The constitutive model of Larson for the stress tensor based on nonaffine motion

THE CONSTITUTIVE MODEL OF LARSON FOR THE STRESS TENSOR BASED ON NONAFFINE MOTION

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Introduction

This paper deals with the constitutive equation for the stress tensor as proposed by Larson. This equation is based on the notion of partial extending strands in a polymer melt. In the limit cases, the model contains the Upper–convected Maxwell model and the differential approximation of the Doi–Edwards model. First, an expression for the stress tensor in terms of global moleculair quantities is derived. The constitutive equation is then obtained in the same way as Larson did, although with a different result. This equation is partially formulated in terms moleculair quantities. Approximations are formulated that contain only averaged variables. Next, alternative deriviations are given, one based on a formalism as proposed by Peters, the others on energy considerations, both yielding the same results as with the first derivation. All deriviations are restricted to a steplike deformation. Incorporation of the relaxation terms is straight forward but left out for convenience.

The stress tensor

The free elastic energy is given by:

$$W = W_S + W_C$$

W_S orginates from the internal energy of structural elements and W_C orginates from the combinatorial entropy of the elements. The structural elements are considered as linear springs:

$$\vec{f}(\vec{R}) = a\vec{R}$$

The free energy in one chain is:

$$U(|\vec{R}|)_{chain} = \frac{a}{2}\vec{R}\cdot\vec{R}$$

The free energy W_s in a unit volume is therefore:

$$W_s = \nu\frac{a}{2}<\vec{R}\cdot\vec{R}>$$

where ν is the number of chains per unit volume. The rate $\dot{W}_s$, using the expression for $\dot{\vec{R}} = \mathbf{L}\cdot\vec{R} - \xi(\vec{n}\vec{n}:\mathbf{D})\vec{R}$ in a steplike deformation, is:

$$\dot{W}_s = \nu a<\dot{\vec{R}}\cdot\vec{R}> = \nu a<\mathbf{D}:\vec{R}\vec{R} - \xi(\vec{n}\vec{n}:\mathbf{D})\vec{R}\cdot\vec{R}> = \nu a(1-\xi)<\vec{R}\vec{R}>:\mathbf{D}$$

For $\xi = 0$, the motion of the structural element is affine, for $\xi = 1$ the Doi/Edwards limit is obtained.

The proces of a steplike deformation is, in this case, a reversible proces. The stress tensor σ_s can therefore be defined from:

$$\dot{W}_s = \sigma_s:\mathbf{D} = \nu a(1-\xi)<\vec{R}\vec{R}>:\mathbf{D} \quad \rightarrow \quad \sigma_s = \nu a(1-\xi)<\vec{R}\vec{R}>$$

For a entropic spring $a = 2kT\beta^2$:

$$\sigma_s = 2\nu kT\beta^2(1-\xi)<\vec{R}\vec{R}>$$

For the rate $\dot{W}_c$ it holds in general:

$$\dot{W}_c = \nu kT\ \mathrm{tr}(<\mathbf{A}> - \mathbf{D}))$$

In case of a steplike deformation, and incompressible material, i.e. $tr(\mathbf{D}) = 0$ this becomes:

$$\dot{W}_c = \nu kT\ tr(<A(\mathbf{D} \rightarrow \infty)>) = \nu kT\ \mathbf{I}:\xi(<\vec{n}\vec{n}>:\mathbf{D})\mathbf{I} = 3\nu kT\ \xi<\vec{n}\vec{n}>:\mathbf{D}$$

This, again, is a reversible proces. The stress tensor σ_c can therefore be defined from:

$$\dot{W}_c = \sigma_c:\mathbf{D} = 3\nu kT\ \xi<\vec{n}\vec{n}>:\mathbf{D} \quad \rightarrow \quad \sigma_c = 3\nu kT\xi<\vec{n}\vec{n}>$$

The macroscopic stress is the sum of the two contributions σ_s and σ_c:

$$\sigma = \sigma_s + \sigma_c = 2G\beta^2(1-\xi)\ <\vec{R}\vec{R}> + 3G\xi\ <\vec{n}\vec{n}>; \qquad G = \nu kT$$

The constitutive equation for a steplike deformation

The deriviation given is restricted to a steplike deformation. Incorporation of the relaxation terms is straight forward but left out for convenience.

The configuration continuity equation reads:

$$\frac{\partial\psi}{\partial t} + \frac{\partial}{\partial\vec{R}}\cdot(\dot{\vec{R}}\psi) = 0$$

The equation for the rate of the structural element end–to–end vector for a steplike deformation is postulated as:

$$\dot{\vec{R}} = \mathbf{L}\cdot\vec{R} - \xi(\vec{n}\vec{n}:\mathbf{D})\ \vec{R}; \qquad \vec{n} = \vec{R}/|\vec{R}|$$

where ξ is the slip parameter. Combining both expressions :

$$\frac{\partial\psi}{\partial t} + \frac{\partial}{\partial\vec{R}}\cdot(\psi\mathbf{L}\cdot\vec{R} - \psi\xi(\vec{n}\vec{n}:\mathbf{D})\,\vec{R}) = 0$$

Multiply with $(A\vec{R}\vec{R} + B\vec{n}\vec{n})$, where A and B are constants, and integrate over the configuration space Ω:

$$\int_\Omega [A\vec{R}\vec{R}\,\frac{\partial\psi}{\partial t} + A\vec{R}\vec{R}\,\frac{\partial}{\partial\vec{R}}\cdot(\psi\mathbf{L}\cdot\vec{R}) - A\vec{R}\vec{R}\,\frac{\partial}{\partial\vec{R}}\cdot(\psi\xi(\vec{n}\vec{n}:\mathbf{D})\,\vec{R}) +$$

$$B\vec{n}\vec{n}\,\frac{\partial\psi}{\partial t} + B\vec{n}\vec{n}\,\frac{\partial}{\partial\vec{R}}\cdot(\psi\mathbf{L}\cdot\vec{R}) - B\vec{n}\vec{n}\,\frac{\partial}{\partial\vec{R}}\cdot(\psi\xi(\vec{n}\vec{n}:\mathbf{D})\,\vec{R})\,d\vec{R}^3 = 0$$

The first term:

$$\int_\Omega A\vec{R}\vec{R}\,\frac{\partial\psi}{\partial t}\,d\vec{R}^3 = \frac{d}{dt}(\int_\Omega A\vec{R}\vec{R}\psi\,d\vec{R}^3) = \frac{d}{dt}<A\vec{R}\vec{R}>$$

intermezzo

Consider a function $f(\vec{R})$ in the configuration space, for example $f(\vec{R}) = A\vec{R}\vec{R}$, and a function $\psi(\vec{R},t)$. Then:

$$\frac{\partial}{\partial t}(f\psi) = \frac{\partial f}{\partial t}\,\psi + f\,\frac{\partial\psi}{\partial t}; \qquad \frac{\partial f}{\partial t} = 0$$

from which it follows:

$$f\,\frac{\partial\psi}{\partial t} = \frac{\partial}{\partial t}(f\psi)$$

Notice that $\frac{\partial f}{\partial t} = 0$ but $\frac{\partial}{\partial t} \langle f \rangle \neq 0$.

The second term. Integration by parts:

$$\int_\Omega A\vec{R}\vec{R}\,\frac{\partial}{\partial\vec{R}}\cdot(\psi\mathbf{L}\cdot\vec{R}\,)\,d\vec{R}^3 = \int_\Omega \frac{\partial}{\partial\vec{R}}\cdot(A\vec{R}\vec{R}\,\psi\mathbf{L}\cdot\vec{R})\,d\vec{R}^3 - \int_\Omega \psi\mathbf{L}\cdot\vec{R}\cdot\frac{\partial}{\partial\vec{R}}(A\vec{R}\vec{R})\,d\vec{R}^3$$

$$= - \langle \mathbf{L}\cdot\vec{R}\cdot\frac{\partial}{\partial\vec{R}}(A\vec{R}\vec{R})\rangle = -\mathbf{L}\cdot\langle A\vec{R}\vec{R}\rangle - \langle A\vec{R}\vec{R}\rangle\cdot\mathbf{L}^c$$

intermezzo

In the foregoing use is made of:

a) $\frac{\partial}{\partial\vec{R}}\cdot(\vec{a}\mathbf{A}) = (\frac{\partial}{\partial\vec{R}}\cdot\vec{a})\mathbf{A} + \vec{a}\cdot(\frac{\partial}{\partial\vec{R}}\mathbf{A})$

b)
$$\begin{aligned}\vec{a}\cdot\frac{\partial}{\partial\vec{R}}(\vec{R}\vec{R}) &= \vec{a}\cdot\mathbf{I}\vec{R} + \vec{R}\vec{R}\,(\vec{a}\cdot\frac{\partial}{\partial\vec{R}})\\ &= \vec{a}\vec{R} + \vec{R}\vec{R}\,(\frac{\partial}{\partial\vec{R}}\cdot\vec{a})\\ &= \vec{a}\vec{R} + \vec{R}\mathbf{I}\cdot\vec{a}\\ &= \vec{a}\vec{R} + \vec{R}\vec{a}\end{aligned}$$

c) The first integral on the right side equals zero because ψ goes to zero at large $|\vec{R}|$.

The third term:

$$-\int_\Omega A\vec{R}\vec{R}\,\frac{\partial}{\partial\vec{R}}\cdot(\psi\xi(\vec{n}\vec{n}:\mathbf{D})\,\vec{R})\,d\vec{R}^3 =$$

$$-\int_\Omega \frac{\partial}{\partial\vec{R}}\cdot(A\vec{R}\vec{R}\cdot\psi\xi(\vec{n}\vec{n}:\mathbf{D})\,\vec{R})\,d\vec{R}^3 + \int_\Omega \psi\xi(\vec{n}\vec{n}:\mathbf{D})\vec{R}\cdot\frac{\partial}{\partial\vec{R}}(A\vec{R}\vec{R})\,d\vec{R}^3 =$$

$$<\xi(\vec{n}\vec{n}:\mathbf{D})\vec{R}\cdot\frac{\partial}{\partial\vec{R}}(A\vec{R}\vec{R})> = 2<\xi(\vec{n}\vec{n}:\mathbf{D})A\vec{R}\vec{R}>$$

The fourth term:

$$\int_\Omega B\vec{n}\vec{n}\,\frac{\partial\psi}{\partial t}\,d\vec{R}^3 = \frac{d}{dt}\Big(\int_\Omega B\vec{n}\vec{n}\psi\,d\vec{R}^3\Big) = \frac{d}{dt}<B\vec{n}\vec{n}>$$

The fifth term:

$$\int_\Omega B\vec{n}\vec{n}\,\frac{\partial}{\partial\vec{R}}\cdot(\psi\mathbf{L}\cdot\vec{R})\,d\vec{R}^3 = \int_\Omega \frac{\partial}{\partial\vec{R}}\cdot(B\vec{n}\vec{n}\;\psi\mathbf{L}\cdot\vec{R})\,d\vec{R}^3 - \int_\Omega (\psi\mathbf{L}\cdot\vec{R})\cdot\frac{\partial}{\partial\vec{R}}(B\vec{n}\vec{n})\,d\vec{R}^3 =$$

$$-<(\mathbf{L}\cdot\vec{R})\cdot\frac{B}{\vec{R}}(\mathbf{I}-\vec{n}\vec{n})\vec{n} + \vec{n}\frac{B}{\vec{R}}(\mathbf{I}-\vec{n}\vec{n})\cdot(\vec{R}\cdot\mathbf{L}^c)>$$

$$-<B\mathbf{L}\cdot\vec{n}\vec{n} + B\vec{n}\vec{n}\cdot\mathbf{L}^c - 2B(\vec{n}\cdot\mathbf{D}\cdot\vec{n})\vec{n}\vec{n}>$$

intermezzo

In the foregoing use is made of:

a) $\frac{\partial}{\partial\vec{R}}\cdot(B\vec{n}\vec{n}) = B\frac{\partial}{\partial\vec{R}}(\vec{n}\vec{n})$

b) $\frac{\partial}{\partial\vec{R}}\vec{n} = \frac{\partial}{\partial\vec{R}}(\vec{R}/|\vec{R}|) = \frac{1}{\vec{R}}(\mathbf{I}-\vec{n}\vec{n})$

c) $\vec{n}\cdot\mathbf{L}\cdot\vec{n} = \vec{n}\cdot\mathbf{D}\cdot\vec{n}$

The sixth term:

$$-\int_{\Omega} B\vec{n}\vec{n}\,\frac{\partial}{\partial\vec{R}}\cdot(\psi\xi(\vec{n}\vec{n}:\mathbf{D})\,\vec{R})\;d\vec{R}^3 =$$

$$-\int_{\Omega} \frac{\partial}{\partial\vec{R}}(B\vec{n}\vec{n}\cdot\psi\xi(\vec{n}\vec{n}:\mathbf{D})\vec{R})\;d\vec{R}^3 + \int_{\Omega} \psi\xi(\vec{n}\vec{n}:\mathbf{D})\vec{R}\cdot\frac{\partial}{\partial\vec{R}}(B\vec{n}\vec{n})\;d\vec{R}^3 =$$

$$<\xi(\vec{n}\vec{n}:\mathbf{D})\vec{R}\cdot\frac{\partial}{\partial\vec{R}}(B\vec{n}\vec{n})> \;=\; <\xi(\vec{n}\vec{n}:\mathbf{D})(\vec{R}\cdot\frac{B}{\vec{R}}(I-\vec{n}\vec{n})\vec{n} + \vec{n}\frac{B}{\vec{R}}(I-\vec{n}\vec{n})\cdot\vec{R})> \;=$$

$$<\xi(\vec{n}\vec{n}:\mathbf{D})(B(\vec{n}-\vec{n})\vec{n} + B\vec{n}(\vec{n}-\vec{n})\cdot\vec{R})> = \mathbf{0}$$

Putting things together:

$$\frac{d}{dt}<\underset{\downarrow\atop 1}{\underline{A\vec{R}\vec{R}}} + \underset{\downarrow\atop 4}{\underline{B\vec{n}\vec{n}}}> - \underline{L}\cdot<\underset{\downarrow\atop 2}{\underline{A\vec{R}\vec{R}}} + \underset{\downarrow\atop 5}{\underline{B\vec{n}\vec{n}}}> - <\underset{\downarrow\atop 2}{\underline{A\vec{R}\vec{R}}} + \underset{\downarrow\atop 5}{\underline{B\vec{n}\vec{n}}}>\cdot\underline{L}^c +$$

$$\underset{\downarrow\atop 3}{\underline{2<\xi(\vec{n}\vec{n}:D)(A\vec{R}\vec{R}}} + \underset{\downarrow\atop a}{\underline{B\vec{n}\vec{n}}})> + \underset{\downarrow\atop 5}{\underline{2<B(\vec{n}\vec{n}:D)\vec{n}\vec{n}>}} - \underset{\downarrow\atop a}{\underline{2<\xi(\vec{n}\vec{n}:D)B\vec{n}\vec{n}>}}$$

The numbers idicate the contribution of the different terms, Notice that an extra term, indicated with an 'a', is added to the contribution of the third term and subtracted at the end.

Using the definition of the upper convected derivative:

$$\overset{\nabla}{<A\vec{R}\vec{R} + B\vec{n}\vec{n}>} + 2<\xi(\vec{n}\vec{n}:\mathbf{D})(A\vec{R}\vec{R} + B\vec{n}\vec{n})> + \underline{2B(1-\xi)<(\vec{n}\vec{n}:D)\vec{n}\vec{n}>} = \mathbf{0}$$

This result differs from the equation as found by Larson (Larson 1984, (32)). The extra term as found here is underlined.

The stress is given by (Larson 1984):

$$\sigma = 2G\beta^2(1-\xi)\langle\vec{R}\vec{R}\rangle + 3G\xi\langle\vec{n}\vec{n}\rangle; \qquad G = \nu kT$$

Using the approximations:

$$\langle\xi(\vec{n}\vec{n}:D)(A\vec{R}\vec{R} + B\vec{n}\vec{n})\rangle = \langle\xi\vec{n}\vec{n}:D\rangle\langle A\vec{R}\vec{R} + B\vec{n}\vec{n}\rangle$$

$$\langle(\vec{n}\vec{n}:D)\vec{n}\vec{n}\rangle = \langle\vec{n}\vec{n}:D\rangle\langle\vec{n}\vec{n}\rangle$$

it follows, for a steplike deformation:

$$\overset{\nabla}{\sigma} + 2\xi\langle\vec{n}\vec{n}\rangle:D\ \sigma + 6G\xi(1-\xi)\langle\vec{n}\vec{n}:D\rangle\langle\vec{n}\vec{n}\rangle = 0$$

Notice that for $\xi = 0$ the classical equation $\overset{\nabla}{\sigma} = 0$ for rubber elasticity is obtained. For $\xi = 1$ the Doi/Edwards differential approximation is found.

Using the definition:

$$\langle\vec{n}\vec{n}\rangle = \frac{1}{3G\xi}\,\sigma_c$$

this equation can be rewritten as:

$$\overset{\nabla}{\sigma} + \frac{2}{3G}(\sigma_c\!:\!D)\ \sigma + \frac{2(1-\xi)}{3G\xi}(\sigma_c\!:\!D)\ \sigma_c = 0$$

With the definition:

$$\sigma_s = 2G\beta^2(1-\xi)<\vec{R}\vec{R}>$$

this can also be written as two coupled equations:

$$\text{a)}\quad \overset{\nabla}{\sigma_c} + \frac{2}{3G\xi}(\sigma_c\!:\!D)\ \sigma_c = 0$$

$$\text{b)}\quad \overset{\nabla}{\sigma_s} + \frac{2}{3G}(\sigma_c\!:\!D)\ \sigma_s = 0$$

Larson used the following approximation:

$$<\vec{n}\vec{n}> = <\frac{2(1-\xi)\beta^2\vec{R}\vec{R}}{2(1-\xi)\beta^2\vec{R}\cdot\vec{R}}> \approx <\frac{2(1-\xi)\beta^2\vec{R}\vec{R}\ +\ 3\xi\vec{n}\vec{n}}{2(1-\xi)\beta^2\vec{R}\cdot\vec{R}\ +\ 3\xi}> \approx$$

$$\frac{<2(1-\xi)\beta^2\vec{R}\vec{R}\ +\ 3\xi\vec{n}\vec{n}>}{<2(1-\xi)\beta^2\vec{R}\cdot\vec{R}\ +\ 3\xi>} = \frac{\sigma}{\mathrm{tr}(\sigma)}$$

Using this approximation, the original equation can be written as:

$$\overset{\nabla}{\sigma} + \left[\frac{2\xi}{\mathrm{tr}(\sigma)} + \frac{6G\xi(1-\xi)}{\mathrm{tr}^2(\sigma)}\right](\sigma\!:\!D)\ \sigma = 0$$

This result differs from the equation derived by Larson who found:

$$\overset{\nabla}{\sigma} + \frac{2\xi}{\mathrm{tr}(\sigma)}(\sigma{:}\mathrm{D})\ \sigma = 0$$

With a similar approximation as used before, the system of two coupled equations can be decoupled, giving a two mode version of Larsons constitutive equation:

$$\sigma_c = 3\xi G<\vec{n}\vec{n}> = 3\xi G<\frac{2(1-\xi)G\beta^2\ \vec{R}\vec{R}}{2(1-\xi)G\beta^2\vec{R}\cdot\vec{R}}> \approx 3\xi G\frac{<2(1-\xi)G\beta^2\ \vec{R}\vec{R}>}{<2(1-\xi)G\beta^2\vec{R}\cdot\vec{R})} = 3\xi G\ \frac{\sigma_s}{\mathrm{tr}(\sigma_s)}$$

Using this gives the appproximated decoupled set:

a) $$\overset{\nabla}{\sigma}_c + \frac{2}{3G\xi}(\sigma_c{:}\mathrm{D})\ \sigma_c = 0$$

b) $$\overset{\nabla}{\sigma}_s + \frac{2\xi}{\mathrm{tr}(\sigma_s)}(\sigma_s{:}\mathrm{D})\ \sigma_s = 0$$

Again, with the approximation for σ_c, with:

$$\mathrm{tr}(\sigma) = \mathrm{I}{:}(\mathrm{A}<\vec{R}\vec{R}> + \mathrm{B}<\vec{n}\vec{n}>) = \mathrm{A}<\vec{R}\cdot\vec{R}> + \mathrm{B} \quad \rightarrow \quad <\vec{R}\cdot\vec{R}> = \frac{1}{\mathrm{A}}(\mathrm{tr}(\sigma - \mathrm{B})$$

and the approximation:

$$\sigma = \mathrm{A}<\vec{R}\vec{R}> + \mathrm{B}<\vec{n}\vec{n}> = \mathrm{A}<\vec{R}\vec{R}> + \mathrm{B}<\frac{1}{|\vec{R}|^2}\vec{R}\vec{R}> \approx (\mathrm{A} + \mathrm{B}\ \frac{1}{<|\vec{R}|^2>})\ <\vec{R}\vec{R}> =$$

$$\frac{\mathrm{A}\ \mathrm{tr}(\sigma)}{\mathrm{tr}(\sigma) - \mathrm{B}}<\vec{R}\vec{R}> \quad \rightarrow \quad \sigma_s \approx (1 - \frac{3\xi G}{\mathrm{tr}(\sigma)})\ \sigma$$

these two equations can be replaced by the one equation in terms of σ only as derived before.

An alternative derivation of the Larson model

The deriviation given is restricted to a steplike deformation. Incorporation of the relaxation terms is straight forward but left out for convenience.

The time derivative of the stress tensor $\sigma = \mathrm{A}\langle\vec{\mathrm{R}}\vec{\mathrm{R}}\rangle + \mathrm{B}\langle\vec{\mathrm{n}}\vec{\mathrm{n}}\rangle$ is:

$$\dot{\sigma} = \mathrm{A}(\langle\dot{\vec{\mathrm{R}}}\vec{\mathrm{R}}\rangle + \mathrm{A}\langle\vec{\mathrm{R}}\dot{\vec{\mathrm{R}}}\rangle) + \mathrm{B}(\langle\dot{\vec{\mathrm{n}}}\vec{\mathrm{n}}\rangle + \langle\vec{\mathrm{n}}\dot{\vec{\mathrm{n}}}\rangle)$$

where $\mathrm{n} = \frac{\vec{\mathrm{R}}}{|\vec{\mathrm{R}}|}$. With:

$$\dot{\vec{\mathrm{R}}} = \mathbf{L}\cdot\vec{\mathrm{R}} - \xi(\vec{\mathrm{n}}\vec{\mathrm{n}}:\mathbf{D})\vec{\mathrm{R}}; \qquad \dot{\vec{\mathrm{n}}} = \frac{1}{|\vec{\mathrm{R}}|}(\mathbf{I} - \vec{\mathrm{n}}\vec{\mathrm{n}})\cdot\dot{\vec{\mathrm{R}}}$$

the expression for the time derivative $\dot{\sigma}$ can be rewritten as:

$$\dot{\sigma} = \mathbf{L}\cdot\sigma + \sigma\cdot\mathbf{L}^{c} - 2\xi\langle(\vec{\mathrm{n}}\vec{\mathrm{n}}:\mathbf{D})(\mathrm{A}\vec{\mathrm{R}}\vec{\mathrm{R}} + \mathrm{B}\vec{\mathrm{n}}\vec{\mathrm{n}})\rangle - 2\mathrm{B}(1-\xi)\langle(\vec{\mathrm{n}}\vec{\mathrm{n}}:\mathbf{D})\vec{\mathrm{n}}\vec{\mathrm{n}}\rangle$$

Using the definition for the upper convected derivative, this becomes:

$$\overset{\nabla}{\sigma} + 2\xi\langle(\vec{\mathrm{n}}\vec{\mathrm{n}}:\mathbf{D})(\mathrm{A}\vec{\mathrm{R}}\vec{\mathrm{R}} + \mathrm{B}\vec{\mathrm{n}}\vec{\mathrm{n}})\rangle + 2\mathrm{B}(1-\xi)\langle(\vec{\mathrm{n}}\vec{\mathrm{n}}:\mathbf{D})\vec{\mathrm{n}}\vec{\mathrm{n}}\rangle = 0$$

The term $<(\vec{n}\vec{n}:\mathbf{D})(A<\vec{R}\vec{R}> + B<\vec{n}\vec{n}>)>$ is approximated as:

$$<(\vec{n}\vec{n}:\mathbf{D})(A\vec{R}\vec{R} + B\vec{n}\vec{n})> \approx (<\vec{n}\vec{n}>:\mathbf{D})(A<\vec{R}\vec{R}> + B<\vec{n}\vec{n}>)> = (<\vec{n}\vec{n}>:\mathbf{D})\ \sigma$$

By definition:

$$<\vec{n}\vec{n}> = \frac{1}{B}\sigma_c$$

Using this gives:

$$\overset{\nabla}{\sigma} + \frac{2\xi}{B}(\sigma_c:\mathbf{D})\ \sigma + \frac{2(1-\xi)}{B}(\sigma_c:\mathbf{D})\ \sigma_c = 0$$

With $B = 3\xi G$ the same expression is obtained as derived before.

An alternative derivation of the Larson model based on energy considerations

A constituve equation for $\dot{\vec{R}}$ is postulated in terms of a slip tensor **A** which is only a function of averaged values and given by:

$$\dot{\vec{R}} = \mathbf{L}\cdot\vec{R} - \mathbf{A}\cdot\vec{R}; \qquad \mathbf{A} = f(\sigma)(\sigma_c:\mathbf{D})\mathbf{I}$$

The rate of the internal free elastic energy for the case of linear springs is:

$$\dot{W}_s = 2\nu kT\beta^2 <\vec{R}\cdot\dot{\vec{R}}> = 2\nu kT\beta^2 (\mathbf{D}:<\vec{R}\vec{R}> - f(\sigma)(\sigma_c:\mathbf{D})\vec{R}\cdot\vec{R})$$

For a steplike deformation it holds:

$$\dot{W}_s = \sigma_s{:}\mathbf{D}$$

With the stresses $\sigma_s = 2\nu kT\beta^2 <\vec{R}\vec{R}>$ and $\sigma_c = 3\xi G <\vec{n}\vec{n}>$ it follows:

$$f(\sigma) = \frac{<\vec{R}\vec{R}>:\mathbf{D}}{3G<\vec{R}\cdot\vec{R}><\vec{n}\vec{n}:\mathbf{D}>} \approx \frac{<\vec{R}\vec{R}>:\mathbf{D}}{3G<\vec{R}\cdot\vec{R}\ \ \vec{n}\vec{n}:\mathbf{D}>} = \frac{1}{3G}$$

Using this result for the derivation of the constitutive equation for σ_s, the original equation for steplike deformations is obtained:

$$\overset{\nabla}{\sigma_s} + \frac{2}{3G}(\sigma_c{:}\mathbf{D})\ \sigma_s = 0$$

The rate of the combinatorial free elastic energy is:

$$\dot{W}_c = \nu kT\ \mathrm{tr}(\mathbf{A})$$

With $\mathbf{A} = f(\sigma)(\sigma_c{:}\mathbf{D})\mathbf{I}$:

$$\dot{W}_c = 3\nu kT\ f(\sigma)(\sigma_c{:}\mathbf{D})$$

For a steplike deformation it holds:

$$\dot{W}_c = \sigma_c{:}\mathbf{D}$$

Combining both expressions:

$$3\nu kT\ f(\sigma) = 1 \quad \rightarrow \quad f(\sigma) = \frac{1}{3G}$$

which is in agreement with the result obtained for the internal free elastic energy. Using this result for the derivation of the constitutive equation for σ_C, the original equation for steplike deformations is obtained:

$$\overset{\nabla}{\sigma}_C + \frac{2}{3G\xi}(\sigma_C{:}\mathbf{D})\ \sigma_C = 0$$

In order to attain one constitutive equation, instead of the two coupled equations, a constituve equation for $\dot{\vec{R}}$ is postulated in terms of a slip tensor **A** which is only a function of σ.

$$\dot{\vec{R}} = \mathbf{L}\cdot\vec{R} - f(\sigma)(\sigma{:}\mathbf{D})\vec{R}$$

The rates of the free elastic energies for the case of linear springs is:

$$\dot{W}_s = 2\nu kT\beta^2 <\vec{R}\cdot\dot{\vec{R}}> = 2\nu kT\beta^2\ (\mathbf{D}{:}<\vec{R}\vec{R}> - f(\sigma)(\sigma{:}\mathbf{D})\vec{R}\cdot\vec{R})$$

$$\dot{W}_c = 3\nu kT\ f(\sigma)(\sigma{:}\mathbf{D})$$

For a steplike deformation it holds, using G= νkT:

$$\dot{W} = \sigma{:}\mathbf{D} = \dot{W}_s + \dot{W}_c = 2G\beta^2\ \mathbf{D}{:}<\vec{R}\vec{R}> - 2G\beta^2\ f(\sigma)(\sigma{:}\mathbf{D})\vec{R}\cdot\vec{R} + 3G\ f(\sigma)(\sigma{:}\mathbf{D})$$

From this it follows:

$$f(\sigma) = \frac{\sigma{:}\mathbf{D} \;\; -2G\beta^2 \;\; \mathbf{D}{:}<\vec{R}\vec{R}>}{\sigma{:}\mathbf{D}(3G \; - \; 2G\beta^2<\vec{R}\cdot\vec{R}>)}$$

Using $tr(\sigma_s) = tr(\sigma) - 3\xi G$ and the approximation for σ_s in terms of σ, the function $f(\sigma)$ can be rewritten as:

$$f(\sigma) = \frac{\xi}{tr(\sigma)}$$

Using this result for the derivation of the constitutive equation for σ, suprisingly the constitutive equation for steplike deformations is obtained as found by Larson.

Reference:

– Larson, R.G., A Constitutive Equation for Polymer Melts Based on Partially Extending Strand Convection, Journal of Rheology, 28(5), 545–571 (1984).