

Large fluctuations of disentanglement force and implications for polymer dynamics

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Abstract. – This paper examines the effect of cooling on disentanglement forces in polymers and the implications for both single chain pullout and polymer dynamics. I derive the explicit dependence of the distribution of these forces on temperature, which is found to exhibit a rich behaviour. Most significantly, it is shown to be dominated by large fluctuations up to a certain temperature T_0 that can be determined from molecular parameters.

The effects of these fluctuations on chain friction are analysed and they are argued to undermine traditional melt-based models that rely on a typical chain friction coefficient. A direct implication for first principles calculation of viscosity is discussed. This quantifies the limit of validity of descriptions such as Rouse dynamics and the tube model and paves the way to model polymer dynamics around the glass transition temperature.

Polymer chain dynamics in dense melts are described quite well by Rouse dynamics and the tube model [1] [2] that have become the accepted paradigm. The latter assumes that a chain moves in an effective tube formed by nearby chains and against friction produced by disentanglement from the rest of the network. This mean field type of description becomes increasingly inaccurate upon cooling and loses validity altogether around the glass transition. While there have been attempts to improve the model by considering more than one chain (e.g., through constraint release [3]), it is worthwhile to explore extensions to the one chain picture before rushing to more complicated models. A detailed understanding of chain dynamics over a wide range of temperatures is also required to interpret recent experiments of single chain pullout [4]. A model for the latter has been proposed recently [5] in which the chain's mean field environment is replaced by a detailed consideration of the local dynamics of disentanglement of non-permanent entanglement points (EPs). An intriguing result of reference [5] is that at low temperatures (well below the glass transition) the disentanglement force distribution is dominated by large fluctuations. This result raises several questions: (1) while it is evident that the fluctuations must decay with increasing temperature, it is unknown how, and at what rate, this happens, nor is it known up to what temperature do the fluctuations persist. (2) is it possible to quantify the effect of the large fluctuations on rheological properties such as viscosity and so determine the range of validity of melt-based models? The latter issue is essential to modelling polymer dynamics around the glass transition temperature.

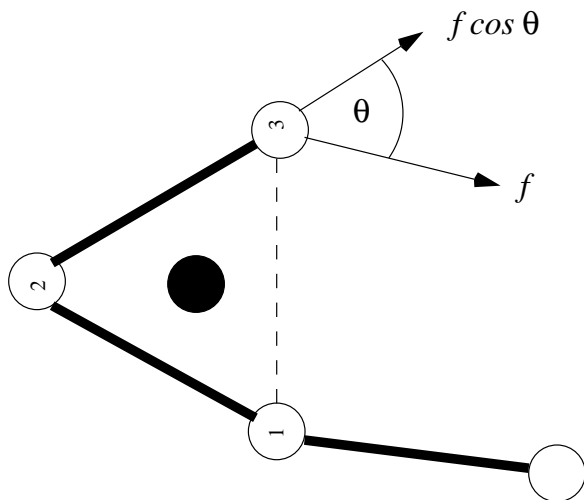


Fig. 1 – A non-permanent entanglement: the black circle is an anchor perpendicular to the page plane around which the disentangling chain slides.

These issues are the subject of this Letter. I derive the probability density function (PDF) of the disentanglement forces and its temperature dependence. It is found to exhibit a rich behaviour: At high temperatures it is sharply peaked around very small forces, as expected, but upon cooling the disentanglement forces increase and a broad local maximum develops. Below some temperature a gap appears at the low forces end which gradually increases until it becomes complete at very low temperatures. When this happens the PDF diverges at a value, f_0 , which is determined by *molecular data*. An algebraic tail then appears at the large forces end of the PDF. I discuss the implications of these results for calculation of the viscosity from molecular information and derive the friction of individual polymer chains. The connection between the broadening of the PDF and appearance of large fluctuations in chain friction is used to quantify how melt-based models break down in this regime.

We start by deriving the disentanglement threshold force distribution using the model introduced in [5]. In this model a non-permanent EP is regarded as a wrapping of a (primary) chain around an anchor chain which is fixed by the surrounding network⁽¹⁾. Disentanglement occurs when the pulled chain slides around the anchor under a pulling force, as shown in fig. 1. The activation energy required to move m segments one position clockwise, $E_b = mE$, is determined by the molecular interactions ($m = 2$ in fig. 1). Tugging at bead 3 with an increasing force f at an arbitrary direction exerts a force $f \cos \theta$ along the 2-3 link. The disentanglement force is defined as the value of f when sliding starts. For simplicity, it is assumed that once a chain starts sliding it continues to do so until disentanglement is complete, but this simplification is not crucial. Once disintegrated, the chain segment immediately after the EP starts uncoiling, building stress on the next EP. This process continues until either the entire chain is unraveled or a topological entanglement is encountered. At very low temperature, slipping occurs when the work needed to move the chain by one segment a is equal to the activation energy E_b , $f \cos \theta = E_b/a \equiv f_0$. The value of E_b/k_B (k_B being Boltzmann constant) is expected to depend only weakly on molecular weight. Here we investigate the

⁽¹⁾The anchor is a chain that initially moves with the pull of the primary chain until it is stuck by the rest of the network. A mobile anchor leads to *non-local* dynamics which is beyond the scope of this discussion

effect of both the distribution of θ and the thermal fluctuations on the distribution of f .

Equilibrated polymer networks are isotropic down to the scale of a few monomers so the angle θ is uniformly distributed but only the range $0 < \theta < \theta_{max} \equiv \pi/2 - \epsilon$ need be considered. This is because: (i) $\theta < 0$ leads to unwrapping rather than sliding, and (ii) when θ is too close to $\pi/2$ the chain cannot be disentangled before scission occurs,

$$\cos \theta_{max} = f_0 / f_{scission} \equiv \epsilon \ll 1 \quad (1)$$

where $f_{scission}$ is the force to rupture the chain and a is Kuhn's length. With pulling, the force on the EP increases steadily and sliding starts when the input of work is larger than $(E_b - af \cos \theta)$. The probability of disentanglement to occur is proportional to $e^{-\beta(E_b - af \cos \theta)}$ when $f \cos \theta < f_0$ and identically unity otherwise. The probability of the former scenario is

$$P_1 = \int_{\gamma(f)}^{\theta_{max}} e^{-\beta(E_b - af \cos \theta)} \left[1 - \int_0^f e^{-\beta(E_b - af' \cos \theta)} df' \right] d\theta \quad (2)$$

and the probability of the latter one is

$$P_2 = \frac{1}{f \sqrt{(f/f_0)^2 - 1}} \left[1 - \int_0^f e^{-\beta(E_b - af' \cos(\gamma(f)))} df' \right] \delta[\gamma(f) - \theta]. \quad (3)$$

In these and the following expressions $\beta = 1/k_B T$, $\gamma(f) = \arccos(f_0/f)$, $\delta(x)$ is Dirac's delta-function and $H(x)$ is the step function which is 1 for $x > 0$ and 0 otherwise. The PDF that disentanglement occurs exactly when the pulling force reaches a value between f and $f + df$ is therefore

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

where

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

and the normalization constant is

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

When $T \rightarrow 0$ $C \rightarrow 1/\theta_{max}$ and the PDF converges to the first term, reproducing in this limit the result of reference [5]. The second term gives the probability density of thermally assisted disentanglement and governs the range $f < f_0$.

Fig. 2 shows $P(f, T)$ generated numerically at $T = 0.05, 0.1, 0.15, 0.2, 0.4$ and 0.9 , measured in units of E_b/k_B . At $T = 0.9$ the PDF is narrowly peaked around $f \approx 0.05 f_0$. As the temperature decreases it develops a maximum which moves towards higher values of f . When $T \approx 0.2$ the PDF is smeared almost over the entire range $0 < f < f_0$ with a broad hump around $f \approx 0.5 f_0$. With further cooling the maximum sharpens again while moving to higher values of f . Another notable feature is the appearance of a gap at small values of f as the temperature drops below $T = 0.2$, corresponding to an exponentially low probability

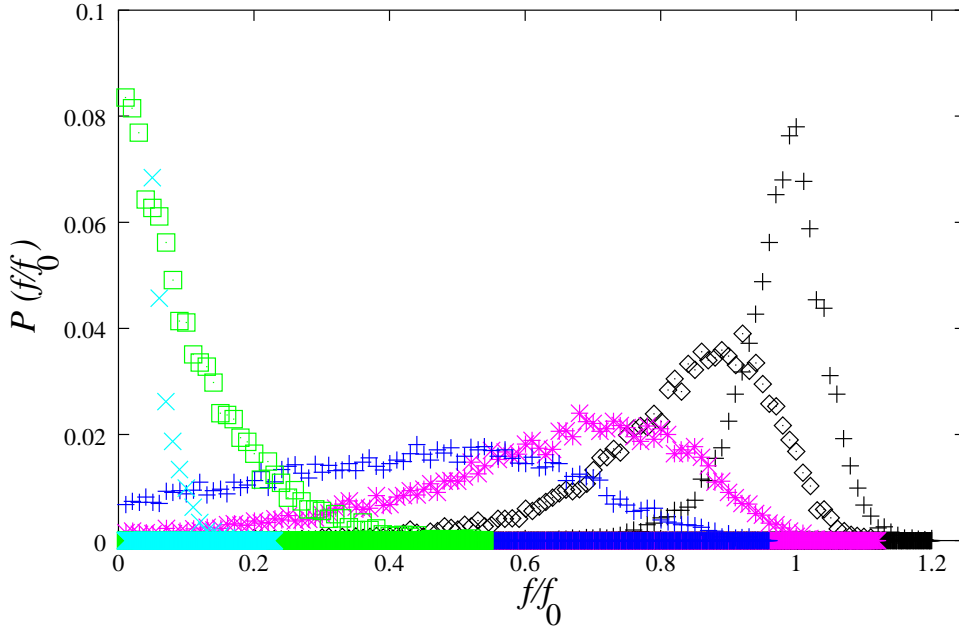


Fig. 2 – The PDF of the disentanglement forces $P_f(f)$ for $T = 0.05(+)$, $0.1(\diamond)$, $0.15(*)$, $0.2(+)$, $0.4(\square)$ and $0.9(\times)$ βE_b . Note the broadening and the development of a local maximum, which moves to larger forces with decreasing temperature.

of disentanglement by small forces. Around the same temperature a tail starts growing for $f > f_0$. Finally, as $T \rightarrow 0$, the gap is complete and no force below f_0 can disentangle. The PDF is then sharply peaked at f_0 converging to the algebraic form of the first term in eq. (4). Fig. 3 shows the dependence of the mean force, $F = \langle f/f_0 \rangle$, on temperature for $N = 100$. In principle, $\langle f(T) \rangle$ should be computable directly from the PDF but the resulting expressions are cumbersome. Empirically, the data can be fitted well by

$$\langle f/f_0 \rangle = AT^x e^{-yT} + B, \quad (5)$$

where $A = 9 \pm 1$, $x = 0.57 \pm 0.03$, $y = 11.2 \pm 0.3$ and $B = 0.037 \pm 0.002$. These parameters depend only on molecular data through the dimensionless quantity $\epsilon = E_b/(af_{scission})$. This intriguingly suggests that changing the chemistry to vary E_b and $f_{scission}$ changes $\langle f \rangle$ with strong effects on the dynamics and rheology in the manner described below. The very low-temperature behavior ($T < 0.1$) is dominated by large fluctuations of the form

$$\sqrt{\langle \delta^2 f \rangle} \sim \frac{1}{\sqrt{\epsilon}} + O(e^{-\beta E_b}). \quad (6)$$

As the temperature increases the moments of f get smaller, the second term in eq. (6) becomes dominant, and the sensitivity to ϵ is washed out. Both the long tail at low temperatures and the broad distribution at intermediate temperatures point to large fluctuations dominating below some temperature T_0 .

To estimate the crossover temperature T_0 let us consider the relative width of the PDF, $\Gamma \equiv \langle \delta f^2 \rangle^{1/2} / \langle f \rangle$. $\Gamma \ll 1$ means that fluctuations are insignificant and the force is well characterised by a typical value, f_{typ} . When Γ is of order 1, fluctuations dominate and this

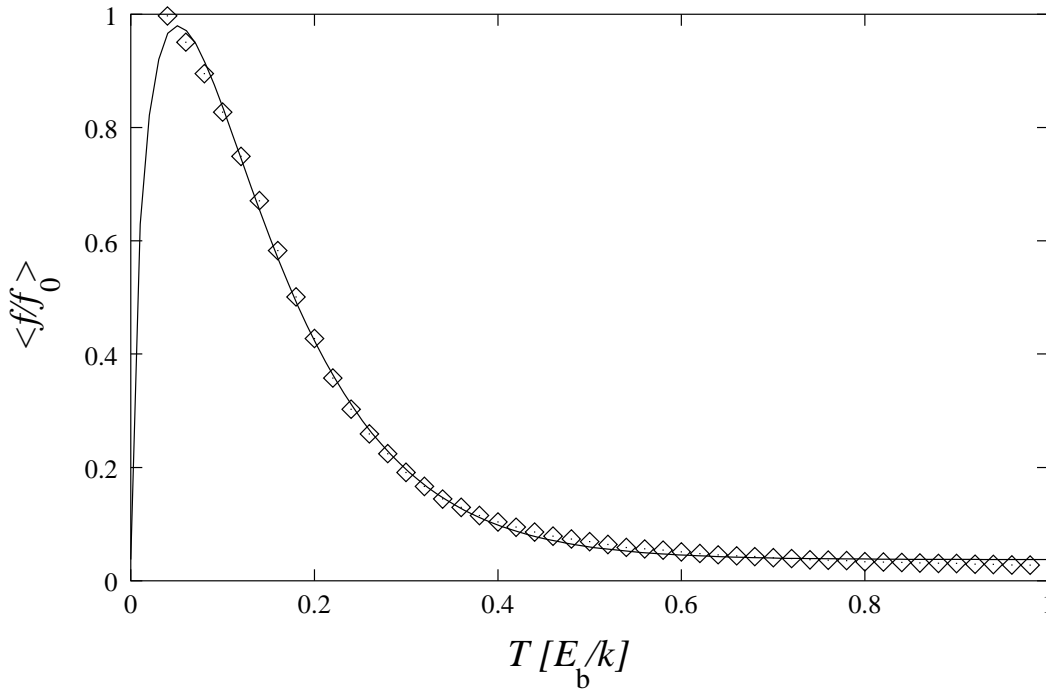


Fig. 3 – The mean disentanglement force as a function of temperature. The points are obtained from a numerical calculation and the line is a power-exponential fit, eq. (5). Note that this curve is also proportional to the viscosity ξ , eq. (7).

is not a good approximation. Figure 4 shows that Γ increases steadily with temperature up to $T \approx 0.4$ and then saturates to $\Gamma \approx 0.8$. Thus, fluctuations play a significant role at all temperatures up to $T = 1$. However, above $T \approx 0.4$ the mean force is quite small and even the fluctuations cannot make it significantly large. Thus, we can estimate $T_0 \approx 0.4E_b/k_B$ as the crossover temperature. Below it is shown that large force fluctuations lead to significant fluctuations of the chain friction coefficient. Above T_0 thermal noise overwhelms the activation energy, the forces become negligibly small and melt dynamics is recovered.

To link these results to rheological behaviour we need to first establish a relation between chain friction and the force PDF. Pulling a chain at a rate v consists of alternating uncoiling and disentanglement processes, giving rise to a fluctuating pulling force. As the $(n-1)$ th EP disentangles the segment following it uncoils behaving as an entropic spring whose effective length is the chain segment between the pulling point, $n=0$, and the n th EP. Once the force reaches the threshold force of the n th EP it disentangles and the force drops. Presuming equilibration on the time scale of this process, the drop of the force is to the value consistent with elasticity of an entropic spring which is longer by the segment between the n th and $(n+1)$ th EP. The number of EPs disentangled per unit time τ is $N = (v\tau/l_0)$, where l_0 is the typical distance along the chain (measured in units of Kuhn's length a) between two successive EPs [6]. The mean force is then

$$F = \tau^{-1} \sum_{n=1}^N \int_0^{t_n} f_n(t) dt = \langle f \rangle_N \quad (7)$$

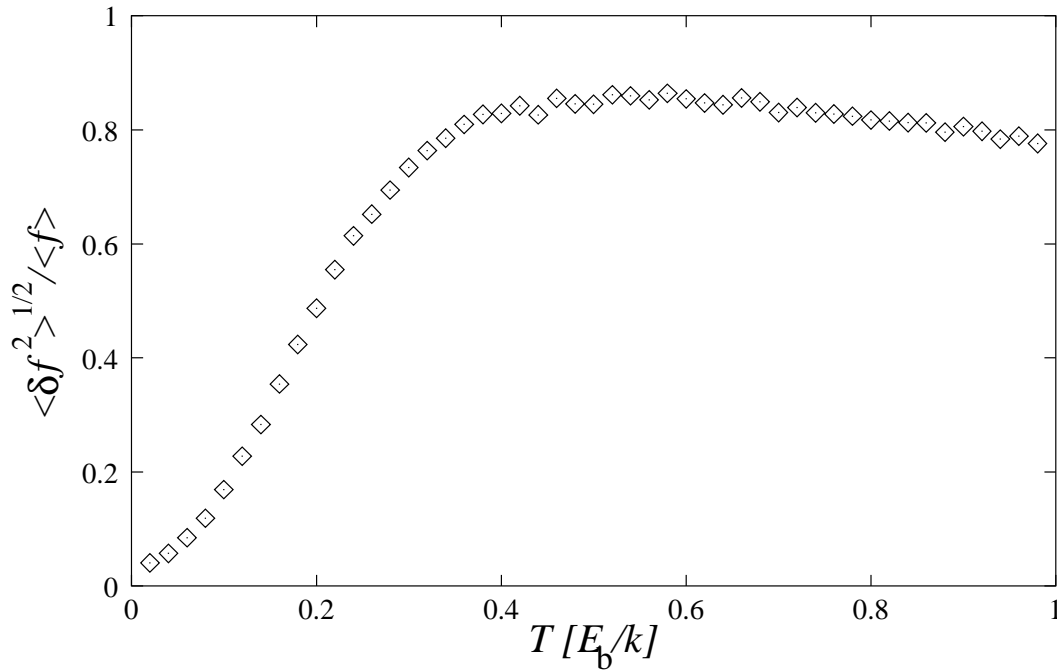


Fig. 4 – The relative width, $\Gamma = \langle \delta f^2 \rangle^{1/2} / \langle f \rangle$ as a function of temperature.

where t_n is the time between the disentanglements of the $(n - 1)$ th and n th EPs, $f_n(t)$ is the force during the time interval t_n , and $\langle \dots \rangle_N$ indicates a time average for a given number of EPs N . To maintain a constant pulling rate, v , this force is balanced by friction and therefore $\xi v = F$. It follows that fig. 3 gives in fact $\xi(T)$! If the terms on the right hand side of eq. (7) have a typical value, g , then the friction is g/l_0 . If, however, f_n is broadly distributed then Eq. (7) makes it immediately apparent that ξ can also suffer large fluctuations with its measured value depending nontrivially on N . Moreover, the sensitivity of the distribution of f_n to temperature is directly reflected by the mean and fluctuations of ξ . We therefore expect ξ to be characterised well by a typical value only above T_0 , while below T_0 its measured value should appear noisy.

Large fluctuations in ξ undermine melt-based models of polymer dynamics. For example, Rouse dynamics are based on a Langevin-type equation where ξ is presumed to have a typical value, and this description breaks down when the fluctuations of ξ become relevant. It is therefore suggested here that, in the absence of other mechanisms for the dynamics ⁽²⁾, $T_0 \approx 0.4$ is the crossover temperature below which melt-based models for polymer dynamics break down. Since one expects melt based models to fail around the glass transition it is tempting to conjecture that $T_g \approx T_0$ and therefore that T_g may be found from *molecular data*. For example, for polystyrene $T_g \approx 370K$ and therefore $E_b/k_B \approx 950K$, giving $f_0 \approx 50pN$, which can be tested experimentally using recent techniques of single chains pullout.

To conclude, I have derived the distribution of forces required to disentangle non-permanent entanglement points as a function of temperature. I have shown that this distribution is narrowly peaked around small forces for temperatures in the melt and it broadens with cooling.

⁽²⁾Note that other molecular mechanisms, such as originating in permanent or topological entanglements may increase the friction coefficient and affect its statistical properties

At low temperatures a gap develops which corresponds to the increasing difficulty to disentangle at low pulling forces, as one would expect. The distribution, and consequently the dynamics, have been shown to depend on temperature and on only two molecular quantities: E_b , the barrier energy needed to slide one chain across another, and $\epsilon = E_b/(af_{scission})$. The pulling force fluctuations have been found to dominate the dynamics below $T_0 \approx 0.4E_b/k_B$ and the implications of these results to viscosity on the molecular level have been discussed. This analysis pinpoints the range of validity of melt-based models by quantifying how and at what temperature they break down. It also forms a basis to construct a consistent model that can bridge between the dynamics in the melt and glass states. The present description holds as long as the chain consists of both coils and non-permanent entanglement points and is not valid for too slow an equilibration or too fast a pulling rate.

Since the dynamics of the molecular chains are fundamental to most aspects of polymer systems these results are expected to have a wide range of applications. For example, they enable to compute directly the mean force required to pull an ensemble of chains along an interface in the interior of a polymer system, which is directly relevant to yield stresses of glassy polymers. Carrying a similar analysis on interfaces between different polymer materials (joined by welding, grafting, or any other method) would give the strength of such joints. An application to the relaxation behaviour of single polymer chains is being currently considered by this author. On a fundamental level, it is possible to re-analyse the Rouse dynamics with a noisy friction coefficient using the results obtained here, extending the usefulness of the traditional approach to lower temperatures than it is currently valid for. This analysis also paves the way to first principles calculations of the viscosity around the glass transition directly from molecular information.

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