Large fluctuations of disentaglement force and implications for polymer dynamics

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Abstract. – This paper examines the effect of cooling on disentanglement forces and the implications for polymer dynamics. The temperature dependent distribution of disentanglement threshold forces is derived explicitly and it is shown to be dominated by fluctuations up to a certain temperature T_0 governed by molecular parameters. At low temperatures this distribution develops a gap at small forces and a long tail at large ones. The upper cutoff of the fluctuations is also shown to be determined by molecular parameters. 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 melt based descriptions such as the Rouse and tube models, and (ii) improve modeling of polymer dynamics in the intermediate regime between the low temperature glassy and the melt states.

Polymer chain dynamics are described quite well in the melt 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, other models are available which specialize in the glassy state. One of the main reasons for the breakdown of the high-temperature description is that on the molecular level chain friction 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 and hopefully gain insight that 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. In the melt this distribution is narrow which means that a typical force and hence a linear viscosity term provide a good description. With decreasing temperature, these forces become broadly distributed, leading to large fluctuations of the viscosity force. Here I address this issue and derive 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 low forces 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 large forces. 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 proceeding to the main discussion, let us establish the relation between friction and the disentanglement force distribution. The chain is envisaged as a series of coiled segments between successive non-topological EPs. A force is required to pull the chain in order to overcome both the entropic elasticity of the coils and disentanglement threshold forces. Chain pulling is then a series of alternating uncoiling and disentanglement processes. Under a constant 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. It is this sum that determines the friction statistics. If the terms in the sum have a typical value, as would be suggested by a narrow distribution of the threshold forces, then the friction force is $F = (1/T)\sum_{n=1}^{N} f_{typ}\tau_{typ} = \xi v$ where $\xi = f_{typ}\tau_{typ}/l_0$. If, however, f_n fluctuates wildly then F is broadly distributed which should be taken explicitly into consideration in the equation governing the dynamics (e.g., the traditional Langevin equation). Thus, it is the distribution of these forces and its explicit temperature dependence that this paper is after.

On the molecular level, a non-topological EP comprises 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 consists of the chain sliding around the anchor under a pulling force, as shown in fig. 1. The anchor is normal to the page plane and is presumed immobile throughout the process. If it is initially mobile then the pull would adjust 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. The activation energy required to move m segments one position clockwise, $E_b = mE$, is determined by the molecular interactions. 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 disentanglement threshold force is the value of f when sliding starts. 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 E_b, or $f\cos\theta = E_b/a$. The temperature E_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 $f_0 \equiv E_b/a \approx 2\times10^{-11}$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 that

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

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

With pulling, the force on the EP steadily increases and we wish to derive the probability, $P(f,T)$, that disentanglement initiates when the force reaches a value between f and $f+df$. Sliding initiates when the energy input is larger than $(E_b - af\cos\theta)$ and so the probability of disentanglement is proportional to $e^{-\beta(E_b - af\cos\theta)}$ when $f\cos\theta < E_b/a \equiv f_0$ ($\beta = 1/k_B T$) and 1 otherwise. 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

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

and (ii) the probability that disentanglement occurred at $f < f_0/\cos\theta$

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

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

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

where

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

and

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

is a normalization constant. Note that when $T \to 0$ $C \to 1/\theta_{max}$ and the PDF converges to the first term in eq. (4), reproducing in this limit the result of 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 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. Cooling to below $T = 0.2E_b/k_B$ gives rise to a gap at small f, which reflects the exponentially low probability of disentanglement by small forces. Simultaneously, a tail starts growing towards large values of f. 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 of the first term in eq. (4). Both the long tail at low temperatures and the broad PDFs at intermediate temperatures point to the fact that *the typical force approximation fails* below some T_0 whose value is found below.

The very low-temperature behavior ($T < 0.1 E_b/k_B$)is dominated by large fluctuations

$$\sqrt{\langle \delta^2 f \rangle} \sim \frac{1}{\sqrt{\epsilon}} + O\left(e^{-\beta E_b}\right) \tag{5}$$

and as the temperature increases the moments of f 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 eq. (3). This, however, turns out to be cumbersome, and the resulting expressions are impossible to write down in terms of simple functions. Resorting to a numerical investigation reveals that the mean force can be fitted excellently by

$$\langle f/f_0 \rangle = B_1 (k_B T/E_b)^{\beta_1} e^{-\beta_2 k_B T/E_b} + C_2 \ , \tag{6}$$

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 values of the parameters depend on molecular data through the dimensionless quantity $\epsilon = E_b/(a f_{scission})$. The smaller ϵ gets the larger the fluctuations and therefore the higher the temperature where reptation dynamics break down. This has the intriguing implication that changing the chemistry to vary E_b and $f_{scission}$ can have strong effects on the dynamics and rheology.

To identify the temperature, T_0, above ehich fluctuations become unimportant it is useful to consider the relative spread 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 and vice versa if Γ becomes 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, as one would naively expect, it saturates to 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 far-reaching implications for the high temperature models. Moreover, since $m E_b/k_B$ 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. This in turn implies that it may be possible to test some aspects of the results obtained here by viscosity measurements just above the glass transition. Above T_0 thermal fluctuations overwhelm the activation energy, Γ drops sharply and 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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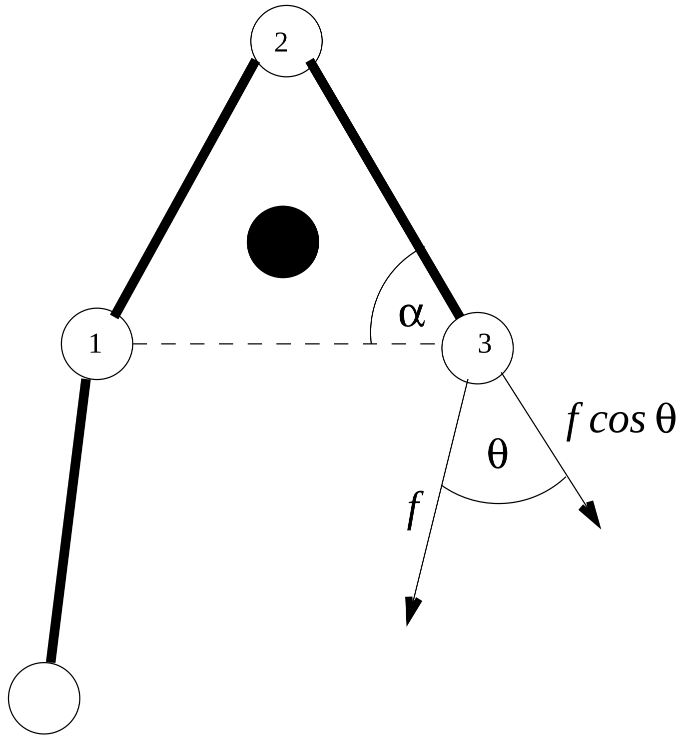

Fig. 1 – A disentanglement configuration: the black circle is an anchor perpendicular to the page plane around which the disentangling chain moves.

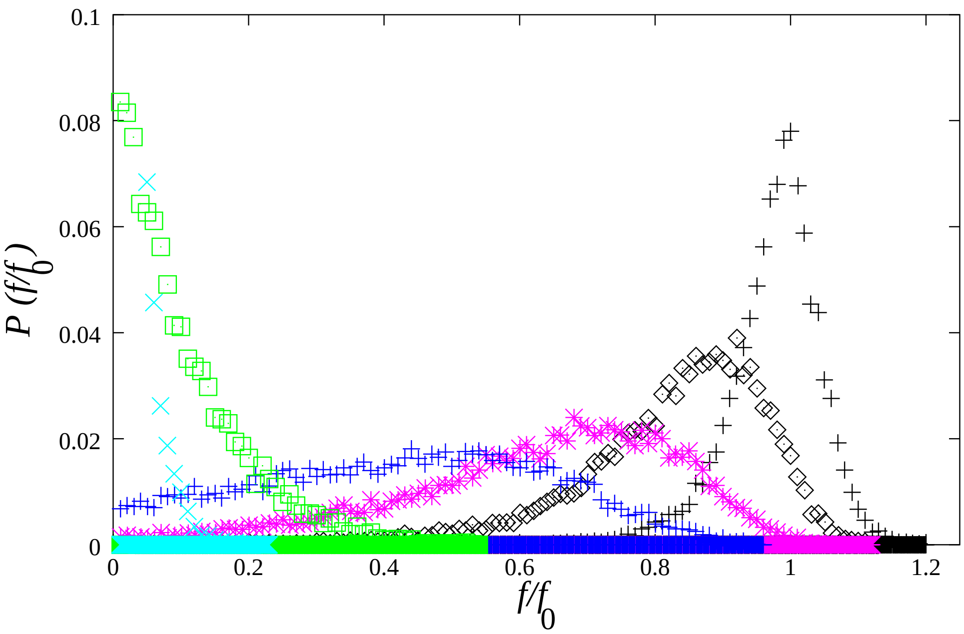

Fig. 2 – The PDF of the threshold forces $P_f(f)$ for $k_BT/E_b = 0.05, 0.1, 0.15, 0.2, 0.4$ and 0.9.

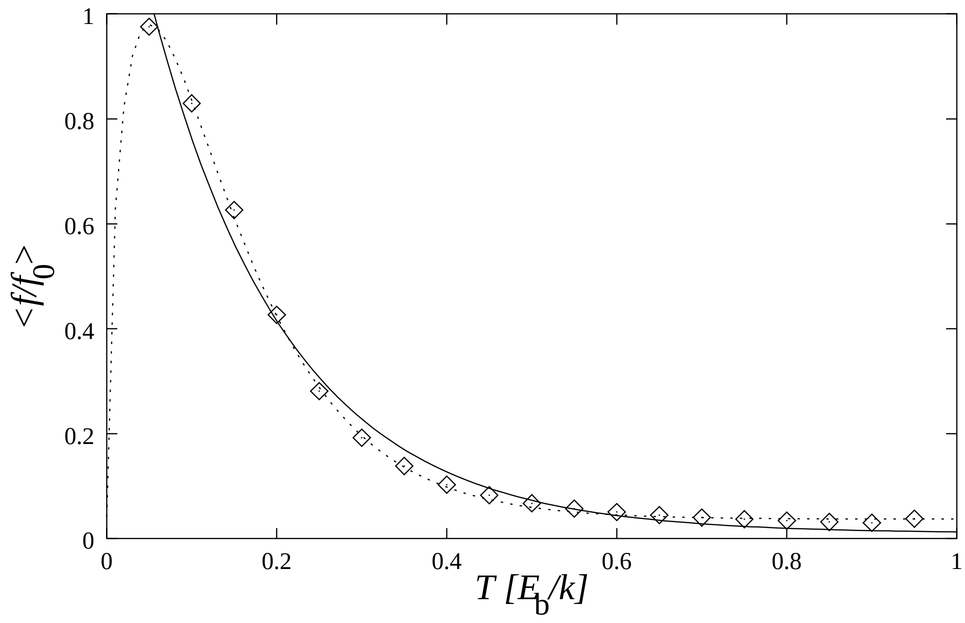

Fig. 3 – The mean disentanglement force as a function of temperature. The points are obtained from a numerical calculation and the lines are an exponential (solid) and a power-exponential (dotted) fits.

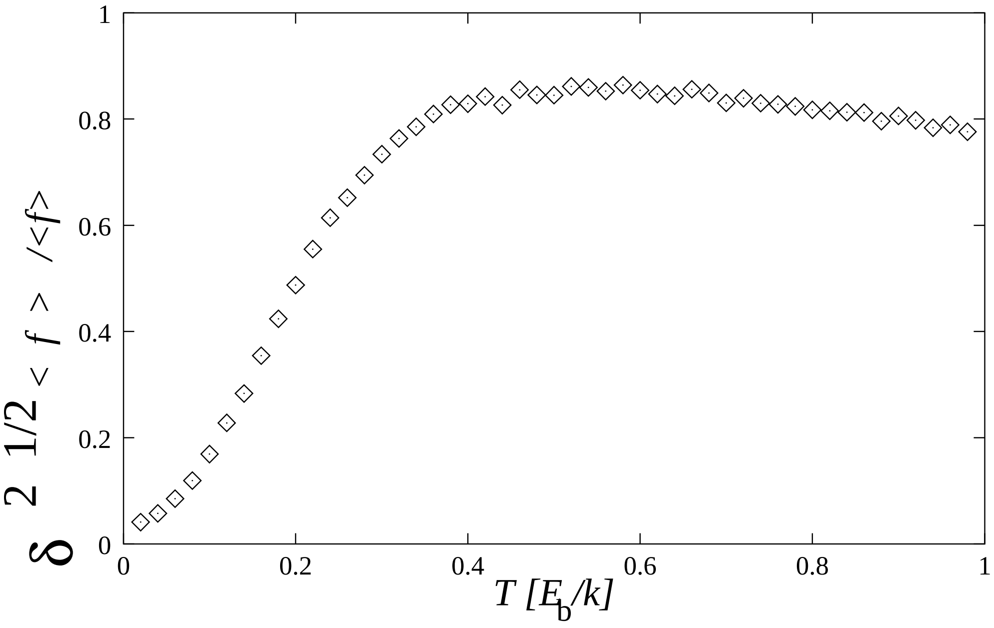

Fig. 4 – The relative width, $\langle \delta^2 f\rangle^{1/2}/\langle f\rangle$ as a function of temperature.

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