

# A Molecular Based Model for Polymer Viscoelasticity: Intra- and Inter-Molecular Variability

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## **Abstract**

We develop dynamic equations for rubber viscoelasticity based on a stick-slip continuum molecular-based model. The model developed is a continuum tube reptation model in which a chemically cross-linked (CC) system of molecules act as constraint box per unit volume for a physically constrained (PC) system of molecules. The CC-system carries along the PC-system during instantaneous step deformations. The subsequent relaxation of the PC-system is determined by the configuration of the CC-system, its own configuration and confirmation, and external force fields. Conversely, the deformation of the PC-system acts as an internal variable affecting the deformations of the constraining CC-system. We model the relationship between these processes to derive a model of viscoelasticity in rubber deformation. In developing a relaxation process for the PC-system, we start from the fact that the PC-system is composed of long molecular chains. The dynamics of these molecular chains are developed by modeling them as chains of beads connected by springs, which represent inter-molecular potentials. Various segments of the molecular chains relax at different rates. In addition, variability in relaxation times across molecular chains is permitted.

# 1 Introduction

Various molecular and phenomenological models have been developed to model both small and large deformations in rubber ([3],[4],[5],[6],[7],[13],[14]). Many of these efforts involve uniform molecular relaxation times even though there is substantial experimental evidence ([2],[10],[15],[17],[20]) to suggest that the assumption of uniform relaxation time is not valid. The focus here is to develop models accounting for the multiple relaxation times observed in experiments dealing with the relaxation of elastomers.

In our effort to account for multiple relaxation times, we integrate and extend ideas from molecular models of Doi and Edwards [9] and Johnson and Stacer [12] and derive a class of nonlinear distributed parameter systems (partial differential equations) with internal strain dynamics that are related to the pseudo-phenomenological models of [6],[7]. These latter models have provided good agreement with both quasi-static and dynamic data for rubber in uniaxial tension and in shear.

The dynamic model for rubber viscoelasticity presented here is based on the continuum version [12] of a tube reptation model considered in [9]. In [9], step-strain relaxation of polymers is modeled with a constraint (stick-slip) theory in which PC-molecules deform with CC-molecules during a large step-strain. Then the PC-molecules contract and creep to return to a lower energy and higher entropy state. As a result, the total energy density at a constraint strain dissipates in time and a viscoelastic theory results. These models are based on cross-linking of rubber network theories for rubbers and other polymers [14],[16],[18]. Here we refine our previous model [3] by accounting for the presence of multiple relaxation times and including them in the relaxation process consistent with the reptation mechanism for the relaxation of the PC-molecule. This is accomplished by a closer study of the dynamics of the PC-molecules.

The continuum molecular model of rubber viscoelasticity proposed in [12] is based on considering the chemically cross-linked molecules as providing cells or boxes with entrapped PC-molecular segments. The model involves placing a unit cell or box at each point of the rubber continuum and deriving subsequent equations for the associated principal stretches. The model developed here employs this fundamental idea.

## 2 Variability of relaxation rates across the length of a constrained molecule

We model a typical PC-molecule by a chain of  $N$ -beads connected by springs. Let the position of the  $i$ -th bead be given by

$$R_i = \sum_{k=1}^N A_{ik} q_k, \quad (1)$$

with, for example,  $A_{ik} \approx \exp(-a^2|i-k|b^2)$ , where throughout we use the notation  $f \approx g$  to indicate that  $f$  behaves like or can be approximated by  $g$ .

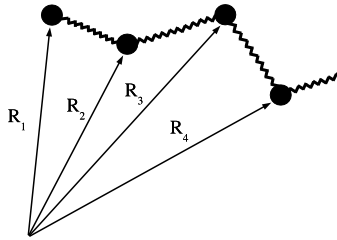


Figure 1: Vector representation of nodes in a polymer molecule.

Thus, the most dominant contribution to  $R_i$  comes from  $q_i$ . In (1) we have

$$q_k = \sum_{\mu=1}^3 q_{k\mu} e_{\mu}, \quad (2)$$

where  $e_{\mu}$  is a unit vector in the direction of the  $\mu$ -th coordinate axis.

Let

$$S = \{(m, n) | m = 1, 2, \dots, N; n = 1, 2, 3\}$$

$$T = \{1, 2, \dots, 3N\}$$

and  $\tilde{h}$  a bijection from  $S$  onto  $T$ .

Let

$$g(ai, bj) = \sum_{\ell=1}^N \frac{\partial R_{\ell}}{\partial q_{ai}} \frac{\partial R_{\ell}}{\partial q_{bj}}, \quad 1 \leq a, b \leq N, \quad 1 \leq i, j \leq 3.$$

Define the  $3N \times 3N$  matrices

$$G\left(\tilde{h}(a, i), \tilde{h}(b, j)\right) = g(ai, bj),$$

$$h_{ajib} = G^{-1}\left(\tilde{h}(a, i), \tilde{h}(b, j)\right).$$

We are interested in the dynamics of the bead-spring chain model. For that we seek the relevant configurational distribution of the chain. We consider a configurational distribution for a chain that is in a fairly general medium possibly subjected to an external force field.

In the case when the mobility matrix is  $H_{nm} = \frac{1}{\zeta}I\delta_{nm}$ , where  $I$  is the identity matrix and  $\zeta$  is the friction constant ([9]), the configurational distribution  $\psi$  of the chain can be shown to obey the equation ([9], page 79, see equation (3.162))

$$\frac{\partial\psi}{\partial t} = \zeta h_{ajib} k_B T \frac{\partial}{\partial q_{ai}} \left( \frac{\partial\psi}{\partial q_{bj}} \right) + \zeta h_{ajib} \frac{\partial}{\partial q_{ai}} \left( \frac{\partial U}{\partial q_{bj}} \right) - \frac{\partial}{\partial q_{ai}} \left( V_{ai}^{(V)} \psi \right), \quad (3)$$

where  $k_B$  is Boltzmann's constant,  $T$  temperature, and  $U$  is potential that includes intermolecular potential as well as possible contributions due to external driving fields. Finally, the medium viscosity is given by

$$V_{ai}^{(V)} = \zeta h_{aibk} \frac{\partial R_n}{\partial q_{bk}} \cdot (H^{-1})_{nm} \cdot (\kappa \cdot R_m), \quad (4)$$

([9], page 78), where  $\kappa$  is velocity gradient tensor. In (3) and (4) we sum over repeated indices (Einstein notation).

In the case when the intermolecular potential is modified by adding a Lennard-Jones type potential and there is an external electric field,  $E = (E_1, E_2, E_3)$ , which induces a dipole going from one molecule (bead) to the next, oriented in the same direction, we have

$$\begin{aligned} \frac{d}{dt} \langle q_{lr} \rangle &= -\zeta k^* C_{lr dk} \langle q_{dk} \rangle \\ &+ \zeta \mu_2 E_k h_{lr bk} (A_{m+1, b} - A_{m, b}) (A_{m+1, j} - A_{m, j}) E_\nu \langle q_{j\nu} \rangle \\ &+ \zeta \mu_1 E_k h_{lr bk} \sum_{n=1}^{N-1} (A_{n+1, b} - A_{n, b}) \\ &+ \zeta h_{lr bk} A_{nb} A_{nl'} \kappa_{k\nu} \langle q_{l'\nu} \rangle \\ &- \zeta h_{lr bk} \sum_{n=1}^{N-1} K_n (A_{nb} - A_{n+1, b}) \sum_m [(A_{n, m} - A_{n+1, m}) \langle q_{mk} \rangle]. \end{aligned} \quad (5)$$

Here  $\langle q_{lr} \rangle$  represents the average of  $q_{lr}$ , i.e.,  $\langle q_{lr} \rangle = \int \psi q_{lr} dq$ ,

$$C_{lr dk} = \sum_{n=2}^N \sum_{b=1}^N h_{lr bk} (A_{n-1,d} - A_{n,d})(A_{n-1,b} - A_{n,b}),$$

and

$$K_n = 12\tilde{\epsilon}(r^*)^6 \widehat{R}_n^{-8} \left(1 - (r^*)^6 \widehat{R}_n^{-6}\right)$$

is the Lennard-Jones potential, where the constant  $\tilde{\epsilon}$  is the depth of the well and  $r^*$  is the separation at which  $\widehat{R}_n$  is a minimum where  $\widehat{R}_n = |R_n - R_{n+1}|$ .

Because we have the formulation of our  $A_{ik}$  weighted so that its largest value occurs when  $i = k$ , e.g.,  $A_{ik} \approx \exp(-a^2|i - k|^{b^2})$ , the system presented in equation (5) can be thought of as almost diagonal.

Let  $\Phi(t, s)$  be the fundamental solution of (5). The time dependent off-diagonal elements of the coefficient matrix in (5) are assumed to be small quantities compared to the diagonal elements. In fact, we take these quantities to be zero in subsequent discussions. Since the off-diagonal elements are assumed to be much smaller quantities than the diagonal elements, we have

$$\begin{aligned} \langle q_{k\mu}(t) \rangle &\approx e^{-(t-s)/\tau_{k\mu}} \Phi_{k\mu}(t, s) \langle q_{k\mu}(s) \rangle, \\ \Phi_{k\mu}(t, t') \Phi_{k\mu}(t', t_0) &\approx \Phi_{k\mu}(t, t_0), \quad \Phi_{k\mu}(t, t) = 1, \\ \Phi_{k\mu}(t, t_0) &\geq 0, \quad Re(\tau_{k\mu}) > 0. \end{aligned}$$

The parameters  $\tau_{k\mu}$ ,  $k = 1, \dots, N$ ,  $\mu = 1, 2, 3$  are the relaxation parameters of interest. In the case where we ignore the hydrodynamic effect (the velocity field in the surrounding medium caused by the motion of one particle which could effect the motion of the other particles) and time dependent external fields in the dynamics of the molecular chain, we will have

$$\langle q_{k\mu}(t) \rangle \approx e^{-(t-s)/\tau_{k\mu}} \langle q_{k\mu}(s) \rangle,$$

which amounts to setting

$$\Phi_{k\mu} \equiv 1.$$

### 3 Extending the continuum model of Johnson and Stacer

We recall that the PC-molecule is modeled by  $N$  beads connected by springs, and the position of the  $i$ -th bead is given by

$$R_i = \sum_{k=1}^N A_{ik} q_k, \quad (6)$$

or

$$R_i = \sum_{\mu=1}^3 R_{i\mu} e_{\mu}. \quad (7)$$

We also recall from Section 2 that

$$\langle q_{k\mu}(t) \rangle \approx e^{-(t-s)/\tau_{k\mu}} \Phi_{k\mu}(t, s) \langle q_{k\mu}(s) \rangle. \quad (8)$$

We note that

$$\langle R_i(t) \rangle = \sum_{\mu} \sum_k A_{ik} \langle q_{k\mu} \rangle e_{\mu}. \quad (9)$$

We would like our generalization of the continuum model of Johnson and Stacer to reflect the presence of multiple relaxation parameters  $\tau_{k\mu}$  (see (8)). On the basis of (7) and (8) we expect the extension at a given point of the PC-molecule to be a superposition of extensions across the length of the PC-molecule.

Let the CC-constraint-tube have length  $L(t)$  and the trapped PC-molecule have length  $\ell(t)$ . We may consider  $\ell(t)$  as composed of  $N$  segments  $(\alpha_k \ell)(t)$ ,  $k = 1, \dots, N$ ,  $\alpha_k \geq 0$ ,  $\sum_{k=1}^N \alpha_k = 1$ , where  $(\alpha_k \ell)(t)$  relaxes in the direction of  $e_{\mu}$  with relaxation parameter  $\tau_{k\mu}$ . We relate the stretches in the constraining CC-molecule and the PC-molecule by the linear relationship (for a discussion of nonlinear analogues, see [4])

$$\begin{aligned} \Delta(\alpha_k \ell) &= \frac{(\alpha_k \ell)}{(\alpha_k L)} \Delta(\alpha_k L) \\ &= \frac{\ell}{L} \Delta(\alpha_k L). \end{aligned} \quad (10)$$

In what follows we will, without loss of generality, drop the “ $\mu$ ” in  $\tau_{k\mu}$  and  $\Phi_{k\mu}$ , and consider  $\tau_k \in \mathbb{R}$ .

In the time interval  $t_0 \leq t \leq t_1$ , we use (8) for segments of the CC-tube to obtain

$$(\alpha_k \ell)(t) = (\alpha_k \ell)(t_0) + \frac{\ell(t_0)}{L(t_0)} \Delta(\alpha_k L)(t_0) e^{-(t-t_0)/\tau_k} \Phi_k(t, t_0), \quad k = 1, \dots, N.$$

Here we follow [12] and consider a sequence of instantaneous step tensile deformations at times  $\{t_i\}$  in the constraint tube. We write  $\ell_i$  for  $\ell(t_i)$ ,  $L_i$  for  $L(t_i)$ ,  $(\alpha_k \ell)_i$  for  $(\alpha_k \ell)(t_i)$ , and  $(\alpha_k L)_i$  for  $\alpha_k L(t_i)$  for  $i = 0, 1, \dots$ . Then we have

$$(\alpha_k \ell)_1 = (\alpha_k \ell)_0 + \frac{\ell_0}{L_0} \Delta(\alpha_k L)_0 e^{-(t_1 - t_0)/\tau_k} \Phi_k(t_1, t_0).$$

Set

$$L_1 = L_0 + \Delta L_0.$$

In the time interval  $t_1 \leq t \leq t_2$ , we obtain

$$\begin{aligned} (\alpha_k \ell)(t) &= (\alpha_k \ell)_0 + [(\alpha_k \ell)_1 + \Delta(\alpha_k \ell)_1 - (\alpha_k \ell)_0] e^{-(t - t_1)/\tau_k} \Phi_k(t, t_1) \\ &= (\alpha_k \ell)_0 + \left[ \frac{\ell_0}{L_0} \Delta(\alpha_k L)_0 e^{-(t_1 - t_0)/\tau_k} \Phi_k(t_1, t_0) + \Delta(\alpha_k \ell)_1 \right] e^{-(t - t_1)/\tau_k} \Phi_k(t, t_1) \\ &= (\alpha_k \ell)_0 + \frac{\ell_0}{L_0} \Delta(\alpha_k L)_0 e^{-(t - t_0)/\tau_k} \Phi_k(t, t_0) + \frac{\ell_1}{L_1} \Delta(\alpha_k L)_1 e^{-(t - t_1)/\tau_k} \Phi_k(t, t_1). \end{aligned}$$

In the continuum limit (again see [12]), we arrive at an expression for the length of the  $k^{\text{th}}$  segment of the PC-molecule

$$(\alpha_k \ell)(t) = (\alpha_k \ell)_0 + \int_0^t \frac{\ell(s)}{L(s)} \frac{d}{ds} (\alpha_k L)(s) e^{-(t-s)/\tau_k} \Phi_k(s, t_0) ds.$$

Summing from  $k = 1, \dots, N$  and writing the resulting formula in differential form, we obtain for tensile deformations

$$\frac{d\ell}{dt} = \sum_{k=1}^N \alpha_k \Phi_k(t, t_0) \frac{\ell(t)}{L(t)} \frac{dL(t)}{dt} - \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) \ell(t) + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) \ell_0. \quad (11)$$

## 4 Strain Energy Density

We recall here the discussion on strain energy density and stick-slip model found in [3] for tensile deformations in the context of segmented PC-molecules.

To use the stick-slip model in continuum simulation of the reptation model of rubber elasticity, one considers a network of cells or boxes in the rubber continuum with sides  $\lambda_{1c}$ ,  $\lambda_{2c}$ , and  $\lambda_{3c}$ . The CC-box will have positive strain energy density  $W_{cc}(\lambda_{1c}, \lambda_{2c}, \lambda_{3c})$  for all stretches except when  $\lambda_{1c} = \lambda_{2c} =$

$\lambda_{3c} = 1$ . Moreover, a box for the PC-system with sides parallel to those of the CC-box is defined by sides  $\lambda_{1p}$ ,  $\lambda_{2p}$ , and  $\lambda_{3p}$  along with an energy density  $W_{pc}(\lambda_{1p}, \lambda_{2p}, \lambda_{3p})$ .

Stresses are calculated from the strain energy density [19] by determining how the energy density function changes with respect to changes in the stretches or displacements. In the model considered, the strain energy density of the rubber continuum is assumed to have the form

$$\begin{aligned} W &= W_{cc} + W_{pc} \\ &= W_{cc}(\lambda_{1c}, \lambda_{2c}, \lambda_{3c}) + W_{pc}(\lambda_{1p}, \lambda_{2p}, \lambda_{3p}). \end{aligned} \quad (12)$$

To find the stresses at a generic point of the rubber continuum, one must determine how  $W$  changes with respect to stretches of the CC-system. The stretches of the PC-boxes are then treated as internal variables depending on the stretches of the CC-system.

The Cauchy stress in the principal direction  $e_j$  is given by

$$\Sigma_j = \lambda_{jc} \frac{\partial W}{\partial \lambda_{jc}} - P, \quad (13)$$

where  $P$  is the hydrostatic stress. If we consider (12) with the  $\lambda_{ip}$  as internal variables depending on the  $\lambda_{ic}$ , then (13) becomes

$$\Sigma_j = \lambda_{jc} \frac{\partial W_{cc}}{\partial \lambda_{jc}} + \lambda_{jc} \sum_{i=1}^3 \frac{\partial W_{pc}}{\partial \lambda_{ip}} \frac{\partial \lambda_{ip}}{\partial \lambda_{jc}} - P. \quad (14)$$

In obtaining (11), we have related the instantaneous tensile deformations  $\Delta(\alpha_k \ell)(t_\nu) = \Delta(\alpha_k \ell)_\nu$  and  $\Delta(\alpha_k L)(t_\nu) = \Delta(\alpha_k L)_\nu$  according to the formula

$$\frac{\Delta(\alpha_k \ell)_\nu}{\Delta(\alpha_k L)_\nu} = \frac{(\alpha_k \ell)_\nu}{(\alpha_k L)_\nu}. \quad (15)$$

Using this observation in the analogy of  $\Delta(\alpha_k \ell)_\nu$ ,  $\Delta(\alpha_k L)_\nu$  with principal stretches  $\lambda_{ip}$ ,  $\lambda_{ic}$ , respectively, we may write

$$\frac{\partial \lambda_{jp}}{\partial \lambda_{ic}} = \frac{\lambda_{jp}}{\lambda_{ic}} \delta_{ji}. \quad (16)$$

In the case of tensile deformations, choosing  $j = 1$  for the direction of loading and using (12) and (16) in (14), we have

$$\Sigma_2 = \Sigma_3 = 0 = \lambda_{2c} \frac{\partial W_{cc}}{\partial \lambda_{2c}} + \lambda_{2p} \frac{\partial W_{cc}}{\partial \lambda_{2p}} - P. \quad (17)$$



With the hydrostatic stress determined by (17), the tensile Cauchy stress is thus given by

$$\Sigma_1 = \lambda_{1c} \frac{\partial W_{cc}}{\partial \lambda_{1c}} - \lambda_{2c} \frac{\partial W_{cc}}{\partial \lambda_{2c}} + \lambda_{1p} \frac{\partial W_{pc}}{\partial \lambda_{1p}} - \lambda_{2p} \frac{\partial W_{pc}}{\partial \lambda_{2p}}. \quad (18)$$

## 5 A dynamic continuum model

To develop a dynamic continuum model for the analysis of rubber/elastomer undergoing large deformations, we use specific forms of the strain energy functions  $W_{cc}$ ,  $W_{pc}$  introduced in Section 4.

We will use parameterized expressions (for motivation, see [7]) for  $W_{cc}$  and  $W_{pc}$  in terms of invariants of the deformations. In particular, we assume

$$\begin{aligned} W_{pc} &= A_1(I_{pc,1} - 3) + A_2(I_{pc,2} - 3) \\ &\quad + A_3(I_{pc,1} - 3)^2 + A_4(I_{pc,2} - 3)^2, \end{aligned} \quad (19)$$

$$A_i \geq 0, \quad i = 1, 2, 3, 4,$$

$$\begin{aligned} W_{cc} &= B_1(I_{cc,1} - 3) + B_2(I_{cc,2} - 3) \\ &\quad + B_3(I_{cc,1} - 3)^2 + B_4(I_{cc,2} - 3)^2, \end{aligned} \quad (20)$$

$$B_i \geq 0, \quad i = 1, 2, 3, 4,$$

where we use the invariants

$$I_{pc,1} = \lambda_{1p}^2 + \lambda_{2p}^2 + \lambda_{3p}^2, \quad (21)$$

$$I_{cc,1} = \lambda_{1c}^2 + \lambda_{2c}^2 + \lambda_{3c}^2, \quad (22)$$

$$I_{pc,2} = \lambda_{1p}^2 \lambda_{2p}^2 + \lambda_{1p}^2 \lambda_{3p}^2 + \lambda_{2p}^2 \lambda_{3p}^2, \quad (23)$$

$$I_{cc,2} = \lambda_{1c}^2 \lambda_{2c}^2 + \lambda_{1c}^2 \lambda_{3c}^2 + \lambda_{2c}^2 \lambda_{3c}^2. \quad (24)$$

We also impose incompressibility conditions  $\lambda_{1c} \lambda_{2c} \lambda_{3c} = 1$ ,  $\lambda_{1p} \lambda_{2p} \lambda_{3p} = 1$ . In what follows, we use the relationships (for the tensile deformation case)

$$\lambda_{2c} = \lambda_{3c} = \frac{1}{\sqrt{\lambda_{1c}}}, \quad (25)$$

$$\lambda_{2p} = \lambda_{3p} = \frac{1}{\sqrt{\lambda_{1p}}}, \quad (26)$$

which satisfy these incompressibility conditions. From (18), the engineering stress  $\Sigma = \Sigma_1/\lambda_{1c}$  is given by

$$\Sigma = \frac{\partial W_{cc}}{\partial \lambda_{1c}} - \frac{\lambda_{2c}}{\lambda_{1c}} \frac{\partial W_{cc}}{\partial \lambda_{2c}} + \frac{\lambda_{1p}}{\lambda_{1c}} \frac{\partial W_{pc}}{\partial \lambda_{1p}} - \frac{\lambda_{2p}}{\lambda_{1c}} \frac{\partial W_{pc}}{\partial \lambda_{2p}}. \quad (27)$$

Thus, to approximate the engineering stress, we set

$$\begin{aligned} \ell &= 1 + \partial_x u_p, & L &= 1 + \partial_x u_c, \\ \epsilon_1 &= \partial_x u_p, & \epsilon &= \partial_x u_c. \end{aligned}$$

Then using (27), we make the approximation

$$\begin{aligned} \Sigma(\epsilon, \epsilon_1) &= \sigma_e(\epsilon) + \sigma_{ve}(\epsilon, \epsilon_1), \\ &= 6(B_1 + B_2)\partial_x u_c + 6(A_1 + A_2)(\partial_x u_p - \partial_x u_c \partial_x u_p) + \dots \\ &\approx 6(B_1 + B_2)\partial_x u_c + 6(A_1 + A_2)\partial_x u_p \end{aligned} \quad (28)$$

where we have divided the stress into elastic  $\sigma_e$  and viscoelastic  $\sigma_{ve}$  components (see [7] for detailed discussions).

From (11), we have

$$\dot{\epsilon}_1 + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) \epsilon_1 = \frac{1 + \epsilon_1}{1 + \epsilon} \dot{\epsilon} \sum_{k=1}^N \alpha_k \Phi_k(t, t_0),$$

and we note that

$$\frac{1 + \epsilon_1}{1 + \epsilon} \approx (1 + \epsilon_1)(1 - \epsilon) = 1 + \epsilon_1 - \epsilon - \epsilon\epsilon_1.$$

Thus,

$$\dot{\epsilon}_1 + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) \epsilon_1 \approx \dot{\epsilon} \sum_{k=1}^N \alpha_k \Phi_k(t, t_0). \quad (29)$$

From (29), under the assumption that  $\epsilon_1(t_0) = 0$ , we have

$$\begin{aligned} \epsilon_1(t) &= \epsilon(t) \sum_{k=1}^N \alpha_k \Phi_k(t, t_0) \\ &\quad - \int_{t_0}^t \epsilon(s) \partial_s \left[ e^{-\left(\sum_{k=1}^N \frac{\alpha_k}{\tau_k}\right)(t-s)} \sum_k \alpha_k \Phi_k(s, t_0) \right] ds. \end{aligned} \quad (30)$$

In terms of the deformations  $\partial_x u_p$ ,  $\partial_x u_c$  (30) is written as

$$\begin{aligned} \partial_x u_p &= \partial_x u_c \sum_{k=1}^N \alpha_k \Phi_k(t, t_0) \\ &\quad - \int_{t_0}^t \partial_x u_c(s, x) \partial_s \left[ e^{-\left(\sum_{k=1}^N \frac{\alpha_k}{\tau_k}\right)(t-s)} \sum_k \alpha_k \Phi_k(s, t_0) \right] ds. \end{aligned} \quad (31)$$

We next consider the longitudinal vibration of a rubber rod with (undeformed) cross-sectional area  $A_c$  and mass density  $\rho$ . Using (28) we write the equation of motion (recall that  $S = A_c \Sigma$  is the engineering stress resultant - see (2.1) of [7])

$$\rho A_c \partial_t^2 u_c - A_c \partial_x [6(B_1 + B_2) \partial_x u_c + 6(A_1 + A_2) \partial_x u_p] = F, \quad (32)$$

where  $F$  is the applied load (in force/unit length) and this equation must be solved with (31).

In summary, the full nonlinear approximate model we derive for the CC-PC molecular system in tensile deformations for a rod has the form

$$\rho \partial_t^2 u_c - \partial_x \Sigma(\epsilon, \epsilon_1) = F/A_c \quad (33)$$

$$\Sigma(\epsilon, \epsilon_1) = 6(B_1 + B_2) \partial_x u_c + 6(A_1 + A_2) (\partial_x u_p - \partial_x u_c \partial_x u_p) + \dots \quad (34)$$

$$\dot{\epsilon}_1 + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) \epsilon_1 = \frac{1 + \epsilon_1}{1 + \epsilon} \dot{\epsilon} \sum_{k=1}^N \alpha_k \Phi_k(t, t_0). \quad (35)$$

We remark that the system (33)-(35) can be viewed as a member of a class of systems similar to those treated in [1] and the methods presented there can be used to guarantee well-posedness (existence and uniqueness) of the corresponding variational forms of this system. Indeed, the models treated in [1] can be properly viewed as generalizations of (33)-(35) that permit (see [4]) nonlinear instantaneous elastic responses as well as other refinements.

To this point in our development for models with intra-molecular variability, we have treated a rubber sample as consisting of identical CC-molecules and identical PC-molecules and have ignored the possibility of any inter-molecular variation. The CC-molecules, which are forced, are not part of the relaxation phenomena and have a contribution to the elastic part  $\sigma_e$  of the stress that depends only on the infinitesimal strain  $\epsilon$ . However, the PC-molecules contribute in a significant way to the relaxation and they may have

variable (across the population of molecules) relaxation characteristics. If, for example, one has  $M$  distinct classes of PC-molecules with strains  $\epsilon_j$  for the  $j^{\text{th}}$  class contributing to the viscoelastic stress component, then the stress  $\Sigma(\epsilon, \epsilon_1)$  in (33) should be replaced by

$$\begin{aligned}\Sigma(\epsilon, \epsilon_1, \dots, \epsilon_M) &= \sigma_e(\epsilon) + \sigma_{ve}(\epsilon, \epsilon_1, \dots, \epsilon_M) \\ &= \sigma_e(\epsilon) + \sum_{j=1}^M \xi_j \sigma_j(\epsilon, \epsilon_j),\end{aligned}$$

where  $\sigma_j(\epsilon, \epsilon_j)$  is the  $\epsilon_j$  dependent contribution to the overall stress in the CC-tube and  $\xi_j$  is the frequency or proportion of the  $j^{\text{th}}$  class in the PC-molecule population.

There are several ways in which the PC-molecules might inherently differ, even if they have similar molecular composition; they might differ in the number of nodes  $N$  and in the relaxation parameters themselves. We introduce additional notation which can be used to more easily formulate this variation.

We allow the values of  $N$ , the number of nodes in the molecule, and the parameters  $\alpha$ ,  $\tau$  and  $\Phi$  to vary from one molecule to another. We further assume that there are  $j = 1, \dots, M$  such types or classes of molecules, each with its own set of  $N^j$  nodes and parameters  $\alpha_k^j$ ,  $\tau_k^j$  and  $\Phi_k^j$ , for  $k = 1, \dots, N^j$ . With this in mind, we can extend the nonlinear model for the CC-PC molecular system by

$$\begin{aligned}\rho \partial_t^2 u_c - \partial_x \Sigma(\epsilon, \epsilon_1, \dots, \epsilon_M) &= F/A_c, \\ \Sigma(\epsilon, \epsilon_1, \dots, \epsilon_M) &= \sigma_e(\epsilon) + \sum_{j=1}^M \xi_j \sigma_j(\epsilon, \epsilon_j) \\ &\approx 6(B_1 + B_2)\epsilon + 6(A_1 + A_2) \sum_{j=1}^M \xi_j \epsilon_j, \\ \dot{\epsilon}_j + \left( \sum_{k=1}^{N^j} \frac{\alpha_k^j}{\tau_k^j} \right) \epsilon_j &= \frac{1 + \epsilon_j}{1 + \epsilon} \dot{\epsilon} \sum_{k=1}^{N^j} \alpha_k^j \Phi_k^j(t, t_0).\end{aligned}$$

We can simplify the above system of equations by making a few substitutions. First we define

$$\frac{1}{\mathcal{J}^j} = \sum_{k=1}^{N^j} \frac{\alpha_k^j}{\tau_k^j},$$

and next we define

$$\Phi^j(t, t_0; \{\alpha_k^j\}, \{\Phi_k^j\}) = \sum_{k=1}^{N^j} \alpha_k^j \Phi_k^j(t, t_0).$$

Thus, we have the following model, based on these discrete variabilities

$$\rho \partial_t^2 u_c - \partial_x \Sigma(\epsilon, \epsilon_1, \dots, \epsilon_M) = F/A_c, \quad (36)$$

$$\Sigma(\epsilon, \epsilon_1, \dots, \epsilon_M) \approx 6(B_1 + B_2)\epsilon + 6(A_1 + A_2)\sum_{j=1}^M \xi_j \epsilon_j, \quad (37)$$

$$\dot{\epsilon}_j + \frac{1}{\mathcal{T}^j} \epsilon_j = \frac{1 + \epsilon_j}{1 + \epsilon} \dot{\epsilon} \Phi^j(t, t_0; \{\alpha_k^j\}, \{\Phi_k^j\}), \quad (38)$$

$$\text{for } j = 1, \dots, M, \text{ where } \xi_j \geq 0 \text{ and } \sum_{j=1}^M \xi_j = 1.$$

The above generalization permits only a finite number of different possibilities of relaxation parameters (corresponding to the  $M$  types of molecules we are considering). We may further generalize our system to a continuum of types of molecules with arbitrary but finite length by using a probability distribution formulation. To do this, we must first determine the space over which such a distribution would be defined.

We first observe that we would like to be able to vary the number of nodes in a molecule,  $N^j$ . These numbers,  $N^j$ , are positive integers and we assume there exists an upper bound for all  $N^j$  dependent on the particular type of elastomer considered. We shall call this upper bound  $N^*$  and thus we define the space

$$\mathcal{N} = \{N \mid N \in \mathbb{Z} \text{ and } 0 < N \leq N^*\}$$

to be the space of all possible chain lengths.

We next need to specify the spaces in which the variable parameters reside. Although we have simplified our model to be in terms of  $\mathcal{T}^j$  and  $\Phi^j$ , we recall that these new parameters are based on the parameters  $\alpha_k^j$ ,  $\tau_k^j$  and  $\Phi_k^j$ . For each term, we define an admissible set of parameters as follows:

$$A = \left\{ \vec{\alpha} = \{\alpha_k\}_{k=1}^{N^*} \mid \alpha_k \in \mathbb{R}, \alpha_k \geq 0 \text{ for all } k, \sum_{k=1}^{N^*} \alpha_k = 1 \right\},$$

$$D = \left\{ \vec{\tau} = \{\tau_k\}_{k=1}^{N^*} \mid \tau_k \in \mathbb{R}, \tau_k \geq 0 \text{ for all } k \right\},$$

$$\mathcal{F}_{\mathbf{T}} = \left\{ f \mid f(t, t')f(t', t_0) = f(t, t_0), f(t, t) = 1, f(t, t_0) \in \mathbb{R}^+ \right\},$$

$$\mathcal{F} = \left\{ \vec{\Phi} = \{\Phi_k\}_{k=1}^{N^*} \mid \Phi_k \in \mathcal{F}_{\mathbf{T}} \text{ and } \Phi_k \in C^n, \text{ for all } k \right\}.$$

We note that the time dependence of the functions  $\Phi_k$  depends on the velocity gradient,  $\kappa$ , and the electric/external field,  $E$  (see (5)). Thus the functions  $\Phi_k$  should all be as smooth as  $\kappa$  and  $E$ . We may assume that the velocity gradient and the electric/external field, if present, are at least continuous. Thus we may assume that  $\mathcal{F}$  is a subset of the  $C^n$  functions on  $[0, \infty) \times [0, \infty)$  for some  $n \geq 1$ .

We define  $\mathcal{T}$ , which is the space of all possible sets of relaxation parameters, to be

$$\mathcal{T} = \left\{ (\vec{\alpha}, \vec{\tau}, \vec{\Phi}) \mid \vec{\alpha} \in A, \vec{\tau} \in D, \text{ and } \vec{\Phi} \in \mathcal{F} \right\},$$

with subspaces defined to be

$$\mathcal{T}_N = \left\{ T \in \mathcal{T} \mid \alpha_k = 0, k = N + 1 \cdots N^* \right\}.$$

Finally, we define the combined space,  $\mathcal{N} \times \mathcal{T}$ , by

$$\mathcal{N} \times \mathcal{T} = \left\{ (N, T) \mid N \in \mathcal{N}, T \in \mathcal{T} \right\}.$$

Using this space we are able to represent the parameters for any molecule of admissible length without having to introduce separate spaces for each possible number of nodes. This can be done by defining a distribution on  $\mathcal{N} \times \mathcal{T}$ , which we will refer to as  $\mathcal{P}(N, T)$ , for  $N \in \mathcal{N}$  and  $T \in \mathcal{T}$ , that must have the following condition:

$$\mathcal{P}(N, T) = 0 \text{ for } (N, T) \text{ such that } T \notin \mathcal{T}_N.$$

Using this probability, we have the following new equation for the stress

$$\Sigma(\epsilon, \mathcal{P}) = 6(B_1 + B_2)\epsilon + 6(A_1 + A_2) \int_{\mathcal{N} \times \mathcal{T}} \tilde{\epsilon}(\epsilon, N, T) d\mathcal{P}(N, T) \quad (39)$$

where  $(N, T) \in \mathcal{N} \times \mathcal{T}$  and  $\tilde{\epsilon}$  satisfies

$$\dot{\tilde{\epsilon}} + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) \tilde{\epsilon} = \frac{1 + \tilde{\epsilon}}{1 + \epsilon} \dot{\epsilon} \sum_{k=1}^N \alpha_k \Phi_k(t, t_0). \quad (40)$$

This randomly distributed model incorporates both intra-molecular variability of relaxation parameters and inter-molecular variability of relaxation parameters and composition of the molecules. It is thus a continuum extension of the model given in (36)-(38) where there are only discrete possibilities.

## 6 Qualitative analysis of the model

In this section, we provide a brief analysis of the model derived in the previous section. In particular, we consider equations (32) subject to (31). Similar analysis can be performed on the model given in equations (36)-(38) and those ideas are summarized at the end of the following analysis.

We set (see (31) and (32))

$$P_1 = 6(B_1 + B_2) \quad (41)$$

$$P_2 = 6(A_1 + A_2) \quad (42)$$

$$R = \sum_{k=1}^N \alpha_k \Phi_k(t, t_0). \quad (43)$$

In the case when we ignore hydrodynamic effect and external time dependent fields in the dynamics of the molecular chain (PC-chain), we set  $\Phi_k(t, t_0) = 1$  and hence  $R = 1$  in (43).

In what follows, we set  $t_0 = 0$ . Thus, from (32) and (31) we have

$$\begin{aligned} & \rho \partial_t^2 u_c - [P_1 + P_2] \partial_x^2 u_c \\ & + \int_0^t P_2 \partial_s \left\{ e^{-\left(\sum_{k=1}^N \frac{\alpha_k}{\tau_k}\right)(t-s)} \right\} \partial_x^2 u_c(s) ds = \frac{F}{A_c}. \end{aligned} \quad (44)$$

We define

$$\begin{aligned} v &= [P_1 + P_2] u_c - \int_0^t P_2 \partial_s \left\{ e^{-\left(\sum_{k=1}^N \frac{\alpha_k}{\tau_k}\right)(t-s)} \right\} u_c(s) ds \\ &= [P_1 + P_2] u_c - \int_0^t P_2 e^{-\left(\sum_{k=1}^N \frac{\alpha_k}{\tau_k}\right)(t-s)} \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) u_c(s) ds. \end{aligned} \quad (45)$$

Then, setting

$$c = \sum_{k=1}^N \frac{\alpha_k}{\tau_k} P_1 / (P_1 + P_2), \quad (46)$$

$$\beta(t) = ct, \quad (47)$$

we have

$$\begin{aligned}
v_{tt} + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) v_t - c \left( v_t + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) v \right) - \frac{1}{\rho} (P_1 + P_2) v_{xx} \\
+ c^2 \int_0^t e^{-(\beta(t)-\beta(s))} \left( v_s + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) v \right) ds \\
= (P_1 + P_2) \left\{ \frac{F}{A_c \rho} - c^2 e^{-\beta(t)} u_c(0) \right\}.
\end{aligned} \tag{48}$$

Rewriting (48), we find

$$\begin{aligned}
v_{tt} + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) v_t - c \left( v_t + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) v \right) - \frac{1}{\rho} (P_1 + P_2) v_{xx} \\
+ c^2 \int_0^t e^{-c(t-s)} \left( v_s + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) v \right) ds = f,
\end{aligned} \tag{49}$$

where

$$f = (P_1 + P_2) \left\{ \frac{F}{A_c \rho} - c^2 e^{-ct} u_c(0) \right\}.$$

Next, we consider the standard Sturm-Liouville problem

$$\begin{aligned}
-y'' - \lambda y &= 0 \\
y(a) - h_0 y'(a) &= 0, \quad h_0 \geq 0 \\
y(b) - h_1 y'(b) &= 0, \quad h_1 \geq 0.
\end{aligned} \tag{50}$$

For this problem, it is known [8] that there is a sequence of eigenvalues  $0 < \lambda_1 < \lambda_2 < \dots < \lambda_n < \dots \nearrow \infty$  and a corresponding complete family of orthonormal eigenfunctions  $\varphi_1, \varphi_2, \dots, \varphi_n, \dots$ .

We will explore (49) with an appropriate Sturm-Liouville problem such as (50). Thus, let us consider a solution of (49) in the form

$$v(t, x) = \sum_{n=1}^{\infty} v_n(t) \varphi_n(x). \tag{51}$$

Also, expanding the function

$$f(t, x) = \sum_{n=1}^{\infty} f_n(t) \varphi_n(x), \tag{52}$$



we formally obtain

$$\begin{aligned} \ddot{v}_n + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) \dot{v}_n - c \left( \dot{v}_n + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) v_n \right) + \frac{1}{\rho} (P_1 + P_2) \lambda_n v_n \\ + c^2 \int_0^t e^{-c(t-s)} \left[ \dot{v}_n + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) v_n \right] ds = f_n. \end{aligned} \quad (53)$$

Let

$$w_n = c^2 \int_0^t e^{-c(t-s)} \left[ \dot{v}_n + \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) v_n \right] ds \quad (54)$$

and

$$\begin{cases} u_1^n(t) = v_n(t) \\ u_2^n(t) = \dot{v}_n(t) \\ u_3^n(t) = w_n(t). \end{cases} \quad (55)$$

Then

$$\frac{d}{dt} \begin{bmatrix} u_1^n \\ u_2^n \\ u_3^n \end{bmatrix} = A_n \begin{bmatrix} u_1^n \\ u_2^n \\ u_3^n \end{bmatrix} + \begin{bmatrix} 0 \\ f_n \\ 0 \end{bmatrix}, \quad (56)$$

where

$$A_n = \begin{bmatrix} 0 & 1 & 0 \\ \left[ c \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) - \frac{1}{\rho} (P_1 + P_2) \lambda_n \right] & \left[ c - \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right] & -1 \\ c^2 \left( \sum_{k=1}^N \frac{\alpha_k}{\tau_k} \right) & c^2 & -c \end{bmatrix}.$$

We have

$$|\zeta I - A_n| = \zeta^3 + \zeta^2 \sum_{k=1}^N \frac{\alpha_k}{\tau_k} + \zeta \frac{1}{\rho} (P_1 + P_2) \lambda_n + \frac{1}{\rho} (P_1 + P_2) \lambda_n c. \quad (57)$$

The Routh-Hurwitz Theorem [11] guarantees that the roots of the polynomial equation

$$z^3 + a_2 z^2 + a_1 z + a_0 = 0$$

have negative real parts if the following conditions are met:

- (i)  $a_0 > 0$

$$(ii) \begin{vmatrix} a_2 & a_0 \\ 1 & a_1 \end{vmatrix} > 0$$

$$(iii) a_2 > 0$$

Thus, the roots of  $|\zeta I - A_n| = 0$  have negative real parts if

$$\frac{1}{\rho}(P_1 + P_2)\lambda_n \left[ \left( \sum_k \frac{\alpha_k}{\tau_k} \right) - c \right] > 0,$$

which is the case. It can further be shown that  $Re(\zeta) < -\mathcal{M}$ ,  $\mathcal{M} > 0$ .

To study the stability property of the model presented in (36)-(38), we follow the recipe in Section 6, which leads to (57). Corresponding to (57), we are led to examine the location of the roots of the system of characteristic polynomials given by the recursive definition

$$\begin{aligned} \Delta_1(\zeta) &= \zeta^3 + \zeta^2 \frac{1}{\mathcal{T}^1} + \zeta \frac{(P_1 + P_2)\lambda_n}{\rho} + \frac{\lambda_n P_1}{\rho \mathcal{T}^1}, \\ \Delta_{M+1}(\zeta) &= \left( \zeta + \frac{1}{\mathcal{T}^{M+1}} \right) \Delta_M + \frac{\lambda_n P_2 \xi_{M+1}}{\rho \mathcal{T}^{M+1}} \prod_{j=1}^M \left( \zeta + \frac{1}{\mathcal{T}^j} \right). \end{aligned}$$

We can directly verify that the roots of the polynomials  $\Delta_1$  and  $\Delta_2$  all have negative real parts. Using the recursion formula we can verify that there exist a positive number  $\mathcal{M}$  and nonnegative numbers  $\bar{\xi}_1, \bar{\xi}_2, \bar{\xi}_3, \dots$ , such that, for any  $\xi_i, i = 1, 2, 3, \dots$ , where  $0 \leq \xi_1 \leq \bar{\xi}_1, 0 \leq \xi_2 \leq \bar{\xi}_2, 0 \leq \xi_3 \leq \bar{\xi}_3, \dots, \sum \xi_i = 1$ , the roots of the polynomials  $\Delta_1(\zeta), \Delta_2(\zeta), \Delta_3(\zeta), i = 1, 2, 3, \dots$ , are all less than  $-\mathcal{M}$ .

## 7 Conclusion

We have presented a dynamic model of rubber viscoelasticity based on reptation models. Deformed molecular chains or segments entrapped between cross-linked molecules or molecular chains tend to return to their original undeformed positions. This is due to the fact that their original positions are positions of lower energy and higher entropy. However, due to the physical and electrostatic barriers created as a result of new configurations and conformations, the entrapped and strained molecules only creep to their original confirmation. The models presented here adhere to these observations

and also account for multiple relaxation times that have been experimentally observed. The approach proposed here indicates how to treat relaxation parameters as statistical quantities. These models can be related in a direct manner to previously derived (pseudo-phenomenological) models based on data from quasi-static and dynamic experiments with rubber rods in uniaxial tension and in shear as detailed in [4],[5],[7]. While the models developed here are based on linear material relationships between CC-system and PC-system stretches, extension to the nonlinear models in [4],[5] should be possible. Finally, the models lend themselves directly to computational methods for deformations of viscoelastic materials. Computations based on these ideas are currently and successfully underway and will be reported on in future publications.

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## References

- [1] A.S. Ackleh, H.T. Banks, and G.A. Pinter, Well-posedness results for models of elastomers, *Journal of Mathematical Analysis and Applications*, 268:440–456, 2002.
- [2] R.D. Andrews, Correlation of dynamic and static measurements on rubberlike materials, *Ind. Engr. Chem.*, 44: 707–715, 1952.
- [3] H.T. Banks and N.G. Medhin, A molecular based dynamic model for viscoelastic responses of rubber in tensile deformation, *Communications on Applied Nonlinear Analysis*, 8:1–18, 2001.
- [4] H.T. Banks, N.G. Medhin, and G.A. Pinter, Nonlinear reptation in molecular based hysteresis models for polymers, *Quarterly of Applied Mathematics*, 62:767–779, 2004.
- [5] H.T. Banks, N.G. Medhin, and G.A. Pinter, Multiscale considerations in modeling of nonlinear elastomers, *Journal of Computational Methods in Science and Engineering*, to appear.

- [6] H.T. Banks, G.A. Pinter, and L.K. Potter, Existence of unique weak solutions to a dynamic system for nonlinear elastomers with hysteresis, *Differential and Integral Equations*, 13:1001–1024, 2000.
- [7] H.T. Banks, G.A. Pinter, L.K. Potter, M.J. Gaitens, and L.C. Yanyo, Modeling of nonlinear hysteresis in elastomers under uniaxial tension, *Journal of Intelligent Material Systems and Structure*, 10:116–134, 1999.
- [8] E. Coddington and N. Levinson, *Theory of Ordinary Differential Equations*, McGraw-Hill, New York, 1955.
- [9] M.DoI and S.F. Edwards, *The Theory of Polymer Dynamics*, Oxford, New York, 1986.
- [10] J.D. Ferry, E.R. Fitzgerald, L.D. Grandine and M.L. Williams, Temperature dependence of dynamic properties of elastomers: relaxation distributions, *Ind. Engr. Chem.*, 44:703–706, 1952.
- [11] F.R. Gantmacher, *Matrix Theory*, volume 2, Chelsea Publishing Company, New York, 1959.
- [12] A.R. Johnson and R.G. Stacer, Rubber viscoelasticity using the physically constrained system’s stretches as internal variables, *Rubber Chemistry and Technology*, 66:567–577, 1993.
- [13] A.R. Johnson, Modeling and viscoelasticity materials using internal variables, *The Shock and Vibration Digest*, 31:91–100, 1999.
- [14] E. Riande, R. Diaz-Calleja, M.G.Prolongo, R.M. Masegosa, and C. Salom, *Polymer Viscoelasticity - Stress and Strain in Practice*, Marcel Dekker, Inc, New York, 2000.
- [15] F. Schwarzl and A.J. Staverman, Higher approximation methods for the relaxation spectrum from static and dynamic measurements of viscoelastic materials, *Appl. Sci. Res.*, A4:127–141, 1953.
- [16] L.H. Sperling, *Introduction to Physical Polymer Science*, John Wiley & Sons, 1992.
- [17] D. Ter Haar, A phenomenological theory of viscoelastic behavior, *Physica* 16:839–850, 1950.

- [18] L.R.G. Treloar, *The Physics of Rubber Elasticity*, Oxford, Clarendon, 1975.
- [19] K.C. Valanis and R.F. Landel, The strain-energy function of a hyper-elastic material in terms of the extension ratios, *J. Applied physics*, 38:2997–3002, 1967.
- [20] M.L. Williams and J.D. Ferry, Second approximation calculations of mechanical and electrical relaxation and retardation distributions, *J. Poly. Sci.*, 11:169–175, 1953.