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Memorandum No. 1693

A rigorous model for constraint release in the bulk and the near-wall region

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December, 2003

ISSN 0169-2690

A rigorous model for constraint release in the bulk and the near-wall region.

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Abstract: In the present work an attempt is made to build a rigorous theoretical model for the constraint release mechanism found to play an important role in the dynamics of polymer melts. Our goal is a formalism free of adjustable parameters and "ad-hoc" assumptions which are inherent to existing theories for constraint release. Our model is capable to describe both thermal and convective constraint release. These processes have the same effect on chains and accordingly can be unified in a single framework. Since polymer chains in the bulk and in the near-wall layer may experience different types of constraint release, the latter case is studied separately. This topic is closely related to the long-standing problem of polymer melt flow instabilities encountered during extrusion. Nowadays it is believed that constraint release plays a crucial role in the dynamics of tethered chains preventing them from being squeezed against the wall. The resulting non-monotonous slip-law is the most probable reason of the so-called spurt instability.

Keywords: polymer flow instabilities, polymer extrusion, entanglements, reptation, (convective) constraint release, bond vector, boundary layer, bond vector probability distribution function, constitutive equation

AMS Classification: 35Q35, 76A10, 35K55, 76D10, 60G15, 65P40

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Introduction

Found to possess a unique variety of properties, polymers soon became an object of intensive research, encouraged by growing demands of industry. Despite their dramatical complexity, some successful models for polymer melt behaviour were proposed, based on simple physical assumptions. E.g., the model proposed by Rouse in [1], valid for dilute polymer solutions, treats a polymer molecule as a number of beads connected by elastic springs. Interacting with particles of the solvent this molecule displays a Brownian-like motion, and the corresponding microscopic equations of motion (Langevin equations) could be written out. But a reliable theoretical model for more complicated highly-entangled systems (such as polymer melts) was still lacking. Attempts to generalize the Rouse model and incorporate interaction between different polymer chains were not very successful resulting in excessive complication of the formalism. The tube concept proposed by De Gennes in 1971 in [2] was a theoretical 'break-through' in the modelling of concentrated entangled systems and had a huge impact on subsequent models. During the past few decades there has been a large number of papers based on the tube concept and extending the original ideas of De Gennes by incorporating additional relaxation mechanisms. For more details, the interested reader is referred to the excellent review by Watanabe [3]. The most recent models by Joshi, Lele [4], and Mead, Larson, Doi [5] include all the major mechanisms such as reptation, retraction, convective motion, and constraint release.

It is constraint release on which we would like to focus in this paper. We remind that constraint release is a sudden removal of a constraint imposed on a chain possibly resulting in a local jump over a distance of the order of the mean tube diameter. Constraints can be released by either reptation or shrinking of surrounding polymer molecules that constitute the tube. We emphasize that these processes have the same effect on the chain. Nevertheless, they have different physical origins and consequently different time scales. This is the reason why they will be studied separately hereafter. In the literature, constraint removal due to retraction of surrounding chains is often referred to as convective constraint release (CCR), in contrast to thermal constraint release arising from reptation (CR).

Because of the extraordinary intricate and diverse nature of constraint release, it has always been a "stumbling block" on the way to a quantitative theoretical model that could further be used to obtain a constitutive equation for polymer melts. Early efforts to describe constraint release mathematically and to incorporate it into existing tube theories (see, for example, the work by Marucci [6]) were mostly based on scaling analysis, and were purely phenomenological. The model by Mead, Larson, Doi [5], and Rubinstein, Colby [7] treats constraint release as a Rouse like motion of the tube itself. But even these advanced theories still contain plenty of 'ad-hoc' assumptions and adjustable parameters, and so a reasonable quantitative model is still lacking.

In the present paper we will develop a rigorous approach to modelling of constraint release. Inspired by the work of Rubinstein and Colby [7] we will introduce the so-called segment mobility distribution function and derive the corresponding equation of motion. The proposed analysis is performed within the new findings in mathematical modelling of chain dynamics described in detail in [9, 10, 11].

The s_0-representation of a chain.

In order to develop a mathematical model that describes real physical processes in the melt, we need a reliable description of a single chain behavior valid for a wide range of flow regimes. In particular, since we do not want to restrict ourselves to slow flows, our analysis cannot be based on the assumption of inextensible chains (see, for example [8]). This follows from simple physical arguments. Fast flows stretch polymer molecules. Since all the molecules in the ensemble have different spatial conformations and, as a consequence, experience different drag forces, they are "allowed" to have different lengths. Therefore, the arclength of a segment (the curvilinear coordinate along the primitive path), which is often used in the theory to measure the segment position, becomes 'chain-dependent'.

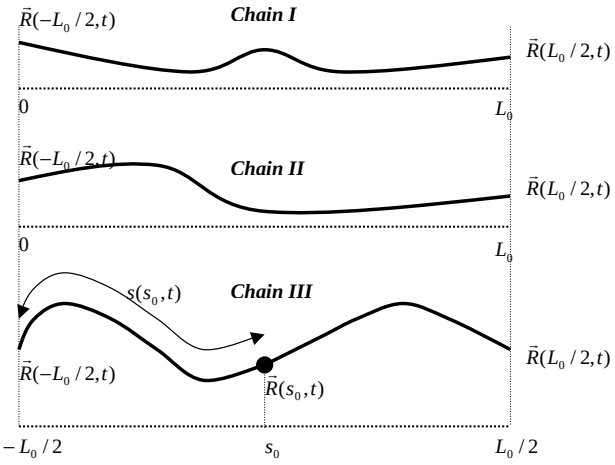

Figure 1: Parameterized curves: s and $\mathbf{R}(s_0,t)$ is the physical arclength and the position vector of segment s_0, respectively; L_0 the equilibrium length of the chain.

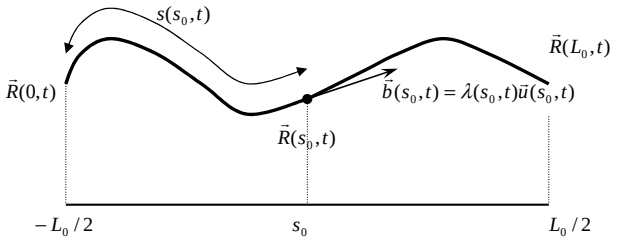

Figure 2: The bond vector of the parameterized chain: $\lambda(s_0,t)$ and $\mathbf{u}(s_0,t)$ is the local stretching and the unit tangent vector at point s_0, respectively.

To eliminate this difficulty and still use a "global" coordinate system even under fast flows, we will represent our molecules as parameterized curves with a parameter running over a certain *fixed* interval. That is to say, every chain in the melt is described by a set of position vectors $\hat{\mathbf{R}}(s_0,t)$ where the parameter s_0 runs from $-L_0/2$ to $L_0/2$ (see, Fig.1). Here, L_0 can be chosen arbitrarily. Note that the s_0-description of a chain was introduced in [9, 10, 11] where it was productively used to derive the equations of motion for the so-called bond vector probability distribution functions and the bond vector correlators.

We outline that s_0 is not the physical position of a segment along the primitive chain, but acts as a 'label'. In contrast to the physical coordinate $\hat{s}(s_0,t)$, which measures arclength along the actual chain (see, Fig.1), this label is unique and marks *the same physical segment at all times*. But, since we have freedom in choosing this label, to make a physical interpretation possible it is very convenient to "address" every segment via its mean equilibrium arclength. Consequently, we choose L_0 as the ensemble averaged equilibrium

length of a molecule.

Note that every chain has its own spatial configuration (see, Fig.1) and accordingly its own parametrization function $\hat{\mathbf{R}}(s_0, t)$ which reflects its time evolution in space. Since this function pertains to a single chain we may think of it as being stochastic. In principle, if we know the explicit form of every parametrization function in the ensemble at any time, dynamics of the whole system of chains is completely defined.

Therefore, there are two types of variables present in our theory: deterministic variables (such as, s_0 and L_0) and stochastic (i.e. chain-dependent) (for example, $\hat{\mathbf{R}}(s_0, t)$). Hereafter, in order to distinguish between them, the latter will be indicated by the hat sign above.

With s_0 chosen as the mean equilibrium arclength of a chain segment along the primitive path, we can introduce two important variables that can be used to describe the spatial conformations of the molecules. These are the local stretching $\hat{\lambda}(s_0, t)$ and the bond vector $\hat{\mathbf{b}}(s_0, t)$ at point s_0. We define them as follows

$$\hat{\mathbf{b}}(s_0, t) = \frac{\partial \hat{\mathbf{R}}(s_0, t)}{\partial s_0}, \quad \hat{\lambda}(s_0, t) = |\hat{\mathbf{b}}(s_0, t)| = \frac{\partial \hat{s}(s_0, t)}{\partial s_0} \tag{1}$$

Here $\hat{s}(s_0, t)$ is the *physical* arclength of the segment s_0. It is obvious that at rest, when the chain is not stretched, $\hat{\lambda} = 1$. Note that the direction and length of the bond vector at a certain point coincides with the unit tangent to the contour and the local stretching at this point (see, Fig.2), respectively. Since that both the local stretching and the bond vector pertain to a single chain, and therefore can be treated as stochastic, they go with the hat sign.

Now, we have introduced all the basic concepts and variables on which the whole formalism will be built: the s_0 coordinate, the parametrization functions, the local stretching and the bond vector. Notice that this formalism is universal, and can be applied to both bulk and tethered polymer molecules. In the next sections we will show how it can be used to describe constraint release effects and calculate the tube survival probability introduced by Doi and Edwards for pure reptation [8] in the absence of flow.

Thermal constraint release

To demonstrate the advantages of the s_0-description, we first consider the case of no flow. Then, chains are not stretched ($\hat{\lambda} = 1$) and constraints can only be released via reptation of surrounding molecules, that is, thermal constraint release (CR). We begin with the simple model of an inextensible chain reptating in a fixed network (built out of fixed constraints). This model was studied in detail by Doi and Edwards in [8]. Their analysis was based on the so-called tube survival probability $G(s, t)$ which is the probability for a segment of the initial tube to 'survive' at time $t > 0$. Note that for inextensible chains $G(s, t)$ also gives the chance that segment s of the chain still stays in the initial tube, since the part of the chain that has left the tube at one side is as long as the part of the tube that did not survive at the other side. The parameter s is the *physical* arclength (the curvilinear

coordinate) of the tube segment. As was found, $G(s,t)$ obeys the following equation of motion and boundary conditions:

$$\begin{aligned} &\frac{\partial G(s,t)}{\partial t} = D_c \frac{\partial^2 G(s,t)}{\partial s^2} \\ &G(s,t=0) = 1, \quad G(\pm L/2, t>0) = 0 \end{aligned} \tag{2}$$

Here, L is the mean equilibrium length of the chain. This equation represents reptation as an one-dimensional Brownian-like motion of the chain inside its tube, and correspondingly has the form of a stochastic process (Fick's law) with the diffusion D_c taken from the Rouse model (see, for example, [8]).

As was mentioned in the previous section, in the absence of flow (or, equivalently, stretching) the s and s_0 coordinates coincide. Therefore, the results by Doi and Edwards can be easily rewritten in the s_0-representation by simply replacing s with s_0. For example, the solution of (2), that is to say, the explicit form of $G(s_0,t)$ is given by

$$G(s_0,t) = \sum_{n=1,3,5,}^{\infty} \frac{4}{\pi n} \sin\left(\frac{\pi n}{2}\right) \cos\left(\frac{\pi n s_0}{L_0}\right) exp\left(-\frac{n^2 t}{t_{rept}}\right), \quad t_{rept} = \frac{L_0^2}{\pi^2 D_c} \tag{3}$$

According to the boundary conditions (2), $G(s_0,t)$ turns to zero at both chain ends which means that the segments at the free ends leave the initial tube almost instantaneously. This arises from the fact they experience a very fast equilibration process with the time scale equal to the Rouse time of a single segment whereas the tube concept only describes a time-averaged behavior on a much larger time scale.

Given $G(s_0,t)$, it is possible to provide a quantitative description of the dynamics of a chain moving in a fixed network. As is seen from (3), as times passes chains leave their initial tubes (i.e. tubes at time $t=0$), and after about time t_{rept} the whole tube will be "abandoned". This implies that t_{rept} is the time needed for a chain to reptate a distance equal to its equilibrium length. Next, we assume that each segment can be assigned a certain characteristic life-time $\bar{\tau}(s_0)$ (in the initial tube) due to this reptative motion. The exact segment survival probability $G(s_0,t)$ (3) can be approximated by

$$G(s_0,t) \cong \exp\left(-t/\bar{\tau}(s_0)\right) \tag{4}$$

It is reasonable to expect that segments at the ends have smaller life-times than that close to the central point $s_0 = 0$. In order to satisfy the boundary conditions (2) we must set $\bar{\tau}(\pm L_0/2) = 0$. From (3), one can find the explicit form of $\bar{\tau}(s_0)$:

$$\bar{\tau}(s_0) = \int_0^{\infty} dt G(s_0,t) = t_{rept} \sum_{n=1,3,5,}^{\infty} \frac{4}{\pi n^3} \sin\left(\frac{\pi n}{2}\right) \cos\left(\frac{\pi n s_0}{L_0}\right) \tag{5}$$

We stress that $\bar{\tau}(s_0)$ has a simple physical meaning, namely it is the mean first passage time for the segment s_0. As follows from (5), $\bar{\tau}(s_0)$ is presented by a series of terms. Note

that the first term (with $n = 1$) on the RHS of (5) is dominant in the sum, and the higher modes (with $n > 1$) have only a minor effect on $\bar{\tau}(s_0)$. Note also that $\bar{\tau}(s_0)$ is an even function of s_0. This is the result of a symmetry inherent to the ensemble of bulk chains.

Until now, we have studied the simple model of a chain reptating in a *fixed* network. We were able to find the characteristic life-time of a segment due to this motion (see, Eq.(5)), and proposed a plausible approximation of the life-time of a segment (see, Eq.(4)). Let us show now how to calculate the finite life time of a *constraint* due to thermal constraint release in a network with possible loss of entanglements. First, we remind that in this network a chain is moving inside its tube which is in turn built out of other chains. Their movement results in sudden release of constraints on the test chain. After a constraint is released, the test chain may experience a random local jump over a distance of the order of the mean tube diameter. In the simplest model we may think that all the constraints have the same finite characteristic life-time, that is, the single life-time approximation.

In order to find this life-time, let us assume that having moved a distance equal to the mean entanglement spacing a_0 the test chain releases one (if entanglements are pair-wise contacts) or more constraints on other chains. Next, we point out a unit volume in the melt. Let N be the number of polymer molecules in this volume. Since every molecule has on average Z_0 segments, the total number of entanglements in the chosen volume is $Z_0N/2$ (for simplicity, we assume that all the entanglements are pair-wise contacts). Note that entanglement creation mechanism is not relevant for the chain dynamics, so that we can only focus on loss of entanglements. From (5) one can infer that the mean time needed for a chain to reptate the distance a_0 is $\bar{\tau}(L_0/2 - a_0)$. Since the number of entanglements at time $t = 0$ is $N_{ent}(0) = Z_0N/2$, the number of entanglements at time $t = \bar{\tau}(L_0/2 - a_0)$ is given by

$$N_{ent}(t = \bar{\tau}(L_0/2 - a_0)) = \frac{Z_0N}{2} - N$$

Let τ_{CR} be the mean life-time of an entanglement due to CR. Then, we have

$$\frac{N_{ent}(t = \bar{\tau}(L_0/2 - a_0)) - N_{ent}(t = 0)}{N_{ent}(t = 0)} = -\frac{\bar{\tau}(L_0/2 - a_0)}{\tau_{CR}} = -\frac{2}{Z_0} \tag{6}$$

From (6), one finds that

$$\tau_{CR} = \frac{Z_0}{2}\bar{\tau}(L_0/2 - a_0) \tag{7}$$

Taking into account (5) and (7), we eventually find the explicit expression for τ_{CR}

$$\tau_{CR} = \frac{Z_0}{2}t_{rept}\sum_{n=1,3,5,}^{\infty}\frac{4}{\pi n^3}\sin\left(\frac{\pi n a_0}{L_0}\right) \tag{8}$$

As in the case of $\bar{\tau}(s_0)$, τ_{CR} is presented as a sum with the first term ($n = 1$) being dominant. Neglecting higher mode terms with $n > 1$, one can approximate τ_{CR} as follows

$$\tau_{CR} \approx 2t_{rept} \tag{9}$$

We see that the characteristic life-time of a constraint τ_{CR} is approximately twice the reptation time. One should realize, however, that the explicit form of $\bar{\tau}_{CR}$ (8) was obtained using the results of the fixed network model. In other words, a perturbation theory was used when deriving (8). This implies that equations (8) and (9) are valid only if the rate at which constraints are removed is much smaller then the inverse reptation time. In order to check whether this condition is satisfied, let us first write down the characteristic relaxation time due to CR. According to the Verdier-Stockmayer model (see, for example, [8]), it is given by

$$t_{CR} = Z_0^2 \tau_{CR} = Z_0^2 t_{rept} \tag{10}$$

For long molecules t_{CR} is much larger then the reptation time, and the perturbation theory is applicable.

So we have calculated the characteristic life-time of an entanglement due to CR presuming that movement of a single molecule over a distance equal to a_0 will release one entanglement. In this formalism every entanglement is assigned the same characteristic relaxation time. In reality, however, all entanglements will be built out of different parts of chains and have different life-times. For example, constraints built out of chain parts close to the free end $s_0 \approx \pm L_0/2$ will relax faster then those from parts close to the chain center $s_0 = 0$.

Rubinstein and Colby [7] developed a rigorous self-consistent model for CR capable to take into account the above mentioned distribution over entanglement life-times. Their formalism involves the *constraint* mobility distribution function $\Psi(\varepsilon)$ which is the fraction of constraints with mobility ε per single chain. The constraint mobility is defined as its inverse life time. They did not derive any equation for it assuming that this function can be extracted from pure computer simulations of a Rouse-like motion of the tube. Inspired by the idea of such a distribution function we will try now to develop a theoretical model that can naturally take into account different life-times (equivalently, mobilities) of the segments.

In order to find the explicit expression for $\Psi(\varepsilon)$, we again consider the case of a chain reptating in a fixed network. Let us introduce the segment mobility distribution function $P(\varepsilon)$ which is the fraction of segments per single chain with mobility equal to ε. It is important to realize that the introduced functions $\Psi(\varepsilon)$ and $P(\varepsilon)$ have different physical meaning. Namely, $\Psi(\varepsilon)$ is related to the Brownian-like motion of the tube due to CR, whereas $P(\varepsilon)$ to the motion of a chain inside its tube due to reptation. Both functions do not depend on time and consequently should depend on equilibrium variables only. Besides that, they are normalized as follows:

$$\int_0^\infty d\varepsilon \Psi(\varepsilon) = 1, \quad \int_0^\infty d\varepsilon P(\varepsilon) = 1 \tag{11}$$

In order to illustrate the model, we will consider the simple discrete representation of a chain with Z_0 being the mean number of segments per chain. Note that every segment has a certain characteristic life-time (mobility) defined in (5). As was found, it depends on the segment position along the chain contour and is an even function of s_0.

From the above arguments one can find that the total number of possible mobilities per chain is given by $K = Z_0/2$. Since every segment of the chain has its own mobility, in the discrete representation the segment mobility distribution function $P(\varepsilon)$ is given by

$$P(\varepsilon_k) = \frac{1}{K} \tag{12}$$

We remark that $P(\varepsilon_k)$ in (12) is normalized in accordance with (11). In what follows, for certainty we set

$$\varepsilon_1 < \varepsilon_2 < \varepsilon_3 < \ldots < \varepsilon_K$$

which means that the mobilities ε_1 and ε_K are associated with segment $s_0 = 0$ and $s_0 = \pm L_0/2$, respectively.

We again consider an unit volume that contains N polymer molecules. For simplicity, we assume that all the entanglements in this volume are pair-wise contacts. Then, it is very convenient to think that every chain "carries half-entanglements" (see, Fig.3). Each half-

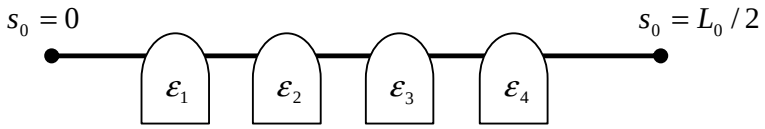

Figure 3: Half-entanglements.

entanglement has its own mobility. Since the number of half-entanglements with mobility ε_i per chain is $Z_0 P(\varepsilon_i)$, the total number of half-entanglements with mobility ε_i in this unit volume is $NZ_0P(\varepsilon_i)$. On interacting, two different half-entanglements will form a full entanglement. Note that the half-entanglements constituting one entanglement may have different mobilities (life-times). The mobility of an *entanglement* is equal to the *minimum* of the corresponding half entanglements.

Next, we introduce the volume fractions of different sorts of entanglements $W(\varepsilon_i, \varepsilon_j)$ where ε_i and ε_j is the mobility of the first and the second half-entanglement, respectively. They can be presented as

$$\begin{aligned} W(\varepsilon_i, \varepsilon_j) &= W(\varepsilon_i)W(\varepsilon_j) \quad i = j \\ W(\varepsilon_i, \varepsilon_j) &= 2W(\varepsilon_i)W(\varepsilon_j) \quad i \neq j \end{aligned} \tag{13}$$

Here, $W(\varepsilon_i)$ is the volume fraction of segments with mobility ε_i. The factor 2 in the expression for $W(\varepsilon_i, \varepsilon_j)$ stems from the fact that $W(\varepsilon_i, \varepsilon_j) = W(\varepsilon_j, \varepsilon_i)$. By definition, $W(\varepsilon_i)$ is given by

$$W(\varepsilon_i) = \frac{NZ_0P(\varepsilon_i)}{NZ_0} = P(\varepsilon_i) \tag{14}$$

So it is clear that the volume fraction of half-entanglements coincides with the segment mobility distribution function $P(\varepsilon_i)$ related to a single chain. As was mentioned already, the mobility of an entanglement is equal to the minimum of the corresponding constitutive

half-entanglements. Therefore, the fraction of constraints with the mobility ε_k in the chosen volume $\Psi(\varepsilon_k)$ can be written out as (we remind that $\varepsilon_k < \varepsilon_{k+1} < \dots$)

$$\Psi(\varepsilon_k) = \sum_{i=k}^{K} W(\varepsilon_k, \varepsilon_i) \tag{15}$$

From (13) and (14), it follows that

$$\Psi(\varepsilon_k) = P(\varepsilon_k)P(\varepsilon_k) + 2\sum_{i=k+1}^{K} P(\varepsilon_i)P(\varepsilon_k) \tag{16}$$

Note that this $\Psi(\varepsilon_k)$ is normalized, so that (compare, Eq.(11)):

$$\sum_{k=1}^{K} \Psi(\varepsilon_k) = 1 \tag{17}$$

From (12) and (16), one can find the explicit expression for $\Psi(\varepsilon_k)$

$$\Psi(\varepsilon_k) = \frac{2}{K^2}\left(K - k + \frac{1}{2}\right) \tag{18}$$

By now we have been able to find the volume fraction of entanglements with the mobility ε_k given the mobility distribution per chain. One should realize that $\Psi(\varepsilon_k)$ is also the distribution over constraint mobilities imposed on a single chain. Namely, the number of ε_k-constraints per chain is equal to $Z_0\Psi(\varepsilon_k)$. We emphasize that in the absence of flow the entanglements can be lost due to reptation only, so that $\Psi(\varepsilon_k)$ describes distribution over mobilities due to thermal CR.

We find it convenient to write down the explicit form for $\Psi(\varepsilon_k)$ in the continuous representation. Multiplying both sides of eqn (18) by $[d\varepsilon_k/dk]^{-1}$ and noticing that $\varepsilon = 1/\bar{\tau}$, from (5) and (18), we have

$$\Psi(\varepsilon) \approx \frac{4}{\pi}\left[1 - \frac{2}{\pi}\arccos\left(\varepsilon_{min}/\varepsilon\right)\right]\frac{\varepsilon_{min}/\varepsilon^2}{\sqrt{1-\left(\varepsilon_{min}/\varepsilon\right)^2}}, \quad \varepsilon_{min} = \frac{\pi}{4t_{rept}} \tag{19}$$

Here, ε_{min} is the minimal possible segment mobility (equivalently, the maximal possible life-time) corresponding to the center of the chain. The characteristic behavior of $\Psi(\varepsilon)$ defined in (19) is depicted in Fig.4. As is seen, it is a monotonous function with the maximum at $\varepsilon = \varepsilon_{min}$. This means that the concentration of entanglements with a very large mobility is much smaller than that with a small mobility. We remind that constraints with small mobilities consist out of chain parts far from the free ends and visa versa.

Given the distribution $\Psi(\varepsilon)$ (19), it is possible to find the mean constraint mobility:

$$\bar{\varepsilon} = \int_{\varepsilon_{min}}^{\infty} d\varepsilon\, \varepsilon\Psi(\varepsilon) \tag{20}$$

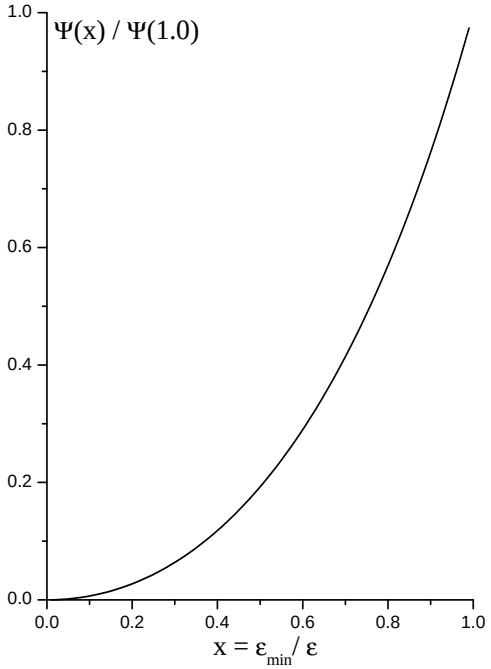

Figure 4: The constraint mobility distribution function.

From (19) and (20), one can find the estimate of $\bar{\varepsilon}$

$$\bar{\varepsilon} \approx \frac{4}{3}\varepsilon_{min} \ln Z_0^3 \approx t_{rept}^{-1} \ln Z_0^3 \tag{21}$$

In the derivation of (21) use was made of the fact that in reality segments at the free ends have a finite life time of the order of the Rouse time of a single segment, so that it is possible to introduce the maximum possible mobility of an entanglement. Note that we have already calculated the mean mobility under the single-life time approximation (see, (9)). By comparing (9) and (21) we see that taking into account the constraint mobility distribution results in an increase in the mean constraint mobility, and correspondingly in a decrease in the mean life-time, as expected.

Before we move to the next section, we find it useful to derive the continuous form of the segment mobility distribution function $P(\varepsilon)$. First, let us write down an explicit equation for the total length of the initial tube that is still present at time t. Using (4), we have

$$L_S(t) = \int_{-L_0/2}^{L_0/2} ds_0 \, e^{-t/\bar{\tau}(s_0)} \tag{22}$$

where $\bar{\tau}(s_0)$ is the life-time of the segment s_0. Note that $L_S(t)$ can also be rewritten in

terms of the segment mobility distribution function

$$L(t) = L_0 \int\limits_{\varepsilon_{min}}^{\infty} d\varepsilon P(\varepsilon) e^{-\varepsilon t} \tag{23}$$

Since $\bar{\tau}(s_0)$ is an even function of s_0, (22) can be rewritten in the form similar to (23)

$$L(t) = 2 \int\limits_{1/\tau(0)}^{\infty} d\varepsilon \left\{ \frac{ds_0(\varepsilon)}{d\varepsilon} \right\} e^{-\varepsilon t} \tag{24}$$

By definition $\varepsilon_{min} = 1/\bar{\tau}(0)$ and therefore from (23) and (24) we end up with

$$P(\varepsilon) = \frac{2}{L_0} \left\{ \frac{ds_0(\varepsilon)}{d\varepsilon} \right\} \tag{25}$$

Note that this function satisfies (11). If we put $\tau = 1/\varepsilon$ and neglect higher modes with $n = 3, 5 \ldots$ in (5), the following explicit expression for $P(\varepsilon)$ comes out

$$P(\varepsilon) \approx \frac{2}{\pi} \frac{\varepsilon_{min}/\varepsilon^2}{\sqrt{1 - (\varepsilon_{min}/\varepsilon)^2}} \tag{26}$$

This equation gives the segment mobility distribution function $P(\varepsilon)$ in the continuous representation. Its discrete form was presented earlier in (12). Note that the 'continuous limit' is only allowed for fairly long chains.

The tube segment survival probability

In the previous section we considered the simple model of no flow. In this regime polymer molecules are not stretched and consequently it is possible to use the results by Doi and Edwards obtained for the case of inextensible molecules. In particular, due to the fact that for inextensible chains the physical s and s_0 coordinates are equivalent, the explicit form of the tube survival probability in the s_0-description was simply obtained by replacing s with s_0. In the presence of flow the physical coordinates become undefined because of stretching and one should only deal with the s_0 ones.

In the absence of flow constraints can only be released by reptation of surrounding chains. As was shown, given the *segment* survival probability function $G(s_0, t)$ it is possible to calculate the constraint mobility distribution function $\Psi(\varepsilon)$ and then find the mean characteristic life-time of a constraint due to CR. The flow may also affect the rate at which constraints are removed via an additional relaxation mechanism, that is, the convective constraint release mechanism. Later we will show that as in the case of CR, the formalism for CCR can also be built in terms of the segment survival probability calculated self-consistently in the presence of flow. The objective of this section is to derive a more

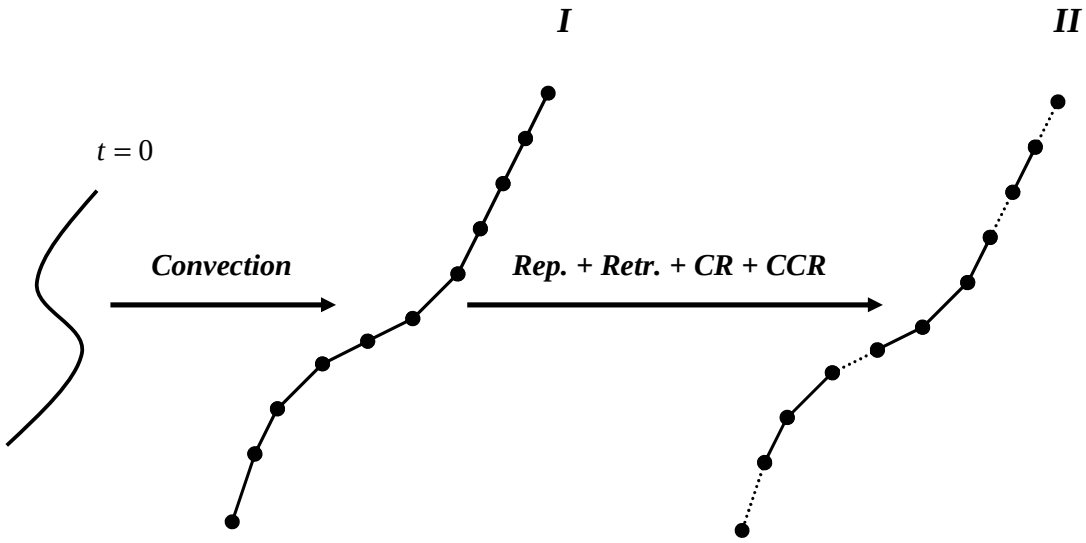

Figure 5: The time evolution of the test chain. The thin dotted lines show missing segments.

general equation of motion for $G(s_0, t)$ valid for wide range of flow rates. It is important to remark that CCR may have the same time scale as reptation, so that our analysis cannot be based on a perturbation theory as in the case of thermal constraint release.

In order to calculate $G(s_0, t)$ in the presence of flow, we point out a single molecule in the melt which will be regarded as the test chain. Let us follow its time evolution in space. To this end, we will consider the time interval between $t = 0$ and t (see, Fig.5). It is important to realize that during this time interval the motion of the chain is affected by the following mechanisms: convection, reptation, retraction, and constraint release. All these processes happen simultaneously. But without loss of generality, it is possible to consider their effects separately. Namely, we split the "transform" from the initial chain at time $t = 0$ to the final chain at time t into two stages. In the first stage, the initial chain is deformed by the flow in the absence of reptation, retraction and constraint release. We will call this chain *intermediate*. In the second stage, the intermediate chain is deformed by retraction, reptation and constraint release in the absence of convection. These effects result in loss of a certain number of segments of the intermediate chain (see, the dotted lines on the final chain in Fig.5). Note that the parts that are close to the free ends are lost due to reptation, retraction and probably due to constraint release, whilst those in the middle due to constraint release only.

In order to describe this loss of segments quantitatively, we introduce two unit vectors. The first one is the unit vector of the intermediate chain $\hat{\mathbf{u}}_I(s_0, t)$. By definition, at time t it is given by

$$\hat{\mathbf{u}}^I(s_0, t) = \frac{\bar{\bar{\mathbf{E}}}(t, 0)\hat{\mathbf{b}}(s_0, 0)}{\left|\bar{\bar{\mathbf{E}}}(t, 0)\hat{\mathbf{b}}(s_0, 0)\right|} \tag{27}$$

Here, $\hat{\mathbf{b}}(s_0, t)$ is the bond vector and $\bar{\bar{\mathbf{E}}}(t, 0)$ the deformation tensor which describes con-

vective motion of the chain produced by the flow over the time interval from $t = 0$ to t. The unit vector of the final chain (i.e. the test chain at time t) is

$$\hat{\mathbf{u}}(s_0, t) = \frac{\hat{\mathbf{b}}(s_0, t)}{\left|\hat{\mathbf{b}}(s_0, t)\right|} \tag{28}$$

We stress that the time evolution of $\hat{\mathbf{u}}$ is determined by retraction, reptation, convection and constraint release in contrast to $\hat{\mathbf{u}}^I$ determined by convection only. Since $\bar{\bar{\mathbf{E}}}(t, 0)$ at time $t = 0$ is simply the unit tensor, $\hat{\mathbf{u}}^I(s_0, t = 0)$ and $\hat{\mathbf{u}}(s_0, t = 0)$ coincide for every s_0.

Now, consider the segment s_0' on the initial chain. Let us follow its time evolution along the contour. First, we consider the transformation from the initial chain to the intermediate chain. In [9] it was found that in the case of pure convection given the coordinate and the position vector of a segment, it is possible to predict its spatial position at any later time. This does not hold for the second stage, that is, the transformation from the intermediate chain to the final chain since reptation, retraction and constraint release are involved. As was showed in [9], all these processes lead to the motion of the chosen segment along the primitive path. As a result, the only one segment s_0 of the final chain that is correlated with the segment s_0' of the initial chain is given by

$$s_0 = s_0' + \widehat{\square} s_0(s_0', t) \tag{29}$$

Here, $\widehat{\square} s_0(s_0', t)$ is the distance in the s_0 space "passed" by the segment s_0' over the time interval from $t = 0$ to t due to retraction and reptation. We stress that $\hat{\Delta} s_0(s_0', t)$ is chain-dependent and hence should be treated as a stochastic variable. Therefore, for the segments s_0' and s_0 that satisfy (29) the following equality should hold

$$\left\langle \hat{\mathbf{u}}^I(s_0', t) \cdot \hat{\mathbf{u}}(s_0, t) \right\rangle = 1 \tag{30}$$

Here, the averaging is taken over the whole ensemble of chains. In (30) we did not take into account the probability for a chain segment to leave the initial tube between $t = 0$ and t. If so, the direction of $\hat{\mathbf{u}}(s_0, t)$ is completely uncorrelated with that of $\hat{\mathbf{u}}^I(s_0', t)$ even if the condition (29) is satisfied, and consequently

$$\left\langle \hat{\mathbf{u}}^I(s_0', t) \cdot \hat{\mathbf{u}}(s_0, t) \right\rangle = 0 \tag{31}$$

Therefore, (30) and (31) can be used as criteria for a chain segment to stay in the initial tube. In particular, the explicit expression for $G(s_0, t)$ which is the probability for the segment s_0 to stay in the initial tube at time t is given by (in discrete representation)

$$G(s_0, t) = \sum_{s_0'} \left\langle \hat{\mathbf{u}}^I(s_0', t) \cdot \hat{\mathbf{u}}(s_0, t) \right\rangle \tag{32}$$

Here, an important comment must be made regarding the initial tube. In the previous section devoted to the no flow case we defined the initial tube as the tube that contains

the test chain at time $t = 0$. That tube is fixed in space and time. In the case of flow, we define the initial tube as the tube that would contain the test chain in the absence of retraction, reptation, and constraint release (see, Fig.5). It is not fixed in time and space. Instead, its evolution is determined by the deformation tensor $\bar{\bar{\mathbf{E}}}(t,0)$. Note that $\hat{\mathbf{u}}^I(s_0',t)$ are in fact the unit tangent vectors of the deforming initial chain.

So we have found that the segment survival probability function $G(s_0,t)$ is defined as the correlator built out of the unit vectors of the final and the intermediate chain. Given their time evolution, it is possible to derive the equation of motion for $G(s_0,t)$. But hereafter, we will use a more convenient approximation of the exact expression (32) written in terms of the bond vectors. In order to rewrite (32) using the bond vectors, let us introduce $\bar{L}_S(t)$ which is the total length of the chain segments that are still present in the initial tube at time t. From the same physical arguments that were used to derive (32), one can find that

$$\bar{L}_S(t) = \frac{1}{a_0} \int\limits_{-L_0/2}^{L_0/2} ds_0' \int\limits_{-L_0/2}^{L_0/2} ds_0 \left\langle \hat{\mathbf{u}}^I(s_0',t) \cdot \hat{\mathbf{b}}(s_0,t) \right\rangle \tag{33}$$

Next, one should recognize that the probability for the segment s_0 to stay in the initial tube at time t does not depend on its stretching. But, due to retraction, it may depend on the local stretching of the chain segments that are closer to the origin $s_0 = 0$ i.e. $s_0' < s_0$.

Therefore, the probability for a chain segment to stay in the initial tube at time t and to have the local stretching equal to λ is given by

$$f(\lambda, s_0, t)\, G(s_0,t) \tag{34}$$

where $f(\lambda, s_0, t)$ is the local stretching probability distribution function introduced in [10]. Using (34), one can easily find another expression for $\bar{L}_S(t)$

$$\bar{L}_S(t) = \int\limits_0^\infty d\lambda \int\limits_{-L_0/2}^{L_0/2} ds_0 \lambda\, f(\lambda, s_0, t)\, G(s_0,t) \tag{35}$$

Comparison of (33) and (35) yields

$$\bar{\lambda}(s_0,t) G(s_0,t) = \frac{1}{a_0} \int\limits_{-L_0/2}^{L_0/2} ds_0' \left\langle \hat{\mathbf{u}}^I(s_0',t) \cdot \hat{\mathbf{b}}(s_0,t) \right\rangle \tag{36}$$

Here, $\bar{\lambda}(s_0,t)$ is the ensemble-averaged local stretching of segment s_0 defined as

$$\bar{\lambda} = \int\limits_0^\infty d\lambda\, f(\lambda, s_0, t) \tag{37}$$

Note that the averaging in (37) is taken over all s_0 segments, not only over those that are still in the initial tube. Note also that (36) gives in fact another representation of $G(s_0,t)$.

Later on it will be used to derive the equation of motion for $G(s_0,t)$. Besides that, use will be made of the following equality which stems from (32) and (36)

$$\bar{\lambda}(s_0,t)\left\langle \hat{\mathbf{u}}^I(s_0',t)\cdot\hat{\mathbf{u}}(s_0,t)\right\rangle = \left\langle \hat{\mathbf{u}}^I(s_0',t)\cdot\hat{\mathbf{b}}(s_0,t)\right\rangle \tag{38}$$

Equation of motion for $G(s_0,t)$.

The goal of this section is to derive the time evolution equation for the segment survival probability. We start by introducing the auxiliary correlator $\phi_{\alpha\beta}(s_0,t|s_0')$:

$$\phi_{\alpha\beta}(s_0,t|s_0') = \left\langle \hat{u}^I_\alpha(s_0',t)\hat{b}_\beta(s_0,t)\right\rangle \tag{39}$$

where the averaging is taken over the whole ensemble of chains. Given $\phi_{\alpha\beta}(s_0,t|s_0')$, one can easily find $G(s_0,t)$ as follows

$$G(s_0,t) = \frac{1}{a_0\bar{\lambda}(s_0,t)}\int\limits_{-L_0/2}^{L_0/2} ds_0'\ \phi_{\alpha\alpha}(s_0,t|s_0') \tag{40}$$

Here, use was made of (36), (38), and (39). Notice that in (40) summation is assumed over repeating indexes. In order to figure out how $\phi_{\alpha\beta}(s_0,t|s_0')$ changes in time, we will study its evolution over the small time interval between t and $t+\Delta t$. According to (27), at time $t+\Delta t$ for $\hat{u}^I_\alpha(s_0',t)$ we have

$$\begin{aligned}\hat{u}^I_\alpha(s_0',t+\Delta t) = \hat{u}^I_\alpha(s_0',t) &+ \Delta t\, K_{\alpha m}(t)\hat{u}^I_m(s_0',t)\\ &- \hat{u}^I_\alpha(s_0',t)\left\{K_{ij}(t)\hat{u}^I_i(s_0',t)\hat{u}^I_j(s_0',t)\right\}\Delta t\end{aligned} \tag{41}$$

where we used the fact that the deformation tensor $\bar{\bar{\mathbf{E}}}(t+\Delta t,t)$ for small Δt can be expanded into the Fourier series with respect to Δt. Then, discarding second order terms

$$\bar{\bar{\mathbf{E}}}(t+\Delta t,t) \approx \bar{\bar{I}} + \bar{\bar{K}}\Delta t$$

Here, $\bar{\bar{I}}$ and $\bar{\bar{K}}$ are the unit and the gradient velocity tensor, respectively. From (39) and (41) one can find that at time $t+\Delta t$ the correlator $\phi_{\alpha\beta}(s_0,t|s_0')$ is given by

$$\begin{aligned}\phi_{\alpha\beta}(s_0,t+\Delta t|s_0') = &\left\langle \hat{u}^I_\alpha(s_0',t+\Delta t)\hat{b}_\beta(s_0,t+\Delta t)\right\rangle =\\ &\left\langle \hat{u}^I_\alpha(s_0',t)\hat{b}_\beta(s_0,t+\Delta t)\right\rangle + \Delta t\, K_{\alpha m}(t)\left\langle \hat{u}^I_m(s_0',t)\hat{b}_\beta(s_0,t)\right\rangle -\\ &-\Delta t\, K_{ij}(t)\left\langle \hat{u}^I_i(s_0',t)\hat{u}^I_j(s_0',t)\hat{u}^I_\alpha(s_0',t)\hat{b}_\beta(s_0,t)\right\rangle\end{aligned} \tag{42}$$

The second term on the RHS simply gives $\phi_{\alpha\beta}$ at time t. Based on symmetry arguments and relation (38), the last term in (42) can be rewritten as

$$\begin{aligned}&\sum_{s_0'}\left\langle \hat{u}^I_i(s_0',t)\hat{u}^I_j(s_0',t)\hat{u}^I_\alpha(s_0',t)\hat{b}_\beta(s_0,t)\right\rangle =\\ &= G(s_0,t)\,\bar{\lambda}(s_0,t)\ \langle \hat{u}_i(s_0,t)\hat{u}_j(s_0,t)\hat{u}_\alpha(s_0,t)\hat{u}_\beta(s_0,t)\rangle_S =\\ &= \delta_{ij}\delta_{\alpha\beta}A(i,\alpha,s_0,t) + \delta_{i\alpha}\delta_{j\beta}A(i,j,s_0,t) + \delta_{i\beta}\delta_{j\alpha}A(i,\alpha,s_0,t)\end{aligned} \tag{43}$$

Here $\langle \ldots \rangle_S$ stands for the averaging over the chains that still have the segment s_0 in the initial tube at time t. It is possible to show that the coefficients $A(i,j,s_0,t)$ satisfy a certain system of linear equations. For example, the first three equations of this system are given by $(i = 0, 1, 2)$:

$$\sum_{s_0'} \left\langle \hat{u}_i^I(s_0',t)\hat{b}_i(s_0,t) \right\rangle = A(i,0,s_0,t) + A(i,1,s_0,t) + A(i,2,s_0,t) + 2A(i,i,s_0,t) \qquad (44)$$

Comparing (39) and (44) we come to the conclusion that the coefficients $A(i,j,s_0,t)$ are in fact functions of the corresponding correlators $\phi_{\alpha\alpha}$ $(\alpha = 0,1,2)$. Further, we find it important to emphasize that the total trace of the last two terms on the RHS of (42) is equal to zero, so that they do not contribute to the equation for $G(s_0,t)$ directly. This does not mean that the flow cannot change the life time of a chain segment. As we will see later, it may well affect the dynamics of the bond vectors, so that the first term in (42) should depend on the flow parameters.

Now we focus on the first term on the RHS of (42). As was mentioned earlier, it is determined by the dynamics of the bond vector only. We have already derived the equation of motion for $\hat{b}_\beta(s_0,t)$ when studying the bond vector probability distribution function of bulk molecules (see, for example, [11])

$$\hat{b}_\beta(s_0,t+\Delta t) = \hat{b}_\beta\big(s_0 + \Delta\hat{s}_0, t\big) + \left(\frac{\partial \Delta\hat{s}_0}{\partial s_0}\right)\hat{b}_\beta(s_0,t) + \Delta t K_{\beta m}(t)\hat{b}_m(s_0,t) \qquad (45)$$

where $\Delta\hat{s}_0$ is the displacement of the segment s_0 due to reptation and retraction over the time interval from t to $t+\Delta t$

$$\Delta\hat{s}_0(s_0,t) = -\frac{1}{\hat{\lambda}(s_0,t)}\int\limits_0^{s_0} dx \frac{\hat{\lambda}(x,t)-1}{T_{eff}}\Delta t + \frac{\Delta\hat{\xi}(s_0,t)}{\hat{\lambda}(s_0,t)} \qquad (46)$$

The first term on the RHS describes displacement of segment s_0 due to retraction over the small time interval Δt, and consequently vanishes in the absence of flow. T_{eff} stands for the effective relaxation time of the local stretching. The second term arises from reptation and is present even in the absence of flow. It is described by the zero-mean gaussian random noise $\Delta\hat{\xi}(s_0,t)$ which is in fact the *physical* shift of the segment s_0 due to reptation.

After substitution of (45) into (42) we arrive at the following time evolution equation for $\phi_{\alpha\beta}(s_0,t|s_0')$ obtained in the absence of constraint release

$$\begin{aligned}\phi_{\alpha\beta}(t+\Delta t) = \phi_{\alpha\beta}(t) &+ \Delta t\, K_{\alpha m}(t)\phi_{m\beta}(t) + \Delta t\, K_{\beta m}(t)\phi_{\alpha m}(t) + \\ &+ \frac{\partial}{\partial s_0}\left[\langle \Delta\hat{s}_0(s_0,t)\rangle\, \phi_{\alpha\beta}(t)\right] + \frac{1}{2}\left\langle \Delta\hat{s}_0^2(s_0,t)\right\rangle \frac{\partial^2\phi_{\alpha\beta}(t)}{\partial s_0^2} - \\ &- -\Delta t\, K_{ij}(t)\left\langle \hat{u}_i^I(s_0',t)\hat{u}_j^I(s_0',t)\hat{u}_\alpha^I(s_0',t)\hat{b}_\beta(s_0,t)\right\rangle\end{aligned} \qquad (47)$$

Notice that in the derivation of (47) use was made of relation (38). Besides that, we assumed that the noise $\Delta\hat{\xi}(s_0,t)$ can be thought of as being uncorrelated with the corresponding bond vector at the same point, so that they can be averaged separately. This

implies that reptation does not contribute to the fourth term on the RHS of (47). In contrast, it is only reptation that contributes to the last term. This originates from the fact that the retraction part in Δs_0 is proportional to Δt (see, Eq.(46)) whereas the reptation goes with $\sqrt{\Delta t}$ because of the gaussian nature of $\Delta\hat{\xi}(s_0,t)$.

Taking into account the above comments we may now write out the explicit form for the fourth and the last term on the RHS of (47). From (38) and (46) one can find that

$$\langle \Delta\hat{s}_0(s_0,t)\rangle\, \phi_{\alpha\beta}(t) = -\frac{1}{\bar{\lambda}(s_0,t)}\int\limits_0^{s_0} dx \left[\frac{\bar{\lambda}-1}{T_{eff}}\right]\Delta t\ \phi_{\alpha\beta}(t) \tag{48}$$

Here, for compactness we have denoted the averaging over the ensemble by the bar sign. We remind that T_{eff} in (46) is the effective relaxation time of the local stretching due to retraction and constraint release. Further, let us consider the last term on the RHS of (47). Since reptation can be represented as an one-dimensional Rouse-like motion we have

$$\langle \Delta\hat{\xi}^2\rangle = 2D_c\Delta t$$

where D_c is the diffusion coefficient of the free Rouse motion, and therefore

$$\frac{1}{2}\left\langle \Delta\hat{s}_0^2(s_0,t)\right\rangle \frac{\partial^2\phi_{\alpha\beta}(t)}{\partial s_0^2} \approx D_c\frac{\partial^2\phi_{\alpha\beta}(t)}{\partial s_0^2}\Delta t \tag{49}$$

In this term the local stretching has been neglected since reptation is only relevant for slow flows when molecules are hardly stretched.

By now we have derived the equation of motion for the correlator $\phi_{\alpha\beta}(s_0,t|s_0')$ (47) in the absence of constraint release. In order to incorporate possible loss of entanglements, we, following the proposal by Milner, McLeish and Likhtman [13], will represent motion of the *tube* itself due to CR as a free Rouse-like motion. The reason for this is that constraint removal causes the tube to make local random jumps with a certain frequency. This resembles a Brownian motion of a polymer molecule in a solvent. Let ν be the characteristic frequency of constraint release events, then

$$\hat{\mathbf{b}}(s_0,t+\Delta t) = \hat{\mathbf{b}}(s_0,t) + \Delta t\left(\frac{3\nu a_0^2}{2}\frac{\partial^2\hat{\mathbf{b}}(s_0,t)}{\partial s_0^2} + \mathbf{g}(s_0,t)\right) \tag{50}$$

Here $\mathbf{g}(s_0,t)$ is a zero-mean random noise. Note that all constraints imposed on a chain are, in general, built out of different chain parts and accordingly have different life-times. But at the same time we stress that these constraints are distributed arbitrarily along the chain contour, so that on average ν does not depend on s_0.

Finally, from (47), (48), (49) and (50) one can find the full equation of motion for the

correlator $\phi_{\alpha\beta}(s_0,t|s_0')$

$$\begin{aligned}\frac{\partial\phi_{\alpha\beta}}{\partial t} &= K_{\alpha m}(t)\phi_{m\beta}+K_{\beta m}(t)\phi_{\alpha m}- \\ &- \frac{\partial}{\partial s_0}\left[\frac{\phi_{\alpha\beta}}{\bar{\lambda}(s_0,t)}\int\limits_0^{s_0}dx\left\{\frac{\bar{\lambda}-1}{T_{eff}}\right\}\right]+ \\ &+ D_c\frac{\partial^2\phi_{\alpha\beta}}{\partial s_0^2}+\frac{3\nu a_0^2}{2}\frac{\partial^2\phi_{\alpha\beta}}{\partial s_0^2}- \\ &- K_{ij}(t)\left\langle\hat{u}_i^I(s_0',t)\hat{u}_j^I(s_0',t)\hat{u}_\alpha^I(s_0',t)\hat{b}_\beta(s_0,t)\right\rangle\end{aligned} \tag{51}$$

When deriving (51) use was made of the fact that the random noise $\mathbf{g}(s_0,t)$ is not correlated with the unit vector of the intermediate chain, and consequently does not contribute to the equation of motion for $\phi_{\alpha\beta}(s_0,t|s_0')$. We emphasize that (51) now includes all the major mechanisms pertaining to bulk chains such as reptation, retraction, convection and constraint release. Note that all the components of the correlator $\phi_{\alpha\beta}(s_0,t|s_0')$ are coupled via the gradient velocity tensor, so that one should solve the whole system of equations. The corollary is that in general there is no closed equation for the segment survival probability $G(s_0,t)$. In other words, to find $G(s_0,t)$ one should first solve the whole system (51) and then compute $G(s_0,t)$ with the help of (40). But as will be shown hereafter, under assumption of small stretching it is possible to derive the close equation of motion for $G(s_0,t)$.

Some comments should be made on (51). In [11] we derived the equation of motion for the mean local stretching $\bar{\lambda}$. It is determined by the flow parameters and the bond vector probability distribution function $f(\mathbf{b},s_0,t)$. This means that the corresponding equations of motion for $\bar{\lambda}$, $\phi_{\alpha\beta}$ and f are coupled and hence should be solved simultaneously. Next, we emphasize that the contributions due to reptation and constraint release have the form of a diffusion process (Fick's law). The reptation diffusion coefficient is given by that of the free Rouse motion. The diffusion coefficient of the constraint release term contains in fact two contributions, namely due to thermal and convective constraint release:

$$\nu = \nu_{CR} + \nu_{CCR}$$

In the previous section we calculated the mean constraint mobility due to CR, that is, ν_{CR} (see, Eq.(21)). This analysis was based on the segment survival probability function taken from the theory of Doi and Edwrads. We will show later that even in a more general case with considerable or fast flow ν can also be expressed via $G(s_0,t)$. This implies that the equation of motion for $\phi_{\alpha\beta}(s_0,t|s_0')$ (51) is a *non-linear* partial-differential equation.

In order to solve (51) one should also specify the initial and boundary conditions for $\phi_{\alpha\beta}(s_0,t|s_0')$. The initial condition follows from the fact that at time $t=0$ the correlation function $\phi_{\alpha\beta}(s_0,t|s_0')$ is non-zero only if $s_0'=s_0$, and so

$$\phi_{\alpha\beta}(s_0,0|s_0') = \left\langle\hat{u}_\alpha(s_0,0)\hat{b}_\beta(s_0,0)\right\rangle\delta(s_0-s_0') \tag{52}$$

Here, the correlator in brackets can be calculated with the help of the bond vector probability distribution function (see, for example, [9, 10]). In the absence of flow, (52) boils down to

$$\phi_{\alpha\beta}(s_0, 0|s_0') = \frac{1}{3}\delta_{\alpha\beta}\,\delta(s_0 - s_0') \tag{53}$$

Next, as was mentioned earlier, due to very fast equilibration processes active at the free ends of a chain, the corresponding segments leave the initial tube almost instantaneously, and so

$$\phi_{\alpha\beta}(s_0 = \pm L_0/2, t|s_0') = 0 \tag{54}$$

Note that these boundary conditions lead to that proposed by Doi and Edwards for $G(s_0, t)$ by integrating over s_0' in accordance with (40).

The slow flow regime

In the previous section we derived the equation of motion for the correlator $\phi_{\alpha\beta}$ valid for a wide range of flow rates. We found that the obtained system of equations for $\phi_{\alpha\beta}$ could not be reduced to a single equation for the segment survival probability function. Here we will study the simpler example of slow flow when a simplification of the theory is expected. In this regime the polymer molecules are only little stretched.

Let us show how under assumption of small stretching it is possible to derive the close equation for the segment survival probability $G(s_0, t)$. We begin with the definition of $G(s_0, t)$. From (36) it follows that $G(s_0, t)$ is proportional to the following sum

$$\sum_{s_0'} \left\langle \hat{\mathbf{u}}^I(s_0', t) \cdot \hat{\mathbf{b}}(s_0, t) \right\rangle \tag{55}$$

where the averaging is taken over the whole ensemble of chains. Let N_{all} be the total number of chains in the ensemble. Therefore, (55) can be rewritten as

$$\sum_{s_0'} \frac{1}{N_{all}} \sum_{surv} \hat{\mathbf{u}}^I(s_0', t) \cdot \hat{\mathbf{b}}(s_0, t) + \sum_{s_0'} \frac{1}{N_{all}} \sum_{left} \hat{\mathbf{u}}^I(s_0', t) \cdot \hat{\mathbf{u}}(s_0, t)\, \hat{\lambda}(s_0, t) \tag{56}$$

Here, in the first term on the RHS the summation is taken over the chains that still have the segment s_0 in the initial tube (we denote their number as N_{surv}). In contrast, the sum in the second term is over the chains whose segment s_0 has already left the tube. We assume that if a chain segment leaves the initial tube then its stretching is completely relaxed. Besides that, the slow flow cannot stretch this segment significantly at any later time. Therefore, taking into account the fact that after leaving the initial tube the orientation of the segment is uncorrelated with $\hat{\mathbf{u}}^I(s_0', t)$, we come to the conclusion that the second term in (56) vanishes (compare (31)). In addition, from (30) for the chains that still have the segment s_0 in the initial tube we have

$$\sum_{s_0'} \hat{\mathbf{u}}^I(s_0', t) \cdot \hat{\mathbf{u}}(s_0, t) = 1 \tag{57}$$

Therefore, the sum in (56) boils down to

$$\frac{1}{N_{all}}\sum_{surv}\hat{\lambda}(s_0,t)=\frac{N_{surv}}{N_{all}}\cdot\frac{1}{N_{surv}}\sum_{surv}\hat{\lambda}(s_0,t) \tag{58}$$

The first factor on the RHS is equivalent to the segment survival probability $G(s_0,t)$. The second one gives the mean local stretching of the segment s_0 where the averaging is only taken over the chains with the segment s_0 still in the initial tube. We denote it as $\bar{\lambda}_S(s_0,t)$. Finally, from (55) and (58) we end up with

$$G(s_0,t)=\frac{1}{\bar{\lambda}_S(s_0,t)}\sum_{s_0'}\left\langle\hat{\mathbf{u}}^I(s_0',t)\cdot\hat{\mathbf{b}}(s_0,t)\right\rangle=\frac{1}{\bar{\lambda}_S}\sum_{s_0'}\phi_{\alpha\alpha} \tag{59}$$

Differentiating both sides of (59) with respect to time, we arrive at

$$\frac{\partial G}{\partial t}=\frac{1}{\bar{\lambda}_S}\sum_{s_0'}\frac{\partial\phi_{\alpha\alpha}}{\partial t}-\left\{\frac{\partial\bar{\lambda}_S}{\partial t}\right\}\sum_{s_0'}\frac{\phi_{\alpha\alpha}}{\bar{\lambda}_S^2} \tag{60}$$

Note that we have already studied the correlator $\phi_{\alpha\alpha}$ and derived the corresponding equation of motion (see (51)). Therefore, the last step for us to take is to derive the equation of motion for $\bar{\lambda}_S$. To this end, we remind that in [9] the following equation of motion for the local stretching was found by representing the chain inside its tube as one-dimensional Rouse chain:

$$\frac{\partial\hat{\lambda}}{\partial t}=K_{\alpha\beta}\hat{u}_\alpha\hat{u}_\beta\hat{\lambda}-\frac{\hat{\lambda}-1}{T_{eff}} \tag{61}$$

This equation describes the dynamics of the local stretching of a *single* chain with T_{eff} being the local stretching effective relaxation time due to shrinking and constraint release. Further, from the definition of $\bar{\lambda}_S$ (56) and (61) one can easily find that

$$\frac{\partial\bar{\lambda}_S}{\partial t}=\bar{\lambda}_S\,\frac{K_{\alpha\beta}\phi_{\alpha\beta}}{\phi_{\alpha\alpha}}-\frac{\bar{\lambda}_S-1}{T_R} \tag{62}$$

Here, summation is assumed over repeated indexes. We stress that in contrast to (60) which is valid for all chains, this equation describes the dynamics of the mean local stretching of segments that are still present in the initial tube. Since these segments do not experience constraint release and accordingly can only relax their stretching via shrinking, we have replaced T_{eff} with T_R which is the corresponding relaxation time in the absence of constraint release. Note that in the absence of flow $\bar{\lambda}_S=1$. If the flow is present, molecules are stretched inside their tubes, and then $\bar{\lambda}_S>1$.

Finally, substituting (51) and (62) into (60), the following equation of motion for $G(s_0,t)$ comes out:

$$\frac{\partial G}{\partial t}=D_c\frac{\partial^2G(s_0,t)}{\partial s_0^2}+\frac{3\nu a_0^2}{2}\frac{1}{\bar{\lambda}}\frac{\partial^2}{\partial s_0^2}\left[\bar{\lambda}G(s_0,t)\right]+\int_0^{s_0}dx\left\{\frac{\bar{\lambda}-1}{T_R}\right\}\cdot\frac{\partial G(s_0,t)}{\partial s_0} \tag{63}$$

Here, we have neglected the effect of stretching on the first term on the RHS since reptation becomes irrelevant if the chains are stretched. Besides that, under the assumption of small stretching one can neglect $\bar{\lambda}_S$ in the denominator of the last term on the RHS.

Notice that we have replaced $\bar{\lambda}_S$ with $\bar{\lambda}$ in (63). We point out that (59) which is valid in the slow flow regime, coincides with the more general result in (36) which is based on the fact that the probability for a chain segment to survive in the initial tube does not depend on its local stretching. Therefore, we argue that in the slow flow regime $\bar{\lambda}_S \approx \bar{\lambda}$.

Some comments must be made on the second term on the RHS pertaining to constraint release. One can see that it has the form of a diffusion process with the coefficient depending on the local stretching. Mead, Larson and Doi [5] proposed to introduce the so-called "switch function" $f(\bar{\lambda}) = 1/\bar{\lambda}$ to weaken the effect of constraint release as random tube reorganization for stretched chains. Our result (63) also contains this switch function as a prefactor. But in addition there is another $\bar{\lambda}$ in the numerator. Since in the slow flow regime $\bar{\lambda}$ is a very smooth function of s_0, in zero approximation it can be replaced with the averaged (along the contour) stretching and then taken out of the derivative. Therefore, we come to the conclusion that incorporation of such a function is inconsistent for regimes of small stretching.

Next, as will be shown further, the frequency of constraint release ν can in turn be expressed via the segment survival probability $G(s_0, t)$, so that (63) is actually a non-linear partial differential equation. The corresponding initial and boundary conditions were presented earlier in (2).

In the absence of flow, the equation of motion for $G(s_0, t)$ (63) boils down to

$$\frac{\partial G}{\partial t} = D_c \frac{\partial^2 G(s_0, t)}{\partial s_0^2} + \frac{3\nu a_0^2}{2} \frac{\partial^2 G(s_0, t)}{\partial s_0^2} \tag{64}$$

where ν is now the frequency of thermal constraint release events. As was shown before, the second term is small and can be dropped, so that (64) coincides with the above mentioned result by Doi and Edwards (see, (2)) derived for pure reptation in a fixed network.

Constraint release in the presence of flow

In one of the previous sections we derived the time evolution equation for the correlator $\phi_{\alpha\beta}(s_0, t|s_0')$ that can further be used to calculate the segment survival probability. It is a non-linear partial-differential equation of the second order with all the major mechanisms relevant to bulk chains taken into account.

When studying thermal constraint release, we established that the mean life-time of a constraint could be expressed via the tube survival probability function $G(s_0, t)$ which was obtained for the case of pure reptation in a fixed network in the absence of flow. In this section we will show how it is possible to calculate the frequency of constraint release ν given $G(s_0, t)$ in the more general case with flow and convective constraint release.

As in the case of CR, we begin our analysis with the segment mobility distribution function. Note that the mean mobility of segment s_0 in the presence of flow contains three

contributions

$$\bar{\varepsilon}(s_0) = \bar{\varepsilon}_{(cr+ccr)} + \bar{\varepsilon}_{(retr)}(s_0) + \bar{\varepsilon}_{(rept)}(s_0) \tag{65}$$

Here, the first one pertains to constraint release. As was explained above, due to the arbitrary "distribution of life-times" along the chain contour, on average this mobility does not depend on s_0. In contrast, the second and the third contributions are functions of s_0. The second term stems from shrinking of a stretched chain inside its tube resulting in vacation of segments close to the free ends. Therefore, we expect that

$$\bar{\varepsilon}_{(retr)}(s_0) = \bar{\varepsilon}_{(retr)} \left(\int_0^{s_0} dx \, (\bar{\lambda} - 1) \right) \tag{66}$$

We see that the mobility of the segment s_0 due to retraction is determined by the stretching of segments with $s_0' < s_0$, and therefore is a non-local process with respect to s_0. The last term on the RHS of (65) arises from reptation. We have already calculated its explicit form in (5) (the mobility is the inverse life-time of a constraint).

Some comments ought to be made on formula (65). First, one can see that the "total" mobility of a segment is simply the sum of the mobilities due to different relaxation processes which is not the case for the life-times. This addition rule holds for mobilities because probabilities of independent processes simply sum up. Second, as was shown earlier, the mobility due to thermal constraint release is much smaller then that due to reptation for long bulk chains.

Next, let us show now how given the segment survival probability we can find the constraint mobility distribution function $\Psi(\varepsilon)$ for the case with flow. We have already derived its explicit form in the case of thermal constraint release (see, (19)). This derivation was based on a perturbation theory assuming that the rate at which constraints are removed is much smaller then the inverse reptation time. But the time scale of CCR depends on the flow rate and can be of the order, or even exceed that of reptation. In this situation perturbation theory may not be applicable any more, and one has to find another way to calculate the mean segment mobility (65).

In order to find $\bar{\varepsilon}(s_0)$ without using perturbation theory, we will represent $G(s_0, t)$ in the form of the inverse Laplace transform

$$G(s_0, t) = \int_0^{\infty} d\varepsilon \, P(\varepsilon, s_0) e^{-\varepsilon t} \tag{67}$$

Here, $P(\varepsilon, s_0)$ can be treated as the probability for the segment s_0 to have the mobility equal to ε. Note that from the initial condition for $G(s_0, t)$ (see, (2)) one can find that it is normalized, and so

$$\int_0^{\infty} d\varepsilon \, P(\varepsilon, s_0) = 1$$

We emphasize that $P(\varepsilon, s_0)$ does not depend on time and consequently should be expressed via equilibrium values only. Known $P(\varepsilon, s_0)$, one can easily calculate the mean life-time of the segment s_0 as follows

$$\bar{\tau}(s_0) = \int_0^\infty dt\, G(s_0, t) = \int_0^\infty \frac{d\varepsilon}{\varepsilon} P(\varepsilon, s_0) \tag{68}$$

Thus, given the segment survival probability one can find $P(\varepsilon, s_0)$ and then the mean-life time of a segment according to (68). Unfortunately, in general, there is no close equation for $G(s_0, t)$ and one should first the full system of equations (51). But under assumption of small stretching it is possible to derive the close equation of motion for $G(s_0, t)$ (63). In this case, it is possible to make one step further and write down the close equation for $\bar{\tau}(s_0)$. We will restrict ourselves to the steady-state problem when the flow rate does not depend on time. Then, the mean local stretching $\bar{\lambda}$ is a function of s_0 only. From integration of (63) and use of (68) it immediately follows that

$$D_c \frac{\partial^2 \bar{\tau}(s_0, t)}{\partial s_0^2} + \frac{3\nu a_0^2}{2} \frac{1}{\bar{\lambda}} \frac{\partial^2}{\partial s_0^2} \left[\bar{\lambda} \bar{\tau}(s_0, t) \right] + \int_0^{s_0} dx \left\{ \frac{\bar{\lambda} - 1}{T_R} \right\} \cdot \frac{\partial \bar{\tau}(s_0, t)}{\partial s_0} + 1 = 0 \tag{69}$$

The first three terms on the LHS correspond to reptation, constraint release and retraction, respectively. As was mentioned before, under slow flows the local stretching is a smooth function of s_0, so that the second term on the LHS can be thought of as being independent of $\bar{\lambda}$. As a result, the mean life-time of the segment s_0 will only depend on $\bar{\lambda}(s_0')$ with $s_0' < s_0$ (compare (66)). We remind that due to the fast equilibration processes active at the free ends, the boundary conditions should be taken as $\bar{\tau}(\pm L_0/2) = 0$.

In the absence of flow, we may drop the third term on the LHS of (69). The solution of the resulting equation again yields the result (5) calculated via time integration of the Doi and Edwards segment probability function (2).

Further, we expect that the frequency of constraint release events ν should also depend on $\bar{\tau}$ so that (69) is a non-linear partial-differential equation. To establish this dependence we repeat the procedure listed in the first section devoted to thermal constraint release. Namely, we introduce the constraint mobility distribution function $\Psi(\varepsilon)$ which has the following form

$$\Psi(\varepsilon_k) = \frac{2}{K^2} \left(K - k + \frac{1}{2} \right)$$

Note that the explicit form of $\Psi(\varepsilon)$ in the *discrete* representation is exactly the same as we had before in (18) in the absence of flow. Here, $K = Z_0/2$ is the number of possible "sorts" of mobilities in our ensemble. But since $\bar{\varepsilon}(s_0)$ now contains retraction, constraint release and reptation, the explicit form of $\Psi(\varepsilon)$ written in the continuous representation will be different from (19). Given the solution of (69), one can find the continuous form of $\Psi(\varepsilon)$ and therefore compute the characteristic frequency of constraint release events ν as

follows

$$\nu = \int_0^\infty d\varepsilon\, \varepsilon \Psi(\varepsilon) \tag{70}$$

This equation makes it obvious that ν does not depend on s_0. Taking into account the explicit form of $\Psi(\varepsilon)$, one can also write down (70) in the discrete format:

$$\nu = \frac{2}{K^2} \sum_{k=1}^{K} \frac{1}{\bar{\tau}(a_0 k - a_0/2)} \left(K - k + \frac{1}{2} \right) \tag{71}$$

Here a_0 is the mean entanglement spacing, or equivalently the length of one segment. In (71) the summation is taken over all possible mobilities in the ensemble. We remind that the total number of possible mobilities is $K = Z_0/2$. It is important to mention that since $\bar{\tau}$ is a function of ν, eqn (71) is in fact a non-linear equation for ν. Its solution gives us the frequency of constraint release events experienced by bulk chains in the presence of flow.

In the single life-time approximation, solving (71) yields

$$\nu = \frac{2}{L_0} \int_0^{L_0/2} dx \frac{\bar{\lambda} - 1}{T_R} \tag{72}$$

In [11], we already derived this expression basing on the known time evolution of a chain inside its tube.

Constraint release in the near-wall layer.

In the previous chapters a detailed analysis was made of constraint release experienced by bulk molecules, that is, molecules far from a wall. We were able to calculate the constraint mobility distribution function and then find the mean life-time of a constraint.

The goal of this section is constraint release in the interfacial layer. In particular, the results obtained for the bulk chains will be further used to calculate the frequency of constraint release for the chains grafted on the wall the so-called tethered chains. We begin with simple physical arguments. First, when studying the bulk flow we dealt with only one sort of molecules, namely bulk chains. In contrast, in the interfacial layer there are two sorts of molecules: bulk and tethered. As a result, one should consider three types of entanglements, namely bulk-bulk (B-B), bulk-tethered (B-T) and tethered-tethered (T-T). Since the dynamics of tethered molecules is different from that of bulk ones (see, for example, Joshi and Lele [4]), it is obvious that we should distinguish between them. Second, as one of the ends of the tethered chain is attached to the wall, the relaxation time for tethered-tethered entanglements is much larger then that of bulk-tethered type. Therefore, it is reasonable to neglect loss of tethered-tethered entanglements presuming that only bulk-bulk and bulk-tethered constraints can be released.

To build a quantitative description of constraint release on tethered molecules, we have to introduce the relative fraction of bulk-tethered constraints per tethered molecule. It can be defined as follows

$$\Phi_Z = \frac{Z_{B-T}}{Z_{B-T} + Z_{T-T}} \tag{73}$$

Here, Z_{T-T} and Z_{B-T} are the mean numbers of tethered-tethered and bulk-tethered constraints per one tethered chain, respectively.

One may expect that Φ_Z should depend on the grafting density of tethered chains. At low surface coverage (the so-called mushroom regime) bulk molecules dominate in the interfacial layer (see, Fig.6). In this regime the tethered chains are hardly entangled with

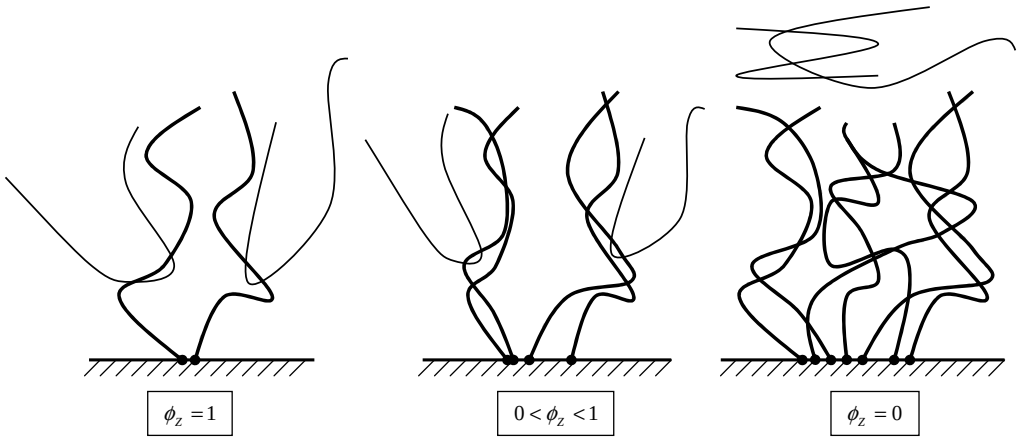

Figure 6: Different grafting regimes. Thick and thin lines stand for the tethered and bulk molecules, respectively

each other and consequently all the constraints imposed on a tethered chain are of the bulk-tethered type ($\phi_Z = 1$). At higher grafting densities different tethered chains start interacting with each other and then some of the entanglements will be of the tethered-tethered type ($\phi_Z < 1$). At extremely high grafting densities (the so-called dry brush regime), the bulk molecules are completely driven out from the interfacial layer and all entanglements are of tethered-tethered type ($\phi_Z = 0$). Obviously, there is no constraint release in this regime. Later on we will see show that Φ_Z is also a function of molecular parameters of bulk and tethered molecules.

In order to find the explicit form of Φ_Z, let us carry out a simple thought experiment. Suppose for a moment that there is no interaction between the polymer melt and the wall. If N_B is the number of monomers per bulk molecule, then from the freely-jointed chain model it directly follows that in the absence of flow every bulk molecule has on average a coiled shape with the radius R_B:

$$R_B = \sqrt{N_B} b$$

Here, b is the monomer length (the Kuhn length). As a consequence, the near-wall layer of thickness R_B will contain on average *only whole* bulk molecules (see, Fig.7). Given the

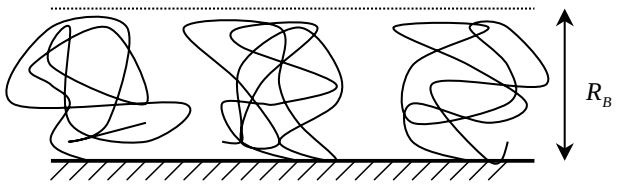

Figure 7: No polymer-wall interaction

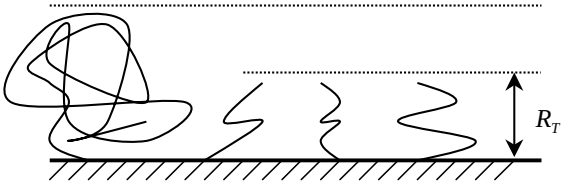

Figure 8: Polymer-wall interaction

mean spacing between adjacent entanglements a_0 one may find the number of bulk chains per unit area Σ_B, that is to say, the surface density of bulk molecules. For certainty, we assume that all entanglements are pair-wise contacts, so that each bulk chain brings in $Z_B/2$ entanglements (Z_B is the mean number of entanglements per bulk chain). Then,

$$\Sigma_B = \frac{R_B}{a_0^3}\frac{4}{Z_B} \tag{74}$$

Here, use was made of the fact that in general the chosen unit volume contains different parts of the "external" bulk chains traversing it. The mean number of entanglements per one part is $Z_B/2$.

Now we "switch on" interaction between the polymer melt and the wall. Then, the bulk molecules that touch the wall will become tethered. Note that in general a tethered molecule has more than one connection with the wall forming the so-called tails and loops. In this paper we will neglect existence of loops and will only consider tails. From the above one may infer that the average number of monomers per tail N_T is smaller then N_B. Therefore, the layer in which the tethered molecules can be found has the thickness of the order of $R_T = \sqrt{N_T}b < R_B$ (see, Fig.8). If Σ_T is the surface density of tethered molecules, then the total number of entanglements per unit area in the near-surface layer of thickness R_B is given by

$$\frac{1}{2}\left[Z_T\Sigma_T + \frac{Z_B\Sigma_B}{2}\right] \tag{75}$$

Here, Z_T is the mean number of entanglements per tethered chain. We remind again that all the entanglements are assumed to be pair-wise contacts. On the other hand, the same number can in turn be expressed via the mean entanglement spacing as follows

$$\frac{R_B}{a_0^3} \tag{76}$$

Therefore, by comparing (75) and (76) one can find that the surface density of bulk molecules in the presence of tethered chains is given by

$$\Sigma_B = \left\{\frac{2R_B}{a_0^3} - Z_T\Sigma_T\right\}\frac{2}{Z_B} \tag{77}$$

Joshi and Lele [15] showed that in the case of low grafting densities, that is, the mushroom regime each tethered chain makes connections with separate bulk chains, so that the following equality must hold

$$Z_T\Sigma_T = \Sigma_B \tag{78}$$

From (77) and (78) one can easily find the corresponding critical grafting density to which the mushroom regime extends

$$\Sigma_T^{(cr)} = \frac{4R_B}{a_0^3}\frac{1}{Z_T Z_B} \tag{79}$$

We find it useful to calculate ϕ_T which is the volume fraction of tethered molecules in the layer of thickness R_B. By definition it is given by

$$\phi_T = \frac{\Sigma_T}{\Sigma_T + \Sigma_B} = \frac{\Sigma_T}{\Sigma_T + 2\big\{2R_B a_0^{-3} - Z_T\Sigma_T\big\}Z_B^{-1}} \tag{80}$$

From (79) and (80), it directly follows that in the mushroom regime the volume fraction of tethered chains is

$$\phi_T \leq \frac{1}{1+Z_T} \tag{81}$$

So it is clear that if the tethered chains are long enough, the interfacial layer is "manned" mostly by the bulk molecules. This is in agreement with the earlier assumption that one tethered chain makes entanglements with separate tethered chains.

Given Σ_T and Σ_B (77) we may now find the explicit expression for Φ_Z. To this end, we will again represent the entanglement network as a gas of interacting "half-entanglements". As was mentioned before, there are two types of chains in the interfacial layer: bulk and tethered. So we introduce two types of half-entanglements, namely black and white (see, Fig.9). Every bulk chain "carries" $Z_B/2$ white half-entanglements, whilst every tethered $Z_T/2$ black ones (see, Fig.10).

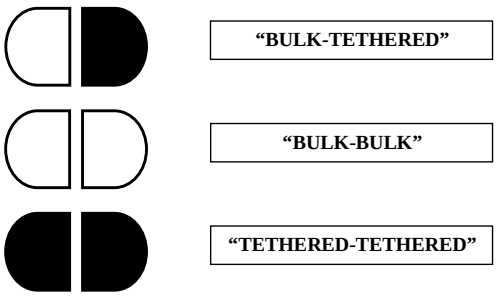

Figure 9: Three types of entanglements

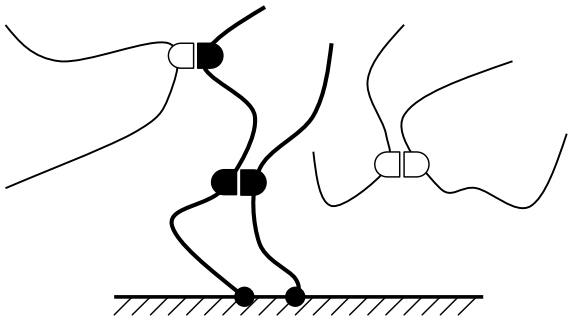

Figure 10: Black and white half-entanglements.

Having interacted two half-entanglements build the whole entanglement one of the three types. The volume fraction of entanglements of each type in the layer of thickness R_B is given by

$$W_{BB} = W_B W_B \qquad W_{BT} = 2W_B W_T \qquad W_{TT} = W_T W_T \tag{82}$$

Here, W_T and W_B is the corresponding volume fraction of half-entanglements pertaining to tethered and bulk molecules, respectively. The factor 2 in the expression for W_{BT} simply

indicates that $W_{BT} = W_{TB}$. Given Σ_T and Σ_B, the explicit form of W_T and W_B is

$$W_T = \frac{Z_T \Sigma_T}{Z_T \Sigma_T + Z_B \Sigma_B R_T R_B^{-1}/2} \tag{83}$$

$$W_B = \frac{Z_B \Sigma_B R_T R_B^{-1}/2}{Z_T \Sigma_T + Z_B \Sigma_B R_T R_B^{-1}/2} \tag{84}$$

So by now we have found that there are three different types of entanglements in the interfacial layer: bulk-bulk, bulk-tethered and tethered-tethered. We derived their volume fractions in the interfacial layer and showed that they could expressed via the volume fractions of half-entanglements. Now we are able to calculate Φ_Z which is the fraction of bulk-tethered constraints per tethered molecule. It is expressed via W_{BT}, W_{TT} and W_{BB} as follows

$$\Phi_Z = \frac{W_{BT}}{W_{TT} + W_{BT}} = \left\{ 1 + \sqrt{\frac{Z_T}{Z_B}} \cdot \frac{\Sigma_T}{\Sigma_B} \right\}^{-1} \tag{85}$$

Note that in the mushroom regime

$$\Phi_Z = \frac{\sqrt{Z_B Z_T}}{1 + \sqrt{Z_B Z_T}} \cong 1 \tag{86}$$

As is seen from (86), even at the critical grafting density (79) almost all constraints imposed on a tethered chain are of the bulk-tethered type.

Next, given the mean life time of a bulk constraint imposed on a tethered chain ν_0 it is possible to find the effective hopping rate at which constraints are released on the tethered chain. We propose the following relation

$$\nu_{eff} = \nu_0 \Phi_Z \tag{87}$$

Note that in the dry brush regime when $\Phi_Z = 0$ the effective frequency is zero, so that no constraint release may occur. Moreover, as was argued by Joshi and Lele [15], tethered molecules are more easily oriented by flow than bulk ones. Accordingly, we also have to incorporate the entanglement network dilution effects, that is, loss of entanglements due to alignment of the chains with the flow. In the case of simple shear flow it can be incorporated this by the additional prefactor

$$\nu_{eff} = \nu_0 \Phi_Z \frac{h}{h_{eq}} \tag{88}$$

Here, an explicit assumption was made that flow can only change the number of entanglements in the direction perpendicular to that of flow. From (88) one can see that for the tethered chains squeezed against the wall $h \approx 0$ when all the entanglements with the bulk chains are lost, the frequency ν is zero.

Conclusion

In the present paper we have developed the formalism that enables us to calculate the constraint mobility distribution function $\Psi(\varepsilon)$ given the segment survival probability $G(s_0, t)$. First, we consider the simple case of no flow when constraints can only be released via reptation of surrounding chains forming the tube. We show that in this case the mean life-time of a constraint can be found using perturbation theory. Namely, given the segment survival probability in a fixed network, it is possible to calculate the constraint mobility distribution function Ψ, and then find the characteristic life time of a constraint. Note that a similar result was obtained using the so-called single exponential approximation. Their comparison gives that incorporation of the distribution over constraints mobilities results in a decrease in the life-time of a constraint.

Later, the more general case with the flow was considered. In this regime another relaxation mechanism is active. This is the release of constraints arising from shrinking of stretched surrounding molecules in their tubes. Since the time scale of this process can be comparable or even exceed that of reptation, the perturbation theory on which the result for CR was based is no more applicable. We proposed another way to calculate the mean segment mobility. Given it, we can repeat the procedure used when studying thermal constraint release and find the constraint mobility distribution function. We stress that in the discrete representation it has exactly the same form as in the case of CR. But since the mean mobility has now a much more complicated form with retraction and constraint release taken into account, we expect the explicit form for Ψ to be different from that obtained when studying CR.

We emphasize that in both situations, the analysis was based on the segment survival probability $G(s_0, t)$. In contrast to the case of no flow, in general there is no close equation for $G(s_0, t)$ in a flow. It means that one should solve the whole system of equations (51) for correlator $\phi_{\alpha\beta}(s_0, t|s_0')$ with the initial and boundary conditions given in (52) and (54), respectively. But under the assumption of small stretching it is possible to derive a close equation for $G(s_0, t)$, and then find the relation for the mean-life time of a segment (71). In the single life-time approximation, its solution is given by (72).

At the end, we considered constraint release experienced by molecules grafted on a solid wall. We saw that at high grafting densities tethered molecules become entangled with each other, so that the effective number of constraints that can be released is reduced assuming that constraints of the "tethered-tethered" type cannot be lost. Therefore, tethered chains may experience the so-called "suppressed" constraint release. We argue that the effective frequency of constraint release on tethered chains is proportional to ϕ_0 which is the relative fraction of constraints per of the "bulk-tethered" type per tethered chain.

Besides that, as was argued by Joshi and Lele, the tethered chains are more easily oriented by flow than bulk, so that one should also take into account the dynamic dilution of the entanglement network in the layer at high flow rates. In case of simple shear flow we proposed a simple estimate of this effect in (88).

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