Large fluctuations of disentaglement forces and implications for polymer dynamics

Raphael Blumenfeld

Polymers and Colloids, Cavendish Laboratory

Madingley Road, Cambridge CB3 0HE, UK

Abstract

This paper examines the effect of cooling on disentanglement forces and the implications for polymer dynamics. The distribution of disentanglement threshold forces is derived from a molecular model and it is shown to be dominated by fluctuations up to a temperature T_0 determined from molecular parameters. At low temperatures this distribution develops a gap at the small force end and a long tail at the large force end. The upper cutoff of the fluctuations is also given explicitly by molecular parameters. It is argued that these results invalidate the traditional typical friction force approximation below T_0 and bear directly on rheological and relaxation behaviors. The present analysis is useful to: (i) identify the limits of friction-based descriptions (e.g., Rouse and tube models), and (ii) improve modeling of the dynamics in the intermediate regime between the low temperature glassy and the melt states.

Email: rbb11@phy.cam.ac.uk

Polymer chain dynamics are described quite well above the glass transition temperature by Rouse dynamics and the tube model [1]. Fundamental to these models is the assumption that chains move against friction produced by disentanglement from the surrounding network. With cooling, this description becomes inaccurate and, well below the glass transition, it is replaced by models that specialize in the glassy state. The reason for the break down of the high-temperature description is that the chains cannot be usefully modeled by a typical force. The aim of this work is to examine and quantify the deterioration of the typical friction approximation from a molecular point of view and this will suggest ways to bridge between high and low temperature models. At the heart of the problem lies the issue of the distribution of threshold forces needed to disentangle a non-permanent entanglement point (EP) when a chain is subjected to an external force. When this distribution is narrow, a typical-value approximation holds good which means that a linear viscosity term provides a faithful description. However, it has been argued recently [2] that these forces are broadly distributed, leading to large fluctuations of the viscosity force. To clarify the issue I derive here the distribution of the disentanglement threshold forces and its temperature dependence in isotropic systems. It is found that: (i) at high temperatures the probability density function (PDF) is sharply peaked at very small forces; (ii) with cooling the PDF moves towards larger forces and develops a local maximum which broadens, giving rise to large fluctuations; (iii) below some temperature, a gap appears at the low forces end which increases gradually; (iv) as the temperature approaches zero the gap is complete, the PDF diverges at a value that is determined by molecular parameters and an algebraic tail grows at the large forces end. These results explain the divergence, with decreasing temperature, of the dynamics from the traditional Rouse and reptation models and allow to identify their range of validity. More importantly, these results suggest ways to model disentanglement dominated dynamics in the intermediate regime between the glassy and melt states.

Before the main discussion, let us establish the relation between friction and the disentanglement force distribution. Under a constant chain pulling rate, v, the number of EPs disentangled per unit time T is $N = (vT/l_0)$, where l_0 is the typical chain length in units of Kuhn's length, a, between two successive EPs [3]. The force invested in this is $F = T^{-1}\sum_{n=1}^{N}\int_0^{t_n} f_n(t)dt$, where t_n is the time between the disentanglements of the $(n-1)$th and nth EPs and $f_n(t)$ is the force during the nth uncoiling and disentanglement process [4]. If the terms in the sum have a typical value, as would be suggested by a narrow distribution of the threshold forces, then $F^{fr} = (1/T)\sum_{n=1}^{N} f_{typ}\tau_{typ} = \xi v$ where $\xi = f_{typ}\tau_{typ}/l_0$. However, if f_n fluctuates wildly then F^{fr} has a broad distribution, which should be taken explicitly into consideration in the Langevin equation governing the dynamics.

To derive the distribution of threshold forces I focus on non-topological EPs consisting of a chain wrapped around one or more chains (anchor) that are fixed by the surrounding network. The wrapping is over an angle lying between zero and 2π. Disentanglement is envisaged as the chain sliding around the anchor under the application of a pulling force, as shown in fig. 1. The anchor is taken to be normal to the page plane and is assumed to be immobile throughout the process. If it is initially mobile then the pull would cause a local adjustment of the chains until the anchor could not move any further. Disentanglement commences when the beads move one position clockwise around the anchor and, for simplicity, it is assumed that once a chain starts slipping it continues to do so until the EP disappears. Further refinement of the model is unnecessary at this stage since this already suffices to capture the essential features. Mmolecular interactions give rise to an activation energy required to move m segments one position clockwise, mE_b. For anchors consisting of one chain $m = 2$ is expected while for thicker anchors $m > 2$ ($m = 2$ in fig 1). Tugging at bead 3 with an increasing force f in an arbitrary direction exerts a force $(f\cos\theta)$ along the 2-3 link. The value of f when sliding starts is the disentanglement threshold force. Equilibrated polymer networks are isotropic down to the scale of a few monomers and, therefore, θ is uniformly distributed. In the absence of thermal fluctuations, slipping occurs when the work needed to move the chain by one segment a is equal to the activation energy mE_b, or $f \cos\theta = mE_b/a$. The temperature mE_b/k_B (k_B being Boltzmann constant) is expected to be around the glass transition temperature and hardly dependent on molecular weight. Taking it to be about $370K$ for Polystyrene and with $a \approx 5\mathring{A}$ gives $f_0 \approx m \times 10^{-11}$N. The distribution of the angles θ and the thermal fluctuations give rise to a distribution of f. In the following only values of θ in the range $0 < \theta < \theta_{max} \equiv \pi/2 - \epsilon$ are considered. The range $\theta < 0$ is excluded because it leads to unwrapping rather than sliding. Values of θ that are too close to $\pi/2$ are irrelevant because the forces that are required to overcome the threshold f_0 in this regime are too large and would lead to scission before sliding occurs. It follows from this argument that θ_{max} is given by

$$\cos\theta_{max} = mE_b/(af_{scission}) \equiv \epsilon \ll 1 \ , \tag{1}$$

where $f_{scission}$ is the force to rupture one bond.

As a chain is pulled there is a steady increase of the force on the EP. Let us derive the probability, $P(f,T)$, that disentanglement initiates when the force reaches a value between f and $f + df$. Imagine the EP as a system in a potential well of depth mE_b. Sliding starts when the barrier $(mE_b - af\cos\theta)$ is overcome. Therefore the probability of disentanglement, given this force, is proportional to $e^{-\beta(mE_b - af\cos\theta)}$ when $f\cos\theta < mE_b/a \equiv f_0$ ($\beta = 1/k_BT$) and it is 1 otherwise. Moreover, for disentanglement to occur at a particular value of f there should have been no sliding at a smaller force. Since different forces at different angles can give rise to the same value of $f\cos\theta$, the probability of disentanglement at f is the sum of: (i) the probability that the force has reached $f_0/\cos\theta$ without disentanglement

$$P_1 = \frac{1}{f\sqrt{(f/f_0)^2 - 1}} \left[1 - \int_0^f e^{-\beta(mE_b - af'\cos(\gamma(f))}\right] \delta[\gamma(f) - \theta] \ , \tag{2}$$

and (ii) the probability that disentanglement occurred at $f < f_0/\cos\theta$ but not before that

$$P_2 = \int_{\gamma(f)}^{\theta_{max}} e^{-\beta(mE_b - af\cos\theta)} \left[1 - \int_0^f e^{-\beta(mE_b - af'\cos\theta)} df'\right] d\theta \ . \qquad (3)$$

In these and the following expressions $\gamma(f) = \arccos(f_0/f)$, $\delta(x)$ is Dirac's delta-function and $H(x)$ is the Heavyside function which is 1 for $x > 0$ and 0 otherwise. The PDF is therefore

$$P(f,T)df = C(P_1 + P_2)df = C\left[\frac{H(f-f_0)}{f\sqrt{(f/f_0)^2 - 1}} + e^{-\beta mE_b} S\right] df \ , \qquad (4)$$

where

$$S = -\frac{H(f-f_0)}{\sqrt{(f/f_0)^2-1}} \frac{e^{\beta af_0} - 1}{\beta af_0} + \int_{\gamma(f)}^{\theta_{max}} e^{\beta af\cos\theta}\left[1 - \frac{e^{\beta af\cos\theta} - 1}{\beta a\cos\theta} e^{-\beta mE_b}\right] d\theta \ ,$$

and

$$C = \left(\theta_{max} + e^{-\beta mE_b}\int_0^{f_0/\epsilon} S df\right)^{-1} \ ,$$

is a normalization constant. Note that $C \to 1/\theta_{max}$ as $T \to 0$ and that in this limit the PDF is given by the first term in (4), as found in ref. [2]. The second term gives the probability density of thermally assisted disentanglement and governs the range $f < f_0$. Fig. 2 shows the PDFs of f/f_0 at $T = 0.05, 0.1, 0.15, 0.2, 0.4$ and $0.9E_b/k_B$. When $T \to 1E_b/k_B$ $P(f,T)$ has a narrow peak around $f \approx 0.05f_0$. As the temperature decreases the PDF broadens and starts to develop a maximum which moves towards higher values of f. Around $T \approx 0.2E_b/k_B$ the PDF is smeared over the entire range $0 < f < f_0$ with a shallow hump around $f \approx 0.5f_0$. With further cooling the maximum sharpens again and keeps moving to higher values of f. Below $T = 0.2E_b/k_B$ a noticeable gap starts to develop at small f, corresponding to the exponentially low probability of disentanglement by small forces. Simultaneously, a tail starts growing at the large f end. Finally, as T approaches zero, the gap is complete in the sense that no force below f_0 can cause disentanglement, the PDF is sharply peaked at f_0 and the tail assumes the algebraic form specified in the first term of (4) (fig. 2b). The long tail at low temperatures and the broad PDFs at intermediate temperatures both indicate that approximating the force by a typical value cannot be useful below some T_0, to be determined below.

The very low-temperature behavior ($T \lesssim 0.1 E_b/k_B$)is dominated by large fluctuations that manifest in a strong dependence of the moments on the upper cutoff $1/\epsilon$:

$$\begin{aligned} \langle f \rangle &\sim \ln(1/\epsilon) + O\left(e^{-m\beta E_b}\right) \\ \langle f^k \rangle &\sim 1/\epsilon^{k-1} + O\left(e^{-m\beta E_b}\right) \\ \sqrt{\langle \delta^2 f \rangle} &\sim \frac{1}{\sqrt{\epsilon}} + O\left(e^{-m\beta E_b}\right) \ . \end{aligned} \tag{5}$$

With heating up the temperature dependent terms gain weight, the moments decrease and the sensitivity to ϵ is washed out. Fig. 3 shows the dependence of $\langle f/f_0 \rangle$ on temperature. In principle, it is possible to derive all the moments, and their temperature dependence directly from (3). This, however, turns out to be cumbersome, leading to expressions that are impossible to write down in terms of simple functions. Resorting to numerical analysis we have found that the mean force can be fitted excellently by either

$$\langle f/f_0 \rangle = A_1 e^{-\alpha k_B T/E_b} + C_1 \ , \tag{6}$$

where $A_1 = 1.40 \pm 0.05$, $\alpha = 6.2 \pm 0.4$ and $C_1 = 0.01 \pm 0.01$, or

$$\langle f/f_0 \rangle = B_1 (k_B T/E_b)^{\beta_1} e^{-\beta_2 k_B T/E_b} + C_2 \ , \tag{7}$$

where $B_1 = 9.1 \pm 0.9$, $\beta_1 = 0.57 \pm 0.03$, $\beta_2 = 11.2 \pm 0.3$ and $C_2 = 0.037 \pm 0.002$. The second form fits somewhat better than the simple exponential one and both fits are superposed on fig. 3. The values of the parameters depend on the dimensionless quantity $\epsilon = (mE_b)/(af_{scission})$ and consequently on molecular parameters. AS ϵ becomes smaller the fluctuations grow and the temperature where reptation dynamics break down increases.

This suggests that varying E_b and $f_{scission}$ by changing the chemistry can have strong effects on the dynamics.

To identify the temperature, T_0, where fluctuations become unimportant it is useful to define the relative width of the PDF, $\Gamma \equiv \langle \delta^2 f \rangle^{1/2} / \langle f \rangle$. When $\Gamma \ll 1$ the fluctuations are much smaller than the mean and a typical force is a good approximation, but not if Γ is of order 1. The graph of Γ (fig. 4) reveals a surprise: it increases steadily with temperature up to $T \approx 0.4 E_b/k_B$ but then instead of dropping again it saturates into a plateau, $\Gamma_p \approx 0.8$. Thus, fluctuations play a significant role up to $T_0 \approx 1 E_b/k_B$, a result that has obvious implications for the high-temperature models. Moreover, since mE_b/k_B is expected to be around T_g, the mechanism of disentanglement discussed here may still be relevant within a small range of temperatures above the glass transition. It follows that it may be possible to test some aspects of the results obtained here by viscosity measurements in the melt. Above T_0 thermal fluctuations should overwhelm the activation energy, Γ should drop sharply and therefore the dynamics are expected to converge to the Rouse and tube models. This closes a circle and supports the estimate made above of $T_0 \approx T_g$. More intriguingly, this also links between the macroscopic glass transition temperature and the molecular parameters E_b and a. It is therefore tempting to conjecture that the glass transition could be determined from this molecular information, a conjecture that it would be very interesting to test.

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4. The distributions of both these quantities at low temperatures has been discussed in ref. [2].

FIGURE CAPTIONS

Fig.1: A disentanglement configuration: the black circle is an anchor perpendicular to the page plane around which the disentangling chain moves.

Fig.2: The PDF of the threshold forces $P_f(f)$ for: (a) $k_BT/E_b = 0.05, 0.1, 0.15, 0.2, 0.4$ and 0.9 and (b) $T = 0$.

Fig.3: The mean disentanglement force as a function of temperature. The points are obtained from a numerical calculation and the lines are an exponential (solid) and a power-exponential (dotted) fits.

Fig.4: The relative width, $\langle \delta^2 f\rangle^{1/2}/\langle f\rangle$ as a function of temperature.