ENGINEERING MECHANICS 2009
National Conference with International Participation
Svratka, Czech Republic, May 11 – 14, 2009

pp. 645–650
Paper **#194**

A REMARK TO THE REPTATION THEORY

A.A. Kharlamov*, P. Filip*, P. Švrčinová*

Summary: *Avoiding the Independent Alignment (IA) approximation in the classical Doi-Edwards model causes the computation extremely time and hardware consuming. Nevertheless some flow situations cannot be modelled with the IA approximation. This contribution presents a probabilistic approach not taking into account the IA approximation.*

1. Introduction

The classical Doi-Edwards (DE) model with Independent Alignment (IA) approximation describes dynamics of strands between entanglements of a polymer molecule. Under external deformation of a sample the strands are deformed affinely, and then they retract to their original lengths, preserving their directions, Doi & Edwards (1986). The same stresses are achieved if the whole molecules are deformed in this way. However, retraction does not preserve direction of the end-to-end vector of a molecule, see Fig.1. This resulted in alternatives to the classical DE model, i.e. the DE model without taking into account the IA approximation.

Fig. 1 Influence of the primitive path of a molecule on its final end-to-end vector $\underline{R}$

In this contribution a probabilistic approach - instead of the IA approximation - is applied. The probability density function of an end-to-end molecule vector after deformation is calculated using geometrical considerations of reptating motion and a conformation of the molecule. Some molecules that decrease their path lengths under affine deformation do not retract but deform affinely and contribute to the stress less than according to the DE theory with the IA approximation. The present model also respects non-retractility of these molecules.

---

* Alexander A. Kharlamov, Petr Filip, Petra Švrčinová: Institute of Hydrodynamics AS CR, v.v.i.; Pod Paťankou 5; 16612 Praha 6; tel.: +420.233 109 011, fax: +420.224 333 361; e-mail: kharlamov@ih.cas.cz; filip@ih.cas.cz; svrcinova@ih.cas.cz

2. The probabilistic model

Let us suppose that a polymeric chain exposed to the deformation gradient $\underline{\underline{F}}^{-1} = \dfrac{\partial \underline{r}}{\partial \underline{r}'}$ is confined in a tube. In contrast to a tube that is redeformed affinely after deformation the chain is not due to retraction. Let us denote the chain end-to-end vectors before and after deformation as $\underline{R}'$ and $\underline{R}$, respectively. The chain is supposed to be unstretchable, hence the primitive path lengths of the chain before and after deformation are the same and equal to L'. Let us denote the virtual primitive path length of 'extended' chain after affine deformation but before retraction by *L*.

After retraction the molecule end-to-end vector $\underline{R}$ is not directed along the end-to-end vector corresponding to the situation after affine deformation $\underline{R}' \cdot \underline{\underline{F}}^{-1}$ but before retraction. The dot denotes the dot-product between vectors or tensors. Depending on its primitive path for fixed $\underline{R}'$ and $\underline{\underline{F}}^{-1}$, vector $\underline{R}$ represents different directions and lengths, see Fig.1 for illustration.

Due to retraction the end-to-end vector $\underline{R}$ is not defined unambiguously by the deformation gradient and the end-to-end vector before deformation. It is a probabilistic variable and is distributed with probability $\Psi_r\left(\underline{R}\right)$, index *r* relates to retraction.

Not only $\underline{R}$ but also the primitive path length *L* is a probabilistically distributed value, however in this study we assume that $L = L' \dfrac{\left|\underline{R}' \cdot \underline{\underline{F}}^{-1}\right|}{\left|\underline{R}'\right|}$, in other words, we assume conservation of a ratio primitive path length vs. chain end-to-end vector before and after affine deformation (preceding to retraction). The more an undeformed chain is stretched, the more this assumption is justified.

In the following the probability $\Psi_r\left(\underline{R}\right)$ will be determined.

Let us denote the initial and end points of vector $\underline{R}$ after retraction by *P* and *Q*, respectively, and the corresponding vectors (starting at the origin of coordinates) $\underline{P}$ and $\underline{Q}$ where the initial point of the chain end-to-end vector is chosen as the origin of coordinates, see Fig. 2. The primitive path length of the molecule section *PQ* equals L'.

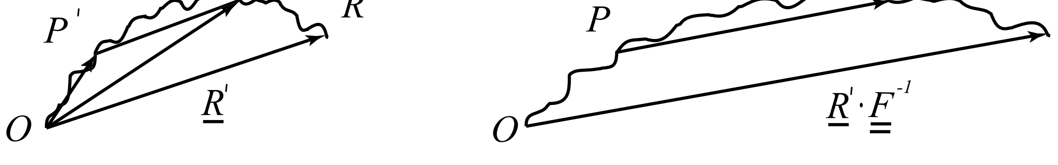

Fig. 2 Topology of a molecule before deformation, after affine deformation, and after retraction.

Both vectors $\underline{P}$ and $\underline{Q}$ represent probabilistic variables. They correspond to the vectors $\underline{P}' = \underline{P} \cdot \underline{\underline{F}}$ and $\underline{Q}' = \underline{Q} \cdot \underline{\underline{F}}$ before deformation, where $\underline{\underline{F}}$ is an inverse deformation gradient tensor. The points P' and Q' lie on a primitive path of the undeformed chain, and the length of the chain segment $P'Q'$ equals kL', where $k = \dfrac{L'}{L} = \dfrac{\left|\underline{R}'\right|}{\left|\underline{R}' \cdot \underline{\underline{F}}^{-1}\right|} = \dfrac{1}{\left|\underline{u}' \cdot \underline{\underline{F}}^{-1}\right|}$, $\underline{u}'$ is unity vector in the direction $\underline{R}'$.

First let us consider those vectors $\underline{R}'$ for which retraction occurs, i.e. $k < 1$. For any deformation due to volume conservation there are vectors $\underline{R}'$ for which $k \geq 1$ and retraction does not occur, these vectors will be treated later.

Due to arbitrariness of a primitive path, vector $\underline{P'Q'}$ is distributed with probability density function $\Psi'_r\left(\underline{P'Q'}\right)$. With respect to volume conservation it is connected to $\Psi_r\left(\underline{R}\right)$ as

$$\Psi_r\left(\underline{R}\right) = \Psi'_r\left(\underline{P'Q'}\right) = \Psi'_r\left(\underline{R} \cdot \underline{\underline{F}}\right) \tag{1}$$

First let us find the probability distribution functions of the vectors $\underline{P}'$ and $\underline{Q}'$ denoted as $\Psi_{P'}\left(\underline{P}'\right)$ and $\Psi_{Q'}\left(\underline{Q}'\right)$, respectively. Let us note that the point P' is achieved by random walk from the point O as well as from the point R'. Thus the probability of vector $\underline{P}'$ with its end in the infinitesimal vicinity of the point P' is proportional to a product of the probabilities arriving to the same point by random walks from the points O and R'

$$\Psi_{P'}\left(\underline{P}'\right) \sim \Psi_{OP'}\left(\underline{P}'\right)\Psi_{R'P'}\left(\underline{P}'\right), \tag{2}$$

where

$$\Psi_{OP'}\left(\underline{P}'\right) \sim \exp\left(-\beta_{OP'}^2 \underline{P}'^2\right), \tag{3}$$

$$\Psi_{R'P'}\left(\underline{P}'\right) \sim \exp\left[-\beta_{R'P'}^2 \left(\underline{P}' - \underline{R}'\right)^2\right]. \tag{4}$$

From the definition of a random walk parameter β, $\beta^2 = \dfrac{3}{2N_k b^2}$, where b is a random walk step, and from the definition of primitive path $L' = N_k b$ it follows that

$$\beta_{OP'} = \beta\sqrt{\frac{2}{1-k}}, \tag{5}$$

$$\beta_{R'P'} = \beta\sqrt{\frac{2}{1+k}}. \tag{6}$$

After normalisation, we obtain

$$\Psi_{P'}\left(\underline{P}'\right) = \left(\frac{2\beta}{\sqrt{\pi}\sqrt{1-k^2}}\right)^3 \exp\left[-\frac{4\beta^2}{1-k^2}\left(\underline{P}' - \frac{1-k}{2}\underline{R}'\right)^2\right]. \tag{7}$$

Analogously $\underline{Q}'$ is distributed

$$\Psi_{Q'}\left(\underline{Q}'\right)=\left(\frac{2\beta}{\sqrt{\pi}\sqrt{1-k^2}}\right)^3 \exp\left[-\frac{4\beta^2}{1-k^2}\left(\underline{Q}'-\frac{1+k}{2}\underline{R}'\right)^2\right]. \tag{8}$$

To find the probability $\Psi'_r\left(\underline{P'Q'}\right)$ from a vector sum $\underline{Q}'$ and $-\underline{P}'$ we consider the probability $\Psi_{P'}\left(-\underline{P}'\right)=\Psi^-_{P'}\left(\underline{P}'\right)$ shifted in such a way that the vector $-\underline{P}'$ starts at the point $\underline{Q}'$. Let us integrate the attained probability over the initial point $\underline{Q}'$ with density $\Psi_{Q'}\left(\underline{Q}'\right)$, see Fig.3

$$\Psi'_r\left(\underline{P'Q'}\right)=\int\Psi^-_{P'}\left(\underline{P'Q'}-\underline{Q}'\right)\Psi_{Q'}\left(\underline{Q}'\right)\mathrm{d}^3\underline{Q}'=$$
$$\left(\frac{2\beta}{\sqrt{\pi}\sqrt{1-k^2}}\right)^6\int\exp\left[-\frac{4\beta^2}{1-k^2}\left(\underline{P'Q'}-\underline{Q}'+\frac{1-k}{2}\underline{R}'\right)^2\right]\exp\left[-\frac{4\beta^2}{1-k^2}\left(\underline{Q}'-\frac{1+k}{2}\underline{R}'\right)^2\right]\mathrm{d}^3\underline{Q}' \tag{9}$$

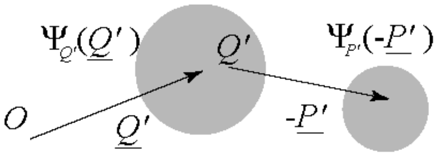

Fig. 3 Calculation of the probability of a vector sum.

In fact we calculate convolution of the functions $\Psi^-_{P'}\left(\underline{P}'\right)$ and $\Psi_{Q'}\left(\underline{Q}'\right)$. After integration we get

$$\Psi'_r\left(\underline{P'Q'}\right)=\left(\frac{\sqrt{2}\beta}{\sqrt{\pi}\sqrt{1-k^2}}\right)^3\exp\left[-\frac{2\beta^2}{1-k^2}\left(\underline{P'Q'}-k\underline{R}'\right)^2\right]=\left(\frac{\beta_k}{\sqrt{\pi}}\right)^3\mathrm{e}^{-\beta_k^2\left(\underline{P'Q'}-k\underline{R}'\right)^2}, \tag{10}$$

where

$$\beta_k=\beta\sqrt{\frac{2}{1-k^2}}. \tag{11}$$

Hence, the vector $\underline{R}'$ - if $k<1$ after deformation - is distributed with the probability density function

$$\Psi_r\left(\underline{R}\right)=\Psi_r\left(\underline{R}\,|\,\underline{R}'\right)=\left(\frac{\beta_k}{\sqrt{\pi}}\right)^3\mathrm{e}^{-\beta_k^2\left(\underline{R}\cdot\underline{\underline{F}}-k\underline{R}'\right)^2}. \tag{12}$$

For the case $k=1$ the probability density function $\Psi'_r\left(\underline{P'Q'}\right)$ reduces to the Dirac δ function, i.e. that vector $\underline{R}'$ and deformation $\underline{\underline{F}}^{-1}$ unambiguously define a vector $\underline{R}$.

If $k\geq 1$ then the molecule end-to-end vector after deformation is supposed not to scatter and to deform affinely; the molecule folds itself, but preserves its primitive path length. This results in putting $k=1$ in Eq.(12).

Now let us determine a probability distribution function $\Psi\left(\underline{R}\right)$ to which the probability function $\Psi_0\left(\underline{R}'\right)=\left(\frac{\beta}{\sqrt{\pi}}\right)^3\exp\left(-\beta^2\underline{R}'^2\right)$ transforms after step deformation. First it is necessary to sum all the probability functions $\Psi_r\left(\underline{R}\middle|\underline{R}'\right)$ with all vectors $\underline{R}'$ scattering, over all the vectors $\underline{R}'$. In other words we calculate a convolution of the functions $\Psi_0\left(\underline{R}'\right)$ and $\Psi_r\left(\underline{R}\middle|\underline{R}'\right)$

$$\Psi\left(\underline{R}\right)=\int\Psi_0\left(\underline{R}'\right)\Psi_r\left(\underline{R}\middle|\underline{R}'\right)\mathrm{d}^3\underline{R}'. \tag{13}$$

Splitting this integral into the regions where $k<1$ and $k\geq 1$ we derive a final expression for probability distribution function of the end-to-end molecule vector after step deformation

$$\Psi\left(\underline{R}\right)=\iiint A_k\left(\frac{\beta}{\sqrt{\pi}}\right)^3\mathrm{e}^{-\beta^2\underline{R}'^2}\left(\frac{\beta_k}{\sqrt{\pi}}\right)^3\mathrm{e}^{-\beta_k^2\left(\underline{R}\cdot\underline{\underline{F}}-k\underline{R}'\right)^2}\mathrm{d}^3\underline{R}'+\left(1-A_k\right)\left(\frac{\beta}{\sqrt{\pi}}\right)^3\mathrm{e}^{-\beta^2\left(\underline{R}\cdot\underline{\underline{F}}\right)^2},$$

$$A_k=\begin{cases}1, & k<1\\ 0, & k\geq 1\end{cases}, \qquad k=\frac{1}{\left|\underline{u}'\cdot\underline{\underline{F}}^{-1}\right|}. \tag{14}$$

Treating molecules as Gaussian chains, stress tensor after step deformation is

$$\underline{\underline{\sigma}}=2kTv\beta^2\left\langle\underline{R}\underline{R}\right\rangle, \tag{15}$$

where

$$\left\langle\cdot\right\rangle=\iiint\cdot\Psi\left(\underline{R}\right)\mathrm{d}^3\underline{R}, \tag{16}$$

the dot denotes the quantity being averaged.

If we take into account relaxation spectrum then for arbitrary deformation history it holds

$$\underline{\underline{\sigma}}=G_N^0\int_{-\infty}^{t}m\left(t-t'\right)2kTv\beta^2\left\langle\underline{R}\underline{R}\right\rangle\mathrm{d}t'. \tag{17}$$

3. Conclusions

There is presented a new, probabilistic approach to reptation. After reptation a molecule end-to-end vector becomes a probabilistic variable, due to the probabilistic nature of conformation of the molecule. Taking into consideration the geometry of conformation of a molecule (random walk) the probability distribution function of end-to-end vector of the molecule after deformation was calculated. The probability distribution function of end-to-end vectors of the whole multitude of molecules is calculated as a convolution of the probability function for undeformed state and the probability distribution function for individual molecule after deformation.

The constitutive equation is expressed by a double integral over space. Using this new model the shear dumping function is lower than that corresponding to the DE model at strain of order of unity and is higher for higher strains.

4. Acknowledgement

This work has been supported by Grant Agency of the Czech Republic, Grant No. 103/09/2066 and the Institutional Research Plan No. AV0Z20600510.

5. References

Doi, M. & Edwards, S.F. (1986) *The Theory of Polymer Dynamics*. Clarendon Press, Oxford.