



HAL
open science

On the bridge hypothesis in the glass transition of freestanding polymer films

Haggai Bonneau, Maxence Arutkin, Rainni Chen, James A Forrest, Elie Raphael, Thomas Salez

► **To cite this version:**

Haggai Bonneau, Maxence Arutkin, Rainni Chen, James A Forrest, Elie Raphael, et al.. On the bridge hypothesis in the glass transition of freestanding polymer films. *European Physical Journal E: Soft matter and biological physics*, 2023, 46, pp.8. hal-03889405

HAL Id: hal-03889405

<https://cnrs.hal.science/hal-03889405>

Submitted on 8 Dec 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

On the bridge hypothesis in the glass transition of freestanding polymer films

Haggai Bonneau,¹ Maxence Arutkin,² Rainni Chen,³ James A. Forrest,³ Elie Raphaël,¹ and Thomas Salez^{4,*}

¹*Gulliver, CNRS UMR 7083, ESPCI Paris, Univ. PSL, 75005 Paris.*

²*School of Chemistry, Center for the Physics & Chemistry of Living Systems, Ratner Institute for Single Molecule Chemistry, and the Sackler Center for Computational Molecular & Materials Science, Tel Aviv University, 6997801, Israel.*

³*Department of Physics & Astronomy, University of Waterloo, N2L 3G1, Ontario, Canada.*

⁴*Univ. Bordeaux, CNRS, LOMA, UMR 5798, F-33400, Talence, France.*

Freestanding thin polymer films with high molecular weights exhibit an anomalous decrease in the glass-transition temperature with film thickness. Specifically, in such materials, the measured glass-transition temperature evolves in an affine way with the film thickness, with a slope that weakly depends on the molecular weight. De Gennes proposed a sliding mechanism as the hypothetical dominant relaxation process in these systems, where stress kinks could propagate in a reptation-like fashion through so called bridges, *i.e.* from one free interface to the other along the backbones of polymer macromolecules. Here, by considering the exact statistics of finite-sized random walks within a confined box, we investigate in details the bridge hypothesis. We show that the sliding mechanism cannot reproduce the basic features appearing in the experiments, and we exhibit the fundamental reasons behind such a fact.

I. INTRODUCTION

Some liquids do not undergo a first-order phase transition to the crystalline solid state when being quenched in temperature, but rather exhibit a supercooled liquid-like behaviour with sharply increasing relaxation times as the temperature is reduced [1–5] – a phenomenon known as the glass transition [6, 7]. While recent theoretical breakthroughs have shown the existence of an ideal glass transition in infinite space dimensions [8], a complete understanding of the formation of real glassy materials remains a central unsolved problem in condensed matter physics [9]. In addition to the interest in this fundamental problem, glassy materials find widespread use and their rheology and stability have significant technological importance.

In the supercooled liquid state, particles are crowded and must move in a correlated way to allow for a reorganisation or a relaxation event [10]. This phenomenology has been used to suggest the emergence of a dynamical cooperative length scale [11]. To probe this hypothetical length scale, besides bulk numerical simulations [12], or mimetic jammed colloidal systems [13, 14], an alternative strategy consisted in studying finite-size effects on the glass-transition temperature T_g , *i.e.* through systems with a similar nanometric size as the cooperative length at stake [15–18]. In particular, experiments and numerical studies investigating thin glassy polymer films have been performed [19–29], and have revealed a set of rich and exotic phenomena. Most notably, a reduction of T_g in thin films of many materials was observed and was further attributed to a combination of the dynamical correlation length with an enhanced liquid-like surface mobility in glasses. These observations have been studied from a theoretical point of view as well, but there is no

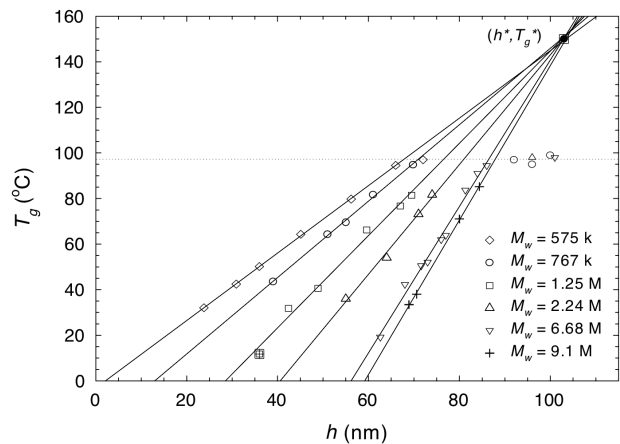


FIG. 1. Glass-transition temperature T_g of freestanding polystyrene films as a function of film thickness h , for various average molecular weights M_w . By extrapolating the low-thickness linear regimes towards larger thicknesses, one empirically finds a universal crossing point, denoted by (h^*, T_g^*) . Figure reproduced from Ref. [43].

definitive consensus yet on the exact underlying mechanisms at play [30–40].

Moreover, beyond the above generic confinement and interfacial behaviours of glassy materials made of small molecules or oligomers, and apart from possible residual stresses and artefacts induced by sample-preparation protocols [41], whether or not specific polymeric effects exist within the glassy physics is an interesting fundamental question with important practical implications given the widespread use of thin plastic films. Accordingly, freestanding polymer films with a thickness h comparable to the macromolecular radius of gyration R_g were experimentally studied [42–46]. The experiments showed that, for molecular weights $M_w < 378 \times 10^3$ – *i.e.* ~ 3600 monomeric units – T_g does not exhibit any dependence on M_w , and the curves can be mapped onto the one for

* thomas.salez@cnrs.fr

low- M_w supported films. However, for larger M_w , the T_g dependence on h and M_w becomes non-trivial, as shown in Fig. 1: at large thicknesses, T_g is equal to the bulk value T_g^{bulk} ; at small thicknesses, T_g decreases in an affine way with decreasing h , together with a slope moderately increasing with M_w . As such, the glass-transition temperature follows the empirical law:

$$T_g = T_g^* + f(M_w)(h - h^*), \quad (1)$$

for $h < h_c$, where $h_c = h^* + (T_g^{\text{bulk}} - T_g^*)/f(M_w)$ is a M_w -dependent critical thickness separating the two regimes, with f a slowly increasing function of M_w , and where h^* and T_g^* are the coordinates of an apparent universal crossing point obtained by extrapolating the low-thickness linear regime of Eq. (1) towards larger thicknesses (see Fig. 1). The function $f(M_w)$ was suggested to be logarithmic-like [42], a form which, perhaps coincidentally, is also present in other interfacial polymeric effects [47]. The existence of such a sharp transition in thin supercooled polymeric films suggests a change of dominating relaxation mechanism around h_c , from a generic bulk molecular one above h_c , to a purely confinement-induced polymeric one below h_c – indicating a probable connexion between h_c and some typical macromolecular polymeric length scale. In addition, the empirical trends suggest that the polymeric mechanism starts to be present below the universal onset thickness h^* , but remains less efficient than the bulk one for $h_c < h < h^*$. Moreover, it was proposed that the polymeric relaxation mechanism in thin supercooled polymer films requires two free interfaces to be connected by bridges consisting of individual macromolecules [42] – which we refer to as the *bridge hypothesis*.

The glass transition in thin polymer films was further shown to have even a finer structure, with in fact two glass transitions occurring with some finite temperature gap in between them [48], corroborating the existence of three competing distinct relaxation mechanisms [49]: a bulk one, a confined molecular/monomeric one, and a confined polymeric one. These features are consistent with the observations made in Ref. [43], where a flow behavior in thin freestanding polymer films was only measured near the bulk value of T_g – independently of the actually-measured T_g . Moreover, by removing one of the two free interfaces of a freestanding polymer film, it was experimentally shown that the polymeric behaviour totally disappears [46, 50], which seems to corroborate the seminal bridge hypothesis. As a side remark, we note that the coupling between different relaxation mechanisms in the bulk was experimentally investigated in details recently, and revealed the role of intramolecular cooperative dynamics in the bulk polymeric glass transition [51].

As an early attempt to rationalize the affine trend in Eq. (1), de Gennes sketched a model based on free-volume arguments and an original *sliding mechanism* involving the reptation-like propagation of stress kinks along the macromolecular bridges [52, 53]. This

model assumed an infinite molecular weight, as well as a Gaussian-tail distribution of the free volumes along the chain backbone, and involved an ideal-random walk scaling for the average bridge length. Despite its merits, the sliding model suffered from intrinsic limitations, and could not reproduce all the experimental observations [46]. Milner and Lipson suggested a *delayed-glassification model* [54], extending the sliding model and computing the bridge-length distribution for infinite molecular weights, that led to a depth-dependent T_g and a decrease in the overall measured T_g [55]. But, once again, while the qualitative picture seemed appealing, the model could not reproduce the experimental data in a quantitative fashion.

To date, there is actually no model which quantitatively captures the M_w dependence of T_g in thin polymer films. In his seminal work [52], de Gennes suggested to refine his approach by performing a complete statistical treatment of the bridge distribution for finite-sized polymer chains in a thin film. This is thus the topic of the present article, where we compute the bridge-length distribution, its mean value, and its proportion within a film, and use the obtained results in order to critically revisit de Gennes' sliding mechanism. We note that *loops*, *i.e.* chain portions connecting two points of a single interface, are not considered here for two reasons. First, supported films also contain loops but do not show the M_w behaviour of freestanding films [42, 46, 50]. Secondly, adding loops to the calculation does not change the M_w dependence.

II. SLIDING MECHANISM

Here, we first briefly recall the main ingredients of the sliding model [52]. Therein, the relaxation time τ is essentially set by the time required for a *kink*, *i.e.* some localised stress, to travel along a *bridge*, *i.e.* a portion of polymer chain connecting the two free interfaces. The kink travels along the chain backbone using successive jumps involving a series of volumes ω_i , which are assumed to be normally and identically Gaussian-tail distributed, as:

$$p(\omega_i) = \sqrt{\frac{2}{\pi\omega_0^2}} e^{-\frac{\omega_i^2}{2\omega_0^2}}, \quad (2)$$

where the standard deviation ω_0 is assumed to be small compared to the monomer size $\sim a^3$, in order to reflect the fact that relaxation along the chain is easier than bulk molecular relaxation. The average relaxation time of this sequential process thus reads:

$$\tau = \tau_0 \left\langle \exp \left(\frac{1}{v_f(T)} \sum_i \omega_i \right) \right\rangle_{\mathcal{P}}, \quad (3)$$

where the average is made over the ensemble $\{\omega_i\}$ against the distributions $\mathcal{P} = \prod_i p(\omega_i)$, and where $v_f(T)$ is the

free volume at temperature T . As classically done, v_f is assumed to vanish at a finite temperature T_V and to evolve in an affine way with temperature, so that:

$$v_f(T) = \alpha a^3 (T - T_V), \quad (4)$$

where α is the expansion coefficient. Assuming that the process happens along a bridge of average number of units $\langle b \rangle$, one eventually finds:

$$T_g - T_V \propto \sqrt{\langle b \rangle}. \quad (5)$$

Introducing the film thickness h , and assuming that $\langle b \rangle \sim h^2$ – which is only valid for infinite ideal random walks – then leads to the affine trend with h in Eq. (1). We now aim at calculating the exact bridge-length distribution for finite-sized polymer chains, in order to investigate whether or not the M_w dependence in Eq. (1) can also be captured by the sliding model.

III. BRIDGE STATISTICS

We consider a film made of a dense (supercooled) polymer melt consisting of identical chains, containing N monomers of size a (*e.g.* for polystyrene, one has a rescaled ideal monomeric size $a \approx 0.75$ nm) each. The film is assumed to be infinite in the (x, y) -plane, and to have two flat free interfaces located at the dimensionless vertical coordinates $z = 0$ and $z = H = h/a$. We define a bridge as a segment of a polymer chain that connects the two free interfaces, as shown in Fig. 2.

First, we are interested in the probability density of the dimensionless bridge length $B = b/a$, at a certain position z inside the film. We start by picking a monomer at a distance z from the lower interface. This monomer belongs to a polymer chain. From the position of the picked monomer, there are two branches of the polymer chain. As we deal with a (supercooled) polymer melt, these two branches can be properly described by Gaussian statistics [56]. For large N , *i.e.* high molecular weight, one can invoke the continuous description of Brownian motion. As such, the probability density of the bridge length can be constructed using a constrained sum of the first-passage “times” of two Brownian motions. The polymer chain is of total length N , so that the test monomer considered above is at a distance P from one end of the chain, and at a distance $N - P$ from the other end (see Fig. 2), with P uniformly distributed in $[0, N]$. Denoting l_1 and l_2 the first-passage “times” of the chain from the test monomer to the $z = 0$ and $z = H$ interfaces, respectively, with $l_1 \leq P$ and $l_2 \leq N - P$, the bridge length reads $B = l_1 + l_2$. Therefore, the probability density $\rho(N, H, B, P, z)$ that a monomer located at a distance z from the bottom interface, and at position P along a chain of total length N , belongs to a bridge of length B ,

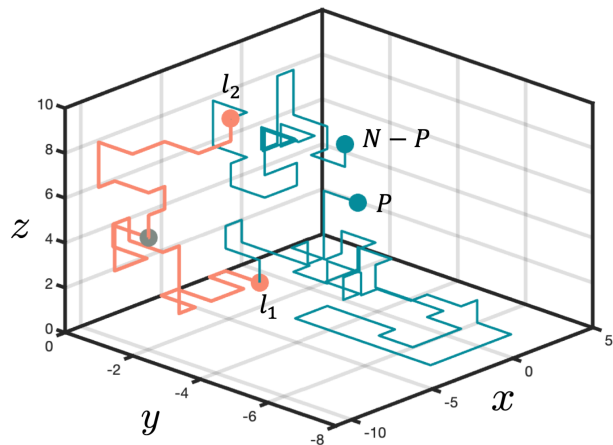


FIG. 2. Sketch of the problem studied, as obtained from numerical simulation. We consider an ideal random walk with N steps in a box of dimensionless thickness $H = 10$ along the z -axis. A randomly chosen monomer (grey), located at an altitude z , is P steps away from one of the walk ends, and $N - P$ steps away from the other end. The chosen monomer is connected to both the $z = 0$ and $z = H$ interfaces, with paths of dimensionless lengths l_1 and l_2 , respectively, forming a bridge (orange) of dimensionless length $B = l_1 + l_2$. Another part (blue) of the random walk does not belong to the bridge.

reads:

$$\rho = 2 \iint_{I_1 \times I_2} dl_1 dl_2 \delta(l_1 + l_2 - B) f_0(z, l_1) f_H(z, l_2), \quad (6)$$

with $I_1 = [0, P]$, $I_2 = [0, N - P]$, where the factor 2 accounts for the possibility of the two bridge subparts to be exchanged, and where $f_0(z, l_1)$ and $f_H(z, l_2)$ are the first-passage-time probability densities to the bottom and top interfaces, after “times” l_1 and l_2 , respectively, when starting at a distance z from the bottom interface [57]. By performing one of the two integrations, Eq. (6) becomes:

$$\rho = 2 \int_I dl f_0(z, l) f_H(z, B - l). \quad (7)$$

with $I = [\max(0, B - N + P), \min(B, P)]$. Then, uniformly averaging Eq. (7) with respect to P and z , gives the probability density $\bar{\rho}(N, H, B)$ that a randomly chosen monomer inside the film belongs to a bridge of length B , between 0 and N , as:

$$\bar{\rho} = \frac{4\pi^2 D^2 (N - B) B}{H^4 N} \sum_{k=1}^{\infty} k^2 (-1)^{k+1} e^{-D\lambda_k^2 B}, \quad (8)$$

where $\lambda_k = \frac{k\pi}{H}$ and $D = \frac{1}{2d}$, with $d = 3$ the space dimension. By integrating Eq. (8) over B , from 0 to N , one gets the fraction $\phi(N, H)$ of monomers belonging to

bridges, as:

$$\phi = \frac{1}{3} - \frac{7H^2}{90DN} \quad (9)$$

$$+ \frac{4}{\pi^2} \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k^2} e^{-D\lambda_k^2 N} \left(1 + \frac{2H^2}{\pi^2 DN k^2} \right), \quad (10)$$

where we note the expected diffusive-like self-similarity in the variable H/\sqrt{DN} . The limit 1/3 at infinite N is intuitive, since any sub-part of the chain containing a given monomer then touches two interfaces, either twice the top one, or twice the bottom one, or once each of the two interfaces, with equal chances.

We now turn to the central quantity of interest in this work, *i.e.* the average dimensionless bridge length $\langle B \rangle$, which is a function of N and H . It can be directly computed from Eq. (8), leading to:

$$\langle B \rangle = \frac{1}{\phi(N, H)} \left[\frac{7H^2}{90D} - \frac{31H^4}{1260ND^2} + \frac{4N}{\pi^2} \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k^2} u_k(N, H) e^{-D\lambda_k^2 N} \right], \quad (11)$$

where, for convenience, we invoked the auxiliary function:

$$u_k = 1 + \frac{4H^2}{\pi^2 DN k^2} + \frac{6H^4}{\pi^4 D^2 N^2 k^4}. \quad (12)$$

By expanding Eq. (11), one finds in particular the large- N asymptotic behavior:

$$\langle B \rangle \simeq \frac{7H^2}{30D} - \frac{61H^4}{3150D^2 N} + O\left(\frac{1}{N^2}\right), \quad (13)$$

that exhibits the $\langle B \rangle \sim H^2$ scaling invoked in the sliding model [52], as well as the first finite-size correction to it.

IV. FINITE-SIZE SLIDING MECHANISM

We now examine the modification of the sliding mechanism for polymer chains of finite length. By plugging Eq. (11) into Eq. (5), one can get an exact expression (not shown) for $T_g(H, N)$ from the sliding mechanism. Expanding the latter, one gets the large- N asymptotic behavior:

$$T_g - T_V \propto \frac{H}{\sqrt{D}} \left(1 - \frac{61H^2}{735DN} \right)^{1/2}. \quad (14)$$

In Fig. 3, we plot $\sqrt{\langle B \rangle}$ as a function of H , for different values of N , by numerically evaluating Eq. (11). While we recover the linear behaviour introduced in Ref. [52] in the strong-confinement regime, the leading term in the large- N asymptotics is independent of N . In other words – and even without discussing the intercept – the slope of the affine regime cannot exhibit the logarithmic-like dependence in N seen in the experiments [42, 43] (see

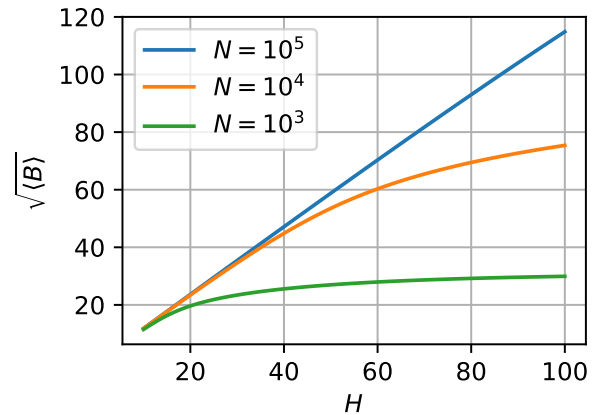


FIG. 3. Square root of the average dimensionless bridge length $\langle B \rangle$ as a function of dimensionless film thickness H , for three chain lengths N , obtained from the numerical evaluation of Eq. (11) using a cut-off after 100 terms in the sum. The results have been checked to weakly depend on the cut-off value in this range.

Fig. 1 and Eq. (1)), preventing the current refined sliding mechanism from explaining them, even qualitatively. We stress that Eq. (11) is essentially of the form:

$$\langle B \rangle = \frac{H^2}{D} \mathcal{F} \left(\frac{H}{\sqrt{ND}} \right), \quad (15)$$

with \mathcal{F} a scaling function, which, combined with Eq. (5), cannot lead to the factorized form of Eq. (1). We also stress that including loops in addition, or exclusively, does not help too, as all these types of paths can be seen under the same category of survival processes, and therefore exhibit a large- N saturation of their average lengths around the value of the film thickness.

V. DISCUSSION

In an attempt to generalize our findings to some variations in the sliding mechanism, we assume that the relaxation time is of the generalized form:

$$\tau = \tau_0 \mathcal{H} \left[\langle B \rangle, \frac{a^3}{v_f(T)} \right], \quad (16)$$

where τ_0 is a reference time scale, and \mathcal{H} is an increasing function of both its arguments. Indeed, the relaxation time is expected to increase with increasing bridge length or decreasing free volume. Therefore, and because the effective glass-transition temperature T_g of a film is assumed to be reached when τ reaches the reference relaxation time of a bulk material at T_g^{bulk} [52], a relation of the following form must be satisfied:

$$v_f(T_g) = a^3 \mathcal{G}(\langle B \rangle), \quad (17)$$

where \mathcal{G} is an increasing function. In the sliding model [52], one has $\mathcal{G}(x) \propto \sqrt{x}$ for instance. For comparison, in the delayed-glassification model [54], one has $\mathcal{G}(x) \propto \log(x)$. As a side remark, a linear relation between free volume v_f and temperature T was assumed (see Eq. (4)), in view of thermal expansion in a sufficiently narrow temperature range, but we stress that any behavior of the form $v_f \sim (T - T_V)^\beta$ with a positive exponent β would lead to the same conclusion.

Let us now exhibit a necessary condition that should be satisfied by a model to ensure its applicability for describing experimental facts. The trends in Fig. (1) are consistent with Eq. (1), and a factor $f(M_w)$ slowly diverging with M_w [42]. Assuming the latter divergence to be true implies that:

$$\lim_{M_w \rightarrow \infty} \frac{\partial T_g}{\partial h} = +\infty. \quad (18)$$

Combining the latter with Eq. (4), and assuming T_V and α to be independent of h , leads to:

$$\lim_{N \rightarrow \infty} \frac{1}{a^3} \frac{\partial v_f(T_g)}{\partial H} = +\infty. \quad (19)$$

Finally, by combining Eq. (19) with Eq (17), one gets:

$$\lim_{N \rightarrow \infty} \mathcal{G}'(\langle B \rangle) \frac{\partial \langle B \rangle}{\partial H} = +\infty. \quad (20)$$

From Eq. (13), we see that the left-hand side of Eq. (20) equals $[7H/(15D)]\mathcal{G}'[7H^2/(30D)]$, which is positive, but finite. Hence, even a generalized formulation of the sliding model following Eq. (16) cannot describe the experimental data. As a result, within the Gaussian framework, we can conclude that a different mechanism is needed to explain the M_w dependence of the T_g reductions in thin freestanding polymer films.

VI. CONCLUSION

We have computed the probability density function of the bridge length in a thin film made of a dense equilibrium assembly of identical finite-sized polymer chains. The calculations were performed in the Gaussian-chain framework. We have then used the obtained expressions in order to refine and critically discuss the sliding model

for the anomalous glass transition in thin freestanding polymer films. Our analysis suggests that the sliding model, as well as similar models based on free-volume arguments, can not capture the intricate chain-length dependence of the experimental data. Another key physical ingredient, with a dependence on the molecular weight, seems to be missing. Finally, we note that: i) the remarkable stability of the films above the measured M_w -dependent T_g ; ii) the proposed existence of a second T_g , more closely associated with flow; and iii) the coincidence of T_g^* with the temperature of the $\alpha - \beta$ splitting in polystyrene, may all suggest that the M_w -dependent T_g in freestanding polymer films is associated with a local, rather than segmental, relaxation.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the European Union through the European Research Council under EMetBrown (ERCCoG-101039103) grant. The authors also acknowledge financial support from the Agence Nationale de la Recherche under EMetBrown (ANR-21-ERCC-0010-01), Softer (ANR-21-CE06-0029) and Fricolas (ANR-21-CE06-0039) grants, as well as from the UHJ-France association and the Scopus Foundation. Finally, they thank the Soft Matter Collaborative Research Unit, Frontier Research Center for Advanced Material and Life Science, Faculty of Advanced Life Science at Hokkaido University, Sapporo, Japan, as well as the Natural Sciences and Engineering Research Council of Canada.

AUTHOR CONTRIBUTION STATEMENT

J.F., E.R. and T.S. conceived the study. H.B. and M.A. performed the analytical research. R.C. performed the numerical simulations. H.B. wrote the first draft of the manuscript. All the authors discussed the results and contributed to the writing of the manuscript.

DATA AVAILABILITY STATEMENT

Data produced for this article are available upon reasonable request to the authors.

-
- [1] H. Vogel, The law of the relationship between viscosity of liquids and the temperature, *Physikalische Zeitschrift*, 22, 645, 1921.
 [2] G. S. Fulcher, Analysis of recent measurements of the viscosity of glasses, *Journal of the American Ceramic Society*, 8, 6, 339, 1925.

- [3] G. Tammann and W. Hesse, Die Abhängigkeit der Viskosität von der Temperatur bei unterkühlten Flüssigkeiten, *Zeitschrift für Anorganische und Allgemeine Chemie*, 156, 245, 1926.
 [4] M. L. Williams, R. F. Landel, and J. D. Ferry, The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids, *Journal*

- of the American Chemical Society, 77, 3701, 1955.
- [5] C. A. Angell, Formation of glasses from liquids and biopolymers, *Science*, 267, 1924, 1995.
 - [6] L. Berthier and G. Biroli, Theoretical perspective on the glass transition and amorphous materials, *Review of Modern Physics*, 83, 587, 2011.
 - [7] M. D. Ediger and P. Harrowell, Perspective: Supercooled liquids and glasses, *The Journal of Chemical Physics*, 137, 2012.
 - [8] G. Parisi, P. Urbani, and F. Zamponi, Theory of simple glasses: exact solutions in infinite dimensions, *Cambridge University Press*, 2020.
 - [9] P. Anderson, Through the glass lightly, *Science* 267, 1615, 1995.
 - [10] G. Adam and J. H. Gibbs, On the temperature dependence of cooperative relaxation properties in glass-forming liquids, *The Journal of Chemical Physics*, 43, 139, 1965.
 - [11] E. Donth, Characteristic length of the glass-transition, *Journal of Polymer Science: Part B: Polymer Physics*, 34, 2881, 1996.
 - [12] J. D. Stevenson, J. Schmalian, and P. G. Wolynes, The shapes of cooperatively rearranging regions in glass-forming liquids, *Nature Physics*, 2, 268, 2006.
 - [13] A. J. Liu and S. R. Nagel, The jamming transition and the marginally jammed solid, *Annual Review of Condensed Matter Physics*, 1, 2010.
 - [14] Z. Zhang, P. J. Yunker, P. Habdas, and A. G. Yodh, Cooperative Rearrangement Regions and Dynamical Heterogeneities in Colloidal Glasses with Attractive Versus Repulsive Interactions, *Physical Review Letters*, 107, 208303, 2011.
 - [15] J. Bares, Glass transition of the polymer microphase, *Macromolecules* 8, 244, 1975.
 - [16] C. L. Jackson and G. B. McKenna, The melting behavior of organic materials confined in porous solids, *The Journal of Chemical Physics*, 93, 12, 9002, 1990.
 - [17] P. Scheidler, W. Kob, and K. Binder, The relaxation dynamics of a simple glass former confined in a pore, *Europhysics Letters*, 52, 277, 2000.
 - [18] L. Berthier, Finite-size scaling analysis of the glass transition, *Physical Review Letters*, 91, 055701, 2003.
 - [19] J. L. Keddie, R. A. L. Jones, and R. A. Cory, Size-dependent depression of the glass transition temperature in polymer films, *Europhysics Letters*, 27, 1, 59, 1994.
 - [20] J. A. Forrest and K. Dalnoki-Veress, The glass transition in thin polymer films, *Advances in Colloid and Interface Science*, 94, 167, 2001.
 - [21] F. Varnik, J. Baschnagel, and K. Binder, Reduction of the glass transition temperature in polymer films: A molecular-dynamics study, *Physical Review E*, 65, 021507, 2002.
 - [22] C. J. Ellison and J. M. Torkelson, The distribution of glass-transition temperatures in nanoscopically confined glass formers, *Nature Materials*, 2, 695, 2003.
 - [23] J. Baschnagel and F. Varnik, Computer simulations of super-cooled polymer melts in the bulk and in confined geometry, *Journal of Physics: Condensed Matter*, 17, R851, 2005.
 - [24] M. Alcoutlabi and G. B. McKenna, Effects of confinement on material behaviour at the nanometre size scale, *Journal of Physics: Condensed Matter*, 17, R461, 2005.
 - [25] Z. Fakhraai and J. A. Forrest, Measuring the surface dynamics of glassy polymers, *Science*, 319, 600, 2008.
 - [26] Z. Yang, Y. Fujii, F. K. Lee, C.-H. Lam, and O. K. C. Tsui, Glass transition dynamics and surface layer mobility in unentangled polystyrene films, *Science*, 328, 1676, 2010.
 - [27] Y. Chai, T. Salez, J. D. McGraw, M. Benzaquen, K. Dalnoki-Veress, E. Raphaël, and J. A. Forrest, A direct quantitative measure of surface mobility in a glassy polymer, *Science*, 343, 994, 2014.
 - [28] H. Yoon and G. B. McKenna, Substrate effects on glass transition and free surface viscoelasticity of ultrathin polystyrene films, *Macromolecules*, 47, 8808, 2014.
 - [29] M. D. Ediger and J. A. Forrest, Dynamics near free surfaces and the glass transition in thin polymer films: A view to the future, *Macromolecules*, 47, 471, 2014.
 - [30] K. Ngai, A. Rizos, and D. Plazek, Reduction of the glass temperature of thin freely standing polymer films caused by the decrease of the coupling parameter in the coupling model, *Journal of Non-Crystalline Solids*, 235, 435, 1998.
 - [31] D. Long and F. Lequeux, Heterogeneous dynamics at the glass transition in van der Waals liquids, in the bulk and in thin films, *European Physical Journal E*, 4, 371, 2001.
 - [32] S. Herminghaus, K. Jacobs, and R. Seemann, The glass transition of thin polymer films: some questions, and a possible answer, *European Physical Journal E*, 5, 531, 2001.
 - [33] J. E. G. Lipson and S. T. Milner, Percolation model of interfacial effects in polymeric glasses, *European Physical Journal B*, 72, 133, 2009.
 - [34] J. A. Forrest, What can we learn about a dynamical length scale in glasses from measurements of surface mobility?, *The Journal of Chemical Physics*, 139, 084702, 2013.
 - [35] C.-H. Lam and O. K. Tsui, Crossover to surface flow in supercooled unentangled polymer films, *Physical Review E*, 88, 042604, 2013.
 - [36] J. A. Forrest and K. Dalnoki-Veress, When does a glass transition temperature not signify a glass transition?, *ACS Macro Letters*, 3, 310, 2014.
 - [37] S. Mirigian and K. S. Schweizer, Communication: Slow relaxation, spatial mobility gradients, and vitrification in confined films, *The Journal of Chemical Physics*, 141, 161103, 2014.
 - [38] T. Salez, J. Salez, K. Dalnoki-Veress, E. Raphaël, and J. A. Forrest, Cooperative strings and glassy interfaces, *Proceedings of the National Academy of Sciences*, 112, 8227, 2015.
 - [39] Z. Hanakata, B. A. Pazminõ Betancourt, J. F. Douglas, and F. W. Starr, A unifying framework to quantify the effects of substrate interactions, stiffness, and roughness on the dynamics of thin supported polymer films, *The Journal of Chemical Physics*, 142, 234907, 2015.
 - [40] M. Arutkin, E. Raphaël, J. A. Forrest, and T. Salez, Cooperative strings and glassy dynamics in various confined geometries, *Physical Review E*, 101, 032122, 2020.
 - [41] G. Reiter, M. Hamieh, P. Damman, S. Sclavons, S. Gabriele, T. Vilmin, and E. Raphaël, Residual stresses in thin polymer films cause rupture and dominate early stages of dewetting, *Nature Materials*, 4, 754, 2005.
 - [42] K. Dalnoki-Veress, J. A. Forrest, P.-G. de Gennes, J. R. Dutcher, Glass Transition Reductions in Thin Freely-standing Polymer Films: a Scaling Analysis of Chain Confinement Effects, *Journal de Physique*, IV, 10, 221, 2000.

- [43] J. A. Forrest and K. Dalnoki-Veress, The glass transition in thin polymer films, *Advances in Colloid and Interface Science*, 94, 167, 2001.
- [44] C. B. Roth and J. R. Dutcher, Glass transition temperature of freely-standing films of atactic poly (methyl methacrylate), *European Physical Journal E*, 12, 103, 2003.
- [45] C. B. Roth, A. Pound, S. W. Kamp, C. A. Murray, and J. R. Dutcher, Molecular-weight dependence of the glass transition temperature of freely-standing poly(methyl methacrylate) films, *European Physical Journal E*, 20, 441, 2006.
- [46] S. Kim and J. M. Torkelson, Distribution of Glass Transition Temperatures in Free-Standing, Nanoconfined Polystyrene Films: A Test of de Gennes' Sliding Motion Mechanism, *Macromolecules*, 44, 4546, 2011.
- [47] M. Aubouy, M. Manghi, and E. Raphaël, Interfacial Properties of Polymeric Liquids, *Physical Review Letters*, 84, 4858, 2000.
- [48] J. E. Pye and C. B. Roth, Two Simultaneous Mechanisms Causing Glass Transition Temperature Reductions in High Molecular Weight Freestanding Polymer Films as Measured by Transmission Ellipsometry, *Physical Review Letters*, 107, 235701, 2011.
- [49] O. Tsui, Anomalous dynamics of polymer films, in *Polymer Thin Films*, *World Scientific*, 267, 2008.
- [50] O. Bäumchen, J. D. McGraw, J. A. Forrest, and K. Dalnoki-Veress, Reduced Glass Transition Temperatures in Thin Polymer Films: Surface Effect or Artifact?, *Physical Review Letters*, 109, 055701, 2012.
- [51] D. L. Baker, M. Reynolds, R. Masurel, P. D. Olmsted, and J. Mattsson, Cooperative Intramolecular Dynamics Control the Chain-Length-Dependent Glass Transition in Polymers, *Physical Review X*, 12, 021047, 2022.
- [52] P.-G. de Gennes, Glass transitions in thin polymer films, *The European Physical Journal E*, 2, 201, 2000.
- [53] P.-G. de Gennes, Glass transitions of freely suspended polymer films, *Comptes Rendus de l'Académie des Sciences*, 1, IV, 1179, 2000.
- [54] S. T. Milner and J. E. Lipson, Delayed glassification model for free-surface suppression of Tg in polymer glasses, *Macromolecules*, 43, 9865, 2010.
- [55] J. E. Lipson and S. T. Milner, Local and Average Glass Transitions in Polymer Thin Films, *Macromolecules*, 43, 9874, 2010.
- [56] M. Doi and S. F. Edwards, The theory of polymer dynamics, *Oxford university press*, 73, 1988.
- [57] S. Redner, A guide to first-passage processes, *Cambridge university press*, 2001.