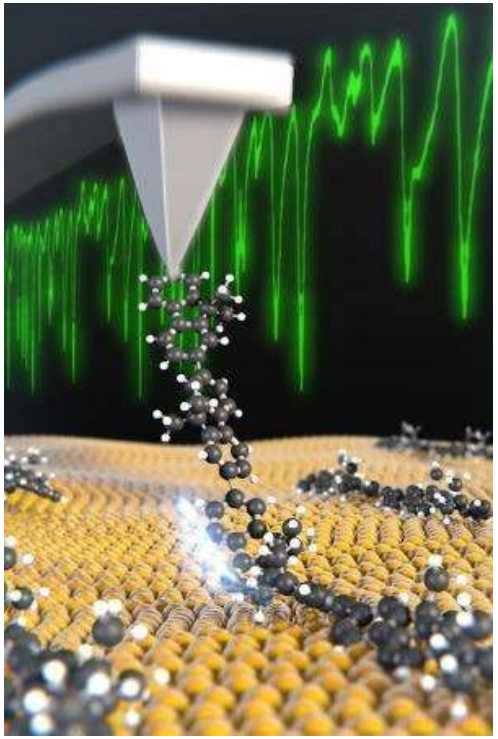
Ideal (and other) Polymers near Attractive and Repulsive Surfaces

Yacov Kantor (TAU) and Mehran Kardar (MIT)



with:

Yosi Hammer (TAU)

Mohammad F. Maghrebi, NIST

Nir Alfasi, Technion

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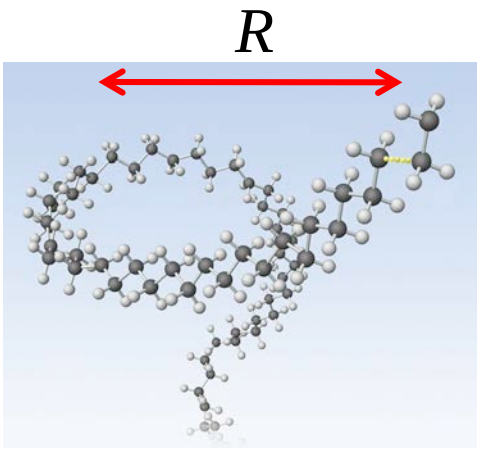
Tel Aviv University, December 25, 2016

Universal properties of a single polymer in "free space"

$$R = aN^{\nu}$$
$$\mathcal{N},\ \mathcal{Z} = bz^{N}N^{\gamma-1}$$

ν	γ	
$\frac{3}{4}$	$\frac{43}{32}$	self - avoiding polymer in $d=2$
0.59	1.16	self - avoiding polymer in $d=3$
$\frac{1}{2}$	1	ideal polymer in any d
$\frac{4}{7}$	$\frac{8}{7}$	θ - polymer in $d=2$

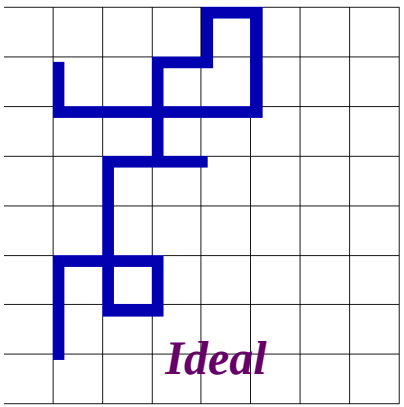


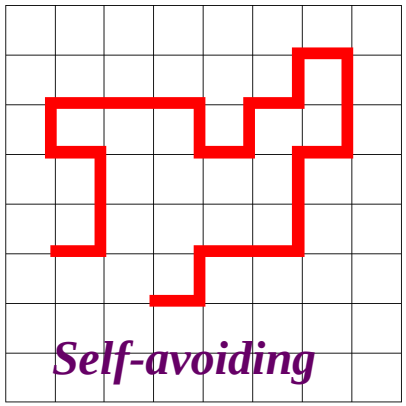
Ideal polymer ***↔ Random walk (RW)***

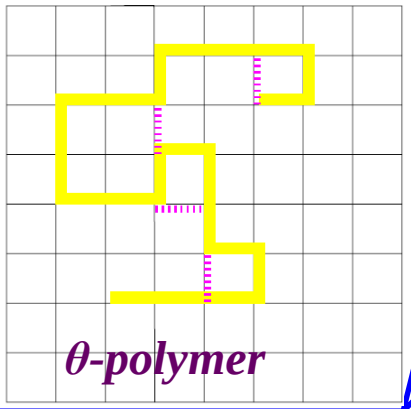
Polymer in good solvent ***↔ Self-avoiding walk (SAW)***

θ-polymer ***↔ Self-avoiding walk with a tuned nearest neighbor attraction***

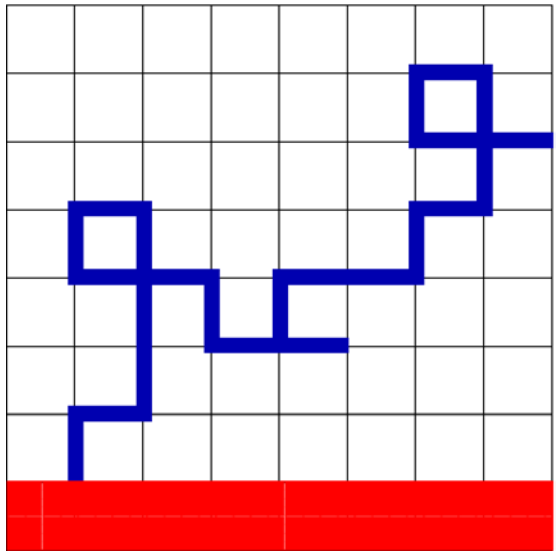
$$F = -k_BT\ln\mathcal{Z} = -k_BTN\ln z - (\gamma-1)k_BT\ln N + \ldots$$







Universal properties of a single polymer near a repulsive plane



$$\mathcal{N}_1,\ \mathcal{Z}_1 = bz^N N^{\gamma_1 - 1}$$

$$F_1 = -k_B T \ln \mathcal{Z}_1 = -k_B T N \ln z - (\gamma_1 - 1) k_B T \ln N + \ldots$$

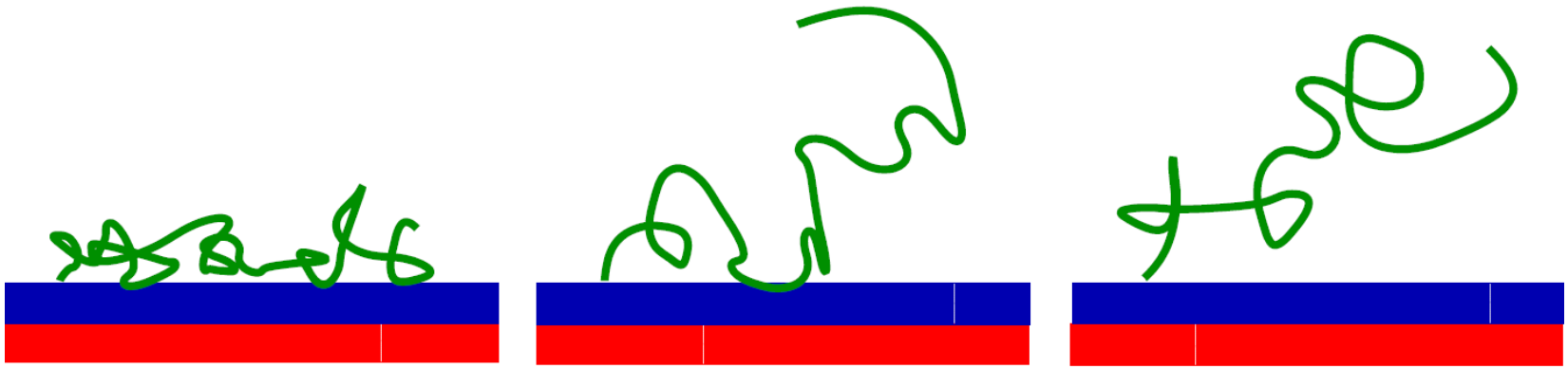
$$F_1 - F = (\gamma - \gamma_1) k_B T \ln N$$

$\gamma_1 < \gamma$, i.e. the wall repels

γ_1	γ	
$\frac{61}{64}$	$\frac{43}{32}$	self - avoiding polymer in $d = 2$
0.70	1.16	self - avoiding polymer in $d = 3$
$\frac{1}{2}$	1	ideal polymer in any d
0.53	$\frac{8}{7}$	θ - polymer in $d = 2$

E.Eisenriegler, K.Kremer, K.Binder,
J.Chem.Phys. 77,6296 (82)
Also see, K. Binder *in Phase Transitions and Critical Phenomena* (83)
K. De'Bell and T. Lookman, RPM 65, 87 (93)
E.Eisenriegler, Polymers near Surfaces (93)

Polymer near an attractive surface. Adsorption transition.



$T<T_c$ adsorbed ***$T=T_c$ transition*** ***$T>T_c$ repulsive regime***

P.G. de Gennes, Rep.Prog.Phys., **32**, 187 (69)

$$\begin{aligned} \mathcal{Z}_a &= b z^N N^{\gamma_a - 1} \\ F_a &= -k_B T \ln \mathcal{Z}_a = -k_B T N \ln z - (\gamma_a - 1) k_B T \ln N + \dots \\ F_a - F &= (\gamma - \gamma_a) k_B T \ln N \end{aligned}$$

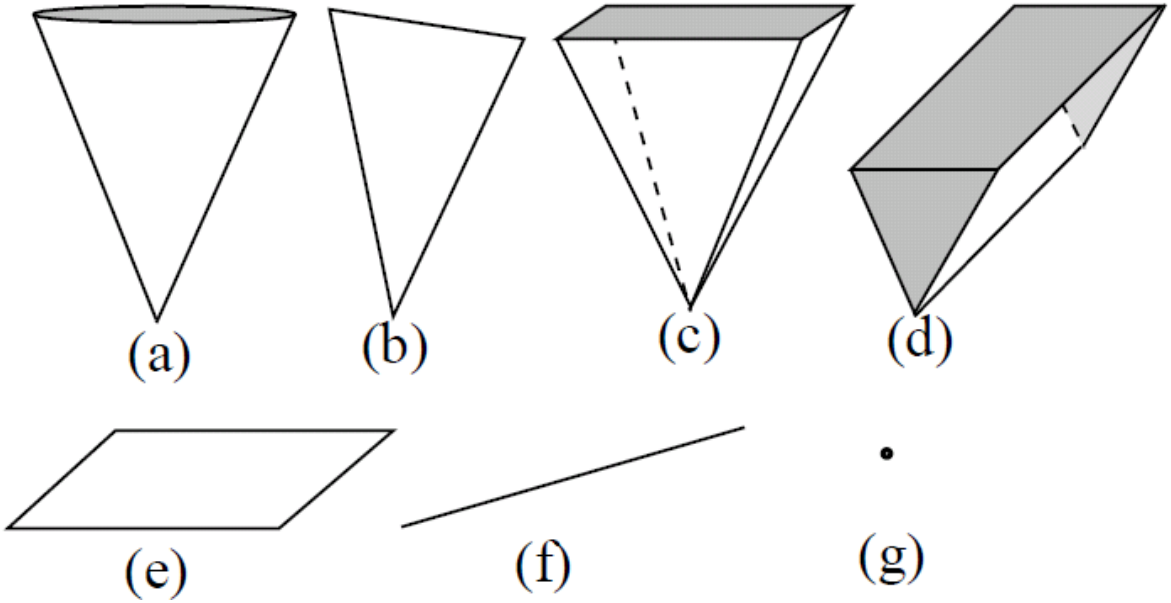
$\gamma_a \geq \gamma$, i.e. the wall attracts

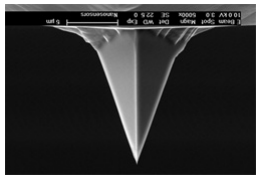
See, E.J. Jense van Rensburg, *The Stat.Mech. of Interacting Walks…*

Polymer near scale free surfaces

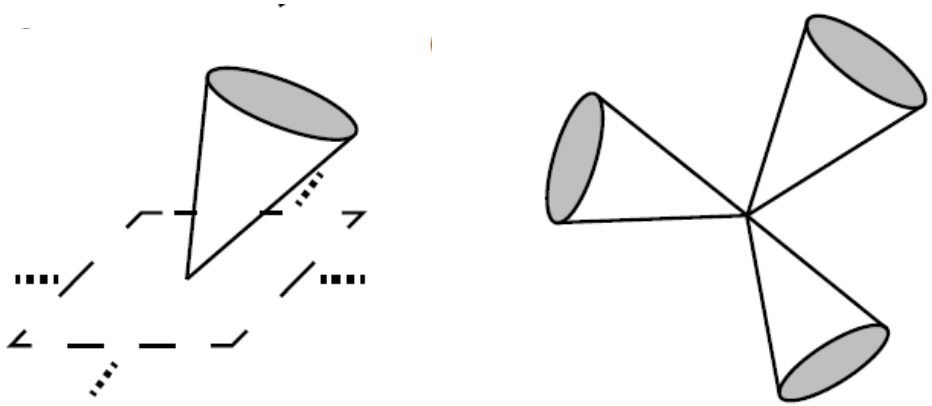
$\mathbf{r} \to \lambda \mathbf{r}$ does not change the geometry

$$\mathcal{Z}_s = bz^N N^{\gamma_s - 1}, \qquad \gamma_s = (2 - \eta_s)\nu$$

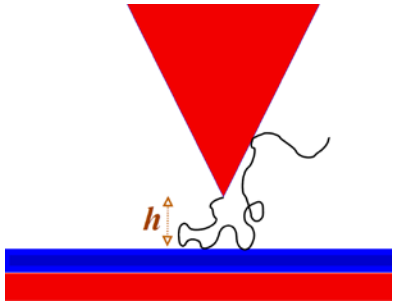




Nano&More AFM tip



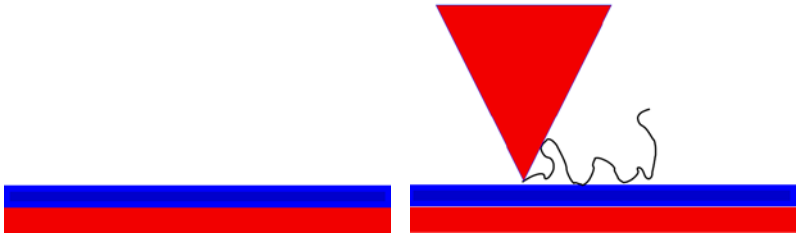
Constant in a polymer mediated force



$$f = \mathcal{A}\frac{k_B T}{h}, \qquad \text{for} \qquad a \ll h \ll R$$

$$\mathcal{Z}_s = b z^N N^{\gamma_s - 1}, \qquad \gamma_s = (2 - \eta_s)\nu$$

$$\begin{aligned} F_{\text{close}} - F_{\text{far away}} &= -k_B T(\ln \mathcal{Z}_{\text{close}} - \ln \mathcal{Z}_{\text{far away}}) \\ &= (\gamma_{\text{far away}} - \gamma_{\text{close}}) k_B T \ln N \\ &= \int_a^R f(h)dh = \mathcal{A} k_B T \ln \frac{R}{a} \end{aligned}$$



$$R = a N^{\nu}$$

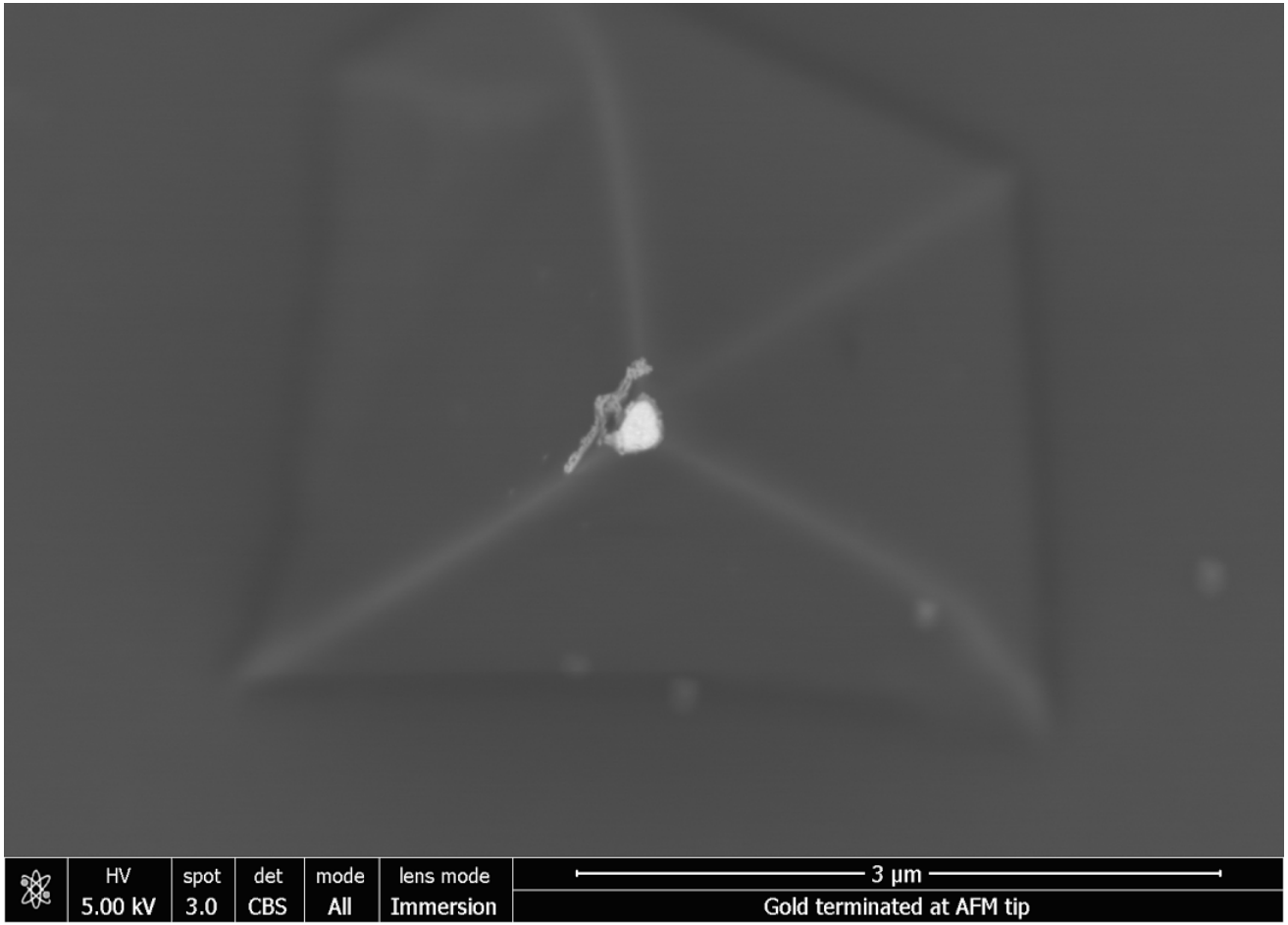
$$\mathcal{A} = \frac{\gamma_{\text{far away}} - \gamma_{\text{close}}}{\nu} = \eta_{\text{close}} - \eta_{\text{far away}}$$

Y. Kantor, M. Kardar (16)

$\mathcal{A} > 0$ repulsion; $\mathcal{A} < 0$ attraction

For repulsive surfaces see,
M. F. Maghrebi, Y. Kantor, M. Kardar,
EPL**96**,66002 (11)

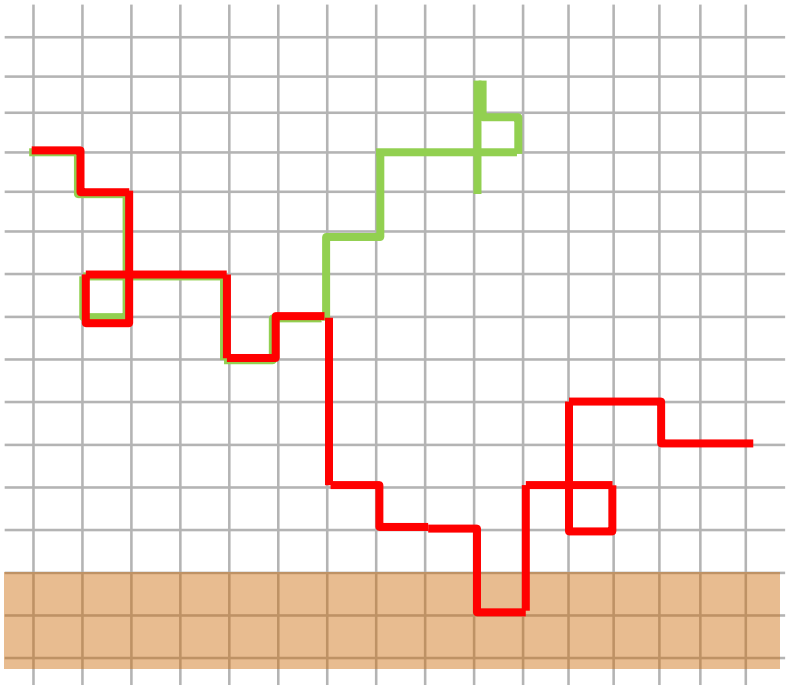
Experiment: polymers in good solvent attached to pyramidal tip



U. Mohideen,
UCR (2015-16)

Parameters:
AFM tip with polymers
Silicon pyramid, gold patch
R_g=1-7nm
MW=350-40,000
(N=8-900)
Surface roughness 2-6nm
polymers=4000-5000

Ideal polymers near repulsive surface as a diffusion problem

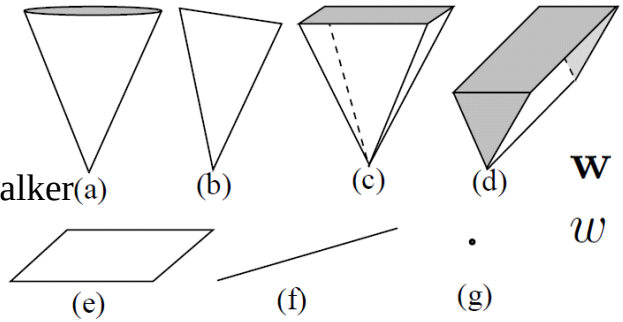


Stat.Mech.	$\Leftrightarrow$	Diffusion
N	$\Leftrightarrow$	t
Repulsive boundary	$\Leftrightarrow$	Absorbing boundary

$$\frac{\partial S(\mathbf{r},t)}{\partial t} = D\nabla^2 S(\mathbf{r},t)$$

$$\mathcal{N}(\mathbf{r},N) = z^N S(\mathbf{r},kN)$$

$$k = a^2/2dD$$



S - survival probability of a random walker that at time $t=0$ was at position $\vec{r}$,

$\mathcal{N}$ - number of configurations,

D - diffusion constant, t - time,

N - number of steps, a - step size,

z - coordination number.

$$\mathbf{w} = \mathbf{r}/\sqrt{Dt}, \quad S(\mathbf{r},t) = H(\mathbf{w})$$

$$w \ll 1 \quad \Rightarrow \quad H(\mathbf{w}) \approx w^{\eta}\psi(\hat{\mathbf{w}})$$

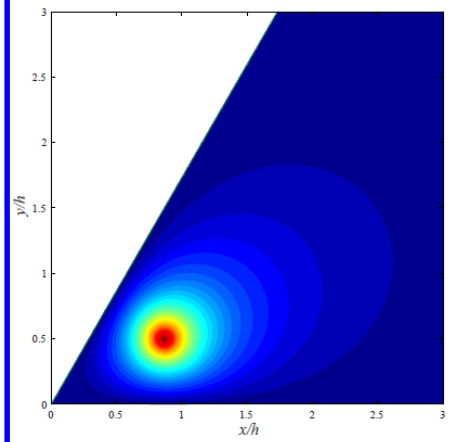
$$\nabla^2_{\mathbf{w}} H = 0$$

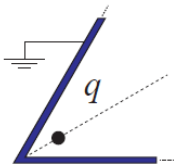
M. F. Maghrebi, Y. Kantor, M. Kardar, PRE**86**,061801(12)

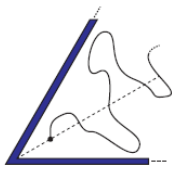
See, S. Redner, *A Guide to First Passage Processes*

Electrostatic potential and monomer density inside a (two-dimensional) wedge

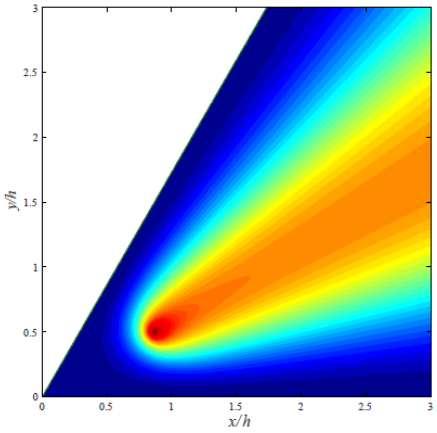
Φ

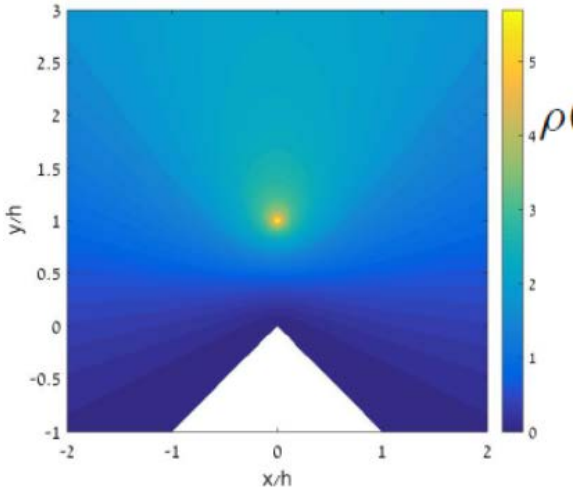






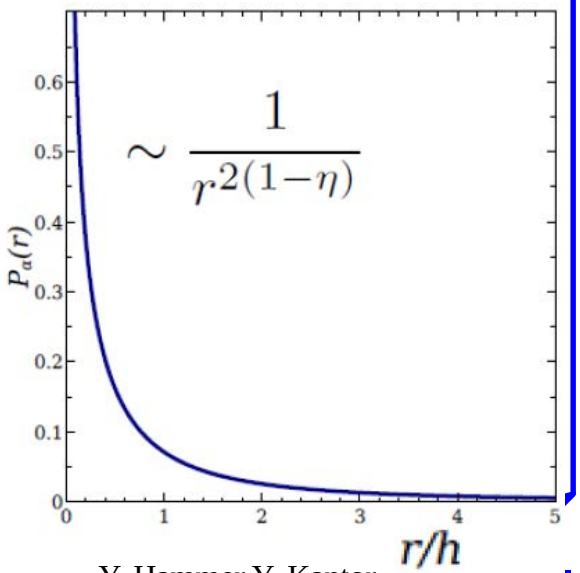
ρ





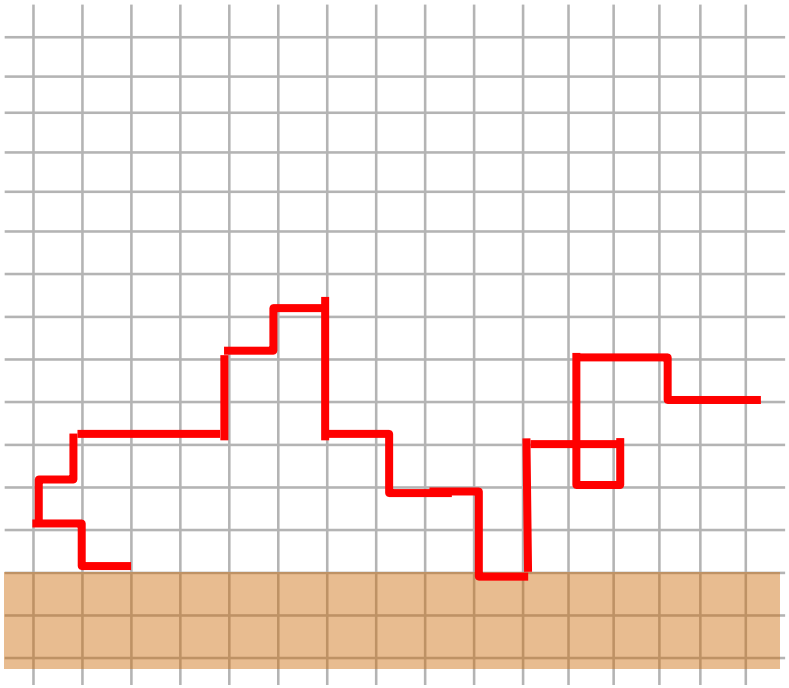
$$\rho(\mathbf{h},\mathbf{r}) = \frac{\Theta(\hat{\mathbf{r}})}{\Theta(\hat{\mathbf{h}})}\left(\frac{r}{h}\right)^{\eta}\Phi(\mathbf{h},\mathbf{r})$$

Y. Hammer (12)



Y. Hammer,Y. Kantor,
PRE **89**,02261 (14)

Ideal polymers near critical attractive surface as a diffusion problem



Stat.Mech.	$\Leftrightarrow$	Diffusion
N	$\Leftrightarrow$	t
Adsorbing boundary	$\Leftrightarrow$	Reflecting boundary

$$\frac{\partial S(\mathbf{r},t)}{\partial t} = D\nabla^2 S(\mathbf{r},t)$$

$$\mathcal{Z}(\mathbf{r},N) = z^N S(\mathbf{r},kN)$$

$$k = a^2/2dD$$

$$\mathbf{w} = \mathbf{r}/\sqrt{Dt}, \quad S(\mathbf{r},t) = H(\mathbf{w})$$

$$w \ll 1 \quad \Rightarrow \quad H(\mathbf{w}) \approx w^\eta \psi(\hat{\mathbf{w}})$$

$$\nabla^2_{\mathbf{w}} H = 0$$

S - survival probability of a random walker that at time $t = 0$ was at position $\vec{r}$,

$\mathcal{N}$ - number of configurations,

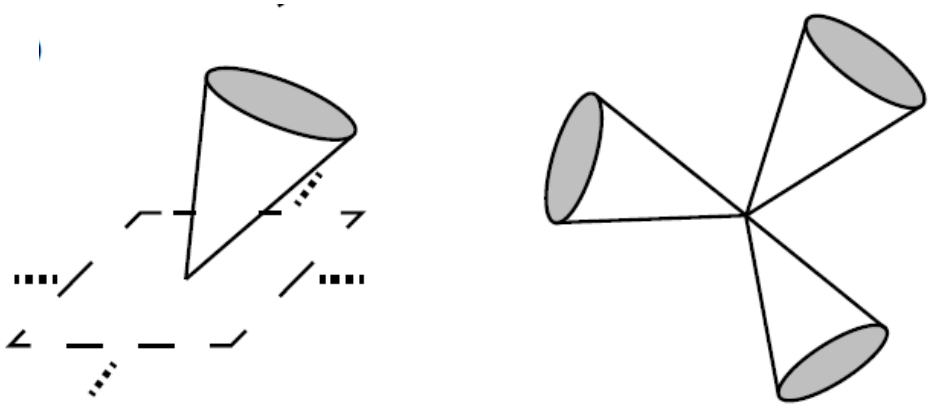
D - diffusion constant, t - time,

N - number of steps, a - step size,

z - coordination number.

R.J. Rubin, J.Chem.Phys. **33**, 2392 (65);
AIP Conf. Proc. **109**, 73 (84)

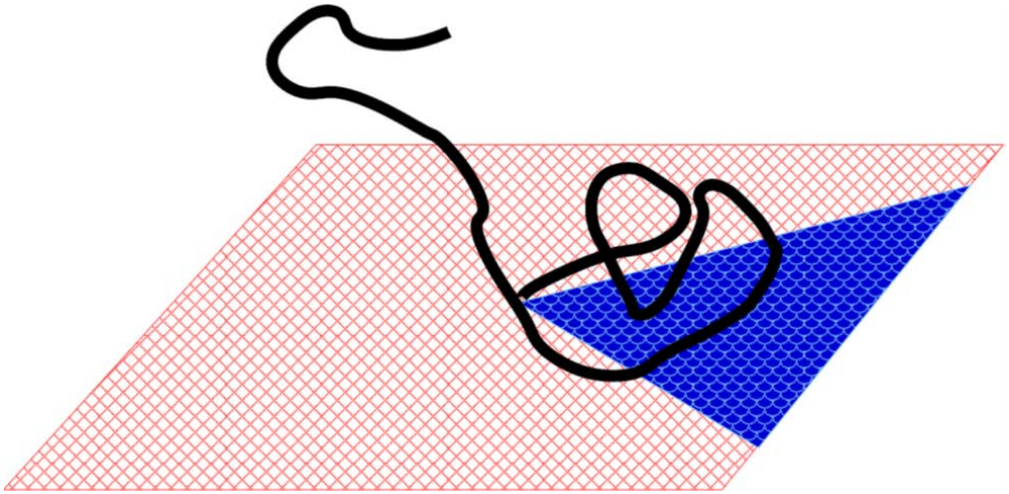
Ideal-polymer-mediated force constant between critical attractive surfaces always vanishes

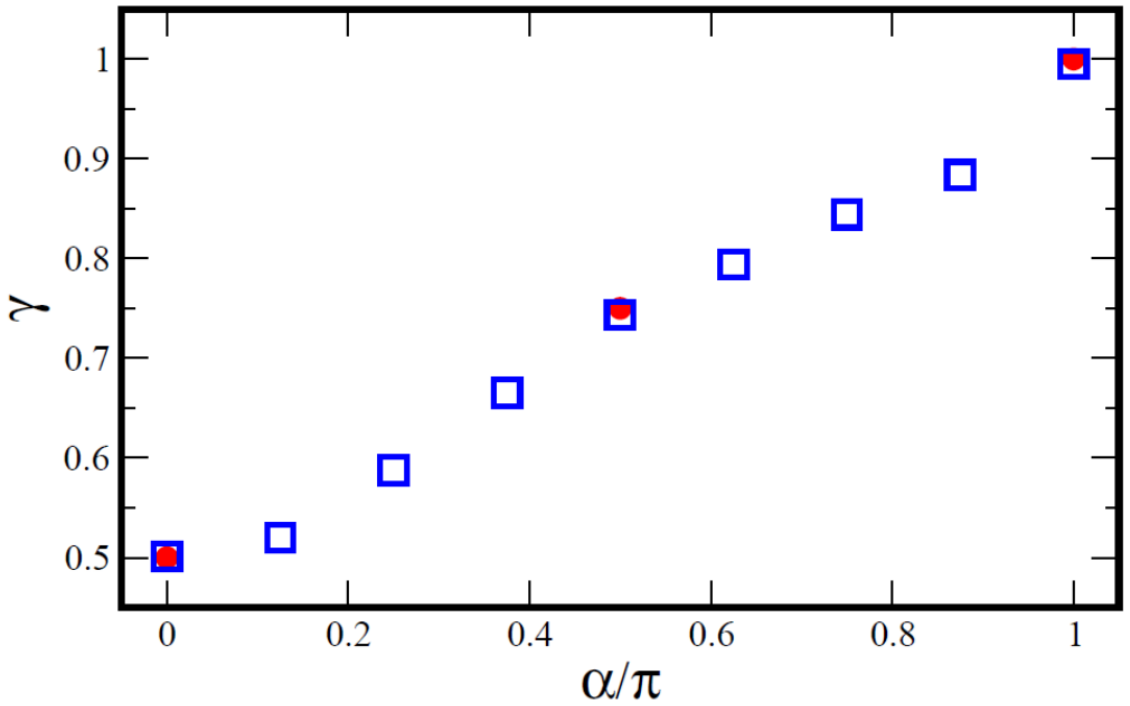


$$\mathbf{w} = \mathbf{r}/\sqrt{Dt}, \qquad S(\mathbf{r},t) = H(\mathbf{w})$$
$$w \ll 1 \quad \Rightarrow \quad H(\mathbf{w}) \approx w^{\eta}\psi(\hat{\mathbf{w}})$$
$$\nabla_{\mathbf{w}}^2 H = 0$$

The equation for H with vanishing normal derivative is solved by H=const., leading to $\eta=0$ (or $\gamma=1$) and $\mathcal{A}=0$.

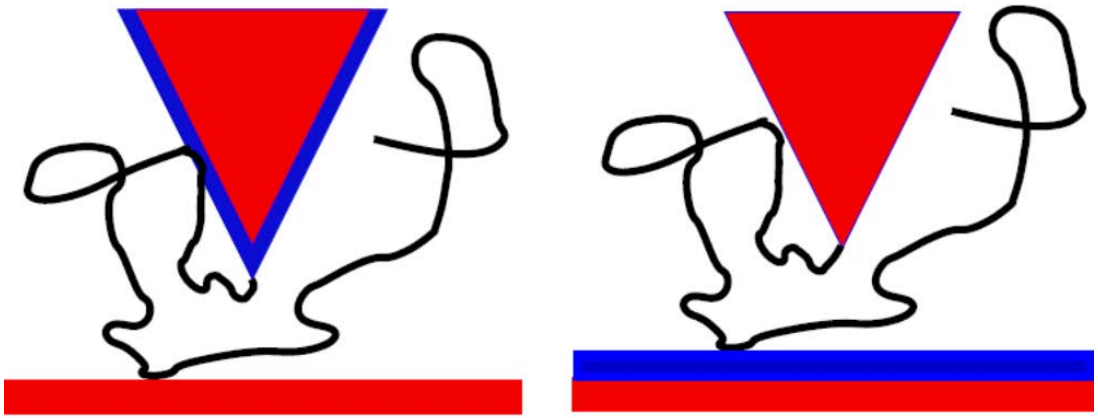
Repulsive plane decorated by a critical attractive sector

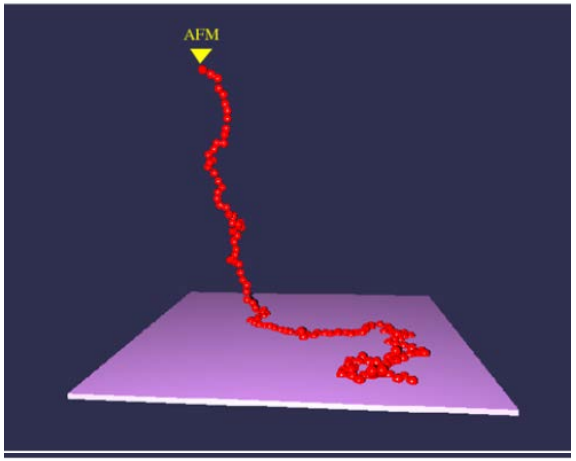




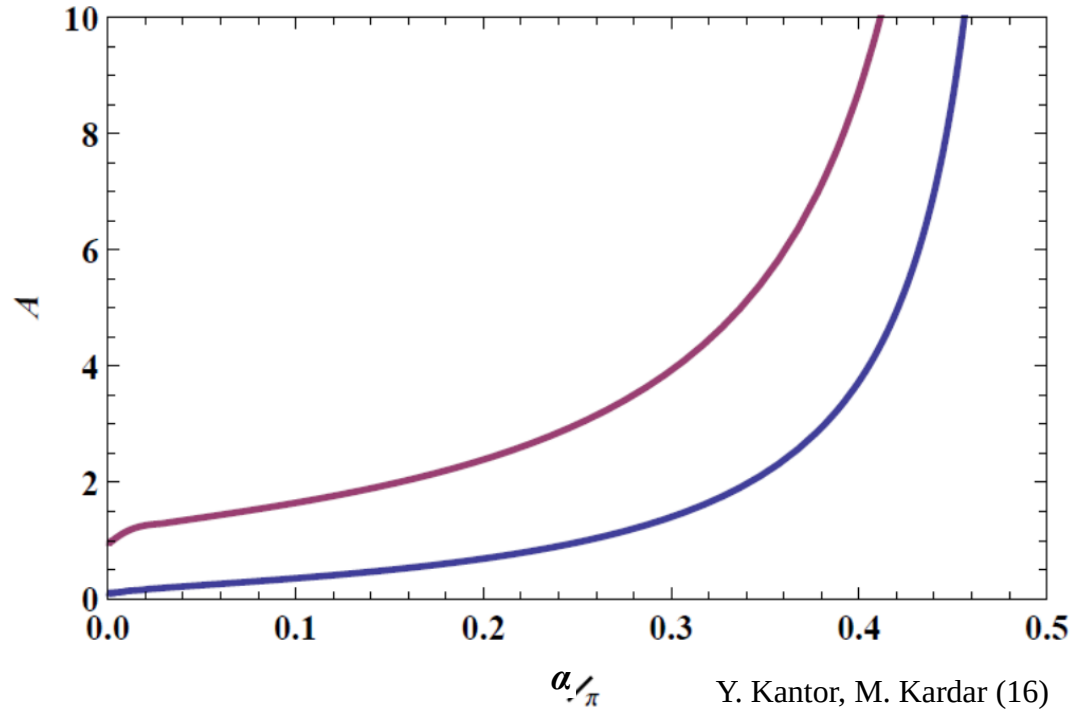
Y. Kantor, M. Kardar (16)

Ideal-polymer-mediated force constant between attractive and repulsive surfaces





S. Bhattacharya, V.G. Rostiashvili, A. Milchev, T.A. Vilgis:, Eur. Phys. J. E**29**, 28 (09)



Y. Kantor, M. Kardar (16)

Conclusions & prospects

- *Probe shapes influence force constants of polymers and polymer-mediated interactions between surfaces*
- *For scale invariant surfaces prefactor of the force law can be calculated exactly if the surfaces are repulsive or at adsorption transition point.*
- *By decorating surfaces it is possible to change exponent γ and, consequently, the force constant.*
- *For ideal polymers the force constants are non-negative but for self-avoiding polymers they can be both positive and negative.*
- *By a suitable selection of geometries and surface coverage it is possible to get a vanishing force constant.*
- *Away from the exact critical point – well-defined crossovers appear.*