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LETTER TO THE EDITOR

The glass transition of nanoscale polymeric films

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Abstract

On the basis of the nanoscale fluctuations of the excess number density of holes (free volumes), a theoretical model is developed to describe the glass transition temperature (T_g) of polymeric films with the thickness <100 nm. A Langevin equation is used in the derivation that helps us to understand the dependence of T_g not only on film thickness but also on molecular weight. Substrates have a strong influence on T_g and the diffusion coefficient of nanofilms, and the surface concentration of adsorbed chain ends depends on the strength of polymer–substrate interactions.

The glass transition temperature (T_g) is perhaps the most important physical parameter of amorphous polymers because a marked change in physical properties is associated with this transition. The influence of system size on the materials properties has gained importance with the advent of nanotechnology. Polymeric thin films are widely used in many applications ranging from microelectronics to nanoscale devices in which the size is already approaching 100 nm and can be expected to decrease further in the future.

The change in the glass transition of freely standing nanofilms and its dependence on the polymer–substrate interactions is an interesting current unexplained problem in polymer physics. It has been observed experimentally that T_g may increase or decrease in thin films from the bulk value depending on the nature of the substrate [1–6]. Molecular simulations of the glass transition in polymer films under confinement have been reported [7,8], and an analytical expression for the shift as a function of the film thickness has been discussed for spherical molecules [9]. The unexpected strong influence of molecular weight measured recently [3] adds a new level of interest to the problem. Besides, there are contradictory reports about the increase in segment mobility and the change in the diffusion coefficient as film thickness decreases. A theoretical understanding of the nanosize phenomena coupled with molecular weight dependence and substrate interactions is needed to help elucidate these open questions.

The glassy state represents a situation of frozen-in disorder and is a result of the significant change in the mobility of molecular segments, which can be described by the hole (free volume) motion [10]. Amorphous polymer consists of holes and polymer chains. The conformational activation energy controlling the hindered rotational relaxation for bonds of main chain in the macromolecule is between one and two orders of magnitude lower than the hole activation energy, which results in much faster relaxation for the flex bonds. Therefore, the dominant contribution to the structural relaxation is from the hole as an amorphous melt is cooled from liquid to solid, which involves the slow relaxation of the frozen-in structure. When the film thickness is comparable to the radius of gyration of polymer chains, the fluctuations of excessive hole density become important in the analysis of the glass transition. In this letter, we shall use a Langevin equation to derive the thickness and molecular weight dependence of T_g. The influence of substrates will be analysed by using a self-consistent field of polymer layers formed by adsorbing polymer ends to a surface. The effects of polymer–substrate interactions on T_g and the diffusion coefficient as a function of film thickness will then be calculated.

Two different views can be found in the literature in the molecular interpretation of T_g. One view is directed at the nonequilibrium character of structural relaxation and physical aging [10]. The other considers the condition of relaxation processes occurring so slowly that T_g can be treated as a time-independent phenomenon. According to Gibbs and DiMarzio's time-independent theory [11], glasses are formed as a result of a system losing its configuration entropy, which is the difference in entropy between the supercooled liquid (S^{liquid}) and glass (S^{glass}). The configuration entropy of nanofilms depends not only on temperature (T) but also on the film thickness (h). By setting the entropy $S^{glass}(h, T) = S^{glass}(h \to \infty, T) = 0$ at the glass transition, the change in the glass transition temperature from the bulk value, $T_{g\infty} \equiv T_g(h \to \infty)$, can be determined by the change in the entropy in the liquid states:

$$\ln\left[T_g(h)/T_{g\infty}\right] = -[S(h) - S(h \to \infty)]\Delta C_p, \tag{1}$$

where $S \equiv S^{liquid}$ is a function of h, but the difference in heat capacity ΔC_p between the supercooled liquid and glass is approximated to be independent of temperature and film thickness. The entropy is related to the excess number density of holes, $\delta n = n - \langle n\rangle$, where $\langle n\rangle$ is the homogeneous average, by [12]

$$S(h) = S_0 - \beta\langle[\delta n(h)]^2\rangle/2, \tag{2}$$

where S_0 is a constant and β depends on molecular weight.

In the study of thickness dependence, consider the change of excess number density, which is governed by the Langevin-like stochastic equation

$$\frac{\mathrm{d}(\delta n)}{\mathrm{d}h} = -\frac{\delta n}{2h_c} + \mu(h), \tag{3}$$

where μ is the noise term that is the source of fluctuations for δn, and the critical film thickness h_c is the correlation length of the fluctuations. In the de Gennes theory [4] based on sliding motion of a chain in a thin film, the molecular weight dependence is involved through $h_c = R_g$ where R_g is the radius of gyration of polymer chains. Thus, $h_c(N) = a\sqrt{N} = h_{c0}\sqrt{NN_0}$ where N is the number of monomer segments per polymer chain, a is the average length of monomer, and the subscript '0' refers to the condition at a reference molecular weight. Integrating equation (3), squaring it and taking the mean, we get

$$\begin{aligned}\langle[\delta n(h)]^2\rangle &= \exp(-h/h_c)\int_0^h\int_0^h \exp\left(\frac{h_1+h_2}{2h_c}\right)\langle\mu(h_1)\mu(h_2)\rangle\,\mathrm{d}h_1\,\mathrm{d}h_2\\ &= \sigma^2[1-\exp(-h/h_c)],\end{aligned} \tag{4}$$

where the standard deviation $\sigma = \sqrt{\langle[\delta n(h \to \infty)]^2\rangle}$. The noise in the above equation has been assumed to be the uncorrelated white noise with $\langle\mu\rangle = 0$ and

$$\langle\mu(0)\mu(h)\rangle = (\sigma^2/h_c^2)\delta(h). \tag{5}$$

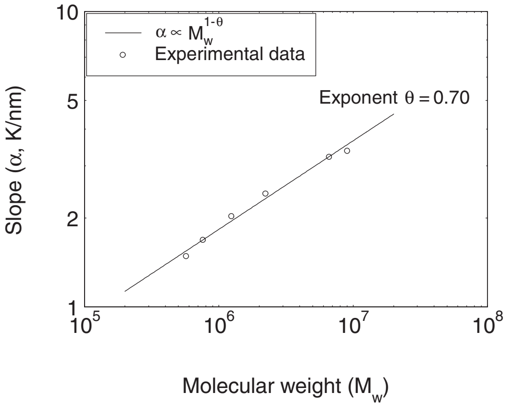

Figure 1. The determination of the exponent θ, which characterizes the nature of cooperative phenomenon, from the molecular-weight-dependent data for freely standing films in table 1 of [3].

When the noise has long-range correlation, it will be more convenient for us to analyse the problem by looking at $\langle[\delta n(h)]^2\rangle - \langle[\delta n(h \to \infty)]^2\rangle = -\sigma^2\psi(h)$ where ψ is the correlation of fluctuations of $\delta n(h)$ and goes to zero when the film thickness is significantly larger than a critical value h_c. Each Langevin equation has a corresponding Fokker–Planck equation. From this, we can have an integral equation that establishes the relation between the autocorrelation function ψ and the noise correlation function [10]:

$$\frac{\mathrm{d}\psi(h)}{\mathrm{d}h} = -\frac{1}{\sigma^2}\int_0^h \langle\mu(0)\mu(h-s)\rangle\psi(s)\,\mathrm{d}s. \tag{6}$$

Let us consider a general expression of the noise correlation function that includes the long-range correlation and is expressed in terms of the Laplace transform [13]

$$\overline{\langle\mu(0)\mu(q)\rangle} = \int_0^\infty \langle\mu(0)\mu(h)\rangle \exp(-qh)dh = -\frac{\sigma^2}{h_c^2}\frac{q\sum_{l=1}^{\infty}(-1)^l\frac{\Gamma(2\theta l+1)}{l!q^{2\theta l}}}{1+\sum_{l=1}^{\infty}(-1)^l\frac{\Gamma(2\theta l+1)}{l!q^{2\theta l}}}, \tag{7}$$

where Γ is the gamma function and $\theta \leqslant 1$. The independent parameter θ describes the range of spatial correlation of the quenched disorder. When $\theta = 1/2$, we get $\overline{\langle\mu(0)\mu(q)\rangle}/(\sigma^2/h_c^2) = 1$ whose Laplace inversion is the delta function mentioned in equation (5)—uncorrelated local noise. To see the physical meaning of θ more clearly, let us look at the Laplace inversion of the leading term in equation (7). We obtain the long-range noise correlation function $\langle\mu(0)\mu(h)\rangle \sim (h/h_c)^{2\theta-2}$ for $1/2 < \theta < 1$. The presence of this long-range correlation suggests a cooperative phenomenon. Putting equations (1), (2), (6) and (7) together, we get

$$\ln\left[\frac{T_g(h,N)}{T_{g\infty}}\right] = -\frac{kN}{2N_0\Delta C_p}\exp\left[-\left(\frac{h}{h_{c0}}\sqrt{\frac{N_0}{N}}\right)^{2\theta}\right], \tag{8}$$

where k is the Boltzmann constant and $h_{c0} = R_{g0}$ is a constant. When $|T_g - T_{g\infty}|/T_{g\infty} \ll 1$ and $h/h_c \ll 1$, equation (8) gives the slope $\alpha = \partial T_g/\partial h \sim N^{1-\theta}$. The exponent $\theta = 0.7$ is determined in figure 1 by fitting this simple scaling relation to recently published data for polystyrene [3]. The value of this exponent (>1/2) confirms that the glass transition in nanofilms is indeed a cooperative phenomenon as in bulk polymers. The properties of polystyrene are $\Delta C_p = 6.45$ cal mol^{-1} K^{-1}, and $R_{g0} = 15$ nm for $M_w = 228\,400$ measured by small-angle neutron scattering at a temperature of 393 K above $T_{g\infty} = 373$ K [14]. Figure 2 shows the calculated depression of the glass transition temperatures from the bulk value of thin

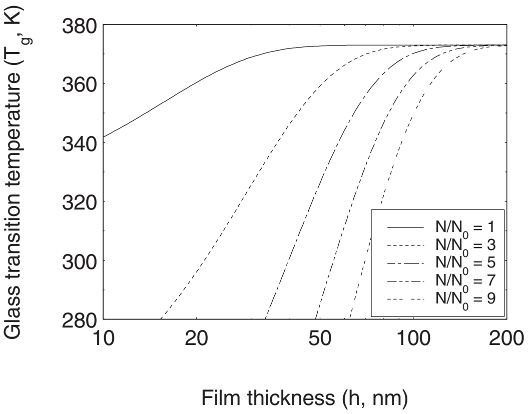

Figure 2. The depression of the glass transition temperature of polystyrene films calculated from equation (8) as a function of film thickness and molecular weight.

films due to the combined effects of the film thickness and molecular weight. Curve 1 (i.e. $N/N_0 = 1$) describes the thickness-dependent T_g data at lower molecular weight [1]. Curves 3–9 provide a theoretical interpretation of the effect of higher molecular weight on T_g observed recently [3]. In the rest of this letter, we shall discuss the influence of substrates by using the same set of input parameters and choosing $N/N_0 = 1$ to illustrate the numerical predictions of our theory.

Based on the idea of a self-consistent field, our next step is to analyse the interacting polymer chains that are attached at one end to an absorbing surface. We consider the typical case where all monomers are chemically identical and the interactions are repulsive and local. It may be worthwhile to mention that the chains in a melt are Gaussian and ideal. When we inscribe our chain on a Flory–Huggins lattice, the pertinent partial differential equation for ideal chains under external potentials is [15]

$$\frac{a^2}{6}\nabla^2 G = \frac{\partial G}{\partial N} + \frac{U(\vec{r})}{T}G. \tag{9}$$

When a certain concentration profile $c(\vec{r})$ is assumed, one can describe each attached chain as an ideal chain subjected to a self-consistent external potential:

$$U(\vec{r}) = mTvc(\vec{r})/A, \tag{10}$$

where m is the number of macromolecules, $v = a^3/N$ is the excluded volume parameter of polymer melts and A is the surface area. The solution of equation (9) is an expansion in the orthonormal eigenfunctions u_i:

$$G(\vec{r}\,', \vec{r}; N) = a^3 \sum_i u_i * (\vec{r}\,')u_i(\vec{r})\exp(-N\lambda_i). \tag{11}$$

The eigenfunction expansion contains an exponential factor that tends to give the maximum weight to the ground-state eigenfunction $u_1(\vec{r})$ for which the eigenvalue $\lambda_i = \lambda_1$ is the minimum. In our situation, the ground state ($i = 1$) dominates. If we retain only u_1 in equation (11) we arrive at $c(\vec{r}) = Nu_1^2$ that is needed in equations (9) and (10). If we put the surface at $z = 0$, the ground-state eignfunction is ruled by

$$\frac{a^2}{6}\frac{\mathrm{d}^2 u_1}{\mathrm{d}z^2} = (m/A)vNu_1^3 - \lambda_1 u_1. \tag{12}$$

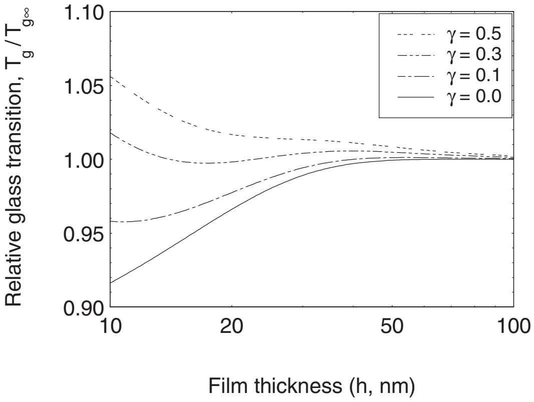

Figure 3. The effect of polymer–substrate interactions on the relative glass transition as a function of the film thickness. The energy of hole formation $\varepsilon = 3.58$ kcal mol^{-1} for polystyrene [10].

This equation can be interpreted as the equation of motion of a particle with mass $a^2/6$. The right-hand side is the force with the corresponding potential energy $V(u_1) = \frac{1}{2}\lambda_1 u_1^2 - \frac{1}{4}(m/a)vNu_1^4$. This potential has a minimum at $u_1(\mathrm{min}) = 0$ and a maximum at $u_1(\mathrm{max}) = \sqrt{2A\lambda_1/mvN}$, which satisfy the boundary conditions: $u_1(0) = 0$ and $u_1(h) = u_1(\mathrm{max})$. Thus, the ground-state eignfunction can be approximated as $u_1(z) \cong \sqrt{2A\lambda_1/mvN}$ for nearly the entire range across the film thickness that is consistent with the numerical solution of the nonlinear differential equation (12). Using the normalization condition, $\int_0^h c(z)\,\mathrm{d}z = N$, we obtain the ground-state eigenvalue, $\lambda_1 = mNv/2Ah$, which gives the free energy $F = -mTS \cong mkTN\lambda_1$. The statistical weight, $\exp(-N\lambda_1)$, in equation (11) gives the entropy reduction. The pressure created in the thin films that is formed by adsorbing polymer ends to the surface of a substrate is determined by

$$p(h) = -(1/A)(\partial F/\partial h)_{N,m,T} = (kTv/2)(mN/Ah)^2. \tag{13}$$

By analysing the deformational contribution to the entropy change during the glass formation [10], the pressure-induced change in the glass transition temperature has been determined as

$$\Delta T_g = (kT_{g\infty}^2/\varepsilon)[1 - \exp(-pv_L/kT_{g\infty})]. \tag{14}$$

Here ε is the mean energy of hole formation and the lattice volume $v_L = a^3 = Nv$. The above equation shows that the glass transition temperature increases with pressure. Substituting equation (13) into (14) and then combining it with equation (8), we finally obtain

$$\frac{T_g(h, N, \gamma)}{T_{g\infty}} = \frac{T_g(h, N, 0)}{T_{g\infty}} + \frac{kT_{g\infty}}{\varepsilon}\left\{1 - \exp\left[-\gamma\left(\frac{h_c(N)}{h}\right)^2\right]\right\}, \tag{15}$$

where the first term on the right-hand side is given by equation (8) and the strength of polymer–substrate interactions is characterized by

$$\gamma = (ma^2/A)^2/2 \tag{16}$$

that depends on the surface concentration of adsorbed chain ends. Clearly, we have $0 \leqslant \gamma \leqslant 1/2$ with $\gamma = 0$ for freely standing films. Figure 3 reveals that substrates have strong influence on the increase or decrease of T_g in nanofilms from the bulk value. A similar trend of the T_g shift related to the polymer–substrate interactions has also been seen from a recent molecular simulation [7].

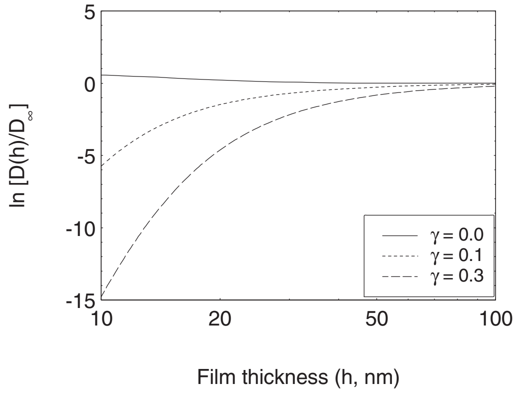

Figure 4. The effect of polymer–substrate interactions on the relative diffusion coefficient as a function of the film thickness. The hole fraction at the glass transition $f_{g\infty} = 0.032$ for polystyrene [18].

There is a simple experiment of an ultra-thin polystyrene film dewetted on a silicon wafer substrate. Dewetting takes place when a continuous film in the glassy state is heated. The temperature at which dewetting occurs is found to decrease as the film becomes thinner [16]. This is a different method of analysing the thickness-dependent T_g. When the film reaches the liquid state, the level of dewetting depends not only on the melt flow of the film but also on the interfacial energy, which is strongly influenced by adsorbing polymer ends to a surface.

On the basis of mesoscopic fluctuation [17], the shear viscosity η is related to the fluctuations of excessive hole density by $\ln[\eta(h)/\eta_\infty] \sim \langle[\delta n(h)]^2\rangle/f\langle n\rangle^2$ for $\delta n/\langle n\rangle \ll 1$ and $\langle\delta n\rangle = 0$, where f is the free volume fraction. Since the diffusion coefficient (D) is inversely proportional to the viscosity, we obtain

$$\ln[D(h)/D_\infty] \cong -[1 - f_g(h)/f_{g\infty}]/f_{g\infty} + \psi(h)/f_{g\infty}\langle n\rangle^2, \tag{17}$$

where $f_g(h) = f_{g\infty}\exp(-pv_L/kT_{g\infty})$ and the pressure p is given by equation (13). By noting $\sigma^2/\langle n\rangle^2 = kT_{g\infty}\Delta\kappa/v = f_{g\infty}$ where $\Delta\kappa$ is the excessive compressibility, equation (17) becomes

$$\ln\left[\frac{D(h,N,\gamma)}{D_\infty}\right] = \exp\left[-\left(\frac{h}{h_c(N)}\right)^{2\theta}\right] - \frac{1}{f_{g\infty}}\left\{1 - \exp\left[-\gamma\left(\frac{h_c(N)}{h}\right)^2\right]\right\}. \tag{18}$$

In figure 4, equation (18) predicts reductions in the diffusion coefficient of ultra-thin polymeric films supported on substrates as size decreases except in the case of weak polymer–substrate interactions including freely standing films.

Based on fundamental principles, we provide new theoretical predictions and interpretations of the glass transition temperature and the diffusion coefficient of ultra-thin films as a function of film thickness, molecular weight and polymer–substrate interactions. When the correlation length of the fluctuations of excessive hole density is comparable to the radius of gyration of polymer chains, the physical properties of the film can differ significantly from the bulk. Indeed, the glass transition temperature can increase or decrease with decreasing film thickness depending on the strength of polymer–substrate interactions.

References

[1] Keddie J L, Jones R A and Cory R A 1994 *Europhys. Lett.* **27** 59
[2] Forrest J A, Dalnoki-Veress K, Stevens J R and Dutcher J R 1996 *Phys. Rev. Lett.* **77** 2002

[3] Dalnoki-Veress K, Forrest J A, Murray C, Gigault C and Dutcher J R 2001 *Phys. Rev.* E **63** 031801
[4] de Gennes P G 2000 *Eur. Phys. J.* E **2** 201
[5] Lin E R, Kolb R, Satija S K and Wu W 1999 *Macromolecules* **32** 3753
[6] DeMaggio G B, Friese W E, Gidley D W, Zhu M, Hristov H A and Yee A F 1997 *Phys. Rev. Lett.* **78** 1524
[7] Torres J A, Nealey P F and de Pablo J J 2000 *Phys. Rev. Lett.* **85** 3221
[8] Mischler C, Baschnagel J and Binder K 2001 *Adv. Colloid Interface* **94** 197
Varnik F, Baschnagel J and Binder K 2002 *Phys. Rev.* E **65** 021507
[9] Fehr T and Lowen H 1995 *Phys. Rev.* E **52** 4016
[10] Chow T S 2000 *Mesoscopic Physics of Complex Materials* (New York: Springer)
[11] Gibbs J H and DiMarzio E A 1958 *J. Chem. Phys.* **28** 373
[12] Landau L D and Lifshitz E M 1969 *Statistical Physics* (Oxford: Pergamon)
[13] Chow T S 1997 *Phys. Rev. Lett.* **79** 1086
[14] Tangari C, Ullman R, King J S and Wingnall G D 1990 *Macromolecules* **23** 5266
[15] de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
[16] Reiter G 1993 *Europhys. Lett.* **23** 579
[17] Chow T S 2000 *Phys. Rev.* E **62** 2475
[18] Ferry J D 1980 *Viscoelastic Properties of Polymers* 3rd edn (New York: Wiley)