APPENDIX II.7

PREDICTION OF LINEAR VISCOELASTICITY FOR MIXTURES OF LINEAR AND STAR MOLECULES: DESCRIPTION OF THE ALGORITHM.

7.1 INTRODUCTION

In appendix II.4, the model that we have develop to predict the linear viscoelasticity of mixture of linear and (a)symmetric star molecules has been presented. In this appendix, we present its structure by means of a graph, which allows seeing clearly the different interactions between all the variables. This graph in linked to the appendix II.4, using the same notations and referring directly to its equations by the symbols ().

In this example, we analyze the resolution of the problem for a blend of two asymmetric stars. Indeed, linear and symmetric star molecules can be included in this class. Moreover, to solve the problem with more than two molecules does not change the algorithm.

Before the presentation of the algorithm in Section 7.4., input data of the model are determined in Section 7.2 and the main variables are defined in Section 7.3.

7.2 INPUT DATA

In this model, the input data are:

- The complete description of the molecules. These ones must be presented in a matrix ***M***: each row represents a molecule and each column is linked to one of its arms. These must be classified from the smallest one to the longest one.

Therefore, in this specific case of a mixture of two asymmetric stars *A* and *B*, the matrix *M* is:

$$M = \begin{pmatrix} M_{A,1} & M_{A,2} & M_{A,3} \\ M_{B,1} & M_{B,2} & M_{B,3} \end{pmatrix},$$

with $M_{A,3} \geq M_{A,2} \geq M_{A,1}$ and $M_{B,3} \geq M_{B,2} \geq M_{B,1}$. For example, $M_{A,1}$ is the molecular weight of the smallest arm of the molecule *A*.

- The volumetric fraction of each kind of molecules:

$$P = \begin{pmatrix} P_A \\ P_B \end{pmatrix},$$

with, in this case, $P_A = 1\text{-}P_B$. This matrix is directly transformed into a matrix called *PROP*, in order to know the volumetric fraction of each arm in the polymer:

$$PROP = \begin{pmatrix} \dfrac{M_{A,1} \cdot P_A}{M_{A,1} + M_{A,2} + M_{A,3}} & \dfrac{M_{A,2} \cdot P_A}{M_{A,1} + M_{A,2} + M_{A,3}} & \dfrac{M_{A,3} \cdot P_A}{M_{A,1} + M_{A,2} + M_{A,3}} \\ \dfrac{M_{B,1} \cdot P_B}{M_{B,1} + M_{B,2} + M_{B,3}} & \dfrac{M_{B,2} \cdot P_B}{M_{B,1} + M_{B,2} + M_{B,3}} & \dfrac{M_{B,3} \cdot P_B}{M_{B,1} + M_{B,2} + M_{B,3}} \end{pmatrix}$$

- The material parameters:

G_N^0 : the plateau modulus,

τ_e : the Rouse time of a segment,

M_e : the molecular weight between two entanglements.

7.3 VARIABLES

We have to determine, at each time step, which is the relaxed part of each arm. In order to do that, we have chosen to divide each arm in 100 segments and to calculate the survival probability of each of them. Thus, the first segment is located between the normalized variable *x=0* and *x=1/100* and the last one, between *x=99/100* and *1*. These segments are not the segments between two entanglements. They represent subchains of the molecule and contain a fixed number of monomers.

In the algorithm, the main variables are the matrixes $p_{rept,}$ p_{fluc} and $p_{envir.,}$ which represent the survival probabilities of all the segments of all the arms, after the reptation, fluctuation and the constraint release processes. They contain one row per molecule and 100 columns for each segment:

$$p_{rept} = \begin{pmatrix} p_{rept,A}(x=\frac{1}{100}) & p_{rept,A}(x=\frac{2}{100}) & \dots & p_{rept,A}(x=\frac{100}{100}) \\ p_{rept,B}(x=\frac{1}{100}) & p_{rept,B}(x=\frac{2}{100}) & \dots & p_{rept,B}(x=\frac{100}{100}) \end{pmatrix}$$

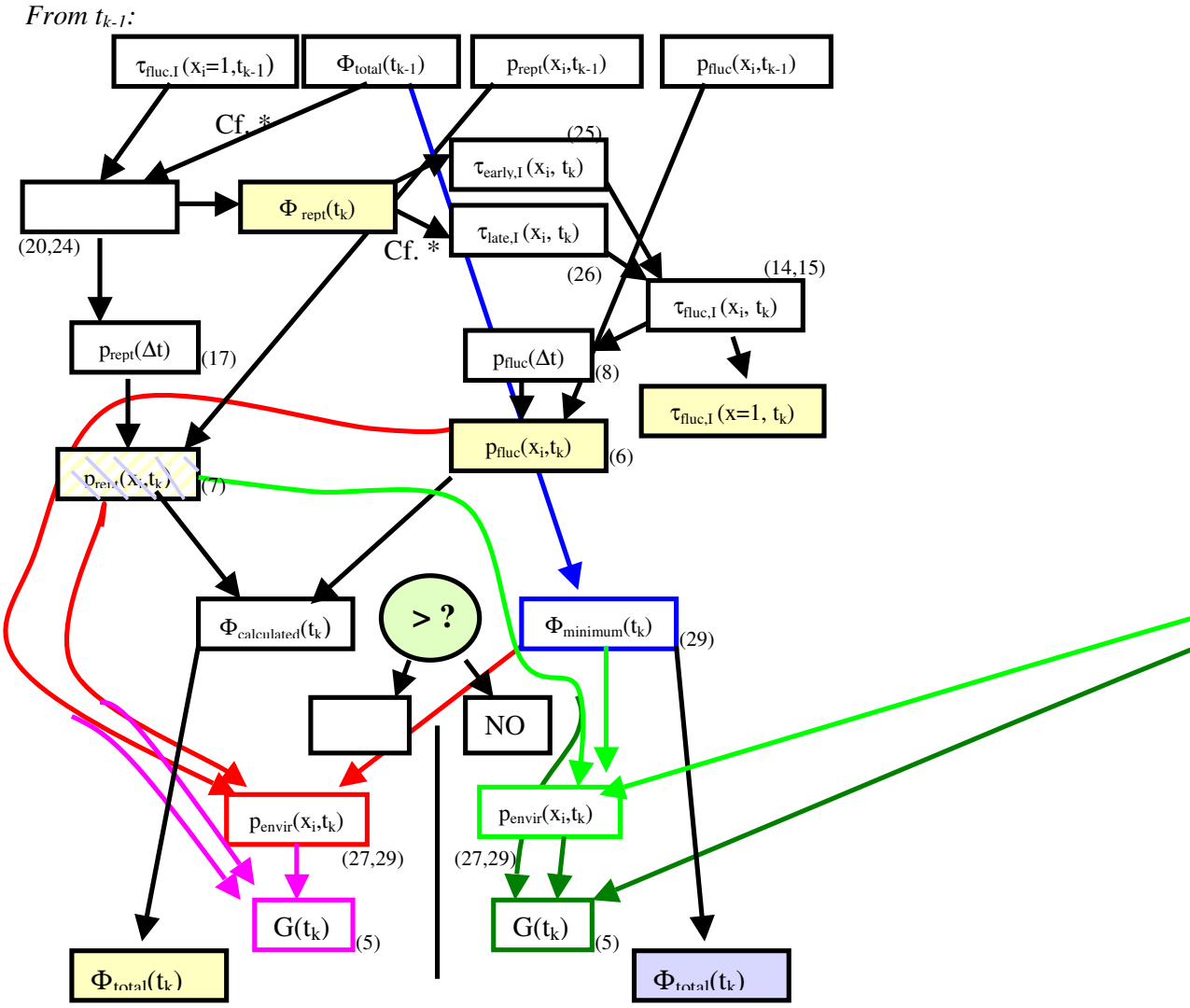
The matrixes p_{fluc} and p_{envir} have exactly the same structure. Their values vary through the time.

Other important variables are $\Phi_{total}(t_{k-1})$, $\Phi_{min}(t_k)$ and $\Phi_{calculated}(t_k)$. $\Phi_{total}(t_{k-1})$ represents the total unrelaxed fraction of the polymer at time t_{k-1}. Then, from this value, at the next time step (i.e. t_k), we determine $\Phi_{min}(t_k)$, the smallest value that can have $\Phi_{total}(t_k)$ in order to respect the equation 29 in appendix II.4. Next, we calculate $\Phi_{calculated}(t_k)$, the unrelaxed fraction of the polymer at time t_k, without any restriction of the rate of enlargement of the tube, and compare this value with $\Phi_{min}(t_k)$. If it is larger than this last one, the motions of the molecule are not quicker than the Rouse process. $\Phi_{total}(t_k)$ is thus equal to $\Phi_{calculated}(t_k)$. On the contrary, if $\Phi_{calculated}(t_k)$ is smaller than $\Phi_{min}(t_k)$, we have to recalculate the survival fluctuation probabilities without upgrading the value of the solvent coming from reptation (see graph), and $\Phi_{total}(t_k)$ becomes equal to the minimum value it can take, $\Phi_{min}(t_k)$. In addition to that, to assure a tube dilation slower than by the Rouse process, we add a lower boundary for the values $p_{envir}(x_i,t_k)$. Indeed, these last ones cannot be smaller than $\Phi_{min}(t_k)$.

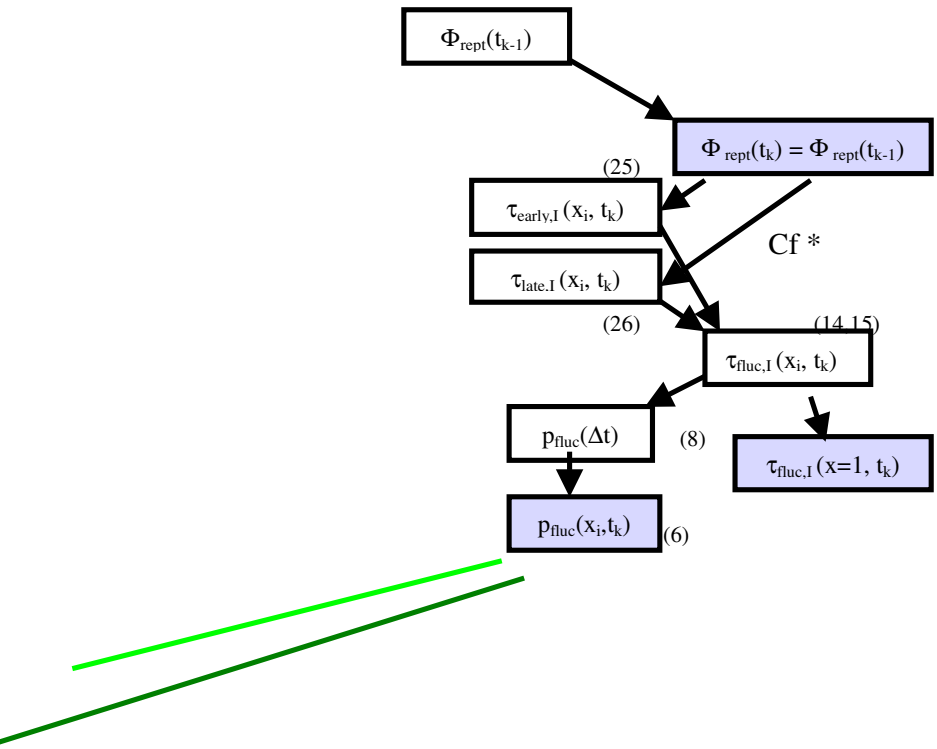
7.4 ALGORITHM

On this graph, the five variables presented above represent the data that we need from the previous time step: $\tau_{fluc,I}$ (where I =A or B), $\Phi_{total}(t_{k-1})$, $p_{rept}(x_i,t_{k-1})$, $p_{fluc}(x_i,t_{k-1})$ and $\Phi_{rept}(t_{k-1})$ (the polymer fraction no relaxed by reptation). The variables in yellow boxes are the one we need in the next time step, if the rate of the tube dilation is smaller

than the Rouse process. Otherwise, we have to consider the blue boxes.


From t_{k-1}:
$\tau_{fluc,I}(x_i=1,t_{k-1})$
$\Phi_{total}(t_{k-1})$
$p_{rept}(x_i,t_{k-1})$
$p_{fluc}(x_i,t_{k-1})$
Cf. *
(25)
$\tau_{early,I}(x_i, t_k)$
$\Phi_{rept}(t_k)$
$\tau_{late,I}(x_i, t_k)$
Cf. *
(20,24)
(26)
(14,15)
$\tau_{fluc,I}(x_i, t_k)$
$p_{rept}(\Delta t)$
(17)
$p_{fluc}(\Delta t)$
(8)
$\tau_{fluc,I}(x=1, t_k)$
$p_{fluc}(x_i,t_k)$
(6)
$p_{rept}(x_i,t_k)$
(7)
$\Phi_{calculated}(t_k)$
> ?
$\Phi_{minimum}(t_k)$
(29)
NO
$p_{envir}(x_i,t_k)$
(27,29)
$p_{envir}(x_i,t_k)$
(27,29)
$G(t_k)$
(5)
$G(t_k)$
(5)
$\Phi_{total}(t_k)$
$\Phi_{total}(t_k)$

*: If the Graessley condition is respected.



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