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

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Abstract 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.

1 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 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], wether or not specific polymeric effects exist within the glassy physics is an interesting fundamental question with important practical implications given the widespread used 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
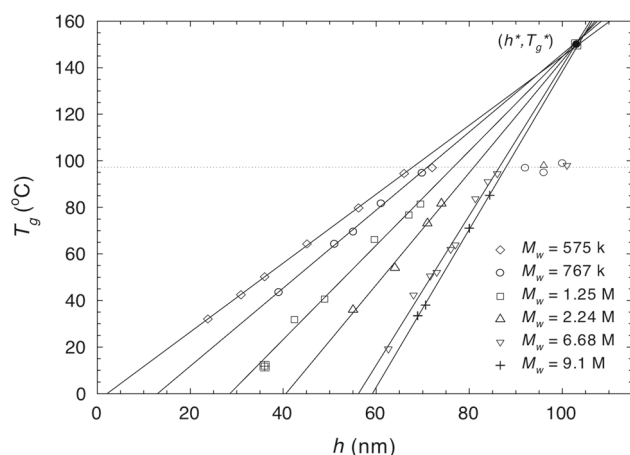
Fig. 1 Glass-transition temperature T_{g} of freestanding polystyrene films as a function of film thickness h, for various average molecular weights M_{w}. By extrapolating the low-thickness linear regimes towards larger thicknesses, one empirically finds a universal crossing point, denoted by (h^*, T_{g}^*). Figure reproduced from Ref. [43]

mapped onto the one for 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 $T_{\mathrm{g}}^{\mathrm{bulk}}$; 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:

$$T_{\mathrm{g}} = T_{\mathrm{g}}^* + f(M_{\mathrm{w}})(h - h^*), \qquad (1)$$

for $h < h_{\mathrm{c}}$, where $h_{\mathrm{c}} = h^* + (T_{\mathrm{g}}^{\mathrm{bulk}} - T_{\mathrm{g}}^*)/f(M_{\mathrm{w}})$ 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 $f(M_{\mathrm{w}})$ was suggested to be logarithmic-like [42], a form which, perhaps coincidently, 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 $h_{\mathrm{c}} < h < h^*$. 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 behaviour in thin freestanding polymer films was only measured near $T_{\mathrm{g}}^{\mathrm{bulk}}$—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]. The focus on bridges is in alignment with the experimental finding that the phenomenon could be dramatically reduced by eliminating one of the free surfaces. 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.

2 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 localized 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 independent jumps indexed by i and involving volumes ω_i, which are assumed to be normally and identically Gaussian-tail distributed, as:

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

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:

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

where the average is made over the ensemble $\{\omega_i\}$ against the distributions $\mathcal{P} = \Pi_i p(\omega_i)$, 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:

$$v_f(T) = \alpha a^3 (T - T_V), \tag{4}$$

where α is the expansion coefficient. Assuming that the process happens along a bridge of average number of units $\langle b \rangle$ gives $\tau/\tau_0 \sim \exp\left[\frac{1}{4} \langle b \rangle \omega_0^2 / v_f^2(T)\right]$. Since the logarithm of the normalized time does not change drastically around the effective glass transition, using Eq. (4) one eventually finds:

$$T_g - T_V \propto \sqrt{\langle b \rangle}. \tag{5}$$

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 wether or not the M_w dependence in Eq. (1) can also be captured by the sliding model.

3 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
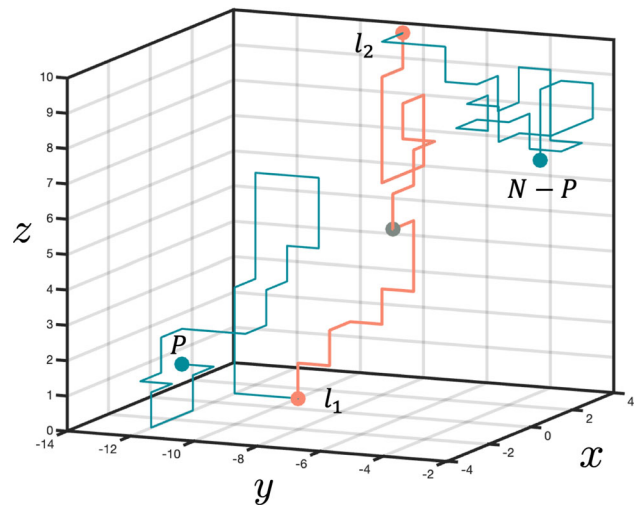

Fig. 2 Sketch of the problem studied, as obtained from numerical simulation. We consider an ideal random walk with N steps in a box of dimensionless thickness $H = 10$ along the z-axis. A randomly chosen monomer (grey), located at an altitude z, is P steps away from one of the walk ends, and $N - P$ 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

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, reads:

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

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:

$$\rho = 2 \int_I \mathrm{d}l f_0(z, l) f_H(z, B - l). \tag{7}$$

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:

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

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:

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

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

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:

$$\langle B \rangle = \frac{1}{\phi(N, H)} \left[\frac{7H^2}{90D} - \frac{31H^4}{1260ND^2} \right.$$

$$\left. + \frac{4N}{\pi^2} \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k^2} u_k(N, H) e^{-D\lambda_k^2 N} \right], \tag{11}$$

where, for convenience, we invoked the auxiliary function:

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

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

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

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.

4 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 behaviour:

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

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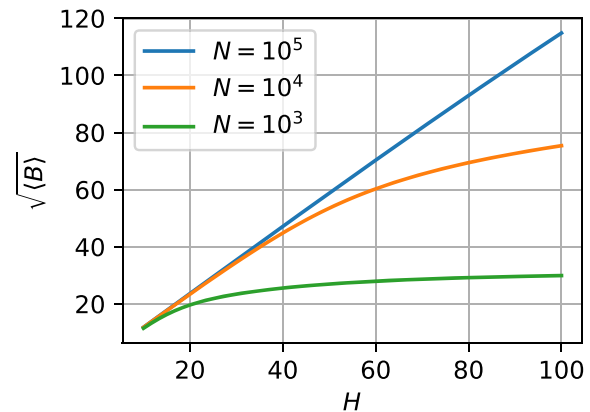

Fig. 3 Square root of the average dimensionless bridge length $\langle B \rangle$ as a function of dimensionless film thickness H, for three chain lengths N, obtained from the numerical evaluation of Eq. (11) using a cut-off after 100 terms in the sum. The results have been checked to weakly depend on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

essentially of the form:

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

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.

5 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:

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

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:

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

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 behaviour 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:

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

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

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

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

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

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.

6 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 segmental, rather than cooperative segmental, relaxation.

Author contribution statement

JF, ER and TS conceived the study. HB and MA performed the analytical research. RC performed the numerical simulations. HB wrote the first draft of the

manuscript. All the authors discussed the results and contributed to the writing of the manuscript.

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