An Evaluation of Single-Segment Reptation Theories for Linear Entangled Polymeric Systems#

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Received: 5.12.2003, Final version: 13.1.2004

#Dedicated to the memory of Piyush G. Gigras

Abstract:
A short synopsis of the recently proposed reptation models based on the Doi and Edwards' tube concept is provided. Specifically, a critical examination of a number of theories like the "simplified" Mead-Larson-Doi model, the Öttinger model and the "Double Convection Reptation" model of Marrucci and coworkers has been performed. These models have been chosen due the fact that are computationally tractable as they mimic the chain dynamics in the tube using unconnected portions of the chain in a mean field way. Overall, we find each of these models to be equally competitive barring a few exceptional cases, where it is suspected that certain critical assumptions, made during the formulation of the model could lead to inaccurate predictions under transient or Lagrangian unsteady settings.

Zusammenfassung:
Ein kurzer Überblick einiger kürzlich vorgeschlagener Reptationsmodelle, welche auf dem Röhrenkonzept von Doi und Edwards basieren, wird vorgestellt. Im speziellen wird eine kritische Untersuchung mehrerer Ansätze durchgeführt, wie dem vereinfachten Modell nach Mead, Larson und Doi, des Modells nach Öttinger und dem Doppelt-Konvektions-Reptations-Modell nach Marrucci und Mitarbeitern. Diese Modelle wurden deswegen ausgewählt, da sie numerisch gelöst werden können. Dies beruht darauf, dass die gesamte Kettendynamik in den Röhren durch einzelne Teile der Kette im Rahmen einer Mean-Feld Approximation behandelt werden kann. Insgesamt findet man, dass von einigen wenigen Ausnahmen abgesehen, alle Modelle vergleichbare Stärken besitzen. Hier wird vermutet, dass gewisse Annahmen, welche bei der Formulierung des Modells gemacht wurden, zu ungenauen Vorhersagen unter transienten oder im Lagrangen Sinne nicht stationären Bedingungen führen.

Résumé:
Un court résumé des modèles récemment proposés de reptation basée sur le concept du tube de Doi et Edwards est présenté. Spécifiquement, un examen critique d'un certain nombre de théories telles que le modèle simplifié de Mead-Larson-Doi, le modèle d'Öttinger et le modèle Double Convection Reptation de Marrucci, a été entrepris. Ces modèles ont été choisis à cause du fait qu'ils sont traitables d'un point de vue numérique, puisqu'ils miment la dynamique de la chaîne dans le tube en utilisant des portions non connectées de la chaîne à la manière d'un champ moyen. En général, nous trouvons que chacun de ces modèles est également compétitif, à l'exception de quelques cas où il est suspecté que certaines hypothèses critiques, faites durant la formulation du modèle, peuvent amener à des prédictions inexactes dans les conditions transitoires ou Lagrangiennes non permanentes.

Key words: Polymer melts, reptation, single segment models, non-linear rheology

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Physical effect/ mathematical term	SMLD	Öttinger	DCR
DR	x	✓	✓
CCR	✓	✓	✓
CCR2	x	x	✓
Avoids IAA	x	✓	x
Multimodal Spectrum	x	✓	x
Relative chain-tube friction (Ωf in Eq. 1)	✓	✓	x
P(s, t, t')	✓	✓	x
Retarction term (Λf in Eq. 1)	x	✓	x
Strain Measure	✓	✓	x
λ_{conv}	✓*	✓*	✓*
λ_{dissip}	x	✓	✓
λ_{extra}	✓	x	x
Non-uniform monomer distribution	x	x	x
Contour length fluctuations	x	x	x

* Lacking concrete details on affine stretch evolution, we consider the Pearson et al. [3] modeling concepts to be correct even though the resulting stretch immediately following a step strain does not agree with the theory.

Table 1: Incorporation of the recent advances on modeling of linear entangled polymers in the recent single segment reptation models: x implies an incorrect inclusion or no inclusion at all, ✓ implies the term has been modeled correctly (SMLD ⟹ Mead et al. [12], Öttinger ⟹ Fang et al. [17], DCR ⟹ Ianniruberto and Marrucci [11]).

However, a similar problem was also encountered in the simplified Mead-Larson-Doi model and it is therefore worthwhile to look for other alternate forms for the affine stretch evolution such as the one proposed by Archer and Mhetar [22].

Among other discrepancies of the model are the ones shared with other single-segment theories such as lack of incorporation of contour length fluctuations, excessive stress relaxation after single step strain due to extra constraint release mechanisms, single mode description although a multimode version can be simply obtained etc.

Given the above facts, the generic applicability of this model to transient or Lagrangian unsteady flows is questionable as evidenced by recent complex flow simulations [26]. While some of the inconsistencies pointed out might not have significant effects on model predictions in the single steady uni-directional flow situations, others have to be definitely corrected in order to get meaningful results from this model in non-trivial flow situations. However, in spite of the above limitations, the model has been successful in bringing out the essential physics for flows beyond the inverse Rouse relaxation time through an elegant incorporation of higher Rouse relaxation mode in the single relaxation time. The shear stress curve has thus been shown to have a monotonic behavior similar to the experiments. The model thus provides new guidelines for future single-segment modeling of entangled polymers.

4 CONCLUSIONS

The field of modeling of linear entangled polymers has gone through a tremendous advance in the past decade. Modeling at the full chain level has provided new essential physics and a framework to test the basic concepts in the tube picture of reptation. However, flow simulations based on full chain concepts have been restricted to homogenous flows due to tremendous computational cost. Although single-segment theories do not capture all the details of the full chain models, they have been very successful in capturing non-linear rheology of entangled polymers. This fact combined with the affordable computational cost associated with the application of single-segment models in complex flows makes modeling at this level of description very attractive. However, one has to be careful in choosing the elements of construction for such models in order to get meaningful results in non-trivial flow situations.

The purpose of this communication has been to critically evaluate a few of the most recent single-segment theories and bring out the merits and shortcomings of such models. In the process we have highlighted issues which question the validity of either certain basic assumptions in the model itself or of the concepts which have been incorporated in the model but have been formulated elsewhere. Specifically, the "simplified" Mead-Larson-Doi model, the "thermo dynamically admissible" reptation model of Öttinger and the "simplified" DCR model of Ianniruberto and Marrucci were examined. While all three of these theories have been found to be equally competetive – one providing better estimates than the other in some situations while lagging behind in others, each of the models has also been found to possess certain shortcomings. A few of these shortcomings even have a common base. For example both the simplified Mead-Larson-Doi model and the simplified DCR model of Ianniruberto and Marrucci do not avoid the controversial independent alignment assumption and incorporate CCR in a controversial manner. Certain modeling aspects are completely absent from all three theories – for example none of the models account for contour length fluctuations and non-uniform monomer distribution. Table 1 provides a summary of our findings in terms of these models.

ACKNOWLEDGEMENTS

This work has been supported by a grant from the National Science Foundation CTS 0095098.

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