

A Spectral View of Polymer Adsorption under Nanoconfinement

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Abstract The number of polymer chains irreversibly adsorbed onto a solid substrate decreases systematically in films thinner than roughly ten macromolecular radii of gyration, an effect attributed to the weakening of the van der Waals interaction under nanoconfinement. Here, we demonstrate that this phenomenology has a precise spectral signature. Within our recently developed framework, the adsorption kinetics are described as a superposition of thermally activated processes, and reducing the film thickness exclusively suppresses the weight of the loop-mediated component of the rate spectrum, leaving the slowest and fastest accessible adsorption rates invariant. The apparent growth rate in the logarithmic regime decreased in proportion to the adsorbed amount and, through the effective Hamaker constant, to the film geometry. Therefore, the rate spectrum is a topological property of the polymer melt, while the amount adsorbed through each pathway is set by the depth of the interfacial potential. Temperature and film geometry act as orthogonal control parameters, tuning the kinetics and adsorbed amount independently, which provides a microscopic basis for the rational design of adsorbed polymer layers.

Keywords Polymer adsorption; Nanoconfinement; Adsorption kinetics; Rate spectrum; Thin films

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INTRODUCTION

Polymer adsorption at solid interfaces controls phenomena of technological relevance,^[1] such as adhesion,^[2] wettability,^[3,4] viscosity,^[5] molecular mobility,^[4,6–10] crystallization,^[11–15] and the long-term mechanical stability of thin-film devices and coatings.^[16,17] The chains of polymer melts deposited onto solid substrates adsorb irreversibly on timescales ranging from hours to years, forming a dense interfacial layer whose thickness h_{ads} increases with annealing time until saturation at a value h_{∞} .^[18–21] The kinetics exhibit a characteristic two-stage behavior: an initial regime of linear growth, governed by direct monomer attachment at the surface up to a crossover thickness $h_{\text{crossover}}$, followed by a pronounced slowdown^[22,23] as available adsorption sites become scarce and newly arriving chains must bridge free sites via loops of progressively increasing size,^[18,19,21,24–27] see the sketch in Fig. 1.

Over a broad intermediate time window, this slowdown manifests as an approximately logarithmic increase in h_{ads} . Logarithmic relaxation has been explained using different approaches, including the early time asymptotics of a single nonlinear relaxation equation^[28] and a uniform distribution of activation energies.^[29] Following the latter path and inspired

by a pink-noise formalism previously established for aging phenomena,^[30,31] we recently established a unified spectral interpretation of the logarithmic growth of adsorbed polymer layers.^[32] Pink noise has a power spectral density proportional to $1/f$, where f is the frequency of the observed fluctuations. In our case, each molecular adsorption event occurs at its own characteristic rate λ , and a single event mainly contributes to noise near the frequency matching its rate. Because the rates λ across all molecules are spread broadly (log-uniformly, meaning roughly equal numbers of events at each order of magnitude of λ), their combined contributions produce a total spectrum that falls off as $1/f$. We proved that the full kinetics of adsorption emerge from a superposition of thermally activated processes sharing a common activation barrier but spanning a log-uniform distribution of prefactors, with two distinct spectral components corresponding to direct monomer attachment and loop-mediated adsorption, respectively.^[32]

A central question in this context is what sets the rate at which the kinetics proceeds, which can be experimentally linked to $v = dh_{\text{ads}}/dt$, evaluated for $h_{\text{ads}} < h_{\text{crossover}}$, setting the adsorption rate in the linear regime. A recent study^[33] showed that v can be quantitatively predicted from bulk molecular dynamics alone, without any knowledge of interfacial chemistry. In the case of polymer layers grown on silicon oxide, the key molecular mechanism is the slow Arrhenius process (SAP), a localized relaxation mode observed in both polymers and small molecules,^[34–36] the thermal barrier of

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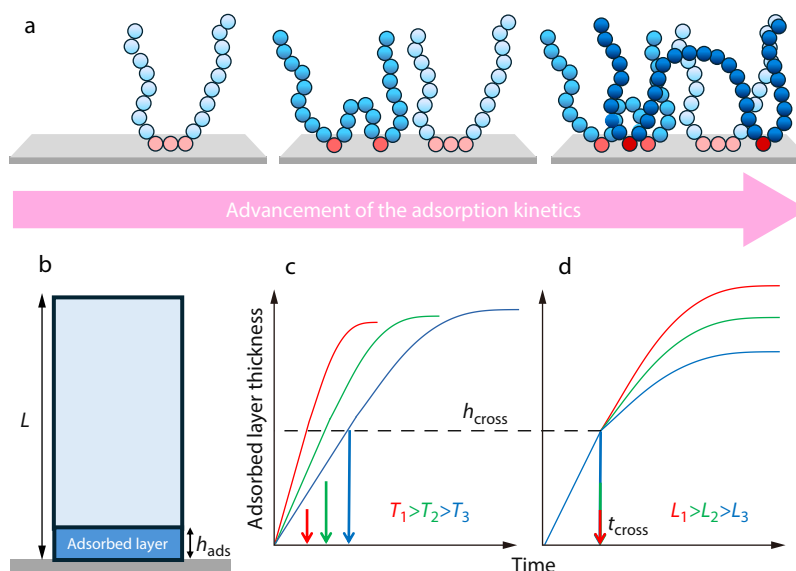


Fig. 1 Spectral origin of confinement effects on polymer adsorption kinetics. (a) Schematic representation of the evolution of chain conformations during adsorption. At short times, chains adsorb predominantly through direct monomer attachment, forming flat train-rich structures (channel 1). As adsorption proceeds and available surface sites become scarce, the interfacial layer grows through the incorporation of loops of progressively increasing size (channel 2). (b) Schematic of the sample geometry, with a film of thickness L and an adsorbed layer of thickness h_{ads} . (c) Sketch of the adsorption kinetics as a function of the temperature of the experiment. Increasing temperature accelerates the kinetics and shifts t_{cross} to shorter times, while leaving h_{cross} and h_{∞} basically unchanged. (d) Sketch of the adsorption kinetics as a function of the whole film thickness, L . Reducing L leaves the early-stage kinetics and h_{cross} invariant, while suppressing the saturation adsorbed amount h_{∞} .

which matches that of adsorption across a broad range of chemically distinct systems. Within this framework, the surface only acts as a geometrical factor. Experiments verified that the number of chains present near the interface per unit area scales as $\rho N^{-1/2}$,^[37,38] and each SAP relaxation event adsorbs a constant, chemistry-independent number of them, yielding $v = Y\rho N^{1/2}f_{SAP}(T)$, where N is the degree of polymerization, ρ is the bulk density, Y is a universal constant, and f_{SAP} is the SAP relaxation frequency,^[19,33,37] which can be predicted from a simple thermodynamic characterization of polymer melts.^[39,40] Crucially, this model exclusively describes the non-equilibrium, short-time growth of the adsorbed layer. At long times, the kinetics eventually saturate at h_{∞} , the value of which is determined by the depth of the interfacial potential,^[21,41] a parameter that the model is not designed to predict.

However, testing the effect of interfacial interactions on adsorption is nontrivial. The most direct approaches, comparing the same polymer on chemically distinct substrates or the same substrate with different polymers, are both complicated by uncontrolled variables. In the former case, the substrate roughness varies across materials and is known to influence the adsorption independently of the interfacial potential.^[19,42–45] In the latter, the total polymer-substrate interaction decomposes into dispersive and polar components that vary simultaneously across pairs, making it difficult to isolate the role of the interaction strength from that of the chemical specificity.^[45,46] A more controlled strategy is to vary the effective interfacial interaction while keeping both the polymer and the substrate fixed. This condition can be achieved by exploiting the geometry of the polymer coating. In a thin polymer layer deposited on a solid substrate, the long-range van der Waals interaction between the polymer and substrate is

screened by the proximity of the polymer-air interface, and its strength therefore depends on the film thickness L . Changing L modifies the interfacial potential in a quantifiable way through the effective Hamaker constant A_{eff} , without introducing any chemical change to the system; more negative values of A_{eff} yield a larger adsorbed amount. When L is reduced below approximately $7R_g$ – $10R_g$, h_{∞} drops substantially below its bulk value^[46,47] reflecting the reduction in the absolute value of A_{eff} as the two interfaces approach each other. Bilayer experiments, in which A_{eff} is tuned by a capping layer without altering L , confirm that h_{∞} depends on A_{eff} alone, and not on the specific film geometry.^[46] Strikingly, v and h_{cross} are unaffected by L , which is consistent with the physical framework described by Thoms *et al.*^[33] where the adsorption rate is insensitive to interfacial interactions. The selective action of interfacial interactions on h_{∞} alone, leaving v and the entire kinetic pathway unchanged,^[46] points to a clean separation between the thermodynamic and dynamical aspects of adsorption, whose spectral content has not been characterized.

Here, we analyze the adsorption kinetics of polymer melts at fixed temperatures for films of varying thickness and find that one-dimensional confinement leaves the full hierarchy of adsorption rates unchanged, while uniformly reducing the amount of material deposited through each loop-mediated pathway. Within the spectral framework, this reduction manifests as a suppression of the spectral weight of the loop-mediated component, with the logarithmic slope of the kinetics scaling linearly with the effective Hamaker constant, whereas the slowest and fastest adsorption rates remain invariant. Therefore, the range of loop sizes accessible to the chain at the interface is governed by chain connectivity and entropic constraints alone, independent of the strength of the polymer-substrate interaction. Our results establish that the hier-

archy of adsorption timescales is a topological property of the chain, whereas the amount of material deposited at each timescale is set by the depth of the interfacial potential. Because these two aspects respond to independent physical controls, the equilibrium adsorbed amount can be tuned through the sample geometry without modifying the kinetics themselves; conversely, the kinetics can be accelerated by temperature without affecting the final adsorbed amount.

SPECTRAL DESCRIPTION OF ADSORPTION KINETICS

In this section, we summarize the spectral framework for the adsorption of polymer melts introduced by Di Leva *et al.*^[32] The adsorbed amount $\Gamma(t)$, which provides the number of chains adsorbed per unit surface, is written as a superposition of independent adsorption channels, each characterized by a spectral density $P^{(i)}(\lambda)$:

$$\Gamma(t) = \sum_i \int [1 - e^{-\lambda t}] P^{(i)}(\lambda) d\lambda \quad (1)$$

where index i labels distinct adsorption regimes with different spectral structures and λ is the rate associated with each elementary process. The adsorbed amount is experimentally tracked through the thickness of the adsorbed layer h_{ads} , which is proportional to Γ , and is measured (e.g., via ellipsometry or atomic force microscopy) after the removal of non-adsorbed chains.^[18,37] For polymer melts, we identify two sequential adsorption channels. Channel (1) governs the early stage, in which the direct monomer attachment builds the adsorbed layer linearly from h_0 (≈ 0 nm) at short times to h_{cross} at the crossover time t_{cross} . Beyond t_{cross} , channel (2) takes over, as adsorption proceeds through the progressive incorporation of loops into the interfacial layer, giving rise to characteristic logarithmic growth. In this late-time regime, the available surface sites where adsorption is possible are scarce and the growth of the interfacial polymer layer is mediated by loops of progressively increasing size.^[24–26] Although the transition between the two regimes is physically smooth, we adopt a minimal description and model it as abrupt on a logarithmic timescale through a sum of Heaviside step functions H , defined as $H(x) = 0$ for $x < 0$ and $H(x) = 1$ for $x \geq 0$. Based on these hypotheses, Eq. (1) expands into an explicit form:

$$\Gamma(t) = \Gamma_1(\min(t, t_{\text{cross}})) + H(t - t_{\text{cross}}) \Gamma_2(t - t_{\text{cross}}) \quad (2)$$

Switching to h_{ads} as the observable leads to two sequential spectral components,^[32]

$$P^{(1)}(\lambda) = \frac{h_{\text{cross}} - h_0}{\lambda_{\text{max}}^{(1)} - \lambda_{\text{min}}^{(1)}} H(\lambda_{\text{max}}^{(1)} - \lambda) H(\lambda - \lambda_{\text{max}}) \quad (3)$$

$$P^{(2)}(\lambda) = \frac{h_{\infty} - h_{\text{cross}}}{\ln(\lambda_{\text{max}}/\lambda_{\text{min}})} \frac{1}{\lambda} H(\lambda_{\text{max}} - \lambda) H(\lambda - \lambda_{\text{min}}) \quad (4)$$

where $P^{(1)}$ is a flat distribution over the interval $[\lambda_{\text{max}}^{(1)}, \lambda_{\text{min}}^{(1)}]$ and $P^{(2)}$ follows a $1/\lambda$ law over $[\lambda_{\text{min}}, \lambda_{\text{max}}]$. Equivalently, in channel (2), each logarithmic interval of adsorption rates contributes equally to the overall adsorption kinetics over $[\lambda_{\text{min}}, \lambda_{\text{max}}]$, as $\lambda^{-1} d\lambda = d\ln\lambda$. Here, $(\lambda_{\text{max}}^{(1)})^{-1}$ is the shortest timescale at which a measurable increase in adsorbed amount can be detected, $\lambda_{\text{max}}^{-1}$ marks the crossover time via $\lambda_{\text{max}} t_{\text{cross}} \sim 1$ and is shared as the boundary between the two spectral components, and $\lambda_{\text{min}}^{-1}$ sets the

time beyond which all accessible modes have relaxed, at which h_{ads} reaches its maximum value h_{∞} . Note that λ_{min} is not identified with a specific polymer relaxation rate (e.g., Rouse, Zimm, or reptation rate). Instead, it is defined as the slowest adsorption rate in the adsorption spectrum, corresponding to the largest loop conformations that remain statistically accessible before the adsorbed layer reaches saturation. The logarithmic width $\ln(\lambda_{\text{max}}/\lambda_{\text{min}})$ encodes the range of accessible loop conformations and is determined by chain topology alone. The distribution of the form $P(\lambda) \sim 1/\lambda$, characteristic of pink-noise spectra, naturally leads to logarithmic time dependencies in a wide range of disordered and out-of-equilibrium systems.^[30,48–51] Substituting $P^{(1)}$ into Eq. (1) and expanding the kernel at short times yields linear kinetics,

$$h_{\text{ads}}(t) \approx h_0 + vt \quad (5)$$

with a constant rate v ,^[18] which is consistent with the early time regime in which surface coverage is low and adsorption proceeds through direct monomer attachment. Substituting $P^{(2)}$ into Eq. (1) gives

$$h_{\text{ads}}(t) = h_{\text{cross}} + (h_{\infty} - h_{\text{cross}}) \frac{\int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} (1 - e^{-\lambda(t-t_{\text{cross}})}) \frac{d\lambda}{\lambda}}{\ln(\lambda_{\text{max}}/\lambda_{\text{min}})} \quad (6)$$

In the intermediate window $\lambda_{\text{max}}^{-1} \ll t - t_{\text{cross}} \ll \lambda_{\text{min}}^{-1}$, where the fastest modes have already relaxed and the slowest remains effectively frozen, Eq. (6) reduces to logarithmic growth:

$$h_{\text{ads}}(t) \approx h_{\text{cross}} + C \ln[(t - t_{\text{cross}})/t_0] \quad (7)$$

where $t_0 = 1$ s ensures dimensional consistency, and $C = (h_{\infty} - h_{\text{cross}})/\ln(\lambda_{\text{max}}/\lambda_{\text{min}})$ measures the total spectral weight of $P^{(2)}$ normalized by the logarithmic width of the rate distribution. We stress that the choice of t_0 is a simple and convenient convention that does not affect the logarithmic slope C . The value extracted experimentally from the logarithmic slope of the kinetics is the lower bound of its asymptotic value. When $\lambda_{\text{max}}/\lambda_{\text{min}}$ is not sufficiently large, the two spectral edges overlap in time, and the observable slope falls below C , although this deviation can be quantified analytically.^[32] Both spectral cutoffs can be extracted directly from the experimentally accessible quantities v , h_{cross} , h_{∞} , and C without fitting the full kinetic expression:^[32]

$$\lambda_{\text{max}} \approx v/h_{\text{cross}}, \quad \lambda_{\text{min}} \approx (v/h_{\text{cross}}) \exp\left(-\frac{h_{\infty} - h_{\text{cross}}}{C}\right) \quad (8)$$

and these relations form the basis of the analysis presented below.

THICKNESS DEPENDENCE AND SPECTRAL PREDICTION

Experiments on films of polystyrene, poly(methyl methacrylate), poly(4-*tert*-butylstyrene), and poly(4-methylstyrene) deposited on silicon oxide have shown that the adsorption kinetics are independent of L up to the crossover time t_{cross} , with the linear growth rate v and the crossover thickness h_{cross} taking the same values regardless of the amount of material available above the substrate.^[19,46] However, beyond t_{cross} , the kinetics depend on L (see Fig. 1). The approach to saturation slows down progressively as L decreases, and the equilibrium value h_{∞} is systematically reduced in thinner films.^[46] The reduction in h_{∞} was ratio-

nalized by noting that nanoconfinement modifies the depth of the interfacial potential through A_{eff} but leaves the molecular mobility unaffected.^[46] Within the framework developed by Thoms *et al.*,^[33] the insensitivity of ν to L is expected on microscopic grounds. Because $\nu(T) \sim f_{\text{SAP}}(T)$ and the SAP relaxation frequency is a bulk quantity that is not appreciably affected by confinement,^[52,53] the adsorption rate is fully determined by bulk dynamics and does not depend on the film geometry.

In spectral terms, the L -independence of ν and h_{cross} implies that *via* Eq. (8), a thickness-independent $\lambda_{\text{max}} \approx \nu/h_{\text{cross}}$, such that $P^{(1)}(\lambda)$ is identical for all film thicknesses and λ_{max} is geometry-invariant, in direct correspondence with the observed superposition of the linear growth regimes. The central question is how the reduction in h_{∞} with decreasing L is distributed between a change in spectral weight and a change in spectral support, that is, whether λ_{min} is affected by confinement.

Several physically distinct scenarios are envisaged. First, confinement could introduce a geometrical cutoff for the accessible loop sizes. In a film of finite thickness, one might expect that loops cannot grow beyond a characteristic size set by the available material; therefore, the slowest accessible adsorption mode is limited by geometry rather than by chain statistics alone. In this case, the largest loops become geometrically inaccessible, the slowest modes disappear from the spectrum, λ_{min} increases toward faster values, and $\ln(\lambda_{\text{max}}/\lambda_{\text{min}})$ decreases with L . The logarithmic slope C then decreases faster than $h_{\infty} - h_{\text{cross}}$, with the ratio $(h_{\infty} - h_{\text{cross}})/C = \ln(\lambda_{\text{max}}/\lambda_{\text{min}})$ shrinking as L is reduced. Second, a more subtle possibility arises if loop formation carries not only an entropic but also an energetic cost. If the probability of forming a loop of a given size is modulated by the depth of the interfacial potential, then the reduction in A_{eff} under confinement would reshape the rate spectrum in a nontrivial manner. In particular, if longer loops are disproportionately penalized by weaker interactions, λ_{min} increases, and the spectral width narrows as L decreases, which is qualitatively similar to the geometrical scenario.

Both scenarios predict that the spectral support $[\lambda_{\text{min}}, \lambda_{\text{max}}]$ is L -dependent and that C and $h_{\infty} - h_{\text{cross}}$ are not simply proportional, providing a clear experimental signature to distinguish them from the simpler case, in which confinement acts only on the spectral weight while leaving the rate hierarchy intact. To discriminate between these possibilities, we examined whether the ratio $(h_{\infty} - h_{\text{cross}})/C$ and the extracted value of λ_{min} remained constant across the film thicknesses. If loop-formation statistics are governed by chain topology alone, independent of the strength of the polymer-substrate interaction, then the spectral width and λ_{min} should be L -invariant, with all thickness dependence absorbed into the amplitude $h_{\infty} - h_{\text{cross}}$. If confinement reshapes the accessible rate distribution, either through a geometrical cutoff of loop sizes or through an energetic modulation of the loop formation probability, deviations from this proportionality will appear.

Under the hypothesis that $\ln(\lambda_{\text{max}}/\lambda_{\text{min}})$ is L -independent, $C(L) \propto h_{\infty}(L) - h_{\text{cross}}$, with λ_{min} remaining invariant. This prediction can be tested by examining the normalized kinetics $\tilde{h}(t) \equiv (h_{\text{ads}}(t) - h_{\text{cross}})/(h_{\infty} - h_{\text{cross}})$. From Eq. (6), $\tilde{h}$ depends on L only through the spectral support $[\lambda_{\text{min}}, \lambda_{\text{max}}]$; if that support is L -

invariant, all kinetic curves collapse onto a single master curve in $\tilde{h}$, regardless of film thickness. We stress that equivalently, the collapse can be verified without knowledge of h_{∞} . If the spectral support is L -invariant, the kinetic curves at different thicknesses differ only by the multiplicative amplitude. This condition implies that for any two thicknesses L_i and L_j a time-independent scalar $a_{ij} = (h_{\infty}(L_i) - h_{\text{cross}})/(h_{\infty}(L_j) - h_{\text{cross}})$ exists, such that $a_{ij}h_{\text{ads}}(t; L_i) - h_{\text{ads}}(t; L_j) = 0$ for all t in the logarithmic regime, which can be checked directly on the raw data without prior knowledge of h_{∞} . If these conditions were verified, nanoconfinement would then act as a uniform rescaling of the spectral weight of $P^{(2)}$. The $1/\lambda$ shape and support $[\lambda_{\text{min}}, \lambda_{\text{max}}]$ are preserved, whereas the prefactor $(h_{\infty} - h_{\text{cross}})/\ln(\lambda_{\text{max}}/\lambda_{\text{min}})$ decreases with L . Because the work of Simavilla *et al.*^[46] establishes a linear relationship between the saturation value of the adsorbed layer thickness and the Hamaker constant, and h_{cross} is L -independent, this directly implies $C(L) \propto |A_{\text{eff}}(L)|$, linking the logarithmic slope of the kinetics to the depth of the interfacial potential.

To assess the validity of these predictions, we analyzed the adsorption kinetics of polystyrene ($M_w = 1000 \text{ kg}\cdot\text{mol}^{-1}$) on SiO_2 at $T = 433 \text{ K}$ for spin-coated thicknesses $L = 130, 235$, and 325 nm (data from Ref. [46]). First, we tested whether the data rescale as predicted. At short timescales, exploiting the thickness-independent overlap of the early-stage kinetics, we performed a global fit and obtained $\nu = (5.4 \pm 0.8) \times 10^{-4} \text{ nm}\cdot\text{s}^{-1}$, consistent with the values extracted from individual datasets; $\nu_{325} = (5.3 \pm 0.8)$, $\nu_{235} = (5.6 \pm 0.7)$, $\nu_{130} = (5.3 \pm 0.5)$, all values expressed in $10^{-4} \text{ nm}\cdot\text{s}^{-1}$. At longer timescales, in agreement with Simavilla *et al.*, we identified a common crossover point $(t_{\text{cross}}, h_{\text{cross}})$ beyond which the kinetics became thickness-dependent, confirming that $\lambda_{\text{max}} \approx t_{\text{cross}}^{-1}$ is confinement-invariant. We then verified whether the post-crossover kinetics collapses onto a master curve by plotting the data in terms of the normalized thickness $\tilde{h}(t)$, defined above, going from zero at h_{cross} to unity at h_{∞} (see Fig. 2). The observed collapse confirms the confinement invariance of λ_{min} and λ_{max} , and we determined their values by fitting the normalized data to

$$\tilde{h}(t) = \frac{\int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} (1 - e^{-\lambda(t-t_{\text{cross}})}) \frac{d\lambda}{\lambda}}{\ln(\lambda_{\text{max}}/\lambda_{\text{min}})} \quad (9)$$

where λ_{min} and λ_{max} are free parameters. The results are shown in Fig. 3 together with the spectral representation of the adsorption kinetics in the lower panels. Consistent results were obtained for the other polymer systems.

DISCUSSION

The invariance of λ_{min} and λ_{max} across all three film thicknesses rules out the aforementioned alternative scenarios. A geometrical cutoff on accessible loop sizes causes λ_{min} to increase systematically as L decreases, shrinking the ratio $(h_{\infty} - h_{\text{cross}})/C = \ln(\lambda_{\text{max}}/\lambda_{\text{min}})$. A size-dependent modulation of the loop formation rate by the interfacial potential would instead deform the spectral shape away from $1/\lambda$ and again shift λ_{min} with L . Neither effect was observed. Confinement acts exclusively on the prefactor C , rescaling the spectral weight of $P^{(2)}$ uniformly without altering the rate hierarchy (see inset of Fig. 3).

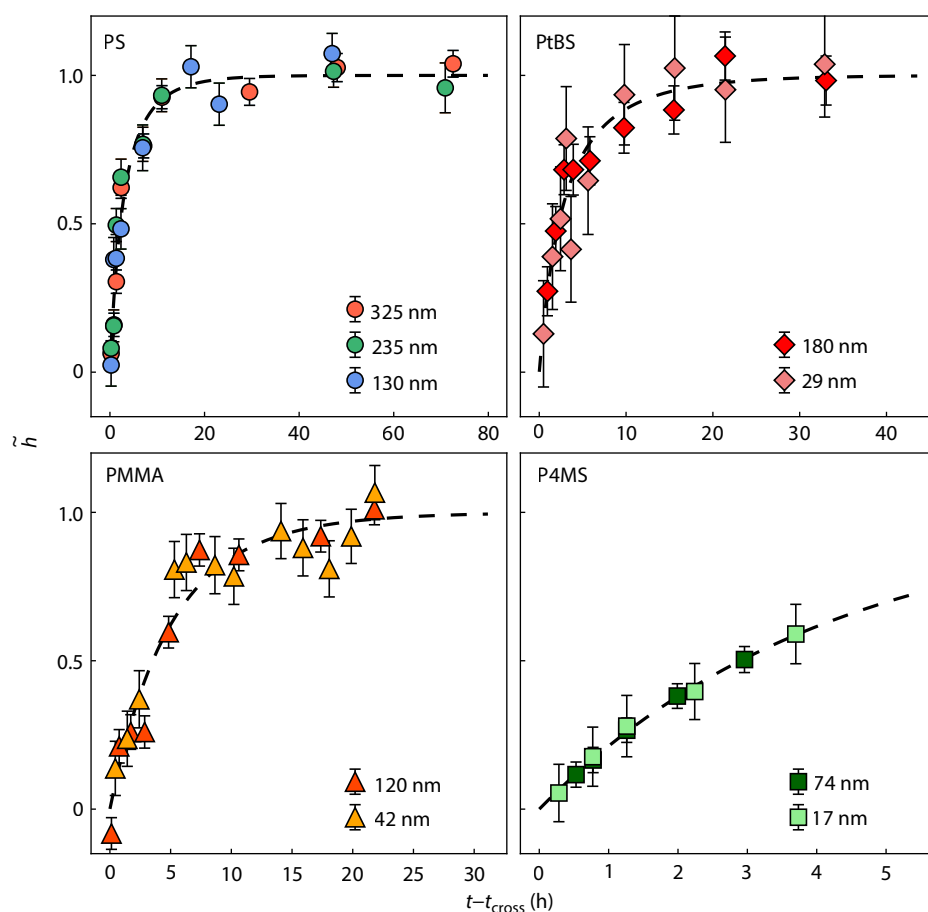


Fig. 2 Normalized adsorption kinetics $\bar{h}(t)$ for four polymers deposited on silicon oxide: polystyrene (PS), poly(4-*tert*-butylstyrene) (PtBS), poly(methyl methacrylate) (PMMA), and poly(4-methylstyrene) (P4MS), measured at different film thicknesses L (indicated in the legend of each panel). The time axis is shifted by t_{cross} to align the onset of the loop-mediated regime. Data collected at different L collapse onto a single master curve in each panel, confirming that the spectral support $[\lambda_{\text{min}}, \lambda_{\text{max}}]$ is L -invariant. The dashed line is the fit to Eq. (9), with λ_{min} and λ_{max} as the only free parameters (data from Ref. [46]).

The physical origin of this separation lies in the decoupling between the conformational statistics of the loops and interfacial potential. The $1/\lambda$ spectrum encodes the conformational landscape accessible to the chain, with each decade of timescale λ^{-1} corresponding to a family of loops, whose relative abundance is set by chain connectivity alone. The interfacial potential controls the overall adsorption yield without reshaping the landscape. Therefore, reducing $|A_{\text{eff}}(L)|$ under confinement suppresses all adsorption pathways by the same factor, leaving the spectral bounds $[\lambda_{\text{min}}, \lambda_{\text{max}}]$ as properties of the chain rather than of the substrate.

The orthogonality between the temperature and geometry as control parameters has direct practical consequences. Properties such as the glass transition temperature,^[54–57] crystallization rate,^[58–60] molecular mobility,^[6–8] and viscosity of thin polymer coatings^[5] are governed by h_{ads} , which can be tuned through the sample geometry without altering the adsorption timescales. Conversely, the time required to reach h_{∞} can be accelerated by temperature without affecting the final adsorbed amount. The spectral framework quantifies this independence. More generally, any experimental handle that modifies A_{eff} without perturbing the chain topology (substrate dielectric environment, capping layer composition,

polymer-substrate chemical affinity within the same van der Waals class, etc.) would shift C while leaving $[\lambda_{\text{min}}, \lambda_{\text{max}}]$ invariant. Modifications that alter the entropic or enthalpic cost of loop formation, such as changes in chain stiffness or molecular weight, are expected to shift λ_{min} and λ_{max} while leaving the proportionality $C \propto |A_{\text{eff}}|$ intact. Regardless of the extent of confinement, a separate consideration applies to the presence of solvent molecules, which screen excluded-volume interactions and thus change the scaling exponent governing loop statistics. Such screening breaks the logarithmic kinetics in dilute solutions, whereas concentrated solutions, where near-ideal statistics are restored, are expected to be retained. Future work should test this crossover experimentally, although we anticipate that experimental uncertainties may obscure the sharp boundary between the two limiting regimes.

CONCLUSIONS

We showed that nanoconfinement modifies the adsorption kinetics of polymer melts exclusively through the spectral weight of the loop-mediated component, leaving the rate spectrum support invariant. At longer times, the apparent growth rate

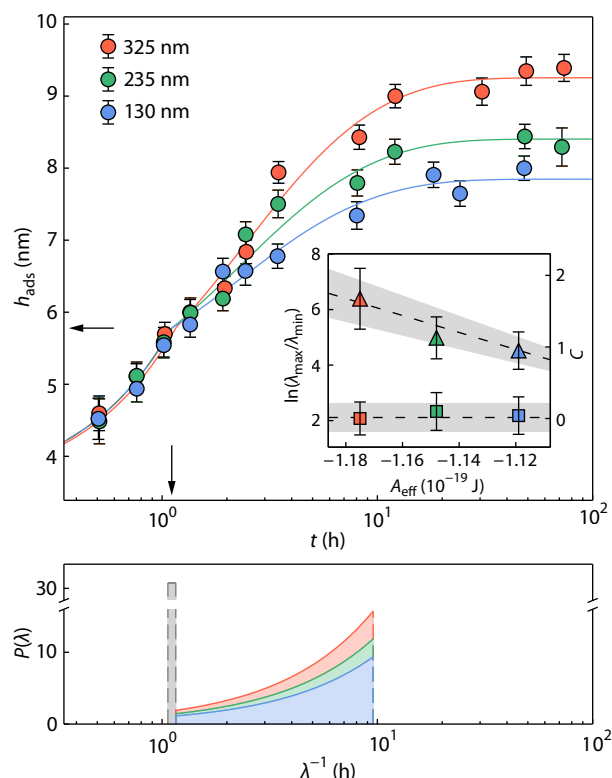


Fig. 3 Top panel: adsorption kinetics of polystyrene on SiO₂ at three film thicknesses (data from Ref. [46]). Solid lines are fits to Eq. (6), with ν , h_0 , h_{cross} , and λ_{max} constrained to be L -independent and h_{∞} and C extracted individually for each thickness. Arrows mark h_{cross} (horizontal) and t_{cross} (vertical). Inset: values of $\ln(\lambda_{\text{max}}/\lambda_{\text{min}})$ (squares) and C (triangles) extracted from individual fits, plotted as a function of the effective Hamaker constant A_{eff} . The gray bands show the results of the global fit constrained across all thicknesses, with the shaded width indicating the fit uncertainty. While C decreases with $|A_{\text{eff}}|$, $\ln(\lambda_{\text{max}}/\lambda_{\text{min}})$ remains constant, confirming that confinement acts exclusively on the spectral weight. Bottom panel: spectral representation $P(\lambda)$ of the adsorption kinetics for the three film thicknesses, constructed from the fitted parameters. The shared λ_{max} (gray dashed line) and the common λ_{min} (blue dashed line) confirm the L -invariance of the spectral support $[\lambda_{\text{min}}, \lambda_{\text{max}}]$. For clarity, $P(\lambda)$ is plotted on a linear vertical scale to facilitate comparison among the three film thicknesses. Note that $P(\lambda)$ remains linear with λ^{-1} .

scales linearly with the effective Hamaker constant, which depends on the sample geometry, whereas the spectral bounds λ_{min} and λ_{max} are not affected by nanoconfinement. The hierarchy of adsorption timescales is, therefore, a topological property of the chain, whereas the amount of material deposited at each timescale depends on thermodynamics. The temperature and film geometry act as orthogonal control parameters, independently tuning the kinetics and adsorbed amount. More generally, in systems where the rate spectrum is generated by chain statistics, the strength of the driving interaction governs only the amplitude of that spectrum and not its structure.

Conflict of Interests

The authors declare no interest conflict.

Data Availability Statement

The experimental data are available in Ref. [46]. Fits to these data are shown as solid lines in Figs. 2 and 3. No additional experimental data were generated as part of this work.

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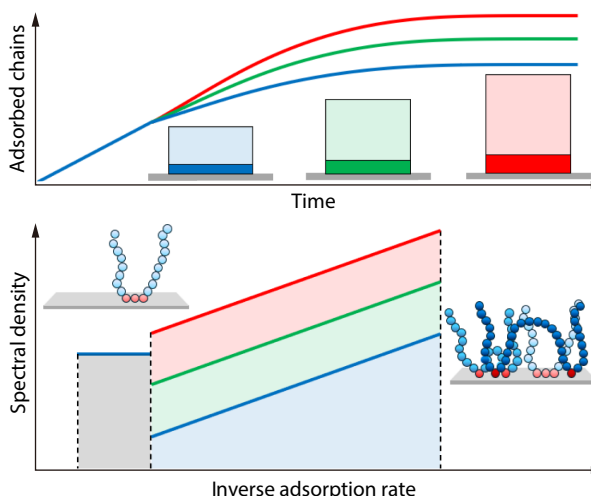
Graphical Abstract

A Spectral View of Polymer Adsorption under Nanoconfinement

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By applying a rate spectral description of polymer adsorption, this study reveals that nanoconfinement suppresses only the spectral weight of loop-mediated adsorption while preserving the rate spectrum. Adsorption is thereby reduced to two orthogonal controls, with interfacial thermodynamics governing the spectral weight and chain topology determining the spectral support.



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