Communications in Applied Analysis **12** (2008), no. 2, 147–160

A MULTISCALE MODEL FOR RUBBER VISCOELASTICITY UNDER SHEAR DEFORMATION

N. G. MEDHIN

Department of Mathematics, North Carolina State University
Raleigh, NC 27695-8205

ABSTRACT. A molecular based model for the viscoelasticity of rubber under shear deformation is developed using a stick-slip continuous molecular model. In our model cross-linked(CC)-system of molcules restrict the motion of entrapped or physically constrained(PC)-molecules. The dynamics of the PC-molecules is modeled by reptation in which the CC-molecules act as constraint boxes and the PC-molecules have to reptate in between the CC-molecules. We assume that a CC-unit cell is placed at each point of the rubber continuum with an entrapped PC-cell inside it. The deformation of the CC-cell causes a deformation of the PC-system which relaxes after removal of the deformation. In the relaxation process the PC-molecules act as internal variables affecting the relaxation process of the CC-system. The Rouse model for relaxing polymers is incorporated into the stick-slip model presented by Johnson and Stacer [13] for describing the dynamics of the entrapped molecule for a short time right after instantneous step-strain of the constraining CC-cell.

1. INTRODUCTION

In the paper by Banks, et. al. [1], [2], [3], [4], [14] model was developed based on molecular models of Johnson and Stacer [13] and Doi and Edwards [8], where strain energy density functions were used to characterize the stress distribution for tensile and shear deformations. In this paper we use a microscopic description of the stress tensor following Doi and Edwards [8] to characterize the stress distribution for a general deformation. In this approach we enforce reptation following the approach of Johnson and Stacer [13] adhering more to the architecture of the constrained polymer and relating its deformation more closely to the constraining CC-cell. In addition the physical parameter of both the polymers in the CC-cell and the PC-molecule can be more readily reflected in the model and the relaxation process of both the PC-molecules as well as the CC-molecules are better described.

The proposed model for a single polymer strand is represented by a series of beads (or nodes) separated by springs, governed by Hooke's Law. The Rouse Model of polymer elasticity was proposed to model the dynamics of polymers by the Brownian motion of these nodes. Such a model can be used to represent the dynamics of a system of chemically cross-linked polymers.

Received May 1, 2008

To develop the model we treat each constrained molecule as a chain of beads connected by springs representing intermolecular potential. Subsequent to an instantneous step strain of the CC-cell the constrained molecule relaxes following the Rouse model for a short time. To enforce reptation we follow the idea of Johnson and Stacer [13]. That is, at each point of the rubber continuum we place a unit cell in the rubber continuum with an entrapped PC-molecule thereby relating the deformation of the entrapped molecule to that of the CC-cell.

As special cases of the general stress formula we give the dynamics of a rubber under tensile deformation and an elastomer/rubber under shear deformation.

2. MODELING OF THE DYNAMICS OF THE PC-MOLECULAR CHAIN

We model a typical PC-molecule by a chain of N-beads connected by a spring. Let $R_n = (R_1, R_2, \ldots, R_N)$ be the position vectors of the beads in the chain. In the model we proceed to develop the dynamics of such a chain for a short period of time after instantaneous step deformation is given by the Rouse model where the motion of the beads be described by the Langevin equation [8]:

$$\frac{\partial}{\partial t} R_n(t) = \sum_m H_{nm} \cdot \left(-\frac{\partial U}{\partial R_m} + f_m(t) \right) + \frac{1}{2} k_B T \sum_m \frac{\partial}{\partial R_m} \cdot H_{nm}, \tag{1}$$

where $f_m(t)$ is a random force term, k_B is Boltzmann's constant, T is the temperature, and the mobility tensor and the interaction potential, are chosen to be

$$H_{nm} = \frac{\delta_{nm}}{\zeta} I,$$

$$U = \frac{k}{2} \sum_{n=2}^{N} \|(R_n - R_{n-1})\|^2,$$

respectively, with

$$k = \frac{3k_B T}{b^2}, \tag{2}$$

where b is the effective segment bond length at equilibrium and ζ is the friction constant of the polymer sample.

If we use the parameters defined above for the mobility tensor, H_{nm}, and for the interaction potential, U, then Equation (1), for the cases when $n = 2, 3, \ldots, N-1$, can be written as

$$\zeta \frac{dR_n}{dt} = -k(2R_n - R_{n+1} - R_{n-1}) + f_n. \tag{3}$$

For the special cases of the extreme ends of the polymer, i.e., the cases when $n = 1$ and $n = N$, we see that (respectively)

$$\zeta \frac{dR_1}{dt} = -k(R_1 - R_2) + f_1, \tag{4}$$

$$\zeta \frac{dR_N}{dt} = -k(R_N - R_{N-1}) + f_N. \tag{5}$$

The term, f_n is a randomly distributed force, which takes into consideration the Brownian motion of the beads. Assume that the random force, f_n, is distributed according to a Gaussian distribution, which is determined by the following moments

$$\langle f_n(t)\rangle = 0,$$
$$\langle f_{n\alpha}(t) f_{m\beta}(t')\rangle = 2\zeta k_B T \delta_{nm}\delta_{\alpha\beta}\delta(t - t'). \tag{6}$$

If we regard n as a continuous variable, it is possible to rewrite Equation (3) using a continuous derivative as

$$\zeta \frac{\partial R_n}{\partial t} = k \frac{\partial^2 R_n}{\partial n^2} + f_n \tag{7}$$
$$\frac{\partial R_n}{\partial n}\Big|_{n=0} = \frac{\partial R_n}{\partial n}\Big|_{n=N} = 0, \tag{8}$$

under the assumption that $R_0 = R_1$ and $R_{N+1} = R_N$.

Define

$$b_n = R_{n+1} - R_n. \tag{9}$$

Then, from (4)–(8), we have

$$\frac{db_n}{dt} = -\frac{3kT}{\zeta b^2} \sum_{k=1}^{N-1} A_{nk} b_k + f_{n+1}(t) - f_n(t), \tag{10}$$

where

$$A_{nk} = 2\delta_{nk} - \delta_{n+1,k} - \delta_{n-1,k} \tag{11}$$

Suppose the rubber medium is subjected to a deformation E. We are going to consider E to be shear deformation. Let V_1, V_2, V_3, be the unit length eigenvectors corresponding to the eigenvalues λ_1, λ_2, λ_3 of E.

Suppose at time t_0 the portion of the PC-molecule between the n-th bead and $(n + 1)$-th bead is contained in a (CC)-cell of dimension L_{ni} in the V_i-direction. Corresponding to this CC-cell we write the vector

$$b_n^{CC}(t_0) = L_{n1}(t_0)V_1 + L_{n2}(t_0)V_2 + L_{n3}(t_0)V_3. \tag{12}$$

For the vector $b_n(t_0)$ we write

$$b_n(t_0) = l_{n1}(t_0)V_1 + l_{n2}(t_0)V_2 + l_{n3}(t_0)V_3. \tag{13}$$

Then,

$$E \cdot b_n^{CC}(t_0) = \lambda_1 L_{n1}(t_0)V_1 + \lambda_2 L_{n2}(t_0)V_2 + \lambda_3 L_{n3}(t_0)V_3 \tag{14}$$
$$E \cdot b_n(t_0) = \lambda_1 l_{n1}(t_0)V_1 + \lambda_2 l_{n2}(t_0)V_2 + \lambda_3 l_{n3}(t_0)V_3. \tag{15}$$

Note that

$$\lambda_i l_{ni}(t_0) - l_{ni}(t_0) = \frac{l_{ni}(t_0)}{L_{ni}(t_0)}(\lambda_i L_{ni}(t_0) - L_{ni}(t_0)). \tag{16}$$

Thus,

$$\Delta l_{ni}(t_0) = \frac{l_{ni}(t_0)}{L_{ni}(t_0)}(\Delta L_{ni}(t_0)). \tag{17}$$

Let

$$U_{mn}(t_0) = \sqrt{\frac{2}{N}} \sin \frac{mn\pi}{N}, \quad m, n = 1, 2, \ldots, N-1, \tag{18}$$

and

$$a_m = 4 \sin^2 \left(\frac{m\pi}{2N}\right), \quad m, n = 1, 2, \ldots, N-1. \tag{19}$$

Then U_{mn} is an orthogonal matrix.

Set

$$q_m = \sum_{n=1}^{N-1} U_{nm} b_n. \tag{20}$$

Then,

$$b_n = \sum_{n=1}^{N-1} U_{nk} q_k, \tag{21}$$

and

$$q'_m(t) = -\frac{3kT}{\zeta b^2} a_m q_m + h_m(t), \tag{22}$$

where

$$h_m(t) = \sum_{l=1}^{N-1} U_{lm}(f_{l+1}(t) - f_l(t)). \tag{23}$$

For ease of notation we set

$$C_m = -\frac{3kT}{\zeta b^2} a_m. \tag{24}$$

Immediately after the rubber medium is subjected to the above deformation at $t = t_0$ we have, for a short interval of time $t_0 < t < t_1$,

$$q_m(t) = U_{rp} b_r(t_0) + e^{-C_p(t-t_0)} U_{rp} \frac{l_{ri(t_0)}}{L_{ri}(t_0)} \Delta L_{ri}(t_0) V_i + \int_{t_0}^{t} e^{-C_p(t-s)} h_p(s) ds, \tag{25}$$

where we sum over repeated indices($r = 1, 2, \ldots, N-1$; $i = 1, 2, 3$).

If the rubber medium is again subjected to instantaneous step deformation at time t_1, then for a short interval of time $t_1 < t < t_2$, we have

$$\begin{aligned} q_m(t) =& U_{rp} b_r(t_0) + U_{rp} \frac{l_{ri(t_0)}}{L_{ri}(t_0)} \Delta L_{ri}(t_0) e^{-C_p(t-t_0)} V_i \\ & U_{rp} \frac{l_{ri(t_1)}}{L_{ri}(t_1)} \Delta L_{ri}(t_1) e^{-C_p(t-t_1)} V_i + \int_{t_0}^{t} e^{-C_p(t-s)} h_p(s) ds, \end{aligned} \tag{26}$$

From (26) we infer, letting $\Delta_n = t_n - t_{n-1}$ tend to zero, that

$$\begin{aligned} q_m(t) = U_{rp} b_r(t_0) + \int_{t_0}^{t} U_{rp} \frac{l_{ri}(s)}{L_{ri}(s)} \frac{dL_{ri}(s)}{ds} e^{-C_p(t-s} V_i \\ + \int_{t_0}^{t} e^{-C_p(t-s)} h_p(s) ds, \end{aligned} \tag{27}$$

From (27), using (21), we have

$$b_n(t) = b_n(t_0) + \int_{t_0}^{t} U_{np} U_{rp} \frac{l_{ri}(s)}{L_{ri}(s)} \frac{dL_{ri}(s)}{ds} e^{-C_p(t-s} V_i$$
$$+ \int_{t_0}^{t} e^{-C_p(t-s)} U_{np} U_{rp} (f_{r+1}(s) - f_r(s)) ds. \quad (28)$$

3. STRAIN ENERGY DENSITY

To calculate the stress in the rubber medium we can use stress energy density function. The stress energy function W consists of a portion W_{cc} from the CC-system of molecules and a portion W_{PC} from the PC-system of molecules. Thus, from (12) and (13) above the strain energy density at the n-th bead has the form

$$W = \sum_{n=1}^{N-1} W_{CC}^n(L_{n1}, L_{n2}, L_{n3+}) + \sum_{n=1}^{N-1} W_{PC}^n(l_{n1}, l_{n2}, l_{n3+}) \quad (29)$$

The Cauchy stress in the principal direction V_j is given by

$$\tau_j = \sum_{n=1}^{N-1} L_{nj} \frac{\partial W_{CC}^n}{\partial L_{nj}} + \sum_{n=1}^{N-1} \sum_{i=1}^{3} \frac{\partial W_{PC}^n}{\partial l_{ni}} \frac{\partial l_{ni}}{\partial L_{nj}} - P, \quad (30)$$

where P is the hydrostatic pressure.

Using (16)

$$\tau_j = \sum_{n=1}^{N-1} \left[L_{nj} \frac{\partial W_{CC}^n}{\partial L_{nj}} + l_{nj} \frac{\partial W_{PC}^n}{\partial l_{nj}} \right] - P \quad (31)$$

4. DYNAMIC MODELS

Suppose that the unit cc-box undergoes a deformation of the type $(x, y, z) \mapsto (x + u(y), y, z)$. The configuration gradient of this map is given by

$$A = \begin{pmatrix} 1 & u'(y) & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The configuration gradient A can be written in a unique way as a product of stretch tensor E and rotation R as

$$A = E\ R,$$

where $E^2 = A^* A$. The eigenvalues ξ_1, ξ_2, ξ_3 of $E^2 = A^* A$ are

$$\begin{aligned} \xi_1 &= 1 + \frac{1}{2} [u'(y)]^2 + u'(y) \sqrt{1 + \frac{1}{4} [u'(y)]^2} \\ \xi_2 &= 1 + \frac{1}{2} [u'(y)]^2 - u'(y) \sqrt{1 + \frac{1}{4} [u'(y)]^2} \\ xi_3 &= 1 \end{aligned}$$

We note that $\xi_1\, \xi_2 = 1$ and thus $\xi_1\xi_2\xi_3 = 1$. For small deformations set

$$\begin{aligned}
\lambda_{1c} &= \sqrt{\xi_1} = 1 + \frac{1}{2}u'(y) + \frac{1}{4}\left[u'(y)\right]^2 + \frac{1}{16}\left[u'(y)\right]^3 + \cdots && (32)\\
\lambda_{2c} &= \sqrt{\xi_2} = 1 - \frac{1}{2}u'(y) + \frac{1}{4}\left[u'(y)\right]^2 - \frac{1}{16}\left[u'(y)\right]^3 + \cdots && (33)\\
\lambda_{3c} &= 1 && (34)
\end{aligned}$$

The quantities $\lambda_{1c}, \lambda_{2c}, \lambda_{3c}$ are the prinicipal stretches. In (31) we set $\tau_3 = 0$. That is

$$\tau_3 = L_3 - \frac{\partial W_{cc}}{\partial L_3} + L_3 \sum_n \frac{\partial W_{pc}}{\partial \ell_{n_j}} - p = 0. \qquad (35)$$

Then, using (35)

$$\begin{aligned}
\tau_1 &= L_{n1}\frac{\partial W_{cc}}{\partial L_{n1}} - L_{n3}\frac{\partial W_{cc}}{\partial L_{n3}} + L_{n1}\frac{\partial W_{pc}^{(n)}}{\partial \ell_{n1}} - L_{n3}\frac{\partial W_{pc}^{(n)}}{\partial \ell_{n3}} && (36)\\
\tau_2 &= L_{n2}\frac{\partial W_{cc}^{(n)}}{\partial L_{n2}} - L_{n3}\frac{\partial W_{cc}^{(n)}}{\partial L_{n3}} + L_{n2}\frac{\partial W_{pc}^{(n)}}{\partial \ell_{n2}} - L_{n3}\frac{\partial W_{pc}^{(n)}}{\partial \ell_{n3}} && (37)\\
\tau_3 &= 0 && (38)
\end{aligned}$$

To develop a dynamic model we assume at each point of the rubber medium we find the entire molecular chain. Using (32)–(34) we have

$$\begin{aligned}
\tau_1 &= \lambda_{1c}\frac{\partial}{\partial \lambda_{1c}} W_{cc}(\lambda_{1c}, \lambda_{2c}, \lambda_{3c}) - \lambda_{3c}\frac{\partial W_{cc}}{\partial \lambda_{3c}}(\lambda_{1c}, \lambda_{2c}, \lambda_{3c}, \ell_{n1}, \ell_{n2}, \ell_{n3}) + \\
&\quad \lambda_{1c}\sum_n \frac{\partial W_{pc}(\ell_{n1}, \ell_{n2}, \ell_{n3}))}{\partial \ell_{n1}} - \lambda_{3c}\sum_n \frac{\partial W_{pc}(\ell_{n1}, \ell_{n2}, \ell_{n3}))}{\partial \ell_{n3}} && (39)\\
\tau_2 &= \lambda_{2c}\frac{\partial W_{cc}(\lambda_{1c}, \lambda_{2c}, \lambda_{3c})}{\partial \lambda_{2c}} - \lambda_{3c}\frac{\partial W_{cc}(\lambda_{1c}, \lambda_{2c}, \lambda_{3c})}{\partial \lambda_{3c}} + \\
&\quad \lambda_{2c}\sum_n \frac{\partial W_{pc}(\ell_{n1}, \ell_{n2}, \ell_{n3}))}{\partial \ell_{n2}} - \lambda_{3c}\sum_n \frac{\partial W_{pc}(\ell_{n1}, \ell_{n2}, \ell_{n3}))}{\partial \ell_{n2}} && (40)
\end{aligned}$$

We enforce incompressibility on the pc-molecular chain by insisting $\ell_{n1}\ell_{n2}\ell_{n3} = 1$.

Eigenvector corresponding to ξ_1 is

$$\left(\frac{1}{\sqrt{2}}, \frac{\sqrt{2}}{2+a}, 0\right)^T$$

corresponding to ξ_2 is

$$\left(\frac{(-1+\frac{1}{2}a)}{(\sqrt{2}(1-\frac{1}{4}a))}, \frac{4}{\sqrt{2}(4-a)}, 0\right)^T \approx \left(-\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right)^T$$

corresponding to ξ_3 is $(0, 0, 1)^T$. We call these vectors v_1, v_2, and v_3 respectively.

Set

$$\ell_{rj} = 1 + \partial_x u_{rj}^{pc}, \quad j = 1, 2, 3. \quad (\text{Note that} \quad \ell_{nj} = b_{nj}.)$$

Now going back to (28) and setting $t_0 = 0$ we have

$$\begin{aligned} b_n(t) = b_n(0) \quad &+ \quad \int_0^t U_{np}U_{rp}\frac{1+\partial_x u^{pc}_{r1}}{1+\frac{1}{2}\partial_y u}\frac{1}{2}\partial_s\partial_y u \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} e^{-c_p(t-s)}\, ds \\ &+ \quad \int_0^t U_{np}U_{rp}\frac{1+\partial_x u^{pc}_{r2}}{1-\frac{1}{2}\partial_y u}\left(-\frac{1}{2}\partial_s\partial_y u\right) \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} e^{-c_p(t-s)}\, ds \\ &+ \quad \int_0^t e^{-c_p(t-s)}U_{np}U_{rp}\left(f_{r+1}(s) - f_r(s)\right)\, ds \end{aligned} \tag{41}$$

Then,

$$\begin{aligned} b_{n1}(t) = b_{n1}(0) + \int_0^t \frac{1}{\sqrt{2}}U_{np}U_{rp}\left(\frac{1+\partial_x u^{pc}_{r_1}}{1+\frac{1}{2}\partial_y u} + \frac{1+\partial_x u^{pc}_{r_2}}{1-\frac{1}{2}\partial_y u}\right)\frac{1}{2}\partial_s\partial_y u\; e^{-c_p(t-s)}\, ds \\ + \int_0^t e^{-c_p(t-s)}U_{np}U_{rp}\left(f^1_{r+1}(s) - f^2_r(s)\right)\, ds \end{aligned} \tag{42}$$

Thus,

$$\begin{aligned} b_{n1}(t) = b_{n1}(0) + \frac{1}{2\sqrt{2}}\int_0^t U_{np}U_{rp}\left[(1+\partial_x u^{pc}_{r1})(1-\frac{1}{2}\partial_y u) + (1+\partial_x u^{pc}_{r_2})(1+\frac{1}{2}\partial_y u)\right]\cdot \\ \cdot\, \partial_s\partial_y u\; e^{-c_p(t-s)}\, ds \\ + \int_0^t e^{-c_p(t-s)}U_{np}U_{rp}\left(f^{(1)}_{r+1}(s) - f^{(2)}_r(s)\right)\, ds \end{aligned}$$

Next,

$$\begin{aligned} b_{n1}(t) = b_{n1}(0) + \frac{1}{2\sqrt{2}}\int_0^t U_{np}U_{rp}\left[1+\partial_x u^{pc}_{r1} - \frac{1}{2}\partial_y u - \frac{1}{2}\partial_x u^{pc}_{r1}\partial_y u + \cdots\right] \\ \times\, \partial^2_{sy} u e^{-c_p(t-s)}\, ds \\ + \frac{1}{2\sqrt{2}}\int_0^t U_{np}U_{rp}\left[1+\partial_x u^{pc}_{r2} + \frac{1}{2}\partial_y u + \frac{1}{2}\partial_x u^{pc}_{r2}\partial_y u + \cdots\right] \\ \times\, \partial^2_{sy} u e^{-c_p(t-s)}\, ds \\ + \int_0^t e^{-c_p(t-s)}U_{np}U_{rp}\left(f^{(1)}_{r+1}(s) - f^{(2)}_r(s)\right)\, ds \end{aligned} \tag{43}$$

Finally,

$$\begin{aligned} b_{n1}(t) \approx b_{n1}(0) + \frac{1}{\sqrt{2}}\int_0^t U_{np}U_{rp}\partial^2_{sy} u e^{-c_p(t-s)}\, ds \\ + \frac{1}{\sqrt{2}}\int_0^t U_{np}U_{rp}\left(\partial_x u^{pc}_{r1} + \partial_x u^{pc}_{r2}\right)\partial^2_{sy} u e^{-c_p(t-s)}\, ds \\ + \int_0^t e^{-c_p(t-s)}U_{np}U_{rp}\left(f^{(1)}_{r+1}(s) - f^{(2)}_r(s)\right)\, ds \end{aligned} \tag{44}$$

Going to the second component we have

$$b_{n2}(t) = b_{n2}(0) + \int_0^t \frac{1}{\sqrt{2}} U_{np}U_{rp}\left[\frac{1+\partial_x u_{r1}^{pc}}{1+\frac{1}{2}\partial_y u}\partial_{sy}^2 u - \frac{1+\partial_x u_{r2}^{pc}}{1-\frac{1}{2}\partial_y u}\partial_{sy}^2 u\right] e^{-c_p(t-s)}\, ds$$
$$+ \int_0^t e^{-c_p(t-s)} u_{np}U_{rp}\left(f_{r+1}^{(2)}(s) - f_r^{(2)}(s)\right)\, ds \tag{45}$$

Finally,

$$b_{n2}(t) \approx b_{n2}(0) + \int_0^t \frac{1}{2\sqrt{2}} U_{np}U_{rp}\left(\partial_x u_{r1}^{pc} - \partial_x u_{r2}^{pc}\right)\partial_{sy}^2$$
$$+ \int_0^t e^{-c_p(t-s)} U_{np}U_{rp}\left(f_{r+1}^{(2)}(s) - f_r^{(2)}(s)\right)\, ds \tag{46}$$

Finally for the third component we have

$$b_{n3}(t) \;=\; b_{n3}(0) + \int_0^t e^{-c_p(t-s)} u_{np}U_{rp}\left(f_{r+1}^{(2)}(s) - f_r^{(2)}(s)\right)\, ds \tag{47}$$

Assuming $\partial_x u(0) = 0$, from (44), we have

$$\begin{aligned}
b_{n1}(t) &= \frac{1}{\sqrt{2}}\int_0^t U_{np}U_{rp}\partial_{sy}^2 u e^{-c_p(t-s)}\, ds + \int_0^t e^{-c_p(t-s)} U_{np}U_{rp}\left(f_{r+1}^{(1)}(s) - f_r^{(2)}(s)\right) ds \\
&= \frac{1}{\sqrt{2}}\partial_y u(y,t) - \frac{1}{\sqrt{2}} U_{np}U_{rp}\partial_y u(y,0)e^{-c_p t} - \frac{1}{\sqrt{2}}\int_0^t U_{np}U_{rp}\partial_y u e^{-c_p(t-s)}\, ds \\
&\quad + \int_0^t e^{-c_p(t-s)} U_{np}U_{rp}\left(f_{r+1}^{(1)}(s) - f_r^{(2)}(s)\right) ds
\end{aligned} \tag{48}$$

We also note that to first order in u_x^{pc} and u_x we have $b_{n1}(t) \approx 1 + \partial_x u^{pc}$, $\partial_x u^{pc}(0) = 0$. The Cauchy stress from (39) is obtained by dividing τ_1 by $\frac{1}{\lambda_{1c}}$. The stress σ_1, using (39) and ignoring the random part, has the form (to first order approximation).

$$A\partial_y u(t,y) - \int_0^t \frac{1}{\sqrt{2}} B_n U_{np}U_{rp}\partial_y u e^{-c_p(t-s)} ds - \frac{1}{\sqrt{2}} B_n U_{np}U_{rp}\partial_y u(y,0)e^{-c_p t}$$

Note that in (28) we sum over repeated indices. We need to sum over r too. To see that we need to sum over see (28). In what follows we write δ_p for $\sum_{r=1}^{N-1} U_{rp}$. Then, the momentum balance equation leads to

$$\rho\partial_t^2 u - A\partial_y^2 u(t,y) + \int_0^t \frac{1}{\sqrt{2}} B_n U_{np}\ \delta_p\ \partial_y u(y,s)e^{-c_p(t-s)}\, ds = \tilde{q}$$

Next we will solve the initial boundary value problem

$$\rho\partial_t^2 u - A\partial_y^2 u(t,y) + \int_0^t \frac{1}{\sqrt{2}} B_n U_{np}\ \delta_p\ \partial_y u(y,s)e^{-c_p(t-s)}\, ds = \tilde{q} \tag{49}$$

$$u(t,0) = 0, \quad \frac{\partial u}{\partial y}(t,b) = F(t), \quad u(0,y) = \partial_t u(0,y) = 0 \tag{50}$$

Let

$$Q(t,y) = u(t,y) - y\ F(t) \tag{51}$$

$$\begin{aligned}
\frac{\partial Q}{\partial y} &= \partial_y u - F(t) \\
\frac{\partial Q}{\partial y}(t,b) &= \partial_y u(t,b) - F(t) = 0 \\
Q(t,0) &= u(t,0) - 0 \cdot F(t) = 0 \\
Q(0,y) &= u(0,y) - y\ F(0) = -y\ F(0) \\
Q_t &= u_t(t,y) y\ F'(t) \\
Q_t(0,y) &= u_t(0,y) - y\ F'(0) = -y\ F'(0).
\end{aligned}$$

$$\rho\ Q_{tt} - A\ \partial_y^2 Q + \int_0^t \frac{1}{\sqrt{2}} B_n U_{np}\ \delta_p\ \partial_y^2 Q(s,y) e^{-c_p(t-s)}\ ds = \tilde{q} \tag{52}$$

$$Q(t,0) = 0 \qquad Q(0,y) = -y\ F(0)$$
$$\frac{\partial Q}{\partial y}(t,b) = 0 \qquad Q_t(0,y) = -y\ F'(0)$$

Consider the Sturm-Liouille problem

$$\begin{aligned}
&-Z'' - \lambda\ Z = 0 \\
&Z(0) = 0 \\
&Z'(b) = 0
\end{aligned} \tag{53}$$

The eigenvalue problem (53) has a system of eigenvalues

$$0 < \mu_1 < \mu_2 < \cdots < \mu_n \cdots \nearrow \infty$$

and a corresponding orthogonal system of eigenfunctions $\psi_1, \psi_2, \ldots, \psi_n, \ldots$.

Set

$$\begin{aligned}
Q^1 &= Q \\
Q^2 &= Q_t
\end{aligned}$$

Then, (45) cn be written as

$$\begin{aligned}
\frac{\partial}{\partial t} Q^1 &= Q^2 \\
\partial_t\ Q^2 &= A \partial_y^2\ Q^1 - \int_0^t \frac{1}{\sqrt{2}} B_m U_{mp}\ \delta_p\ \partial_y^2 Q(s,y) e^{-c_p(t-s)}\ ds + \tilde{q}
\end{aligned} \tag{54}$$

We look for a solution of (54) of the form

$$\begin{aligned}
Q^1 &= \sum_m Q_m^1(t)\ \psi_m(y) \\
Q^2 &= \sum_m Q_m^2(t)\ \psi_m(y)
\end{aligned}$$

Then, using Laplace transform

$$\zeta \hat{Q}_m^1(\zeta) - \hat{Q}_m^1(0) = \hat{Q}_m^2$$

$$\zeta \hat{Q}_m^2(\zeta) = -\mu_m \frac{A}{\rho} + \frac{1}{\sqrt{2}} B_m U_{mp} \delta_p \mu_m \hat{Q}_m \frac{1}{c_p + \zeta} + \tilde{q}$$

$$\zeta^2 \hat{Q}_m^1 - \frac{\frac{1}{\sqrt{2}\rho} B_m U_{np} \delta_p \mu_n}{\rho(c_p + \zeta)} \hat{Q}_m^1 + \frac{\mu_m}{\rho} A \hat{Q}_m^1 = \zeta \hat{Q}_m^1(0) + Q_m^2(0) + \frac{1}{\rho} \hat{\tilde{q}}_m$$

Let

$$\gamma_1 = \sum\nolimits_n U_{n1} B_n$$

We need to investigate the roots of the polynomial

$$\rho\zeta^2(c_1 + \zeta) + \mu_m A (c_1 + \zeta) - \frac{1}{\sqrt{2}} \gamma_1 \delta_1 c_1 \mu_m$$

By Routh-Hurewitz Theorem the roots all have negative real parts provided $\mu_m A c_1 - \frac{1}{\sqrt{2}} \gamma_1 \delta_1 c_1 \mu_m > 0$. Further, the roots will be to the left half a vertical line given by $x = -M$, $M > 0$.

Let

$$\begin{aligned}
\gamma_q &= \sum\nolimits_n U_{nq} B_n \\
D_q &= C_q \gamma_q, \; q = 2, \ldots, N-1 \\
\Gamma(\rho, c_1, \mu_m, \gamma_1, \zeta) &= \rho\zeta^2(c_1 + \zeta) + \mu_m A (c_1 + \zeta) - \frac{1}{\sqrt{2}} \gamma_1 \delta_1 c_1 \mu_m \\
H_1(\rho, c_1, \mu_m, \gamma_1, \zeta) &= \frac{\Gamma}{\zeta(\zeta + C_1)} \\
H_2(\rho, c_1, \mu_m, \gamma_1, \zeta) &= (Q_m'(0)\zeta + Q_m(0)) H_1^{-1} \\
\Theta(t) &= \sum_{q=2}^{\infty} D_q e^{-C_q t}
\end{aligned}$$

Then,

$$H_1 \hat{Q}_m - (Q_m'(0)\zeta + Q_m(0)) = \frac{\mu_m}{\rho} Q_m' \hat{\Theta} + \frac{1}{\rho} \hat{\tilde{q}}_m$$

Taking inverse Laplace transform of H^{-1} and H_2 we have

$$\begin{aligned}
\mathcal{L}(H^{-1})(t) &= \sum_{i=1}^{3} \kappa_{mi} e^{\zeta_{mi} t} \\
\mathcal{L}(H_2)(t) &= \sum_{i=1}^{3} \eta_{mi} e^{\zeta_{mi} t}
\end{aligned}$$

where $Re(\zeta_{mi}) \le -M$, $M > 0$. Then,

$$Q_m(t) = \int_0^t \left[\int_0^s \left(\sum_{i=1}^{3} \kappa_{mi} e^{\zeta_{mi}} (s - r) \right) Q_m(r) dr \right] \Theta(t - s) ds$$

$$+ \sum_{i=1}^{3} \eta_{mi} e^{\zeta_{mi}} t + \frac{1}{\rho} \sum_{i=1}^{3} \kappa_{mi} \int_0^t e^{\zeta_{mi}}(t-s) q_m(s) ds$$

$$= \int_0^t Q_m(s) \sum_{i=1}^{3} \sum_{q=2}^{\infty} \frac{\kappa_i D_q}{\lambda_i + C_q} (e^{\zeta_{mi}}(t-s) - e^{-C_q(t-s)}) ds$$

$$+ \sum_{i=1}^{3} \eta_{mi} e^{\zeta_{mi}} t + \frac{1}{\rho} \sum_{i=1}^{3} \kappa_{mi} \int_0^t e^{\zeta_{mi}}(t-s) q_m(s) ds \tag{55}$$

Now consider the equation

$$w_m(t) = \int_0^t w_m(s) \sum_{i=1}^{3} \sum_{q=2}^{\infty} \frac{\kappa_i D_q}{\lambda_i + C_q} (e^{\zeta_{mi}}(t-s) - e^{-C_q(t-s)}) ds + \sum_{i=1}^{3} \eta_{mi} e^{\zeta_{mi}} t \tag{56}$$

The integral equation (56) can be solved uniquely and

$$|w_m(t)| \leq L_m e^{-K_m t}$$

We also have

$$Q_m(t) - w_m(t) = \int_0^t (Q_m(s) - w_m(s)) \sum_{i=1}^{3} \sum_{q=2}^{\infty} \frac{\kappa_i D_q}{\lambda_i + C_q} (e^{\zeta_{mi}}(t-s) - e^{-C_q(t-s)}) ds$$

$$+ \frac{1}{\rho} \sum_{i=1}^{3} \kappa_{mi} \int_0^t e^{\zeta_{mi}}(t-s) q_m(s) ds \tag{57}$$

If q_m is white noise the second integral in (57) is a Wiener integral. Then,

$$E[Q_m(t) - w_m(t)] = 0$$

Thus,

$$E[Q_m(t)] = w_m(t)$$

Let $R(t, s)$ be the resolvent kernel for the integral equation for (57). Then,

$$Q_m(t) - w_m(t) = \frac{1}{\rho} \sum_{i=1}^{3} \kappa_{mi} \int_0^t e^{\zeta_{mi}}(t-s) q_m(s) ds$$

$$= \int_0^t R(t, s) \frac{1}{\rho} \sum_{i=1}^{3} \kappa_{mi} \int_0^s e^{\zeta_{mi}}(s-r) q_m(r) dr$$

$$= \int_0^t q_m(r) \int_r^t R(t, s) \frac{1}{\rho} \sum_{i=1}^{3} \kappa_{mi} e^{\zeta_{mi}}(s-r) ds dr \tag{58}$$

The inner integral in (58) is bounded by a constant of the form

$$d_m \frac{1}{\rho} |\kappa_{mi}| (e^{Re(\zeta_{mi})t} + e^{Re(\zeta_{mi})r}).$$

Now we see that

$$E(|Q_m(t) - w_m(t)|^2) \leq \Delta_m t \,,$$

$$E(|Q_m(t)|^2) \leq |w_m(t)|^2 + \Delta_m t \,.$$

From the above analysis we see how we may solve the initial boundary value problem (49)–(50) and also obtain qualitative information without explicity solving it. Given u one obtains $b_n(t)$ from (41). We have just shown how one may proceed to deal with the first order apporximation (in u_x^{pc} and u_x) of (41). Next we present how we may approximate the microscopic stress tensor at a given point.

The microscopic stress contribution $\sigma_{\alpha\beta}^{PC}(t)$ to the stress tensor that comes from the PC-molecules as a result of applied strain is given by

$$\sigma_{\alpha\beta}^{PC}(t) = \frac{c}{N}\frac{3k_BT}{b^2}\sum_{n=1}^{N-1}\langle b_{n\alpha}(t)b_{n\beta}(t)\rangle \tag{59}$$

where $\frac{c}{N}$ accounts for the number of polymers in a unit volume. Suppose we take a cell of dimension (in A=Angstrom) $30A \times 30A \times 30A$. Then, we may put a molecular chain of end to end length of $a = 30A$ in the cell. If the Kuhn length is $15A$ we expect 4 segments in the chain. Thus, we may take a bead to bead distance of about $15A$. If we think of polyethylene we need about 10 monomer units between beads or per segment, or about 40 monomer units per chain of end to end distance of $30A$. We expect polyethylene of density 35kg per cubic meter will place about 40 monomers in a cell of the above dimension. Suppose we subject the r-th constraining cell to a shear deformation $(x, y, z) \mapsto (x + u(t, y), y, z)$ where $u(t, y) = t * y * \cos((t-1) * \pi * t) * 1.707 * (1 - (t-1) * (t)^2)$ at time t. Using (46)–(48) we calculate $b_n(t)$(see (28)). We used (28) and (59) to get the stess contributions. The figures below show stress contributions by the constrained molecules as a result of the applied shear.

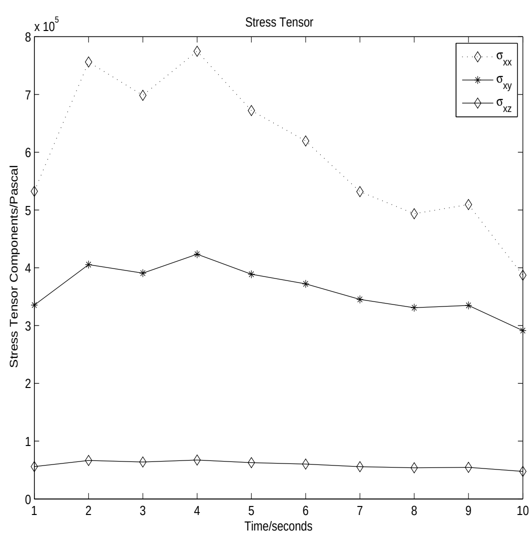

FIGURE 1

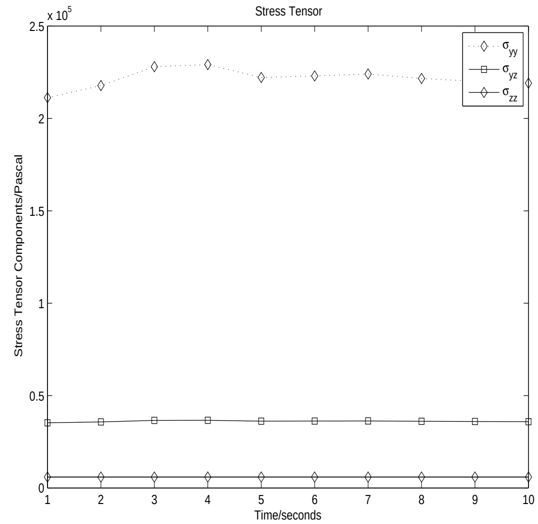

FIGURE 2

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