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Memorandum No. 1677

A universal constitutive model for the interfacial layer between a polymer melt and a solid wall

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May, 2003

ISSN 0169-2690

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A universal constitutive model for the interfacial layer between a polymer melt and a solid wall.

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Abstract: In a preceeding report we derived the evolution equation for the bond vector probability distribution function (BVPDF) of tethered molecules. It describes the behavior of polymer molecules attached to a solid wall interacting with an adjacent flowing melt of bulk polymer molecules and includes all the major relaxation mechanisms such as constraint release, retraction and convection. The derived equation is quite universal and valid for all flow regimes. In the present paper the developed formalism is further analyzed. We begin our analysis with the simple case of slow flows. Then, as expected, a remarkable reduction of the theory is possible. Later on the more general case is considered.

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

Previous studies of polymer melt flow near solid walls have shown that two different flow regions could be distinguished. The first one is far from the wall and populated by bulk molecules only. It is often referred to as the bulk flow area. The second sides with the solid wall and contains, in general, both bulk and tethered chains. We will address it as the interfacial layer.

The scope of our previous work [1] was the interfacial layer. We developed a quantitative theory which enabled us to predict its thickness given flow characteristics and molecular parameters. It was found that the behaviour of molecules attached to the solid wall can be successfully described in terms of the so-called bond vector probability distribution function $f(\mathbf{b}, s_0, t)$, which is actually the probability for the bond vector at position s_0 along the backbone and time t to have the direction $\mathbf{b}$. The bond vector, i.e. the vector tangent to the primitive path, defines both the spatial conformation of the molecule (via its direction) and the local stretching along the chain (via its length). We were able to derive the corresponding equation of motion for f based on only one assumption, namely that only neighbouring segments along the chain contour can interact. This equation contains a lot of information about the dynamics of the tethered chains near the wall and includes all the major relevant relaxation mechanisms such as retraction, constraint release and convection.

We remind that in our preceeding work [1] this equation was already used to derive the time evolution equation for the thickness of the interfacial layer. One should realize, however, that the equation for f is quite general and, for example, can also be used to compute the local stress near the solid boundary produced by the bulk flow. It is important to outline that this analysis is closely related to the so-called "stick-slip" transition observed during polymer melt extrusion. As is shown in [2], it is the stick-slip transition that causes flow instabilities (spurt) when processesing melts. That is the reason why the ability to predict the local stress in the interfacial layer is not only of fundamental, but also of practical interest.

As was shown before in [1], the evolution equation for the bond vector probability distribution function f is a non-linear partial differential equation and, as a consequance, is rather difficult to solve, even numerically. So, to begin with, we will first consider the simple case of slow flow, in which the local stretching of the tethered chain is small and the theory may be remarkably reduced.

The present problem is not totally new and some progress has already been made. Therefore, it is not necessary to build a theory from scratch. Instead, our model will be a plausible refinement of existing theories. We start with the classical work by Doi and Edwards [3]. They derived the most general expression for the stress tensor

$$\sigma_{\alpha\beta} = \frac{G^0}{L_0} \int_0^{L_0} dx \, S_{\alpha\beta}(x,t) \tag{1}$$

Here, G^0 is the plateau modulus and L_0 the equilibrium length of the chain. Both G^0 and L_0 are functions of the molecular parameters. We do not specify any explicit expressions

for them here, but assume that these data may be extracted from experiments on polymer melts. The tensor $S_{\alpha\beta}$ is the bond vector correlator defined as

$$S_{\alpha\beta}(x,t) =< \hat{b}_\alpha(x,t)\hat{b}_\beta(x,t) > \tag{2}$$

Here, $\hat{b}_\alpha(x,t)$ is the α-component of the bond vector at position x and time t. The hat sign indicates that it is stochastic in nature. We remind that the direction of the bond vector at a particular point x coincides with the corresponding tangent to the primitive path. Besides that, its length is equal to the local stretching at that point. The averaging in (2) is taken over the whole ensemble of attached chains.

We point out that equation (1) is quite general and valid for both bulk and interfacial regions. But some care must be taken in the latter case. Namely, from the theory of rubber elasticity it follows that the plateau modulus G^0 is proportional to the number of entanglements per unit volume. In the bulk flow region all the entanglements are of the "bulk - bulk" kind and one can provide a reasonable estimate of G^0. In contrast, in the interfacial layer there are two types of entanglements: "bulk-bulk" and "bulk-tethered". Following the proposal by Joshi [4] we argue that only "bulk-tethered" entanglements give a contribution to the wall stress. Consequently, the plateau modulus of the interfacial region should depend on the relative fraction of "bulk-tethered" entanglements.

From (1) it is obvious that given the tensor $S_{\alpha\beta}$ one can easily find the explicit expression for the wall stress. So, our objective at this moment is to compute the correlator (2). To begin with, we note that averaging over the ensemble of tethered chains in (2) is equivalent to integrating over all possible values of the bond vector with the bond vector probability distribution function f as the weight

$$S_{\alpha\beta}(x,t) = \int\limits_{\mathbb{R}^3} d^3\mathbf{b}\, b_\alpha b_\beta f(\mathbf{b},x,t) \tag{3}$$

Equation (3) makes it clear that the results of our previous work [1] could also be used to compute the local stress near the wall. Namely, the evolution equation for the correlator $S_{\alpha\beta}$ can be obtained directly from that for $f(\mathbf{b},x,t)$. So, it is worth quoting some of our previous results because we will need them afterwards. We begin with the equation of motion for the bond vector distribution function f which has the following form

$$\begin{aligned}\frac{\partial f(\mathbf{b},s_0,t)}{\partial t} =& \frac{3\nu a^2}{4}\frac{\partial^2 f}{\partial s_0^2} - \frac{1}{T_{eff}}\frac{\bar{\lambda}(s_0,t)-b}{b}f + \frac{1}{b}\left\{\int_0^{s_0} dx\bar{\dot{\xi}}(x,t)\right\}\frac{\partial f}{\partial s_0} + \\ &+\frac{\partial\bar{\lambda}(s_0,t)}{\partial s_0}\left\{\int_0^{s_0} dx\bar{\dot{\xi}}(x,t)\right\}\frac{f}{b^2} - \frac{\partial}{\partial\mathbf{b}}\cdot\left(\mathbf{\Gamma}(\mathbf{b})f(\mathbf{b},s_0,t)\right)\end{aligned} \tag{4}$$

where

$$\begin{aligned}\bar{\dot{\xi}}(x,t) &= \frac{\partial\bar{\lambda}(x,t)}{\partial t} - K_{\alpha\beta} < \hat{u}_\alpha(x,t)\hat{u}_\beta(x,t)\hat{\lambda}(x,t) > \\ \mathbf{\Gamma}(\mathbf{b}) &= \left\{\bar{\bar{\mathbf{K}}} - \frac{1}{T_{eff}}\frac{b-1}{b}\bar{\bar{\mathbf{I}}} - \frac{1}{b^2}\frac{\partial\bar{\lambda}(s_0,t)}{\partial s_0}\int_0^{s_0} dx\,\bar{\dot{\xi}}(x,t)\,\bar{\bar{\mathbf{I}}}\right\}\mathbf{b}\end{aligned} \tag{5}$$

Here, $\bar{\bar{\mathbf{K}}}$ and $\bar{\bar{\mathbf{I}}}$ is the velocity gradient and unit tensors, respectively. The first term on the right hand side of (4) pertains to the constraint release (CR) relaxation mechanism, i.e. the random tube reorientation process due to release of the constraints imposed on the tethered chain. It has the form of a diffusion process with the diffusion coefficient equal to $3\nu a^2/4$ (a is the mean tube diameter and ν is the hopping rate). Some comments should be made on this hopping rate ν. Mead, Larson and Doi [5] proposed a phenomenological expression for ν based on simple physical arguments. They show that ν is determined by the dynamics of the bulk chains and argue that a constraint removal process can be manifested as a random tube reorientation only for the case of small stretching. It actually implies that the mentioned ν does not only depend on the molecular parameters of bulk chains and the flow rate, but also on the stretching in the tethered chains. Later on these effects will be taken into account in our formalism.
The second term arises from the one-dimensional motion of the monomers along the primitive path of the chain due to retraction. This mechanism results in local equilibrium at a certain point s_0 along the chain and has a characteristic time T_{eff}. According to a suggestion by Mead, Larson and Doi [5] CR can also affect the retraction rate via removal of constraints on a "tout" piece of chain which results in its fast relaxation with characteristic time τ_e (the Rouse time of a single chain segment). This means that T_{eff} is actually a function of the flow rate and should be equal to the corresponding Rouse time in the case of a fixed network. The $\bar{\lambda}(s_0, t)$ in (4) is the averaged (over the ensemble of tethered chains) local stretching at location s_0. Note that it can also be expressed via the bond vector probability distribution function

$$\bar{\lambda} = \int\limits_{\mathbb{R}^3} d^3\mathbf{b}\, b\, f(\mathbf{b}, s_0, t)$$

This implies that (4) is a non-linear partial integro-differential equation.
It is also important to remind that s_0 is not the real arclength of a segment along the backbone. We represent the spatial comformation of a tethered chain by a parameterized curve $\mathbf{R}(s_0, t)$, $0 \le s_0 \le L_0$, where parameter s_0 "labels" the same physical segment at all times and does not change from chain to chain in contrast to real coordinates. Since we have some freedom in choosing the "label", it is very convenient to take s_0 as the *equilibrium* arclength of the segment.
The third and fourth terms also stem from stretching. They vanish when the chain is fully relaxed. These are "non-local" processes which correspond to coordinated motion of the different chain segments.

The bond vector distribution in slow flow

Up to now we have considered the general theory valid for all flow regimes. In this section we will study the simple case of slow flow. First, let us define what is meant by slow flow. We note that the retraction relaxation mechanism has the time scale of the free Rouse

motion (see, for instance, [6]). Therefore, in the case of flows with rates much less then the inverse Rouse time the chain has time to relax and accordingly can be thought of as having a length close to its equilibrium value. Apparently, this is the regime of small stretching. In contrast, when the flow rate exceeds the inverse Rouse time, there are two concurring processes: stretching (since the tube is elongated by the shearing flow) and axial shrinking. In this regime chains can be significantly stretched. Hence, we define the slow flow regime as the regime with the flow rate much less then the inverse Rouse time and, as a consequence, with small stretching.

We begin our analysis with equation (4) for the bond vector probabilty distribution function f. Since we will use it to derive the bond correlation function $S_{\alpha\beta}$, it is important to examine its major features in slow flows. In slow flows, from (4) one can infer that the bond vector probability distribution $f(\mathbf{b}, s_0, t)$ can be approximated by the product

$$f(\mathbf{b}, s_0, t) = f^{(b)}(b, s_0, t) f^{(\mathbf{u})}(\mathbf{u}, s_0, t) \tag{6}$$

Here, the first function $f^{(b)}(b, s_0, t)$ depends on the length of the bond vector only. Actually, it is the distribution over local stretching at point s_0 and time t (we remind that $|\mathbf{b}(s_0, t)| = \lambda(s_0, t)$). Next, $f^{(\mathbf{u})}(\mathbf{u}, s_0, t)$ is only a function of the unit tangent vector $\mathbf{u}$ and pertains to the purely orientational distribution. It is important to note that equation (6) displays that the local stretching and the local orientation of a segment may be considered as being independent in slow flow. As will be shown later, the accuracy of this approximation decreases with increasing flow rate.

The corresponding equations of motion for $f^{(\lambda)}$ and $f^{(\mathbf{u})}$ may be obtained directly from (4) and have the form

$$\frac{\partial f^{(b)}(\lambda, s_0, t)}{\partial t} = \frac{3\nu a^2}{4} \frac{\partial^2 f^{(b)}}{\partial s_0^2} + \frac{1}{\lambda} \int_0^{s_0} dx \bar{\dot{\xi}}_1(x, t) \frac{\partial f^{(b)}}{\partial s_0} + \frac{1}{\lambda} \frac{\partial \bar{\lambda}(s_0, t)}{\partial s_0} \int_0^{s_0} dx \bar{\dot{\xi}}_1(x, t) \frac{\partial f^{(b)}}{\partial \lambda} \tag{7}$$

$$\begin{aligned} \frac{\partial f^{(\mathbf{u})}(\mathbf{u}, s_0, t)}{\partial t} =& \frac{3\nu a^2}{4} \frac{\partial^2 f^{(\mathbf{u})}}{\partial s_0^2} + \left\{ \int_0^{s_0} dx \bar{\dot{\xi}}_2(x, t) \right\} \frac{\partial f^{(\mathbf{u})}}{\partial s_0} - \frac{\partial}{\partial \mathbf{u}} \cdot \left(\mathbf{\Gamma}(\mathbf{u}) f^{(\mathbf{u})}(\mathbf{u}, s_0, t) \right) + \\ &+ K_{\alpha\beta} \left\{ u_\alpha u_\beta - \langle u_\alpha u_\beta \rangle \right\} f^{(\mathbf{u})} \end{aligned} \tag{8}$$

where

$$\begin{aligned} &\bar{\dot{\xi}}_1(x, t) = -\frac{\bar{\lambda}(x, t) - 1}{T_{eff}} \\ &\bar{\dot{\xi}}_2(x, t) = -K_{\alpha\beta} < \hat{u}_\alpha(x, t) \hat{u}_\beta(x, t) \hat{\lambda}(x, t) > \\ &\mathbf{\Gamma}(\mathbf{u}) = \bar{\bar{\mathbf{K}}} \mathbf{u} - (K_{\alpha\beta} u_\alpha u_\beta) \, \mathbf{u} \end{aligned} \tag{9}$$

Here, use has been made of the fact that in the slow flow regime the fast retraction motion (with the time scale of the Rouse time) can be thought as instantaneous in comparison to the deformation of the chain by the flow. Therefore, considering the behavior of the attached molecules at the time scale of the flow, the time derivative of the local stretching

in (5) may be dropped. In other words, due to the fast retraction processes one can think of the chain as being at local equilibrium at any moment of time.
Here, we would like to make some comments on the bond length probability distribution function $f^{(b)}$ in (6). From (7) it follows that in the stationary case and in the absence of constraint release, it satisfies the very simple relation

$$\frac{\partial f^{(b)}}{\partial s_0} + \frac{\partial \bar{\lambda}(s_0,t)}{\partial s_0}\frac{\partial f^{(b)}}{\partial \lambda} = 0 \tag{10}$$

Let us neglect the width of the bond length distribution at equilibrium, that is to say we assume that is has the form of a delta function. Then a solution of (10) is given by

$$f^{(b)}(\lambda, s_0) \propto exp\left\{ -\frac{\left[\lambda - \bar{\lambda}(s_0)\right]^2}{\left[L_0^{-1}\int\limits_0^{L_0} dx\bar{\lambda}(x) - 1\right]} \right\} \tag{11}$$

Here, a fact has been used that the delta function can be approximated by

$$\delta(x - x_0) \propto exp\left\{ -\frac{(x-x_0)^2}{\Delta t} \right\} \; if \; \Delta t \to 0$$

Thus, in the absence of constraint removal the distribution function for the local stretching in slow flow has the Gaussian form (note that $\bar{\lambda} \geq 1$). One can see that in the absence of flow (or, equivalently, in the absence of stretching) this distribution has the form of a delta function, as expected.
Note that the standard deviation is proportional to the local stretching. As a consequence, in the slow flow regime the following approximation comes out

$$< \lambda^2 > \cong < \lambda >^2$$

In addition, we note that the accuracy of the pre-averaged approximation

$$< b_\alpha(s_0,t) b_\beta(s_0,t) > \cong \left(\bar{\lambda}(s_0,t)\right)^2 < u_\alpha(s_0,t) u_\beta(s_0,t) > \tag{12}$$

decreases when the flow rate is increased. Therefore, in the fast flow regime it may cause a significant error and, consequently, one should deal with the full correlator $< b_\alpha b_\beta >$.
Further, some remarks ought to be made on the distribution function for tangent vectors $f^{(\mathbf{u})}$ (8). The equation of motion (8) coincides completely (except for the CR term) with the result obtained by Doi, Edwards [3] where they studied the behavior of an inextensible chain under imposed deformation. They also proposed a convenient integral representation of the solution of (8). Interesting though it is, this integral transformation merits a special consideration and is not discussed here (an interested reader may find the details in the original work by Doi [7]).

The constitutive equation in slow flow

Above, we have established all the necessary "ingredients" needed to calculate the wall stress. In particular, we have studied the bond vector probability distribution function f in the slow flow regime and have shown that the bond vector correlation function $S_{\alpha\beta}$ (3) can be expressed via a second moment of f. In this chapter an attempt will be made to derive an equation for $S_{\alpha\beta}$ taking the equation for f as a starting point. Multipling both sides of (4) by $b_\alpha b_\beta$ and integrating over all possible values of the bond vector, one finds that

$$\begin{aligned}\frac{\partial S_{\alpha\beta}(s_0,t)}{\partial t} =& \frac{3\nu a^2}{4}\frac{\partial^2 S_{\alpha\beta}}{\partial s_0^2} - 2\frac{\bar{\lambda}(s_0,t)-1}{T_{eff}}S_{\alpha\beta}(s_0,t) + K_{\alpha\gamma}S_{\beta\gamma}(s_0,t) + K_{\beta\gamma}S_{\alpha\gamma}(s_0,t) + \\ &+ \left\{\int_0^{s_0} dx\bar{\dot{\xi}}(x,t)\right\}\frac{\partial S_{\alpha\beta}(s_0,t)}{\partial s_0}\end{aligned} \tag{13}$$

When deriving (13) use has been made of the pre-averaged approximation (12) which is valid in the slow flow regime. The first term on the right hand side of (13) describes the effect of constraint release on tethered chains. As was mentioned before, removal of constraints may result in random tube reorganisation or in fast retraction of a "tout" part of the chain depending on the local stretching. In this section we focus on the slow flow regime when the attached molecule has a length close to its equilibrium value. Accordingly, fast retraction motion due to the constraint removal can be neglected and T_{eff} may be replaced with the corresponding Rouse time of the tethered chain. Note that the Rouse time of a tethered chain is two times larger then that of a bulk chain with the same number of monomers.

The second and the last term in (13) describes one-dimensional retraction motion of segments along the primitive path. The factor 2 in the second term arises from the fact that $S_{\alpha\beta}$ is a bilinear function of the bond vector.

The terms with $K_{\alpha\beta}$ describe convection produced by the flow. The tensor $K_{\alpha\beta}$ is the velocity gradient tensor [3] characterizing how fast the averaged velocity of the medium changes in space. From (13) it is clear that in the presence of flow all the components of the correlator $S_{\alpha\beta}$ are coupled and one has to solve a system of equations.

Note that, we outline that at rest a solution of (13) is, in general, a linear function of s_0. This stems from the fact that the boundary conditions for the tethered and the free end of a chain attached to the wall are different. We emphasize that even in the absence of any flow the tensor $S_{\alpha\beta}$ is not isotropic (i.e. $S_{\alpha\beta} \neq S\,\delta_{\alpha\beta}$). This also follows from the boundary conditions for the tethered chain. In contrast, for bulk chains at rest $S_{\alpha\beta}$ does not depend on s_0 and is isotropic. Note that in view of (1) formula (13) can easily be transformed into the time evolution equation for the stress near the solid wall by integrating both sides over $0 \leq s_0 \leq L_0$.

The correlation function $S_{\alpha\beta}$ in Fourier space

Until now, we have considered the simple case of slow flow. In this regime the stretching of the tethered chain is small and, as a result, a significant reduction of the formalism is obtained. We derived the closed equation for the bond correlator $S_{\alpha\beta}$ which enables us to calculate the local stress near the wall.
The question may arise whether we can write down an explicit equation for $S_{\alpha\beta}$ in the general case. Unfortunately, as we can see from (4), when the stretching is not small the local stretching and orientation cannot be considered to be independent and we will have to deal with the full equation of motion (4). Besides that, we mentioned already that in fast flow the pre-averaged approximation (12) is poor and not appropriate.
In this section we will try to build a general theory valid for all flow regimes. We have shown already that all the quantities of practical interest are actually the second moments of the bond vector distribution function $f(\mathbf{b}, s_0, t)$ introduced before. So, we are especially interested in developing a "macroscopic" theory dealing with ensemble averaged variables. Of course, it must be based on the equation of motion for $f(\mathbf{b}, s_0, t)$ which can be considered as the "micro-level". One could indeed simply concentrate on the numerical aspects of the problem by obtaining the solution of (4) via computer simulation and then finding the components of $S_{\alpha\beta}$ via (3). But since we would like to advance our theory as much as possible, further analytical development of the model definitely makes sense.
In order to derive the general equation for the correlator $S_{\alpha\beta}$ we return to formula (4). As we will see later it is more convenient to rewrite it in terms of the Fourier transform of the bond distribution probability function:

$$f(\mathbf{b}, s_0, t) = \int\limits_{\mathbb{R}^3} \frac{d^3\mathbf{p}}{(2\pi)^3} \varphi(\mathbf{p}, s_0, t) e^{i\mathbf{pb}}, \tag{14}$$

where $\varphi(\mathbf{p}, s_0, t)$ is given by

$$\varphi(\mathbf{p}, s_0, t) = \int\limits_{\mathbb{R}^3} d^3\mathbf{b} f(\mathbf{b}, s_0, t) e^{-i\mathbf{pb}} \tag{15}$$

A remark could be made on formula (15). Neglecting extremely stretched states, the bond vector probability distribution function $f(\mathbf{b}, s_0, t)$ is non-vanishing only for those bond vectors that satisfy $|\mathbf{b}| \leq B$, where B is the maximum possible stretch under the given conditions. It actually implies that the corresponding Fourier transform (15) will vanish for $|\mathbf{p}| > 1/B$ and, as a result, the integration over the whole "$\mathbf{p}$"-space in (14) can be approximated by that over a finite volume.
From (15) we see that the equation of motion for $\varphi(\mathbf{p}, s_0, t)$ can be easily obtained from (4) by multiplying the both sides by $exp(-i\mathbf{pb})$ and then integrating over all possible bond vectors $\mathbf{b}$. But, in fact, it is the correlator $S_{\alpha\beta}$ that we are interested in. Hence, it is worth figuring out the apparent relation between the introduced Fourier transform φ and

the required S-tensor. From (3) and (14) we have

$$S_{\alpha\beta}(s_0,t) = <\hat{b}_\alpha(s_0,t)\hat{b}_\beta(s_0,t)> = -\frac{\partial^2\varphi(\mathbf{p},s_0,t)}{\partial p_\alpha\, p_\beta}\bigg|_{\mathbf{p}=0} \tag{16}$$

So, we see that φ can be treated as a generating function for $S_{\alpha\beta}$. If φ is known, one can easily find the desirable $S_{\alpha\beta}$ by simply taking its second order derivative with respect to $\mathbf{p}$ evaluated at the origin. Eventually, from (4) and (14) the following equation for φ is found (for compactness, we leave out the arguments s_0 and t):

$$\begin{aligned}
&\frac{\partial\varphi(\mathbf{k})}{\partial t} = \frac{1}{T_{eff}}\left\{\varphi(\mathbf{k}) - k_\alpha\frac{\partial\varphi(\mathbf{k})}{\partial k_\alpha}\right\} + k_\alpha K_{\alpha\beta}\frac{\partial\varphi(\mathbf{k})}{\partial k_\beta} + \\
&+\frac{1}{4\pi}\left\{\frac{\partial\bar{\lambda}(s_0,t)}{\partial s_0}\int_0^{s_0} dx\bar{\dot{\xi}}(x,t)\right\}\int d^3\mathbf{p}\frac{1}{p}\left[\varphi(\mathbf{k}+\mathbf{p}) - k_\alpha\frac{\partial\varphi(\mathbf{k}+\mathbf{p})}{\partial k_\alpha}\right] - \\
&-\frac{1}{T_{eff}}\frac{1}{2\pi^2}\int d^3\mathbf{p}\frac{1}{p^2}\left\{\bar{\lambda}(s_0,t)\varphi(\mathbf{k}+\mathbf{p}) - k_\alpha\frac{\partial\varphi(\mathbf{k}+\mathbf{p})}{\partial k_\alpha}\right\} + \\
&+\frac{1}{2\pi^2}\left\{\int_0^{s_0} dx\bar{\dot{\xi}}(x,t)\right\}\frac{\partial}{\partial s_0}\int d^3\mathbf{p}\frac{1}{p^2}\varphi(\mathbf{k}+\mathbf{p})
\end{aligned} \tag{17}$$

In deriving of (17) use was made of the integrals

$$\int\limits_{\mathbb{R}^3} d\mathbf{b}e^{i(\mathbf{p}-\mathbf{k})\mathbf{b}}\frac{1}{b^2} = \frac{2\pi^2}{|\mathbf{p}-\mathbf{k}|}$$

$$\int\limits_{\mathbb{R}^3} d\mathbf{b}e^{i(\mathbf{p}-\mathbf{k})\mathbf{b}}\frac{1}{b} = \frac{4\pi}{|\mathbf{p}-\mathbf{k}|^2}$$

By now, we have derived an explicit equation for φ which is the Fourier transform of the bond vector probability distribution function f. Just as in the case of equation (4), the coefficients are determined by the averaged quantities such as $\bar{\dot{\xi}}$ and $\bar{\lambda}$ which, in turn, depend on the probability function f (or, equivalently, on φ). Therefore, (17) is a non-linear integral and partial differential equation.

Next, we will show now that it is still possible to make a small step ahead towards a closed equation for $S_{\alpha\beta}$. To this end, let us introduce the auxiliary tensor $S_{\alpha\beta}(\mathbf{p},s_0,t)$

$$S_{\alpha\beta}(\mathbf{p},s_0,t) = -\frac{\partial^2\varphi(\mathbf{p},s_0,t)}{\partial p_\alpha\, p_\beta} \tag{18}$$

It is a mixed second-order derivative of the Fourier transform φ. From (17) and (18) one can derive the equation of motion for the tensor $S_{\alpha\beta}(\mathbf{p},s_0,t)$. In particular, for the "$\mathbf{p}=\mathbf{0}$"

- components of this tensor we have

$$\begin{aligned}
&\frac{\partial S_{\alpha\beta}(\mathbf{0},s_0,t)}{\partial t} = -\frac{1}{T_{eff}} S_{\alpha\beta}(\mathbf{0},s_0,t) + K_{\alpha\gamma} S_{\beta\gamma}(\mathbf{0},s_0,t) + K_{\beta\gamma} S_{\alpha\gamma}(\mathbf{0},s_0,t) + \\
&+ \frac{1}{2\pi^2}\left\{\int_0^{s_0} dx \bar{\dot{\xi}}(x,t)\right\} \frac{\partial}{\partial s_0} \int d^3\mathbf{p} \frac{1}{p^2} S_{\alpha\beta}(\mathbf{p},s_0,t) - \\
&- \frac{1}{4\pi}\left\{\frac{\bar{\lambda}(s_0,t)}{\partial s_0}\int_0^{s_0} dx \bar{\dot{\xi}}(x,t)\right\} \int d^3\mathbf{p} \frac{1}{p} S_{\alpha\beta}(\mathbf{p},s_0,t) - \\
&- \frac{1}{T_{eff}} \frac{1}{2\pi^2} \int d^3\mathbf{p} \frac{1}{p^2} \left[\bar{\lambda}(s_0,t) - 2\right] S_{\alpha\beta}(\mathbf{p},s_0,t)
\end{aligned} \tag{19}$$

From (19) one can see that all the "$\mathbf{p} = \mathbf{0}$" - components of the tensor $S_{\alpha\beta}(\mathbf{p})$ are coupled via the gradient deformation tensor $K_{\alpha\beta}$. Besides that, they also depend on other "$\mathbf{p} \neq \mathbf{0}$" - components which immediately implies that in order to compute $S_{\alpha\beta}(\mathbf{p})$ we should deal with the whole system of partial differential - integral equations. It is important to point out that (19) contains only ensemble averaged information. To show this, we note that the following relations should hold

$$< u_\alpha(s_0,t) b_\beta(s_0,t) >= \int d^3\mathbf{p}\, S_{\alpha\beta}(\mathbf{p},s_0,t) \frac{1}{2\pi^2 p^2} \tag{20}$$

$$< u_\alpha(s_0,t) u_\beta(s_0,t) >= \int d^3\mathbf{p}\, S_{\alpha\beta}(\mathbf{p},s_0,t) \frac{1}{4\pi p} \tag{21}$$

Therefore, it is clear that description of the ensemble by the tensor $S_{\alpha\beta}(\mathbf{p},s_0,t)$ is "one level higher" then that by the bond vector probability distribution function f since it only constains different second moments of f.
Finally, we notice that equation (19) is valid for all flow regimes and is quite universal. In the previous section we focused on slow flow and could derive the coherent equation set for the bond tensor $S_{\alpha\beta}$ itself (or, equivalently for the "$\mathbf{p} = \mathbf{0}$" components of the auxilary function $S_{\alpha\beta}(\mathbf{p})$). Let us check whether we can get this equation once again from (19). First, we note that in the slow flow regime stretching is small. Besides that averaging over orientation and local stretching can be done separately (12). Taking this into account, one can find that

$$< u_\alpha(s_0,t) b_\beta(s_0,t) >\approx S_{\alpha\beta}(\mathbf{p}=0,s_0,t) \quad < u_\alpha(s_0,t) u_\beta(s_0,t) >\approx S_{\alpha\beta}(\mathbf{p}=0,s_0,t) \tag{22}$$

From (20), (21), (22) it follows that in the slow flow regime we can neglect the contribution of the "$\mathbf{p} \neq 0$"- components of $S_{\alpha\beta}(\mathbf{p})$ in (19) and write down the closed equation for the "$\mathbf{p} = 0$"- components only. So, from (19) we again obtain the previous result (13).
An important comment should also be made on (19). When deriving it we ignored the CR term present in the original equation (4). Some care is needed when incorporating it into equation (19). We mentioned at the beginning that in general the hopping rate ν could

depend on the local stretching. Mead, Larson and Doi [6] proposed for ν the following expression

$$\nu(b) = \frac{\nu_0}{b}$$

where ν_0 does not depend on the local stretching. Note that this relation was obtained in a self-consistent way. Taking into account this result, the extra contribution due to constraint removal to be added to the right hand side of (19) is given by

$$3\pi\nu_0 a^2 \int d^3\mathbf{p} \frac{1}{p^2} \frac{\partial^2 S_{\alpha\beta}(\mathbf{p}, s_0, t)}{\partial s_0^2},$$

Final Remarks

Our objective was to derive an explicit equation (or set of equations) for the bond vector correlation function $S_{\alpha\beta}$. First, we focused on the simple case of slow flow when the stretching of the tethered chain is small. Then a remarkable reduction of the theory is found. One of the main results of this analysis is that the local stretching and orientation may be studied independently. As a consequence, the "full" distribution function $f(\mathbf{b}, s_0, t)$ can be split in two parts, namely, the distribution for the local stretching $f^{(b)}$ and the orientation probability distribution function $f^{(\mathbf{u})}$ (see (6)). We conclude that the pre-averaged approximation (12) can only be used under slow flows. Its accuracy decreases if the flow rate is increased.

We were able to derive the evolution equations for the introduced distributions $f^{(b)}$ and $f^{(\mathbf{u})}$ (equations (7) and (8), respectively). The solution of the equation for the stretching probability distribution function (7) is shown to have the Gaussian distribution in the stationary case and in absence of constraint removal. Its standard deviation is proportional to the local stretching. We point out that the evolution equation for the bond orientation function $f^{(\mathbf{u})}$ is in complete agreement with the result by Doi, Edwards [3] with the CR term left out.

Finally, we were able to write down the equation of motion for the bond vector correlator $S_{\alpha\beta}$ (13). It is a non-linear integral partial differential equation. The solution can probably be obtained only with the help of numerical procedures. We also considered the general case that holds for all flow rates. We introduced the auxiliary tensor $S_{\alpha\beta}(\mathbf{p}, s_0, t)$ (see (18)) and derived the evolution equation for it (see (19)). It is quite universal and in fact based on only a single assumption of locality of interaction between different parts of the tethered chain. As we mentioned before, this equation is "macroscopic" in the sense that it only includes ensemble averaged variables. For example, given $S_{\alpha\beta}(\mathbf{p}, s_0, t)$ one can easily find the correlator $S_{\alpha\beta}$ (3) by simply taking its value at the origin $\mathbf{p} = \mathbf{0}$.

References

[1] Tchesnokov M.A., Molenaar J., Slot J.J.M., Report "Dynamics of molecules grafted on solid wall during polymer melt extrusion".

[2] Dubbeldam J.L and Molenaar J., private communication, 2003, 12pp.

[3] Doi M, Edwards S, The theory of polymer dynamics, Oxford, 1986

[4] Joshi J., Lele A., Mashelkar R., Macromolecules, 34, 2001,p.3412

[5] Mead D., Larson R., Doi M., Macromolecules, 31, 1998, p. 7895

[6] Likhtman A., McLeish T., Macromolecules, 2002, 35, p. 6332

[7] Doi M., J. of Polymer Science, 18, 2055 (1980)