Simple Model to Predict the Adsorption Rate of Polymer Melts

Erik Thoms, Zijian Song, Kai Wang, and Simone Napolitano*
Laboratory of Polymer and Soft Matter Dynamics, Experimental Soft Matter and Thermal Physics (EST),
Université libre de Bruxelles (ULB), Brussels 1050, Belgium

(Received 16 November 2023; revised 16 February 2024; accepted 16 May 2024; published 14 June 2024)

We determine the adsorption rate of polymer melts by means of measurements of molecular mobility. We show that the complex set of molecular rearrangements involved in the adsorption of polymers on flat surfaces can be modeled as an equilibration kinetics driven by the slow Arrhenius process (SAP), a recently discovered molecular mechanism. Our predictive model is based on the single hypothesis that the number of chains adsorbed per unit surface within the timescale of spontaneous fluctuations associated to the SAP is a temperature-invariant constant, not depending on the chemical structure of the polymer. Going beyond the qualitative arguments setting a correlation between equilibrium and nonequilibrium properties, we demonstrate that the rate at which an adsorbed layer grows does not depend on interfacial interactions. By considering simple physical arguments, we demonstrate that this quantity can be straightforwardly determined using the energy barrier of molecular motion as only input.

DOI: 10.1103/PhysRevLett.132.248101

The number of contacts made by molecules of neighboring phases is a key parameter in determining the macroscopic properties of hybrid materials, such as nanocomposites and thin coatings [1]. As a complete microscopic description of the interface is not always available, in the case of adsorbing media, for practical purposes, the number of contacts can be substituted by the adsorbed amount—meaning, the number of molecules adsorbed per unit surface—or, equivalently, in the case of polymer melts, by the thickness of the layer of adsorbed molecules, h_{ads} [2]. Over the past decade or so, a series of correlations between these quantities and relevant materials properties such as wettability [3,4], gas carrying capacity [5], crystallization rate [6], viscosity [7], molecular mobility [8] and glass transition temperature [9], have been identified in polymer melts. These results, achieved via a simple physical approach (thermal annealing), are comparable to those obtained by more cumbersome procedures, requiring chemical modifications [10]. On the other hand, polymer adsorption can be exploited to modify surface chemistry, for example, in the case of sensors based on the nanopore geometry [11] or devices for macromolecular pattern recognition [12]. Despite the possibility to adjust the desired properties of polymers, a rigorous understanding of the processing-property relations at the molecular level is currently lacking. Controlling whole film properties by varying the adsorbed amount requires knowing the rate at which the adsorbed layer grows.

Determining the rate at which polymer chains adsorb is, anyway, particularly challenging. Adsorption of polymer melts presents, in fact, some peculiarities, which complicate the development of quantitative models. Other than for

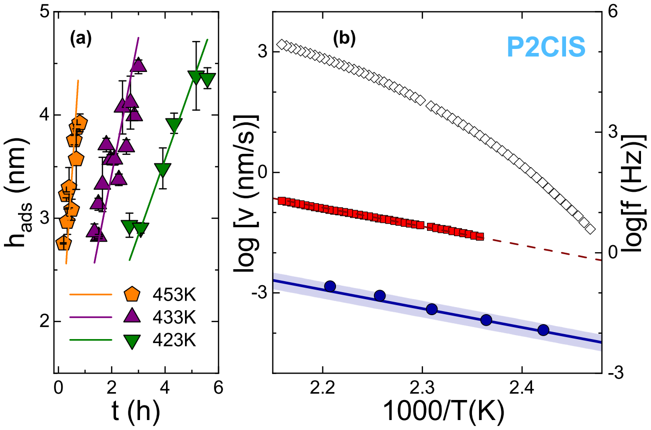

FIG. 1. (a) Kinetics of adsorption of poly(2-chloro styrene) at selected temperatures. Symbols are measured data, while continuous lines provide the expected time evolution of h_{ads} based on the values of v, as predicted by our model and using the value of Υ, see Eq. (2), obtained from measurements conducted on the polymers listed in Fig. 2; see Fig. S2 for more information on the kinetics [13]. (b) The experimental values of the adsorption rates (blue circles) are shown together with molecular rates of the SAP (red squares) and the α-process (white diamonds); the logarithm of these quantities is plotted as a function of the inverse temperature, because in such representation straight lines correspond to constant activation barriers. The continuous blue line depicts the predictions of Eq. (2), with the shaded area indicating 1 standard deviation. The dashed red line provides the temperature dependence of the relaxation rate of the SAP according to an Arrhenius equation $f_{\mathrm{SAP}}(T) = f_0 \exp(-E_{\mathrm{SAP}}/RT)$, with $E_{\mathrm{SAP}} = 90$ kJ/mol and $\log(f_0/\mathrm{Hz}) = -12.24$.

small molecules, because of connectivity, polymer melts can irreversibly adsorb even when the monomer-wall interactions do not exceed the thermal energy, $k_{\mathrm{B}}T$ (with the Boltzmann constant k_{B} and the temperature T) [20]; importantly, the amplitude of the interactions becomes irrelevant as soon as surface affinity exceeds the small threshold necessary to ensure irreversible adsorption [21]. As a consequence, the adsorption rate cannot be easily parametrized in terms of the interfacial potential [22]. Furthermore, other than in dilute solutions and upon imbibition in nanopores [23], adsorption of polymer melts does not require diffusion of macromolecules through the solvent towards the substrate [16]. Adsorption is, nevertheless, not immediate. Molecules already present at the interface need to rearrange before getting pinned onto the substrate: the whole process can get extremely slow [24,25]. For polymer melts deposited on silicon oxide, one of the most used materials in microelectronics [26], formation of a stable adsorbed layer can take up to several days even at temperatures well above the glass transition [17]. These large timescales are commonly associated with the complex set of movements necessary to adsorb large molecules in a crowded environment [27,28]. Chains arriving at later times need to stretch and form longer loops, because the empty spots—where adsorption is still possible—might be available only at distances exceeding several monomer sizes [20]. Additionally, incorporating new chains into the adsorbed layer often involves desorption of monomers appertaining to molecules that adsorbed at an earlier time. Because of that, the overall timescale of adsorption increases with the probability of monomer desorption, which is an exponential term of the monomer-wall interaction [29].

From a kinetic perspective, this complex set of molecular rearrangements can be treated as an equilibration kinetics, and adequately modeled by identifying the molecular process whose thermal barrier matches that of adsorption. This commonly used procedure—based on the intimate link between nonequilibrium and equilibrium properties of a system [30]—requires expressing the rate, at which a physical quantity (e.g., h_{ads}) evolves towards a steady state, in terms of the rate at which molecules spontaneously fluctuate. For example, the stability of amorphous pharmaceuticals is usually predicted based on measurements of the structural (α-)process [31], while the mechanical response of bulk metallic glasses is attributed to so-called β-relaxation [32]. Similarly, recent work [33] shows a correlation between adsorption and slow relaxation modes—namely, the slow Arrhenius process, SAP—present in the liquid dynamics: the timescale of adsorption can be written as a multiple of τ_{SAP}, the characteristic time of the molecular rearrangements associated with this process. This reasoning corresponds to a scaling law of the type $[\mathrm{d}h_{\mathrm{ads}}/\mathrm{d}(t/\tau_{\mathrm{SAP}})] \sim$ const, see Supplemental Material, Fig. S1 [13].

Here, we introduce a methodology capable of going beyond these qualitative arguments and to quantitatively predict equilibration rates, using, as only input, the energy barrier of spontaneous fluctuations. Simple physical arguments allowed us to determine the numerical constant necessary to convert the rate at which the SAP spontaneously relaxes into the rate at which an adsorbed polymer layer grows upon time. Application of this approach to a broad class of commonly employed polymers provides unique information on the physics of interfacial layers: We show that the number of chains adsorbed per unit surface within τ_{SAP} is a constant that does not depend on temperature or on the chemical structure.

At sufficiently short times t, adsorption is not affected by surface coverage and can be described by a zero-order reaction mechanism [16]. These conditions lead to a linear kinetics and to a straightforward determination of the adsorption rate, $v = \mathrm{d}h_{\mathrm{ads}}/\mathrm{d}t$. While the same rate can still describe the overall kinetics, at later times the effective increase in adsorbed amount smoothly decays to zero as the kinetics reach a stable state [17]. In Fig. 1(a), we show the time evolution of h_{ads} upon adsorption of molecules of poly (2-chlorostyrene) (P2ClS) on silicon oxide, at different temperatures; see Supplemental Material for details on sample preparation and on the experimental procedures involved in the characterization of adsorbed layers [13]. Adsorption speeds up as temperature increases, which indicates that, as expected, the phenomenon is governed by molecular mobility rather than by an interfacial potential. Such incremental change with temperature is, however, much smaller than what would be expected assuming a coupling between adsorption and the α-modes, the mechanism commonly responsible for the equilibration of polymer melts. The mismatch in the activation barriers ($= -R\partial \ln v/\partial T^{-1}$, where R is the gas constant) of the two mechanisms is indeed—by far—too large in this temperature range ($E_{\mathrm{ads}} = 99 \pm 5$ kJ/mol for adsorption vs $160 < E_{\alpha} < 430$ kJ/mol for the α-process, see Fig. S3 [13]). On the other hand, we observe a better match with the activation barrier of the slow Arrhenius process ($E_{\mathrm{SAP}} = 90 \pm 1$ kJ/mol), a relaxation process found in dielectric spectra of P2ClS. This molecular mode, which can be detected both in polymers and in small molecules [34], is connected to a multitude of equilibration phenomena [33], such as physical aging [35], dewetting [36], reentanglement, and the formation of the liquid phase upon melting of polymer crystals [37].

The SAP involves small scale rearrangements of independent entities. Collective relaxation of these noninteracting entities allows overcoming molecular barriers similar to those of high temperature flow [38]. While this mechanism might not be efficient in mass transport over length scales exceeding the monomer size, the localized rearrangements associated with this process (e.g., trans/gauche conformational transitions) are sufficient at small enough distance from the interface to bring in molecules that can eventually get pinned onto the adsorbing substrate. Following this framework, we expect that v is proportional to $f_{\mathrm{SAP}}[\sim\tau_{\mathrm{SAP}}^{-1} \sim \exp(-E_{\mathrm{SAP}}/RT)]$, the frequency at which the material relaxes via the SAP. Importantly, this quantity can be directly obtained via an impedance analyzer, in a model free approach, as the maximum of a peak in the dielectric susceptibility [18]; see Supplemental Material for the further information on the experimental procedure used to investigate the SAP dynamics [13]. The T dependence of the adsorption rate can, hence, be expressed as

$$v = v_0 \exp\left(-\frac{E_{\mathrm{SAP}}}{RT}\right). \qquad (1)$$

At present, no theory can predict the exact value of the adsorption rate: the preexponential factor, v_0, remains an elusive quantity. A parametrization of v_0 would require a microscopic model assessing how many molecules get adsorbed per unit surface and unit time. Our approach is capable of determining this parameter based on measurements of the SAP molecular mobility only, meaning without performing measurements of the adsorbed amount. Importantly, the latter type of experiments requires just a few hours and one single sample, while a direct measurement of v involves preparing and processing several polymer films, leading to experimental times easily exceeding several weeks.

To understand how many molecules get adsorbed per unit surface and unit time, we make one simple hypothesis: the SAP acts as internal clock of the material, and each time this process relaxes, a constant number of molecules gets adsorbed. Here, we are assuming that the number of monomers involved in the conformational transition and required to adsorb is temperature independent, which is in line with the Arrhenius character of the process. The hypothesis also anticipates that the length scale over which molecules get rearranged does not (significantly) depend on the chemical nature of the system, meaning that the SAP is a very localized process. To achieve a quantitative picture, we consider that, for a chain of polymerization index N, the probability [14,17] that a monomer is present at the interface for a flat substrate is proportional to $\rho N^{-1/2}$, where ρ is the bulk density. A straightforward way to determine the number of chains adsorbed per unit space in experiments is given by measurements of h_{ads}, an operational parameter proportional to the mass of all the monomers present in the adsorbed layer, meaning both those in direct contact with the substrate ($\sim N^{-1/2}$) and those indirectly adsorbed ($\sim N$). This implies that the apparent adsorption rate grows as $N^{1/2}$, as verified by experiments [17]. Our reasoning provides a quantitative expression of the adsorption rate

$$v(\rho, N, T) = \Upsilon \rho N^{\frac{1}{2}} f_{\mathrm{SAP}}(T), \qquad (2)$$

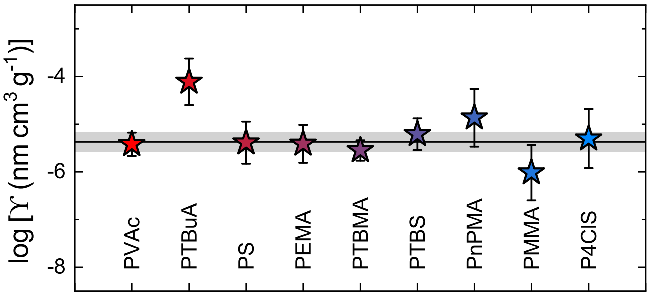

FIG. 2. Value of the parameter Υ for the investigated polymers, see Supplemental Material for the full names [13]. The black horizontal line and the shaded area, respectively, indicate the mean value and the standard deviation of Υ, obtained by averaging 57 individual measurements performed for all systems, excluding PTBuA and PMMA, in a temperature range of 165 K. Please note that, although P2ClS was not considered in this statistics, we could predict its adsorption rate based on this dataset.

where Υ is a constant expressed in units of length over mass density. In the metric of Eq. (2), $\log(\Upsilon)$ expresses the orders of magnitude separating the rate at which adsorbed layers grow ($\approx 10^{-3}$–10^{-5} nm/s, in the temperature range of the experiments) and that at which the SAP relaxes ($\approx$1–100 Hz). If our hypothesis is valid, Υ should not depend on the chemical structure of the polymer or the temperature of the experiment. To assess the strength of this assumption, we verified that for different commonly employed polymers (see Fig. 2), the ratio $v_0/(\rho N^{1/2} f_0)(=\Upsilon)$ is constant; here f_0 is the preexponential factor of $f_{\mathrm{SAP}}(T)$. The lack of T dependence of Υ is further assessed in the Supplemental Material, see Fig. S4 [13]. We stress that, because evaluating the product $\rho N^{1/2} f_{\mathrm{SAP}}$ does not require adsorption experiments, knowing the value of v for one single polymer at one single temperature would be sufficient to determine the adsorption rate of other polymers at different temperatures.

To show the strength of our approach we plug in the mean value of Υ from the dataset in Fig. 2 in Eq. (2) and compare, see Fig. 3, its predictions (lines) with the experimental values (full points) of polymers for which we could obtain f_{SAP} from dielectric data. The same value of Υ was also used to predict the adsorption rates used to reproduce the kinetics in Fig. 1(a). The agreement between our prediction and the experimental results is impressive. For nine systems, we recover the experimental trend within 1 standard deviation by using the same value of Υ. We stress that these polymers have significantly different affinity with the substrate. The binding energy between silicon oxide and PMMA segments is 4 times greater than with PS segments ($\approx 1 k_B T$) [39], which implies that interfacial chemistry does not play a significant role in the formation of adsorbed layers. We also note that, although we can still catch the correct activation barrier,

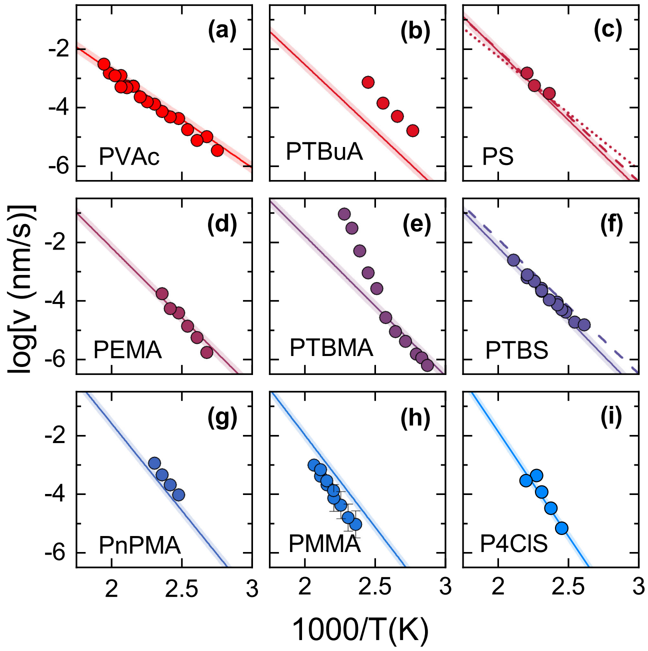

FIG. 3. For 9 different polymers, we provide the logarithm of the adsorption rate determined by experiments (symbols) as a function of the inverse temperature. The continuous lines depict the predictions of Eq. (2), with the shaded area indicating 1 standard deviation. We stress that the uncertainties on modeled quantities are often smaller than those associated to the experimental determination of v. The deviations at high temperatures for the adsorption rate of PTBMA, panel (e), are due to its enslavement to the α process [33]. Additionally, we include the predictions of the adsorption rate based on E_{SAP} values obtained through aging (dashed lines, PS and PTBS) and dewetting (dotted line, PS) experiments *via* the SAP compensation law, parametrized as $\ln(f_0/Hz) = 0.9 + E_{\mathrm{SAP}}/(3.6\ \mathrm{kJ/mol})$ [38].

for PTBuA [see Fig. 3(b)], Eq. (2) underestimates v_0 by more than a factor 10. This trend indicates that while the SAP is still the molecular process driving the formation of the adsorbed layer, the density of contacts made by this polymer with the substrate must be significantly different than for other systems, invalidating the approximations used to derive Eq. (2). Nevertheless, by using the value of Υ found in Fig. 2 as a reference, one achieves precious information on the formation of interfaces also in this system: with respect to the other polymers, a smaller number of contacts is sufficient to incorporate chains of PTBuA in the adsorbed layer, which consequently grows faster than expected.

Importantly, our approach allows estimating the value of the adsorption rate also when dielectric measurements are not available. A recent work [38] has, in fact, highlighted a linear relation between $\ln(f_0)$ and E_{SAP}, a trend due to an entropy-enthalpy compensation behavior (see Fig. S5 [13]) observed in a large number of different systems [40]. Such a property enables one to obtain $f_{\mathrm{SAP}}(T)$ by simply knowing its thermal activation barrier, e.g., through equilibration experiments [33,37]. To illustrate the potential of this method, we added to Fig. 3 the values of adsorption rate predicted employing values of E_{SAP} obtained via measurements of physical aging [33,41] and dewetting [36,42], i.e., equilibration mechanisms mediated by the SAP. While using dielectric data can reproduce more accurately the experimental values of the adsorption rate, the predictions achieved by using other equilibration pathways are, nevertheless, very accurate. Finally, we stress that as E_{SAP} and, hence, τ_{SAP} are not particularly affected by confinement [43,44], it is bulk dynamics to determine how fast molecules rearrange to form interfacial layers. These ideas support models considering that nanoconfinement effects originate in the properties of bulk alone [45].

In conclusion, we present a simple model capable of predicting the rate at which polymer chains adsorb on flat substrates. We tested this framework on various commonly used polymers and found that the formation of adsorbed layers is minimally affected, if at all, by surface chemistry. Moreover, our approach goes well beyond the qualitative arguments connecting equilibration kinetics and molecular mobility, and identifies the exact proportionality between the rate at which an interfacial layer forms and that at which molecules spontaneously fluctuate. We show that the number of chains adsorbed per unit surface is constant if the timescale of the phenomenon is rescaled to the molecular time of the SAP, a relaxation mechanism observed in polymers and small molecules. We stress that this observation is at odds with the common assumption that equilibration phenomena of polymer melts typically follows the structural (segmental, α-) relaxation. New models and simulations aiming at predicting the properties of interfacial polymer layers should consider these experimental findings. Finally, we anticipate that our approach can be extended to other phenomena, including physical aging, permeability, and other transport mechanisms, and we are confident that the solving strategy introduced in this Letter will open the way to new approaches to understand how dynamics affects materials' behavior.

The authors acknowledge financial support from Action de Recherche Concertée ULB under Grant No. ARC 20061 "SADI." S. N. acknowledges support from the Funds 'Piffica Visione' under Grant No. 1023A.

---

[*] simone.napolitano@ulb.be

[1] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, New York, 2010).

[2] Simone Napolitano, Irreversible adsorption of polymer melts and nanoconfinement effects, Soft Matter **16**, 5348 (2020).

[3] Emmanouil Glynos, Bradley Frieberg, and Peter F Green, Wetting of a multiarm star-shaped molecule, Phys. Rev. Lett. **107**, 118303 (2011).

[4] Houkuan Tian, Chaofan Bi, Zhiqiang Li, Chen Wang, and Biao Zuo, Metastable polymer adsorption dictates the dynamical gradients at interfaces, Macromolecules **56**, 4346 (2023).

[5] Christopher DelRe, Hyukhun Hong, Malia B. Wenny, Daniel P. Erdosy, Joy Cho, Byeongdu Lee, and Jarad A. Mason, Design principles for using amphiphilic polymers to create microporous water, J. Am. Chem. Soc. **145**, 19982 (2023).

[6] Yuhui Yang, Houkuan Tian, Simone Napolitano, and Biao Zuo, Crystallization in thin films of polymer glasses: The role of free surfaces, solid interfaces and their competition, Prog. Polymer Sci. **144**, 101725 (2023).

[7] Tadanori Koga, N. Jiang, P. Gin, M. K. Endoh, S. Narayanan, L. B. Lurio, and S. K. Sinha, Impact of an irreversibly adsorbed layer on local viscosity of nanoconfined polymer melts, Phys. Rev. Lett. **107**, 225901 (2011).

[8] Biao Zuo, Hao Zhou, Mary J. B. Davis, Xinping Wang, and Rodney D. Priestley, Effect of local chain conformation in adsorbed nanolayers on confined polymer molecular mobility, Phys. Rev. Lett. **122**, 217801 (2019).

[9] Simone Napolitano and Michael Wübbenhorst, The lifetime of the deviations from bulk behaviour in polymers confined at the nanoscale, Nat. Commun. **2**, 260 (2011).

[10] Sivasurender Chandran, Jörg Baschnagel, Daniele Cangialosi, Koji Fukao, Emmanouil Glynos, Liesbeth M. C. Janssen, Marcus Müller, Murugappan Muthukumar, Ullrich Steiner, Jun Xu *et al.*, Processing pathways decide polymer properties at the molecular level, Macromolecules **52**, 7146 (2019).

[11] Stuart F. Knowles, Nicole E. Weckman, Vincent J. Y. Lim, Douwe J. Bonthuis, Ulrich F. Keyser, and Alice L. Thorneywork, Current fluctuations in nanopores reveal the polymer-wall adsorption potential, Phys. Rev. Lett. **127**, 137801 (2021).

[12] Monika Möddel, Wolfhard Janke, and Michael Bachmann, Adsorption and pattern recognition of polymers at complex surfaces with attractive stripelike motifs, Phys. Rev. Lett. **112**, 148303 (2014).

[13] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.132.248101 for details on sample preparation and on the experimental procedures involved in the characterization of adsorbed layers, which includes Refs. [14–19].

[14] O. Guiselin, Irreversible adsorption of a concentrated polymer solution, Europhys. Lett. **17**, 225 (1992).

[15] Jayanta Kumar Bal, Thomas Beuvier, Aparna Beena Unni, Elvia Anabela Chavez Panduro, Guillaume Vignaud, Nicolas Delorme, Mohamed Souheib Chebil, Yves Grohens, and Alain Gibaud, Stability of polymer ultrathin films (< 7 nm) made by a top-down approach, ACS Nano **9**, 8184 (2015).

[16] Caroline Housmans, Michele Sferrazza, and Simone Napolitano, Kinetics of irreversible chain adsorption, Macromolecules **47**, 390 (2014).

[17] David Nieto Simavilla, Weide Huang, Philippe Vandestrick, Jean-Paul Ryckaert, Michele Sferrazza, and Simone Napolitano, Mechanisms of polymer adsorption onto solid substrates, ACS Macro Lett. **6**, 975 (2017).

[18] Friedrich Kremer and Andreas Schönhals, Analysis of dielectric spectra, in *Broadband Dielectric Spectroscopy* (Springer Science & Business Media, New York, 2002), pp. 59–98, ISBN 9783642561207.

[19] David Nieto Simavilla, Weide Huang, Caroline Housmans, Michele Sferrazza, and Simone Napolitano, Taming the strength of interfacial interactions via nanoconfinement, ACS Central Sci. **4**, 755 (2018).

[20] Ben O'Shaughnessy and Dimitrios Vavylonis, Irreversibility and polymer adsorption, Phys. Rev. Lett. **90**, 056103 (2003).

[21] A. De Virgiliis, A. Milchev, V. G. Rostiashvili, and Thomas A. Vilgis, Structure and dynamics of a polymer melt at an attractive surface, Eur. Phys. J. E **35**, 1 (2012).

[22] Christian Ligoure and Ludwik Leibler, Thermodynamics and kinetics of grafting end-functionalized polymers to an interface, J. Phys. **51**, 1313 (1990).

[23] Chien-Hua Tu, Jiajia Zhou, Masao Doi, Hans-Juergen Butt, and George Floudas, Interfacial interactions during *in situ* polymer imbibition in nanopores, Phys. Rev. Lett. **125**, 127802 (2020).

[24] Peter Frantz and Steve Granick, Kinetics of polymer adsorption and desorption, Phys. Rev. Lett. **66**, 899 (1991).

[25] Nikolaos Patsalidis, George Papamokos, George Floudas, and Vagelis Harmandaris, Structure and dynamics of a polybutadiene melt confined between alumina substrates, Macromolecules **56**, 6552 (2023).

[26] Mark Geoghegan and Georges Hadziioannou, *Polymer Electronics* (Oxford University Press, Oxford, 2013), Vol. 22.

[27] A. Baumgärtner and M. Muthukumar, Effects of surface roughness on adsorbed polymers, J. Chem. Phys. **94**, 4062 (1991).

[28] Maria M. Santore, Dynamics in adsorbed homopolymer layers: Understanding complexity from simple starting points, Curr. Opin. Colloid Interface Sci. **10**, 176 (2005).

[29] Jack F. Douglas, Harry E. Johnson, and Steve Granick, A simple kinetic model of polymer adsorption and desorption, Science **262**, 2010 (1993).

[30] Lars Onsager, Reciprocal relations in irreversible processes. I., Phys. Rev. **37**, 405 (1931).

[31] Marzena Rams-Baron, Renata Jachowicz, Elena Boldyreva, Deliang Zhou, Witold Jamroz, Marian Paluch, Marzena Rams-Baron, Renata Jachowicz, Elena Boldyreva, Deliang Zhou *et al.*, *Amorphous Drugs* (Springer, New York, 2018).

[32] T. Ichitsubo, E. Matsubara, T. Yamamoto, H. S. Chen, N. Nishiyama, J. Saida, and K. Anazawa, Microstructure of fragile metallic glasses inferred from ultrasound-accelerated crystallization in Pd-based metallic glasses, Phys. Rev. Lett. **95**, 245501 (2005).

[33] Zijian Song, Cristian Rodríguez-Tinoco, Allen Mathew, and Simone Napolitano, Fast equilibration mechanisms in disordered materials mediated by slow liquid dynamics, Sci. Adv. **8**, eabm7154 (2022).

[34] Federico Caporaletti and Simone Napolitano, The slow Arrhenius process in small organic molecules, Phys. Chem. Chem. Phys. **26**, 745 (2024).

[35] Valerio Di Lisio, Isabella Gallino, Sascha Sebastian Riegler, Maximilian Frey, Nico Neuber, Golden Kumar, Jan Schroers, Ralf Busch, and Daniele Cangialosi, Size-dependent vitrification in metallic glasses, Nat. Commun. **14** (2023).

[36] Mithun Chowdhury, Paul Freyberg, Falko Ziebert, Arnold C.-M. Yang, Ullrich Steiner, and Günter Reiter, Segmental relaxations have macroscopic consequences in glassy polymer films, Phys. Rev. Lett. **109**, 136102 (2012).

[37] Bao Wang, Matteo Sanviti, Angel Alegría, and Simone Napolitano, Molecular mobility of polymers at the melting transition, ACS Macro Lett. **12**, 389 (2023).

[38] Erik Thoms and Simone Napolitano, Enthalpy-entropy compensation in the slow arrhenius process, J. Chem. Phys. **159**, 161103 (2023).

[39] Jack F. Douglas, Hildegard M. Schneider, Peter Frantz, Robert Lipman, and Steve Granick, The origin and characterization of conformational heterogeneity in adsorbed polymer layers, J. Phys. Condens. Matter **9**, 7699 (1997).

[40] A. Yelon and B. Movaghar, Microscopic explanation of the compensation (Meyer-Neldel) rule, Phys. Rev. Lett. **65**, 618 (1990).

[41] Xavier Monnier and Daniele Cangialosi, Thermodynamic ultrastability of a polymer glass confined at the micrometer length scale, Phys. Rev. Lett. **121**, 137801 (2018).

[42] Sivasurender Chandran and Günter Reiter, Segmental rearrangements relax stresses in nonequilibrated polymer films, ACS Macro Lett. **8**, 646 (2019).

[43] Erik Thoms, Chun Li, and Simone Napolitano, Tracing the slow Arrhenius process deep in the glassy state-quantitative evaluation of the dielectric relaxation of bulk samples and thin polymer films in the temperature domain, J. Chem. Phys. **160**, 034901 (2024).

[44] Erik Thoms, Kai Wang, Sivasurender Chandran, and Simone Napolitano, Fast processing affects the relaxation of polymers: The slow arrhenius process can probe stress at the molecular level, J. Phys. Chem. Lett. **15**, 4838 (2024).

[45] Ronald P. White and Jane E. G. Lipson, To understand film dynamics look to the bulk, Phys. Rev. Lett. **125**, 058002 (2020).