The glass transition of thin polymer films: some questions, and a possible answer

S. Herminghaus[a], K. Jacobs, and R. Seemann

Department of Applied Physics, University of Ulm, 89069 Ulm, Germany

Abstract. A simple and predictive model is put forward explaining the experimentally observed substantial shift of the glass transition temperature, T_g, of sufficiently thin polymer films. It focuses on the limit of small molecular weight, where geometrical 'finite size' effects on the chain conformation can be ruled out. The model is based on the idea that the polymer freezes due to memory effects in the viscoelastic eigenmodes of the film, which are affected by the proximity of the boundaries. The elastic modulus of the polymer at the glass transition turns out to be the only fitting parameter. Quantitative agreement is obtained with our experimental results on short chain polystyrene ($M_W = 2$ kg/mol), as well as with earlier results obtained with larger molecules. Furthermore, the model naturally accounts for the weak dependence of the shift of T_g upon the molecular weight. It explains why supported films must be thinner than free standing ones to yield the same shift, and why the latter depends upon the chemical properties of the substrate. Generalizations for arbitrary experimental geometries are straightforward.

PACS. 64.70.Pf Glass transitions – 68.60.Bs Mechanical and acoustical properties – 81.05.Kf Glasses (including metallic glasses) – 83.10.Bb Kinematics of deformation and flow

1 Introduction

To explain the experimental observation that thin polymer films melt at temperatures strongly different from (usually below) the glass transition temperature of the bulk polymer, T_g^0 [1–4], is one of the major current challenges in the theory of homopolymers. At first glance, one might expect such a behavior, due to the impact of the finite size geometry of a thin film upon objects as large as polymer molecules. In fact, for molecular weights larger than about $M_W = 300$ kg/mol, geometry effects have been recently shown to play a dominant role, resulting in a linear dependence of T_g upon the film thickness, h [4–6]. For smaller molecules, however, the problem is conceptually more intricate, since a noticeable reduction of T_g can be observed at film thicknesses orders of magnitude larger than the radius of gyration of the molecules. Furthermore, the shift $T_g^0 - T_g(h)$ becomes strongly nonlinear and largely independent of molecular weight [3,7], indicating that this regime must be governed by a different mechanism. A fundamental understanding of this effect would be of great interest not only for polymer physics, but potentially also elucidate the physics of the glass transition in a larger class of systems, since it comes into play at small molecular weight.

Many attempts have been undertaken to explain these observations, mostly by considering microscopic models of the inner structure of the films. Long and Lequeux have envisaged the freezing of the film as a percolation of rigid domains [8], mediated by thermal fluctuations [9]. Other models assume a layered structure of the film, with a particularly mobile region close to the free surface of the film [1]. Within this framework, Forrest and Mattsson [7] have recently been able to achieve quite impressive accordance with the experimental data [2,7]. Their model makes use of the so-called cooperativity length, $\xi(T)$, which plays a mayor role in a whole class of theoretical concepts of the glass transition. The only drawback is that there is yet no well established theory of $\xi(T)$. Furthermore, as a consequence of the two-layer structure of the film inherent in the model, it is not completely clear why there should not be two glass transitions, rather than a single one shifted in temperature.

As a complementary approach, computer simulations of polymer films with free surfaces have recently been carried out, and most of the experimental findings were reproduced qualitatively [10]. However, the polymer chains in these simulations were shorter than those used in the experiments up to now. Before attempting to explain the effect theoretically, it is therefore worthwhile to study experimentally the behavior of polymers with short chain length, both to ease comparison with simulation and to explore the range of validity of the apparent independence of the shift of T_g on molecular weight.

Before going into the details of our study, let us take a break and summarize the main questions to be answered.

[a] e-mail: `stephan.herminghaus@physik.uni-ulm.de`

1. What is the principal mechanism responsible for the reduction of T_g in thin films of low molecular weight ($M_W < 300$ kg/mol) polymers?
2. Down to how small molecular weight is this mechanism valid?
3. Why is there no significant dependence of this effect on molecular weight [3]?
4. Why is the effect stronger in free standing films than in supported ones [3]?
5. Why does the effect depend upon the chemical composition of the substrate for supported films [11–13]?
6. Why is there sometimes an increase of T_g in thin films, instead of a reduction [11–13]?

We will try in the present paper to give answers to these questions, or at least show in which direction answers might be found, on the basis of a novel, quite simple model which rests mainly on the viscoelastic eigenmodes of the films. We restrict the discussion to the case of polystyrene (PS), since this is the most thoroughly studied polymer in this context. Furthermore, it is particularly well suited for comparison with theoretical models, since (atactic) polystyrene does not show any propensity to crystallization. In other polymers, which might crystallize at least in part of the film, modelling would be exceedingly difficult, and the main mechanism could well be obscured in experiments.

2 Experiment

Let us first explore the range of validity of the aforementioned effect of reduction of T_g, as to the molecular weight of the polymer. We have investigated the glass transition in thin supported films of atactic PS with a molecular weight as small as 2 kg/mol (≈ 20 monomer units). It was purchased from Polymer Labs (UK) with a polydispersity index $M_W/M_N = 1.05$, the radius of gyration is 1.3 nm. Effects from the molecular geometry are thus expected only for films of few nanometers thickness. The films were spin cast from toluene solution onto silicon wafers (Silchem GmbH, Freiberg/Germany), which were previously cleaned by ultrasonication in acetone, ethanol, and toluene, subsequently. Residual organics were removed with a 1:1 mixture of H_2SO_4 with H_2O_2, and the substrates were thoroughly rinsed with hot millipore water afterwards. Films were investigated with thicknesses ranging from 4 to 160 nm. The roughness of the free surface of the films was less than 0.2 nm, as revealed by scanning force microscopy (SFM).

The glass transition temperature was determined in two different ways, depending on film thickness. The standard procedure of monitoring the thermal expansion of the film *via* ellipsometry, as introduced by Keddy and Jones [1], was used for film thicknesses down to 9.6 nm. Figure 1a shows a typical run. The data were reproducible, irrespective of being taken during heating or cooling. Typical heating or cooling rates were 2 K/min. We plotted the changes in refractive index and thickness of the film in Figure 1b. The solid line represents the Clausius
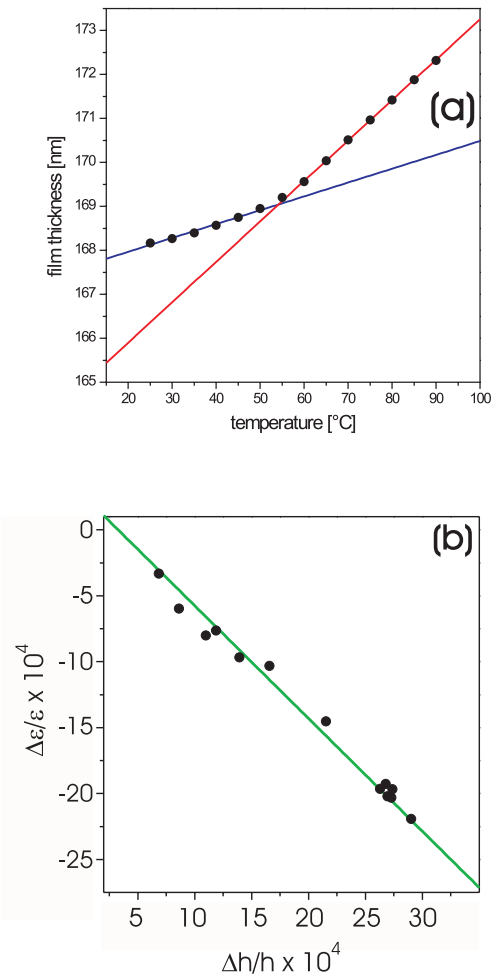

Fig. 1. (a) Ellipsometric dilation measurement of a thin PS film. Typical heating/cooling rates were 2 K/min. (b) The change in film thickness *vs.* the change in the optical dielectric constant, as measured by ellipsometry for various temperatures during a heating/cooling cycle. The good agreement obtained with the Clausius-Mosotti relation represented by the solid line demonstrates the absence of significant loss or degradation of material.

Mosotti relation. Obviously, there is good agreement, suggesting the absence of any loss or degradation of material. This was found invariably for all samples.

In Figure 2 we plotted the thermal expansion coefficients found above and below $T_g(h)$, which corresponds to the kink in Figure 1a. At large film thickness, T_g obtained in this way approached 327 ± 1 K, which is consistent with the temperature at which macroscopic melting is observed in the bulk (T_g^0) for PS with this chain length. The shaded areas represent published data of the expansion coefficients [14]. Good agreement is found both above and below T_g. Small deviations at very small film thickness, as might be concluded from our data, have been reported before [1].
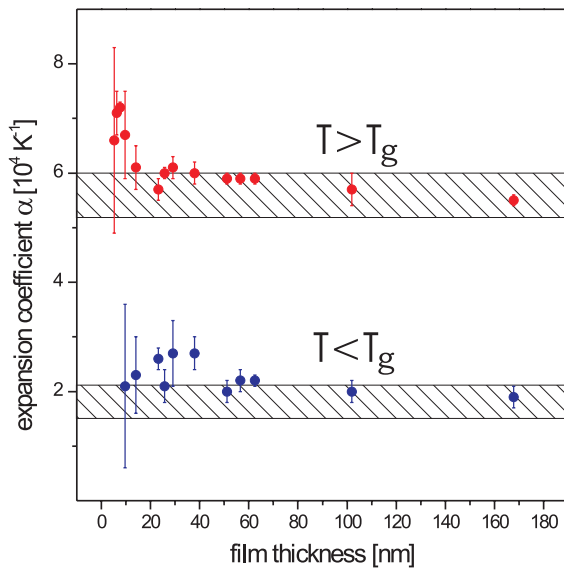
Fig. 2. Thermal expansion coefficients obtained above and below T_g. The shaded areas represent values taken from the literature [14].
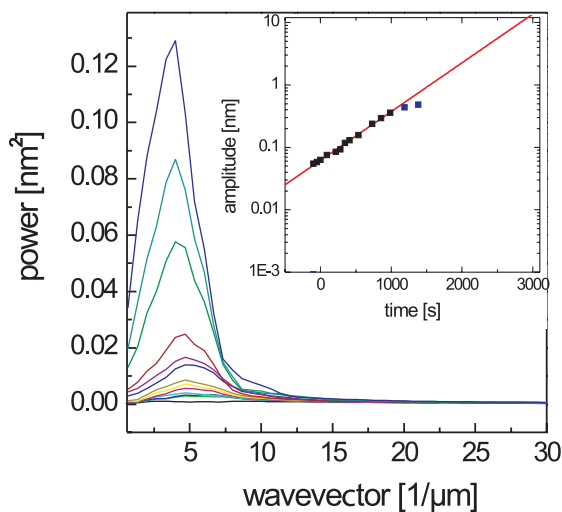

Fig. 3. Temporal evolution of the power spectrum of spinodal dewetting undulations on a PS film exhibiting unstable capillary waves at its free surface. Curves of equidistant times are superimposed to show the gradual increase of the main peak. The inset shows the exponential growth of the latter, from which the viscosity of the film can be inferred.

For films thinner than 9 nm, we determined the melting behaviour of the films by observing the buildup of amplified thermal fluctuations (spinodal dewetting) [15–17]. These processes were monitored by SFM with *in situ* heating. In order to speed up the experiments to a feasible time scale, dewetting was observed at temperatures close to T_g^0. As an example, we show in Figure 3 the temporal evolution of the Fourier transform (spatial power spectrum) of the surface topography. The hallmark feature is the
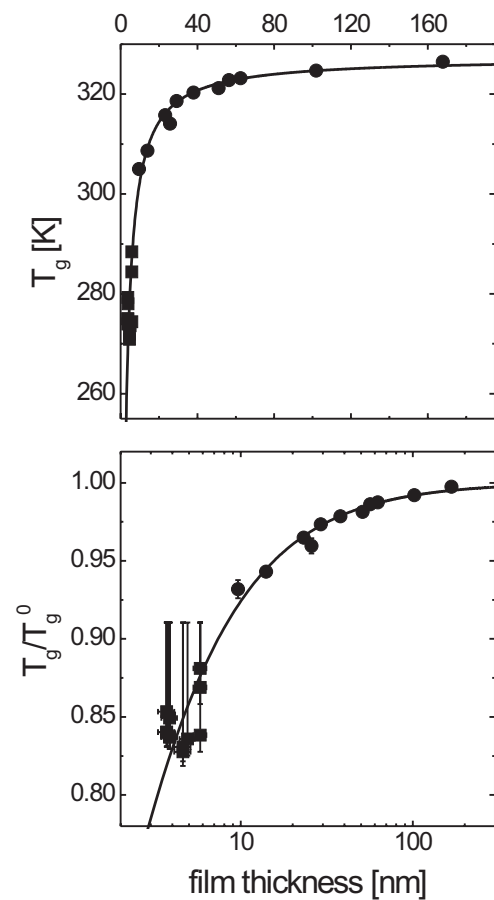

Fig. 4. The glass transition of thin films of 2 kg/mol polystyrene, as determined from thermal expansion (circles) and from the growth of spinodal waves (squares). The solid curve represents our model, which has the elastic modulus governing the dominant modes as its only fitting parameter. It furthermore corresponds to what was found for larger molecular weight PS before [19]. Top: linear scale. Bottom: logarithmic scale, showing more details at small film thickness.

clear peak representing the fastest growing mode. The inset shows the peak intensity as a function of time on logarithmic scale. Exponential growth is clearly observed up to a rather well defined time at which coalescence of holes sets in.

From the slope of the straight line in the inset, and the known effective interface potential [17,18], the viscosity η of the polymer can be determined exploiting well-known theory on thin film dynamics [15]. Measuring the viscosity as a function of temperature, we found that this obeyed a Vogel-Fulcher law, with the Vogel-Fulcher temperature shifted by a certain amount ΔT_{VF}, which depended on the film thickness. We identified $\Delta T_{\mathrm{VF}}(h)$ with the shift in glass temperature. In this way, the apparent glass transition temperature of particularly thin films was inferred from the spinodal dewetting experiments by setting $T_g(h) = T_g^0 - \Delta T_{\mathrm{VF}}(h)$.

Our experimental results are shown in Figure 4 as the full symbols. The circles represent the thermal expansion measurements, the squares were obtained from the spinodal dewetting experiments. As one can clearly see, the glass transition temperature is substantially reduced for all films thinner than about 50 nm. The solid line represents the function

$$T_{\mathrm{g}} = T_{\mathrm{g}}^0 (1 + h_0/h)^{-1} \tag{1}$$

This form has been shown before to account well for the data obtained by others for larger molecular weight films, if $h_0 = 0.68$ nm was assumed for PS [19]. Within experimental scattering, our data exhibit indeed the same dependence of $T_{\mathrm{g}}(h)$ in the full range of film thickness explored. It is remarkable that the data from both the thermal expansion and spinodal dewetting measurements are well fitted by the same curve. This tentatively corroborates the procedure of obtaining T_{g} for very thin films (squares) as discussed above.

Although our polymer chains are roughly by a factor of 50 shorter than those investigated before, we obtain $h_0 = 0.82$ nm from the fit, which is quite close to the above value. This confirms the weak dependence (if there is a significant one at all) of the reduction of the glass transition temperature on the molecular weight of the polymer, down to a molecular weight as small as 2 kg/mol.

We can thus state that the reduction of T_{g} in thin films, as described phenomenologically by equation (1), is observed in a huge range of molecular weight, from molecules as small as 2 kg/mol up to a few hundred kg/mol. This is in accordance with molecular dynamics simulations [10], and rules out mere finite size effects on the individual coils as the main cause of the reduction of T_{g} in this regime. Note that the radius of gyration of our polymer is only 1.3 nm, while T_{g} is significantly reduced at a film thickness of 50 nm already. The fitting parameter used in equation (1), h_0, changes only by about 20% in this range, confirming that the dominant mechanism which is responsible for this effect cannot depend strongly on the molecular weight of the polymer.

3 Eigenmode spectrum of the films

Since it is clear that the behaviour displayed in Figure 4 can in no way be attributed to the geometrical impact of the finite film thickness upon the microscopic conformation of the individual chains, we present here an approach to the problem which intentionally makes as few reference as possible to the molecular structure of the film. The latter is accounted for merely by the strain in the polymer, *i.e.*, the deviation of the *local average* gyration ellipsoids of the molecules from a sphere. By '*local*' we mean a volume much larger than the volume of the backbone of a single molecule, but with a lateral dimension much smaller than the film thickness.

Such a deviation from the equilibrium conformation (*i.e.*, from a Gaussian coil, if self-avoidingness is neglected), which may be viewed as an entropy fluctuation, can decay either by self diffusion of the individual molecules, or by some center-of-mass rearrangement (*i.e.*, flow) of the melt. It is clear that close to a surface, such rearrangements are much easier to accomplish due to coupling of the capillary waves on the free surface to the bulk flow of the polymer. This coupling is effective down to a depth comparable to the wavelength of the capillary modes, which may be *much larger than the coil size of the molecules*. Thus we are provided with a mechanism which affects the motion of the polymer molecules, and naturally can act over distances which are large as compared to molecular dimensions. In order to explore the possible relevance of this mechanism for the reduction of T_{g} in thin films, we have to consider the eigenmode spectrum of the (viscoelastic) polymer film. This can be discussed with all possible boundary conditions at the substrate, such that films with strong slip along the substrate, grafted films, or free standing films, may as well be treated within the same framework.

The spectrum of a viscoelastic thin film can be obtained in a straightforward manner by combining standard theory of elasticity [20] and hydrodynamics [21] in the limit of small Reynolds number (Stokes dynamics). The equation of motion reads

$$\{\partial_t + \omega_0 + \frac{E}{\eta}\}\nabla^2\phi = \frac{\nabla p}{\eta} \tag{2}$$

where E is Young's modulus, η is the viscosity, and ω_0 is the Rouse rate of relaxation of the individual chains into their equilibrium configuration [22,23]. ϕ is a vector field related to the strain tensor, **S**. For the sake of clarity, we restrict our discussion to a simple model, taking into account only a single intrinsic relaxation rate, ω_0, as opposed to more general treatments [24]. Deviations of the real polymer from this simple behaviour will be introduced *a posteriori* farther below.

If we restrict the discussion to one lateral (x) and one normal (z) coordinate, $\phi = (\phi_x, \phi_z)$ is defined *via*

$$\mathbf{S} = \begin{pmatrix} \partial_x\phi_x & \frac{1}{2}(\partial_x\phi_z + \partial_z\phi_x) \\ \frac{1}{2}(\partial_x\phi_z + \partial_z\phi_x) & \partial_z\phi_z \end{pmatrix}. \tag{3}$$

Finally, p is the pressure field.

For harmonic excursions of the free surface, $\zeta(x) = \zeta_0 \exp\{iqx - \omega t\}$, equation (2) has solutions

$$\phi_x \propto [1 + (h + q^{-1})\alpha(q)]\cosh qz - q^{-1}\alpha(q)\sinh qz$$
$$\phi_z \propto [1 + h\alpha(q)]\sinh qz - z\alpha(q)\cosh qz \tag{4}$$

where for the function $\alpha(q)$, we find

$$\alpha(q) = \left(\frac{q}{2}\right)\frac{\mathrm{e}^{2qh} - 1}{\mathrm{e}^{2qh} - 1 + qh} \tag{5}$$

for free standing films (symmetric modes) as well as for supported films with full slippage (zero friction). For supported films with some friction at the substrate, the expressions are of similar form, but considerably more complicated, and will not be discussed here. At the free surface, we used the standard boundary condition of zero

tangential stress, and $p = -\sigma \partial_{xx} \zeta$, where σ is the surface tension of the polymer. Note that for free standing films, h is defined as *half* the film thickness.

For the relaxation rates of the modes, we get

$$
\begin{aligned}
2\omega = \left(\omega_0 + \frac{E}{\eta} + \frac{\sigma q^2}{2\eta\alpha(q)}\right) \\
\pm \sqrt{\left(\omega_0 + \frac{E}{\eta} + \frac{\sigma q^2}{2\eta\alpha(q)}\right)^2 - \omega_0 \frac{2\sigma q^2}{\eta\alpha(q)}} \, .
\end{aligned}
\tag{6}
$$

Since it is only the 'fast' modes which contribute appreciably to the reduction of the glass transition temperature (see below), we consider only the upper branch of equation (6). Observing that $\omega_0 \ll \frac{E}{\eta}$, this is given by

$$
\omega = \omega_0 + \frac{E}{\eta} + \frac{\sigma q^2}{2\eta\alpha(q)},
\tag{7}
$$

as a very good approximation. The dependence of the wave number, q, stems solely form the coupling to the capillary waves on the free film surface. The first major assumption of our model is that $T_g(h)$ is determined by the spectrum of the viscoelastic eigenmodes of the film as given by equation (7).

4 The freezing mechanism: memory effects

The second major assumption is that the physical cause for the melting or freezing of the film, respectively, are *memory effects* in the polymer material. These are of course not included in the linear theory discussed above, and may be formulated in a generic way by means of a suitable memory kernel, as used in a class of theoretical models of the glass transition, called mode coupling models [26,27]. Within this framework, memory effects are taken into account by inserting a convolution integral with the memory kernel $m\{\phi(t)\} = a_1\phi + a_2\phi^2 + a_3\phi^3 + ...$ in the otherwise linear differential equation of motion of the modes considered [28]. In these models, ϕ usually describes density fluctuations. In contrast, we consider the material to be essentially incompressible, and ϕ denotes here the strain in the polymer material, as defined above. It thus describes the local state of the material, similar to what the density does for simple glass forming liquids [26,27,29].

In our case, the equation of motion (2) is of first order in time, hence we have

$$
\phi' + \omega(q)\phi + \int_0^t m\{\phi(\tau)\}\phi'(t-\tau)\mathrm{d}\tau = 0
\tag{8}
$$

as the mode coupling equation. This type of equations has been thoroughly analysed [25–27,30] in relation to the *microscopic* physics of the glass transition (to which we do not refer here), as well as to large scale degrees of freedom [31]. For density fluctuations in glass forming simple liquids, it was found that the coefficients a_i of the memory kernel vary concurrently with temperature, and that upon

crossing a certain border in the space spanned by the a_i, the system freezes into a nonergodic state [27]. The existence of such a freezing transition has been found to be largely independent of the precise form of the memory kernel. In fact, most of the features of a glass transition may be well represented by what has become known as schematic models, which are simple mode coupling equations not referring in their memory kernels to the microscopic physics of the system under study.

It is now worthwhile to contemplate on possible memory effects in a polymer melt, as to their scaling with temperature. Let us first consider a polymer molecule in equilibrium, forming a more or less Gaussian coil. If this is elongated by straining the polymer melt, to what extent will it memorize this process after the strain is released? In the strained state, the molecule will relax to some extent. However, this relaxation will not proceed homogeneously along the molecule, since the activation energy, U, for local rearrangements will depend upon the local topological environment.

In order to discuss the relaxation behaviour of the local molecular geometry, let us define a local geometric exponent of the coil, μ, by the relation

$$
\langle |\Delta\mathbf{r}| \rangle = (\Delta s)^\mu
\tag{9}
$$

where $\langle |\Delta\mathbf{r}| \rangle$ is the typical distance travelled in space upon moving alongside the polymer chain by a distance Δs. In completely stretched parts of the chain, $\mu = 1$, whereas in equilibrated domains, $\mu = \mu_{\text{equilib.}} \approx 0.5$. The variation ΔU of $U(s)$ determines the variation of the relaxation rate of μ towards $\mu_{\text{equilib.}}$. When the strain is released, remnants of this variation will remain, and thus represent a memory of the strain. This holds as long as the strain/release process is fast as compared to the equilibration time, ω_0^{-1}. For the modes to be considered here, this is well fulfilled. When $\Delta U \ll kT$, as we may assume, these remnant variations in $\mu(s)$ scale as $\Delta U/kT$, thus we can conclude that memory effects in the polymer scale as $1/T$. As a direct consequence, we can replace the memory kernel $m\{\phi(\mathbf{t})\}$ of equation (8), the coefficients a_i of which are temperature dependent, with $M\{\phi\}/T$, where M is now independent of temperature.

By proper normalizaton of time, equation (8) can now be rewritten as

$$
\phi' + \phi + \frac{1}{T\omega(q)} \int_0^t M\{\phi(\tau)\}\phi'(t-\tau)\mathrm{d}\tau = 0.
\tag{10}
$$

From this equation, we see directly that the modes with the largest relaxation rate freeze at the lowest temperature. Furthermore, the precise form of M, which might be derived from a detailed analysis of the non-equilibrium dynamics of the polymer molecules, does not need to be considered here any further. It is only required that M belongs to the class of kernels which yield a freezing transition for ϕ at all, *i.e.*, it must be a strictly monotonous function of ϕ for all q [25].

Let us now turn back to the eigenmodes of the film. The relaxation rates, as given by equation (7), are monotonously increasing with q. However, modes with q much larger than the inverse film thickness, h^{-1}, do not penetrate appreciably into the film, such that only a small fraction of the material takes part in these modes. Hence we are led to considering chiefly the modes with $q \approx h^{-1}$, since these are the highest frequency modes comprising all of the film material.

Setting thus $T_g(h)\omega(h^{-1}) = \text{const.}$ as suggested by equation (10), we directly arrive at a simple formula for the glass transition temperature:

$$T_g(h) = T_g^0 \left(1 + \frac{1.16\,\sigma}{h(E + \eta\omega_0)}\right)^{-1}. \tag{11}$$

This is precisely the form of equation (1), and Figure 4 shows that it describes our data very well.

5 Discussion

The quantity $\eta\omega_0$ is on the order of a few kPa and can in general be safely neglected against E. The characteristic length scale which appears here, and which was called h_0 in equation (1), is thus the ratio σ/E, with the surface tension $\sigma = 31$ mN/m for PS. It follows that the elastic modulus determining the dynamics of the relevant modes, E, is *the only physical fitting parameter* in the model. From $h_0 = 0.82$ nm, as obtained from the fit of our model, we find for the elastic modulus $E \approx 44$ MPa, which is, on logarithmic scale, right in between the modulus of the frozen material (a few GPa) and the modulus just above T_g (about 300 kPa). On the basis of the model discussed above, let us now try to formulate answers to the questions asked in the introduction, one after the other.

1. What is the main mechanism responsible for the reduction of T_g in thin films of low molecular weight ($M_W < 300$ kg/mol) polymers? The physical picture which emerges from our model is that as the temperature is increased, melting proceeds as the fastest mode involving all of the film material escapes from its frozen state and fluctuates. This proceeds with the help of the capillary waves on the free film surface, which ease entropy fluctuations in the polymer melt. The concomitantly increased motion of polymer chains reduces the effective viscosity also for modes with smaller q, which, as a consequence, are sped up (η appears in the denominator in Eq. (7)!) and melt in turn. In this way, the film finally melts at all length scales. It is illustrative to note that the softness of the spinodal modes, as used for the determination of T_g at small film thickness, does not contradict our model: these are modes with $q \ll 1/h$, and are thus not the fastest modes, as considered in the melting mechanism.

2. Down to how small molecular weight is this mechanism valid? We found that in agreement with simulation results [10], the effect is present even for molecules as short as about 20 monomer units. This is well below the limit of entanglement. It thus spans a wide range in molecular weight, over more than two orders of magnitude. It is precluded, or obscured, by other effects at molecular weights in excess of about 300 kg/mol [3].

3. Why is there no significant dependence of the effect on molecular weight? The physical property which solely determines the thin film behaviour according to our model is the elastic modulus, E. As it is well known, E displays no marked dependence on the molecular weight [22,32], such that on the basis of our model, $T_g(h)$ is expected as well to be largely independent of molecular weight. To be precise, E is slightly less for smaller molecular weight than for larger [14,32], such that according to equation (11), h_0 should be larger for smaller molecular weight. In fact, we obtained $h_0 = 0.82$ nm for our very short molecules, whereas for larger molecules, $h_0 = 0.68$ nm was found [19]. The observation that the relevant length scale, h_0, decreases with increasing molecular weight is another evidence against geometrical effects on individual chains to be relevant in the regime discussed here. The exact physical significance of the somewhat arbitrary 'choice' of E, which may be viewed as E *at* T_g, is to be investigated in further studies.

4. Why is the effect stronger in free standing films than in supported ones? We have mentioned that the eigenmodes of supported films of thickness h with no friction are identical to those (the symmetric ones) of free standing films of thickness $2h$. Thus our model predicts that the effect in a supported film is just as large as in a free standing film of twice the thickness. This is indeed in accordance with experimental observation [3].

5. Why does the effect depend upon the chemical composition of the substrate for supported films? It is clear that the amount of friction of the film material at the substrate changes the eigenmode spectrum of the film, such that a dependence on the chemical composition of the substrate is indeed expected on the basis of our model. When there is few or no friction with the substrate, even a film between two walls (*i.e.*, without a free surface) might exhibit features in its eigenmode spectrum which are to change the glass transition. It will be interesting to study this case in detail along the lines of the above model, since there are numerous simulation results on this geometry [33–35]. For a quantitative comparison with experimental data, however, the friction coefficients would have to be determined for the systems investigated. One should be aware of the fact that this also induces some uncertainty in the numerical value of E derived from our fit (*cf.* Fig. 4), since we have not characterized the friction of the films on the substrate.

6. Why is there sometimes an increase of T_g in thin films [11–13]? We can try to give a rough idea to what extent effects like this may be accounted for within our model, by including the interaction of the free surface with the substrate *via* long range forces. This is described most conveniently by replacing σq^2 by $\sigma q^2 + \frac{d^2 V}{dh^2}$, where $V(h)$ is the effective interface potential of the film due to long range forces [36,37]. For unretarded van der Waals forces, $V(h) = -A/12\pi h^2$, where A is the Hamaker constant. If $A > 0$, $\frac{d^2 V}{dh^2}$ is negative, such that the van der Waals forces

tend to destabilize film, giving rise to spinodal dewetting for sufficiently thin films. In any case, a positive A will reduce the relaxation rate of all of the modes, including the one at $q = 1/h$, and thereby tend to increase the glass transition temperature. Quantitatively, this effect is obtained by accordingly replacing σ in equation (11) by $\sigma - \frac{A}{2\pi h^2}$. As it turns out, T_g attains a minimum at $h_{min} = 3\sqrt{A/2\pi\sigma}$, and increases sharply for smaller thickness. For $A = 2.2 \times 10^{-20}$ J, representing PS on silicon oxide [18], this is at $h_{min} \approx 1$ nm. An increase of T_g above T_g^0 at a film thickness significantly larger than 1 nm can be explained only with an unphysically large Hamaker constant.

However, one should anyway be cautious with trying to interpret an increase of T_g in thin films in the framework of our model if working with polymers other than PS [10–13]. It is not at all clear what impact a possible crystallization (which is not present in atactic PS) can have on $T_g(h)$. Consequently, possible model systems for studying the mechanism discussed in the present paper have to be carefully chosen to ensure the absence of any pronounced inner texture of the film. Our model can be appropriate only for 'structureless' films, and might break down for films with a pronounced layered texture like, *e.g.*, a Langmuir-Blodgett film [38], or for other polymers which may crystallize at least in some part of the film.

6 Outlook

It is tempting to apply the view developed here also to the surface of a bulk polymer sample, for which the spectrum is obtained setting $\alpha = q/2$. As it is readily seen, one should expect surface melting at the polymer surface, down to a thickness of $h_{sm} = h_0 T_g^0 (T_g^0 - T)^{-1}$ [39]. This is very much along the lines of first ideas which had been put forward to explain the observed reduction of T_g in thin films [1]. To the best of our knowledge, there is yet no conclusive evidence in favor or in disfavor of polymer surface melting.

To confirm the theoretical concept put forward here, an *ab initio* derivation of the memory kernel, $m\{\phi\}$, from the statistics and microscopic transport properties of the individual molecule would be desirable. Furthermore, it is important to elaborate on the significance of Young's elastic modulus, E, at the glass transition. This was determined experimentally using our model to be $E = 44$ MPa, but it is not yet clear what physical principle distinguishes this value. A complete theory of the glass transition on the basis of the proposed model would be rather cumbersome, since it involves two strongly nonlinear mechanisms mutually affecting each other: freezing by the mode coupling mechanism, and non-Newtonian effects on the viscosity. Our model furthermore suggests that the glass transition in a homopolymer may be viewed as a mode-coupling-model freezing of its viscoelastic bulk modes. This needs not to contradict more classical views of the glass transition in homopolymers, but might serve as an interesting, and potentially useful, alternative approach.

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