

Microscopic Theory of Chain Pullout in Amorphous Polymers

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ABSTRACT: The statistical-mechanical problem of chain pullout from an amorphous polymer under the influence of a constant force has been investigated. A simple microscopic model is proposed to describe the pullout process in both polymer glasses and elastomeric materials from a single point of view. A mean-field approximation for the interchain potential is used to account for the entanglements with the polymer network of the chain being pulled out. The chain mobility and the pullout rate were calculated as a function of pullout force, length of the chain, and other model parameters. In glassy polymers the pullout force was found to be almost rate independent at low pullout rates and linear in rate at high pullout rates. For polymer glasses the model also predicts the existence of some characteristic degree of polymerization N_e of the chain being pulled out, such that the pullout force scales as N for $N \ll N_e$ but as N^3 for $N \gg N_e$. In elastomeric materials the pullout force was found to have a nonlinear dependence on both chain length and rate of pullout.

1. Introduction

The mechanical properties of polymers in general, and the fracture of polymers in particular, have received growing attention over the last decade. Although the macroscopic processes involved in the fracture of polymers vary widely depending on the system under consideration, one can always identify the two major processes that control fracture on a microscopic level. These are chain scission and chain pullout. Numerous results concerning chain scission can be found in the literature (see ref 1 for references), but much less has been learned about the microscopic picture of chain pullout.^{2–21}

The pullout process is, however, at least of the same importance as chain scission in determining the mechanical properties of polymers. It has been shown to play an important role in the failure of the interfaces between immiscible polymers, especially those reinforced by diblock copolymers,^{2–7,18,19} in crazing and crack propagation in bulk polymers,^{15,22,23} in friction and lubrication of polymer surfaces,^{16,17,20} and in several other processes.

A number of models have been proposed to describe the process of chain pullout and the relation between chain pullout and the mechanical properties of bulk polymers and their interfaces.^{9–13,16,18,22–24} One can attempt to separate these models into two major groups. The first group of models has its origin in work devoted to polymer adhesion and interfacial toughness.^{9–13} To this end the authors usually consider the process of failure of the diblock-reinforced interface between two immiscible amorphous polymers. The failure of such an interface by crack propagation causes either scission or pullout of diblock copolymer chains entangled in the bulk of polymeric material. Although models of this process differ in their approach to the micromechanical problem of crack propagation, the descriptions of the individual chain pullout process have a number of features in common. For example, the pullout process is dominated by viscous forces, and so the pullout rate is linear in the pullout force. However, it is assumed to be different from a purely viscous process in the sense that the pullout force tends to a nonzero constant as the pullout rate approaches zero.

The second group of models is based on the idea of a random local environment.^{22–24} It is assumed that inside the amorphous polymer the monomers are located in a distribution of local environments which may be modeled as energy wells of different depths. The pullout process starts when the cooperative barriers to chain center-of-mass motion are overcome by the highly localized stress applied along the chain contour. The chain mobility in these models does not represent the effect of simple viscosity and has a quite complicated behavior as a function of applied stress and temperature.

In order to describe known experimental results, all the models assume the existence of some nonzero threshold pullout force. The nature of this force is interpreted, however, in a number of different ways. In the early models of de Gennes^{12,13} it was assumed that the pulled-out chain was chemically connected to the polymeric network, and the threshold force was related to the force necessary to break this connection. In de Gennes' recent models^{10,11} the threshold force is considered to be a result of the competition between elastic and capillary forces. The capillary force tends to "suck" the chain into the tube inside the material. The elastic force, however, tends to pull the chain out in order to reduce the extension of the random coil formed by the pulled-out portion of the chain. Although this mechanism may play an important role in the case of elastomeric materials, it does not seem capable of accounting for the substantial increase in threshold force that occurs in polymer glasses when the chain length is increased.¹⁸

In models based on the idea of a random local environment, the threshold force arises as the force necessary to overcome local barriers and thus naturally depends on the length of the chain being pulled out. There is, however, a problem if one wants to incorporate in these models some recent results concerning elastomeric materials. It was found in some experiments⁴ that a diblock-reinforced interface between elastomers can recover its original toughness at room temperature even after complete mechanical failure. This process has been interpreted^{26,27} in terms of reptation-like diffusion of diblock copolymer chains from the surface to the bulk of the polymer. This interpretation is, however, incompatible with models in which a random local environment inhibits motion of the chain at room

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temperature in the absence of a pullout force that exceeds some threshold value.

It was shown in the work of Washiyama *et al.*¹⁸ that the pullout force grows much more rapidly with chain length for chains longer than some characteristic length N_e than it does for chains shorter than N_e . The authors attributed this phenomenon to additional friction due to chain entanglements. This effect is not predicted by any of the above-mentioned models. There are also some other experimental results, such as the saturation of the interfacial toughness in elastomeric materials at high pullout rates,² that cannot be explained in terms of existing models of chain pullout.

In this study we propose a new model which describes from a single point of view the process of chain pullout in a wide range of amorphous polymers, including both polymer glasses and elastomeric materials. While the model does not encompass all possible complications, such as "knot tightening" and the stochastic nature of the chain environment, it does contain the essential elements of the effects of chain entanglements. The paper is organized as follows. In the next section we describe the model of the pullout process and derive a set of simple equations of motion that allow us to calculate the chain mobility provided the mobility of each monomer is known. In the third section we introduce the concept of the "bumpy channel", which is used to account for chain entanglements with the polymeric network. The fourth section is devoted to the calculation of the monomer mobility along the channel. In the fifth section we return to the equations of motion derived in section 2 and use the monomer mobility derived in the fourth section to calculate the mobility of the whole chain along the channel. In section 6 the results obtained for the mobility of the chain are used to calculate the pullout force as a function of pullout rate, length of the chain, and other model parameters.

2. Model

Microscopic description of the chain pullout process in amorphous polymers poses a number of serious difficulties. The disordered structure of these materials, along with the three-dimensional nature of the problem, makes almost impossible a direct approach similar to the one employed²⁵ in the case of liquid-crystalline polymers. One thus has to resort to the simplest model available. The most successful model capable of describing the dynamics of polymer chains in a dense network is the so-called tube model.^{28,29} In this model the motion of a chain inside a dense network of other chains is assumed to be highly restricted in the direction perpendicular to its contour, as would be the case were it confined in a tube.

The tube model is able to predict a number of important results concerning chain dynamics in amorphous polymers, polymer melts, and solutions.^{30,31} This model can also be seen as the conceptual basis of many of the existing models of chain pullout, in all of which the chain is assumed to move predominantly along its contour during the pullout process. Many of these models assume that a viscous force slows longitudinal motion of the chain. On the basis of the tube model, it is, however, difficult to derive the strong dependence typical for amorphous polymers of the threshold pullout force on the length of the chain. On the other hand, in models based on the concept of a random local environment, a length-dependent threshold force naturally arises as the force necessary to overcome local potential

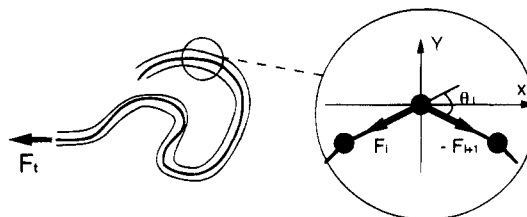


Figure 1. During the pullout process the chain moves predominantly along its length as if confined in a tube. Intermonomer forces are assumed to be central.

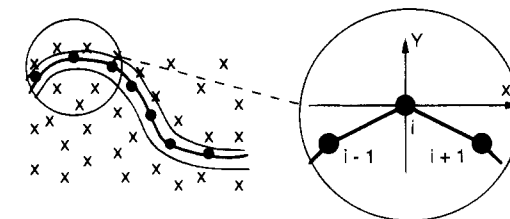


Figure 2. The tube is assumed to be formed by the chains of the random polymeric network.

barriers. These models, however, do not predict the chain reptation at room temperature that has been found in elastomeric materials.

In the model presented here we have tried to incorporate both the concept of the tube and the idea of local barriers. We describe the polymer as a freely jointed chain and, in the spirit of the tube model, assume that the chain is moving predominantly along its contour during the pullout process. We consider a chain of N monomers moving with constant velocity v under the influence of the force F_t applied to the first monomer of the chain (see Figure 1). One can then write a system of equations for the longitudinal and transverse components, $F_{i||}$ and $F_{i\perp}$, of the force acting on the i th monomer of the chain as

$$F_{i\perp} = F_i \theta_i$$

$$F_{i||} = F_i - F_{i+1} \quad (1)$$

with boundary conditions $F_1 = F_t$ and $F_{N+1} = 0$. Here, F_i and F_{i+1} are the forces acting along the bonds connecting the i th monomer to the $(i-1)$ th and $(i+1)$ th monomers, respectively, θ_i is the exterior angle between these bonds, assumed to be small ($\theta_i \ll 1$), and $i = 1, 2, \dots, N$. Here we also neglect the inertia of the chain and assume $F_{i||}/F_i \ll 1$. Let us now define the mobility μ of a monomer as the ratio of its velocity to the longitudinal component of the force acting on it. This mobility will be a function of the position of the monomer as it travels along its path. Then a new set of equations

$$v = \mu_i F_{i||} \quad (2)$$

can be added to eqs 1. Thus if one knows all the local mobilities, then the total chain mobility, defined as $\mu_t = v/F_t$, can be easily derived from eqs 1 and 2 for any configuration of the chain defined by $\{\theta_i\}$.

3. The Concept of the "Bumpy Channel"

In the tube model^{28,29} the chain is assumed to be confined in a "tube" formed by other chains of the polymeric network, as shown in Figure 2. Let us now introduce a local system of coordinates associated with the tube in such a way that the X-axis is tangential to the axis of the tube. The Y-axis at a given monomer

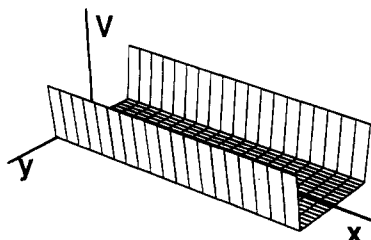


Figure 3. Representation of the tube model in terms of the mean-field potential $V(X,Y)$ defined by eq 3.

site is taken to be normal to the axis of the tube and in the plane defined by the monomer and its two nearest neighbors. Motion in the remaining Z -axis direction is ignored. One can reformulate then the idea of the tube in terms of the mean-field potential $V(X,Y)$ that acts on the i th monomer of the chain by writing

$$V(X,Y) = \begin{cases} \text{const} & |Y| < d \\ +\infty & |Y| \geq d \end{cases} \quad (3)$$

where d is the characteristic radius of the tube (see Figure 3). Indeed, the motion of the chain in such a potential is equivalent to motion inside a tube of diameter $2d$. The potential $V(X,Y)$ defined by eq 3 can be thought of as a zero-order approximation to the mean-field potential of neighboring chains. In actuality, the tube is formed by the chains of a random polymeric network, and thus one can expect the function $V(X,Y = \text{const})$ to be a fluctuating function of X rather than a constant. Also, the restrictions imposed by the network on transverse motion of the chain should not lead to $V(X,Y \geq d) \rightarrow \infty$ since the network chains are not infinitely stiff.

These considerations suggest that one might modify the tube concept by including higher-order corrections to the mean field of neighboring chains. The schematic representation of the procedure we use for this purpose is shown in Figure 4. We first expand $V(X,Y)$ as a power series in Y , so that

$$V(X,Y) = \sum_{n=0}^{\infty} \frac{1}{n!} V_n(X) Y^n \quad (4)$$

where $V_n(X) = \partial^n V / \partial Y^n$. In the tube model the motion of the chain in the Y -direction is assumed to be highly restricted, and so we truncate the series at $n = 4$. The assumption that the motion is symmetric about $Y = 0$ restricts us to even values of n , so that

$$V(X,Y) = \sum_{k=0}^2 \frac{1}{(2k)!} V_{2k}(X) Y^{2k} \quad (5)$$

The functions $V_{2k}(X)$ should really be randomly fluctuating functions of X in order to reflect the disordered local structure of the polymeric network. On the other hand, one can expect them to have a strong Fourier component with the period defined by the average distance a between the chains that form the tube. We choose to retain only this one dominant Fourier component and approximate the functions $V_0(X)$, $V_2(X)$, and $V_4(X)$ as

$$\begin{aligned} V_0(X) &= \vartheta + \epsilon \cos(2\pi X/a) \\ V_2(X) &= \alpha + \beta \cos(2\pi X/a) \\ V_4(X) &= \varrho + \lambda \cos(2\pi X/a) \end{aligned} \quad (6)$$

where ϑ , ϵ , α , β , ϱ , and λ are some parameters which

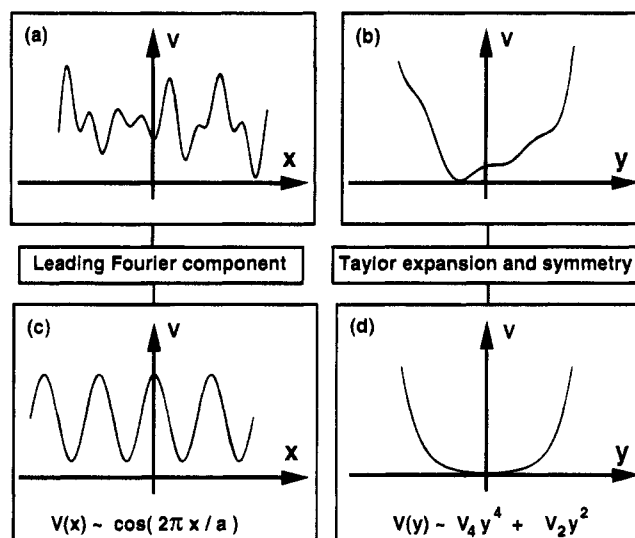


Figure 4. Schematic representation of the procedure used to obtain an approximate mean-field potential $V(X,Y)$. Curves a and b schematically represent the actual potential acting on the i th monomer of the chain. Curves c and d represent a mean-field approximation to the actual potential. See detailed explanation in the text.

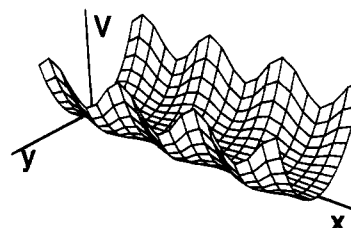


Figure 5. Representation of the "bumpy channel" in terms of the mean-field potential $V(X,Y)$ defined by eq 7. Parameters are chosen as $\lambda = 0$, $\varrho = 1$, $\epsilon = 0$, $\beta = 0.01$, and $\alpha = 0.02$.

characterize the network, and we assume that $V_0(X)$, $V_2(X)$, and $V_4(X)$ have the same period and initial phase. In order for the chain to be confined in the y -direction, the coefficient ϱ should be greater than $|\lambda|$. Substituting eq 6 into eq 5 and omitting the additive constant ϑ , we obtain the mean-field potential $V(X,Y)$ in the form

$$V(X,Y) = \alpha Y^2 + \varrho Y^4 + [\epsilon + \beta Y^2 + \lambda Y^4] \cos(2\pi X/a) \quad (7)$$

A plot of this function at some typical values of the parameters ϵ , α , β , ϱ , and λ is shown in Figure 5. One can see that the potential $V(X,Y)$ defined by eq 7 is similar to the mean-field representation of the tube model (see Figure 3) but has a somewhat more complicated structure. We will refer to a chain in such a potential as being confined in a "bumpy channel".

4. Mobility of a Monomer along the Bumpy Channel

As we have mentioned in section 2, the total mobility of the chain can be calculated if one knows the local mobility of each monomer in the chain. In order to calculate the monomer mobility along the channel, we first note that the transverse component F_{\perp} of the force acting on the monomer from the rest of chain and defined by eq 1 can be represented as a term $F_{\perp} Y$ added to the channel potential $V(X,Y)$ defined by eq 7. If we now introduce the dimensionless coordinates $x = 2\pi X/a$ and $y = 2\pi Y/a$, the channel potential $V(x,y)$ can be rewritten as

$$V(x,y) = f_{\perp}y + \alpha y^2 + \rho y^4 + [\epsilon + \beta y^2 + \lambda y^4] \cos x \quad (8)$$

where $f_{\perp} = F_{\perp}a/(2\pi)$ and ϵ , α , β , ρ , and λ are appropriately renormalized. The mobility of the monomer in such a potential depends not only on the parameters ϵ , α , β , ρ , and λ but also on the force f_{\perp} as well. In the case where $f_{\perp} \rightarrow 0$ and $|\epsilon|$ is not large ($|\epsilon| \lesssim k_B T$), the motion of the monomer along the axis of the channel is effectively unrestricted as shown in Figure 6a. However, if some finite force f_{\perp} is applied, then the motion of the monomer along the axis of the channel is restricted by potential barriers which grow as f_{\perp} increases, as illustrated in Figure 6b.

The approach that we take to finding the mobility of a monomer in such a channel is not one of direct calculation. Instead we make use of the fact that we can turn to the literature to find solutions of closely related problems. One can reasonably well approximate the required mobility as that in the one-dimensional potential

$$V_x(x) = h \cos(x) \quad (9)$$

where $h = (V_{\text{sad}} - V_{\text{min}})/2$ and V_{sad} and V_{min} correspond to the values of $V(x,y)$ in the saddle points and minima, respectively. In the zero-temperature limit, $k_B T/h \rightarrow 0$, the mobility μ of the monomer in the potential $V_x(x)$ can be found from the solution of a Langevin-type equation as³²

$$\gamma\mu = [1 - (h/f_{\parallel})^2]^{1/2} \quad h < f_{\parallel} \\ = 0 \quad h \geq f_{\parallel} \quad (10)$$

where $f_{\parallel} = F_{\parallel}a/(2\pi)$ describes the force acting on the monomer in the X-direction and $1/\gamma$ is the high-temperature monomer mobility. The value of h can be expressed in terms of the parameters of the potential $V(x,y)$,

$$h = \frac{1}{4}\alpha(y_s^2 - y_m^2) + \frac{1}{4}\beta(y_s^2 + y_m^2) + \frac{3}{8}f_{\perp}(y_s - y_m) + \epsilon \quad (11)$$

where

$$y_s = [-q_s/2 + ((p_s/3)^3 + (q_s/2)^2)^{1/2}]^{1/3} - [q_s/2 + ((p_s/3)^3 + (q_s/2)^2)^{1/2}]^{1/3}$$

$$y_m = [-q_m/2 + ((p_m/3)^3 + (q_m/2)^2)^{1/2}]^{1/3} - [q_m/2 + ((p_m/3)^3 + (q_m/2)^2)^{1/2}]^{1/3}$$

$$p_s = 1/2(\alpha + \beta)/(\rho + \lambda), \quad p_m = 1/2(\alpha - \beta)/(\rho - \lambda)$$

$$q_s = 1/4 f_{\perp}/(\rho + \lambda) \quad q_m = 1/4 f_{\perp}/(\rho - \lambda)$$

In the special case of $\lambda = 0$, one can approximate h as

$$h = (\beta/2) \left[1 + \frac{1 - 2\alpha/(3\rho)}{1 + 2\epsilon/\beta} \right] \left(\frac{f_{\perp}}{4\rho} \right)^{2/3} + \epsilon \quad \text{if } |f_{\perp}| \gg |\alpha| + |\beta| \quad (12)$$

$$h = \frac{\beta f_{\perp}^2}{4(\alpha^2 - \beta^2)} + \epsilon \quad \text{if } |f_{\perp}| \ll |\alpha| + |\beta|, \quad |\alpha| > |\beta| \quad (13)$$

Thus one can see that the mobility μ of the monomer along the bumpy channel can be explicitly expressed in terms of the parameters of the channel potential $V(x,y)$

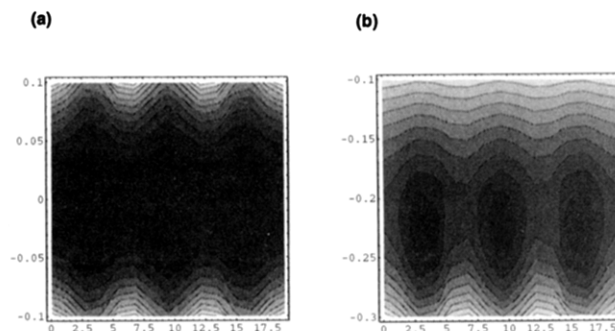


Figure 6. Contour map of the potential $V(x,y)$ defined by eq 8 in the cases where (a) $f_{\perp} = 0$ and (b) $f_{\perp} = 0.05$. The darker regions correspond to smaller values of V . Parameters are chosen as $\lambda = 0$, $\rho = 1$, $\epsilon = 0$, $\beta = 0.01$, and $\alpha = 0.02$.

and the transverse f_{\perp} and longitudinal f_{\parallel} components of the force acting on the monomer from the rest of the chain.

5. Total Mobility of the Chain along the Bumpy Channel

Let us return now to eqs 1 and 2 and calculate the total mobility of the chain along the bumpy channel. One can rewrite these equations as

$$va/(2\pi) = \mu f_{\parallel} \\ f_{\parallel} = f_i - f_{i+1} \\ f_{i\perp} = \theta_i f_i \quad (14)$$

where $f_i = F_i a/(2\pi)$, $f_1 = f$, $f_{N+1} = 0$, the monomer mobility μ_i is now given by eq 10, and $i = 1, 2, \dots, N$. If the chain is long enough, we can treat the index i as a continuous variable and make the approximation

$$f_{i+1} - f_i = \frac{df_i}{di} \quad (15)$$

Substituting eqs 10 and 15 in eqs 14, we then obtain

$$\frac{\gamma va}{2\pi} = \frac{df_i}{di} \left[1 - (h(f_{i\perp}))^2 \left(\frac{df_i}{di} \right)^{-2} \right]^{1/2} \quad (16)$$

where $h(f_{i\perp})$ is given by eq 11. This differential equation can be transformed to a transcendental equation with respect to $\gamma\mu_t$

$$N = \int_{\delta}^1 \left[(\gamma\mu_t)^2 + \left(\frac{h(\theta f_i)}{f_t} \right)^2 \right]^{-1/2} d\left(\frac{f_i}{f_t} \right) \quad (17)$$

where $\delta \equiv (f_N/f_t)$ is defined by

$$\left(\frac{f_N}{f_t} \right)^2 - \left(\frac{h(\theta f_N)}{f_t} \right)^2 - (\gamma\mu_t)^2 = 0$$

$\mu_t = v/F_t$ is the total chain mobility, N is the total number of monomers in the chain, and $h(\theta f_i) = h(f_{i\perp})$. The solution of this equation gives the total chain mobility μ_t as a function of the total force f_t applied to the chain, the high-temperature monomer mobility $1/\gamma$, parameters of the bumpy channel potential $V(x,y)$, and the chain configuration $\{\theta_i\}$.

The angles θ_i describe the local curvature of the chain and will be randomly distributed about some mean value. We shall make the simplification of assuming all the θ_i to be equal, so that $\theta_i = \theta = \text{const}$. We can then consider the mobility of the chain of length N as being a function of the parameters ϵ , α , β , ρ , λ , θ , and γ which characterize the system under consideration and

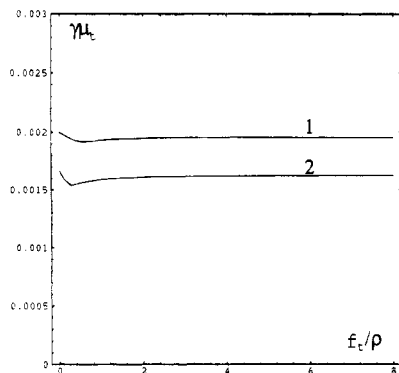


Figure 7. Mobility μ_t of a short chain ($N \ll (1/\theta)(\rho/\beta)^{1/2}$) in an elastomeric material as a function of applied force f_t . Curve 1 corresponds to a chain of $N_1 = 500$ monomers and curve 2 to $N_2 = 600$. Parameters of the potential are chosen as $\alpha/\rho = 0.02$, $\beta/\rho = 0.01$, $\theta = 0.1$, $\epsilon = 0$, and $\lambda = 0$.

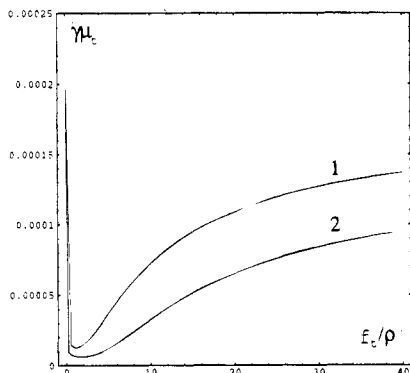


Figure 8. Mobility μ_t of a long chain ($N \gg (1/\theta)(\rho/\beta)^{1/2}$) in an elastomeric material as a function of applied force f_t . Curve 1 corresponds to a chain of $N_1 = 5000$ monomers and curve 2 to $N_2 = 6000$. Parameters of the potential are chosen as $\alpha/\rho = 0.02$, $\beta/\rho = 0.01$, $\theta = 0.1$, $\epsilon = 0$, and $\lambda = 0$.

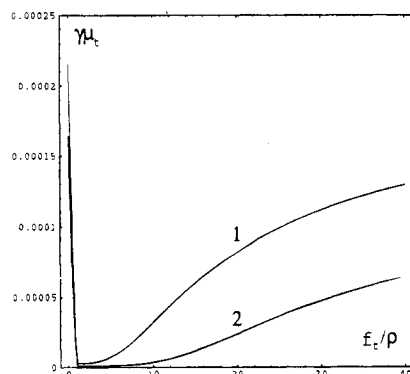


Figure 9. Mobility μ_t of a more sharply curved long chain ($N \gg (1/\theta)(\rho/\beta)^{1/2}$) in an elastomeric material as a function of applied force f_t . Curve 1 corresponds to the chain of $N_1 = 4000$ monomers and curve 2 to $N_2 = 5000$. Parameters of the potential are chosen as $\alpha/\rho = 0.02$, $\beta/\rho = 0.01$, $\theta = 0.2$, $\epsilon = 0$, and $\lambda = 0$.

of the force f_t applied to the chain. We now investigate the influence of these parameters on the chain mobility.

First we consider the case of a soft material in which $\lambda = 0$ and $\epsilon \ll k_B T$ (which is equivalent to $\epsilon = 0$ in a zero-temperature approximation) but retain the steep sides of the channel by choosing $\alpha, \beta \ll \rho$. With these conditions the typical solutions of eq 17 take the form shown in Figure 7–9 for the cases of chains of different lengths (parameter N) and configurations (parameter θ). As one can see from Figure 7, for short chains, defined as those for which $N \ll (1/\theta)(\rho/\beta)^{1/2}$, the total

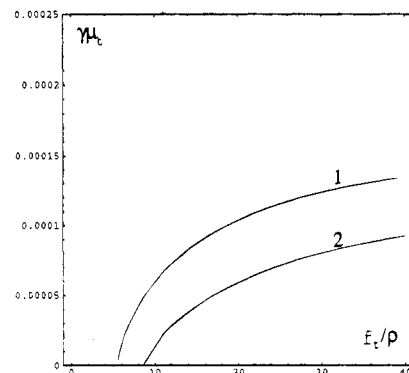


Figure 10. Mobility μ_t of a chain in a polymer glass as a function of applied force f_t . Curve 1 corresponds to a chain of $N_1 = 5000$ monomers and curve 2 to $N_2 = 6000$. Parameters of the potential are chosen as $\alpha/\rho = 0.02$, $\beta/\rho = 0.01$, $\theta = 0.1$, $\epsilon/\rho = 0.0001$, and $\lambda = 0$.

mobility μ_t is basically independent of the pullout force f_t and is equal to the high-temperature chain mobility, $1/(\gamma N)$. For long chains, which have $N \gg (1/\theta)(\rho/\beta)^{1/2}$, there is a very different behavior, as seen in Figures 8 and 9. Although the mobility takes its high-temperature value at extremely small applied forces, there is a rapid decrease in mobility as soon as a modest force is applied. It is only when the force is increased to values of the order of $(N\beta/3)^3\theta^2/(4\rho)^2$ that the mobility begins to increase again and approach its high-temperature value. On the basis of this behavior, we identify the regime in which $\lambda = \epsilon = 0$ as corresponding to an elastomeric material (see section 1), in which reptation can occur.

Because the parameter θ is proportional to the local curvature of the chain, we expect that increasing θ will lead to an increased force necessary to pull out a more tightly coiled chain. This is indeed seen to be the case. Curve 1 of Figure 8 indicates a higher mobility when $\theta = 0.1$ than does curve 2 of Figure 9, which describes a similar chain but with $\theta = 0.2$.

If we choose the parameter $\epsilon \gtrsim k_B T$ (or $\epsilon \neq 0$ in the zero-temperature approximation), the mobility of the chain at $f_t \rightarrow 0$ goes to zero as shown in Figure 10. Although the chain pullout process is still possible if f_t exceeds some threshold value, the chain reptation is now suppressed. In this sense the case $\epsilon \neq 0$ corresponds to chain pullout in a polymeric glass, where no appreciable reptation is found at temperatures below the glass transition.

The coefficient λ determines the strength of the most strongly nonlinear terms in the potential and is the dominant controlling factor in the suppression of chain pullout. For nonzero ϵ , the effect of the term in λ appears analogous to that of the tightening of a knot, and both chain pullout and reptation cease. It is only in the somewhat pathological case shown in Figure 11, in which $\lambda \neq 0$ but $\epsilon = 0$, that some reptation occurs. Because this situation appears unrealistic, we shall put $\lambda = 0$ in the rest of the discussion. This is equivalent to assuming that the local environment of the chain is either flexible enough or in a sufficient state of thermal motion to mitigate this "knot-tightening" phenomenon.

With $\lambda = 0$ one can obtain some useful approximations for the total mobility μ_t . For small values of f_t , where $f_{t\perp} \ll |\alpha| + |\beta|$, the function $h(f_{t\perp})$ can be approximated by eq 13. In this case the integral in eq 17 can be evaluated explicitly as

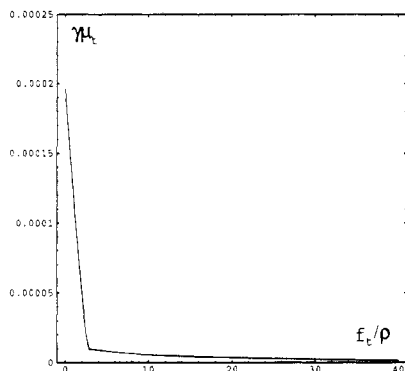


Figure 11. Mobility μ_t of the chain of $N = 5000$ monomers as a function of applied force f_t in the special case where the center of the channel is completely smooth (i.e., $\epsilon = 0$) but the term $\lambda\gamma^4$ in the potential is nonzero. Parameters of the potential are chosen as $\alpha/\rho = 0.02$, $\beta/\rho = 0.01$, $\theta = 0.1$, $\epsilon/\rho = 0$, and $\lambda = 0.1$.

$$N = (2a_2c_2)^{-1}[F(\xi_1, \xi) - F(\xi_2, \xi)] \quad (18)$$

where

$$\xi_1 = \arccos[(f_N/f_t)^2 - a_2^2]/((f_N/f_t)^2 + a_2^2)]$$

$$\xi_2 = \arccos[(1 - a_2^2)/(1 + a_2^2)]$$

$$(f_N/f_t)^2 = (1/2)[c_2^{-2} - 2b_2^2 - ((2b_2^2 - c_2^{-2})^2 - 4(b_2^4 + 4s_2^2))^{1/2}]$$

$$\xi = [1/2 - (1/2)(b_2/a_2)^2]^{1/2}, \quad a_2^2 = (b_2^4 + s_2^2)^{1/2}$$

$$b_2^2 = \epsilon/(c_2 f_t), \quad s_2 = \gamma\mu_t^{(1)}/c_2, \quad c_2 = f_t\theta_2(\beta/4)(\alpha^2 - \beta^2)^{-1}$$

and $F(\xi, \xi)$ denotes the elliptic integral of the first kind. We thus obtain an implicit equation for the total mobility $\mu_t^{(1)}$. For the case of elastomeric materials ($\epsilon = 0$) and small mobilities ($\gamma\mu_t^{(1)} \rightarrow 0$), eq 18 can be further simplified and yields the solution

$$\gamma\mu_t^{(1)} = \left(\frac{2K(1/2^{1/2})}{N}\right)^2 \frac{\alpha^2 - \beta^2}{\beta\theta^2} \frac{1}{f_t} \quad (19)$$

where $K(x)$ denotes a complete elliptic integral, and hence $K(1/2^{1/2}) \approx 2.08$. The plot of $\gamma\mu_t^{(1)}$ is shown in curve 3 of Figure 12 and approximates the exact solution, shown in curve 1, in the range where f_t/ρ is small. Thus when a small but finite force f_t is applied to the chain, its mobility decreases as $1/f_t$ and chain motion is limited to very low rates of pullout.

For large values of f_t , where $f_{t\perp} \gg |\alpha| + |\beta|$, we can use eq 12 for $h(f_{t\perp})$. By substituting eq 12 in eq 17, we obtain an implicit equation for the total mobility $\gamma\mu_t^{(2)}$ of the form

$$N = \frac{3}{c_1} \int_{\delta}^1 \frac{z^2 dz}{[(z^2 + b_1^2)^2 + s_1^2]^{1/2}} \quad (20)$$

where $\delta \equiv f_N/f_t$ is given by

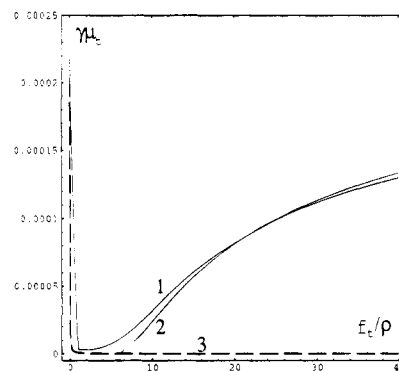


Figure 12. Mobility μ_t of a long chain ($N \gg (1/\theta)(\rho/\beta)^{1/2}$) in an elastomeric material as a function of applied force f_t . Curve 1 represents the exact solution, and curves 2 and 3 are approximations to $\gamma\mu_t$ valid at large and small f_t/ρ , respectively. Parameters of the potential are chosen as $\alpha/\rho = 0.02$, $\beta/\rho = 0.01$, $\theta = 0.2$, $\epsilon = 0$, $\lambda = 0$, and $N = 4000$.

$$\frac{1}{c_1^2} \left(\frac{f_N}{f_t}\right)^2 - \left(b_1^2 + \left(\frac{f_N}{f_t}\right)^{2/3}\right)^2 - \left(\frac{\gamma\mu_t^{(2)}}{c_1}\right)^2 = 0$$

and

$$b_1^2 = \frac{\epsilon}{c_1 f_t}, \quad c_1 = \left(\frac{\theta}{4\rho}\right)^{2/3} \frac{p\beta}{2f_t^{1/3}}$$

$$p = 1 + \frac{1 - 2\alpha/(3\rho)}{1 + 2\epsilon/\beta}, \quad s_1 = \frac{\gamma\mu_t^{(2)}}{c_2}$$

A typical solution of eq 20 for the case of an elastomeric material ($\epsilon = 0$) is shown in curve 2 of Figure 12. As one can see, it describes the region where the appropriate exact solution (see curve 1) increases with increasing f_t . An analytical approximation for the intermediate region, in which μ_t is very small, can be found for the case where $\epsilon = 0$. Then one obtains an approximate solution of eq 20 in the form

$$\gamma\mu_t^{(2)} = \left(\frac{6}{N}\right)^{5/2} \left(\frac{f_t^{**}}{f_t}\right)^{5/6} \left[1 - \left(\frac{f_t^{**}}{f_t}\right)^{1/3}\right]^{1/2} \quad (21)$$

where $f_t^{**} = (Np\beta/6)^3(\theta/(4\rho))^2$. This result can be used to get an estimate of the order of magnitude of the chain mobility in the mobility gap region. On substituting f_t^{**} from eq 21 into eq 19, we find

$$\gamma\mu_t(f_t = f_t^{**}) = \frac{6}{Np^3} \left(\frac{48\rho K(1/2^{1/2})}{\beta\theta^2 N^2}\right)^2 \left(\frac{\alpha^2}{\beta^2} - 1\right) \quad (22)$$

As one can see, for sufficiently long chains, where $N \gg (1/\theta)(\rho/\beta)^{1/2}$, the mobility within the gap can be much smaller than the mobility $1/(\gamma N)$ that the chain has at vanishing pullout force. Thus in the case of elastomeric materials the motion of long chains is strongly suppressed at any pullout force f_t less than some characteristic value f_t^{**} .

In the case where $\epsilon \gg 2N^2\beta^3\theta^2/\rho^2$, which, according to our classification, is an example of a polymer glass, the solution of eq 20 takes the form

$$\gamma\mu_t^{(2)} = \frac{1}{N} \left[1 - \left(\frac{\epsilon N}{f_t}\right)^2\right]^{1/2} \quad (23)$$

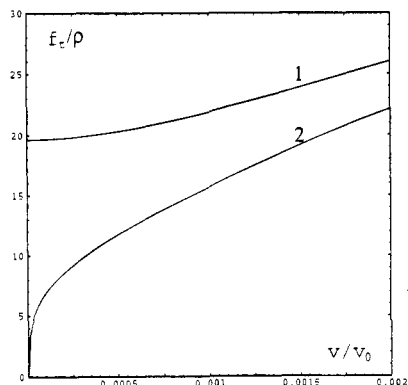


Figure 13. Pullout force f_t as a function of pullout rate v . Curve 1 corresponds to a polymer glass ($\epsilon \neq 0$) and curve (2) to an elastomeric material ($\epsilon = 0$). The number N of monomers in the chain satisfies the criterion for a "long" chain, ($N \gg (1/\theta)(\rho/\beta)^{1/2}$). Pullout rate is expressed in units of $v_0 = (2\pi/a)(\rho/\gamma)$. Parameters of the model are $\alpha/\rho = 0.02$, $\beta/\rho = 0.01$, $\theta = 0.2$, $N = 4000$, $\lambda = 0$, $(\epsilon/\rho)_1 = 0.08$, and $(\epsilon/\rho)_2 = 0$.

Thus f_t must exceed some threshold force ϵN in order for solution of eq 23 to exist. The mobility $\gamma\mu_t^{(2)}$ described by eq 23 is in fact the mobility of the chain in a potential in which the effect of the coefficient β is ignored and hence for which $V(x) = \epsilon \cos(x)$. This means that the only important characteristic of the channel in this case is the parameter ϵ —the amplitude of oscillations of the mean-field potential along the axis of the bumpy channel. In this limit we have in effect recovered the simpler model discussed in ref 25.

6. The Pullout Force

If one knows the mobility μ_t of the chain as a function of the applied force f_t , the relation between rate of pullout v and applied force f_t can be found from the equation

$$\frac{v}{v_0} = \mu_t \frac{f_t}{\rho} \quad (24)$$

where $v_0 = 2\pi\rho/(a\gamma)$. Typical results for $f_t(v)$ are shown in Figure 13 for the cases of elastomeric and glassy materials. As one can see, at high pullout rates v the function $f_t(v)$ is almost linear for both elastomers and glasses. At low pullout rates the behavior of the function $f_t(v)$ is, however, different in glasses and elastomers. In glasses the pullout force f_t is almost rate independent and equal to the threshold pullout force f_t^* when the pullout rate is low. In elastomeric materials, however, the pullout force f_t for long chains is strongly rate dependent at low pullout rates. This difference in the behavior of $f_t(v)$ is the direct consequence of different chain mobilities in glasses and elastomers. In elastomeric materials the mobility μ_t at small pullout forces $f_t \lesssim f_t^*$, i.e., in the gap region in Figures 8 and 9, is small but nonzero. This leads to a very fast growth of $f_t(v)$ at small v as shown in Figure 13. In glassy materials, however, the mobility μ_t is zero for all f_t less than some threshold force f_t^* , but as f_t exceeds f_t^* the mobility starts growing very fast (see Figure 10). This form of $\mu_t(f_t)$ leads to a pullout force that is almost rate independent at low pullout rates.

Let us now concentrate on glassy materials and calculate the threshold pullout force f_t^* as a function of the model parameters α , β , ρ , ϵ , and θ and chain length N . In order to find f_t^* we have to solve eq 20 with $\gamma\mu_t^{(2)}$

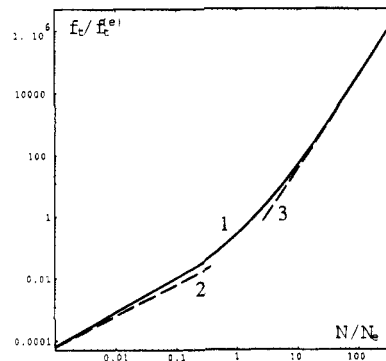


Figure 14. Pullout force f_t^* in a polymer glass as a function of the number N of monomers in the chain. Curve 1 corresponds to the exact solution, curve 2 to $f_t = N\epsilon$, and curve 3 to $f_t = (A/27)N^3$, where $N_e = 4(\epsilon/A)^{1/2}$, $f_t^{(e)} = AN_e^3$, and $A = \rho(p/2)^3(\beta/\rho)^3(\theta/4)^2$.

= 0. In this case eq 20 can be reduced to a set of equations

$$1 - \left(\frac{f_N}{f_t^*}\right)^{1/3} + b_1 \arctan\left(\frac{1}{b_1} \left(\frac{f_N}{f_t^*}\right)^{1/3}\right) - b_1 \arctan\left(\frac{1}{b_1}\right) = Nc_1/3$$

$$\left(\frac{f_N}{f_t^*}\right) - c_1 \left(\frac{f_N}{f_t^*}\right)^{2/3} - c_1 b_1^2 = 0 \quad (25)$$

If the chain is not too short, so that $N \gg (2/p)(\rho/\beta)(\epsilon/\rho)^{1/3}(4/\theta)^{2/3}$, then eqs 25 can be further simplified to the form

$$y^{1/3} = 1/3 + x^{1/2} \arctan \frac{y^{1/3} x^{1/2}}{x + (yx/N)^{1/3}} \quad (26)$$

where $y = f_t^*/(AN^3)$, $x = \epsilon/(AN^2)$, and $A = \rho(p/2)^3(\beta/\rho)^3(\theta/4)^2$. Approximate solution of this transcendental equation takes the form

$$\frac{f_t^*}{f_t^{(e)}} = \left(\frac{N}{N_e}\right)^3 \left[\left(\frac{1}{3} + \pi \left(\frac{x}{4} \right)^{1/2} \right) - x \left(\frac{1}{3} + \pi \left(\frac{x}{4} \right)^{1/2} \right)^{-1} \right]^3$$

if $(N_e/4)^{2/3} \ll N \lesssim N_e$

$$= \left(\frac{N}{N_e}\right)^3 \left[x^{1/3} + \frac{1}{5} + \left(\frac{3}{175} \right) x^{-1/3} \right]^3$$

if $N_e \lesssim N \ll (N_e/4)^2$ (27)

where $N_e = 4(\epsilon/A)^{1/2}$ and $f_t^{(e)} = AN_e^3$. A plot of the function $f_t^*(N)$ defined by eq 27 is shown in Figure 14. One can see that N_e represents a characteristic length of the chain at which the threshold pullout force f_t^* exhibits a transition from the linear law $f_t^* = N\epsilon$, obeyed when $N \ll N_e$, to the cubic law $f_t^* = A(N/3)^3$ for $N \gg N_e$. This leads to a considerable increase in the threshold force f_t^* for chains longer than N_e .

Let us now estimate an order of magnitude of the threshold pullout force. For the chain of $N \sim 10^2$ monomers and model parameters chosen as $a \sim 10^{-9}$ m, $\epsilon \sim 10^2$ K, $\epsilon/\rho \sim 10^{-1}$, $\beta/\rho \sim 10^{-1}$, and $\theta \sim 10^{-1}$, we obtain from eq 27 the threshold force $f_t^* \sim 10^{-9}$ N and a characteristic chain length $N_e \sim 10^2$ or 10^3 monomers. These estimates are compatible with experimental results concerning chain pullout in diblock-reinforced interfaces.^{2,18}

7. Conclusions

A simple microscopic model has been developed to describe from a single point of view the process of chain

pullout in a wide range of polymers including both polymer glasses and elastomeric materials. The new concept of the "bumpy channel" was proposed in order to take into account the influence of chain entanglements on the pullout process. The chain mobility and the rate of pullout were calculated as functions of the pullout force, the length of the chain, and various model parameters. The main predictions of the model are in good qualitative agreement with experimental data.

In the case of glassy materials the model predicts (i) that there is a nonzero threshold pullout force, (ii) that the pullout force is independent of the pullout rate at low rates and linear in the rate at high rates, and (iii) that chain entanglements give rise to a threshold degree of polymerization N_e , such that the pullout force f_t scales as N for $N \ll N_e$ but as N^3 for $N \gg N_e$. In the case of elastomeric materials the model predicts (i) that the pullout force varies rapidly with pullout rate at small rates and varies more slowly at high rates and (ii) that chain entanglements cause an additional frictional force, which varies nonlinearly with both chain length and applied force. The model predicts the correct orders of magnitude for the pullout force, but some additional experimental information is required in order to attempt more precise quantitative predictions.

In the present paper we have restricted ourselves to consideration of a relatively loosely coiled chain ($\theta_i \ll 1$), where nonlocal cooperative effects such as self-tightening knots can be neglected. The other, more subtle limitation of the model comes from the fact that we retained only the leading Fourier component of the random local potential acting on the monomers of the chain. Our model may thus have only limited applicability to the case of amorphous materials with substantial density fluctuations and, as a consequence, ill-defined short-range order.

In this treatment we concentrated on the description of pullout of a single chain and did not consider other potentially important processes involved in the fracture of polymers and their interfaces. In particular, we did not take into account surface effects, which are of considerable importance in describing such processes as crack propagation and crazing. As a result we did not obtain the nonzero threshold pullout force in elastomeric materials, which has been shown by Raphaël and de Gennes¹⁰ to be related to surface effects. The model we proposed in this paper can, however, be extended to describe not only fracture in polymeric materials but also some other properties of polymers, including some aspects of viscoelasticity. This extension of the model will be the subject of a future paper.

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