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Modified Gaussian Model for Rubber Elasticity. 2. The Wormlike Chain†

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ABSTRACT: The modified Gaussian model for the wormlike chain is applied approximately to a three-chain model of rubber elasticity. A closed-form expression for the network free energy is obtained and equations governing the uniaxial extension and solvent swelling are derived. Numerical results for the stress–strain behavior in uniaxial extension are presented.

I. Introduction

In the first paper in this series[1] the modified Gaussian model of the freely jointed chain was applied to a simple model of an elastic network. A simple closed-form expression for the network free energy was obtained and equations governing network behavior in uniaxial extension and in solvent swelling were derived. The solvent swelling equation has proven to be useful in interpreting experimental data on the swelling of bituminous coals.[2]

In this paper the use of the modified Gaussian model in rubber elasticity is extended to the case of the wormlike chain of Porod and Kratky.[3] The wormlike chain allows more freedom in the treatment of non-Gaussian chain statistics because the chain length and the chain stiffness can be varied independently. It also provides a treatment of chain statistics that avoids the use of the concept of statistical segments. This is an advantage for short chains, where the division into statistical segments can be arbitrary and unrealistic. This work has been motivated by three considerations: (1) to see whether the modified Gaussian model could provide useful closed-form expressions for the network free energy for this more complicated chain model; (2) to provide a preliminary theoretical basis for experimental measurements of the elastic properties of networks in which chain stiffness is varied systematically; (3) to provide a more realistic model for interpretation of solvent swelling measurements on bituminous coals.[4]

A variety of non-Gaussian effects have been included in the theory of rubber elasticity but the effect of chain stiffness seems not to have been previously considered explicitly. In this paper we focus only on the effects of single-chain statistics using a simple three-chain affine deformation model and ignore all the complicated and important network effects. Therefore, the equations derived and numerical results presented can only be used for qualitative or semiquantitative comparison with experiment. The results, however, should provide some insight as to where the effects of chain stiffness will be important. In the future we hope to apply the modified Gaussian model to coupled chains in a network to provide a more realistic model. For the present the simple theory presented here must suffice.

II. Modified Gaussian Model

In this section the development of the modified Gaussian model is reviewed briefly and the essential equations presented. For a detailed presentation of the reader is referred to the original paper.[6]

The polymer chain is assumed to contain $N + 1$ identical backbone atoms connected by N bond vectors $\vec{b}_i$, $i = 1, 2, ..., N$. The true backbone potential V is a function of $\{b\}$ and is expressed in units such that $kT = 1$. The chain is subjected to an equilibrium force $\vec{f}$ acting on the end-to-end vector $\vec{R}$

$$\vec{R} = \sum_{i=1}^{N} \vec{b}_i \qquad (1)$$

The exact distribution function of the set $\{b\}$ is

$$\psi_V(f) = \exp(\vec{R}\cdot\vec{f} - V)/Z_V(f) \qquad (2)$$

$$Z_V(f) = \int \exp(\vec{R}\cdot\vec{f} - V)\, \mathrm{d}\{b\} \qquad (3)$$

In the presence of $\vec{f}$ the mean end-to-end vector $\langle\vec{R}\rangle_f$ does not vanish and is calculated

$$\langle\vec{R}\rangle_f = \int \vec{R}\psi_V(f)\, \mathrm{d}\{b\} \qquad (4)$$

$$= \mathrm{d} \ln Z_V(f)/\mathrm{d}\vec{f} \qquad (5)$$

The idea of the modified Gaussian model is that the exact distribution function can be expanded in a series of Hermite-like polynomials orthogonal with respect to a weight function e^{-g}, where

† J.K. dedicates this paper to the memory of Arthur F. Scott, Professor Emeritus of Chemistry at Reed College, who was an inspiration for generations of students.

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$$g = -\vec{R}\cdot\vec{f} + G(f) \quad (6)$$

and $G(f)$ is a quadratic form in the bond vectors $\vec{b}_i$. The quadratic form $G(f)$ is chosen so as to make the first approximation for ψ_V, that is,

$$\psi_V \cong \psi_G = \exp(-g)/Z_G(f) \quad (7)$$

$$Z_G = \int \exp(-g)\ \mathrm{d}\{b\} \quad (8)$$

as good as possible. The condition on G is that the coefficients in the Hermite expansion be made to vanish. For the first coefficient this translates into the condition

$$\langle \vec{b}_i\vec{b}_j\rangle_G = \langle \vec{b}_i\vec{b}_j\rangle_V \quad (9)$$

where $\langle\ \rangle_G$ and $\langle\ \rangle_V$ refer to averages over the distribution functions ψ_G and ψ_V, respectively. For the freely rotating chain (fixed bond lengths and fixed bond angles) eq 9 gives the two conditions

$$\langle b_i^2\rangle_G = \langle b_i^2\rangle_V = l^2 \quad (10)$$

$$\langle \vec{b}_i\cdot\vec{b}_{i\pm1}\rangle_G = \langle \vec{b}_i\cdot\vec{b}_{i\pm1}\rangle_V = l^2\cos\theta \quad (11)$$

where l is the fixed bond length and θ the supplement of the bond angle. $G(f)$ is chosen to be

$$G(f) = \tfrac{1}{2}\alpha l^{-3}\sum_{i=1}^{N-1}|\vec{b}_i - \vec{b}_{i+1}|^2 + \tfrac{1}{2}\beta l^{-1}\sum_{i=1}^{N}|\vec{b}_i|^2 \quad (12)$$

and the constraint eq 10 and 11 are used to determine α and β, which are taken to be functions of the external force. The probability distribution, ψ_G, retains a Gaussian form but the force constants are allowed to depend on f such that the bond length and bond angle remain constant (on the average). Physically, β represents a bond stretching force constant and α represents the bond angle force constant.

The partition function Z_G can be easily evaluated from the eigenvalues of the quadratic form eq 12. The parameters α and β are evaluated from the equations

$$\partial \ln Z_G/\partial\beta = -\tfrac{1}{2}Nl \quad (13)$$

$$\partial \ln Z_G/\partial\alpha = -(N-1)l^{-1}(1-\cos\theta) \quad (14)$$

and $\langle\vec{R}\rangle_f$ is given by

$$\langle\vec{R}\rangle_f = \partial \ln Z_G/\partial\vec{f} = Nl\vec{f}\beta^{-1} \quad (15)$$

In the general case of the freely rotating chain eq 13 and 14 yield a pair of coupled transcendental equations for α and β.

The wormlike chain, which is the continuous chain limit of the freely rotating chain, is obtained in the limit $l \to 0$, $N \to \infty$, with the contour length

$$L = Nl \quad (16)$$

held constant and the bond angle $\pi - \theta \to \pi$

$$\lim_{l\to0}(1-\cos\theta)l^{-1} = 2\Lambda \quad (17)$$

where $(2\Lambda)^{-1}$ is the persistence length and Λ^{-1} the Kuhn statistical segment length. In this limit eq 13 and 14 reduce to

$$\alpha = 3/4\Lambda \quad (18)$$

and

$$L = Lf^2\beta^{-2} + \frac{3}{2}\beta^{-1}\left[1 + L\left(\frac{\beta}{\alpha}\right)^{1/2}\coth L\left(\frac{\beta}{\alpha}\right)^{1/2}\right] \quad (19)$$

The mean-square end-to-end distance for this model is given by

$$\langle R^2\rangle = 3L/\beta(0) \quad (20)$$

The wormlike chain is characterized by two parameters: the contour length L and the persistence length, which is proportional to α. By suitable variation of these parameters chains of any equilibrium conformation from random coil to rigid rod can be modeled.

III. Stress–Strain Relationship and Chain Free Energy

The relationship between extension and applied force is given formally by eq 15. Use of eq 15 requires that eq 19 be solved for β as a function of f. This was done numerically in the original paper by Fixman and Kovac,[6] but our purposes here require a closed-form solution. Because of the presence of the function coth $[L(\beta/\alpha)^{1/2}]$ in eq 19, only an approximate solution can be found. This can be done conveniently in two limits.

The term x coth x has simple behavior in two regions. For small x, corresponding to short, very stiff chains, x coth $x = 1$ and eq 19 can be solved very easily. The resulting equations are identical with those for a freely jointed chain with a single link ($N = 1$) and are therefore a special case of the results derived in the previous paper in this series.[1] This case will not be considered further in this paper.

If $x \geq 2$, then $x \coth x \cong x$ and eq 19 becomes

$$L = Lf^2\beta^{-2} + \frac{3}{2}\beta^{-1}\left[1 + L\left(\frac{\beta}{\alpha}\right)^{1/2}\right] \quad (21)$$

a quartic polynomical in $\beta^{1/2}$ which can be solved in closed form. Since β is an increasing function of f, the practical condition for this limit is

$$L\left(\frac{\beta(0)}{\alpha}\right)^{1/2} \geq 2 \quad (22)$$

This condition should hold all but the shortest and stiffest chains. Therefore, the approximation should be adequate for most cases of practical interest. If there is any ambiguity about whether a particular set of parameters L and α fulfills the condition (22), then eq 19 can be solved numerically to find $\beta(0)$.

Rather than solve eq 21 for β and substitute into eq 15 to obtain $\vec{f}$ as a function of $\vec{R}$, it is simpler to use eq 15 to eliminate β from eq 21 and solve directly for $\vec{f}$. Since $\vec{f}$ is along $\vec{R}$, we can rewrite eq 15 as a scalar equation

$$R \equiv |\langle\vec{R}\rangle_f| = Nlf\beta^{-1} \quad (23)$$

or

$$r \equiv R(Nl)^{-1} \equiv RL^{-1} = f\beta^{-1} \quad (24)$$

Therefore

$$\beta = fr^{-1} \quad (25)$$

Substituting eq 25 into eq 21 yields

$$(1-r^2)f - \frac{3r^{1/2}}{2\alpha^{1/2}}f^{1/2} - \frac{3r}{2L} = 0 \quad (26)$$

This is a quadratic polynomial in $f^{1/2}$ which can be solved easily to obtain

$$f = \left[\frac{\tfrac{3}{4}r^{1/2}\alpha^{-1/2} + \tfrac{3}{4}r^{1/2}\alpha^{-1/2}(1 + \tfrac{8}{3}\alpha r^{-1}(1-r^2))}{1-r^2}\right]^2 \quad (27)$$

Equation 27 represents a force-extension (stress–strain) equation of state for a single wormlike chain. It is essentially the inverse of eq 23. In deriving eq 27 we have assumed that eq 23 is a proper thermodynamic equation of state in which fluctuations do not play a significant role. This, of course, is only strictly true in the thermodynamic limit. It would be interesting to solve for eq 27 directly from the partition function by using an appropriate ensemble transform. This would show whether the assumption is correct.

The force can be assumed to be obtained from the chain free energy (ΔA) by differentiation

$$\vec{f} = \partial \Delta A / \partial \vec{R} \tag{28a}$$

or

$$f = \partial \Delta A / \partial R \tag{28b}$$

so ΔA can be obtained by integration of the stress–strain relationship

$$\Delta A = \int_0^R f(R')\, \mathrm{d}R' + \text{constant} \tag{29}$$

Using eq 27 in eq 29 and performing the integration term by term, we obtain

$$\Delta A = \frac{9}{16}\alpha^{-1}(1 - r^2)^{-1} - \frac{3}{4}L^{-1} \ln (1 - r^2) + \frac{9}{16}\alpha^{-1}(1 - r^2)^{-1}\left(1 + \frac{8}{3}\alpha L^{-1}(1 - r^2)\right)^{1/2} - \frac{3}{4}L^{-1} \ln \left\{\left[\left(1 + \frac{8}{3}\alpha L^{-1}(1 - r^2)\right)^{1/2} - 1\right] \Big/ \left[\left(1 + \frac{8}{3}\alpha L^{-1}(1 - r^2)\right)^{1/2} + 1\right]\right\} + \text{constant} \tag{30}$$

Even though eq 30 is rather complicated, it does represent a closed-form expression for the chain free energy in terms of two parameters L and α and is therefore amenable to the description of a wide variety of chains.

In order to use eq 30 in a network model one also needs to know the equilibrium end-to-end distance of the chain. This is given in terms of $\beta(0)$ by eq 20. $\beta(0)$ can be obtained by putting $f = 0$ in eq 19 and solving the resulting quadratic for β. The result is

$$\beta_0 \equiv \beta(0) = \left[\frac{3}{4}\alpha^{-1/2} + \left(\frac{9}{16}\alpha^{-1} - \frac{3}{2}L^{-1}\right)^{1/2}\right]^2 \tag{31}$$

IV. Simple Network Model

In this section the single-chain free energy eq 30 will be incorporated into a simple three-chain model for a network. Although the three-chain model cannot hope to reproduce the exact behavior of a complicated network, it does provide a closed-form expression of the network free energy which can then be applied to a variety of experimental situations. The predictions of this model should provide at least a qualitative picture of the effects of chain stiffness in rubber elasticity.

A. Network Free Energy. In the three-chain model it is assumed that the random cross-linked network can be represented by three independent sets of equivalent chains directed along each of the coordinate axes. The total network free energy is then written

$$\Delta A_{\text{net}} = \Delta A_x + \Delta A_y + \Delta A_z \tag{32}$$

where ΔA_i is the free energy of the equivalent chains directed along the i axis. Suppose the network contains M chains. It is then assumed that $M/3$ chains are directed along each axis. Using eq 30 for the free energy of a single chain, we have

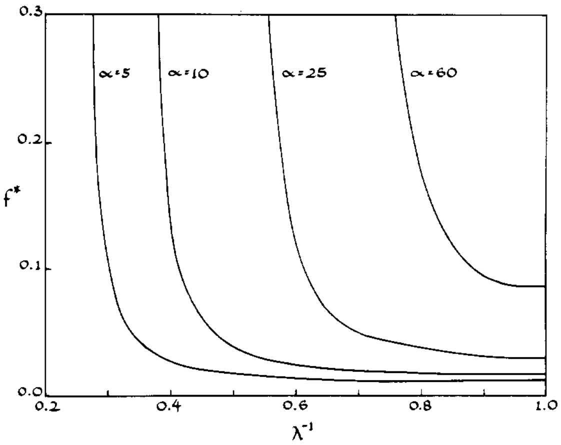

Figure 1. Plot of reduced force $f^* = f/M(\lambda - \lambda^{-2})$ vs. reciprocal elongation λ^{-1} for $L = 100$ and various α. Results calculated from eq 41.

$$\Delta A_{\text{net}} = \frac{M}{3}\left\{\frac{9}{16\alpha}\left[\frac{1}{1 - x^2} + \frac{1}{1 - y^2} + \frac{1}{1 - z^2} + \frac{(1 + {}^8\!/_3\alpha L^{-1}(1 - x^2))^{1/2}}{1 - x^2} + \frac{(1 + {}^8\!/_3\alpha L^{-1}(1 - y^2))^{1/2}}{1 - y^2} + \frac{(1 + {}^8\!/_3\alpha L^{-1}(1 - z^2))^{1/2}}{1 - z^2}\right] - \frac{3}{4}L^{-1}\left[\ln ((1 - x^2)(1 - y^2)(1 - z^2)) + \ln \left[\frac{(1 + {}^8\!/_3\alpha L^{-1}(1 - x^2))^{1/2} - 1}{(1 + {}^8\!/_3\alpha L^{-1}(1 - x^2))^{1/2} + 1} \times \frac{(1 + {}^8\!/_3\alpha L^{-1}(1 - y^2))^{1/2} - 1}{(1 + {}^8\!/_3\alpha L^{-1}(1 - y^2))^{1/2} + 1} \times \frac{(1 + {}^8\!/_3\alpha L^{-1}(1 - z^2))^{1/2} - 1}{(1 + {}^8\!/_3\alpha L^{-1}(1 - z^2))^{1/2} + 1}\right]\right]\right\} \tag{33}$$

where x, y, and z are the reduced extensions of the chains along the axes defined analogously to r.

In the unstrained state each of the equivalent chains is assumed to have its equilibrium end-to-end distance and the chain deformations are assumed to be affine. We then write

$$x = \lambda_1 \langle r^2 \rangle_0^{1/2}$$

$$y = \lambda_2 \langle r^2 \rangle_0^{1/2}$$

$$z = \lambda_3 \langle r^2 \rangle_0^{1/2} \tag{34}$$

where λ_i is the strained length divided by the unstrained length and where $\langle r^2 \rangle_0$ is the reduced equilibrium mean-square and end-to-end distance for the wormlike chain given by

$$\langle r^2 \rangle_0 = L^{-2} \langle R^2 \rangle_0 \tag{35}$$

$$= 3/(L\beta_0) \tag{36}$$

where eq 20 has been used for $\langle R^2 \rangle_0$ and β_0 is given by eq

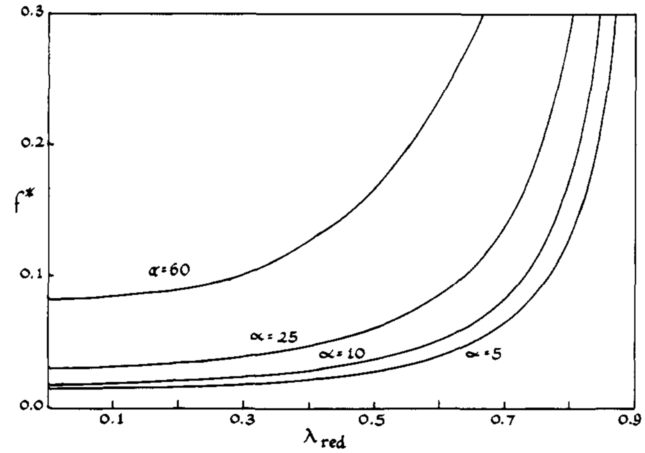

Figure 2. Plot of reduced force $f^* = f/M(\lambda - \lambda^{-2})$ vs. reduced elongation $\lambda_{red} = (\lambda - 1)/(\lambda_{max} - 1)$ for $L = 100$ and various α. Results calculated from eq 41.

31. Substituting eq 34 and 36 into eq 33, one obtains for the network free energy

$$\Delta A_{net}/M = \frac{3}{16\alpha}\left\{\frac{1}{1 - 3\lambda_1^2/L\beta_0} + \frac{1}{1 - 3\lambda_2^2/L\beta_0} + \frac{1}{1 - 3\lambda_3^2/L\beta_0} + \frac{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda_1^2/L\beta_0))^{1/2}}{1 - 3\lambda_1^2/L\beta_0} + \frac{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda_2^2/L\beta_0))^{1/2}}{1 - 3\lambda_2^2/L\beta_0} + \frac{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda_3^2/L\beta_0))^{1/2}}{1 - 3\lambda_3^2/L\beta_0}\right\} - \frac{1}{4}L^{-1} \ln \left\{(1 - 3\lambda_1^2/L\beta_0)(1 - 3\lambda_2^2/L\beta_0)(1 - 3\lambda_3^2/L\beta_0) \times \left[\frac{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda_1^2/L\beta_0))^{1/2} - 1}{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda_1^2/L\beta_0))^{1/2} + 1}\right] \times \left[\frac{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda_2^2/L\beta_0))^{1/2} - 1}{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda_2^2/L\beta_0))^{1/2} + 1}\right] \times \left[\frac{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda_3^2/L\beta_0))^{1/2} - 1}{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda_3^2/L\beta_0))^{1/2} + 1}\right]\right\} \quad (37)$$

The network free energy will be applied to two common experimental situations, uniaxial extension and solvent swelling. Other experimental situations, such as biaxial extension, could be easily considered.

B. Uniaxial Extension. Suppose that the network is stretched along the x axis by a factor λ, that is,

$$\lambda_1 = \lambda \quad (38)$$

Assuming that the network is isotropic and that the volume is constant, we have the condition

$$\lambda_1\lambda_2\lambda_3 = 1 \quad (39)$$

and so

$$\lambda_2 = \lambda_3 = \lambda^{-1/2} \quad (40)$$

Substituting eq 38 and 40 into eq 37, we can evaluate the force as

$$\frac{f}{M} = \frac{\partial}{\partial\lambda}\left(\frac{\Delta A_{net}}{M}\right) = \frac{3}{16\alpha}\left\{\frac{(6\lambda/L\beta_0)(1 + (1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda^2/L\beta_0))^{1/2})}{(1 - 3\lambda^2/L\beta_0)^2} - \frac{(6/\lambda^2 L\beta_0)(1 + (1 + \frac{8}{3}\alpha L^{-1}(1 - 3/\lambda L\beta_0))^{1/2})}{(1 - 3/\lambda L\beta_0)^2} - \frac{8\lambda\alpha/L^2\beta_0}{(1 - 3\lambda^2/L\beta_0)(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda^2/L\beta_0))^{1/2}} + \frac{(8\alpha/L^2\beta_0\lambda^2)}{(1 - 3/L\beta_0\lambda)(1 + \frac{8}{3}\alpha L^{-1}(1 - 3/L\beta_0\lambda))^{1/2}}\right\} + \frac{1}{4L}\left\{\frac{6\lambda/L\beta_0}{1 - 3\lambda^2/L\beta_0} - \frac{6/L\beta_0\lambda^2}{1 - 3/L\beta_0\lambda} + \frac{8\alpha\lambda/L^2\beta_0}{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda^2/L\beta_0))^{1/2}} \times \left[\frac{1}{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda^2/L\beta_0))^{1/2} - 1} - \frac{1}{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda^2/L\beta_0))^{1/2} + 1}\right] - \frac{8\alpha/L^2\beta_0\lambda^2}{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3/L\beta_0\lambda))^{1/2}} \times \left[\frac{1}{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3/L\beta_0\lambda))^{1/2} - 1} - \frac{1}{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3/L\beta_0\lambda))^{1/2} + 1}\right]\right\} \quad (41)$$

Some representative numerical results have been plotted in Figures 1 and 2. These results have been calculated from eq 41 with $L = 100$ and differing values of α as indicated in the figures. Figure 1 is a Mooney–Rivlin plot in which the reduced force $f^* = f/M(\lambda - \lambda^{-2})$ is plotted vs. λ^{-1}. *On this plot Gaussian behavior corresponds to a* horizontal line, so the curves plotted show the deviations from Gaussian behavior. The constraint of finite chain length is shown in the sharp upturn of the curves. This can be seen in Figure 2, in which the same reduced force is plotted against the reduced extension $\lambda_{red} = (\lambda - 1)/(\lambda_{max} - 1)$. In Figure 2 all the curves go asymptotically to infinity as λ_{red} goes to 1.0.

To get an idea whether the non-Gaussian effects might be observed experimentally one should note that for a polymethylene chain α would be between 5 and 10. A polyisoprene or polybutadiene chain would have a value of α about a factor of 2 or 3 larger. The difference can be seen by considering the curves for $\alpha = 10$ and $\alpha = 25$. *These two curves do show significant differences in both* the magnitude of the small-strain modulus and the slope of modulus vs. extension at moderate strain. Experimental work to study this effect is now in progress.

C. Solvent Swelling. The free energy of dilution of a polymer system can be described by the Flory–Huggins equation

$$\Delta G_1 = RT[\ln (1 - v_2) + v_2 + \chi v_2^2] \quad (42)$$

where v_2 is the volume fraction of polymer and χ is the

Flory interaction parameter. For isotropic swelling

$$\lambda_1 = \lambda_2 = \lambda_3 = \lambda \tag{43}$$

and the free energy of the elastic network is

$$\Delta G_e = \frac{RT\rho}{M_c}\left\{\frac{9}{16\alpha} + \frac{1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda^2/L\beta_0)^{1/2} + 1}{1 - 3\lambda^2/L\beta_0} - \frac{9}{4L}\ln\frac{(1 - 3\lambda^2/L\beta_0)((1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda^2/L\beta_0))^{1/2} - 1)}{(1 + \frac{8}{3}\alpha L^{-1}(1 - 3\lambda^2/L\beta_0))^{1/2} + 1}\right\} \tag{44}$$

where we have equated ΔG and ΔA; this is a good approximation in incompressible systems. In eq 44 the factor of RT has been included explicitly and we have written

$$M/N_A = \rho/M_c$$

where ρ is the density of the network prior to swelling, M_c is the chain molecular weight, and N_A is Avogadro's number. The free energy of dilution of the network is calculated as

$$\Delta G_{1e} = \partial\Delta G_e/\partial n_1 \tag{45}$$

where n_1 is the mole fraction of solvent. This derivative can be evaluated with the aid of the substitution

$$v_2^{-1} = \lambda^3 = 1 + n_1 V_1 \tag{46}$$

where V_1 is the molar volume of the solvent. Equation 46 assumes additivity of volumes in the swelling process.

$$\frac{\partial\Delta G_e}{\partial n_1} = -\frac{RT\rho V_1}{M_c}v_2^{-11/3}\left\{\frac{3}{2L\beta_0}\times\frac{1}{\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)\left(1 + \frac{8\alpha}{3L}\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)\right)^{1/2}} - \frac{9}{8L\alpha\beta_0}\frac{\left(1 + \frac{8\alpha}{3L}\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)\right)^{1/2}}{\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)^2} - \frac{9}{2L^2\beta_0}\frac{1}{1 - v_2^{-2/3}\frac{3}{L\beta_0}} - \frac{6\alpha}{L^3\beta_0}\left[1\Big/\left(\left(1 + \frac{8\alpha}{3L}\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)\right)^{1/2} - 1\right)\times\left(1 + \frac{8\alpha}{3L}\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)\right)^{1/2}\right] + \frac{6\alpha}{L^3\beta_0}\left[1\Big/\left(\left(1 + \frac{8\alpha}{3L}\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)\right)^{1/2} + 1\right)\times\left(1 + \frac{8\alpha}{3L}\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)\right)^{1/2}\right]\right\} \tag{47}$$

This assumes that the elastic and mixing free energies are additive,[7] an assumption that may not be universally correct.[8]

The total free energy of the system is the sum of eq 47 and 42. At equilibrium $\Delta G = 0$. This condition yields the following equation relating v_2, M_c, L, and α:

$$\ln(1 - v_2) + v_2 + \chi v_2^2 - \rho V_1 M_c^{-1} v_2^{-11/3}(3/2L\beta_0)\times\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)^{-1}\left(1 + \frac{8\alpha}{3L}\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)\right)^{-1/2} - (9/8L\alpha\beta_0)\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)^{-2}\left(\left(1 + \frac{8\alpha}{3L}\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)\right)^{1/2} + 1\right) - (9/2L^2\beta_0)\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)^{-1}\times(6\alpha/L^3\beta_0)\left(1 + \frac{8\alpha}{3L}\left(1 - v_2^{-2/3}\frac{3}{l\beta_0}\right)\right)^{-1/2}\times\left[\left(\left(1 + \frac{8\alpha}{3L}\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)\right)^{1/2} + 1\right)^{-1} - \left(\left(1 + \frac{8\alpha}{3L}\left(1 - v_2^{-2/3}\frac{3}{L\beta_0}\right)\right)^{1/2} - 1\right)^{-1}\right] = 0 \tag{48}$$

V. Discussion

The purpose of this paper has been to extend the modified Gaussian model of rubber elasticity to the case of the wormlike chain in which the parameter of chain stiffness can be varied independently of chain length. Within the limits of the simple network model used it has been shown that chain stiffness does have a noticeable effect on the form of the stress–strain relationship which might be experimentally detectable. Of course, the work described here is only a first step. Much more work is needed to try to provide a more realistic network model into which the wormlike chain free energy can be incorporated. Despite the simplicity of the model, it is hoped that the equations derived here will be useful in interpreting experimental results on model synthetic networks and in studying the macromolecular structure of bituminous coal. Experimental work on these two problems is in progress.

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