Impact of decoupling approximation between stretch and orientation in rheometrical and complex flow of entangled linear polymers

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Abstract

We study the rheometrical and complex flow response of the coupled version of the double-convection-reptation model with chain stretch. This model for monodisperse entangled linear polymers has recently been proposed by Marrucci and Ianniruberto [Phil. Trans. Roy. Soc. A, 361 (2003) 677–688] to overcome the anomalous shear thickening that was present in an earlier version of the theory. It avoids the decoupling approximation between orientation and stretch. Except for the shear thickening, both coupled and decoupled models show very similar results that are in qualitative agreement with available rheometrical data for two nearly monodisperse polymer solutions. In contraction/expansion flow simulations, however, higher Weissenberg numbers can be attained with the coupled model. Simulations in the stretch-dominated regime predict a dramatic growth of the upstream vortex activity and an increase of the pressure correction.

Key words: tube model, chain stretch, decoupling approximation, numerical simulation

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1 Introduction

Recently, Ianniruberto and Marrucci [1] have proposed a single segment, tube based constitutive equation for linear polymer melts that accounts for most of the currently known physics at that level of description. The so-called double-convection-reptation model with chain stretch (DCR-CS) had a number of deficiencies as shown by Wapperom *et al.* [2]. The most important one is a shear-thickening regime at shear rates of the order of the reciprocal Rouse time.

In response, Marrucci and Ianniruberto [3] concluded that the unphysical shear thickening was caused by the decoupling approximation of orientation and stretch, which is frequently used in tube theories. Indeed, for the newly proposed model that avoids decoupling, the shear viscosity decreases monotonically. To distinguish between the two models, we introduce the nomenclature ‘coupled DCR-CS model’ for the new model, while the previous model is referred to as ‘decoupled DCR-CS model’.

In this paper, we evaluate the coupled DCR-CS model in rheometrical and complex flows, and study in particular the effect of the decoupling approximation. We consider two nearly monodisperse solutions for which it was previously shown that the decoupled DCR-CS model predictions are in qualitative agreement with available experimental data in shear [4] and shear and uniaxial extension [5]. We show that both models predict very similar results in rheometrical flows, except for the anomalous shear thickening. We also consider the start-up flow through a 4:1:4 axisymmetric contraction/expansion geometry. We find that for the coupled DCR-CS model, a stable steady state solution can be reached at much higher values of the Weissenberg number. For one of the fluids this allowed us to reach flow rates at which polymer chains do get stretched. At these high levels of chain stretch, our simulations show a dramatic growth of the vortex activity, as well as an increase of the pressure correction. The coupled DCR-CS model is the first tube-based model that shows this behaviour.

2 Governing equations

2.1 Decoupled DCR-CS model

In the decoupled DCR-CS model [1] orientation and stretch are pre-averaged separately and each is governed by its own evolution equation.

Orientation is governed by a differential equation for the square of the orientation tensor $\boldsymbol{S}$:

$$\frac{D\boldsymbol{S}^2}{Dt} = \boldsymbol{\kappa} \cdot \boldsymbol{S}^2 + \boldsymbol{S}^2 \cdot \boldsymbol{\kappa}^T - 2\boldsymbol{S}^2 \left(\boldsymbol{\kappa} : \boldsymbol{S}\right) - \frac{2}{\tau}\left(\boldsymbol{S}^2 - \frac{1}{3}\boldsymbol{S}\right). \tag{1}$$

Here, D/Dt denotes the material derivative and $\boldsymbol{\kappa} = (\nabla \boldsymbol{v})^T$ is the transpose of the velocity gradient. The right-hand side of Eq. (1) consists of a convective part and a term that describes relaxation. The effective relaxation time τ is given by

$$\tau = \frac{1}{2\left(\frac{1}{\tau_\mathrm{d}} + |\boldsymbol{\kappa} : \boldsymbol{S}|\right)} + \tau_\mathrm{R}. \tag{2}$$

This formulation accounts for reptation (through the reptation time τ_d), for convective constraint release (CCR) (through $|\boldsymbol{\kappa} : \boldsymbol{S}|$), and for the intrinsic friction of the chain (through the Rouse time τ_R). The factor 2 appearing in Eq. (2) expresses double reptation and CCR2. For slow flows, reptation dominates and $\tau \approx \tau_\mathrm{d}/2 + \tau_\mathrm{R}$. For faster flows, CCR which is implemented through the $\boldsymbol{\kappa} : \boldsymbol{S}$ term, decreases the relaxation time τ. To avoid negative relaxation times in reversing flows [6], Marrucci *et al.* have corrected this contribution in an *ad hoc* manner by using the absolute value signs in Eq. (2). For very fast flows, when $|\boldsymbol{\kappa} : \boldsymbol{S}| \gg 1/\tau_\mathrm{d}$, τ reaches a non-vanishing minimum value equal to the Rouse time τ_R.

At flow rates larger than the reciprocal Rouse time, polymer chains get stretched. This is described by a separate evolution equation for the average stretch ratio λ,

$$\frac{D\lambda}{Dt} = \lambda\boldsymbol{\kappa} : \boldsymbol{S} - \frac{1}{\tau_\mathrm{R}}\left(f\lambda - 1\right). \tag{3}$$

The first term on the right-hand side of Eq. (3) accounts for affine deformation of the chain, while the second describes stretch relaxation with the Rouse time taken as the characteristic time. The non-linear factor f accounts for finite extensibility of the polymer chains,

$$f = \frac{\lambda_\mathrm{max} - 1}{\lambda_\mathrm{max} - \lambda}. \tag{4}$$

It is unity at equilibrium and approaches infinity at the upper limit λ_max of chain stretch.

Finally, the polymer contribution to the stress $\boldsymbol{T}$ results from anisotropic orientation and stretch and is given by the following algebraic relation:

$$\boldsymbol{T} = Gf\lambda^2\boldsymbol{S}, \tag{5}$$

where G is a modulus. The single-mode DCR-CS theory thus has four material parameters (G, λ_{max}, τ_{d}, τ_{R}), which can in principle all be determined from linear viscoelasticity data.

2.2 Coupled DCR-CS model

Recently, Marrucci and Ianniruberto proposed a coupled version of the DCR-CS model [3]. This model avoids the decoupling approximation between orientation and stretch. The basic dynamic variable is the second moment $\boldsymbol{A}$ of the distribution of end-to-end vectors of the subchains between consecutive entanglements. It is governed by a single evolution equation:

$$\frac{D\boldsymbol{A}}{Dt} = \boldsymbol{\kappa}\cdot\boldsymbol{A} + \boldsymbol{A}\cdot\boldsymbol{\kappa}^{T} - \frac{f}{\tau}\left(\boldsymbol{A} - \frac{\mathrm{tr}\,\boldsymbol{A}}{3}\boldsymbol{I}\right) - \frac{1}{3\tau_{\mathrm{R}}}\left(f\mathrm{tr}\,\boldsymbol{A} - 1\right)\boldsymbol{I}. \tag{6}$$

Note that tr $\boldsymbol{A}$ corresponds to the square of the stretch, λ^2. The factor f accounts for finite extensibility of the polymer chains and is modeled by

$$f = \frac{b-1}{b - \mathrm{tr}\,\boldsymbol{A}}, \tag{7}$$

where b corresponds to the square of the maximum stretch, λ_{max}.

The effective relaxation time is such that

$$\frac{1}{\tau} = \frac{2}{\tau_{\mathrm{d}}} + \left(\frac{1}{\tau_{\mathrm{R}}} - \frac{2}{\tau_{\mathrm{d}}}\right)\frac{\beta(f\mathrm{tr}\,\boldsymbol{A} - 1)}{1 + \beta(f\mathrm{tr}\,\boldsymbol{A} - 1)}. \tag{8}$$

It accounts for the same physics as the decoupled model, i.e. reptation, convective constraint release, and Rouse relaxation. However, the way these effects are implemented in the effective relaxation time is quite different. First, the effective relaxation time does not have any contribution from the Rouse time at equilibrium, $\tau_{\mathrm{eq}} = \tau_{\mathrm{d}}/2$. Second, convective constraint release which decreases τ to a lower limit, the Rouse time τ_{R}, is now implemented using the trace of the configuration tensor instead of using $\boldsymbol{\kappa} : \boldsymbol{S}$. This has the advantage that no *ad hoc* correction with absolute value signs is necessary to assure a positive relaxation time. Furthermore, in this way the model also becomes consistent with non-equilibrium thermodynamics. The extra numerical parameter β measures CCR effectiveness and should be chosen equal to 2 or larger to guarantee a strictly monotonic viscosity curve [3].

As noted before, stretch is implemented in the model via the trace of $\boldsymbol{A}$. By taking the trace of Eq. (6) we arrive at

$$\frac{D\mathrm{tr}\,\boldsymbol{A}}{Dt} = 2\boldsymbol{\kappa} : \boldsymbol{A} - \frac{1}{\tau_{\mathrm{R}}}(f\mathrm{tr}\,\boldsymbol{A} - 1). \tag{9}$$

Thus stretch has a fixed relaxation time of τ_{R} and is not affected by CCR, similar to the decoupled DCR-CS model.

Finally, the polymer contribution to the stress results from the now undecoupled anisotropic orientation and stretch,

$$\boldsymbol{T} = Gf\boldsymbol{A}, \tag{10}$$

where G is a modulus. The coupled DCR-CS model thus has four material parameters (G, λ_{max}, τ_{d}, τ_{R}), and the numerical CCR-parameter β.

2.3 How to choose equivalent material parameters?

In order to ensure that stretch takes place at the same rates of deformation with both models, the Rouse time in the coupled model has to be chosen half of the Rouse time of the decoupled model. This result can easily be obtained from the equation for stretch, Eq. (9), by using $\boldsymbol{A} = \lambda^2\boldsymbol{S}$ and $\mathrm{tr}\,\boldsymbol{A} = \lambda^2$. Then we arrive at

$$\frac{D\lambda}{Dt} = \lambda\boldsymbol{\kappa} : \boldsymbol{S} - \frac{1}{2\tau_{\mathrm{R}}}\left(f\lambda - \frac{1}{\lambda}\right). \tag{11}$$

If we compare this equation with Eq. (3) for the decoupled model we find that the Rouse time of the coupled model is half the value of the decoupled model. We also remark in passing that the relaxation term in Eq. (11) contains a term $1/\lambda$ instead of a 1 in the decoupled theory.

Since $\mathrm{tr}\,\boldsymbol{A}$ is proportional to the square of stretch, the value of b is taken as λ_{max}^2. The non-linear factor f associated with the finite extensibility of the chain, however, is different for the two models. In terms of λ and λ_{max} the factor f, Eq. (7), can be written as

$$f = \frac{\lambda_{\mathrm{max}}^2 - 1}{\lambda_{\mathrm{max}}^2 - \lambda^2} = \frac{\lambda_{\mathrm{max}} - 1}{\lambda_{\mathrm{max}} - \lambda}\frac{\lambda_{\mathrm{max}} + 1}{\lambda_{\mathrm{max}} + \lambda}, \tag{12}$$

which is always smaller than for the decoupled model Eq. (4).

Also the meaning of the modulus G in both models is not exactly the same. For the decoupled version, the modulus, the relaxation time at equilibrium τ_{eq}, and the zero-shear viscosity are related by

$$\eta_0 = \frac{G\tau_{\mathrm{eq}}}{6}, \tag{13}$$

while for the coupled model we have

$$\eta_0 = \frac{G\tau_{\mathrm{eq}}}{3}. \tag{14}$$

In case we choose the relaxation times at equilibrium equal for both models, the modulus of the decoupled model is exactly twice the modulus of the coupled model. When the reptation times τ_{d} of both models are chosen to be equal, however, this is no longer true. This is caused by a difference in the relaxation time at equilibrium τ_{eq}. For the decoupled model, the Rouse time contributes to τ_{eq},

$$\tau_{\mathrm{eq}} = \tau_{\mathrm{d}}/2 + \tau_{\mathrm{R}}, \tag{15}$$

while for the coupled version it does not,

$$\tau_{\mathrm{eq}} = \tau_{\mathrm{d}}/2. \tag{16}$$

Since for well-entangled polymers τ_{d} is much bigger than τ_{R}, the difference in τ_{eq} will generally be small.

3 Polystyrene solution

Bhattacharjee *et al.* [5] have published experimental data in both shear and extension for a 10 % solution of a 3.9 10^6 molecular weight polystyrene in diethyl phthalate. In addition, they derived the values of the decoupled DCR-CS model parameters. Here, we use the same parameter values except for the modulus. The modulus is chosen such that the zero-shear viscosity of the model equals the zero-shear viscosity of the data, $\eta_0 = 4570$ Pa $\cdot$ s. All model parameters are given in Table 1.

The parameters of the coupled model are chosen based on the discussion in section 2.3. This means that for τ_{R} we take half of the value of the decoupled

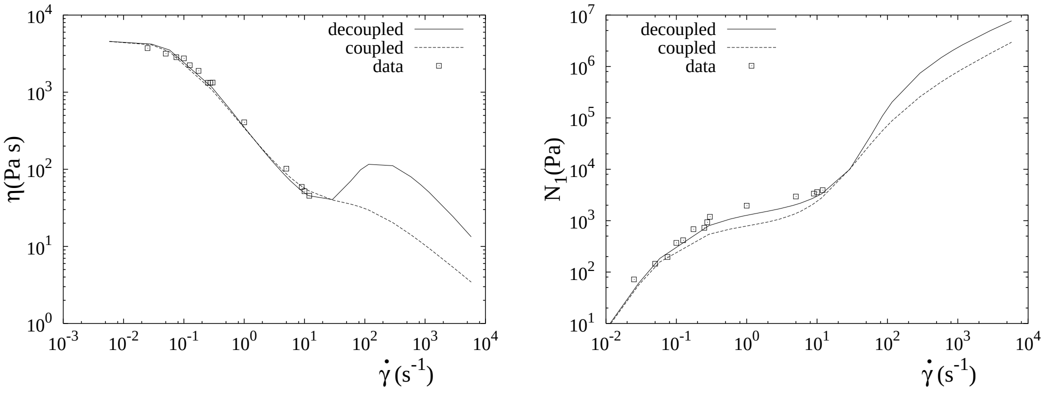
DCR-CS model	G(Pa)	τ_{d}(s)	τ_{R}(s)	stretch	β
decoupled	3083	17.22	0.282	$\lambda_{\max} = 13.6$	-
coupled	1592	17.22	0.141	$b = 184.96$	2

Table 1
Model parameters for the nearly monodisperse polystyrene solution of [5].

model and for b we take $\lambda^2_{\max}$. Furthermore, we take equal values for the reptation time τ_{d} in both models. The value of G is then chosen so that the zero-shear viscosities, Eqs. (13,14), of both models are equal.

3.1 Rheometrical results

In Fig. 1(a) we consider the impact of decoupling on the steady shear viscosity. One of the main drawbacks of the decoupled DCR-CS model is the existence of a shear-thickening regime at shear rates of the order of the reciprocal Rouse time [2] and for significant values of $\lambda_{\max}$. Figure 1(a) shows that for the coupled DCR-CS model the viscosity decreases monotonically as a function of the shear rate. As argued by Marrucci and Ianniruberto [3] this was caused by the decoupling approximation of orientation and stretch and was the main reason to introduce the coupled version of the model. From Fig. 1(a) we conclude that both models are in qualitative agreement with experiments of [5] in the range of shear rates for which experimental data are available, i.e. in the reptation and CCR dominated regimes. In the stretch regime, where both models start to differ significantly, no experimental data are available, unfortunately. Whether the change of slope in viscosity that the coupled DCR-CS



(a) (b)

Fig. 1. Steady-state shear response of the decoupled and coupled DCR-CS models (polystyrene solution): (a) shear viscosity η, and (b) first normal stress difference N_1 as a function of shear rate $\dot{\gamma}$. Data are from [5].

model shows is physical or an artifact of the model therefore remains to be confirmed.

Similar observations can be made for the first normal stress difference N_1 as displayed in Fig. 1(b). In the reptation and CCR dominated regimes the decoupled and coupled DCR-CS models show similar responses in qualitative agreement with the experimental data. When polymer molecules are stretched, both models show an increase in N_1. As for the shear viscosity, this response remains to be verified experimentally.

Figure 2 compares the viscosity in start up of shear at various shear rates. The early-time overshoots at very high shear rates observed previously for the DCR-CS model [2] are also present for the coupled model. They even become apparent at somewhat lower shear rates and are more pronounced. Therefore, this is not an artifact of the decoupling approximation but inherent to the DCR-CS theory. Whether the early-time overshoots, above the linear viscoelastic envelope, are an artifact of the theory needs to be established.

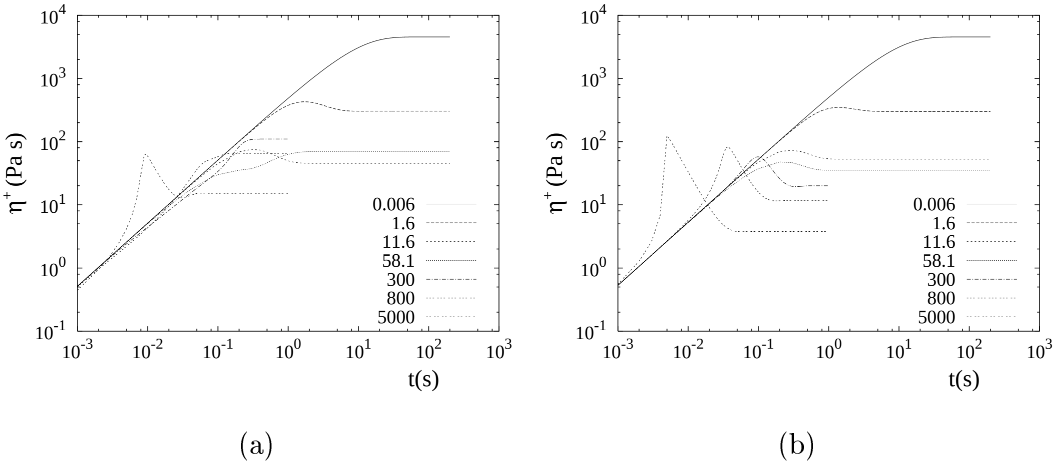


Fig. 2. Model predictions for the transient shear response at shear rates (s^{-1}) given in the legends (polystyrene solution): (a) decoupled DCR-CS and (b) coupled DCR-CS.

Bhattacharjee *et al.* [5] have shown that the decoupled DCR-CS model also shows qualitative agreement with experimental data in steady uniaxial extension. For this flow type, experimental data are not only available in the reptation and CCR dominated regimes, but also in the regime where polymer chains stretch. Figure 3 shows that the coupled DCR-CS model predicts a qualitatively similar steady elongational viscosity, although the results in the CCR-dominated regime are consistently lower than for the decoupled version (and also lower than the experimental data).

In transient uniaxial extensional both models show also a satisfactory agreement with the experimental data. Figure 4 shows the first normal stress dif-

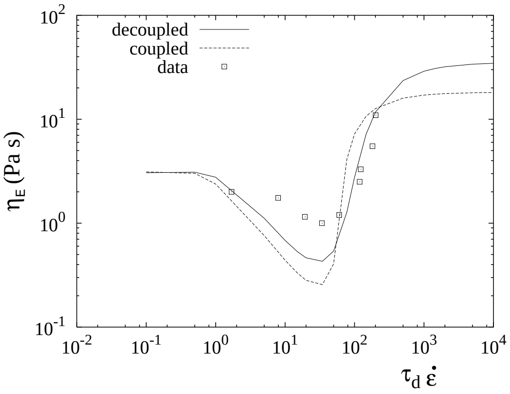
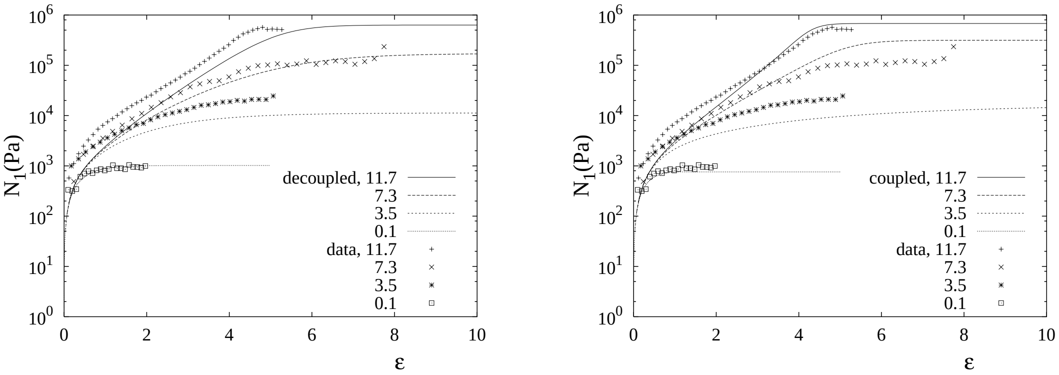


Fig. 3. Steady-state response in uniaxial extension of the decoupled and coupled DCR-CS models (polystyrene solution). Data are from [5].



(a)

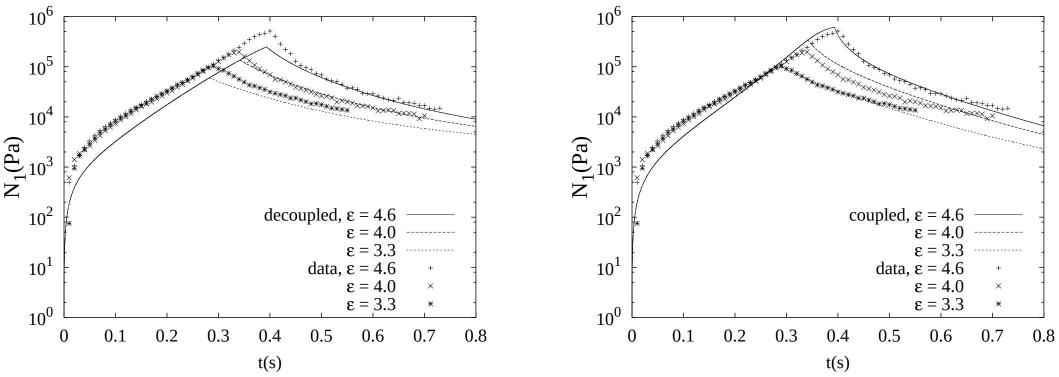
(b)

Fig. 4. Transient response in uniaxial extension at elongation rates (s^{-1}) given in the legends (polystyrene solution): (a) decoupled DCR-CS and (b) coupled DCR-CS. Data are from [5].

ference as a function of the Henky strain. Both models show similar responses and agree qualitatively with the experimental data for various elongation rates. The underprediction at small Henky strains (small times) is inherent to the single segment approximation. In start-up of shear flow, Ianniruberto and Marrucci [4] have shown that a two-segment model that distinguishes between internal and end segments significantly improved the model predictions at small times.

Stress relaxation after cessation of uniaxial extension is displayed in Fig. 5. There we show the first normal stress difference in uniaxial extension at an elongation rate of $\dot{\epsilon} = 11.7\ \mathrm{s}^{-1}$ and up to various Henky strains. Again, a good qualitative agreement with experimental data is observed.

We conclude this section on rheometrical flow predictions for the polystyrene solution by examining the stretch in steady shear and uniaxial extension. The stretch curves, λ for the decoupled and $\sqrt{\mathrm{tr}\,\boldsymbol{A}}$ for the coupled DCR-CS model,



(a) (b)

Fig. 5. Stress relaxation after uniaxial extension at $\dot{\epsilon} = 11.7$ s^{-1} at Henky strains indicated in the legends (polystyrene solution): (a) decoupled DCR-CS and (b) coupled DCR-CS. Data are from [5].

are shown in Fig. 6. As expected, with increasing Weissenberg number both models asymptotically approach the maximum stretch in uniaxial extension. We note for further reference that at identical elongation rates, the coupled DCR-CS model predicts a larger stretch. This appears to be a consequence of the smaller factor f compared to the decoupled model. At steady state, $\boldsymbol{\kappa} : \boldsymbol{S}$ is balanced by f at high elongation rates for both models, see Eqs. (3,11). This requires a larger value of λ for the coupled DCR-CS model as can easily be seen from Eq. (12).

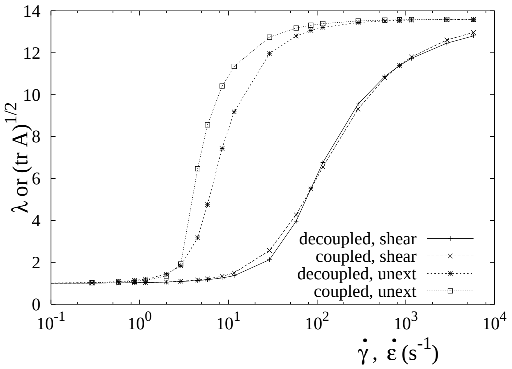


Fig. 6. Model predictions of stretch in steady shear and extension for the decoupled and coupled DCR-CS models (polystyrene solution).

In shear, polymer chains are stretched at larger deformation rates than in extension, as expected. Remark that in shear polymer chains also reach asymptotically the maximum stretch for both the decoupled and coupled DCR-CS model. This is in sharp contrast with the pompom model [7], for example, where the stretch approaches $1 + \tau_s/(2\tau_b)$ at large shear rates. Since the backbone relaxation time τ_b is larger than the stretch relaxation time τ_s, the levels of stretch attained in steady shear flows will be much less. Which type of response is more likely is still an open question.

3.2 Flow in a constriction

We consider the start-up flow through an axisymmetric 4:1:4 constriction with rounded corners, as depicted in Fig. 7 along with the mesh. As a characteristic time we use the contribution of the reptation time to the equilibrium relaxation time, i.e. $\tau_{\mathrm{d}}/2$. The Weissenberg number is then $We = \tau_{\mathrm{d}} U/2R$, with U the average velocity at the section of the smallest gap radius R. We have shown previously [2,6] that the mesh of Fig. 7 is sufficiently fine for the range of Weissenberg numbers considered here. Around the smallest gap radius, the constriction wall is circular with diameter R. The lengths of the inlet and outlet regions are taken $19.5R$, and at both inlet and outlet we impose fully developed velocity boundary conditions, which have been calculated separately. No-slip velocity boundary conditions are specified at the wall and symmetry conditions hold at the centerline. For the decoupled DCR-CS model orientation $\boldsymbol{S}$ and stretch λ are imposed at the inlet. For the coupled DCR-CS model the configuration tensor is specified at the inlet.

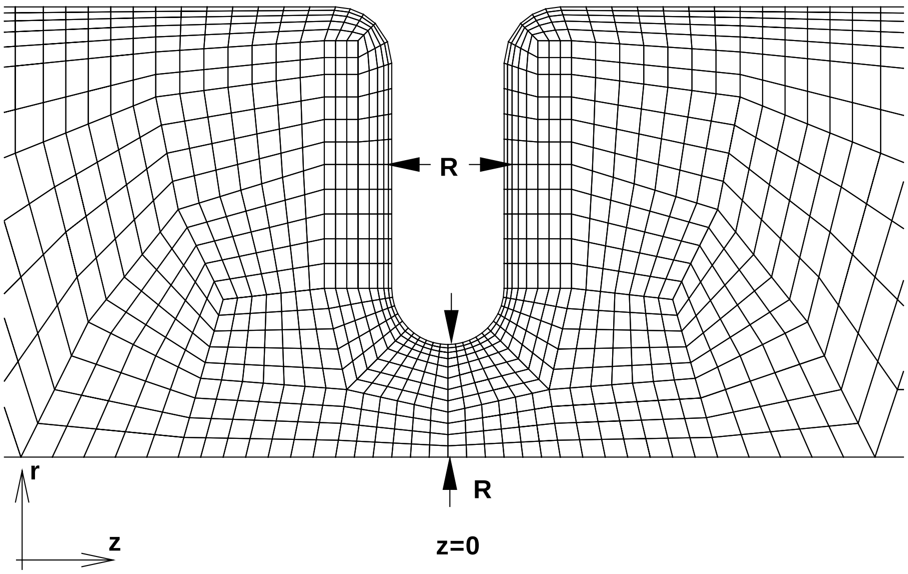
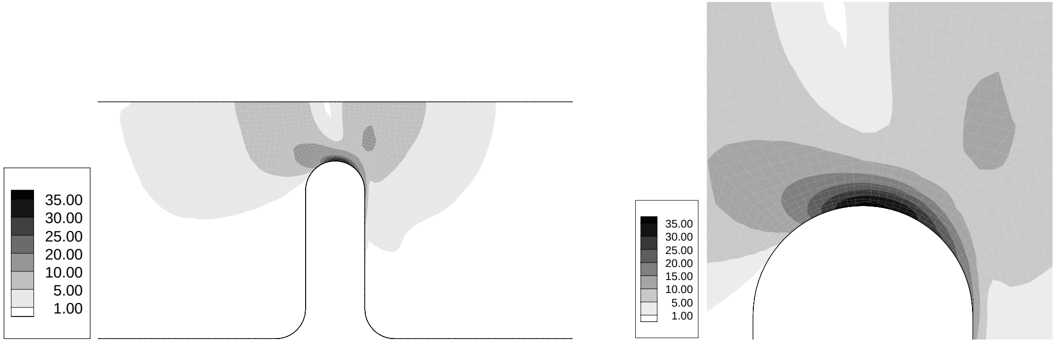


Fig. 7. Zoom of 4:1:4 constriction geometry with rounded corners and medium mesh.

Steady-state regimes are obtained as a long-time limit of transient simulation starting from the equilibrium state. At each time step the conservation laws are decoupled from the constitutive equations. The equations of motion, with the solvent viscosity strictly set to zero, are solved with the DEVSS Galerkin finite element method introduced in [8]. The constitutive equations are solved with the help of the backward-tracking Lagrangian particle method (see [9] for a detailed description of the numerical scheme).

In the 4:1:4 constriction flow, a stable steady state could be obtained up to $We = 50$ for the decoupled model and 100 for the coupled model. Figure 8 displays the contours of the second invariant of the rate-of-deformation tensor at $We = 50$ using the coupled model. The maximum strain rate of 37.5 s^{-1} is located at the constriction wall, while deformation rates near the centerline are considerably smaller. The maximum strain rate at the centreline is approximately 10 s^{-1} which corresponds to an elongation rate of almost 6 s^{-1}. As can be observed from the rheometrical data, simulations are still in the CCR dominated regime at these values of deformation rates so that polymer chains do not become highly stretched. This can be verified in Fig. 9 which shows the stretch contours, i.e. λ for the decoupled and $\sqrt{\mathrm{tr}\,\boldsymbol{A}}$ for the coupled model, at Weissenberg numbers of 10 and 50. As expected, stretch is only moderate at $We = 50$ (note that full stretch corresponds to $\lambda_{\max} = 13.6$), while stretch is practically absent at $We = 10$.

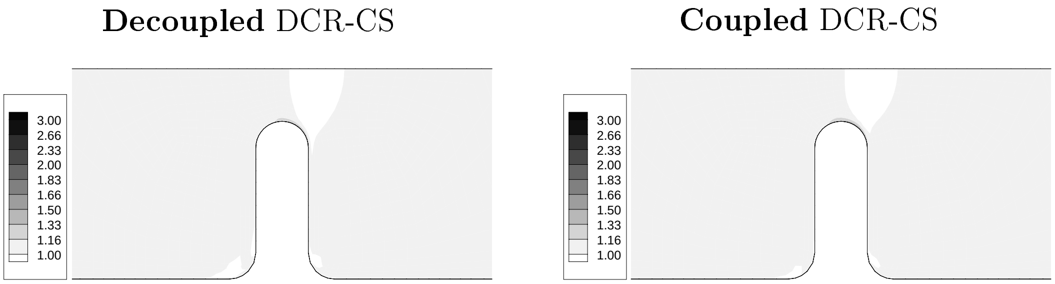


(a) (b)

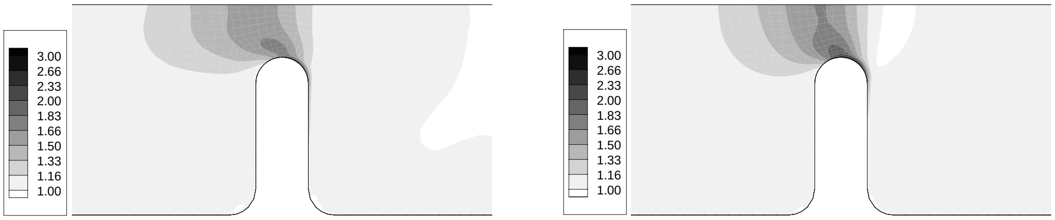
Fig. 8. Second invariant of the rate of deformation tensor for coupled DCR-CS model at $We = 50$ (polystyrene solution), (a) region around the constriction, and (b) zoom at the constriction wall. Flow is from left to right (as in all subsequent figures).

These low levels of chain stretch correlate with a decreasing vortex activity as can be seen from Fig. 10. This result does not come as a surprise and was already found previously in simulations with decoupled versions of the model in the CCR dominated regime [2]. Since the impact of the decoupling approximation of orientation and stretch only becomes apparent when polymer molecules are significantly stretched, the vortex structures of both models are very similar.

For the coupled model, significantly higher Weissenberg numbers of $\mathcal{O}(100)$ could be reached, but these were not large enough to reach the high-stretch regime. For the sake of brevity, these results are not included here. Instead, we will discuss the impact of chain stretch for the polybutadiene solution in section 4 for which we do find stable steady state results when polymer chains are nearly fully stretched.



(a) *We* = 10: Max 1.47 (b) *We* = 10: Max 1.58



(c) *We* = 50: Max 2.41 (d) *We* = 50: Max 3.09

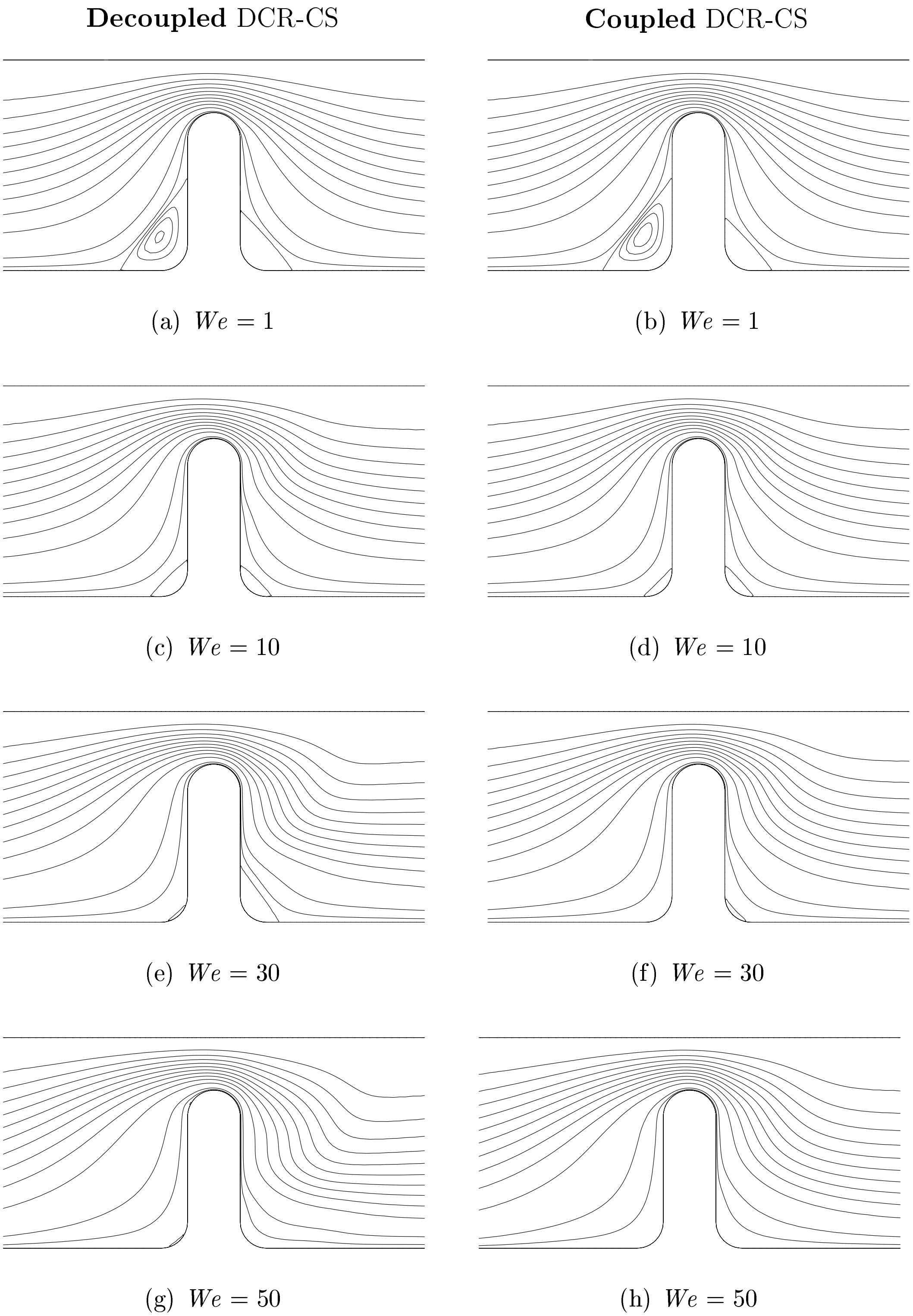
Fig. 9. Steady-state stretch for the decoupled (left) and coupled (right) DCR-CS models at various Weissenberg numbers (polystyrene solution).

DCR-CS model	G(Pa)	τ_d(s)	τ_R(s)	stretch	β
decoupled	9000	1.5	0.5	$\lambda_\mathrm{max} = 2.5$	-
coupled	4500	2.5	0.25	$b = 6.25$	2

Table 2
Model parameters for the decoupled and coupled DCR-CS model for the polybutadiene solution of [10].

4 Polybutadiene solution

For a nearly monodisperse 7.5 % polybutadiene solution of 3.5 10^5 molecular weight in hydrocarbon oil, we use parameter values identified by Ianniruberto & Marrucci [4]. Only shear data are available for this fluid [10] and the parameter values of both the decoupled and coupled DCR-CS model are given in Table 2. To identify the corresponding parameter values of the coupled DCR-CS model we proceed slightly differently than for the polystyrene solution. Since the Rouse time is relatively large compared to the reptation time, the relaxation times at equilibrium differ significantly when equal values of the reptation time are chosen. (Remember that for the decoupled model, the Rouse time contributes to τ_eq whereas it does not for the coupled version.) To obtain the same response at low deformation rates, we therefore choose the equilibrium relaxation time to be equal for both models by adjusting the reptation time τ_d of the coupled model.



(a) $We = 1$ (b) $We = 1$

(c) $We = 10$ (d) $We = 10$

(e) $We = 30$ (f) $We = 30$

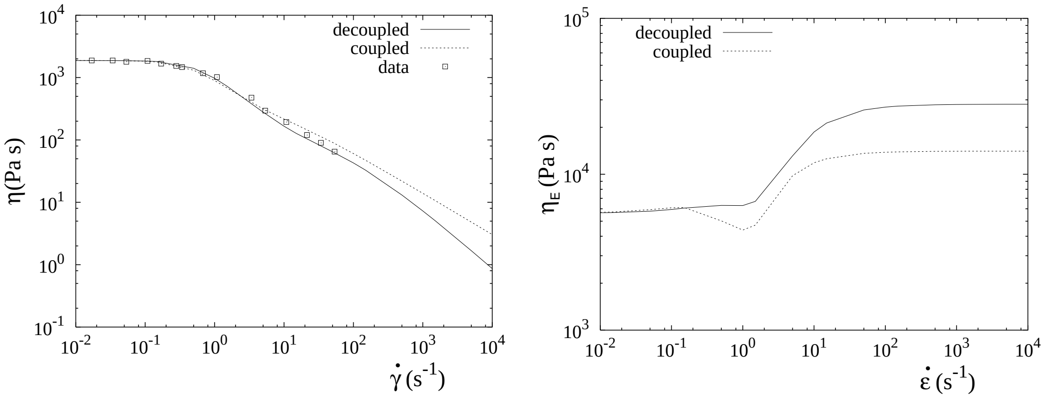
(g) $We = 50$ (h) $We = 50$

Fig. 10. Steady-state streamlines for the decoupled (left) and coupled (right) DCR-CS models at various Weissenberg numbers (polystyrene solution).

The other parameter values are chosen following the same procedure as for the polystyrene solution, i.e. the Rouse time in the coupled model has been chosen half of the Rouse time of the decoupled model, and for the value of b we take again $\lambda_{\max}^2$. The modulus is chosen such that the zero-shear viscosities are equal for both models. Since the relaxation times at equilibrium are equal for the polybutadiene solution, it follows from Eqs. (13,14) that the modulus in the coupled model is exactly half of the value of the decoupled model.

4.1 Rheometrical results

For the shear viscosity in Fig. 11(a), we observe a good agreement with the experimental data in the reptation dominated regime. In the CCR dominated regime, the decoupled and coupled DCR-CS models have a slightly different slope resulting in a slight underprediction and overprediction, respectively. This difference does not come as a surprise since for relatively large values of τ_{R} the effective relaxation time is quite different for both models and we chose to match the relaxation time at equilibrium. We also note that due to the relatively low value of $\lambda_{\max}$, the decoupled model does not show any shear thickening but only a change of slope, just as for the coupled model.

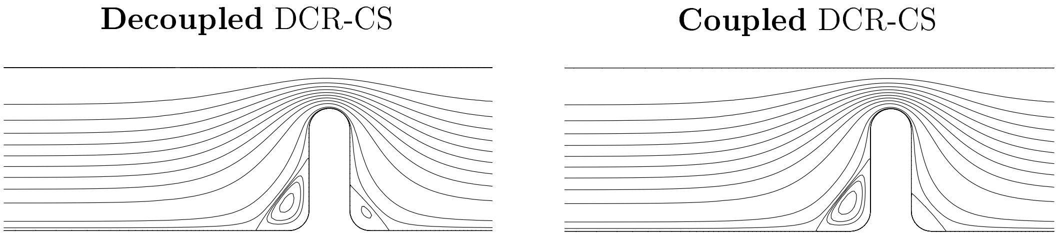


(a) (b)

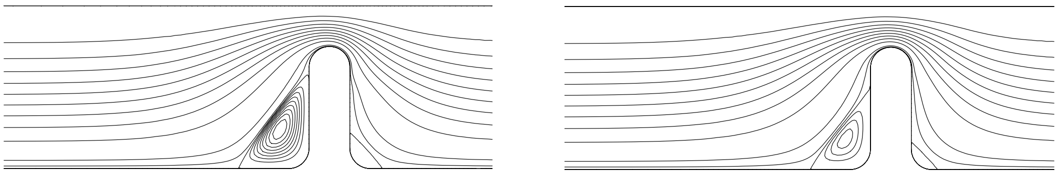
Fig. 11. Steady-state response of the decoupled and coupled DCR-CS models (polybutadiene solution): (a) shear viscosity η, and (b) uniaxial extensional viscosity η_E as a function of shear rate $\dot{\gamma}$ and elongation rate $\dot{\epsilon}$, respectively. Data are from [10].

To better understand the complex flow simulations, we also compare in Fig. 11(b) the model predictions in uniaxial extension. For the decoupled DCR-CS model, the uniaxial extensional viscosity increases monotonically and approaches asymptotically its upper limit. For the parameter values of the coupled model that we have chosen, η_E first goes through a minimum and then approaches a maximum that is considerably lower.

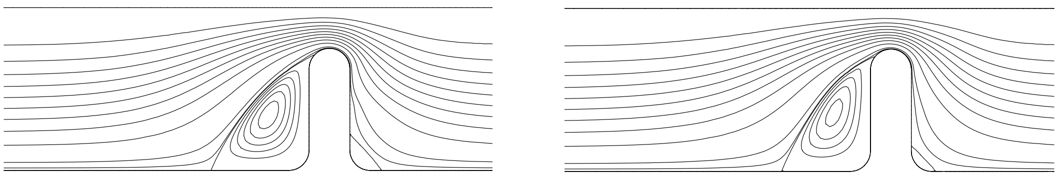
As a characteristic time, we use the equilibrium relaxation time. The Weissenberg then becomes $We = \tau_{\mathrm{eq}} U/R$. For the decoupled DCR-CS model, a stable steady state could be reached for Weissenberg numbers up to 15. From Fig. 12 we observe that for these values of the Weissenberg number a similar



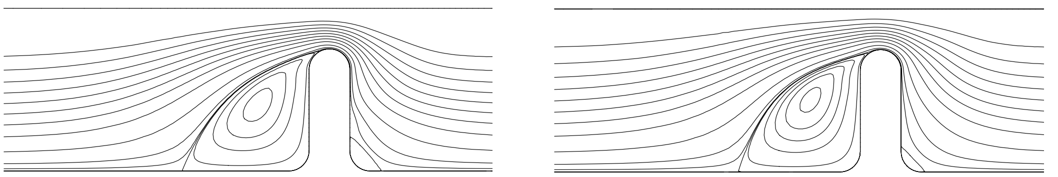
(a) $We = 1$: $I_\psi = 0.002$ (b) $We = 1$: $I_\psi = 0.002$



(c) $We = 5$: $I_\psi = 0.005$ (d) $We = 5$: $I_\psi = 0.002$



(e) $We = 10$: $I_\psi = 0.018$ (f) $We = 10$: $I_\psi = 0.014$



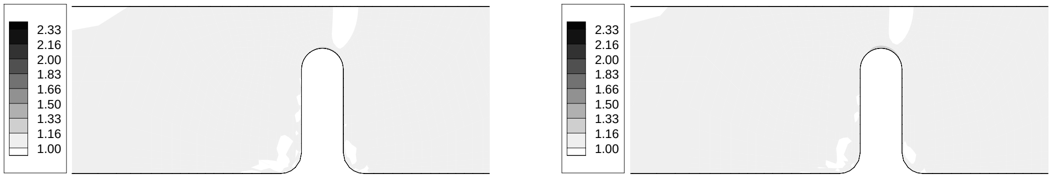
(g) $We = 15$: $I_\psi = 0.034$ (h) $We = 15$: $I_\psi = 0.046$

Fig. 12. Steady-state streamlines for the decoupled (left) and coupled (right) DCR-CS models at various Weissenberg numbers (polybutadiene solution).

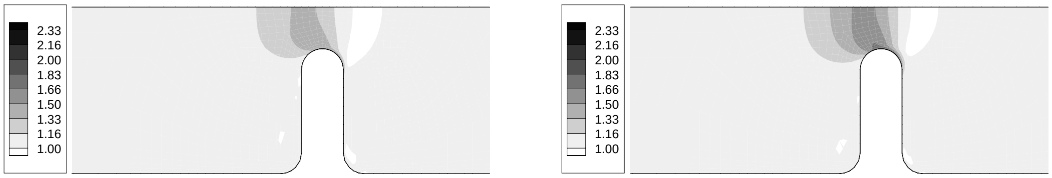
vortex growth of the upstream vortex is predicted by both the coupled and decoupled DCR-CS models. Quantitatively, however, there are some differences like in the vortex intensity I_ψ and the considerably larger vortex at the moderate Weissenberg number of $We = 5$. This is not unexpected since the extensional viscosity of the decoupled model increases monotonically, while for the coupled version η_E goes through a minimum at moderate levels of $\dot{\epsilon}$ before it starts to increase due to chain stretch.

Figure 13 shows the corresponding levels of chain stretch, i.e. λ and $\sqrt{\operatorname{tr} \boldsymbol{A}}$, respectively, at the various Weissenberg numbers. Although the predictions of both models are again in qualitative agreement, the stretch levels in the constriction predicted by the coupled model are consistently higher. However, this does not lead to an earlier apparent breakdown of the numerical scheme.

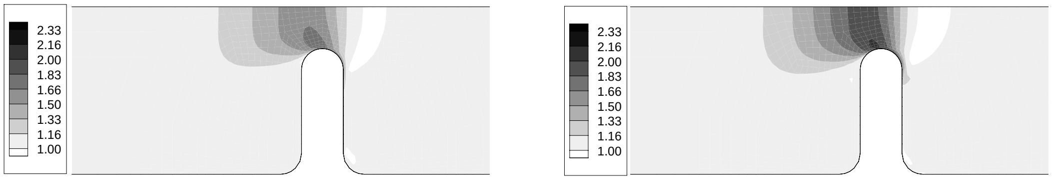
Decoupled DCR-CS **Coupled** DCR-CS



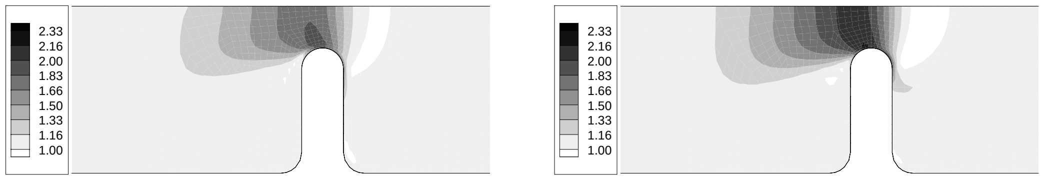
(a) $We = 1$: Max 1.34 (b) $We = 1$: Max 1.44



(c) $We = 5$: Max 1.66 (d) $We = 5$: Max 1.94



(e) $We = 10$: Max 1.85 (f) $We = 10$: Max 2.12



(g) $We = 15$: Max 1.96 (h) $We = 15$: Max 2.21

Fig. 13. Steady-state stretch for the decoupled (left) and coupled (right) DCR-CS models at various Weissenberg numbers (polybutadiene solution).

On the contrary, it is the decoupled model for which no stable steady state can be obtained for Weissenberg numbers larger than 15.

For the coupled model considerably higher levels of We can be attained. Figure 14 displays the contours of the second invariant of the rate-of-deformation tensor at the highest Weissenberg number for which we have performed calculations, $We = 50$. It is clear that we do reach the stretch-dominated regime near the constriction wall as well as near the axis of symmetry.

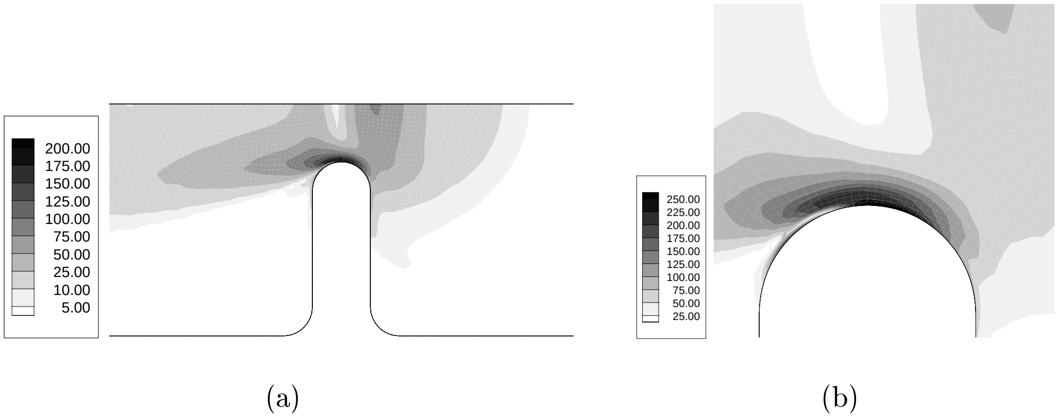
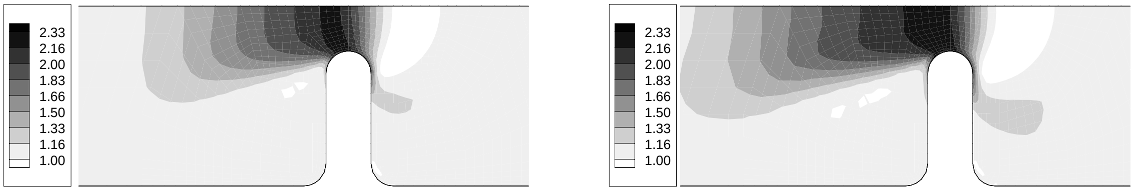


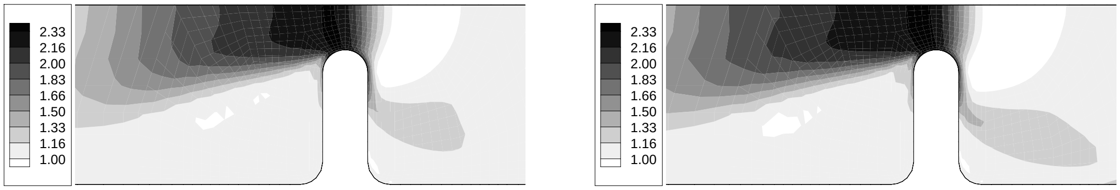
Fig. 14. Second invariant of the rate of deformation tensor for coupled DCR-CS model at $We = 50$ (polybutadiene solution), (a) region around the constriction, and (b) zoom at the constriction wall.

The contours of the stretch $\sqrt{\text{tr}\,\boldsymbol{A}}$ in Fig. 15 show that for Weissenberg numbers between 20 and 50 polymer chains become highly stretched in the constriction region, from the wall to the axis of symmetry. This region extends ever further upstream as the Weissenberg number increases, and at $We = 50$ chain stretch is already significant at a distance of $4R$ upstream of the constriction. Furthermore, full stretch is almost reached at this Weissenberg number. These high levels of stretch correlate with a dramatic growth of both the size and intensity of the upstream vortex as can be observed from Fig. 16.

In our simulations with previous tube models for linear polymer melts, regions with nearly fully extended polymer chains could not be reached and a decreasing pressure correction that is typical for non-elastic shear-thinning fluids was observed [2,6]. Here, the nondimensional pressure correction is defined as $(\Delta p - \Delta p^0)/\Delta p^0$, where Δp is the total pressure drop in the flow domain and Δp^0 corresponds to the pressure drop in a fully-developed Poiseuille flow in a tube without the constriction, i.e. of length $40R$ and radius $4R$. At the high levels of stretch that we can reach with the coupled DCR-CS model, however, we obtain for the first time an increase of the pressure correction (see Fig. 17). After an initial decrease in the CCR dominated regime, the pressure correction starts to increase at about $We = 10$. At corresponding levels of stretch the numerical simulations for the decoupled DCR-CS model do not reach a steady

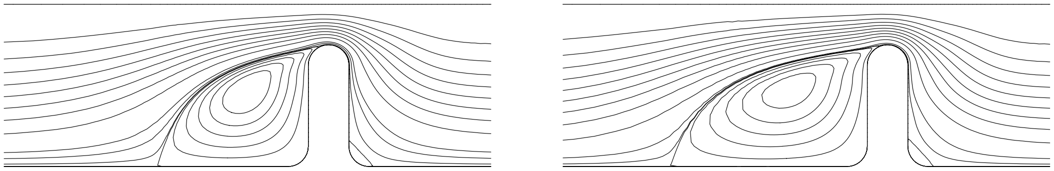


(a) $We = 20$: Max 2.29 (b) $We = 30$: Max 2.43

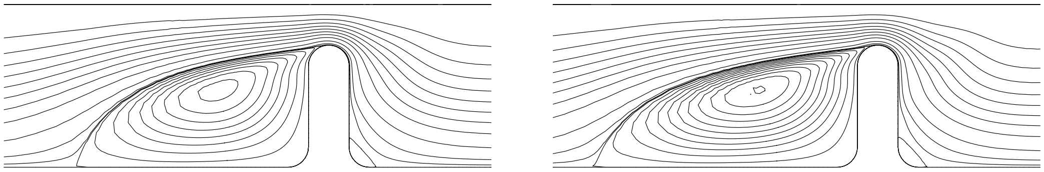


(c) $We = 40$: Max 2.46 (d) $We = 50$: Max 2.47

Fig. 15. Steady-state stretch for the coupled DCR-CS model at high Weissenberg numbers (polybutadiene solution).



(a) $We = 20$: $I_\psi = 0.078$ (b) $We = 30$: $I_\psi = 0.122$



(c) $We = 40$: $I_\psi = 0.148$ (d) $We = 50$: $I_\psi = 0.161$

Fig. 16. Steady-state streamlines for the coupled DCR-CS model at high Weissenberg numbers (polybutadiene solution).

state regime. For comparison we also show in Fig. 17 the pressure correction for the polystyrene solution using the coupled DCR-CS model. In this case, the increase is absent since the maximum Weissenberg number up to which a stable steady state could be reached corresponds to the CCR-dominated regime.

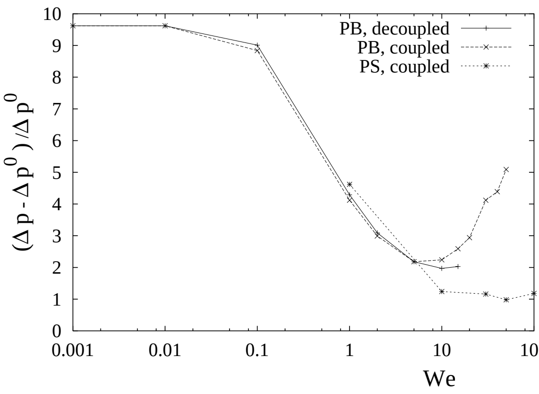


Fig. 17. Non-dimensional pressure correction in the constriction as a function of the Weissenberg number (polybutadiene and polystyrene solutions).

5 Concluding remarks

We have evaluated the impact of the decoupling approximation in the DCR-CS theory describing monodisperse linear polymer melts. For this we considered the response of both a polystyrene and a polybutadiene nearly monodisperse solution in rheometrical and complex flows.

Both coupled and decoupled DCR-CS models yield satisfactory predictions of shear data available within the reptation and CCR-dominated ranges of shear rates. However, the coupled version does not show the anomalous shear thickening behaviour of the decoupled model at shear rates where stretch comes in to play. Instead, its viscosity curve shows a change of slope just outside the experimental range of shear rates. Therefore, shear experiments in the stretch-dominated regime are needed to further evaluate the coupled DCR-CS model. For the polystyrene solution, both models are in qualitative agreement with available uniaxial extension data in the reptation, CCR and stretch-dominated regimes. This holds both for steady, start-up, and stress relaxation experiments.

In a 4:1:4 constriction flow, both models predict very similar results for a particular fluid and at identical Weissenberg numbers. However, stable steady-state solutions can be obtained up to a higher Weissenberg number with the coupled DCR-CS model. Maximum Weissenberg numbers reached for the polystyrene solution are within the reptation and CCR-dominated regimes and correspond to a monotonic decrease of the upstream vortex and very weak stretch. For the polybutadiene solution, however, the high-stretch regime can be reached. The large levels of stretch predicted by the coupled DCR-CS model at high Weissenberg numbers correlate with significant upstream vortex activity. Additionally, the coupled DCR-CS model then predicts an increase of the pressure correction. This is a "first" in the realm of available tube models.

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