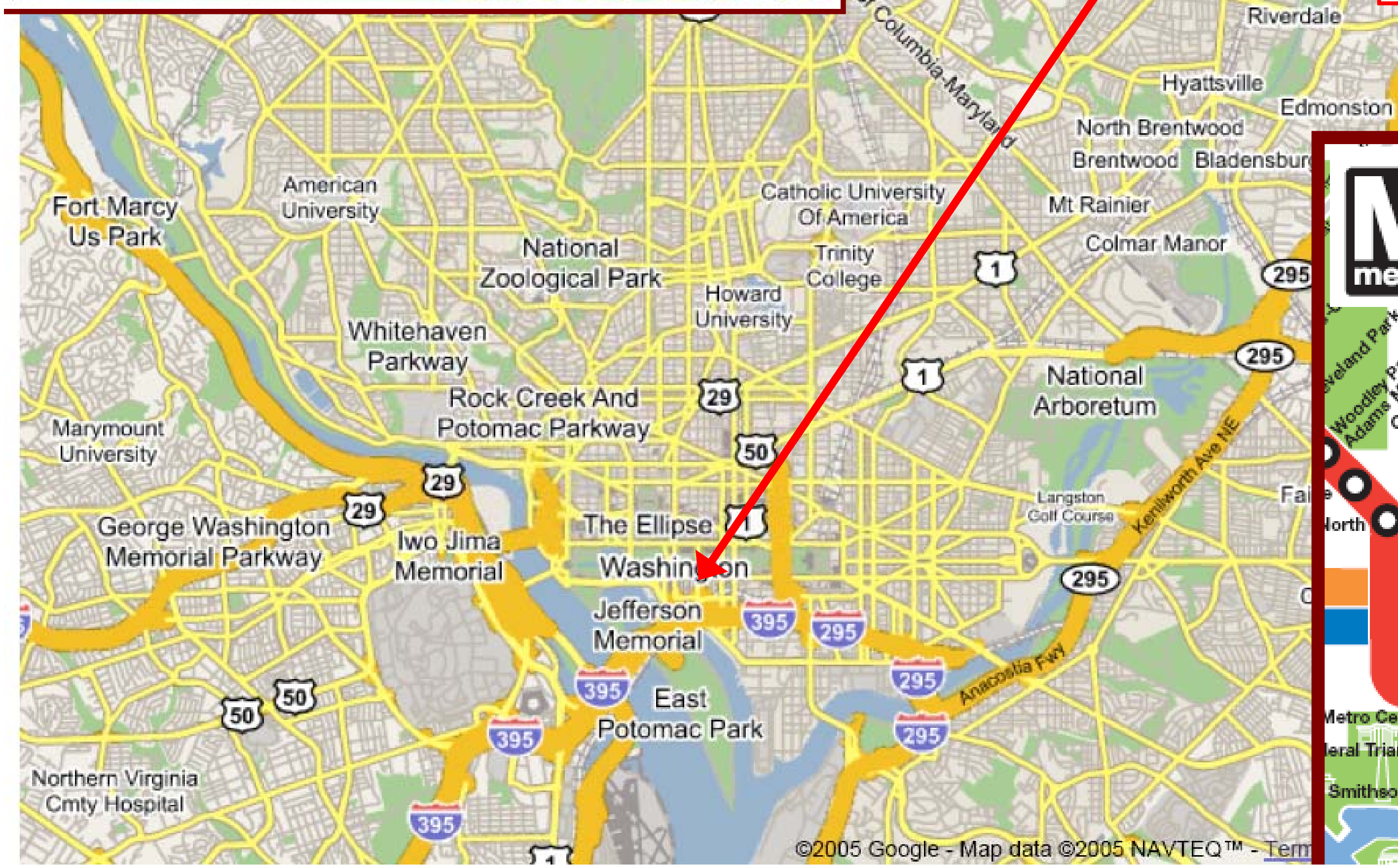
—-T. Frisch

Calanques are not fermions!!

Maryland is on the east coast of the USA. Founded as a Catholic haven, it is one of the original 13 colonies → states. D.C. was carved from it to be the national capital (rather than Philadelphia), as part of the Constitution's "Great Compromise." Its northern border is the Mason-Dixon line, which separated the North from the South, but it was prevented from joining the rebels. Historically conservative, it is now “liberal”; it has the highest mean income of any state.

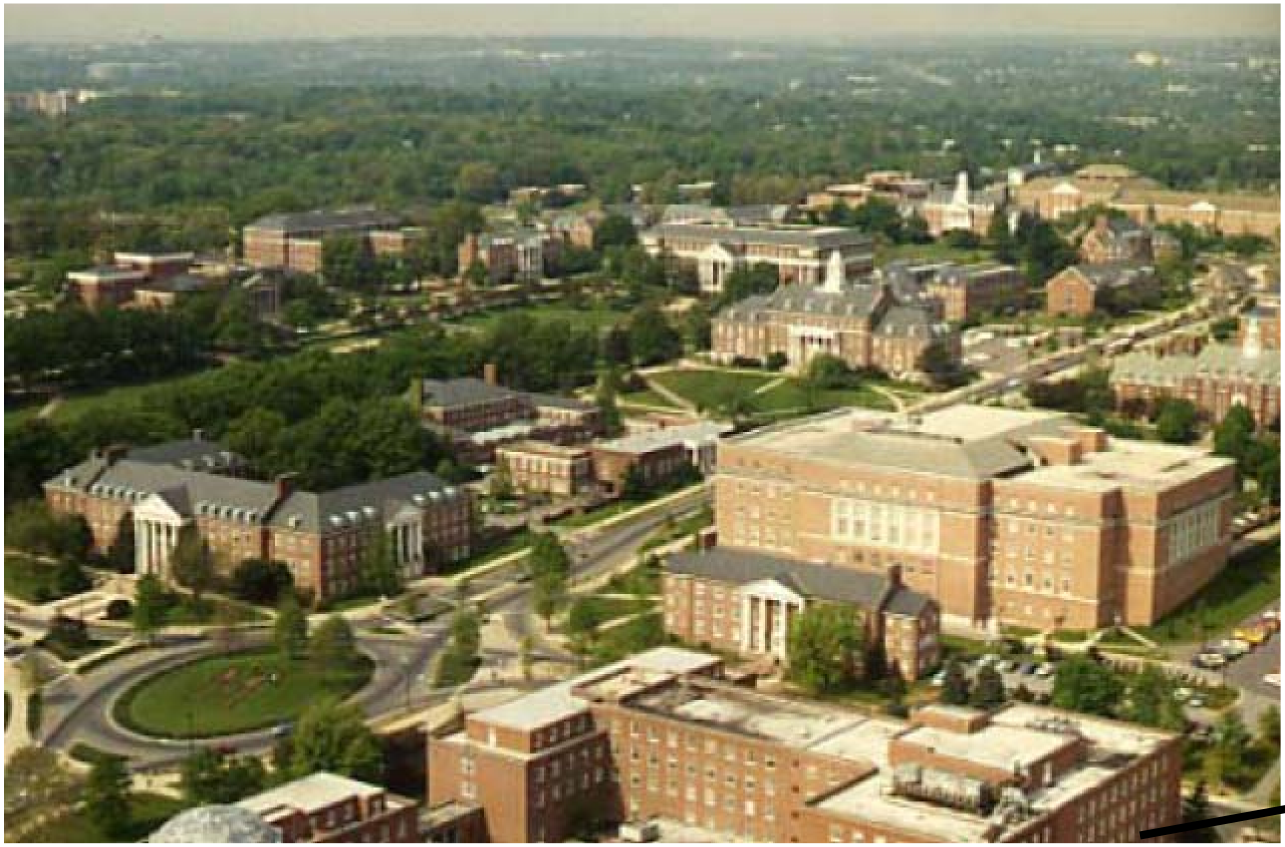






UM is "inside the Beltway".

UM ↔ DC center:
~ 14 km.



Aerial view of UM

Grew large after World War 2

"A good university needs a good football and a good physics department."
--UM Pres. C. Byrd

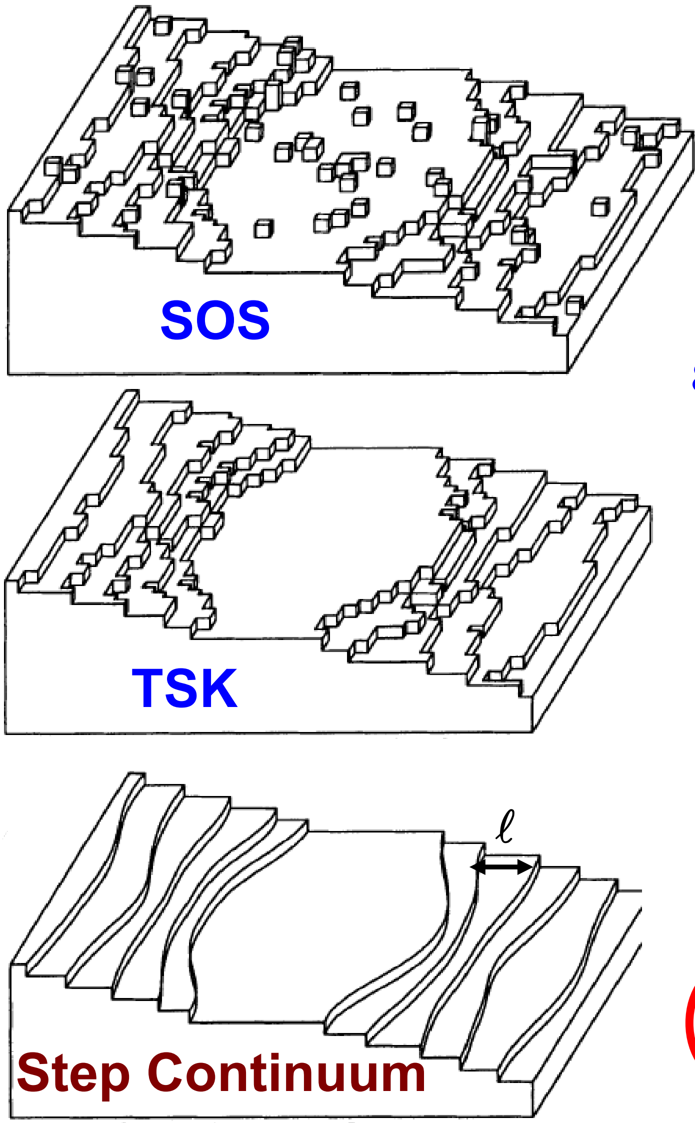
my office, in Physics Bldg

Chartered 1856 as agricultural college

Near College Park Airport, oldest continually operated airport in world (>1909)!

Models & Key Energies

Discrete/atomistic → Step Continuum



ε *energy of unit height difference between NN sites*
+ hopping barriers, attach/detach rates

kink energy

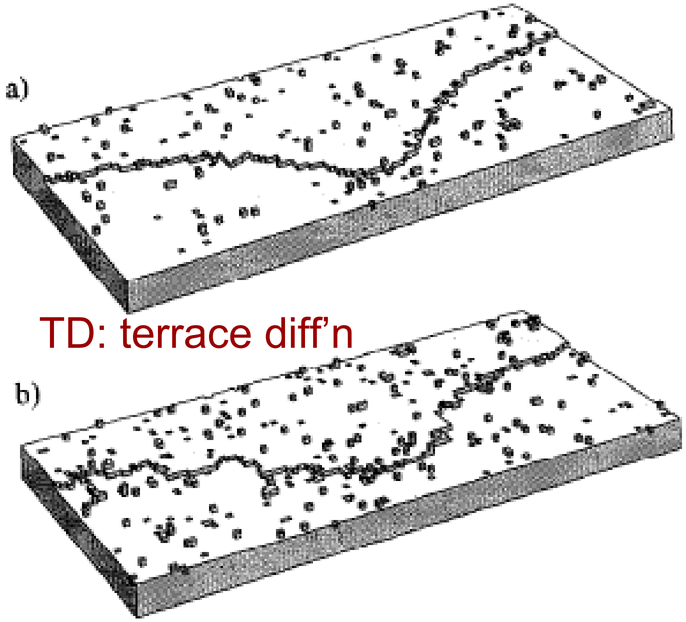
$\tilde{\beta}$ *step stiffness* $\beta(\theta) + \beta''(\theta)$: inertial "mass" of step

A *strength of step-step repulsion* A/ℓ^2

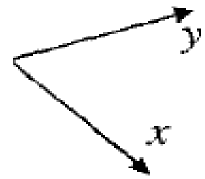
Γ *rate parameter, dependent on microscopic transport mechanism*

Main test: Self-consistency of these 3 parameters to explain many phenomena
Coarse-grain: Relation of 3 nano/mesoscale parameters to atomistic energies??

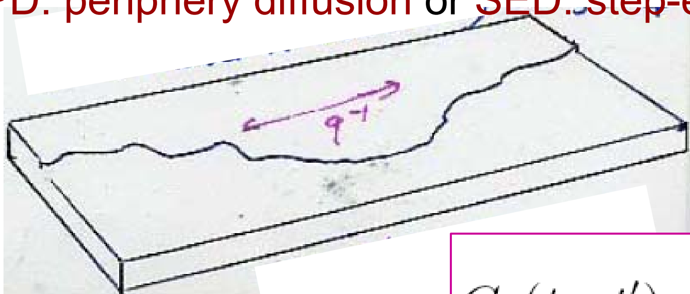
Steps as Brownian strings: *Langevin* "capillary wave" approach



TD: terrace diff'n



PD: periphery diffusion or SED: step-edge diff'n



$$\frac{\partial x(y,t)}{\partial t} = -\text{restoring "force"} + \text{noise}(y,t)$$

e.g. heal curvature

$$x(y,t) = \sum_q \mathrm{e}^{iqy} x_q(t)$$ to deal with ∇y

$$\frac{\partial x_q(t)}{\partial t} = -\frac{x_q(t)}{\tau_q} + \text{noise}(q,t)$$

$$= 2\langle |x_q(t)|^2 \rangle - 2\langle x_q(t) x_q(t')^2 \rangle$$

$$G_q(t-t') \equiv \left\langle \left| x_q(t) - x_q(t') \right|^2 \right\rangle = \frac{2k_B T}{\tilde{\beta} q^2 L_y} \left(1 - \mathrm{e}^{|t-t'|/\tau_q} \right)$$

J. Villain, J. Phys. (Paris) I 1 (1991) 19

saturation $G_q \Rightarrow$ stiffness

Langevin "capillary wave" approach to isolated steps: behaviors

$$G_q(t-t') \equiv \left\langle \left| x_q(t) - x_q(t') \right|^2 \right\rangle = \frac{2k_BT}{\tilde{\beta} q^2 L_y} \left(1 - e^{|t-t'|/\tau_q}\right)$$

$\tau^{-1} \propto q^n$

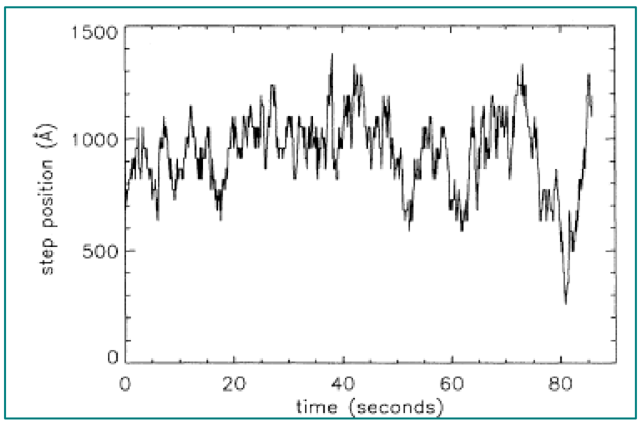
[Maryland notation]

$$\tau_q^{-1} = \frac{\tilde{\beta}}{k_BT} \times \begin{cases} \Gamma_{\mathrm{attach}}\, q^2 & \mathrm{EC/AD:\ curvature\text{-}driven} \\ 2\Gamma_{\mathrm{diffu}}\, |q|^3 & \mathrm{TD} \\ \Gamma_{\mathrm{edge}}\, q^4 & \mathrm{PD/SED:\ \text{-}}\nabla^2\mathrm{curvature} \end{cases}$$

$\tau_q^{-1} \Rightarrow$ transport mode & associated Γ

$$\tau_q^{-1} = (\Omega\tilde{\beta} / k_BT) q^2 \tilde{f}(q); \qquad \tilde{f}(q) = k_+ + k_-,\ 2D_{su}|q|,\ 2a_\perp D_{st} q^2$$

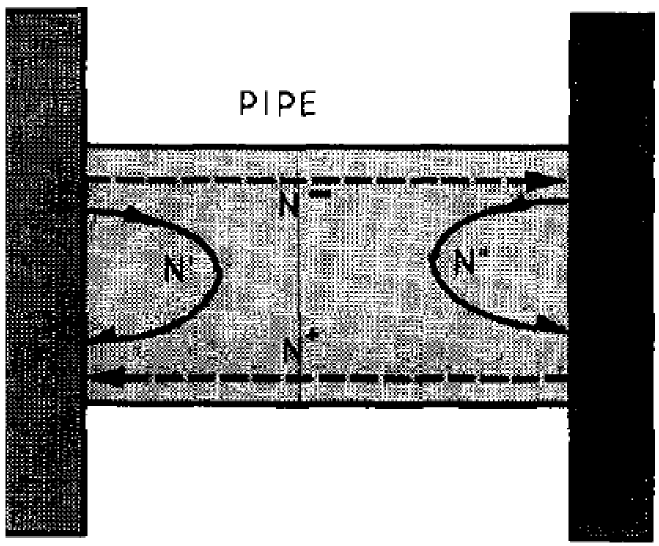
Single value of *y*

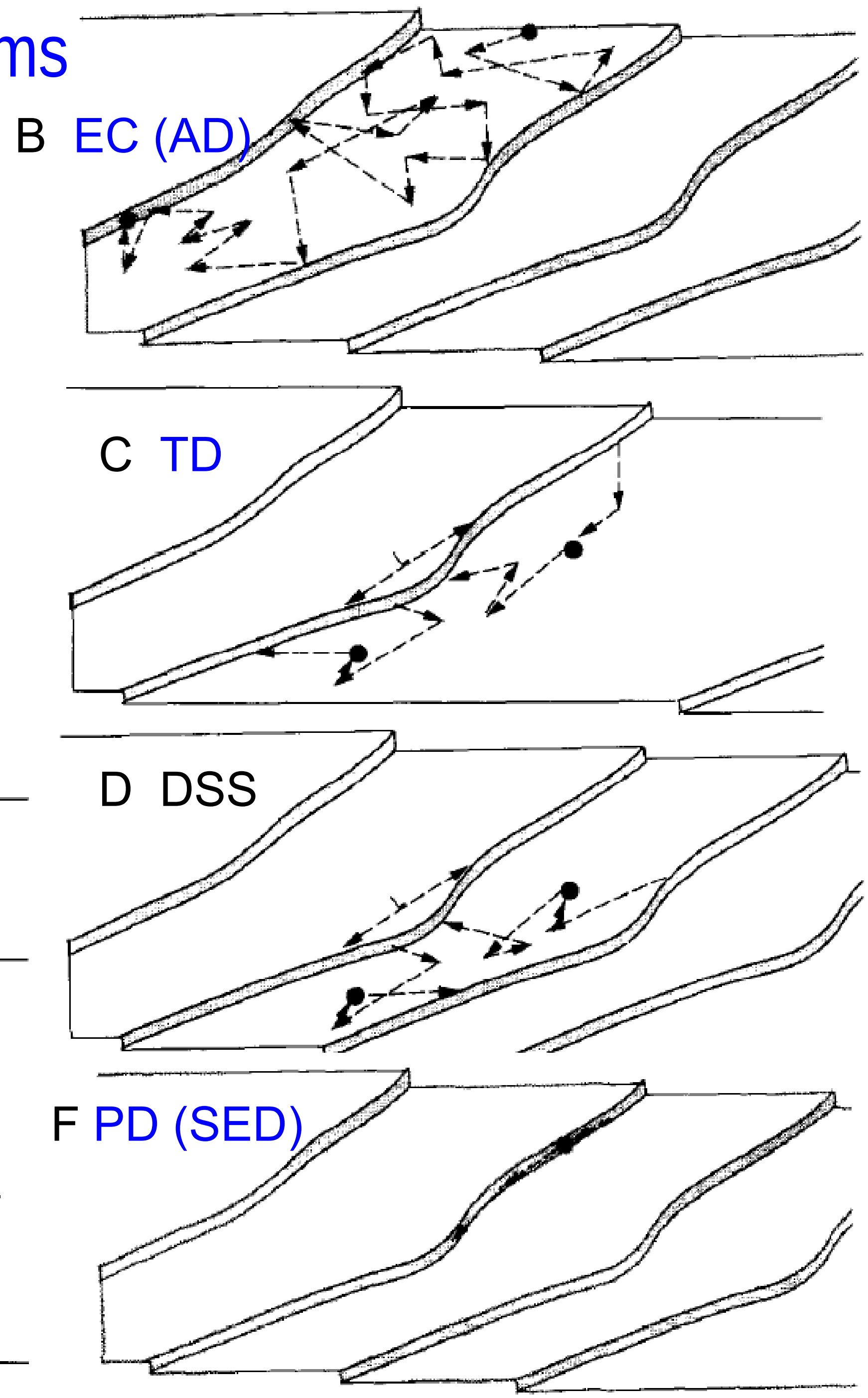


or early-time exponent: $G(t) \propto t^{1/n}$ or $t^{2\beta}$

$$G(t) \equiv \langle [x(t_0+t) - x(t_0)]^2 \rangle_{y_0,\, t_0} \propto \begin{cases} t^{1/2} \\ t^{1/3} \\ t^{1/4} \end{cases}$$

Atomistic Mass Transport Mechanisms

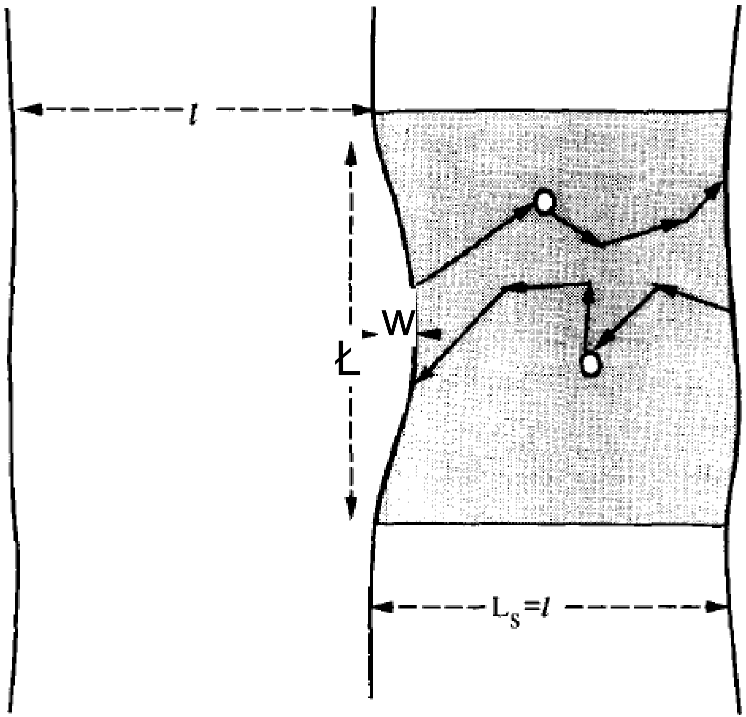




Reservoir	Pipe	Pipe dimension-ality	Case (equation)	$\tau(L)/h^2L$
Surface	Step	1D	B (9, 10)	τ_a
Vapour	Surface	Quasi-1D	A (8)	$1/\alpha l$
Vapour	Surface	2D	A (7)	$1/\alpha\lambda_s$
Same step	Step	1D	F (16)	$L^2/D_g\rho_g$
Same step	Surface	Quasi-1D	E (14)	$(L^2/l)/D_s\rho_s$
Surface	Surface	2D	C (11)	$L/D_s\rho_s$
Other steps	Surface	2D	D (12, 13)	$l/D_s\rho_s$
Vapour	Vapour	3D	(A.9)	$1/D_v\rho_v$

Pimpinelli et al., Surf Sci. 295 ('93) 143

Arguments of Pimpinelli et al. re healing time of bumps



$w^2(Ł) = k_B T\, Ł/6\tilde{\beta}$ for fixed pts Ł apart, assuming $w < \langle \ell \rangle$

Bump: $\delta N(t) \sim \sqrt{N(t)} \sim w\, Ł$

\# impinging = # crossing pipe
$N(t) \approx c_{eq}\, Ł\, L_s\, t/þ$, þ is time to flow through pipe

Time to form bump
$\tau(w, Ł) \approx w^2\, Ł\, þ/c_{eq} L_S$
or $\tau_\ell(Ł) \approx (Ł^2/L_S)(k_B T þ/c_{eq}\tilde{\beta})$

B EC (AD): $L_S \sim 1$
$\Rightarrow \tau \approx k_B T \tau_a Ł^2/\tilde{\beta} \sim q^{-2}$

C (TD): $L_S \sim Ł$, $þ \sim Ł^2/D_s$
$\Rightarrow \tau \approx k_B T Ł^3/\tilde{\beta} c_{eq} D_s \sim q^{-3}$

F PD (SED): $L_S \sim 1$, $þ \sim Ł^2/D_{st}$
$\Rightarrow \tau \approx k_B T Ł^4/\tilde{\beta} c_{st} D_{st} \sim q^{-4}$

D (DSS): $L_S \sim \ell$, $þ \sim \ell^2/D_s$
$\Rightarrow \tau \approx kBTŁ^2 \ell\, /\tilde{\beta} c_{eq} D_s \sim q^{-2}$

Linear Relaxation: Velocity $\propto$ free energy change due to displacement

Evaporation-condensation (attachment-detachment): Model A, non-conserved

$$\frac{\partial x}{\partial t} = -\frac{\Gamma_a}{k_B T}\frac{\delta H}{\delta x} = \frac{\Gamma_a}{k_B T}\widetilde{\beta}\frac{\partial^2 x}{\partial y^2}$$

Add noise, Langevin:

$$\frac{\partial x(y,t)}{\partial t} = \frac{\Gamma_a}{k_B T}\widetilde{\beta}\frac{\partial^2 x}{\partial y^2} + \eta(y,t)$$

$$\langle \eta(y,t)\eta(y',t')\rangle = \frac{2a^3}{\tau_a}\delta(y-y')\delta(t-t')$$

$$\Gamma_a = \frac{2a^3}{\tau_a}$$

$$\tau^{-1}(q) = (\Gamma_a/k_B T)\widetilde{\beta}q^2$$

Edge-Diffusion Limited Case: PD or SED
Model B, conserved dynamics

Particle conservation ⇒ extra $-(\partial^2 x/\partial y^2)$

$$\frac{\partial x(y,t)}{\partial t} = -\frac{\Gamma_{st}}{k_B T}\widetilde{\beta}\frac{\partial^4 x}{\partial y^4} + \eta(y,t)$$

$$\langle \eta(y,t)\eta(y',t')\rangle = \frac{2a^5}{\tau_a}\delta''(y-y')\delta(t-t')$$

$$\tau^{-1}(q) = (\Gamma_{st}/k_B T)\widetilde{\beta}q^4$$

Terrace Diffusion (TD)

Attachment-detachment fast compared to terrace diffusion. Step fluctuations governed by how concentration gradient decays.

$$c(x,y) = c_0 + c_0 a^2(\widetilde{\beta}/k_B T)\Sigma_q q^2 x_q \mathrm{e}^{-|q|x} cos(qy)$$

$$\frac{\partial x}{\partial t} = \frac{2D_s c_s \widetilde{\beta}}{k_B T}\int_{-\infty}^{\infty} -\left(\frac{\partial^2 x}{\partial y^2}\right)_{y'} \frac{a^2(y-y')^2}{[a^2+(y-y')^2]^2} dy' + \eta(y,t)$$

$$\langle \eta(y,t)\eta(y',t')\rangle = \frac{4D_s c_s a^4}{k_B T}\frac{a^2(y-y')^2}{[a^2+(y-y')^2]^2}\delta(t-t')$$

$$\tau^{-1}(q) = 2D_s c_s(a^4/k_B T)\widetilde{\beta}|q|^3$$

Diffusion step-to-step (DSS)

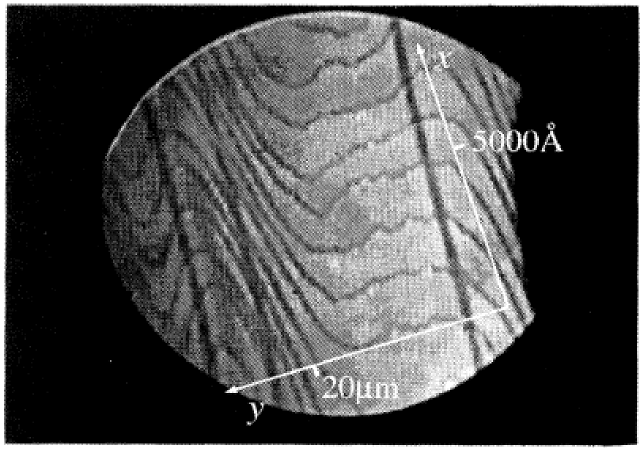
ℓ < diffusion length $\Rightarrow$ q $\rightarrow$ 1/ℓ $\qquad$ $|q|^3 \rightarrow q^2/\ell$

BEHAVIOR OF ISOLATED STEPS

Label	EC	TD	PD
Limiting process	Attachment-detachment (2D) Evaporation-condensation (Model A)	Terrace diffusion	Periphery (edge) diffusion (Model B)
τ_q^{-1}	q^2	q^3	q^4
Adatom (vacancy) concentration	Uniform	Varies near step	≈ 0
(Early-time) width^2	$t^{1/2}$	$t^{1/3}$	$t^{1/4}$
Prefactor	k or $\Gamma_a \sim \frac{1}{\tau_{attach}}$	$D_{su} \sim \frac{1}{\tau_{hop}}$	D_{st} $\Gamma_h \sim \frac{1}{\tau_{hop,step}}$
Energy [microscopic! WARNING]	Step-edge well Sticking coefficient	Diffusion barrier (Exchange barrier)	Barrier along edge Corner barrier
Analogy for sinusoidal corrugation	(3D) Evaporation-condensation	Volume diffusion	Surface diffusion
D(R) for cluster of radius R ASYMPTOTIC	R^{-1} ($N^{-1/2}$)	R^{-2} (N^{-1})	R^{-3} ($N^{-3/2}$)
Examples of vicinals	Si(100) Tromp Si(111) Williams Ag(110) Reutt-Robey Au(110) Frenken	[SOS model]	Pb(111) Frenken • Cu(001) Ibach • Ag(001) Williams Pt(111) Giesen

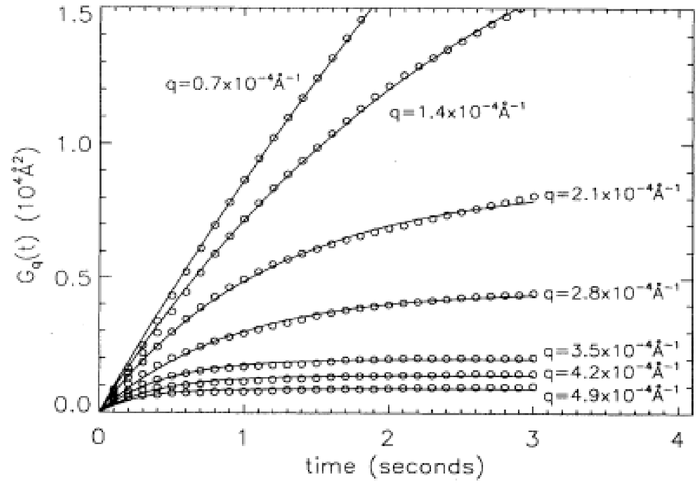
Early Study of Si(111)

N.C. Bartelt,…TLE, E.D. Williams,…J.-J. Métois, PRB 48 ('93) 15453



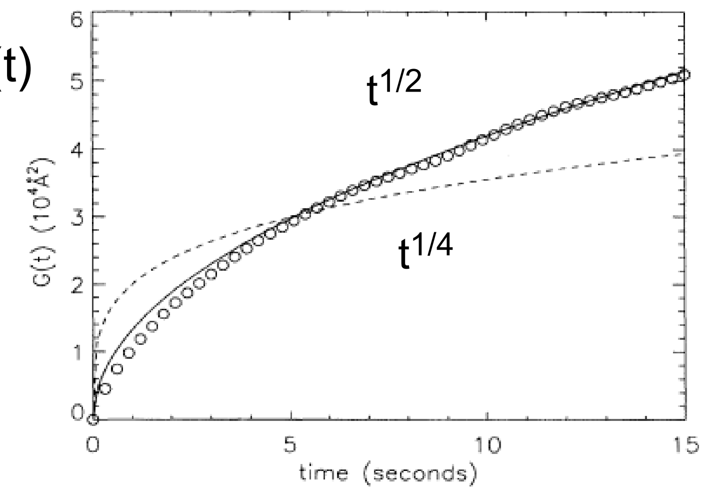
Heyraud, Métois REM image

$G_q(t)$

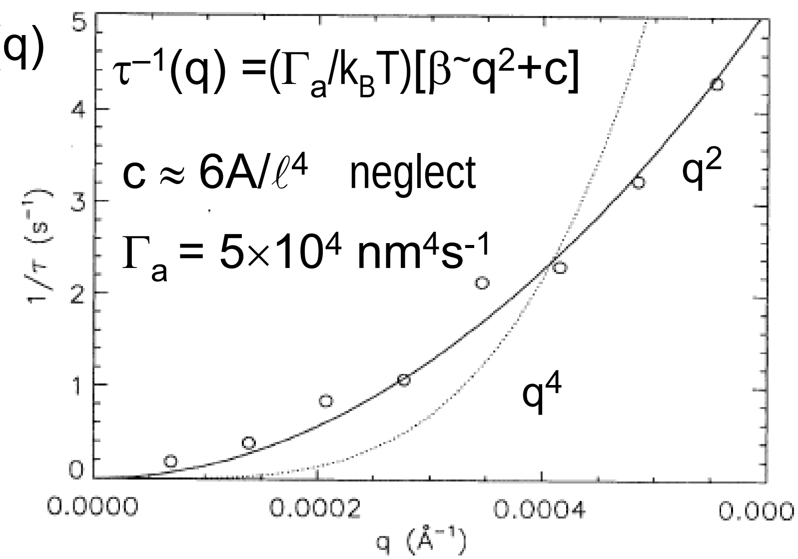


$\tilde{\beta} \approx 30$mev/Å

G(t)



$\tau^{-1}(q)$



$\tau^{-1}(q) = (\Gamma_a/k_BT)[\tilde{\beta} q^2 + c]$

$c \approx 6A/\ell^4$ neglect

$\Gamma_a = 5\times 10^4$ nm^{4}s^{-1}

$$\frac{\partial x}{\partial t} = \frac{\Gamma_a \tilde{\beta}}{kT}\frac{\partial^2 x}{\partial y^2} - \frac{2\Gamma_a c x}{kT} + \eta_a(y,t)$$

Measured time exponent 1/z on late transition & noble metals

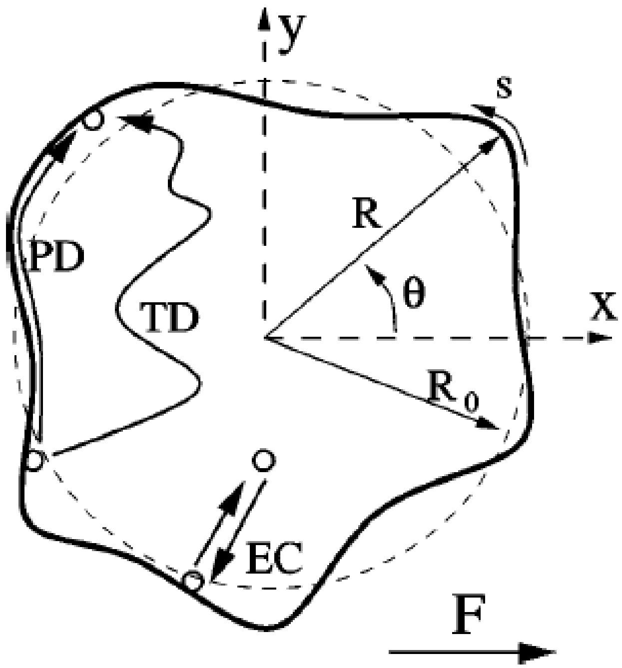
Surface	Temperature range (K)	Time exponent 1/z
Cu(100)[e]		
Cu(100)[e]		
Cu(100)[c]		
Cu(100)[c]		
Cu(100)[c]		
Cu(100)[f]		
Cu(100)[c]		
Cu(119)[e]		
Cu(1111)[‡]	293	
Cu(1111)[‡]	300	1/4
Cu(1113)[‡]	300–370	1/4
Cu(1119)[‡]	310–360	1/4
Cu(1119)[‡]	290–370	
Cu(1179)[‡]	390–600	1/4
Cu(111)[e]		
Cu(111)[c]		
Cu(171719)[‡]	300–500	1/4
Cu(212123)[‡]	300–500	1/4
	600	1/2
Ag(100)[e]		
Ag(100)[f,h]		
Ag(100)[c]		
Ag(119)[e]		
Ag(111)[‡]	300	1/4
Ag(111)[‡]		
Ag(111)[‡]	300	1/4
Ag(111)[‡]	310–390	1/4
	440–590	1/2
Ag(111)[e]		
Ag (110)[‡]	300	1/2
Au(100)[e]		
Au(100)[c]		
Au(111)[e]		
Au(110)[‡]	300–590	1/2
Ni(111)[e]		
Ni(100)[e]		
Ni(100)[e]		
Ni(100)[c]		
Pt(100)[e]		
Pt(111)[‡]	530–800	1/4
Pt(111)[i]		
Pt(111)[j]		
Pt(111)[e]		
Pt(111)[c]		
Pt(111)[h]		
Pt(331)[‡]	~80–300	
Pb(111)[‡]	300	1/4

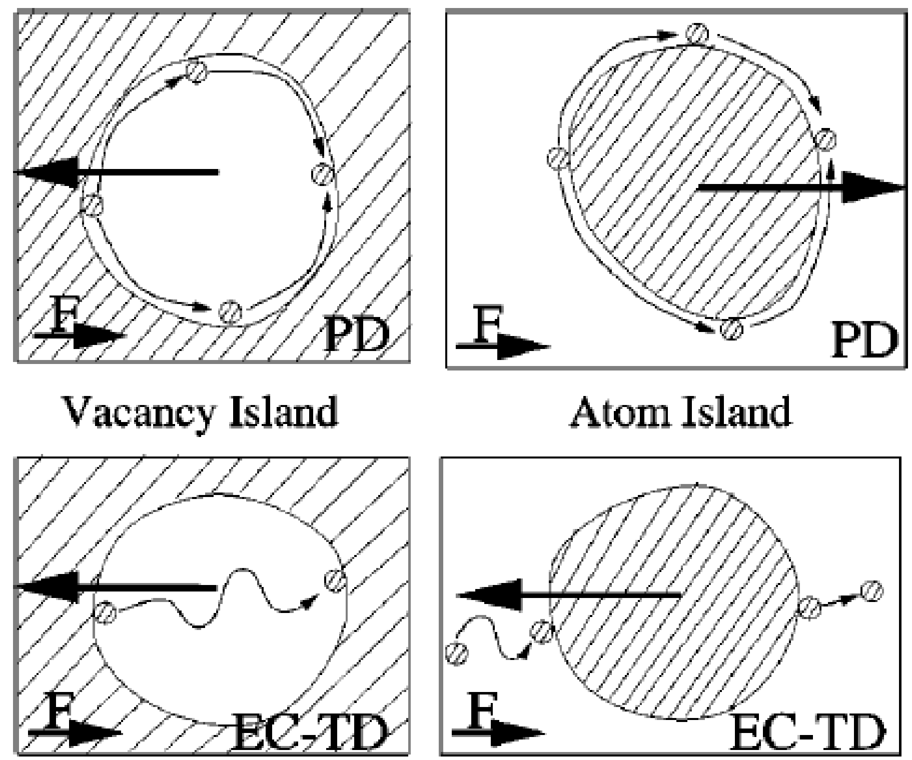
M. Giesen, Prog. Surf. Sci. 68 ('01) 1

Summary of all cases studied in “unified” treatment paper

Case: Limits	Equation	τ_q^{-1}/Sq^2	$(A_q+2B_q)/S$	$(A_q-2B_q)/S$
A ($3dEC$): $D_{st}=0$, $\lvert\Lambda_q\rvert\approx x_s$				
(i) $D_{su}/(x_s k_\pm)\ll 1\ll \ell/x_s$	(35)	$2(D_{su}/\tau_e)^{1/2}$	$\star$	$\star$
(ii) $x_s k_\pm/D_{su}\ll 1\ll \ell/x_s$	(35) w/ $2(D_{su}/\tau_e)^{1/2}\to k_+ + k_-$	$k_+ + k_-$	$\star$	$\star$
(iii) $\ell/x_s\ll 1\ll D_{su}/(x_s k_\pm)$	(36) w/ $4(k_+^{-1}+k_-^{-1})^{-1}$			
such that $D_{su}\ell/(x_s^2 k_\pm)\gg 1$	& $\ell/\tau_e\to k_+ + k_-$	$\star$	$k_+ + k_-$	$k_+ + k_-$
(iv) $\ell/x_s\ll D_{su}/(x_s k_\pm)\ll 1$	(36)	$\star$	$4(k_+^{-1}+k_-^{-1})^{-1}$	ℓ/τ_e
(v) $D_{su}/(x_s k_\pm)\ll \ell/x_s\ll 1$	(37)	$\star$	$4D_{su}/\ell$	$D_{su}(k_+^{-1}+k_-^{-1})/\tau_e$
B (EC): $a_q^\pm\gg 1$ or $b_q^\pm\gg 1$				
(i) $D_{st}=0$, $a_q^\pm\gg 1$	(38), (39)	$k_+ + k_-$	$\star$	$\star$
(ii) $D_{su}=0$, $b_q^\pm\gg 1$	(38), (39)	$k_+ + k_-$	$\star$	$\star$
(iii) $b_q^\pm\gg 1$, $a_q^\pm\gg 1$	(38), (39)	$k_+ + k_-$	$\star$	$\star$
C (ISTD): $D_{st}=0$				
(i) $k_-=0$, $a_q^+\ll 1$	(40), (41) w/ $D_{su}\to D_{su}/2$	$D_{su}\lvert q\rvert$		
(ii) $k_+=0$, $a_q^-\ll 1$	(40), (41) w/ $D_{su}\to D_{su}/2$	$D_{su}\lvert q\rvert$	$\star$	$\star$
(iii) $a_q^\pm\ll 1$	(40), (41)	$2D_{su}\lvert q\rvert$		
D (DSS): $D_{st}=0$, $\lvert q\rvert\ell\ll 1$				
(i) $a_q^\pm\ll\lvert q\rvert\ell$	(42)	$\star$	$4D_{su}/\ell$	$D_{su}^2(k_-^{-1}+k_+^{-1})q^2$
(ii) $\lvert q\rvert\ell\ll a_q^\pm\ll 1$	(43)	$\star$	$4(k_+^{-1}+k_-^{-1})^{-1}$	$D_{su}\ell q^2$
(iii) $a_q^\pm\gg 1$	(43) w/ $4(k_+^{-1}+k_-^{-1})^{-1}$			
such that $a_q^\pm\lvert q\rvert\ell\gg 1$	& $D_{su}\ell q^2\to k_+ + k_-$		$k_+ + k_-$	$k_+ + k_-$
E ($PSTD$): $k_-=0$, $D_{st}=0$				
& $\lvert q\rvert\ell\ll 1\ll 1/a_q^\pm$	(44)	$\star$	$D_{su}\ell q^2$	$D_{su}\ell q^2$
F (PD): $D_{su}=0$				
(i) $b_q^\pm\ll 1$	(45), (46)	$2a_\perp D_{st}q^2$		
(ii) $b_q^-=0$, $b_q^+\ll 1$	(45), (46) w/ $D_{st}\to D_{st}/2$	$a_\perp D_{st}q^2$	$\star$	$\star$
(iii) $b_q^+=0$, $b_q^-\ll 1$	(45), (46) w/ $D_{st}\to D_{st}/2$	$a_\perp D_{st}q^2$		
G ($3dS$): $D_{st}=D_{su}=0$				
& $D_{va}\lvert q_z\rvert/k_\pm\ll 1$	(47)	$D_{va}\lvert q_z\rvert$	$\star$	$\star$

S.V. Khare & TLE, PRB 57 (’98) 4782



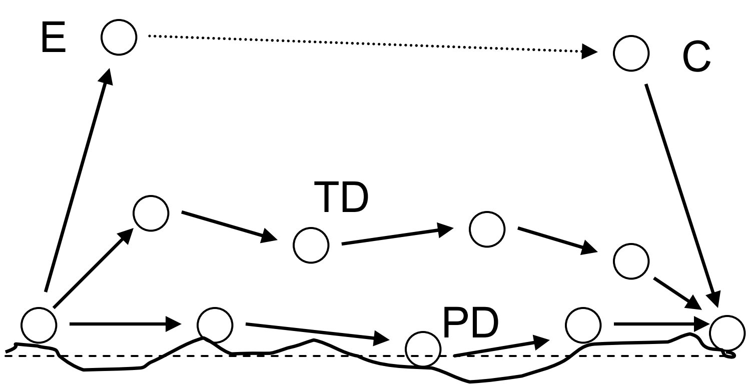


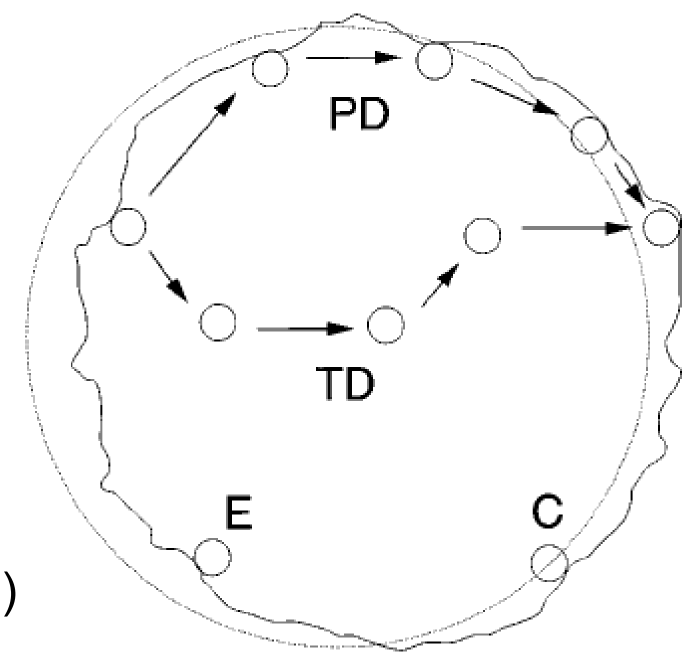
$$R(\theta) = R_0 + \rho(\theta)$$

$$\langle |\rho_n|^2 \rangle_{\mathrm{eq}} = \frac{k_B T R_0}{2\pi(n^2-1)\tilde{\beta}}$$

O. Pierre-Louis & TLE, PRB 62 ('00) 13697

Island – Adatom or Vacancy – Defined by Nearly Circular Step!



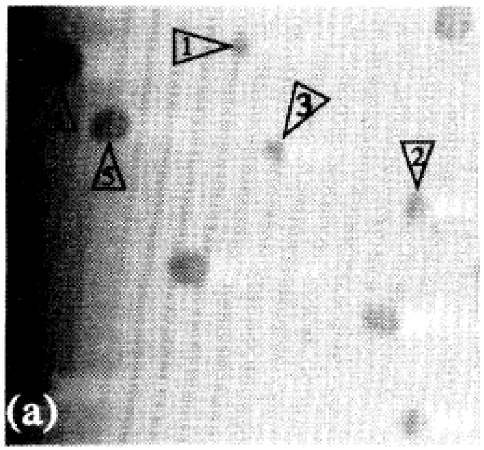


$D_c = D_{c0}R^{-\alpha}$ α = 3 (PD), 2 (TD), 1 (EC)

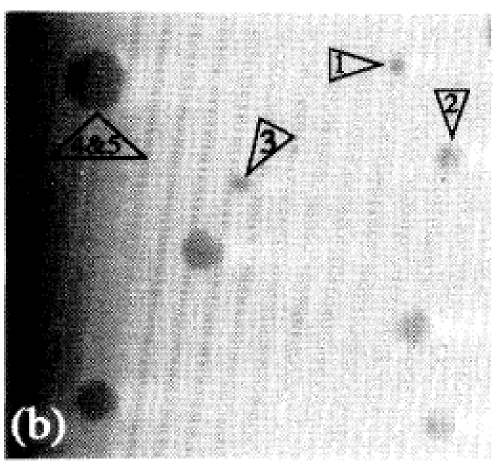
$D_{c0} = D_{st}c_{st}\Omega^2/\pi,\ 2D_sc_s\Omega^2/\pi,\ \Gamma/\pi$

Dependence of cluster diffusion constant on vacancy island size

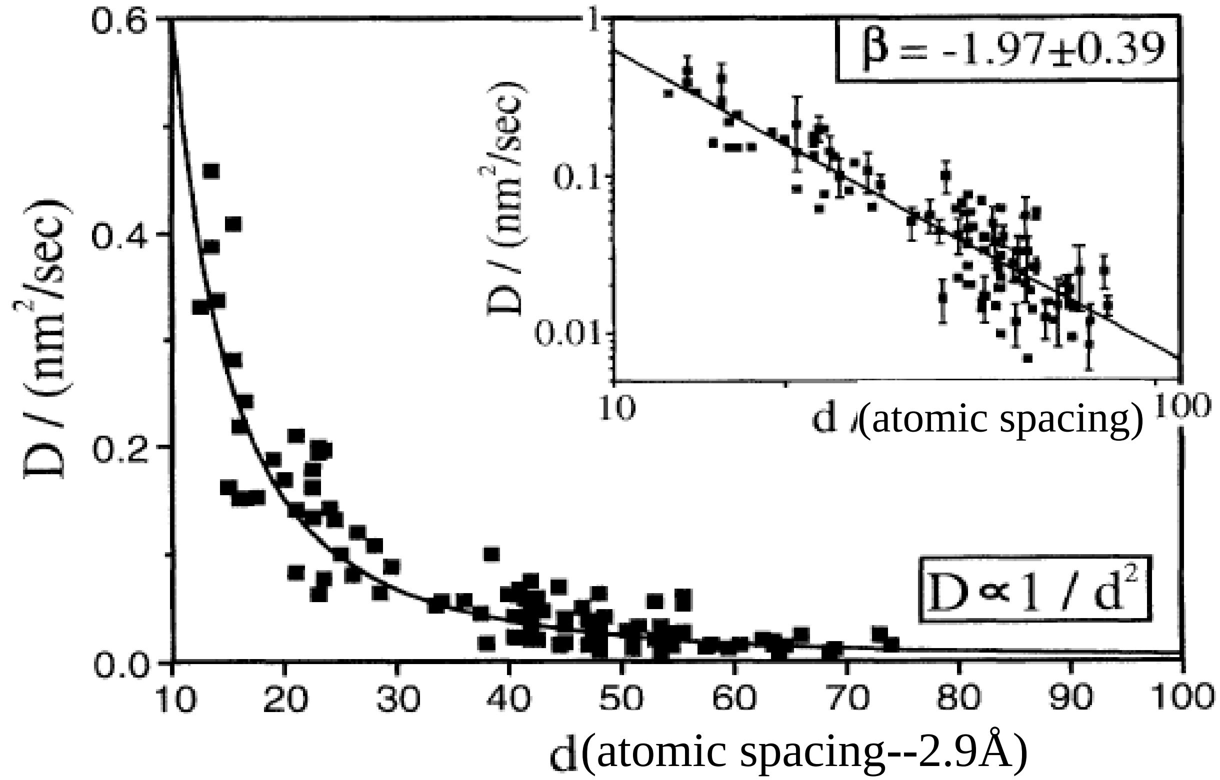
K. Morgenstern,…G. Comsa, PRL 74 (’95) 2058

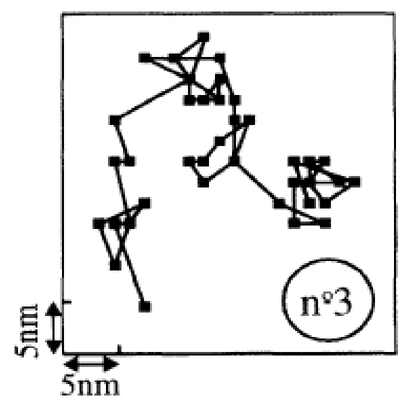


173nm x 173nm

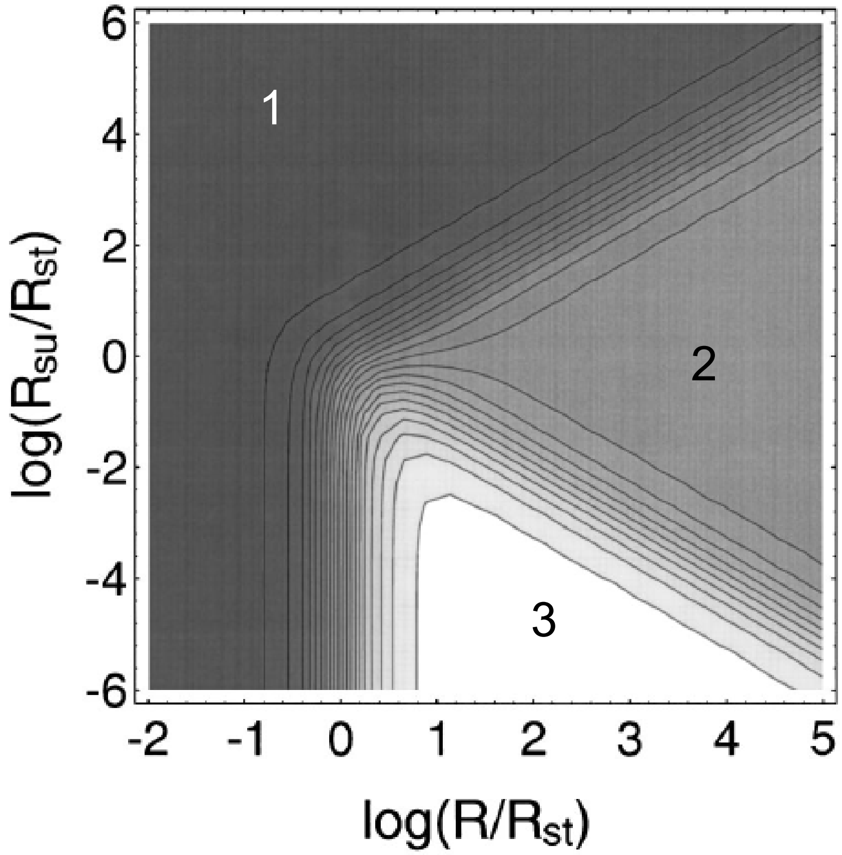


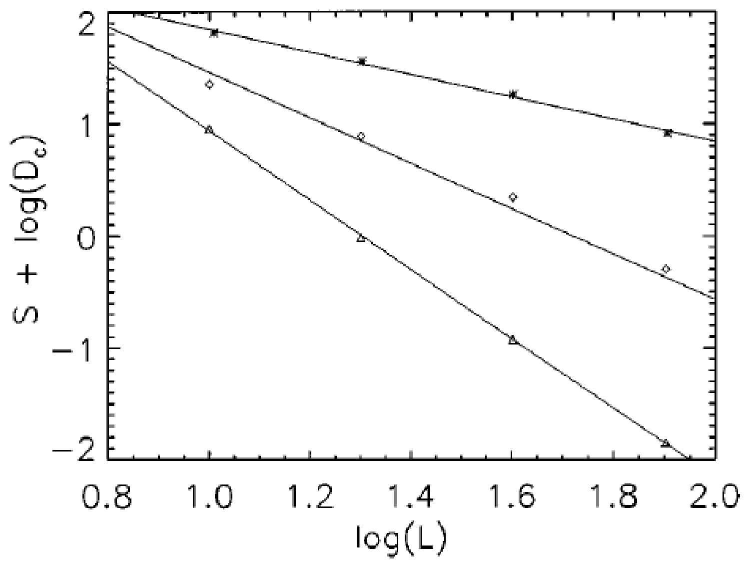
4700 s later than (a),
scans every 100 s

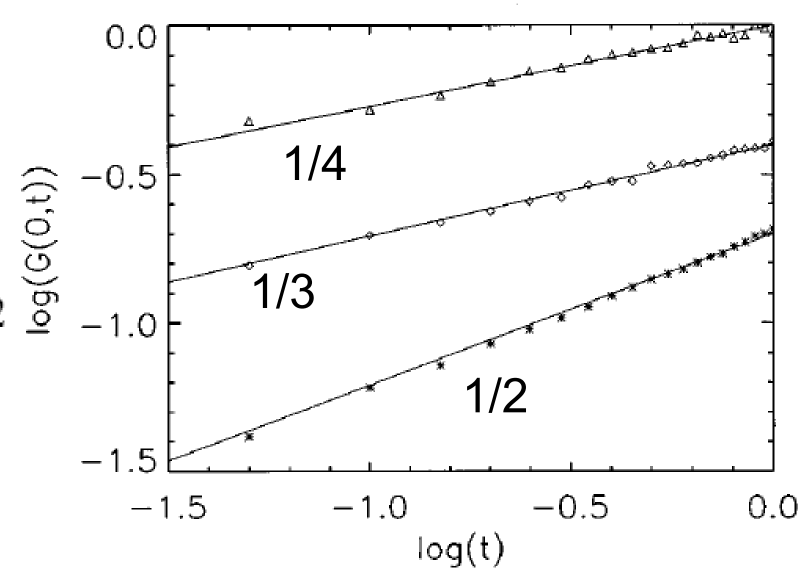




Crossover for cluster diffusion exponent α



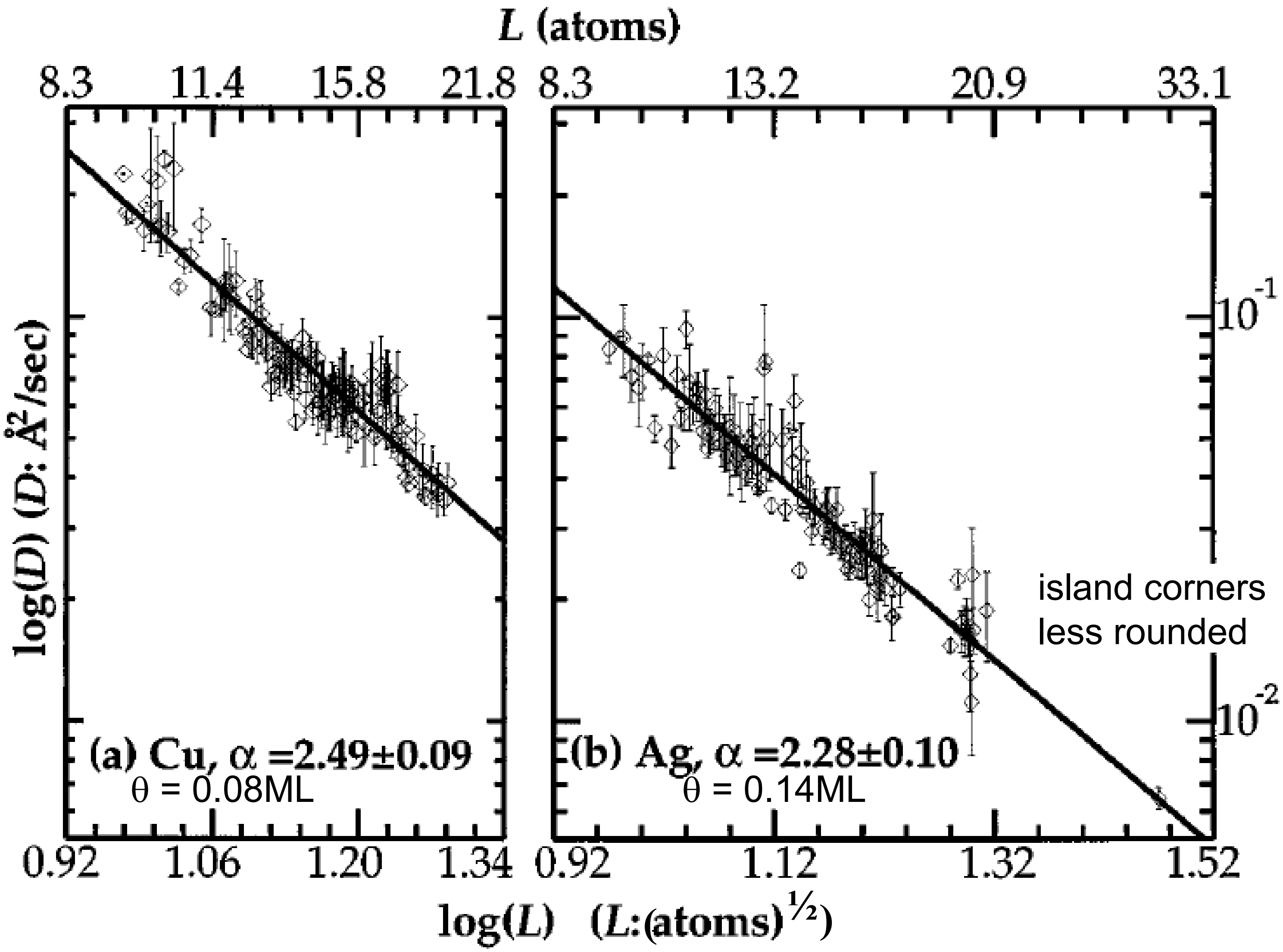




$$R_{su} \equiv D_{su}\Omega/\Gamma_+ \qquad R_{st} \equiv (a_\perp D_{st}\Omega/\Gamma_+)^{1/2}$$

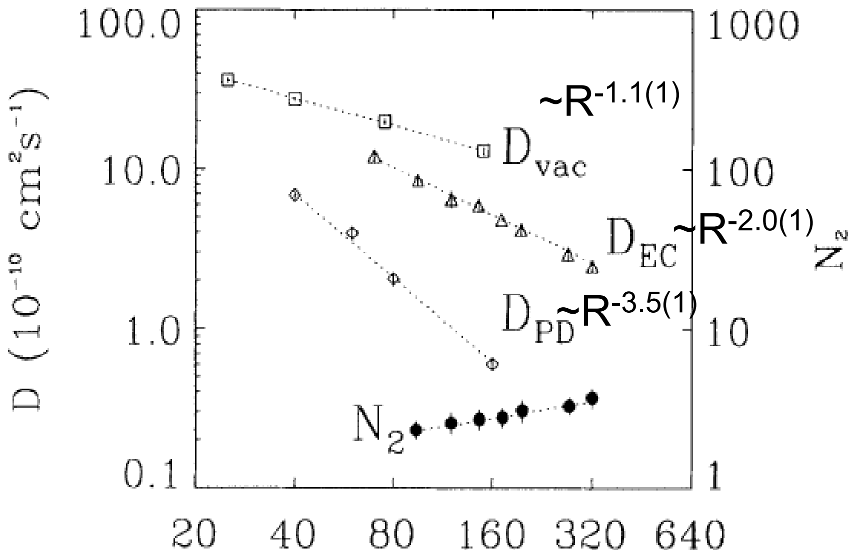
S.V. Khare & TLE, PRB 54 ('96) 11752

Size dependence of diffusion constant of Cu(001) and Ag(001)

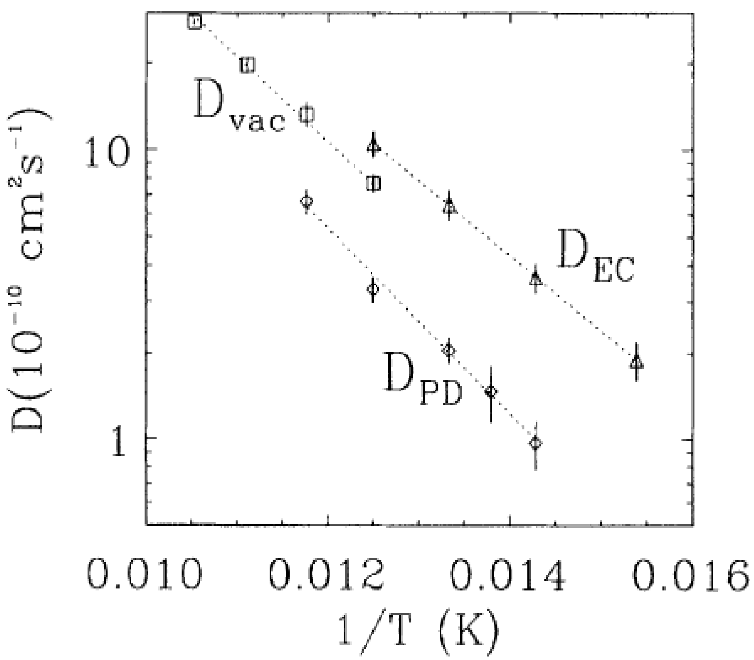


W.W. Pai et al., PRL 79 ('97) 3210

Simulations with rather realistic potentials Xe/Pt(111)



$N=\pi R^2$; R_{max} ~ 10

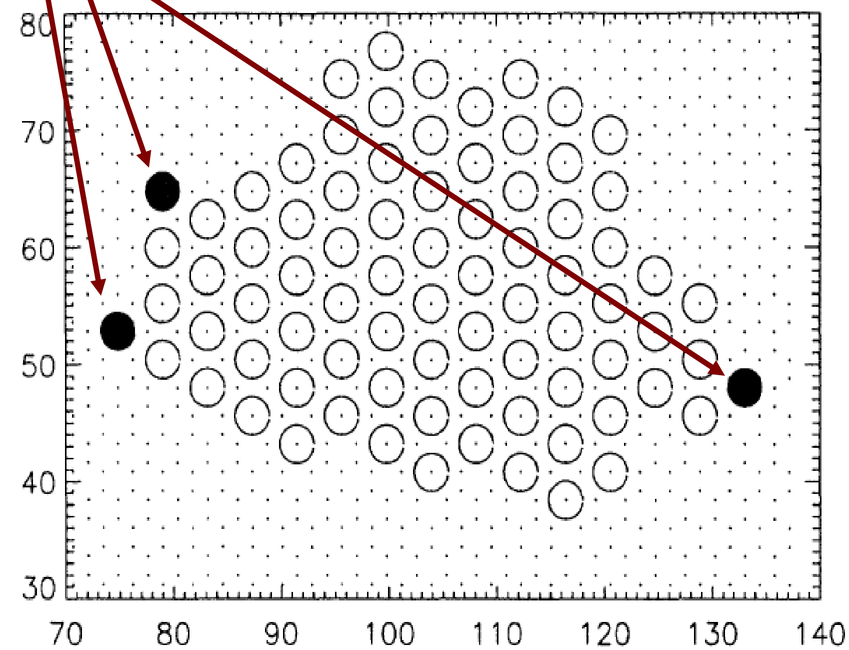


1) Not periphery diffusion

D.S. Sholl and R.T. Skodje, PRL 75 ('95) 1358

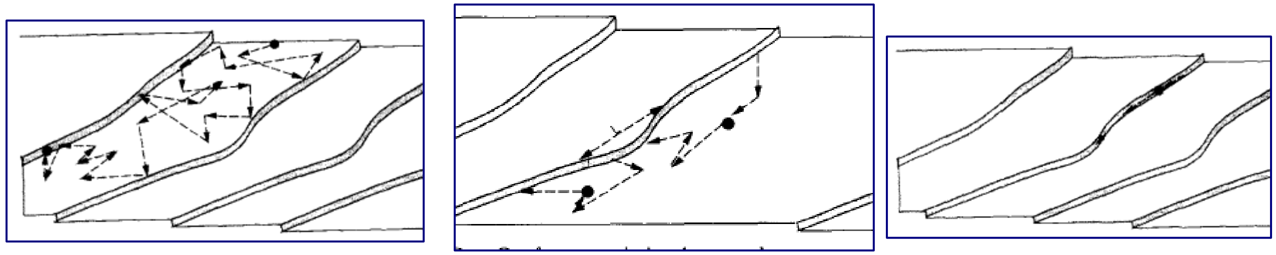
2) N_2 atoms (having 2NN) control detachment

$N_2 \propto R^{\mathbf{0.7(2)}}$, not $R^{\mathbf{1}}$ as in continuum model



Pre-continuum results!

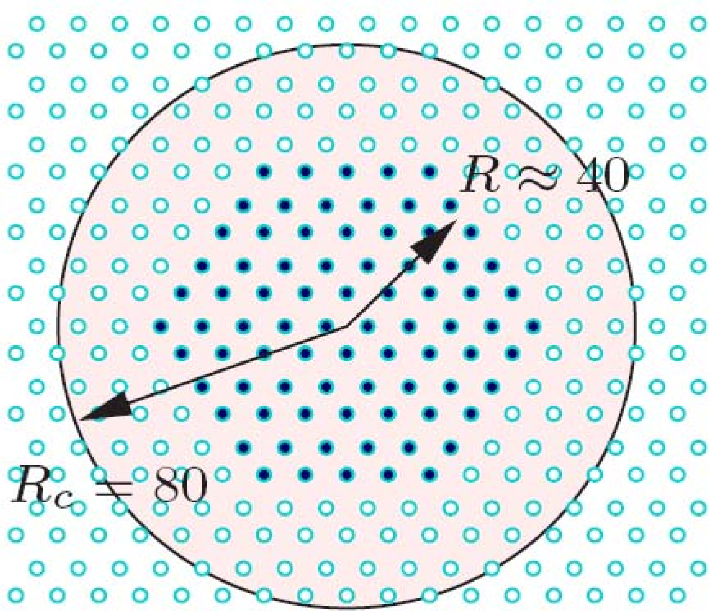
Isolated Step Fluctuations: Signatures of Dominant Mass Transport Mechanism

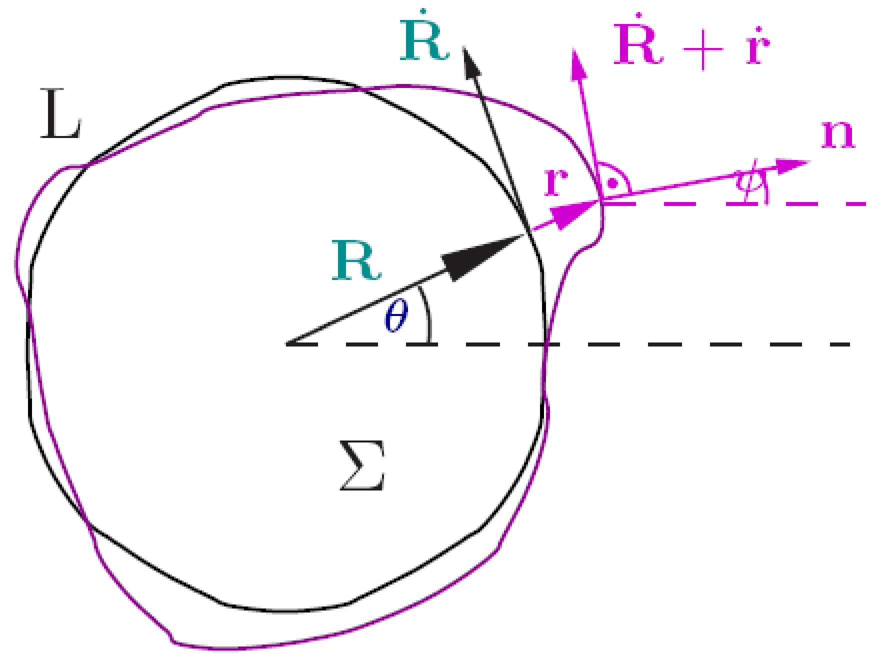


	EC or AD (ADL)	TD (DL)	PD
Limited by	At/de/tach at step	Terrace diffu'n	**Step-edge diffu'n**
Fluctuation healing time--width y	y^2	y^3	y^4
Size dep. of island diffu'n, $R \propto \sqrt{\text{area}}$	R^{-1}	R^{-2}	R^{-3}
w^2(t)	$t^{1/2}$	$t^{1/3}$	$t^{1/4}$
Island area decay	t^{1}	$t^{2/3}$	N/A
Evolution of atom/ vacancy island	Shrink to round point *(Grayson's Thm)*		Wormlike, pinch-off
Height decay of cone ["facet"]	$t^{1/4}$	$t^{1/4}$	N/A
Height decay of paraboloid [rough]	$t^{1/3}$	$t^{2/5}$	N/A

Kinetic Monte Carlo & Analysis

F. Szalma, Hailu Gebremariam, & TLE, PRB 71 ('05) 035422





Process	Energy (meV)	Energy (K)	Break-three energy (K)
Surface diffusion	70	812	812
Edge diffusion	237	2749	2319
Break 1 bond	192	2227	2319
Break 2 bonds	359	4164	3826
Break 3 bonds	467	5417	5333
Attachment			812
Out			70000

Detailed balance

General form of free energy:

$$F[\mathbf{r};t] = 2\pi\lambda \mathbf{r}^\dagger \left(\mathbf{A} + \mathbf{MBN}\right)\mathbf{r}$$

eigenvalues Λ_n

With isotropy, F simplifies greatly:

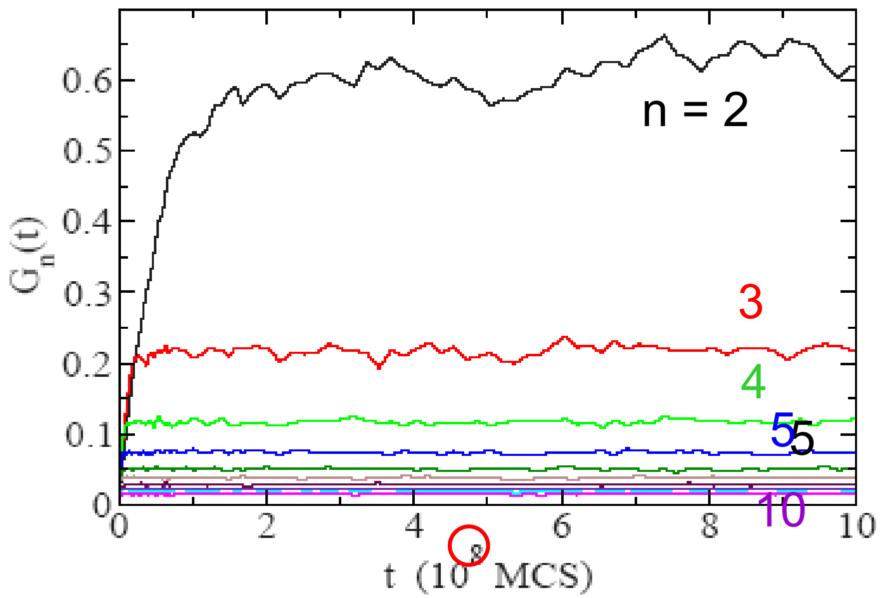
$\mathbf{A} = 0$ $\mathbf{B} = (1/2)\mathbb{1}$

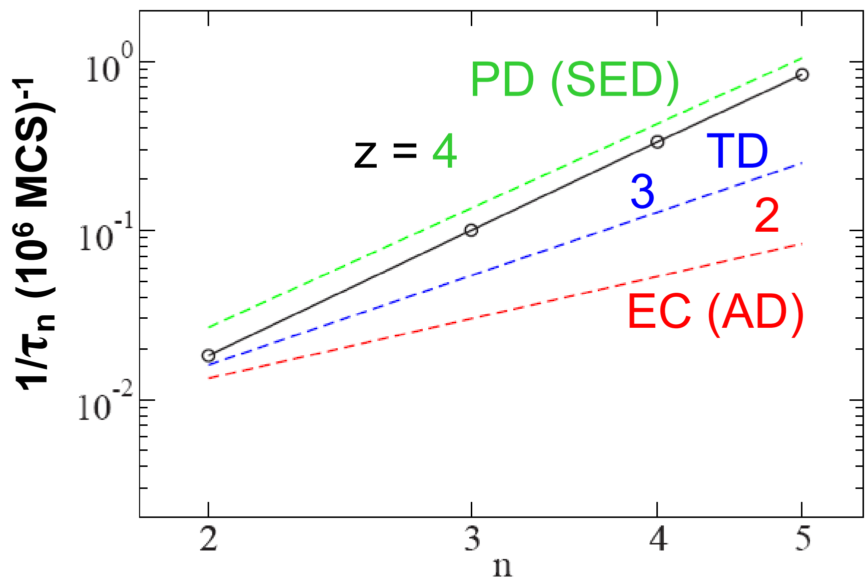
Results of Analysis of KMC Simulation Data

Temporal correlations of "Fourier" modes and their time constants

$$G_n(t) = \left\langle |r_n(t_0) - r_n(t_0+t)|^2 \right\rangle = C_n\left(1 - \exp\left(-|t|/\tau_n\right)\right)$$

$$1/\tau_n \sim n^z$$





T =400K, R=20a_1, R_c=40a_1

$$\tau_2 = 5.5 \times 10^7 \text{ MCS}$$

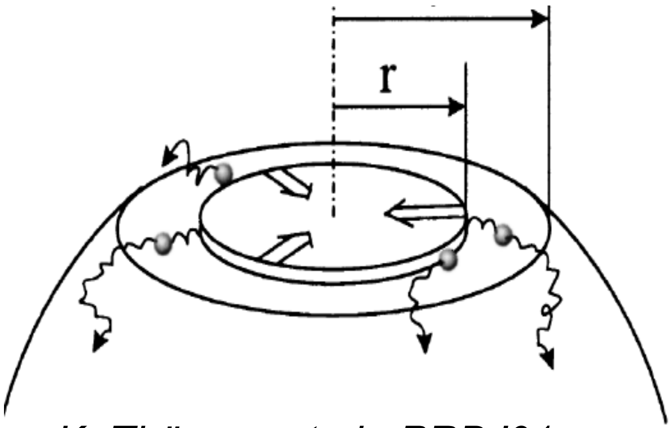
$$\nu = \nu_D \exp[-\beta E_b] \quad \nu_D = 1.83\times10^{12}$$

$$\Rightarrow \tau_2 = 0.030 \text{ msec}$$

$$z = (1/2)/\beta$$

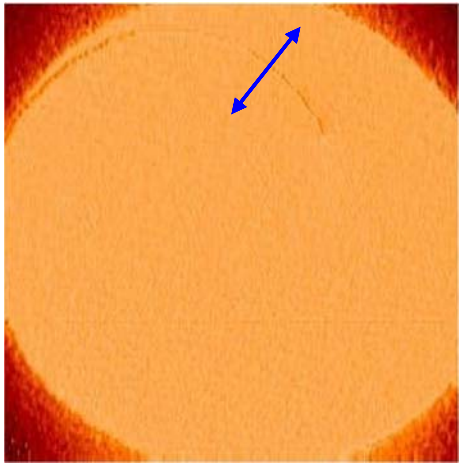
$$G(t) = \left\langle [r(t_0) - r(t_0+t)]^2 \right\rangle \propto t^{2\beta}$$

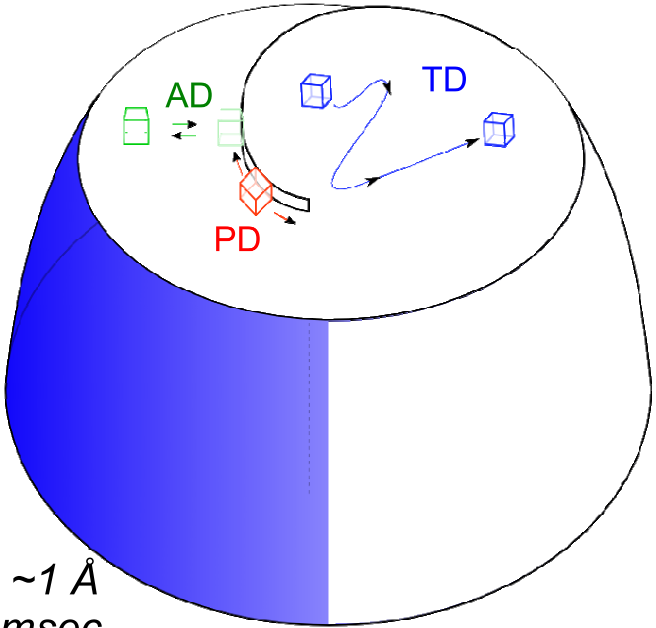
Experiments, resolution



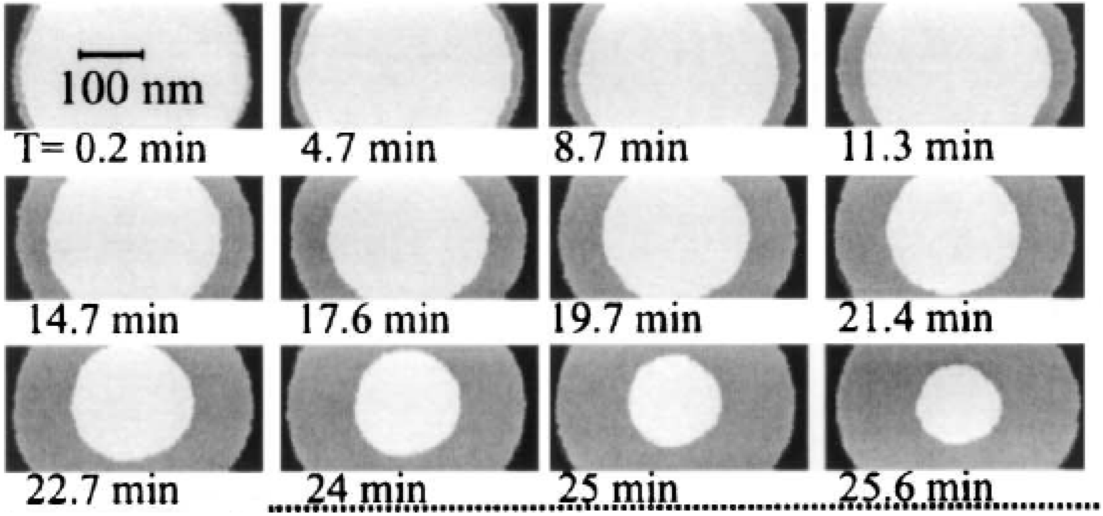
K. Thürmer et al., PRB '01

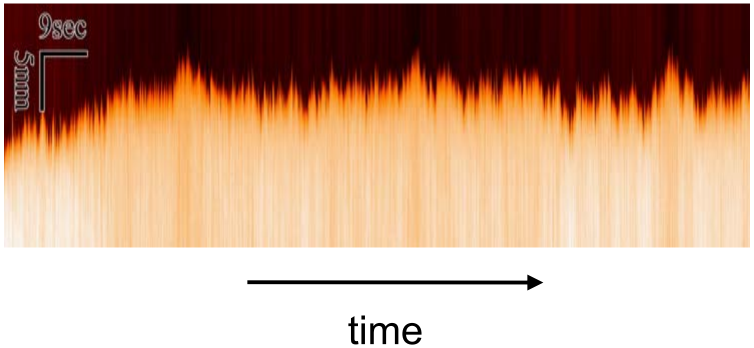
STM, Pb(111) (*D.B.Dougherty, M. Degawa, et al. 05, 06*)





- spatial resolution: *nearly atomic, ~1 Å*
- time resolution: *1 min/frame, 10 msec*
- *no* spatial info along step, line-scan





Linear response, hopping rates

Langevin description of step fluctuations:

$$\frac{\partial x}{\partial t}=\frac{-\Gamma_{PD}\tilde{\beta}}{k_B T}\frac{\partial^4 x}{\partial y^4}+\frac{\Gamma_{AD}\tilde{\beta}}{k_B T}\frac{\partial^2 x}{\partial y^2}+\eta(x,t)$$

$$\langle \eta(y,t)\eta(y',t')\rangle=-2\Gamma_{PD}\frac{\partial^2}{\partial x^2}\delta(y-y')\delta(t-t')+2\Gamma_{AD}\delta(y-y')\delta(t-t')$$

Correlation function:

$$G(t)=\langle[x(t)-x(0)]^2\rangle$$

$$G(t)=2\frac{\Gamma(3/4)}{\pi}\left(\frac{k_B T}{\tilde{\beta}}\right)^{3/4}\Gamma_{PD}^{1/4}\, t^{1/4}$$

$$G_q(t)=\langle|x_q(t)-x_q(0)|^2\rangle$$

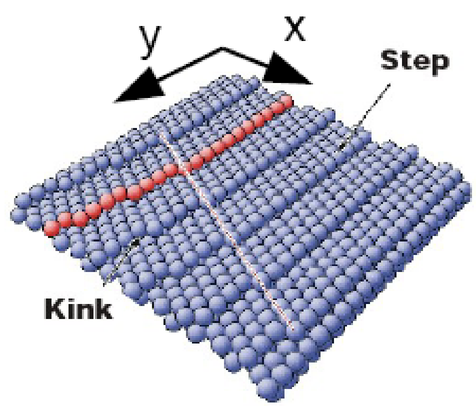
$$G_q(t)=\frac{2k_B T}{L\tilde{\beta}q^2}\left(1-\mathrm{e}^{-|t|/\tau(q)}\right)$$

Hopping rate:

$$\Gamma_{PD}=\Omega^{5/2}/\tau_h$$

$$\tau_h=\left(\frac{2\Gamma(3/4)}{\pi\, c(T)}\right)^4\left(\frac{k_B T}{\tilde{\beta}}\right)^3\Omega^{5/2}$$

$$\tau(q)=\frac{k_B T}{\tilde{\beta}}\frac{\tau_h}{\Omega^{5/2}q^z} \qquad z=4$$



LEEM

STM (line scan)

Atomic resolution

Spatial info

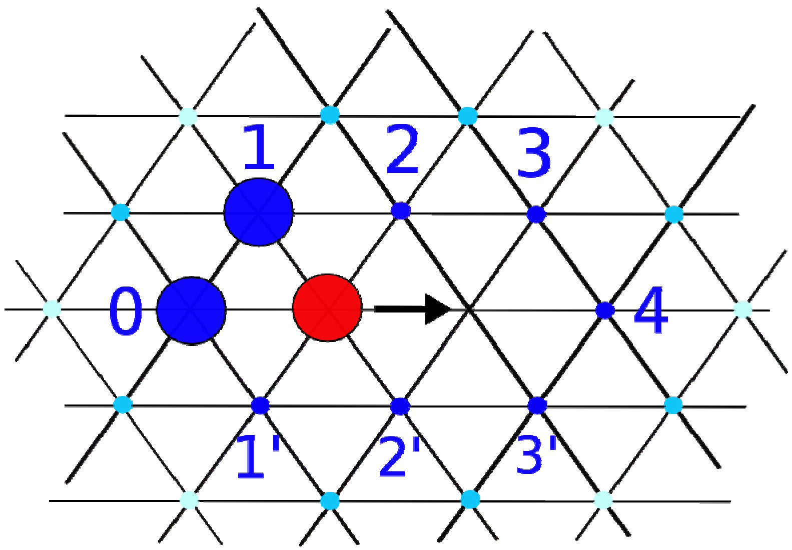
MC

$$\frac{1}{\tau_h}=\nu\mathrm{e}^{-E_h/k_B T}$$

$$E_h=3\epsilon_k+E_d$$

Kinetic Monte Carlo

Hopping barrier: $E_b = E_{TD} + mE_{NN} + nE_{2NN} + kE_{3NN} + \dots$



Pb(111)

E_{TD}=70meV,
E_{NN}=130meV

Break-3 scheme

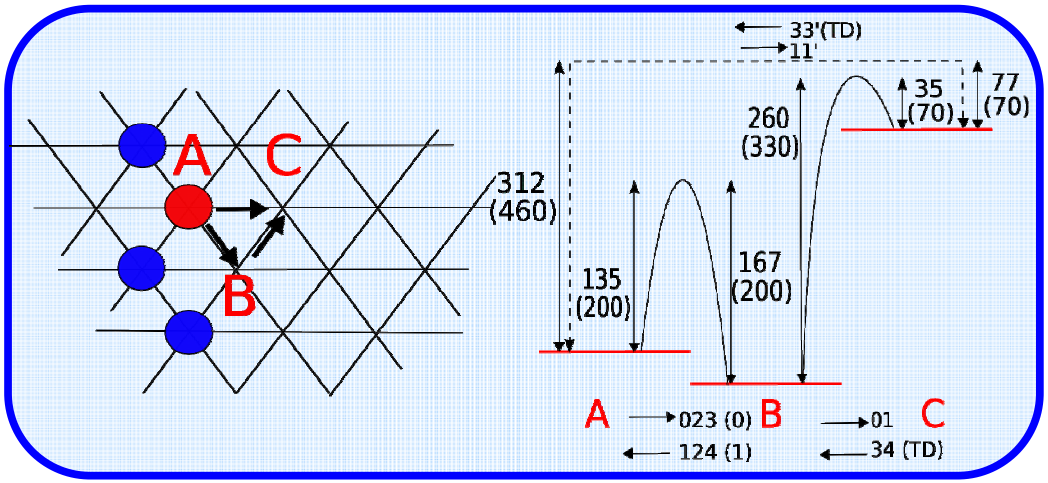
SEAM

Config	E_b^{bb3}	E_b^{bb5}	E_b^{EAM}	$\Delta E_b^{\mathrm{EAM}}$	E_b^{Kaw}
TD	70	70	70	0	70
0	200	200	192	116	200
01	330	330	260	225	330
12	200	330	237	147	200
012	330	460	359	269	330
011′	460	460	467	386	460
123	200	330	108	0	70
011′2	460	590	598	469	460
1234	200	330	141	-162	70
23	70	200	86	-147	70
22′	70	330	130	0	70
11	330	330	312	235	330
023	200	200	135	-32	70

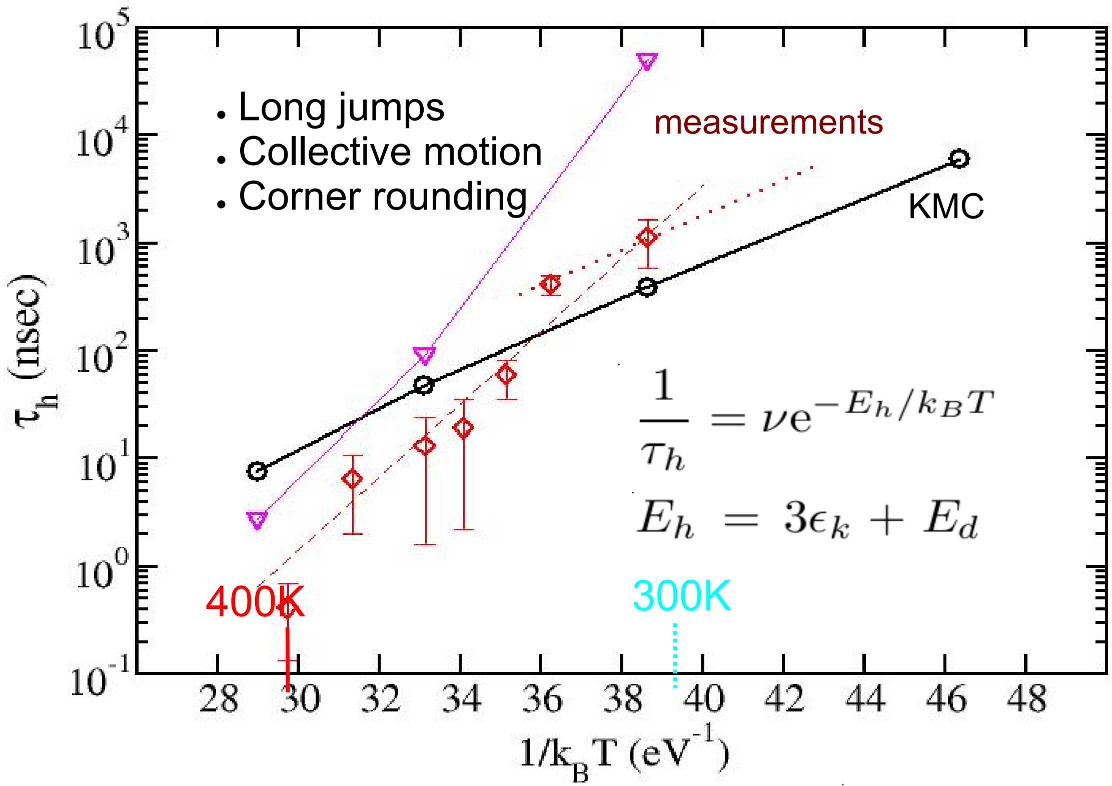
Cu(111) no strong effect of *2NN* on static parameters
T.Stasevich et al. PRB 2005

Cu(111) collective motion of clusters of adatoms
Trushin et al. PRB 2005
Karim et al. condmat/2005

Long jumps in diffusion
G. Antczak, G. Ehrlich, PRB 2005

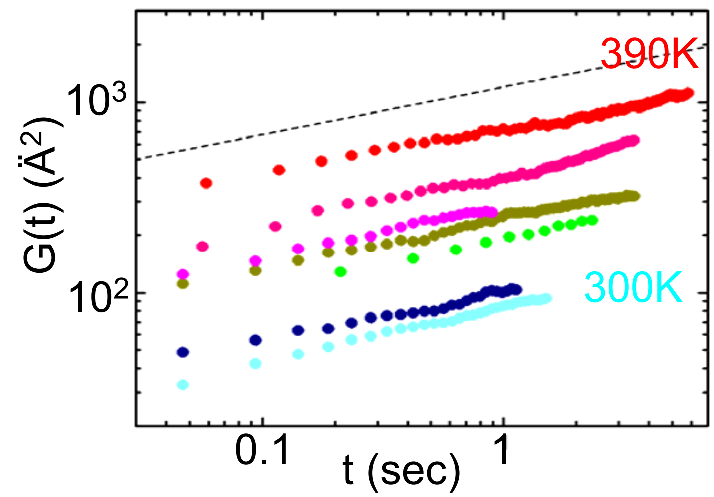


Kinetic parameters



F. Szalma, D.B. Dougherty,…
PRB 73 ('06) 115413

$$G(t) = c(T)\ t^{1/4}$$



T (K)	z	L (Å)	n	λ(Å)	$\tau(\lambda)$	τ_h
250	3.98	879.2	6	146.5	1.26ms	5.91μs
300	3.81	439.6	5	87.9	17.5μs	0.382μs
350	4.02	439.6	5	87.9	3.1μs	47.1ns
400	4.17	439.6	5	87.9	0.66μs	7.59ns

	E_{coh}	ϵ_k^{Exp}	E_d^{Exp}	ϵ_k^{Th}	E_d^{Th}
Pt	5.84[a]	167[b]	1000[b]	161(A) 178(B)[c]	840(A) 900([illegible]
Cu	3.49[a]	128[e] 113[f]	320[e]	90(A) 120(B)[g]	228[h] 290[i]
Ag	2.95[a]	101[j]	0±100[j]	74[k]	220[h]
Pb	2.03[a]	40(A) 60.3(B)[l] 61(A) 87(B)[m]	**585**	41(A) 60(B)[n]	**185**

Conclusions re 2-parameter KMC on Pb(111)

- Static parameters such as line tensions, stiffnesses agree well with experiment
- Low-T kinetics is well modelled by the KMC
- Higher T requires a more complex MC scheme (concerted or collective motion, corner rounding, long jumps)

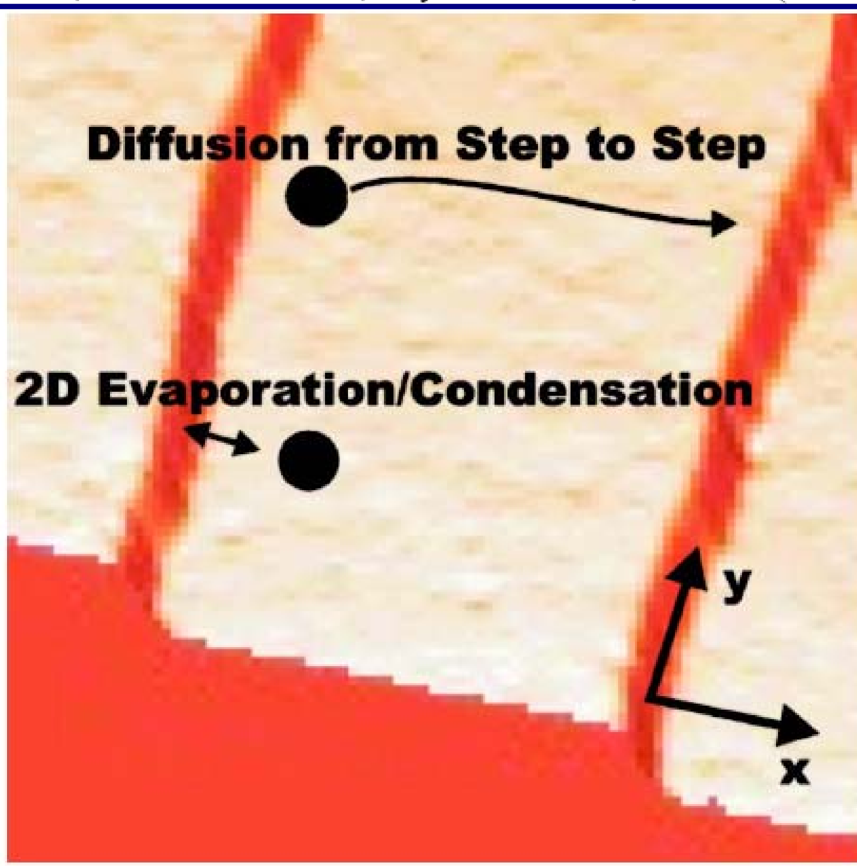
PHYSICAL REVIEW B **70**, 235422 (2004)

Distinguishing step relaxation mechanisms via pair correlation functions

D. B. Dougherty, I. Lyubinetsky,* T. L. Einstein, and E. D. Williams†

Si(111) ($\sqrt{3} \times \sqrt{3}$) R30° Al at 970K

M. Kammler, M. Horn von Högen, N. Voss, M. Tringides, A. Menzel, and E. H. Conrad, Phys. Rev. B **65**, 075312 (2002). suggest DSS, not EC



$$G(t) = \langle [x(y_0, t+t_0) - x(y_0, t_0)]^2 \rangle = ct^{1/z}$$

$$G_{\mathrm{EC}}(t) = \sqrt{\frac{4k_B T a_n^2 a_p t}{\pi \tilde{\beta} \tau_a}}$$

$$G_{\mathrm{DSS}}(t) = \sqrt{\frac{16 D c k_B T \Omega^2 t}{\pi^3 \tilde{\beta} \langle \ell \rangle}}$$

What to do when can't ramp $\langle \ell \rangle$??

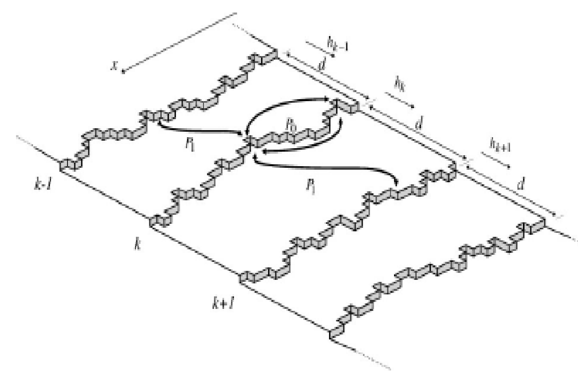
B. Blagojevic & P.M Duxbury, PRE 60 ('99) 1279

TABLE I. Limiting behaviors for $G(0,t)$.

Mass transport mechanism	Time regime	$G(0,t)$
Evaporation-condensation (EC)	$t \to 0$	$\sim t$
	$0 \ll t \ll \tau_s^{\mathrm{ST}}$	$\Omega\left(\frac{a_\perp}{\pi \tilde{s}}\right)^{1/2}\left(\frac{t}{\tau_{\mathrm{EC}}}\right)^{1/2}$
	$t \gg \tau_s^{\mathrm{ST}}$	$\frac{L\Omega}{12\tilde{s}}\left(1-\frac{6}{\pi^2}e^{-t/\tau_s^{\mathrm{EC}}}\right)$
Step-edge diffusion (SE)	$t \to 0$	$\sim t$
	$0 \ll t \ll \tau_s^{\mathrm{SE}}$	$\frac{\Gamma(\frac{3}{4})}{\pi}\left(\frac{\Omega^5 a_\parallel}{\tilde{s}^3}\right)^{1/4}\left(\frac{t}{\tau_{\mathrm{SE}}}\right)$
	$t \gg \tau_s^{\mathrm{SE}}$	$\frac{L\Omega}{12\tilde{s}}\left(1-\frac{6}{\pi^2}e^{-t/\tau_s^{\mathrm{SE}}}\right)$
Terrace diffusion 1 ($T1$) $d \to \infty$	$t \to 0$	$\sim t$
	$0 \ll t \ll t_1^{T1}$	$\Omega a_\perp\left(\frac{\alpha_U+\alpha_L}{\pi \tilde{s}}\right)^{1/2}\left(\frac{t}{\tau_{\mathrm{TD}}}\right)$
(isolated step)	$t_1^{T1} \ll t \ll t_2^{T1}$	$\frac{\Omega\Gamma(\frac{2}{3})}{\pi}\left(\frac{a_\perp^2}{\tilde{s}^2}\right)^{1/3}\left(\frac{t}{\tau_{\mathrm{TD}}}\right)^{1/3}$
	$t_2^{T1} \ll t \ll \tau_s^{T1}$	$\frac{\Omega\Gamma(\frac{2}{3})}{\pi}\left(\frac{2a_\perp^2}{\tilde{s}^2}\right)^{1/3}\left(\frac{t}{\tau_{\mathrm{TD}}}\right)^{1/3}$
	$t \gg \tau_s^{T1}$	$\frac{L}{12\tilde{s}}\left(1-\frac{6}{\pi^2}e^{-t/\tau_s^{T1}}\right)$
Terrace diffusion 2 ($T2$) d finite, $\alpha_U=0$ or $\alpha_L=0$	$t \ll t_1^{T2}$	as for isolated step ($T1$)
	$t_1^{T2} \ll t \ll \tau_s^{T2}$	$\frac{\Omega\Gamma(\frac{3}{4})}{\pi}\left(\frac{d a_\perp^2}{\tilde{s}^3}\right)^{1/4}\left(\frac{t}{\tau_{\mathrm{TD}}}\right)^{1/4}$
(e.g., Schwoebel barrier $=\infty$)	$t \gg \tau_s^{T2}$	$\frac{L}{12\tilde{s}}\left(1-\frac{6}{\pi^2}e^{-t/\tau_s^{T2}}\right)$
Terrace diffusion 3 ($T3$) d finite, $\alpha_{U,L} \neq 0$	$t \ll t_1^{T3}$	as for isolated step ($T1$)
	$t_1^{T3} \ll t \ll \tau_s^{T3}$	$4\Omega a_\perp\left(\frac{1}{\pi^3 \tilde{s}(d+d_0)}\right)^{1/2}\left(\frac{t}{\tau_{\mathrm{TD}}}\right)^{1/2}$
	$t \gg \tau_s^{T3}$	$\frac{L\Omega}{12\tilde{s}}\left\{1-\frac{3L}{2\pi^3}\left(\frac{d+d_0}{\pi a_\perp^2 \tilde{s}}\right)^{1/2}\left(\frac{t}{\tau_{\mathrm{TD}}}\right)^{-1/2} e^{-(2\pi/L)^4 \tilde{s} a_\perp^2 dt/\tau_{\mathrm{TD}}}\right\}$

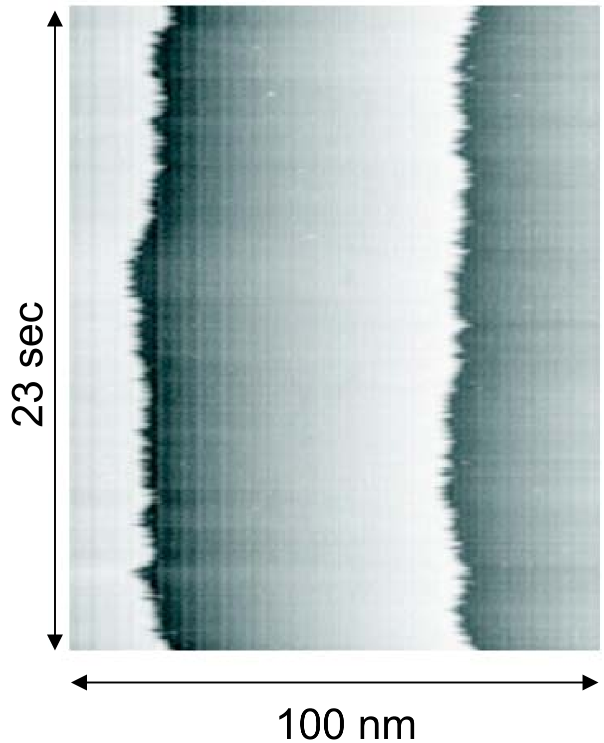
$$J_{k,k}(x,t)=\int_0^{L/2} P_0(l)\{\mu_k(x+l,t)-2\mu_k(x,t)+\mu_k(x-l,t)\}dl,$$

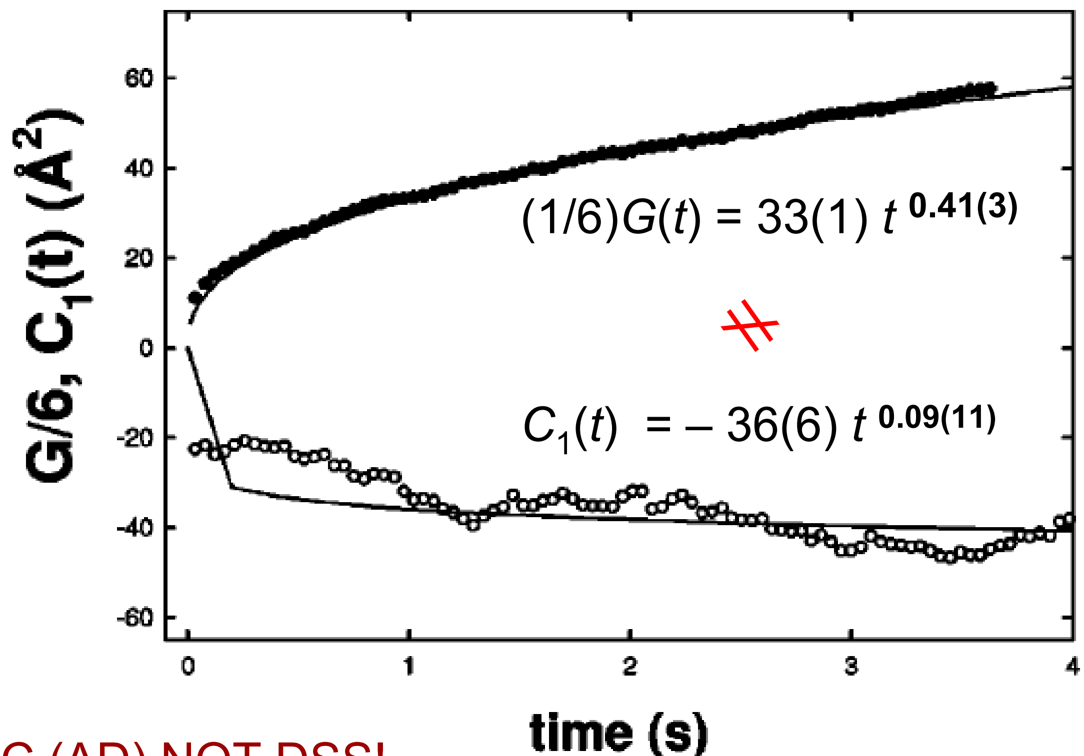
$$J_{k\pm1,k}(x,t)=\int_0^{L/2} P_1(l)\{\mu_{k\pm1}(x+l,t)-2\mu_k(x,t)+\mu_{k\pm1}(x-l,t)\}dl.$$



$$C_1(t) = \langle x_n(y_0, t+t_0)x_{n+1}(y_0, t_0)\rangle = \sqrt{\frac{16Dck_BT\Omega^2 t}{9\pi^3\tilde{\beta}\langle\ell\rangle}} = \frac{1}{6}G_{\mathrm{DSS}}$$

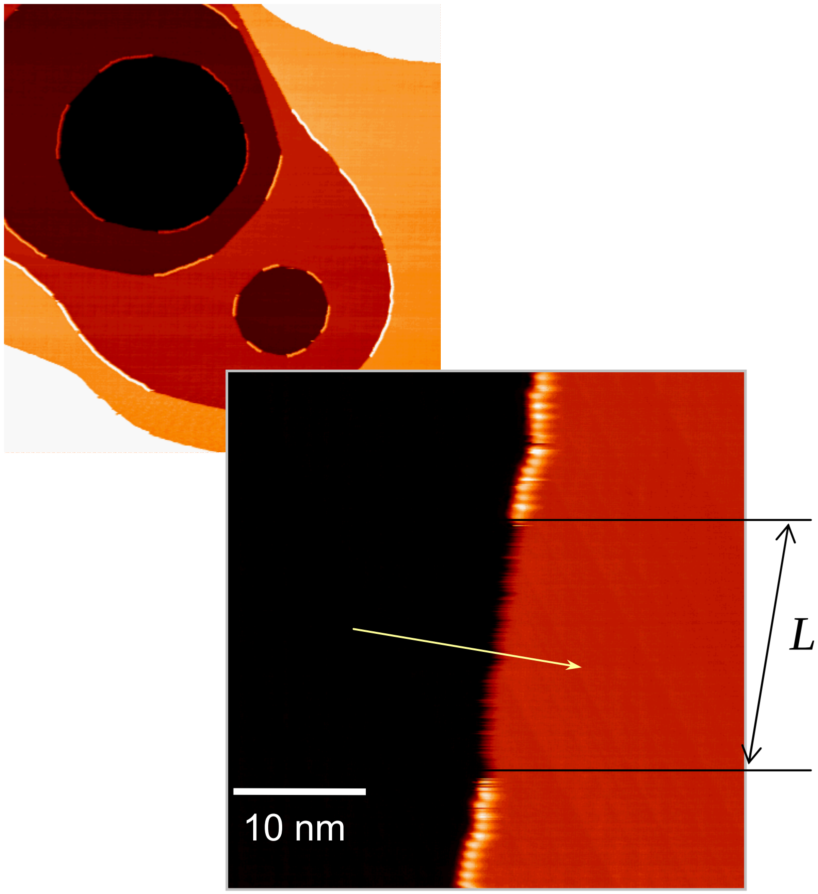
B. Blagojevic & P.M. Duxbury, PRE 60 ('99) 1279





So EC (AD) NOT DSS!

Step-edge Fluctuations: SED by Ag → AD by C_{60}



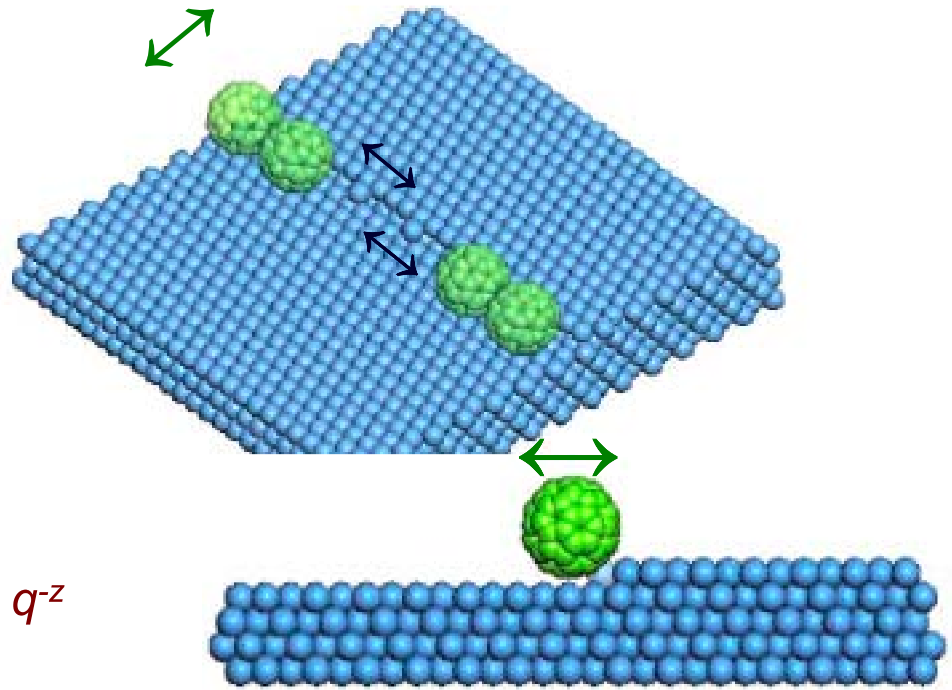
Ag step edges

$$G(t) = \left\langle [x(t+t_0) - x(t_0)]^2 \right\rangle_{t_0} \sim t^{1/4}$$

$z \approx 4$

Step-edge (periphery) diffusion

Conserved noise



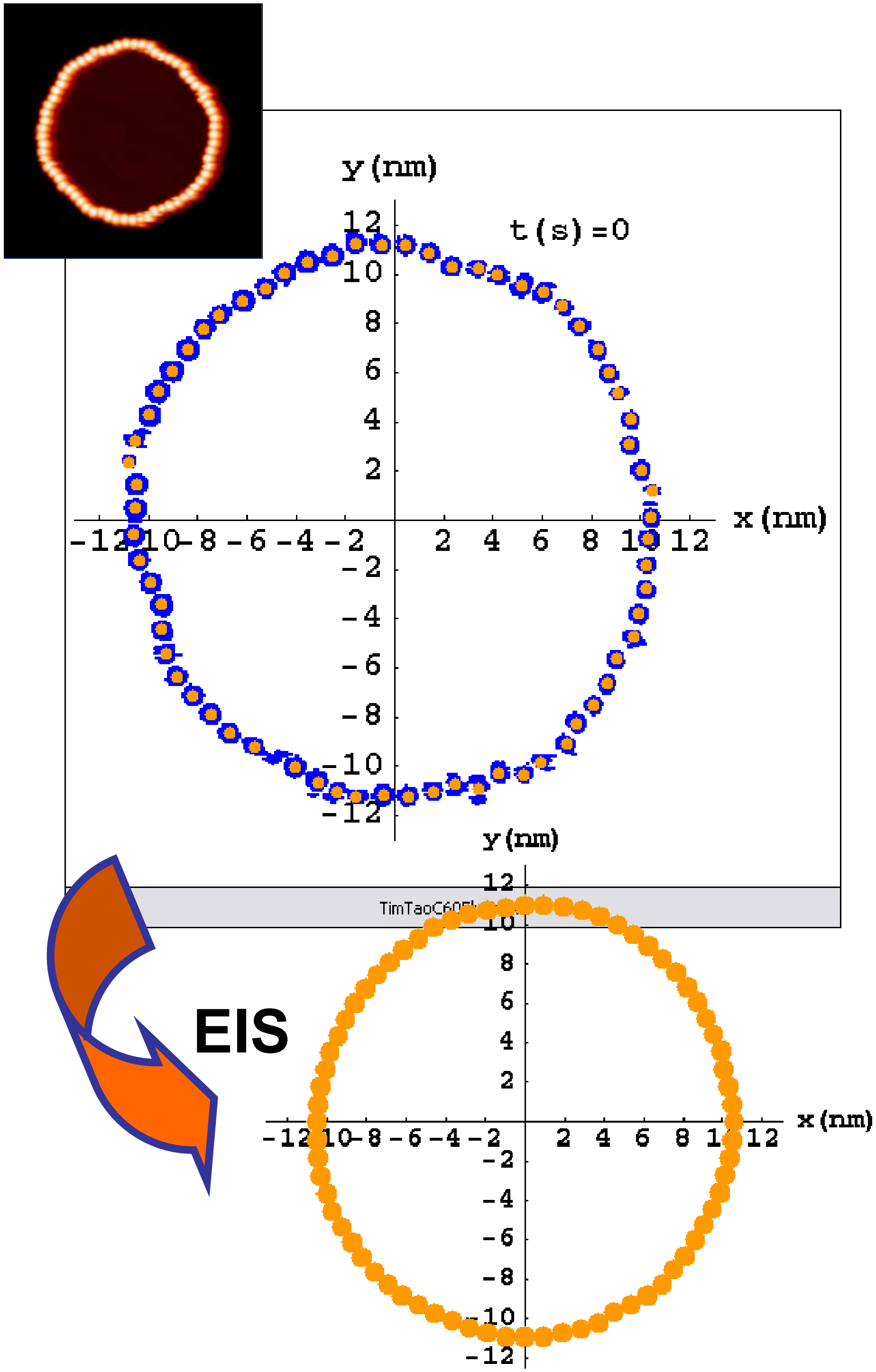
$\tau_q \sim q^{-z}$

$\sim t^{1/2}$ $z = 1.85 \approx 2$

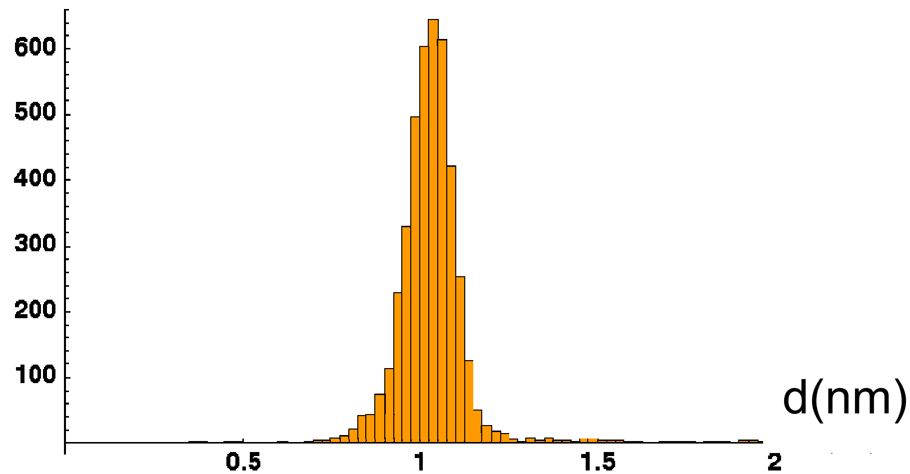
Attachment-detachment ltd., random
Non-conserved noise: Ag kicks C_{60}

C. G. Tao et al., PRB **73**, 125436 (2006)
Nano Lett **7**, 1495 (2007)

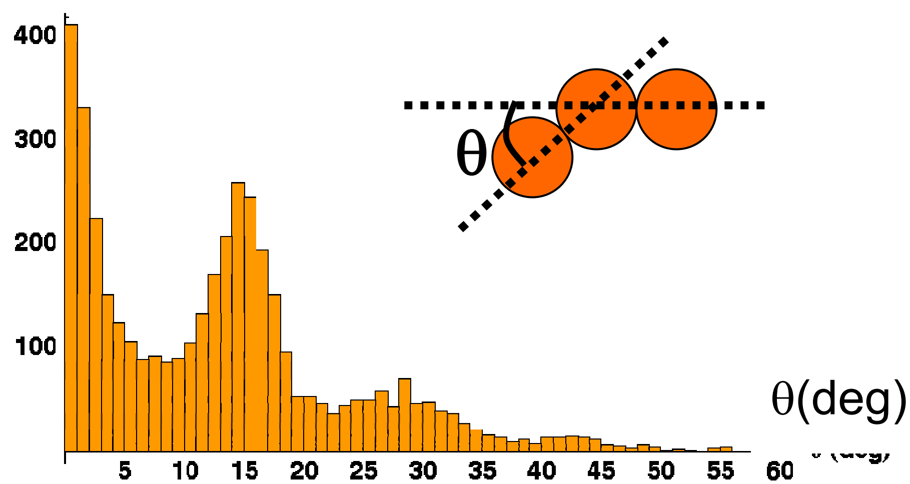
Island Fluctuations



Distribution of Distances between C_{60} NNs

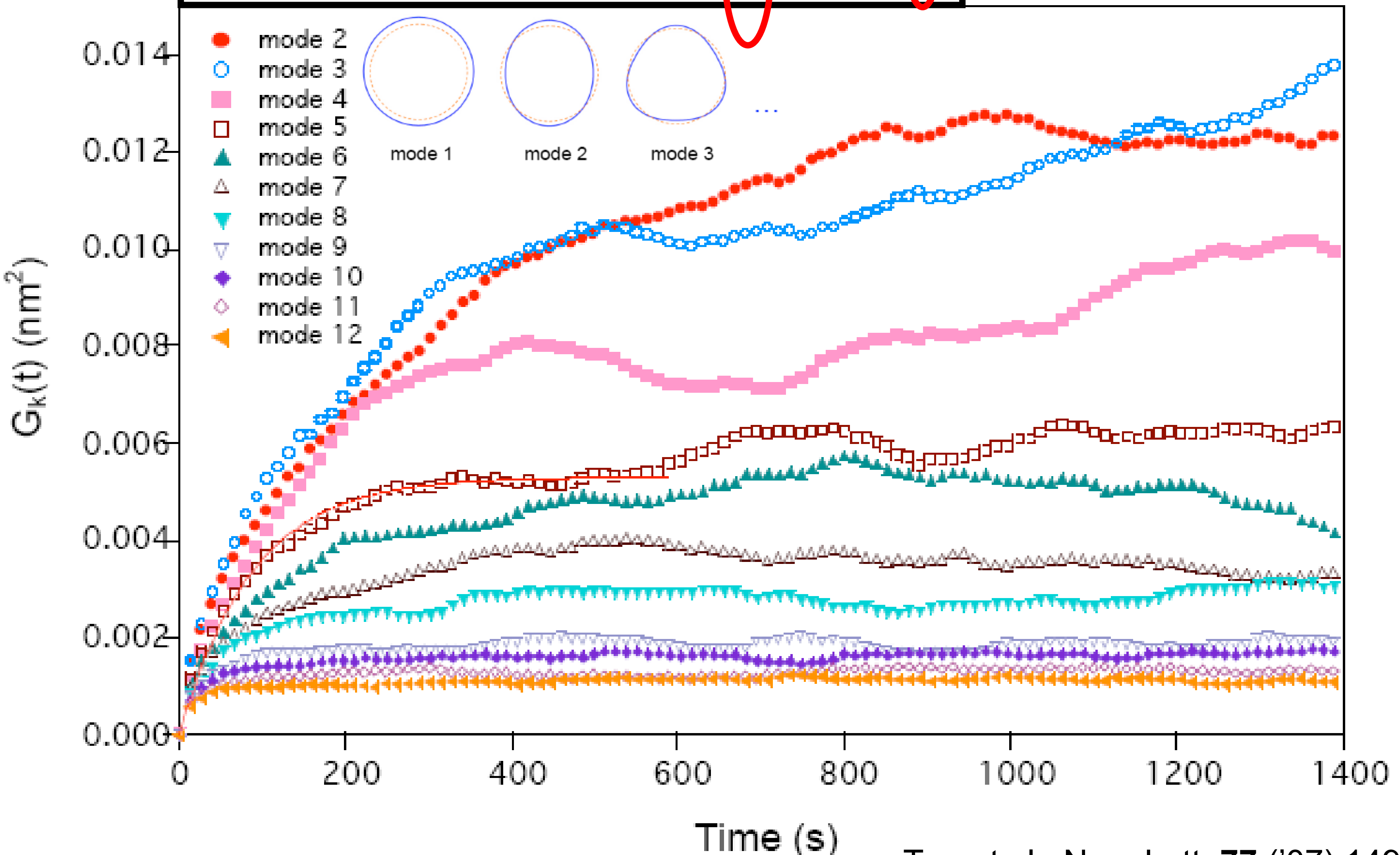


Distribution of Angle of C_{60} Triad



Normal Mode Analysis of Fluctuations of C_{60} Necklace

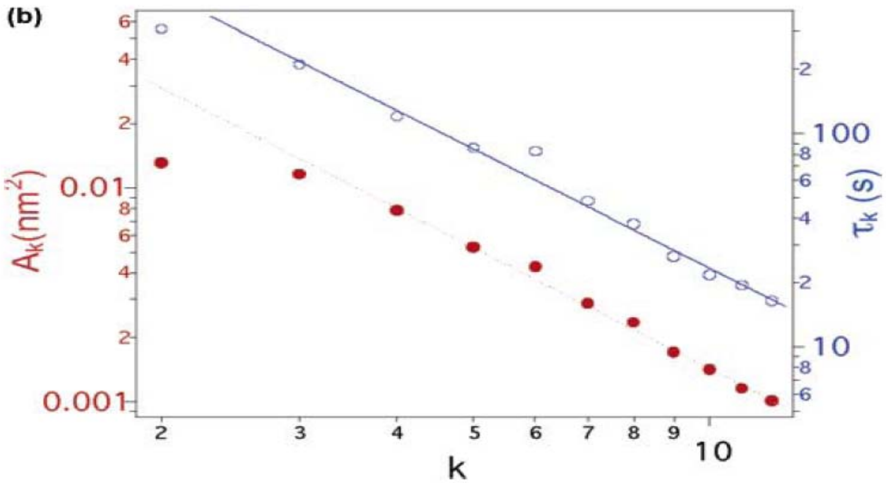
$$G_k(t) = \langle [r_k(t + t_0) - r_k(t_0)]^2 \rangle = A_k(1 - e^{-t/\tau_k})$$



Tao et al., NanoLett. **77** ('07) 1495

Analysis of Fluctuation Modes: Extract stiffness $\Rightarrow \beta \Rightarrow \varepsilon^{CC}$

Non-conserved dynamics [vs. conserved for bare Ag (111) islands]



$$A_k = \frac{k_B T \langle R \rangle}{\pi \tilde{\beta} k^2}$$

Find $A_k = 0.108(2) \times k^{-1.88(1)} \Rightarrow \tilde{\beta} = 65$ meV/Å

$\Rightarrow \varepsilon^{CC} \approx 37$ meV

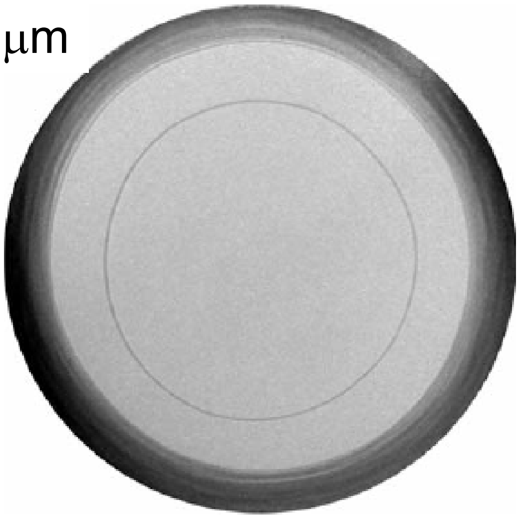
$\varepsilon^{AA} > \varepsilon^{AC} > \varepsilon^{CC}$

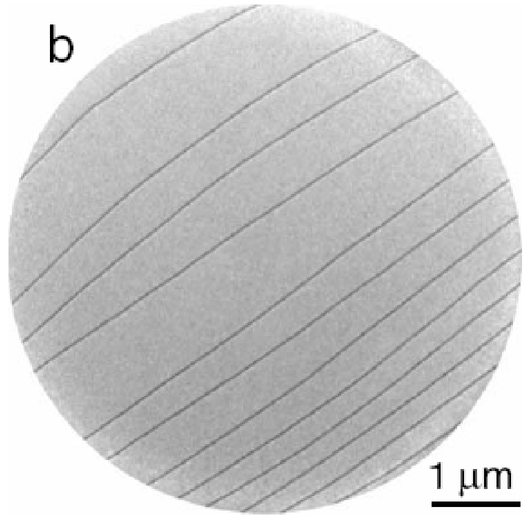
$\tau_k \propto k^{-1.85(5)}$

Si(111) 1x1 Revisited: β(T) & Morphological Evolution

A.B. Pang, K.L. Man, M.S. Altman, T. J. Stasevich, F. Szalma, & TLE, PRB 77 ('08) 115424

R ~ 1.7 μm





LEEM images

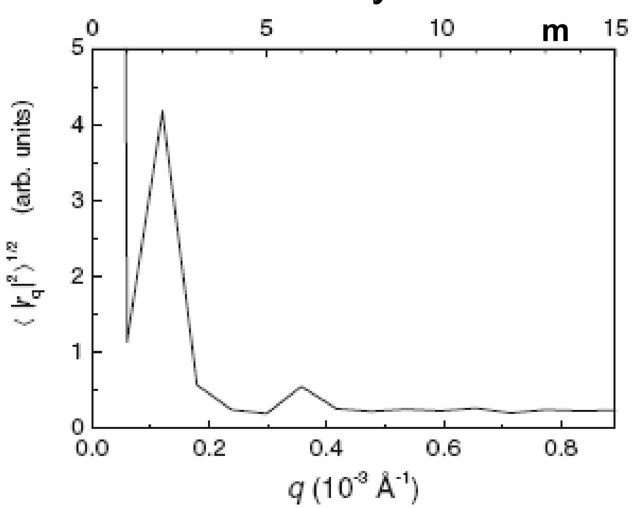
1163K

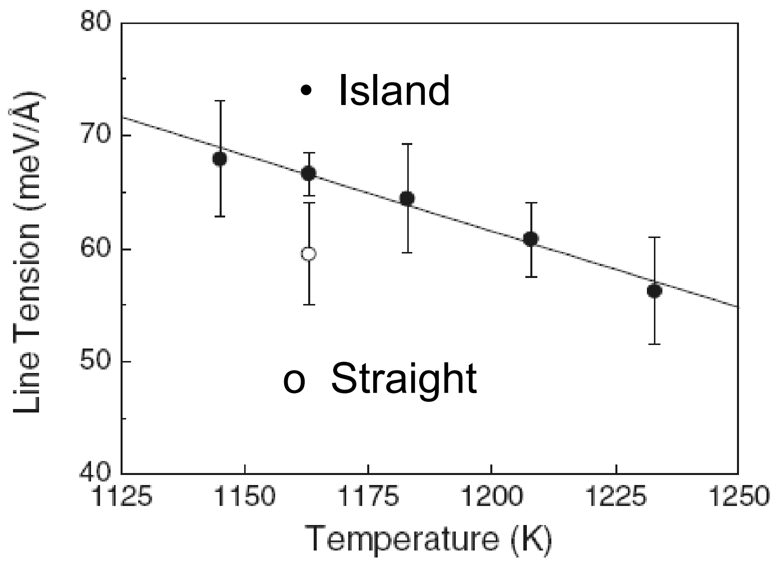
single-height steps

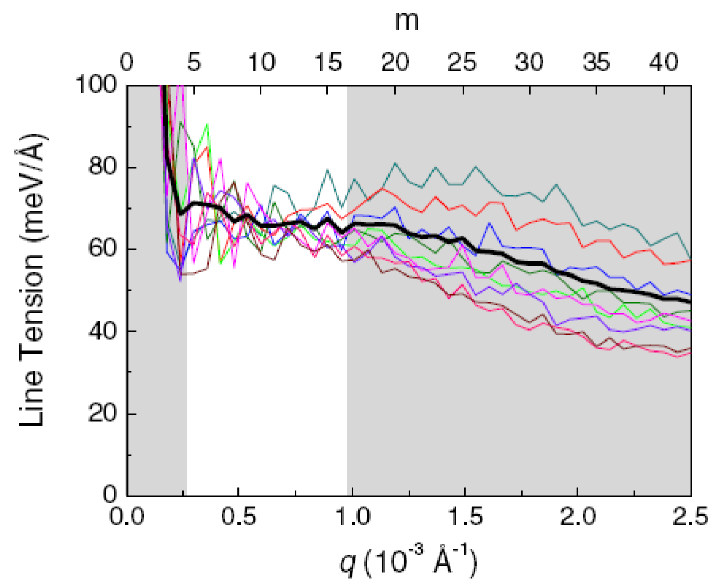
L_y ~ 3400 nm

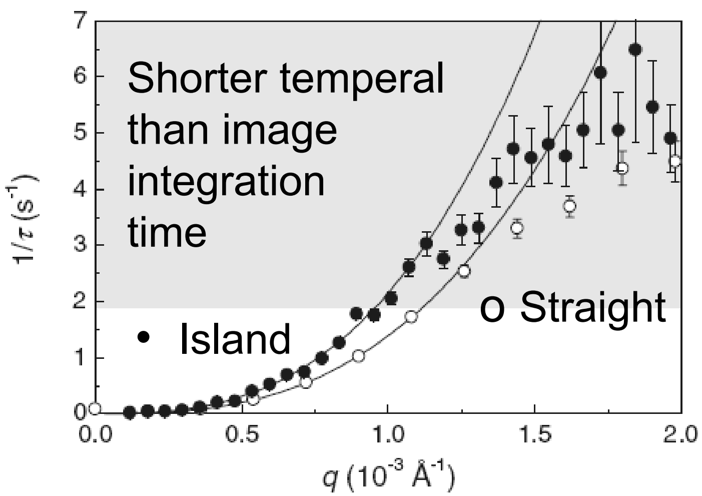
Shape anisotropy < 1% so $\widetilde{\beta}(\theta) \approx \beta(\theta) \approx \beta$

At most 10% decay of R





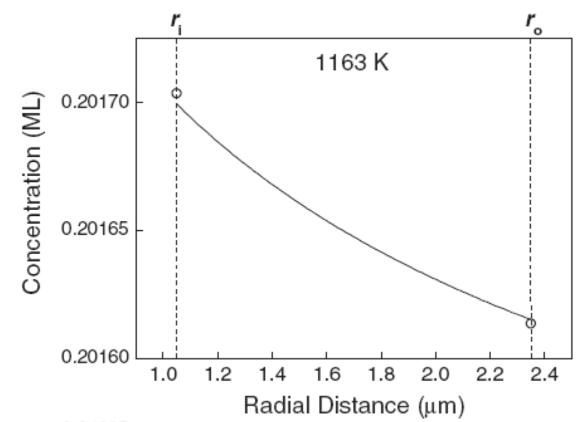


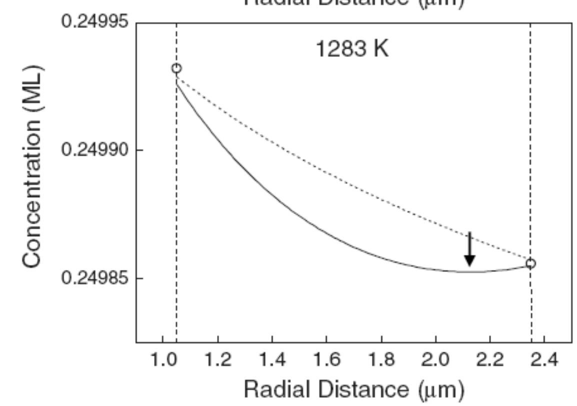


$\tau^{-1}(q) \propto q^z$

$z_{isl} = 2.83(10)$
$z_{str} = 2.74(12)$

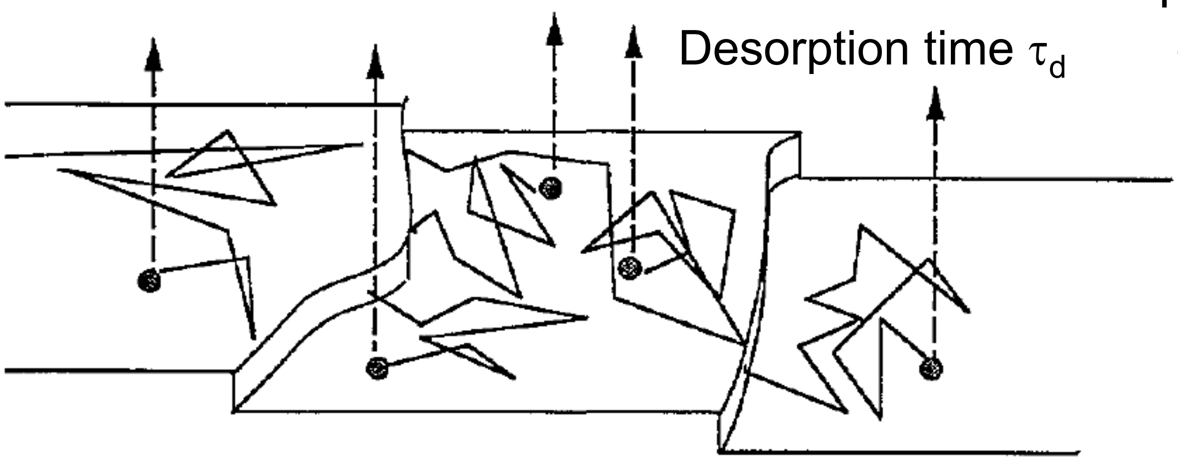
TD, not EC (AD)





Effect of Growth or Evaporation on Dispersion?

A. Pimpinelli, I. Elkinani, A. Karma, C. Misbah, & J. Villain, J. Phys. Cond. Matt. 6 ('94) 2661



Desorption time τ_d

Think of Métois's experiments on Si(111) at high T

BCF with weak and strong ES effect, e.g. limit of isolated step

$$\tau^{-1}(q) \approx D_s\,(c_{eq}{}^0\beta/k_BT)\;q^3$$

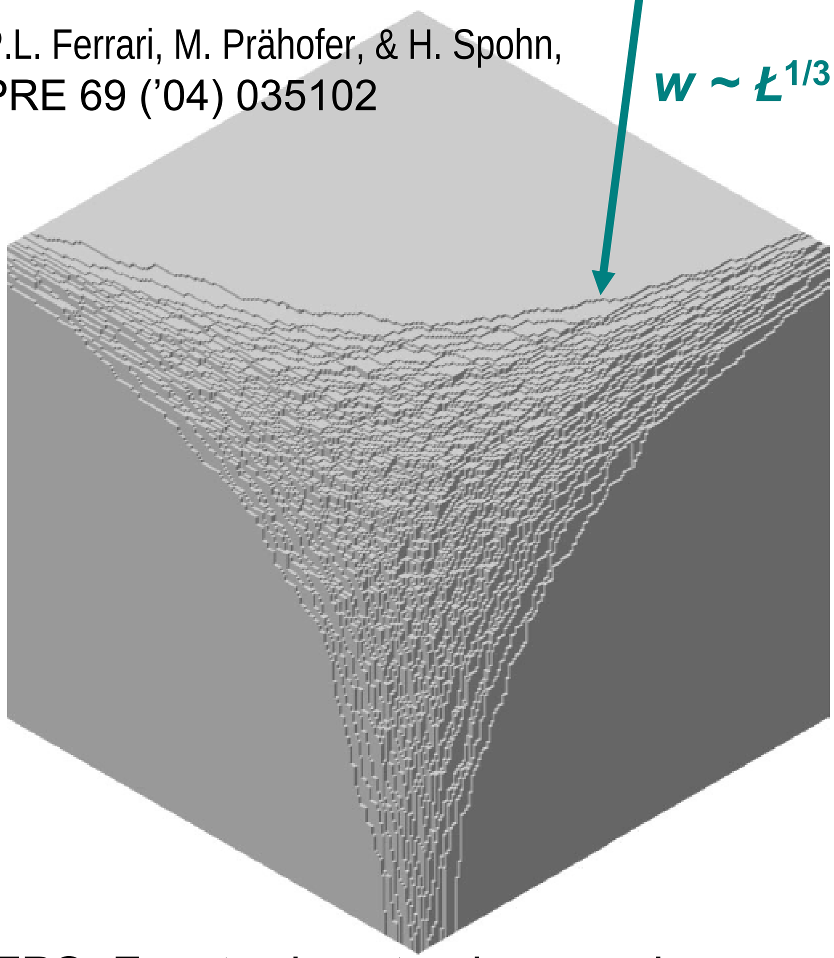
$$\tau^{-1}(q) \approx D_s\,c_{eq}{}^0\kappa\;[(\beta/k_BT)\{q^2+\kappa^2\}^{1/2} + d_S\kappa]\;\;q^2 \qquad\qquad \kappa^{-2} = D_s\tau_d$$

Facet edge vs. isolated step (or single-layer island) & vicinal surface

"On the Beach": facet *"shoreline"*
…by a rough sea!

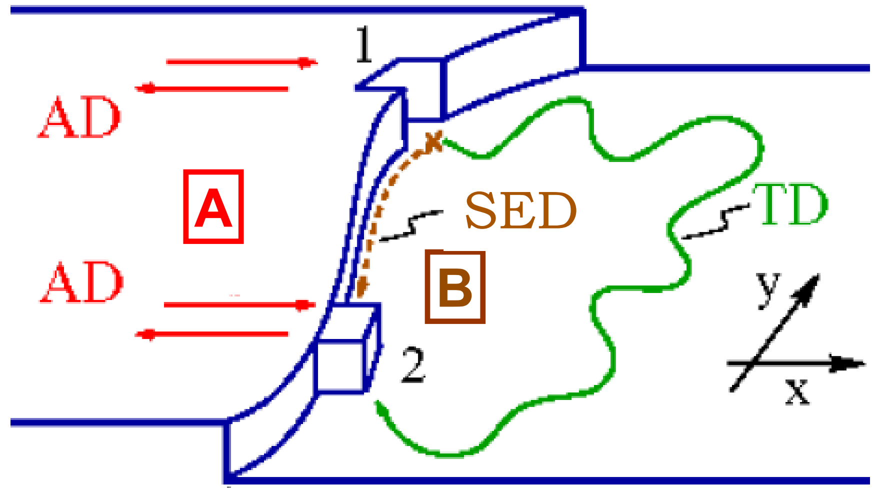
P.L. Ferrari, M. Prähofer, & H. Spohn,
PRE 69 ('04) 035102

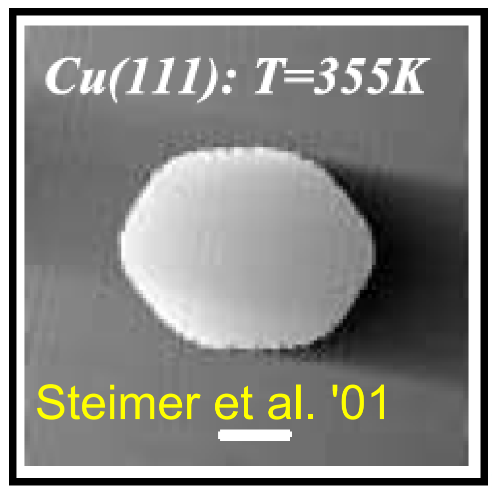
***w* ~ Ł**$^{1/3}$



FPS: Facet-edge step has much more space in which to meander than steps in rounded [rough] region.

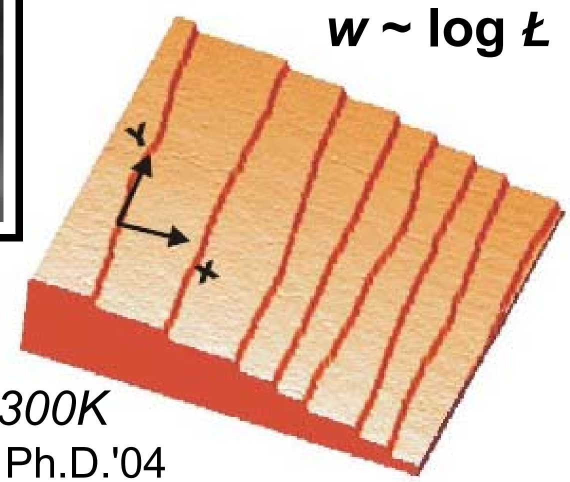
Dynamic mechanisms





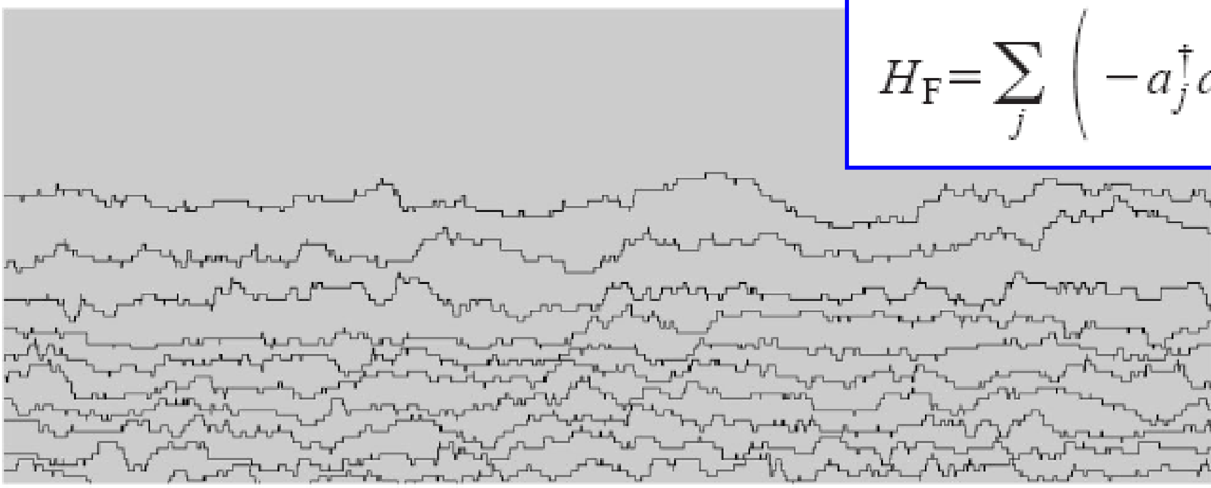
***w* ~ Ł**$^{1/2}$

***w* ~ log Ł**



Al/Si(111): T=300K
D.B. Dougherty Ph.D.'04

FPS Analysis: steps as [free] fermion world lines



$$H_F = \sum_j \left(-a_j^\dagger a_{j+1} - a_{j+1}^\dagger a_j + 2 a_j^\dagger a_j + \frac{j}{\lambda} a_j^\dagger a_j \right)$$

λ^{-1} is Lagrange multiplier
re ***conserved volume,***
→ 0 in macro limit

Exact result for step density $\bar{\rho}_\lambda(j) = \langle \bar{a}_j^\dagger a_j \rangle_\lambda$ in terms of Bessel function J_j & deriv's

Near shoreline, $\lim_{\lambda\to\infty} \lambda^{1/3} \rho_\lambda(\lambda^{1/3} x) = -x \mathrm{Ai}(x)^2 + \mathrm{Ai}'(x)^2$

Shoreline wandering: $\mathrm{Var}[b_\lambda(t) - b_\lambda(0)] \cong \lambda^{2/3} g(\lambda^{-2/3} t)$ *g(s)*: $2|s| \to 1.6264 - 2/s^2$

$$\mathrm{Var}[b_\ell(\ell\tau + x) - b_\ell(\ell\tau)] \cong (\tfrac{1}{2} A \ell)^{2/3} g\left(\frac{A^{1/3}}{2^{1/3} \ell^{2/3}} x \right)$$

$\ell \sim N^{1/3}$ cf. 3-d Ising corner

In scaling regime shoreline fluctuations are *non-Gaussian* & related to GUE multimatrix models.

$\kappa = \frac{1}{2}(\pi \gamma_{PT} k_B T / \tilde{\beta})^2$ where $h = -\frac{2}{3} \gamma_{PT} (r - \rho_0)^{3/2}$ (up to lattice consts)

Heuristic extraction of dynamic/growth exponent β

Isolated steps: $G(t) \equiv \langle [x(t_0+t) - x(t_0)]^2 \rangle_{t_0[,y_0]} \propto t^{2\beta} = \begin{cases} t^{1/2} & \text{A} \\ t^{1/4} & \text{B} \end{cases}$

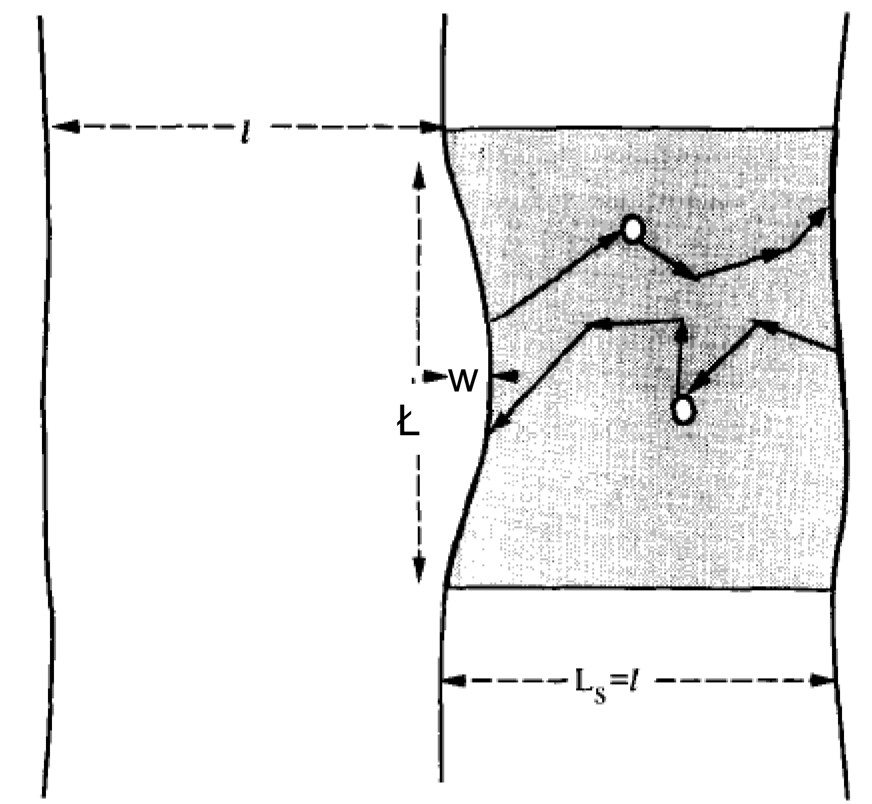


Fig. 1. A stepped surface seen from above. A typical configu-

A. Pimpinelli, J. Villain, et al., Surf. Sci. **295** ('93) 143

- # atoms entering/leaving in t: $N(t) \approx c_{eq} Ł L_s t/\tau^*$
- fluctuating area²: $W^2 Ł^2 \approx (\delta N)^2 \approx N(t)$
- Ferrari *et al.* scaling: $W \sim Ł^{\alpha} \rightarrow Ł^{1/3}$
- $L_s \approx a$

A) Attachment-detachment limited

$1/\tau^* \approx$ kinetic coef.

$w \approx t^{1/5}$ or $G(t) \approx t^{2/5}$

B) Step-edge diffusion limited

$1/\tau^* \approx D_{se}/Ł^2$

$w \approx t^{1/11}$ or $G(t) \approx t^{2/11}$

A. Pimpinelli, M. Degawa, TLE, EDW, Surface Sci. **598**, L355 (2005).

Scaling approach

$$x(y,t) \rightarrow \tilde{r}(\theta,t) = [r(\theta,t) - \rho_0]/\rho_0$$

$$\delta\mu = a^2\tilde{\beta}\left(\kappa - \frac{1}{\rho_0}\right) \approx \frac{a^2\tilde{\beta}}{\rho_0}\left(-\tilde{r}_{\theta\theta} + \frac{1}{2}\tilde{r}_\theta^2\right)$$

Nonlinear KPZ term in Langevin eqns due to curvature

(or from asymmetric potential due to step neighbor on just 1 side)

$$\frac{\partial \tilde{r}(\theta,t)}{\partial t} = \left(\Gamma_{\mathrm{AD}} \ldots\right)\left[\frac{\partial^2 \tilde{r}}{\partial \theta^2} - \frac{1}{2}\left(\frac{\partial \tilde{r}}{\partial \theta}\right)^2\right] + \eta(\theta,t)$$

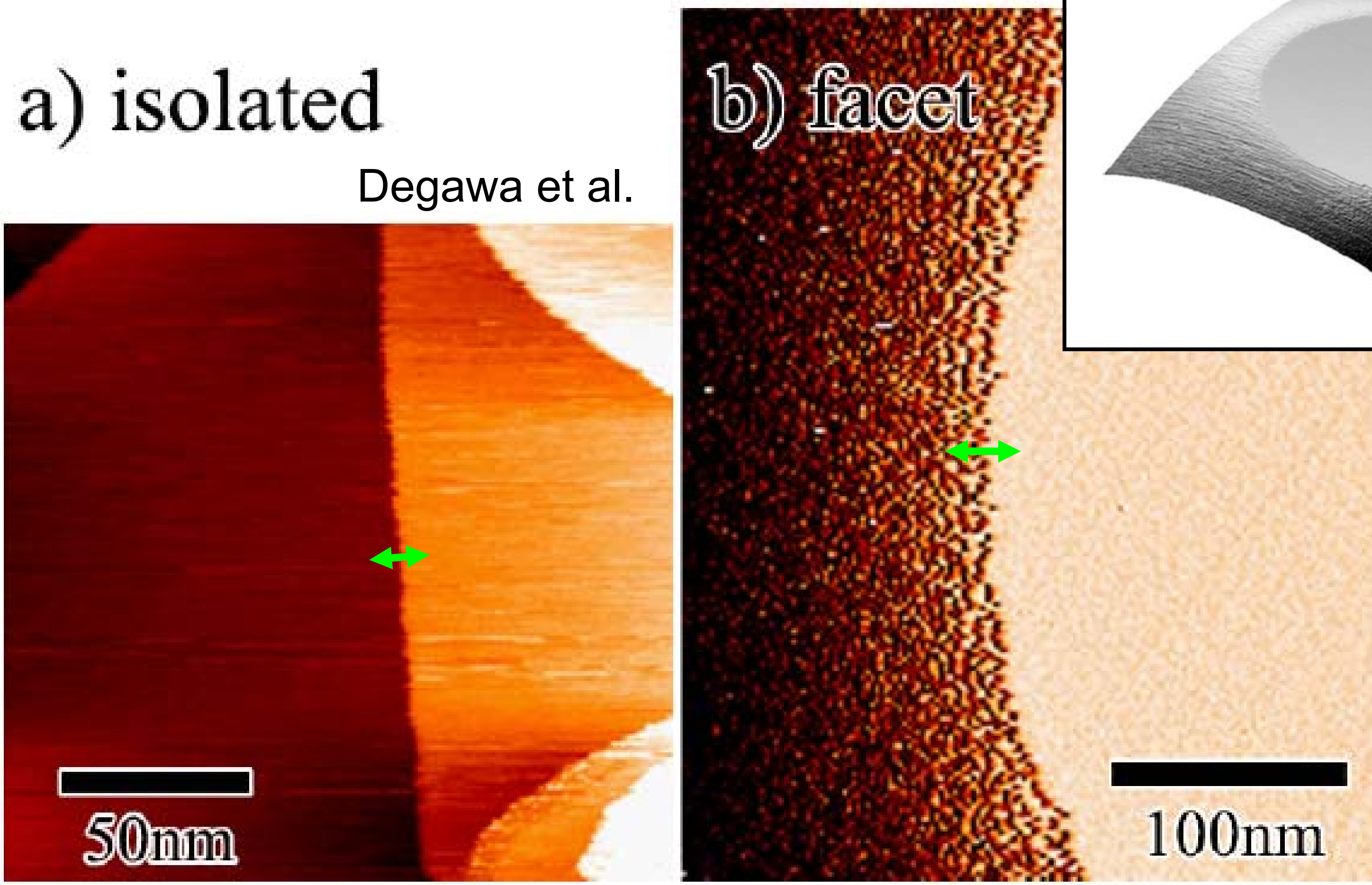
$$\frac{\partial \tilde{r}(\theta,t)}{\partial t} = \left(\Gamma_{\mathrm{SED}} \ldots\right)\left[-\frac{\partial^4 \tilde{r}}{\partial \theta^4} + \frac{1}{2}\frac{\partial^2}{\partial \theta^2}\left(\frac{\partial \tilde{r}}{\partial \theta}\right)^2\right] + \eta_C(\theta,t)$$

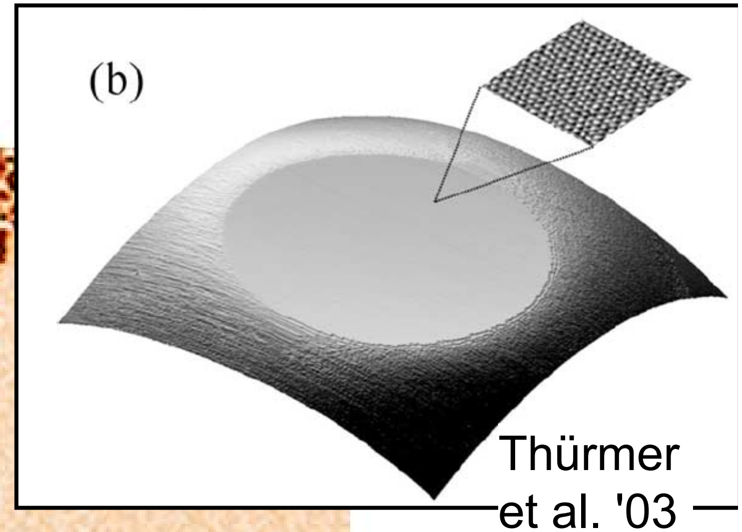
Dilate by *b*, so *Ł' = b Ł*, *w' = b*$^\alpha$ *w*, *t' = b*^{z} *t*; *equate exponents of b*

Class	$\partial/\partial t$	Lin. $\nabla^{2,4}$	NL KPZ	Noise	α	z	$\beta = \alpha/z$
Isolated AD	$\alpha - z$	$\alpha - 2$	-	$-(1+z)/2$	$1/2$	2	$1/4$
Isolated SED	$\alpha - z$	$\alpha - 4$	-	$-(3+z)/2$	$1/2$	4	$1/8$
Train AD	$\alpha - z$	$\alpha - 2$	-	$-(2+z)/2$	0 (ln)	2	0
Asymmtr. AD	$\alpha - z$	$\alpha - 2$	$2\alpha - 2$	$-(1+z)/2$	$1/3$	$5/3$	$1/5$
Asymmtr. SED	$\alpha - z$	$\alpha - 4$	$2\alpha - 4$	$-(3+z)/2$	$1/3$	$11/3$	$1/11$

STM images (scanned, not snapshot): step & facet edge

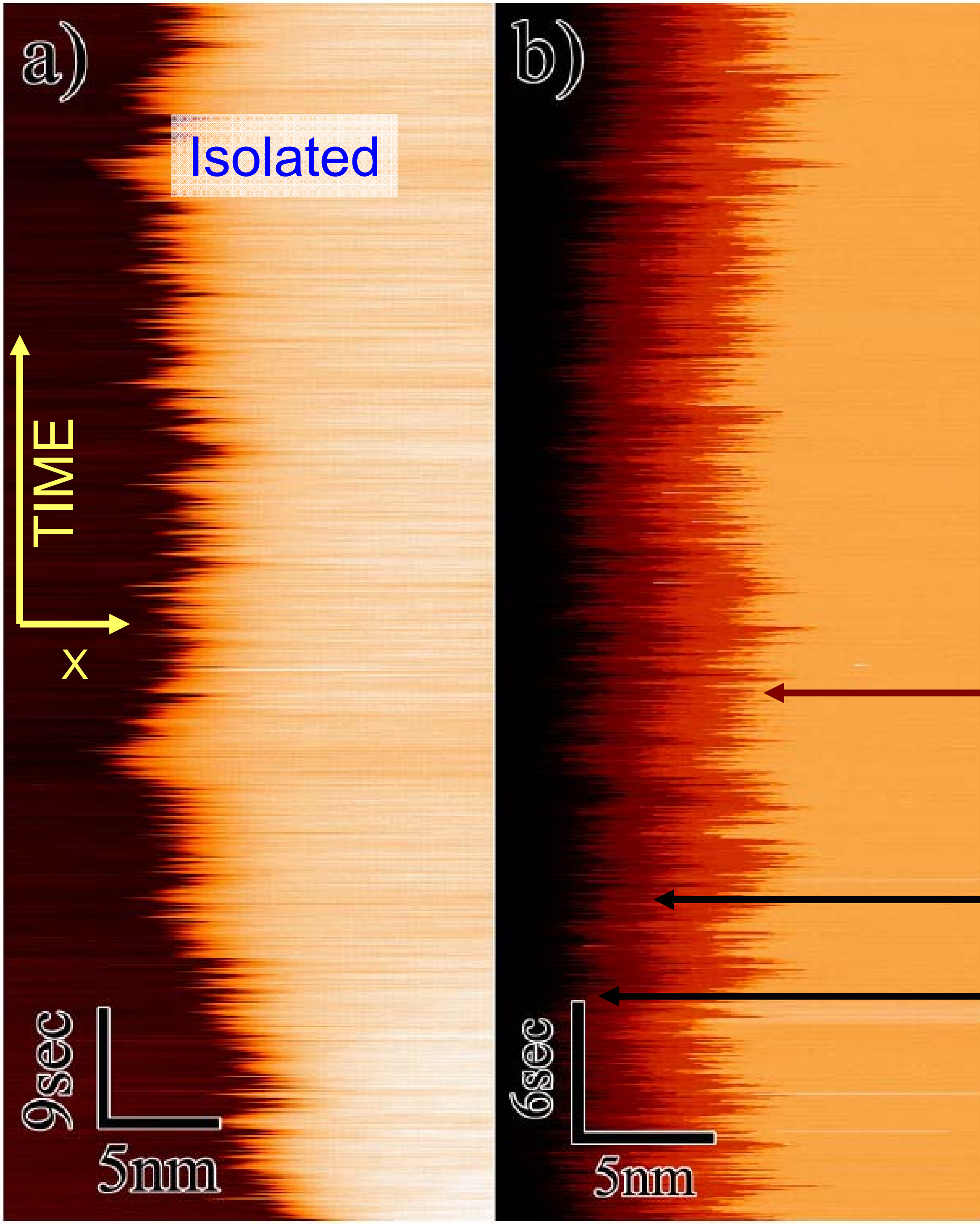
(111) facet [close-packed] on supported Pb crystallite





from screw dislocation

Equilibrium fluctuations studied by F. Szalma et al. '06



STM line-scans (pseudoimages)

$$\langle [x(t_0+t)-x(t_0)]^2 \rangle_{t_0}$$

$$\equiv G(t) \propto t^{2\beta}$$

$w^2 = ½\ G(t\to\infty)$

Facet edge (shoreline)

Analyzed on next slide

Next step edge

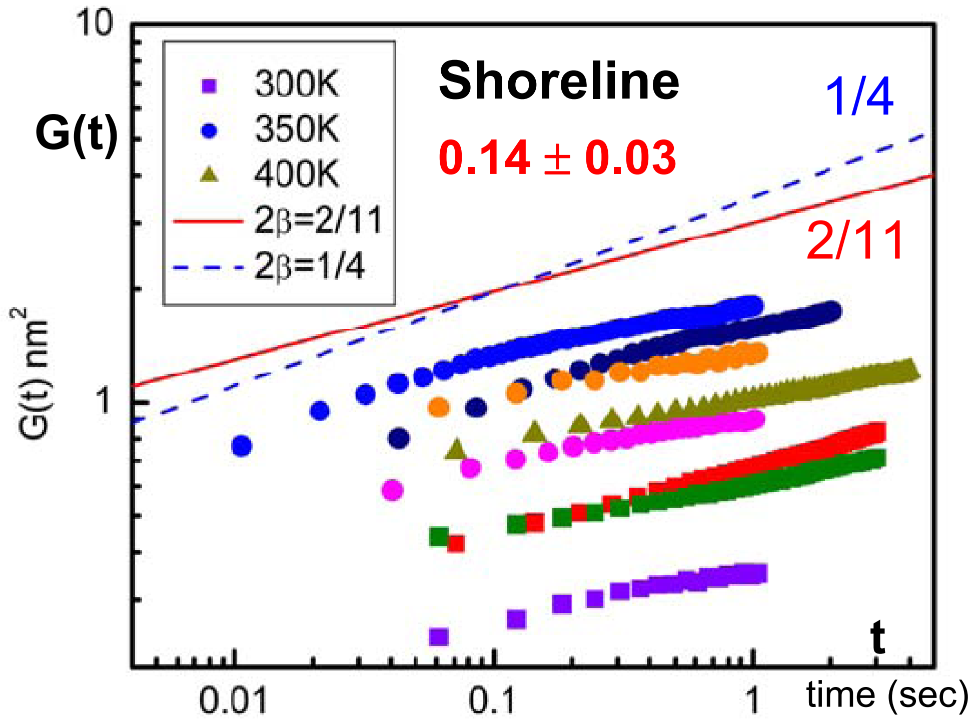
3rd step edge

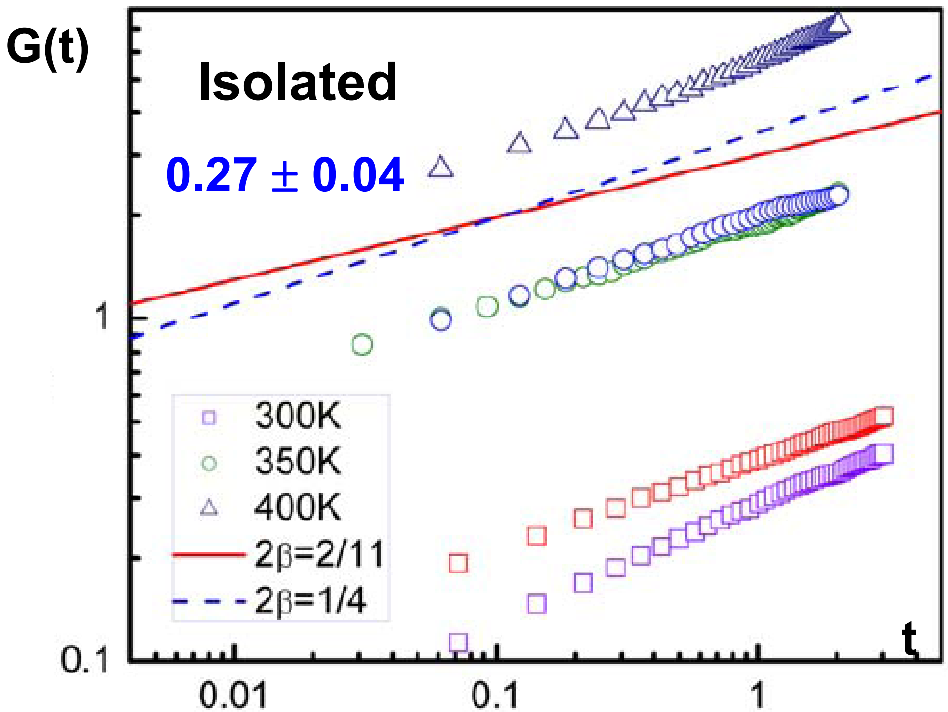
fcc metals (late trans., noble,…):

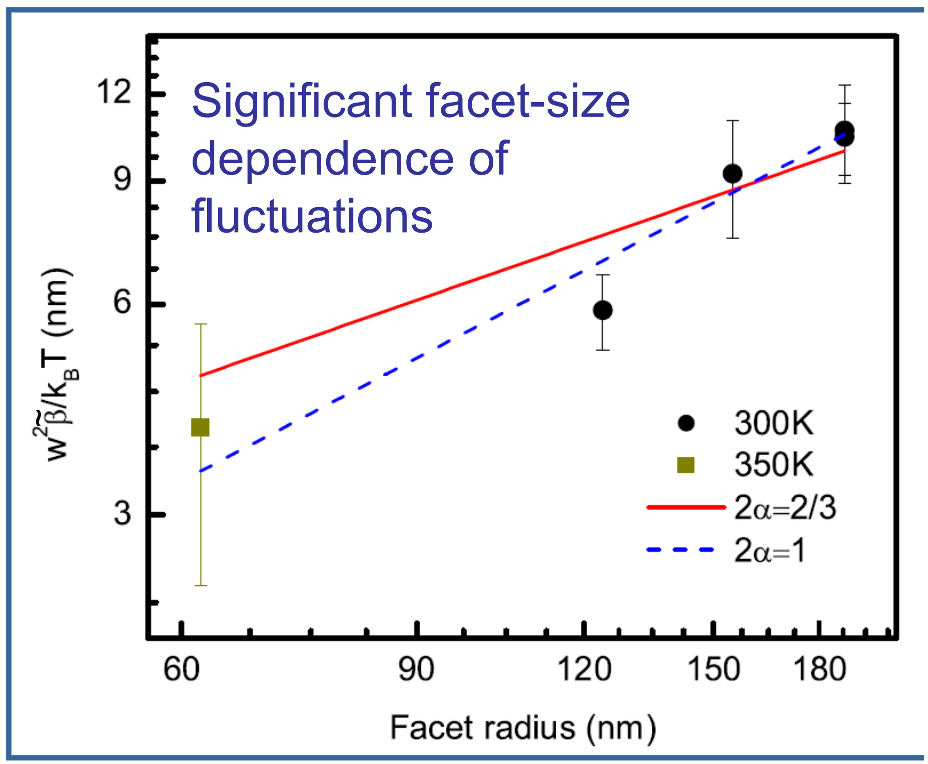
mass transport by SED (B)

Extract 2β from log-log plot of experimental *G(t)*

Exponent for facet edge is significantly smaller than for isolated step, with value consistent with expectation for asymmetric SED







Summary (see http://www2.physics.umd.edu/~einstein)

- Steps are useful for many applications, bear on many problems of current interest, and embody fascinating physics
- Sophisticated experiments, with powerful theoretical and computational calculations, allow for quantitative measurements that yield numerical assessment of key parameters and allow prediction of associated phenomena
- 3 special cases for isolated steps: EC (AD), TD, PD (SED)
- Capillary wave approach and time-dependence of pseudoscans both useful
- Can be hard to distinguish EC and DSS, both have $\tau^{-1} \propto q^2$
- Including anisotropy can be necessary, but not always
- How does growth or evaporation affect equilibrium analysis?
- Shorelines have remarkable physics