

# Evidence of a Transition Layer Between the Free Surface and the Bulk

<sup>\$</sup>Wojciech Ogieglo\*, <sup>\$</sup>Kristianne Tempelman, <sup>#</sup>Simone Napolitano and <sup>\$</sup>Nieck E. Benes

<sup>\$</sup>Films in Fluids, University of Twente, Enschede, The Netherlands

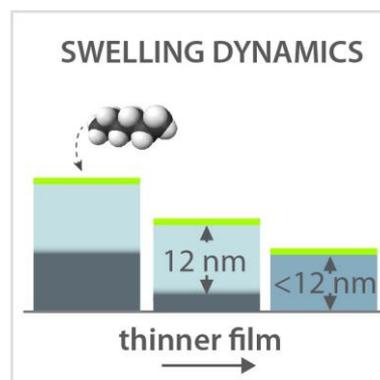
<sup>#</sup> Laboratory of Polymer and Soft Matter Dynamics, Faculté des Sciences, Université libre de Bruxelles (ULB),  
Boulevard du Triomphe, Bâtiment NO, Bruxelles 1050, Belgium

\*corresponding author: [w.ogieglo@gmail.com](mailto:w.ogieglo@gmail.com); Author's current affiliation: Advanced Membranes & Porous Materials Center,  
King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

## Abstract:

The free surface, a very thin layer at the interface between polymer and air, is considered the main source of the perturbations in the properties of ultrathin polymer films, *i.e.* nanoconfinement effects. The structural relaxation of such layer is decoupled from the molecular dynamics of the bulk. The free surface is, in fact, able to stay liquid even below the temperature where the polymer resides in glassy state. Importantly, this surface layer is expected to have a very sharp interface with the underlying bulk. Here, by analyzing the penetration of *n*-hexane into polystyrene films, we report on the existence of a transition region, not observed by previous investigations, extending for 12 nm below the free surface. Presence of such layer permits reconciling the behavior of interfacial layers with current models and has profound implications on the performance of ultra-thin membranes. We show that the expected increase in the flux of the permeating species is actually overruled by nanoconfinement.

## Graphical abstract:



Molecules sitting at the very interface with air (or a gas, or vacuum) exhibit peculiar properties, strongly differing from those of the bulk. Particles can, for example, diffuse faster on surfaces than towards the interior. This feature is shared by polymers, where within the first 2-10 nm<sup>1,2</sup> – interfacial layer, usually referred to as *free surface*<sup>3-5</sup> – structural relaxation occurs at rates exceeding by up to 12 orders of magnitude the bulk rate. The free surface is, hence, capable of demonstrating liquid-like behavior also below the glass transition temperature,  $T_g$ , of the material in bulk. In addition to this, evidence for enhanced flow was confirmed by ingenious viscosity measurements.<sup>6,7</sup> At the state of the art, such a tremendous enhancement in molecular mobility is currently considered as the main cause of the reduction in  $T_g$  commonly observed in thin polymer films.<sup>8</sup> The shift in  $T_g$ , in fact, increases linearly with the thickness of this layer.<sup>9</sup> Recent work has, furthermore, shown that it is possible to tune the properties of the free surface by controlling macromolecular architecture (molecular weight,<sup>10</sup> branching,<sup>11</sup> ...) and the processing conditions (notably the degree of adsorption on the supporting substrate<sup>12-14</sup>). Remarkably, extensive investigation has shown that the structural relaxation at the free surface is totally disentangled from the molecular dynamics of the underlying bulk layer.<sup>3,15</sup> The extreme sharpness of the interface between the surface layer and the bulk is furthermore strengthened by models defined on step-like functions<sup>1,2,6</sup> – thus with an interfacial width virtually equal to zero.

While such a steep transition could be rationalized for small molecules, in the case of high molecular weight polymers, where the macromolecular size ( $2R_g$ , where  $R_g$  is the gyration radius of the polymer) easily exceeds 10 nm, we would expect a broader transition region. It is thus puzzling to think that a transition region between the free surface and the bulk does not exist. Considering the huge amount of investigations in this field, we would rather comment that current methods failed in identifying the transition region because of a small contrast with the bulk region.

In this *Letter*, we introduce a novel method allowing to determine fine variations in the structure of a polymer film, which permitted to verify the existence of a transition region between the free surface and the bulk. Measuring the kinetics of dilation induced by the penetration of *n*-hexane vapor inside thin films of polystyrene (PS) of different thicknesses and molecular weights we determined that the first 15 nm from the interface with air show a peculiar stratification. This region can be divided into two sub layers with distinct extent and dynamics of swelling. The first layer of ~2.5 nm, attributable to the free surface, behaves as a liquid and swells almost 4 times as much as the bulk. Underneath the free surface, a transition layer, swelling just 20% more than the bulk, extends for 12 nm independently on the molecular weight.

Diffusion of small molecules inside a polymer film can be promptly followed by monitoring in time the swelling of the layer<sup>16,17</sup>. This process is limited by both the reorganization of chains while their environment gets filled up by the

penetrants and the availability of free volume holes where the guest molecules can be accommodated. Monitoring the diffusion rate of the penetrant along the whole sample, hence, provides direct information about the spatial variation in the dynamics of polymer chains and in the distribution of free volume<sup>16</sup>. For example, at the interface between polymer and air the reduced topological constraints provide an increase in free volume content with respect to the bulk.<sup>18,19</sup> With these considerations in mind, we attempted to identify the transition region between free surface and bulk by searching for discontinuities in the swelling rate. Based on previous work<sup>20</sup>, however, we considered that the changes in free volume content might be too small (<0.2%) and we could have encountered the same problem as the other techniques at the state of the art.<sup>1</sup>

In our measurements, we achieved in-situ observation of film swelling from the very first moments after contact with the penetrant by combining a very high data acquisition rate ( $\sim 2$  spectrum  $s^{-1}$ ) and the use of a vapor, as opposed to liquid<sup>16</sup>, ambient. To identify the presence of a transition layer we have, in fact, exploited a peculiar feature of the diffusion of vapor molecules at temperatures around the glass transition of the swollen film. Polymer chains swell when surrounded by molecules of a good solvent; this process is usually associated with an increase in molecular mobility due to plasticization. Penetration of small molecules into a glass induces a transition to the rubbery state and as a consequence increase in the diffusion coefficient by 3-4 orders of magnitude. Such a tremendous difference in penetrant mobility might induce an anomalous mechanism, known as Case II, where diffusion of small molecules inside the polymer matrix is not limited by Fickian diffusion of the penetrant, but by chain relaxation at the interface between the rubbery swollen outer layer and the glassy dry inner layer. Swelling, hence, proceeds linearly with time, which sets the signature of Case II anomalous diffusion<sup>21</sup>. In sub  $\mu m$ -thick films, anomalous diffusion occurs at temperatures high enough to ensure plasticization upon swelling; at lower temperatures, the swollen portion of the film remains glassy and diffusion of penetrants proceeds via conventional Fickian dynamics<sup>17</sup>. As the temperature where this change in diffusion mechanism occurs is just above the  $T_g$  of the swollen polymer, Case II diffusion is associated with molecular conformations of the liquid/rubbery state rich in free volume content.

Considering the strong coupling between free volume content and temperature,<sup>22-24</sup> we assumed a similar reasoning in the case of a distribution in materials properties running from the free surface to the bulk. In particular, we considered that, upon optimization of the experimental conditions, we could have forced transport of penetrant molecules in the

---

<sup>1</sup> We considered a thermal expansion coefficient of the free volume content of  $75 \times 10^{-4} K^{-1}$ ,<sup>20</sup> and a shift in  $T_g$  by 4 K between bulk and surface layer

interfacial layer of PS via Case II diffusion and, hence, achieved a magnifying effect on the small variation in free volume content from the free surface to the bulk.

We chose *n*-hexane because in the vapor phase this molecule is able to swell PS. More importantly, upon penetration of these small molecules the  $T_g$  of polystyrene drops to 292 K, allowing to perform experiments at room temperature. In these conditions, we could observe the presence of a layer with higher free volume content than the bulk, where swelling proceeds linearly with time, sitting on top of a bulk-like region, where a small reduction in free volume content was sufficient to inhibit Case II diffusion. The neat passage from linear to the usual square root dependence of swelling with time allowed us to precisely measure the thickness of the transition layer. While the stratification of the interface is likely a general phenomenon in glassy polymer interfaces the careful choice of the experimental conditions allowed for the very high sensitivity of our method. The precision of our method (0.5 – 1 nm) significantly exceeded that of other investigations by fluorescence<sup>25–27</sup> or by dielectric spectroscopy<sup>28</sup> because we were not limited by the minimum dimensions of the labeled layer (15-25 nm). Additionally, we studied the vapor penetration at the film interface not only as function of film thickness but also polymer molecular weight which gave insight into the physical origin of the transition layer.

To quantitatively illustrate our results, in Figure 1, we plotted the time evolution of the increase in film thickness upon swelling,  $\Delta h = h_{\text{swollen}} - h_{\text{dry}}$ . The evidence of three distinct dynamics of swelling regimes confirms the presence of three regions with well distinct properties. Starting from the outer to the inner layer, that is, from the short- to the long-time dilation kinetics, we identify a first layer (the free surface) that almost instantly swells, followed by a transition layer swelling linearly with time (Case II) sitting on top of a (bulk) region where dilation occurs following Fickian diffusion at the rate of very thick films. For all films, the free surface swells by  $\Delta h_{\text{fs}} = 1.5$  nm in approximately 3 seconds, i.e., with a speed of  $\sim 1$  nm·s<sup>-1</sup>, that is more than 2 orders of magnitude faster than the bulk films (0.003 – 0.005 nm·s<sup>-1</sup>).

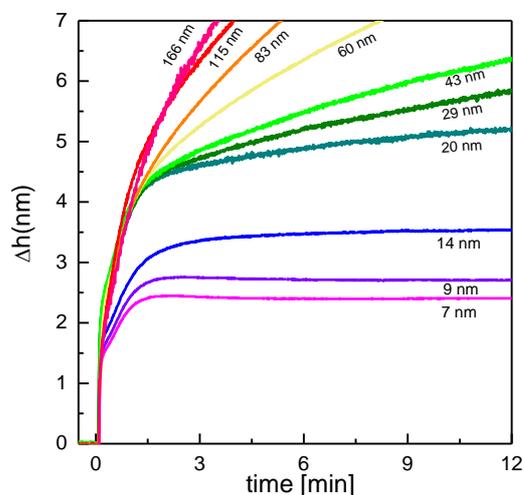


Figure 1 Increase in film thickness upon swelling,  $\Delta h = h_{\text{swollen}} - h_{\text{dry}}$ , as a function of time for polystyrene thin films with  $M_w = 280 \text{ kg}\cdot\text{mol}^{-1}$ ; data show stratification of dynamics with almost instantly swollen free surface, linear in time transition region, and bulk regions going from shortest to longest time

Considering the thickness dependence of the swelling factor,  $SF = h_{\text{swollen}}/h_{\text{dry}}$  see Figure 2, and the value extrapolated to  $h = 0$ , that is  $SF_{t=0} = 1.6$ , this outer free surface layer,  $L_{\text{fs}}$ , extends for 2.5 nm in the dry film. This value is calculated by considering that  $\Delta h_{\text{fs}} + L_{\text{fs}} = L_{\text{fs}} \cdot SF_{t=0}$ . The large increase in swelling corresponding to four times the relative change experienced by thicker films ( $SF_{t=0} = 1.6$  for free surface versus 1.15 for bulk), might be related to the enhanced conformational freedom of the free interfaces of glassy systems, where the matrix expansion is not as much restricted by the neighboring chains and entanglement density is reduced. This is in line with a suggestion<sup>2,6</sup>, that the lack of cooperativity in the dynamics of the free surface relaxed via a simple thermally activated process, and not by a super-Arrhenius fashion as the bulk, lowers the energetic costs upon structural relaxation. By considering the extent and time of dilation, the thickness of this surface layer ( $\sim 2.5 \text{ nm}$ ) is in excellent agreement with previous reports on the altered behavior at the free surface.<sup>7,29,30</sup> No film wrinkling or dewetting as a result of solvent vapor penetration occurred because of the relatively high molecular weight and high viscosity of the used polymer, as well as comparatively low degree of plasticization and swelling. Such morphological changes would have been detected by our experimental technique either by significant loss of signal intensity (light scattering) or deviations in the ellipsometric delta parameter at shorter wavelengths of probing light.

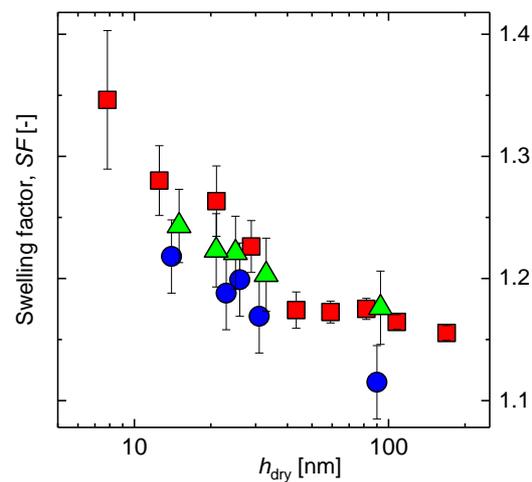


Figure 2 Equilibrium swelling factor,  $SF = h_{\text{swollen}}/h_{\text{dry}}$ , dependence on  $h_{\text{dry}}$  for polystyrene thin films of  $M_w = 280$  (red squares), 500 (green triangles), and 1000 (blue circles)  $\text{kg}\cdot\text{mol}^{-1}$  exposed to *n*-hexane vapor

After the first 3 seconds characterized by fast dynamics, a second regime, of  $\sim 1.5$  minutes, takes place. Here swelling slows down, albeit without recovering bulk rate, and proceeds linearly with time. Linear thickness dilation is associated with the progressive motion of a sharp front between swollen and non-swollen parts of the film, via Case II diffusion. Based on a swelling factor of very thick films ( $SF = 1.15$ , bulk) and the extent of the transition layer-related swelling from Figure 1 ( $\Delta h_{tr} \sim 2$  nm), we measured a value of  $L_{tr} = 12$  nm for the dry thickness of this transition layer by considering that  $\Delta h_{tr} + L_{tr} = L_{tr} \cdot SF$ . This value for the transition layer thickness agrees very well with results of recent molecular dynamics simulations<sup>31</sup>. Experiments performed on samples of different molecular weights allowed verifying that  $L_{tr}$  is independent of chain length for films thicker than  $2R_g$ , see Figure 3. For thinner films, the transition layer shrinks and the velocity of swelling smoothly decreases. Fast swelling dynamics gets, hence, inhibited while approaching the polymer/substrate interface, probably because of a reduction in free volume content. In line with recent work,<sup>14,32,33</sup> we expect that the presence of a layer of PS chains irreversibly adsorbed on the supporting substrate, would favor densification of the film. As free volume content decreases linearly upon adsorption,<sup>34,35</sup> the reduction in  $L_{tr}$  should be sensitive to the adsorbed amount,  $\Gamma$ , that is, number of monomers present in the chains adsorbed per unit surface. This idea is confirmed by Figure 3, where data sets of different molecular weights superimpose when plotting the values of  $L_{tr}$  as a function of the film thickness normalized to thickness of the adsorbed layer ( $\approx 0.5 R_g$ ), a quantity directly proportional to the adsorbed amount. Measurements in films thinner than 15 nm did not show a presence of a bulk-like layer.

Based on these observations, the structure and extension of the transition layer depend on the boundary conditions at both the polymer/air and the polymer/substrate interfaces, while its molecular origin should be attributed to the upper interface only:  $L_{tr}$  is indeed constant for films where the surface layer is far enough from the supporting substrate.

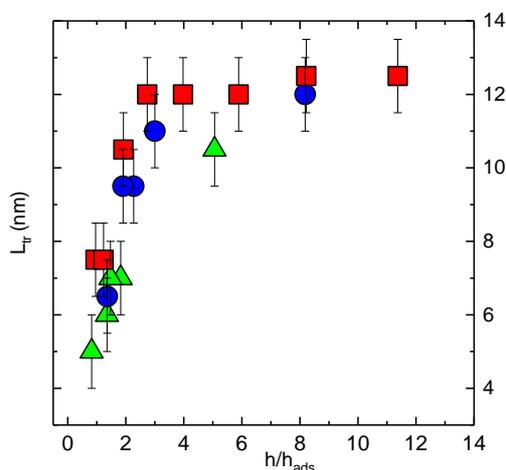


Figure 3 Transition layer thickness,  $L_{tr}$ , as a function of  $h_{dry}$  normalized by the thickness of the adsorbed layer  $h_{ads}$  ( $\approx 0.5 R_g$ ); Symbol designation as in Figure 2;  $R_g$  values used are 14.6, 19.5 and 27.6 nm for  $M_w$  of 280, 500 and 1000 kg·mol<sup>-1</sup>, respectively (taken from literature<sup>36</sup>).

Presence of the transition layer has profound implications on the fabrication of polymer coatings designed to be responsive towards contact with small molecules, such as sensors<sup>37</sup>, or to affect the diffusional transport of small molecules, as in the case of barriers and artificial membrane films for molecular separations<sup>38-40</sup>. In particular, current fabrication trends push towards a reduction in the thickness of membrane films, aiming at an increase of the flux of the permeating species. We stress on the supported character of these membranes, as freestanding films would lack of mechanical stability. Commercial devices with a thickness in the 20-40 nm range for air separation exist already for years and recently, sub-10 nm membranes have been introduced for organic solvent nanofiltration<sup>41</sup>. We anticipate that, depending on the molecular weight of the polymer used, the effect of nanoconfinement-induced stratified dynamics will dominate the separation performance. For such thin films the properties will exclusively be determined by the nanoconfinement, and bulk materials properties are of limited predictive potential for membrane separation performance.

## Materials and methods

Ultrathin films of polystyrene (PS,  $M_w$  ranging from 280 to 1000 kg mol<sup>-1</sup>) in the 7-166 nm thickness range were spincoated onto clean silicon wafers from toluene (Merck, analytical grade). Prior to the deposition, the substrates were treated with a mixture of sulfuric acid and 30% hydrogen peroxide (3:1 v:v), then rinsed with ultra-pure water. The film thickness was adjusted via the solution concentration; the spin coating speed was 2000 rpm. The freshly formed films were dried for one week at room temperature, under nitrogen. Prior to the swelling experiments the films were heated to 150 °C (PS bulk  $T_g \approx 100$  °C), for a period of time sufficient to ease structural relaxation yet short enough to avoid dewetting of especially the thinnest films (5 min for 280 kg mol<sup>-1</sup> and 2 h for 1000 kg mol<sup>-1</sup>). Afterwards, the films were quenched at room temperature, and kept aging in ambient atmosphere for exactly 3 minutes or 3 weeks before the swelling experiments started. Swelling experiments were performed using an M-2000X spectroscopic ellipsometer (J. A. Woollam Co., Inc.). Dynamic data were acquired in a fast mode resulting in a temporal resolution of  $\sim 2$  scan s<sup>-1</sup>. A trapezoidal stainless steel cell with quartz windows was stabilized at 22±0.1 °C. *N*-hexane vapors were generated by flowing purified nitrogen through a bubbler at 21±0.1 °C. The nitrogen flow rate was kept constant throughout each series of measurements. The optical model comprised the silicon substrate with a  $\sim 2$  nm native silicon oxide and atop a

single uniform layer with a Cauchy optical dispersion. The wavelength range was limited to 370–1000 nm, where the polymer can be assumed fully transparent. The ambient refractive index was set to 1.000, assuming no effect of the *n*-hexane vapor. The window birefringence was carefully corrected for. Even though for ultrathin films the accuracy of the simultaneous thickness and refractive index determination is limited, relative variations in thickness can be monitored with a very high precision (<1%). Further information on the ellipsometry analysis can be found in the Supporting Information. The thickness of the adsorbed layer was obtained by literature data<sup>42</sup> of experiments of PS adsorbed on silicon oxide, the same system considered in this work.

**Supporting Information Available:** Experimental considerations related to the sensitivity of the used experimental technique to accurately determine swelling in ultra-thin films and different presentations of data shown in Figure 1 including square root of time on the X-axis and squared extent of thickness change on the Y-axis.

## Acknowledgement

The authors acknowledge financial support of the Dutch Institute for Sustainable Process Design (ISPT). SN acknowledges financial support from the *Fonds de la Recherche Scientifique* – FNRS under Grant no. T.0147.16 “TIACIC”.

## References

- (1) Paeng, K.; Ediger, M. D. Molecular Motion in Free-Standing Thin Films of Poly(methyl Methacrylate), poly(4-Tert-Butylstyrene), Poly( $\alpha$ -Methylstyrene), and poly(2-Vinylpyridine). *Macromolecules* **2011**, *44*, 7034–7042.
- (2) Paeng, K.; Swallen, S. F.; Ediger, M. D. Direct Measurement of Molecular Motion in Freestanding Polystyrene Thin Films. *J. Am. Chem. Soc.* **2011**, *133*, 8444–8447.
- (3) Fakhraai, Z.; Forrest, J. A. Measuring the Surface Dynamics of Glassy Polymers. *Science*. **2008**, *319* (5863), 600–604.
- (4) Yin, H.; Madkour, S.; Schönhals, A. Unambiguous Evidence for a Highly Mobile Surface Layer in Ultrathin Polymer Films by Specific Heat Spectroscopy on Blends. *Macromolecules* **2015**, *48*, 4936–4941.
- (5) Madkour, S.; Yin, H.; Füllbrandt, M.; Schönhals, A. Calorimetric Evidence for a Mobile Surface Layer in Ultrathin Polymeric Films: poly(2-Vinyl Pyridine). *Soft Matter* **2015**, *11*, 7942–7952.
- (6) Yang, Z.; Fujii, Y.; Lee, F. K.; Lam, C.-H.; Tsui, O. K. C. Glass Transition Dynamics and Surface Layer Mobility in Unentangled Polystyrene Films. *Science*. **2010**, *328* (5986), 1676–1679.
- (7) Chai, Y.; Salez, T.; McGraw, J. D.; Benzaquen, M.; Dalnoki-Veress, K.; Raphael, E.; Forrest, J. A. A Direct Quantitative Measure of Surface Mobility in a Glassy Polymer. *Science*. **2014**, *343* (6174), 994–999.
- (8) Ediger, M. D.; Forrest, J. A. Dynamics Near Free Surfaces and the Glass Transition in Thin Polymer Films: A View to the Future. *Macromolecules* **2014**, *47*, 471–478.
- (9) Napolitano, S.; Glynos, E.; Tito, N. B. Glass Transition of Polymers in Bulk, Confined Geometries, and near Interfaces. *Reports Prog.*

*Phys.* **2017**, *80*, 36602.

- (10) Geng, K.; Chen, F.; Tsui, O. K. C. Molecular-Weight Dependent Tg Depression of Silica-Supported Poly( $\alpha$ -Methyl Styrene) Films. *J. Non. Cryst. Solids* **2015**, *407*, 296–301.
- (11) Glynos, E.; Johnson, K. J.; Frieberg, B.; Chremos, A.; Narayanan, S.; Sakellariou, G.; Green, P. F. Free Surface Relaxations of Star-Shaped Polymer Films. *Phys. Rev. Lett.* **2017**, *119*, 227801.
- (12) Burroughs, M. J.; Napolitano, S.; Cangialosi, D.; Priestley, R. D. Direct Measurement of Glass Transition Temperature in Exposed and Buried Adsorbed Polymer Nanolayers. *Macromolecules* **2016**, *49*, 4647–4655.
- (13) Perez-De-Eulate, N. G.; Sferrazza, M.; Cangialosi, D.; Napolitano, S. Irreversible Adsorption Erases the Free Surface Effect on the Tg of Supported Films of Poly(4-Tert-Butylstyrene). *ACS Macro Lett.* **2017**, *6*, 354–358.
- (14) Koga, T.; Jiang, N.; Gin, P.; Endoh, M. K.; Narayanan, S.; Lurio, L. B.; Sinha, S. K. Impact of an Irreversibly Adsorbed Layer on Local Viscosity of Nanoconfined Polymer Melts. *Phys. Rev. Lett.* **2011**, *107*, 1–5.
- (15) Daley, C. R.; Fakhraai, Z.; Ediger, M. D.; Forrest, J. A. Comparing Surface and Bulk Flow of a Molecular Glass Former. *Soft Matter* **2012**, *8*, 2206.
- (16) Ogieglo, W.; Wormeester, H.; Wessling, M.; Benes, N. E. Probing the Surface Swelling in Ultra-Thin Supported Polystyrene Films during Case II Diffusion of N-Hexane. *Macromol. Chem. Phys.* **2013**, *214*, 2480–2488.
- (17) Ogieglo, W.; Wormeester, H.; Wessling, M.; Benes, N. E. Temperature-Induced Transition of the Diffusion Mechanism of N-Hexane in Ultra-Thin Polystyrene Films, Resolved by in-Situ Spectroscopic Ellipsometry. *Polymer*. **2013**, *54*, 341–348.
- (18) Tito, N. B.; Lipson, J. E. G.; Milner, S. T. Lattice Model of Mobility at Interfaces: Free Surfaces, Substrates, and Bilayers. *Soft Matter* **2013**, *9*, 9403.
- (19) Tito, N. B.; Milner, S. T.; Lipson, J. E. G. Enhanced Diffusion and Mobile Fronts in a Simple Lattice Model of Glass-Forming Liquids. *Soft Matter* **2015**, *11*, 7792–7801.
- (20) Hagiwara, K.; Ougizawa, T.; Inoue, T.; Hirata, K.; Kobayashi, Y. Studies on the Free Volume and the Volume Expansion Behavior of Amorphous Polymers. *Radiat. Phys. Chem.* **2000**, *58*, 525–530.
- (21) Thomas, N. L.; Windle, A. H. A Theory of Case II Diffusion. *Polymer*. **1982**, *23*, 529–542.
- (22) White, R. P.; Lipson, J. E. G. Polymer Free Volume and Its Connection to the Glass Transition. *Macromolecules* **2016**, *49*, 3987–4007.
- (23) Boucher, V. M.; Cangialosi, D.; Alegría, A.; Colmenero, J. Complex Nonequilibrium Dynamics of Stacked Polystyrene Films Deep in the Glassy State. *J. Chem. Phys.* **2017**, *146*, 203312
- (24) Cangialosi, D. Dynamics and Thermodynamics of Polymer Glasses. *J. Phys. Condens. Matter* **2014**, *26* (15).
- (25) Ellison, C. J.; Torkelson, J. M. The Distribution of Glass-Transition Temperatures in Nanoscopically Confined Glass Formers. *Nat Mater* **2003**, *2*, 695–700.
- (26) Priestley, R. D.; Ellison, C. J.; Broadbelt, L. J.; Torkelson, J. M.; M., T. J. Structural Relaxation of Polymer Glasses at Surfaces, Interfaces, and In Between. *Science*. **2005**, *309*, 456–459.
- (27) Baglay, R. R.; Roth, C. B. Local Glass Transition Temperature Tg(z) of Polystyrene next to Different Polymers: Hard vs. Soft Confinement. *J. Chem. Phys.* **2017**, *146*, 203307.
- (28) Rotella, C.; Napolitano, S.; De Cremer, L.; Koeckelberghs, G.; Wübbenhorst, M. Distribution of Segmental Mobility in Ultrathin Polymer Films. *Macromolecules* **2010**, *43*, 8686–8691.
- (29) Braatz, M. L.; Infantas Meléndez, L.; Sferrazza, M.; Napolitano, S. Unexpected Impact of Irreversible Adsorption on Thermal Expansion:

Adsorbed Layers Are Not That Dead. *J. Chem. Phys.* **2017**, *146*, 203304.

- (30) Yang, Z.; Clough, A.; Lam, C. H.; Tsui, O. K. C. Glass Transition Dynamics and Surface Mobility of Entangled Polystyrene Films at Equilibrium. *Macromolecules* **2011**, *44*, 8294–8300.
- (31) Hsu, D. D.; Xia, W.; Song, J.; Keten, S. Glass-Transition and Side-Chain Dynamics in Thin Films: Explaining Dissimilar Free Surface Effects for Polystyrene vs Poly(methyl Methacrylate). *ACS Macro Lett.* **2016**, *5*, 481–486.
- (32) Simavilla, D. N.; Huang, W.; Vandestruck, P.; Ryckaert, J. P.; Sferrazza, M.; Napolitano, S. Mechanisms of Polymer Adsorption onto Solid Substrates. *ACS Macro Lett.* **2017**, *6*, 975–979.
- (33) Fujii, Y.; Yang, Z.; Leach, J.; Atarashi, H.; Tanaka, K.; Tsui, O. K. C. Affinity of Polystyrene Films to Hydrogen-Passivated Silicon and Its Relevance to the T<sub>g</sub> of the Films. *Macromolecules* **2009**, *42*, 7418–7422.
- (34) Napolitano, S.; Rotella, C.; Wübbenhorst, M. Can Thickness and Interfacial Interactions Univocally Determine the Behavior of Polymers Confined at the Nanoscale? *ACS Macro Lett.* **2012**, *1*, 1189–1193.
- (35) Napolitano, S.; Capponi, S.; Vanroy, B. Glassy Dynamics of Soft Matter under 1D Confinement: How Irreversible Adsorption Affects Molecular Packing, Mobility Gradients and Orientational Polarization in Thin Films. *Eur. Phys. J. E* **2013**, *36*.
- (36) Terao, K.; Mays, J. W. On-Line Measurement of Molecular Weight and Radius of Gyration of Polystyrene in a Good Solvent and in a Theta Solvent Measured with a Two-Angle Light Scattering Detector. *Eur. Polym. J.* **2004**, *40*, 1623–1627.
- (37) Kimmel, D. W.; LeBlanc, G.; Meschievitz, M. E.; Cliffel, D. E. Electrochemical Sensors and Biosensors. *Anal. Chem.* **2011**, *84*, 685–707.
- (38) Lau, W. J.; Ismail, A. F.; Misdan, N.; Kassim, M. A. A Recent Progress in Thin Film Composite Membrane: A Review. *Desalination* **2012**, *287*, 190–199.
- (39) Horn, N. R.; Paul, D. R. Carbon Dioxide Plasticization and Conditioning of Thin Glassy Polymer Films Monitored by Gas Permeability and Optical Methods. *Macromolecules* **2012**, *45*, 2820–2834.
- (40) Ogieglo, W.; Wormeester, H.; Eichhorn, K. J.; Wessling, M.; Benes, N. E. In Situ Ellipsometry Studies on Swelling of Thin Polymer Films: A Review. *Prog. Polym. Sci.* **2015**, *42*, 42–78.
- (41) Karan, S.; Jiang, Z.; Livingston, A. G. Sub-10 Nm Polyamide Nanofilms with Ultrafast Solvent Transport for Molecular Separation. *Science*. **2015**, *348*, 1347–1351.
- (42) Housmans, C.; Sferrazza, M.; Napolitano, S. Kinetics of Irreversible Chain Adsorption. *Macromolecules* **2014**, *47*, 3390–3393.