

Kinetics of Irreversible Adsorption: Thermodynamics vs Molecular Mobility

David NIETO SIMAVILLA, Weide Huang, Caroline Housmans,
Philippe Vandestruck, JP Ryckaert, Michele Sferrazza
Simone Napolitano

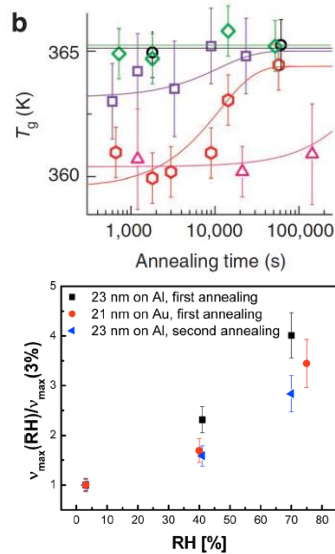
Laboratory of Polymer and Soft Matter Dynamics
Université libre de Bruxelles (ULB)

snapolit@ulb.ac.be
<http://dynamics.ulb.be>

WHY STUDYING ADSORPTION?

Linear relation between the **glass transition temperature** and the adsorbed amount

Napolitano Nat Comm 2010

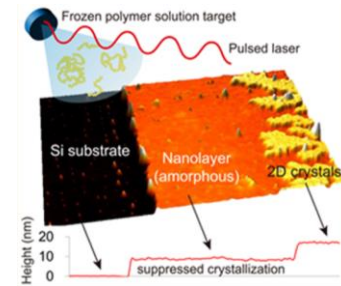
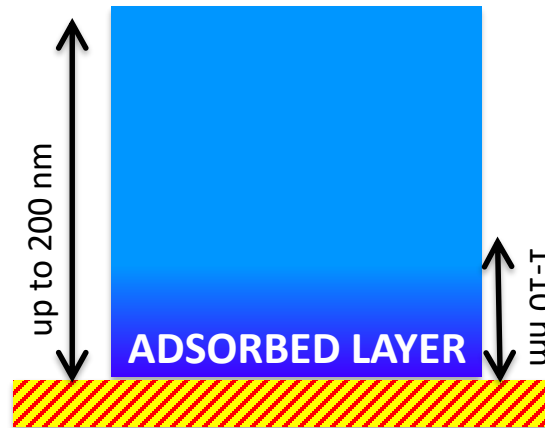
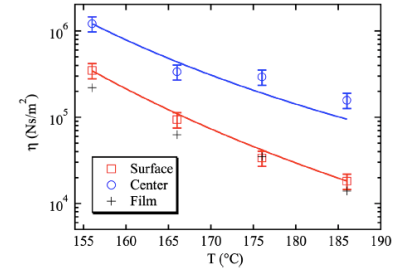


Nguyen Macromolecules 2013

The **water uptake** of thin films of PVAc can be modified upon annealing favoring adsorption

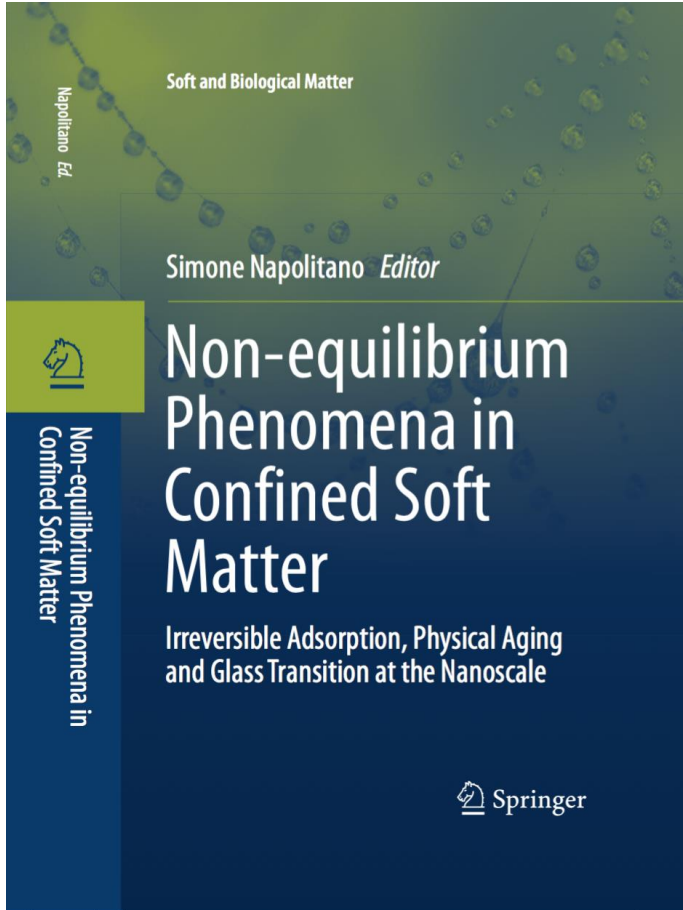
Surface viscosity of a 50 nm thick film of PS is reduced in the presence of a 7nm thick adsorbed layer.

Koga PRL 2011



Jeong JPCL 2013

Crystallization of adsorbed layers prepared via MAPLE is inhibited



Equilibration and physical aging

1. History dependent temporal changes of properties of thin polymer films

Günter Reiter

2. Equilibrium pathway of ultrathin polymer films as revealed by their surface dynamics

Fei Chen, Kung Geng and Ophelia K. C. Tsui

3. Structural Relaxation of Confined Polymers

Yunlong Guo & Rodney Priestley

4. Simulation Understanding of Physical Aging in Ultrathin Polymer Films

Qiyun Tang & Wenbing Hu

Irreversible adsorption

5. Kinetics of irreversible chain adsorption, new insights from experiments and simulations

Caroline Housmans, Philippe Vandestrück Jean-Paul Ryckaert, Michele Sferazza and Simone Napolitano

6. Structure and dynamics of adsorbed polymer layers

Naisheng Jiang, Maya Endoh and Tadanori Koga

7. Irreversibly adsorbed layer in supported ultrathin polymer film investigated by Local Dielectric Spectroscopy

Kim Hung Nguyen, Daniele Prevosto, Massimiliano Labardi, Simone Capaccioli and Mauro Lucchesi

Glass Transition and Material Properties

8. Non-equilibrium structure affects the ferroelectric behavior of confined polymers

Daniel Martinez-Tong, Alejandro Sanz, Jaime Martín, Tiberio A Ezquerro, Aurora Nogales

9. Interfacial role in the increase of structural order of a Discotic Liquid Crystal

Gabin Gbabode & Basab Chattopadhyay

10. 1D confinement of polyols stabilizes non-equilibrium liquid phase with enhanced orientational order

Simona Capponi, Simone Napolitano, Michael Wübberhorst

11. Dynamics of Confined Glass-Forming Liquids in Near Equilibrium Conditions

Sindee Simon

12. Effect of confinement geometry on the out-of-equilibrium glassy dynamics

Daniele Cangialosi

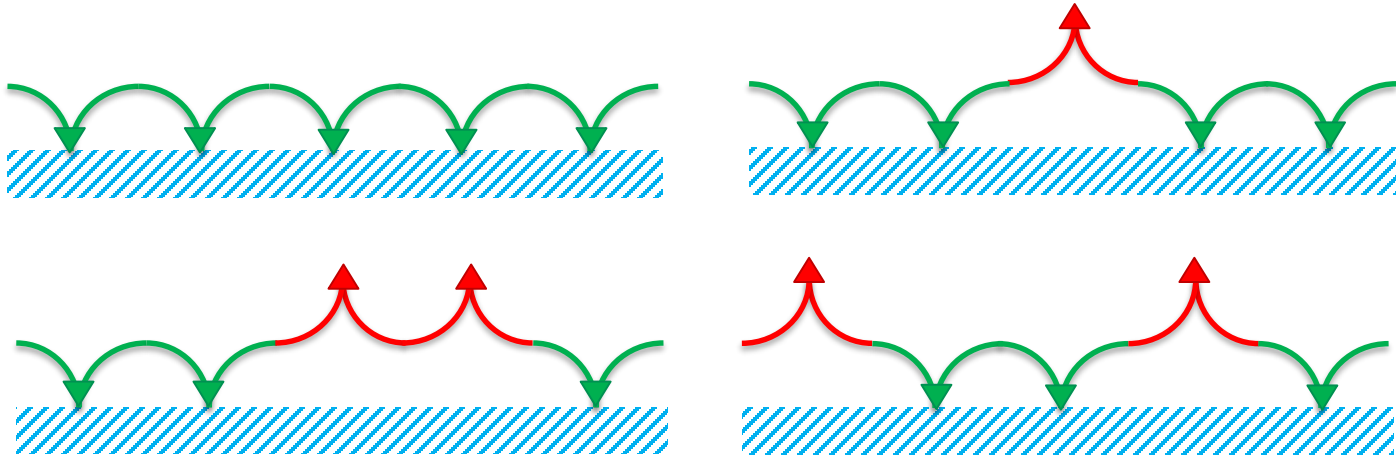
PHYSICS OF IRREVERSIBLE ADSORPTION OF POLYMER MELTS

Adsorption is an **increase in molecular density in proximity of a nonrepulsive interface**. Because of connectivity adsorption is irreversible at chain level, also for monomer/substrate interactions $< k_B T$. Desorption of the whole chain requires cooperative desorption of all the adsorbed monomers.

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EXAMPLE: Let's consider a chain of (at least) 5 **red** monomers which turn **green** when they adsorb onto a **blue** substrate. We fix the monomer/substrate interaction to $0.5 k_B T$ (and we forget about entropy).



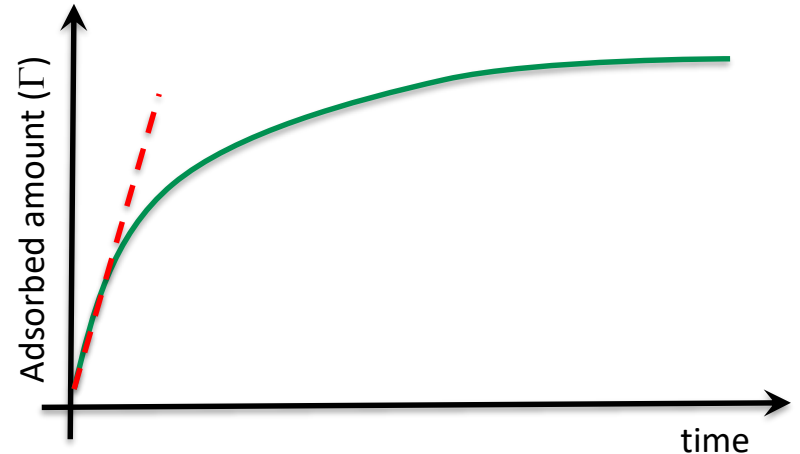
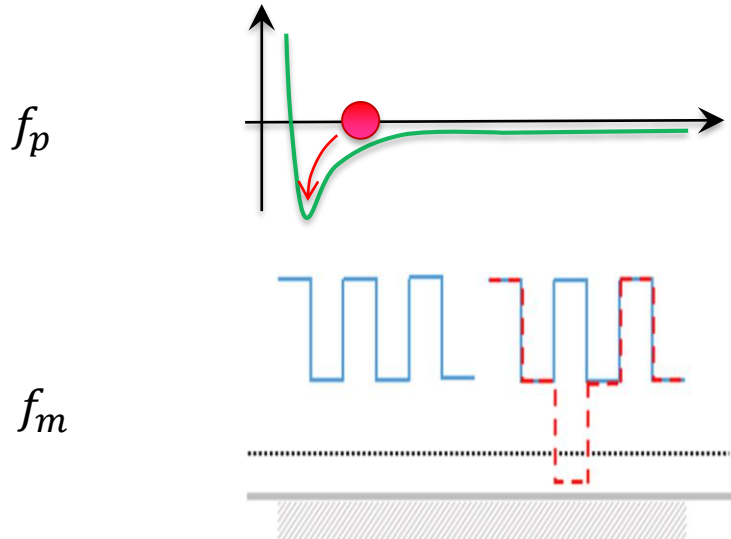
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The kinetics of adsorption is a nonequilibrium process, whose rate is given by the fastest between two mechanisms, related to molecular motion (e.g. a relaxation rate, f_m) and interfacial potential (f_p).

$$q \approx c f_m + c' f_p \quad \frac{\partial f_m}{\partial T} > 0 \quad \frac{\partial f_p}{\partial T} < 0$$

at high T, molecular motion increases while interfacial interactions decrease
 $\rightarrow f_m \ll f_p$



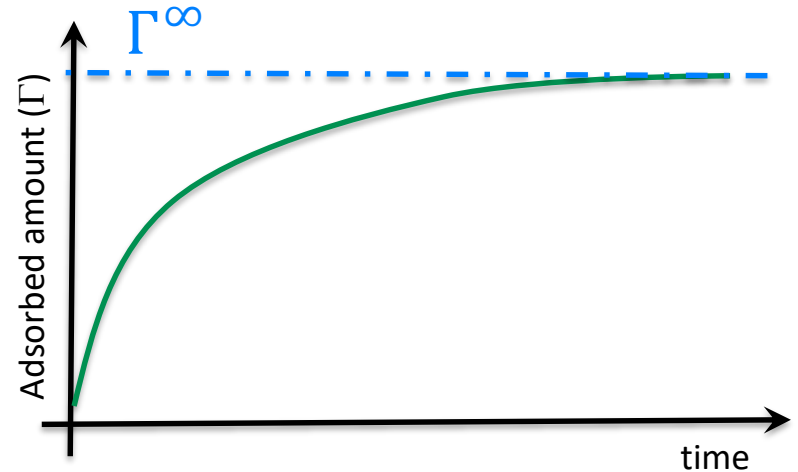
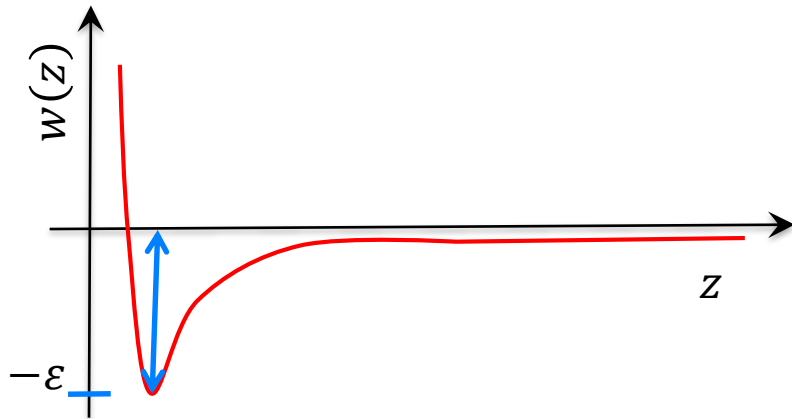
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The kinetics of adsorption is instead a nonequilibrium process, whose rate is given by the fastest between two mechanisms, related to molecular motion and interfacial potential

After long enough (infinite) waiting time, the adsorbed amount saturates to an equilibrium value given by the interfacial potential and the topography (roughness of the substrate)

$$\Gamma^\infty \sim \varepsilon$$



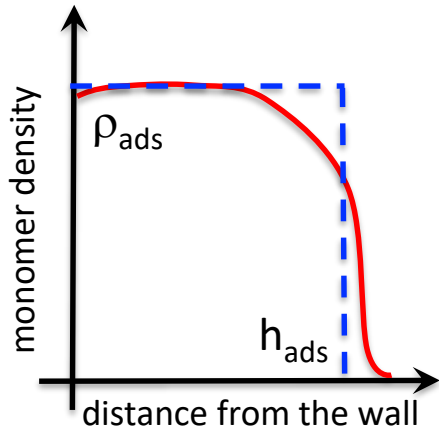
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Adsorption is an increase in molecular density in proximity of a nonrepulsive interface. Because of connectivity adsorption is irreversible at chain level, also for monomer/substrate interactions $< k_B T$. Desorption of the whole chain requires cooperative desorption of the single adsorbed monomers.

The kinetics of adsorption is instead a nonequilibrium process, whose rate is given by the fastest between two mechanisms, related to molecular motion and interfacial potential

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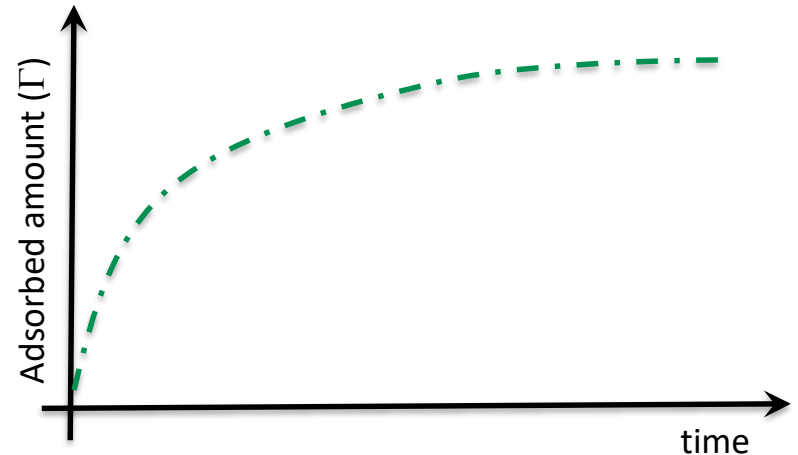
In experiments the adsorption amount can be determined by a measurement of the thickness of the adsorbed layer



$$h_{ads} = \frac{\int_0^{\infty} \Gamma_m(z) dz}{\rho_{ads}}$$

$$\Gamma = \frac{\rho h_{ads}}{N_A} N^{1/2} \approx \frac{\rho h_{ads}}{N_A} \left(\frac{M_w}{m_m} \right)^{1/2}$$

$$\Gamma = \text{const} \times h_{ads}$$



KINETICS OF ADSORPTION

EMPIRICAL EXPRESSIONS FOR THE KINETICS OF IRREVERSIBLE ADSORPTION

The rate of adsorption is proportional to the space available at the interface

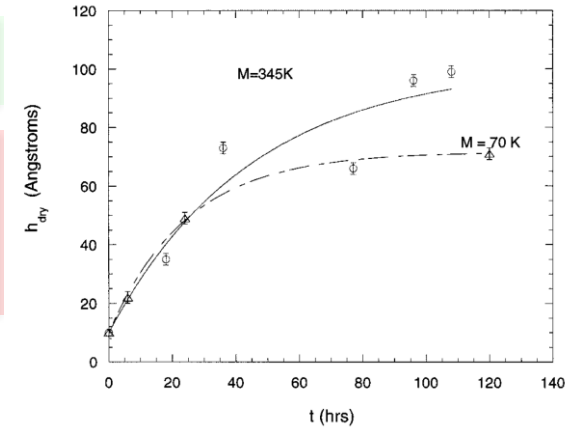
Durning *Langmuir* (1999)

$$\frac{\partial \Gamma}{\partial t} \sim -\Gamma$$

$$\Gamma(t) = \Gamma^\infty [1 - \exp(-t/t_{ads})]$$

It provides a timescale of adsorption

It does not take into account the macromolecular nature of polymers. Conformations of adsorbed chains change with surface coverage



EMPIRICAL EXPRESSIONS FOR THE KINETICS OF IRREVERSIBLE ADSORPTION

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$$\Gamma(t) = \begin{cases} vt & t < t_{cross} \\ \Gamma_{cross} + \Pi \log\left(\frac{t - t_{cross}}{t_0}\right) & t > t_{cross} \end{cases}$$

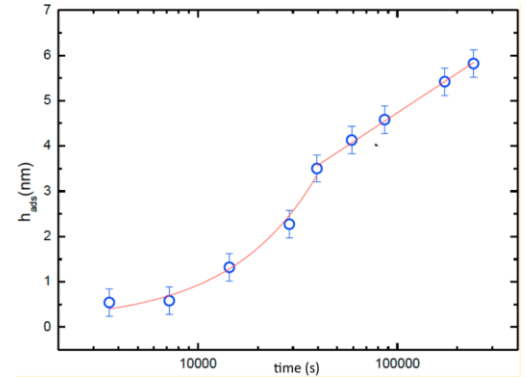
Based on experimental evidence, linear regime at short times, logarithmic at longer times

Housmans *Macromolecules* (2013)

$$\Gamma(t) = \begin{cases} vt & t < t_{cross} \\ \Gamma_{cross} + \Pi \log\left(\frac{t - t_{cross}}{t_0}\right) & t > t_{cross} \end{cases}$$

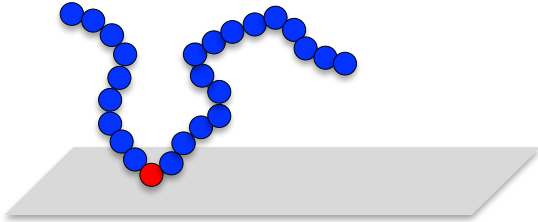
It provides a timescale of adsorption and probably takes into account for changes in conformations.

No saturation. Growth, though much slower, increases as a function of time



A MORE RIGOROUS TREATMENT IS NECESSARY

EARLY STAGE OF ADSORPTION



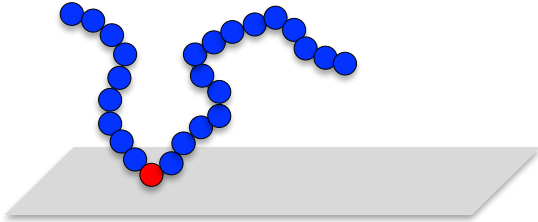
At short times we consider a zero-order adsorption reaction mechanism:

- every monomer in proximity of the interface can adsorb, the timescale of adsorption is given by the monomer adsorption rate q .
- every time a (group of) **monomer**(s) get(s) adsorbed \rightarrow the **whole chain** gets adsorbed

Rate of adsorption = **monomer reaction rate** x **monomer availability** x **connectivity**

$$\frac{\partial \Gamma}{\partial t} = q \rho \frac{Z_{surf}(N)}{Z_{bulk}(N)} N$$

EARLY STAGE OF ADSORPTION



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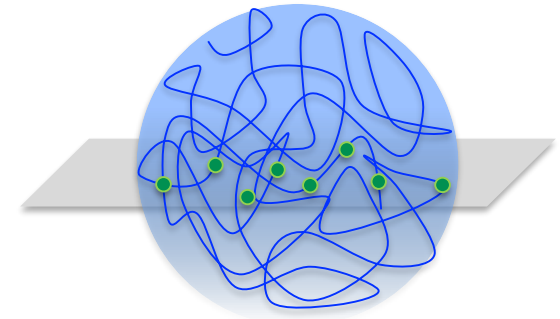
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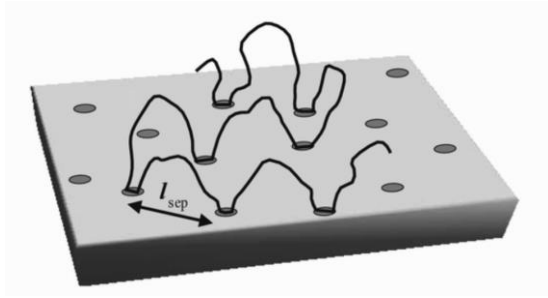
$$\frac{\partial \Gamma}{\partial t} = q \rho \frac{Z_{surf}(N)}{Z_{bulk}(N)} N$$

How many monomers are present at the interface?

$\frac{Z_{surf}(N)}{Z_{bulk}(N)} = N^{-1/2}$ gives to the fraction of available monomers in contact with the surface



$$\Gamma = q\rho N^{1/2} t$$

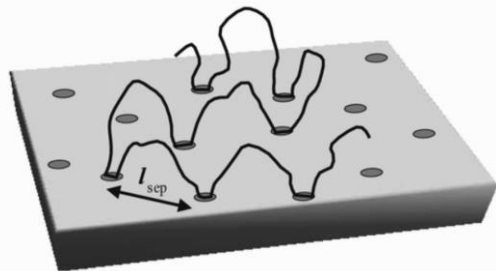


At longer times, surface crowding inhibits zero-order adsorption reaction mechanism

- Same as the tube considered in the dynamics of melts, we approximate the previously-adsorbed chains with a potential opposing to adsorption
- At each time we associated a density of holes (separation length, l_{sep}) where adsorption can take place \rightarrow formation of loops
- The holes density goes to zero (l_{sep} diverges) as the adsorbed amount reaches its equilibrium value \rightarrow longer and longer loops
- We consider a monomer reaction rate Q , which might differ from that in the earlier regime q

Rate of adsorption (time) = **monomer reaction rate** x **monomer availability (time)** x **connectivity**

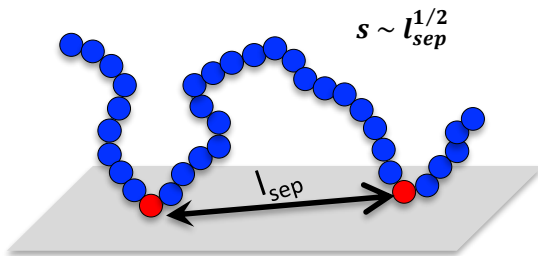
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Rate of adsorption (time) = **monomer reaction rate** x **monomer availability (time)** x **connectivity**

How do loops contribute to the adsorbed amount?



A loop is formed by

- n **directly** adsorbed monomers (Γ_b)
- s **indirectly** adsorbed monomers ($\Gamma - \Gamma_b$)

short times

$$\frac{\partial \Gamma}{\partial t} = q\rho N^{1/2}$$

long times

$$\frac{\partial \Gamma(t)}{\partial t} = Q\rho N^{1/2} \Delta \Gamma_b(t)$$

$$\Delta \Gamma_b(t) = \Gamma_b^\infty - \Gamma_b(t) \quad \text{the remaining space where adsorption is possible}$$

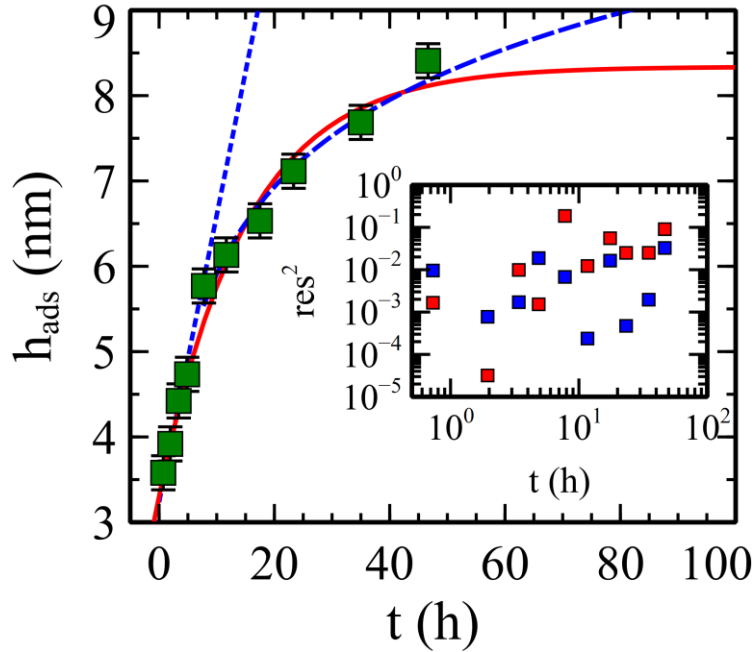
$$\tau = \exp(\Gamma^\infty) / \Phi Q$$

For a polymer melt

$$\Gamma(t) = \Gamma^\infty + \ln \left[1 - \exp\left(-\frac{t - t_{cross}}{\tau}\right) \right]$$

LET'S TEST THIS MODEL!

TESTING THE MODEL



HYPOTHESIS I

Adsorption at $t > t_{\text{cross}}$ proceeds via the formation of loops

HYPOTHESIS II

The monomer adsorption rate is independent on the regime of adsorption. The overall adsorption rate is limited by the availability of space at the interface q and Q (the monomer adsorption rates in the two regimes) are universally bounded. Our model predicts:

$$Q = q \exp(\Gamma^\infty) / \nu\tau$$

EXPERIMENTS

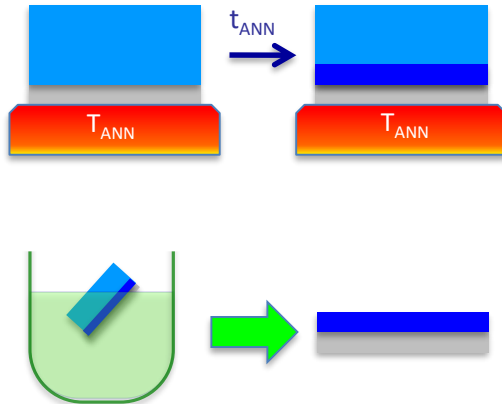
Films of different polymers prepared by spincoating

Thermally equilibrated films were instantaneously brought to the annealing temperature, T_{ANN}

For each polymer we measured the adsorbed amount after different annealing times - 10-15 independent samples per T_{ANN}

Reproducing **GUISELIN EXPERIMENT** we isolated the adsorbed layer and determined the adsorbed amount

More on preparation → Nieto *Macromol Chem Phys* (2018)

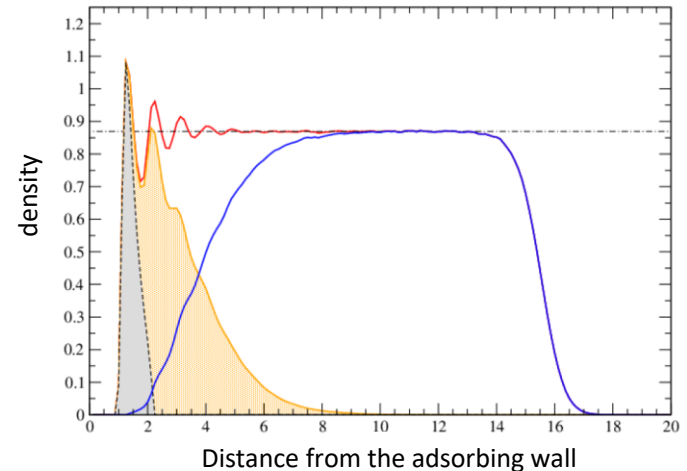


MD SIMULATIONS

Coarse-grained polymer melt & substrate system

Films were equilibrated against a hard wall, with monomer/wall interaction $\varepsilon_W = \varepsilon_0$, then we switched ε_W to $\varepsilon_1 > \varepsilon_0$,

We followed the formation of the adsorbed layer (directly and indirectly adsorbed amount, molecular conformations) while the system equilibrated to the new value of ε_W

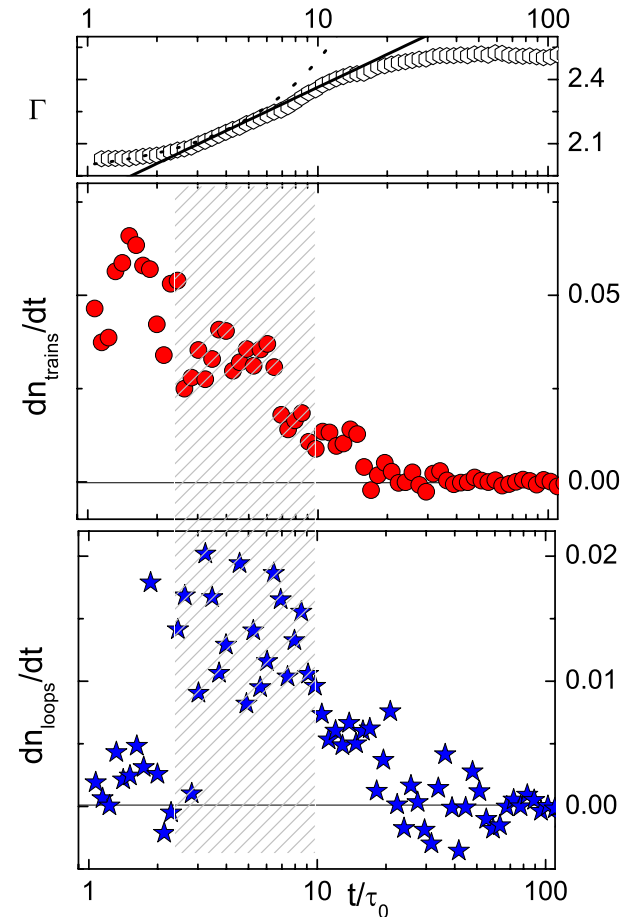


HYPOTHESIS I

HYPOTHESIS Adsorption at $t > t_{\text{cross}}$ proceeds via the formation of loops

METHOD We have analyzed the rate of formation of train loops and tails via MD.

RESULTS Our results confirm that the formation of loops boosts in the “logarithmic regime” ($t_{\text{cross}} < t < \tau$)-



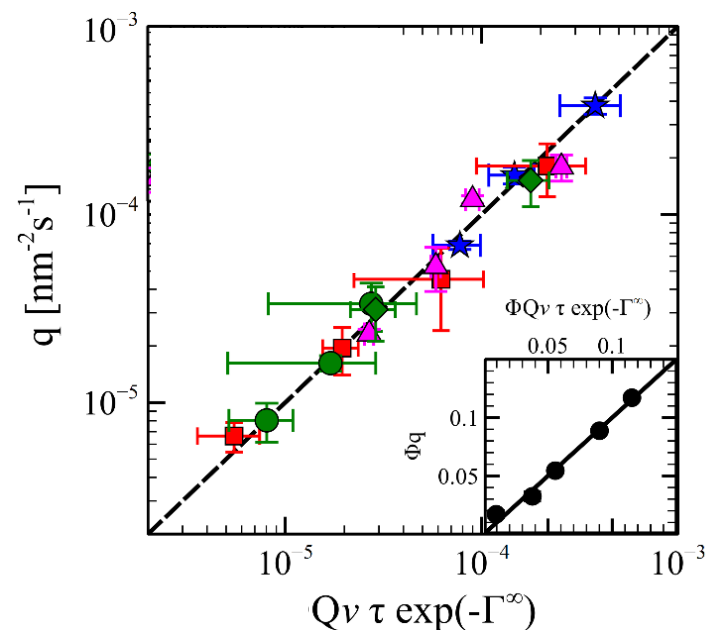
HYPOTHESIS The monomer adsorption rate is independent on the regime of adsorption. The overall adsorption rate is limited by the availability of space at the interface

METHOD If our model is correct, the apparent monomer adsorption rate in the logarithmic regime should be related to that in the linear regime, via the equation

$$Q = q \exp(\Gamma^\infty) / \nu\tau$$

To prove it, we varied the monomer adsorption rate, while keeping constant the polymer/substrate pair, by changing temperature in the experiments and the depth of the interfacial potential in simulations.

RESULTS We found the expected correlation between the predictions of our model and the outcome of experiments & simulations



(first) CONCLUSIONS

The formation of an irreversibly adsorbed layer is described by a nonequilibrium kinetics :

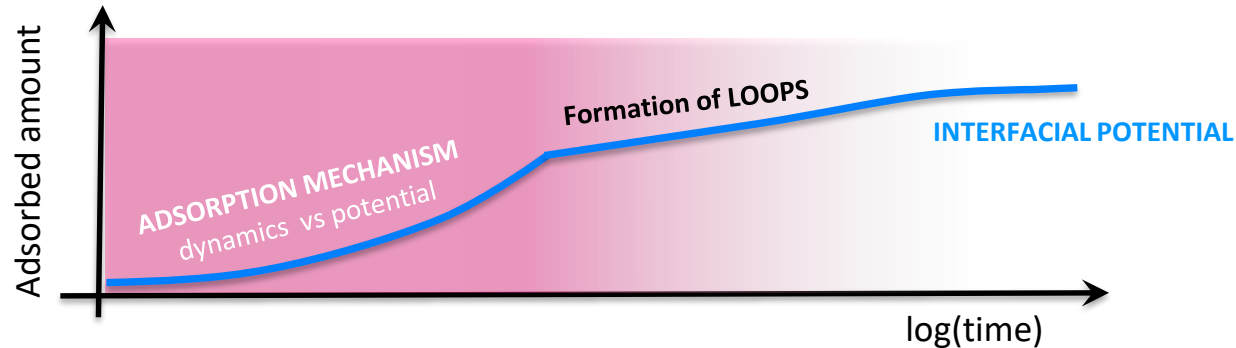
At short times the growth rate is constant → linear growth regime

At longer times the growth rate drops because of the less available state

The logarithmic growth typical of the later stages of adsorption is related to the formation of loops

The first regime is a nonequilibrium phenomenon (constant rate, independent on the final equilibrium value)

The second regime yields equilibration (the rate decreases while approaching equilibrium) towards a final adsorbed amount, which depends on interfacial potential



TOWARDS A CONTROL OF INTERFACIAL INTERACTIONS

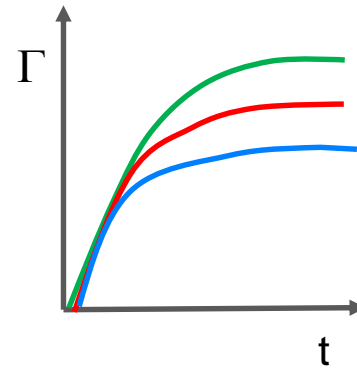
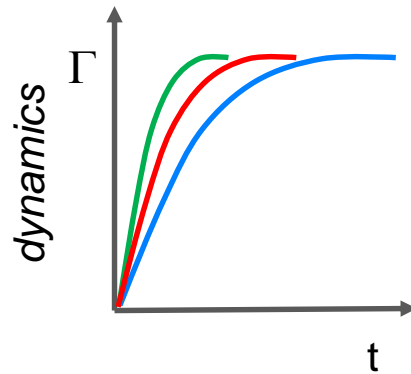
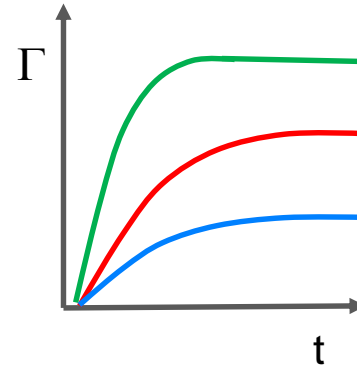
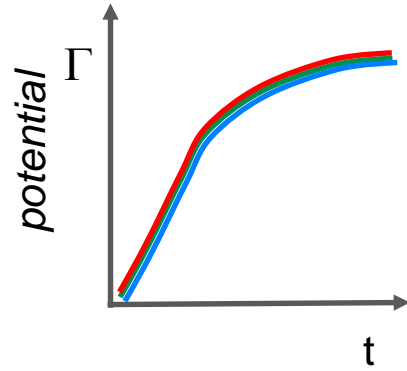
POSSIBLE ADSORPTION SCENARIOS

ADSORPTION MECHANISM

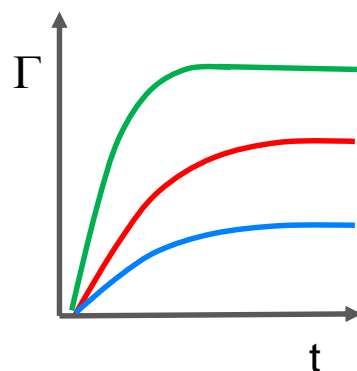
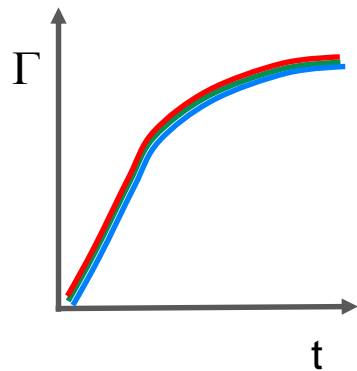
INTERFACIAL INTERACTIONS

constant

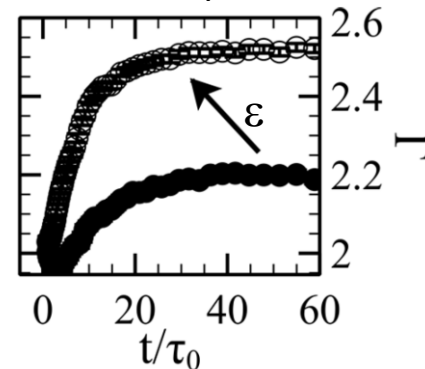
variable



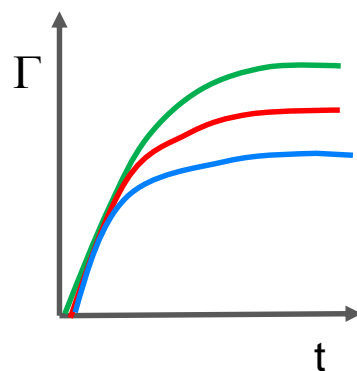
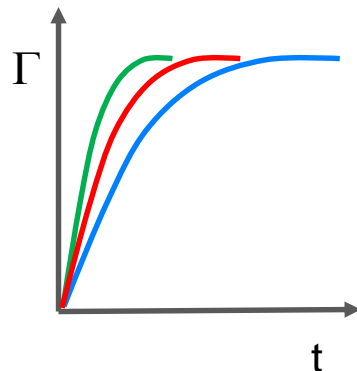
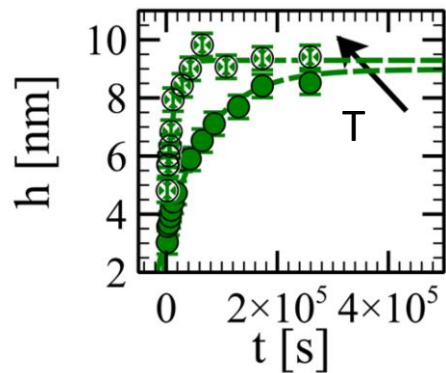
TRIVIAL



By varying interfacial potential



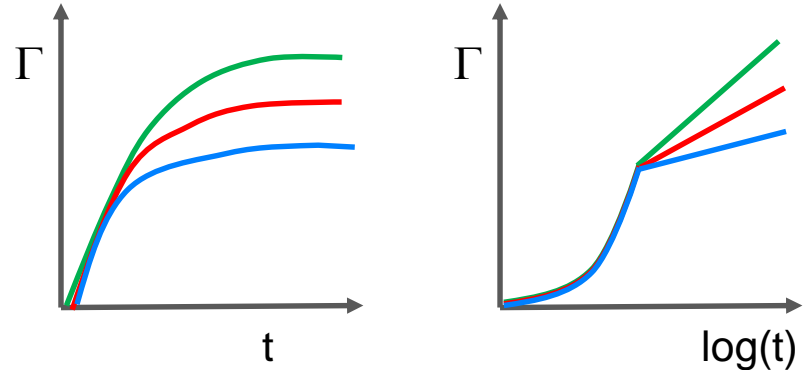
By varying T



UNKNOWN

SEARCHING THE MISSING SCENARIO

This scenario describes the adsorption of systems having the **same** value of monomer **adsorption rate** (nonequilibrium), but **tunable adsorbed amount** in equilibrium conditions



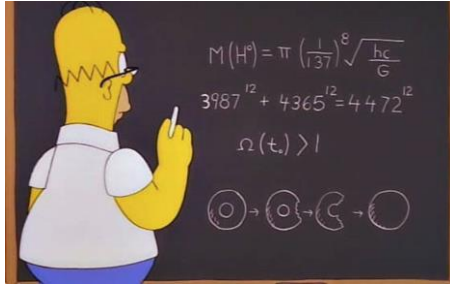
RELEVANCE Existence of such scenario would 1) allow studying the impact of interfacial interactions at invariant dynamics; 2) prove the exactness of our model of adsorption based on two independent regimes. In the saturating exponential scenario the adsorption rate at short time is directly related to the equilibrium adsorbed amount



To reproduce it, we could think of experiments with different polymers, different M_w , different temperatures, different substrates. This procedure would be extremely time consuming and “artificial/trivial”.

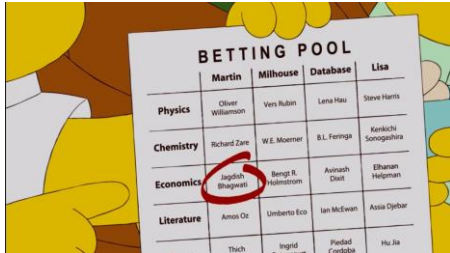
We searched for alternative variables, which would permit to observe this scenario using the same polymer, the same chain length, same substrate. This task seemed quite difficult

SIMPSONS PREDICTED THE MISSING SCENARIO!



(1998) S10E02 The Wizard of Evergreen Terrace

Homer predicted the mass of the Englert/Brout/Higgs Boson 14 years before its measurement



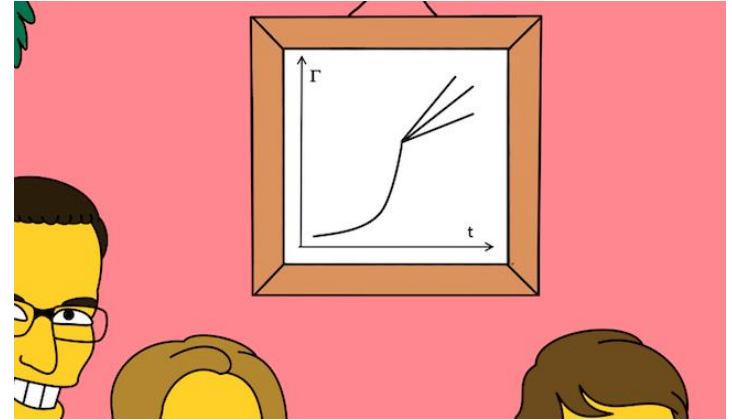
(2010) S22E01 Elementary School

In 2010 Milhouse bet on a Nobel prize for Economics to Bengt Holmstrom, who will be eventually awarded in 2016

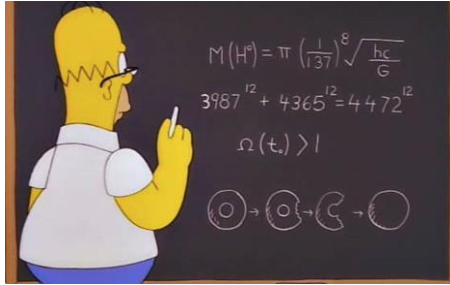


(2000) S11E17 Bart to the Future

Set in the far future, Lisa becomes president of the USA and has to face issues from a previous Trump administration. D Trump became president in 2016

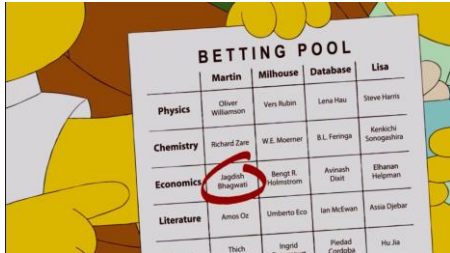


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(2017) New Year Greeting card

A painting picturing the missing scenario is clearly visible in this simpsonised version of the Laboratory of Polymer and Soft Matter Dynamics of ULB.

(HOW DID WE GET THERE?)

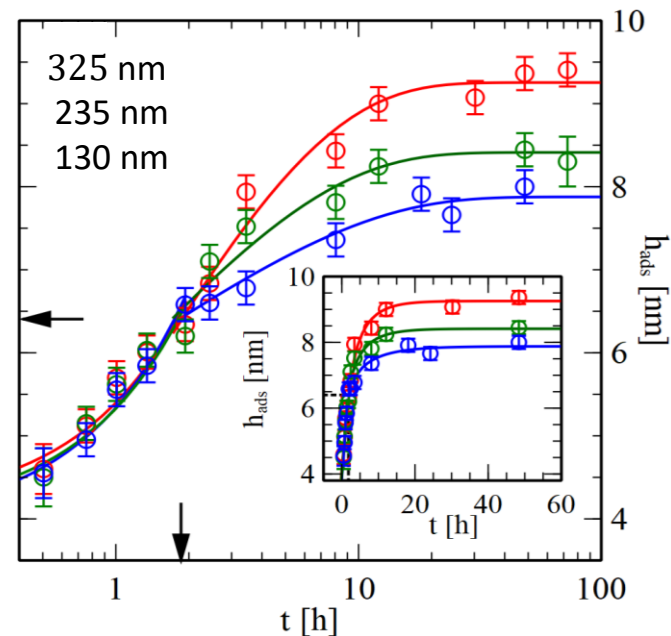
METHOD

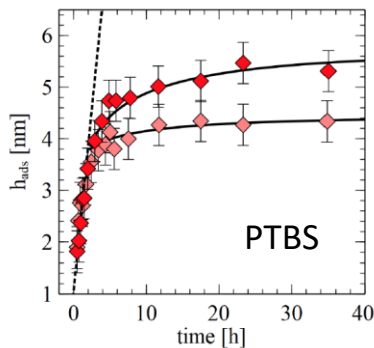
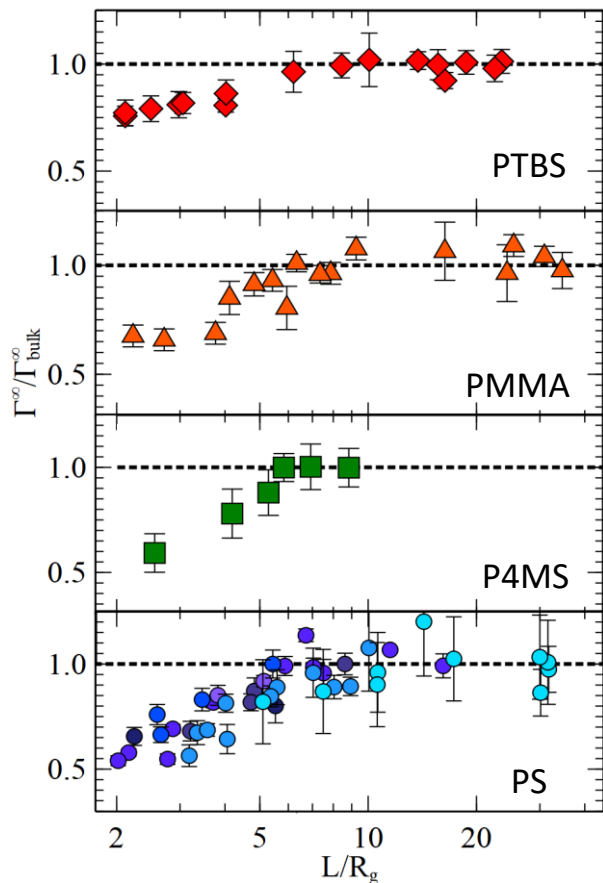
We prepared thin films of PS (1000 kg/mol) of different thickness and measured the kinetics of adsorption in isothermal conditions

RESULTS

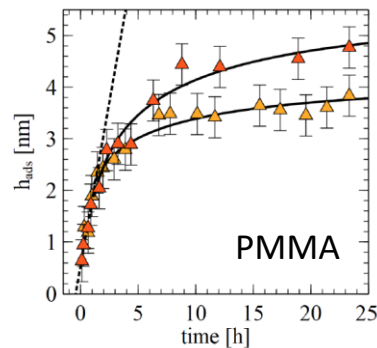
At times shorter than t_{cross} , the kinetics of adsorption show no confinement effect. This indicates that the monomer adsorption rate q is not affected by nanoconfinement.

At longer times the kinetics depend on the thickness of the film: the adsorbed amount of thinner films saturates to smaller values.

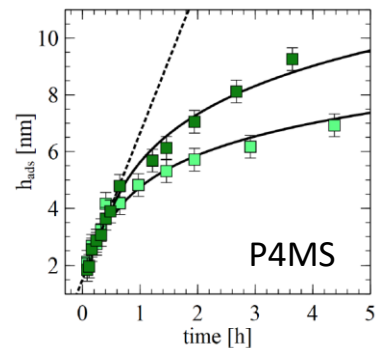




180 nm
29 nm



120 nm
42 nm



74 nm
17 nm

We have performed experiments on different polymers, and on PS of different molecular weight.

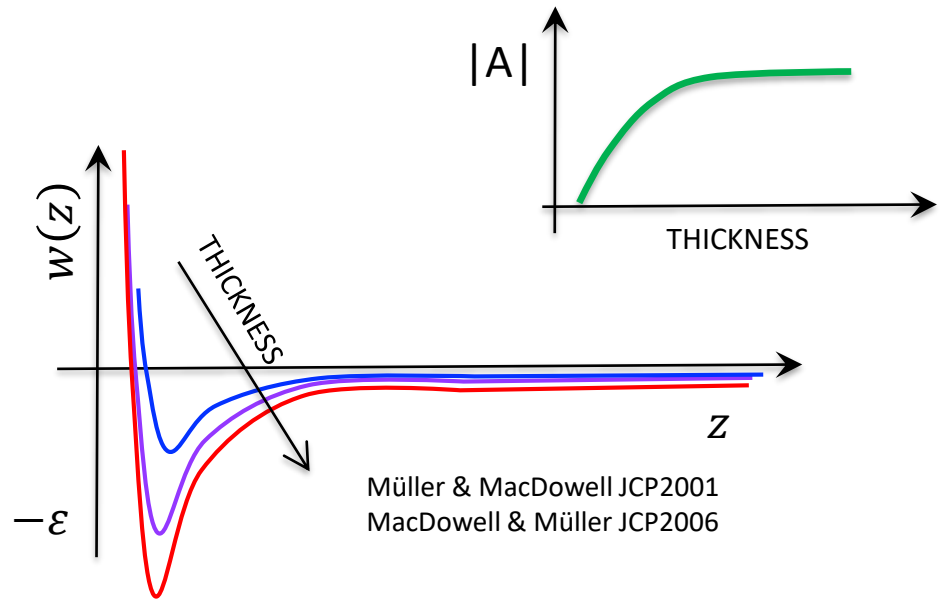
For all the systems investigated, we observed a drop in final adsorbed amount for thicknesses below 6-10 R_g.

NANOCONFINEMENT SCENARIO

This adsorption scenario implies that confinement alters the equilibrium adsorbed amount.

The equilibrium adsorbed amount is directly related to the depth of the interfacial potential

The interaction between polymer chains and substrate decreases upon reduction of the film thickness.



How is this possible?

The dispersive component of the interfacial potential, the one related to van der Waals forces, is size dependent. The amplitude of such forces can be computed \rightarrow Hamaker constant, A . In the case of thin films, A decreases upon reduction of the layer thickness

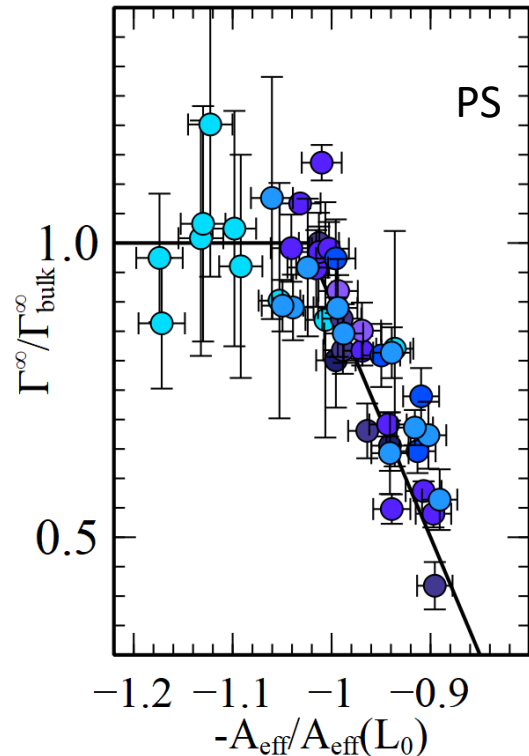
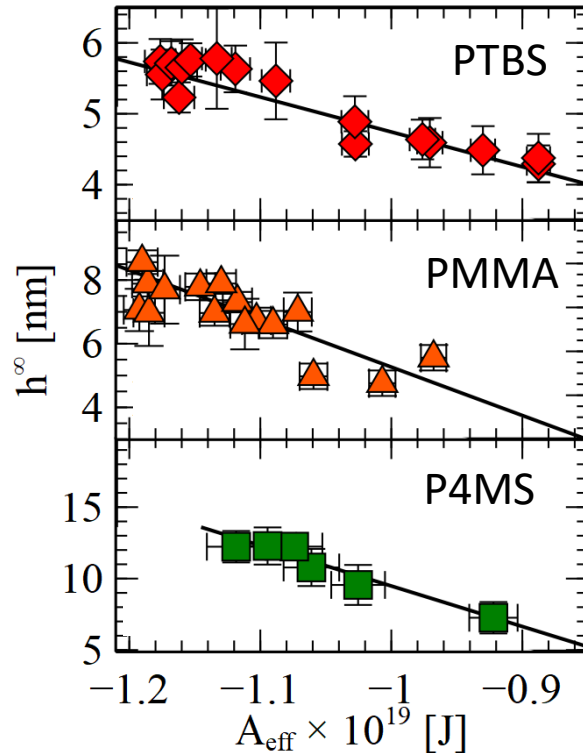
$$\Gamma^\infty \sim \varepsilon \quad \varepsilon \sim |A| \quad \Gamma^\infty \sim |A|$$

The missing scenario can be achieved by changing thickness

INTERFACIAL INTERACTIONS ARE TAMED BY NANOCONFINEMENT

Nieto Simavilla *ACS Central Science* (2018)

$$\Gamma^\infty \sim |A|$$



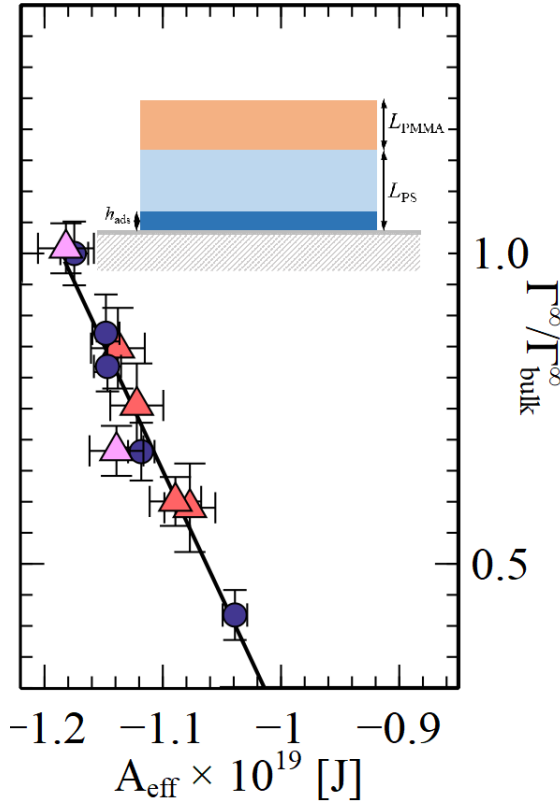
We verified that the reduction in adsorbed amount upon confinement follows the related reduction in negative Hamaker constant.

Thinner films have a less negative Hamaker constant :

- smaller interaction between polymer and substrate
- smaller adsorbed amount

Interfacial interactions can be controlled by changing film thickness, the adsorbed amount is a direct measurement of the interaction between polymer and substrate.

VARYING A AT CONSTANT THICKNESS

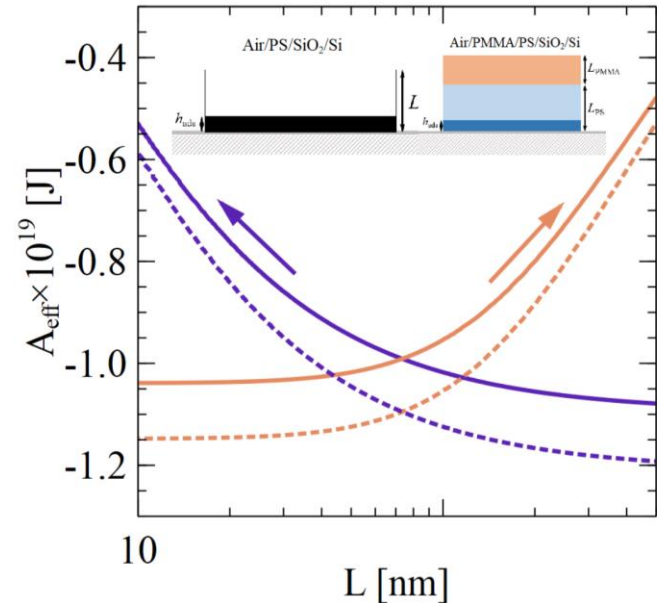


To discard that the trends could be ascribed to finite size effects or any other unknown or uncontrolled parameter from sample preparation, we designed a second type of experiments.

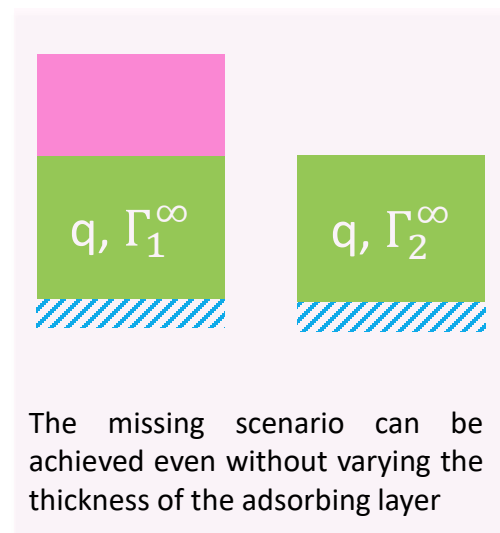
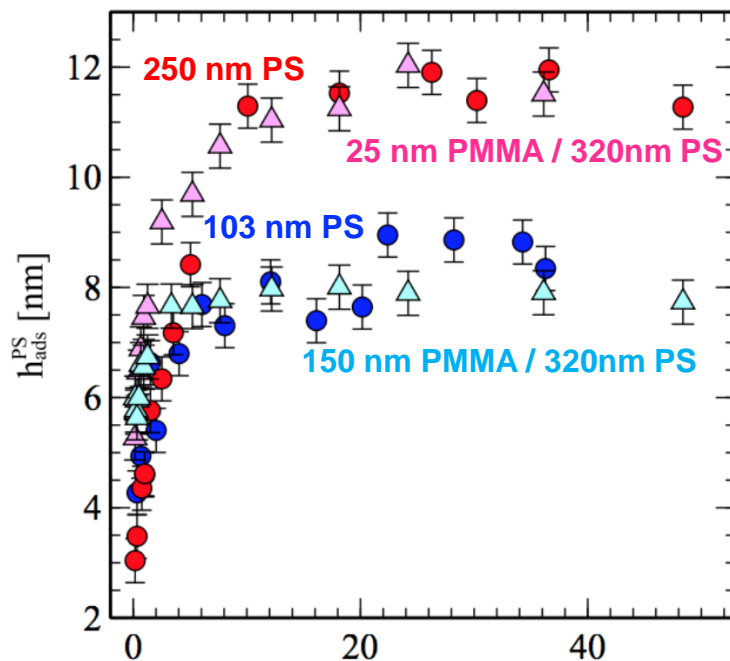
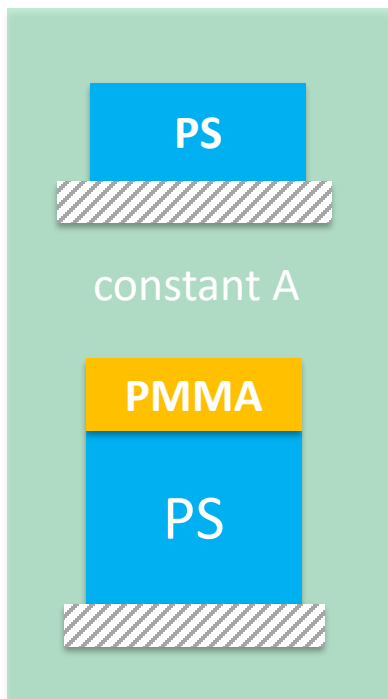
We modified the effective Hamaker constant without altering the thickness of the adsorbing layer.

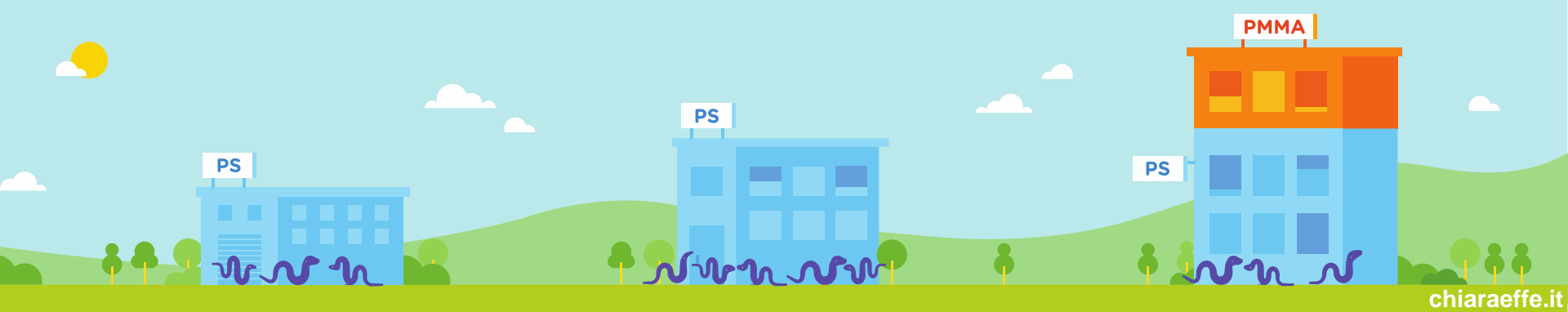
This conditions could be achieved by placing a layer of a different material on top of the adsorbing layer.

We considered the well studied bilayer system PS/PMMA. For bilayer of constant thickness of PS, the Hamaker constant decreases upon increase of the thickness of PMMA.



Our results show that the adsorbed amount and thus the interfacial interactions depend on the Hamaker constant only (and not on thickness, or presence of free surfaces).





CONCLUSIONS

It is possible to adsorb at constant rate (nonequilibrium component) and different interfacial potential (equilibrium component)

The adsorption kinetics includes two different regimes

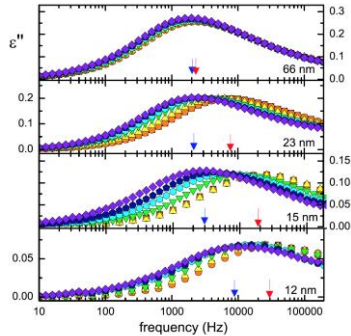
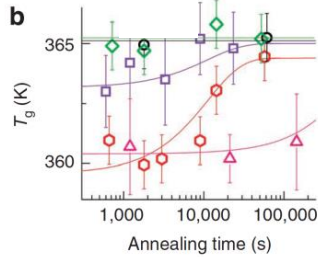
Nanoconfinement tames interfacial interactions

Interfacial interactions do not depend only on the interfacial chemistry, but also on geometry

WHY STUDYING ADSORPTION?

Linear relation between the **glass transition temperature** and the adsorbed amount in **capped films**

Napolitano Nat Comm 2010

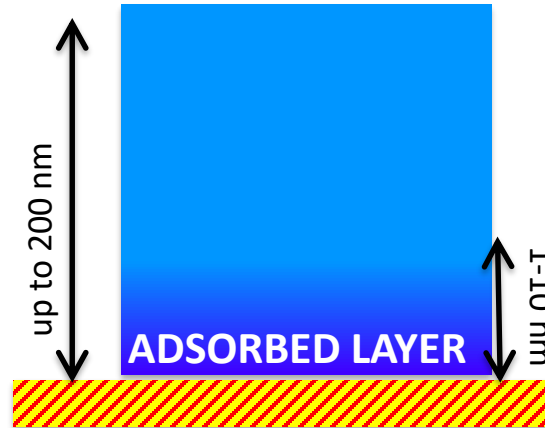
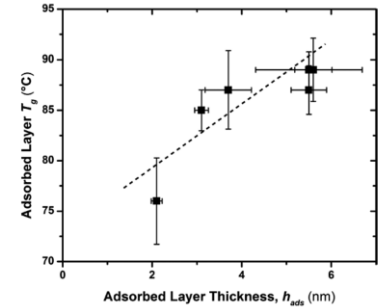


Panagopoulou PRL 2017

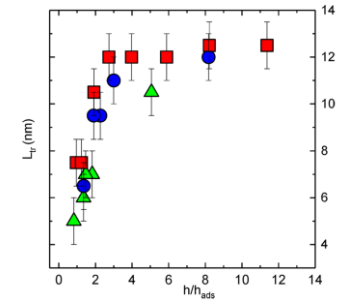
Linear relation between **segmental dynamics** and the adsorbed amount

Linear relation between the **glass transition temperature** and the adsorbed amount in **supported films**

Glycos MM
Burroughs MM 2011
Sun Soft Matter



Perez Eulate ACS Macro 2017
Ogiglio JPCL 2018



The effects of **the free surface** (reduction in T_g , increased permeability) are erased upon **adsorption**.

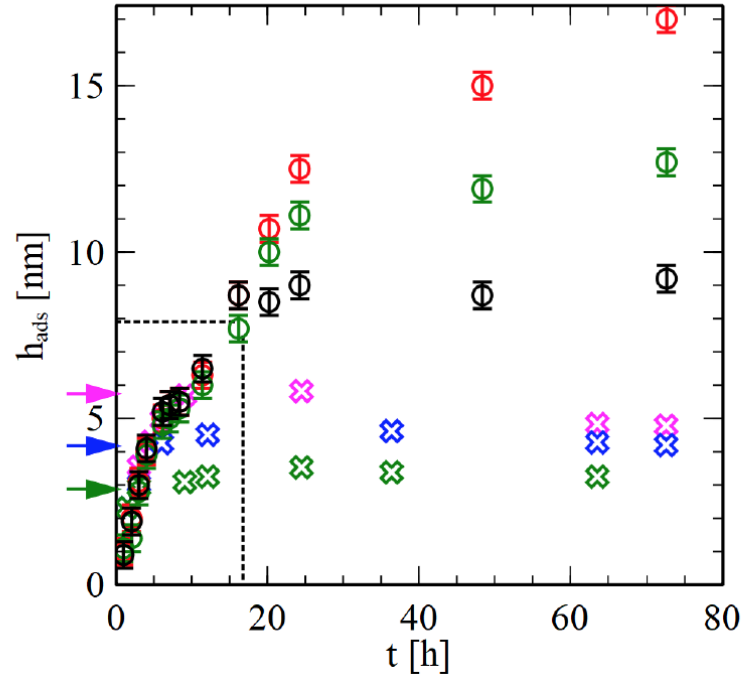
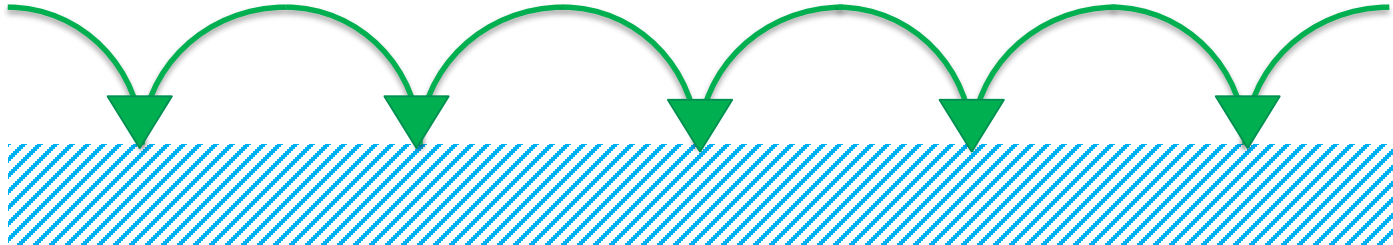


Fig. S10 - Adsorption kinetics for samples of PS325 of different layer thickness, $L = 134$ nm (red circles), 74 nm (green circles) and 35 nm (black circles), $L = 22$ nm (magenta crosses), 15 nm (blue crosses) and 9.6 nm (green crosses). coincide (marked dotted lines). For this molecular weight $R_g \sim 16$. For $L > 2R_g$ (circles), the crossover point (see marked dotted lines) is independent on L . For $L < 2R_g$ (crosses), deviation from the linear regime occurs at progressively shorter times and smaller thicknesses (see colored arrows). At longer times, due to depletion in available adsorbable material, the adsorbed layer thickness quickly saturates to a constant value smaller than $h_{\text{cross}}(L > 2R_g)$.

PHYSICS OF IRREVERSIBLE ADSORPTION OF POLYMER MELTS

Adsorption is an increase in molecular density in proximity of a nonrepulsive interface. Because of connectivity adsorption is irreversible at chain level, also for monomer/substrate interactions $< k_B T$. Desorption of the whole chain requires cooperative desorption of all the adsorbed monomers.

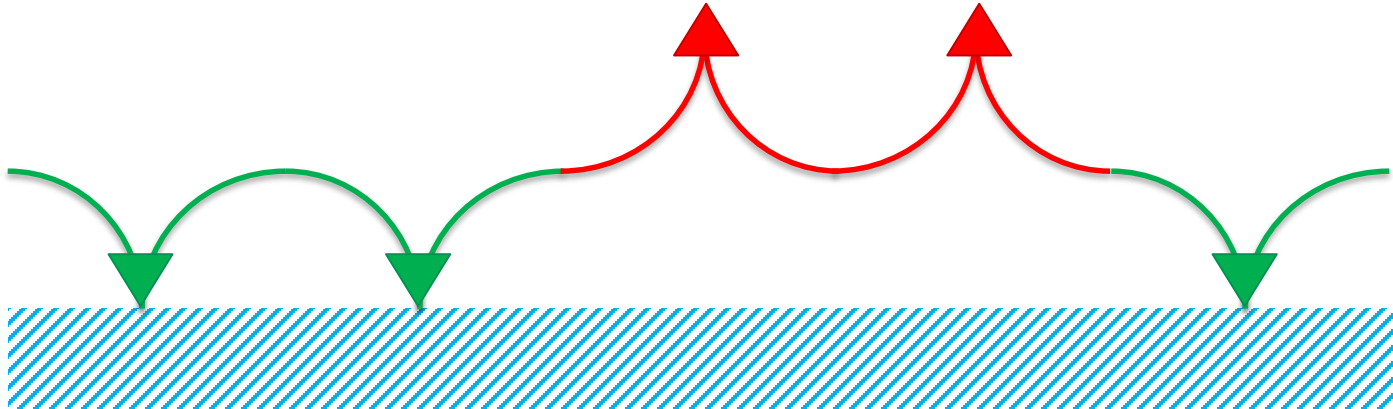
EXAMPLE: Let's consider a chain of (at least) 5 red monomers which turn green when they adsorb onto a blue substrate. We fix the monomer/substrate interaction to $0.5K_B T$ (and we forget about entropy).



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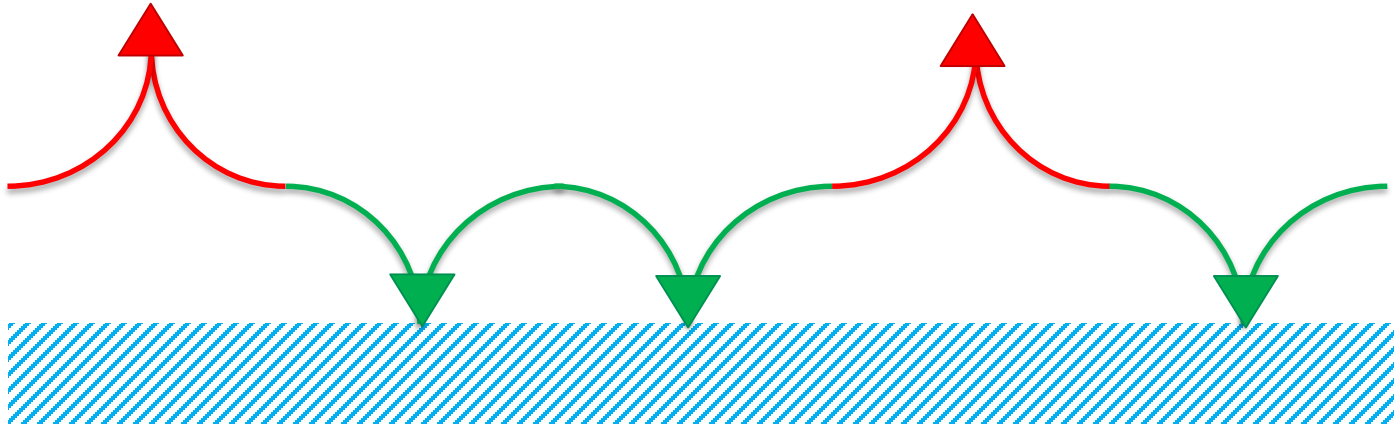
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