

# Thermodynamic Models for Swelling of Heterogeneous Networks

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## Synopsis

The equilibrium swelling behavior of heterogeneous systems consisting of a continuous network phase and a dispersed lamellar, spherical, or cylindrical phase is described using a thermodynamic model. The case of swelling of both phases but to different extents is described. The equilibrium volume fractions of each phase as well as the stresses at equilibrium are predicted as functions of the polymer interaction parameter,  $\chi$ , the modulus,  $G$ , and the geometric character of the networks.

## INTRODUCTION

Equilibrium-swollen crosslinked polymeric systems, otherwise known as gels,<sup>1,2</sup> have become materials of utmost importance in biomedical and high technology applications. Knowledge of their swelling characteristics at equilibrium in relation to their structure is important when one studies the permeation properties. In recent years there have been significant efforts to develop new models for the description of the equilibrium swelling behavior of such systems.<sup>3,4</sup>

The swelling and elastic behavior of homogeneous, polymeric networks was originally addressed by Huggins<sup>5,6</sup> and Flory and Rehner.<sup>7-10</sup> The free energy of a crosslinked polymer (network), swollen to equilibrium was found to be a balance of the networks' compatibility with a solvent, and the retractive contribution from rubberlike elasticity as expressed by its corresponding partial molar Gibbs free energies.

Equilibrium swelling analysis of multiphase heterogeneous polymer networks utilizes some of the concepts used for the development of similar expressions for homogeneous polymer networks. These heterogeneous networks may be treated as quasi-homogeneous systems, with constraints arising from the contact between two dissimilar materials at their interfacial boundaries as well as physical constraints on the macromolecules within each network phase.<sup>11-14</sup> The macroscopic constraints may include: (i) the conformation and relative geometries of the polymer domains; (ii) swelling dimensionality; and (iii) external constraints. Thus, it is necessary to reformulate the thermodynamic models for homogeneous polymer networks in order to account for these effects.

Three types of domains commonly found in heterogeneous two-phase polymer networks, are spherical, cylindrical, and lamellar structures. Each phase is

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composed of a unique polymer which may or may not swell when exposed to an appropriate liquid. Polymer systems which exhibit two-phase behavior may include: (i) block or graft copolymers; (ii) bonded elastomers; or (iii) uncross-linked polymer domains in a crosslinked, elastic continuous phase. Heterogeneous networks, such as block and graft copolymer networks, exhibit phase separation on a microscopic level. This phase separation leads to formation of microdomain structures.

In the work presented here, a two-phase system of homogeneous polymers in contact with each other a sharp discontinuous phase boundary is considered. If a diffuse boundary exists, the theory developed below is easily modified to account for a third phase—the transition region between the bulk portion of the homogeneous polymer phases.

## SWELLING OF HETEROGENEOUS NETWORK SYSTEMS

### Definition of Problem

There are three possible cases of heterogeneous network systems of the type considered above. In the first case, the dispersed phase does not swell in the solvent. The second case involves a network where the continuous or most abundant phase does not swell in the presence of solvent. The prediction of system parameters, such as the equilibrium polymer volume fraction and stresses, in the latter case, may be calculated using an inverse approach to that discussed by Klier and Peppas.<sup>15</sup> In the case where the dispersed or less abundant phase does not swell, Treloar<sup>16</sup> and Klier and Peppas<sup>15</sup> have presented models that fully describe swellable two-phase systems where the core or inner phase restricts the swelling behavior of the surrounding phase. Two-phase swellable block and graft copolymers where one of the phases does not swell in the presence of solvent may also be described in this manner. The third case involves systems in which both phases may swell, albeit to different extents. A development for spherical, cylindrical, and planar geometries for this case is presented here.

Deformations in swellable networks may be measured using the extension ratios,  $\lambda_i$ , the ratio of the length of the deformed sample along the  $i$ th principle axis to the length of the undeformed sample along the  $i$ th principle axis.<sup>17-20</sup> The work required to produce a deformation is expressed as:

$$W = \sum_i w(\lambda_i) \quad (1)$$

where  $w(\lambda_i)$  are the component work functions specific to each of the  $i$  principle axes.

Treloar<sup>21</sup> has shown that the resultant stress,  $\sigma_i$ , along the  $i$ th axis in a swollen material is

$$\sigma_i = \lambda_i v_{2,s} w'(\lambda_i) + p \quad (2)$$

where  $\sigma_i$  is the force per unit area along the  $i$ th principle axis of the deformed material,  $w'(\lambda_i)$  is the first derivative of the  $i$ th component of the work function with respect to  $\lambda_i$ ,  $p$  is an arbitrary isotropic force applied on the system,  $\lambda_i$  are

the extension ratios defined with respect to the unswollen, unstrained network and  $v_{2,s}$  is the equilibrium swollen polymer volume fraction.

To express equilibrium conditions of a network in the swollen state, the force balances for two-phase, swellable, spherical, cylindrical, and planar systems are solved by applying appropriate boundary conditions and specifying a constitutive equation for the stress-strain relationship. In all geometries the boundary condition at the polymer/solvent interface is set so that forces normal to the surface be constant. For simplicity the stress at the polymer/solvent interface is set equal to zero. However, for application purposes, the reader may consider the use of the surface tension of a solvent with a polymer surface as this constant.

### Planar Geometrical Analysis

Consider the deformation of a two-phase polymer network in the slab geometry swollen to equilibrium conditions. The  $x$ ,  $y$ , and  $z$  axes are identified by the subscripts 1, 2, and 3, respectively in the generalized coordinates,  $\zeta_i$ , and swelling is allowed only in the  $x$  direction.

The extension ratios along each of the principle axes are written as follows

$$\lambda_i = d\zeta_i/d\zeta'_i \quad (3)$$

In a system limited to deformations in only the  $x$  direction,

$$\lambda_2 = \lambda_3 = 1 \quad (4)$$

The term  $\zeta_i$  is the position along the  $i$  principle axis of the swollen network, and  $\zeta'_i$  is the corresponding position of the unswollen (dry) network.

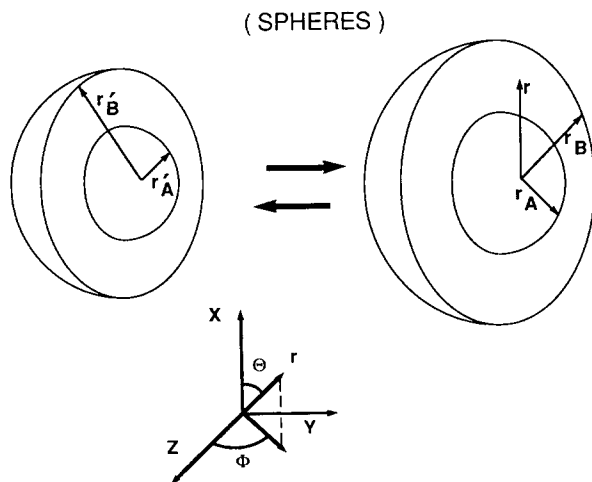


Fig. 1. Spherical microdomain structure of two-phase heterogeneous networks in the dry and equilibrium swollen states.

### Spherical Analysis

For spherical systems Figure 1 shows the equilibrium swollen condition where the  $r$ ,  $\theta$ , and  $\phi$  directions are identified by the subscripts 1, 2, and 3, respectively. The force balance for this type of system has been derived by Rivlin.<sup>22</sup>

$$\frac{d\sigma_1}{dr} = \frac{2}{r} (\sigma_2 - \sigma_1) \quad (5)$$

Geometric constraints were considered to evaluate the extension ratios along each of the three principle directions using the extension ratios  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$ .

$$\lambda_1 = \frac{dr}{dr'} \quad (6)$$

$$\lambda_2 = \frac{r}{r'} \frac{d\theta}{d\theta'} = \frac{r}{r'} \quad (7)$$

$$\lambda_3 = \frac{r}{r'} \frac{\sin \theta}{\sin \theta'} \frac{d\phi}{d\phi'} = \frac{r}{r'} \quad (8)$$

where

$$r_B'^3 = 3 \int_0^{r_B} r^2 v(r)_{2,s} dr \quad (9)$$

In the set of equations above,  $r_B$  is the outer radial position of the swollen polymer, and  $r_B'$  is the corresponding radius of the unswollen network. Similarly,  $r$  and  $r'$  are the radial positions in the swollen and corresponding unswollen networks, respectively, for an arbitrary point in the polymer network. The extension ratios in the  $\theta$  and  $\phi$  direction are equal, resulting in the condition

$$\lambda_2 = \lambda_3 = \frac{r}{r'} \quad (10)$$

For a two-phase system where the inner and outer phases are denoted by A and B respectively, eq. (9) simplifies to

$$(r_B')^3 = 3 \int_0^{r_A} r^2 v_{2,s}(r) dr + 3 \int_{r_A}^{r_B} r^2 v_{2,s}(r) dr \quad (11)$$

Equations (6) through (8) are then re-expressed as

$$\lambda_1 = \frac{dr}{dr'} = \frac{1}{v_{2,s}} \frac{(r')^2}{r^2} = \frac{1}{v_{2,s} \lambda_2^2} \quad (12)$$

and

$$\lambda_2 = \lambda_3 = r \left[ r_A^3 v_{2,s}^A + 3 \int_{r_A}^r r^2 v_{2,s}(r) dr \right]^{-1/3} \quad (13)$$

In all cases the distribution of stresses will be uniform within the inner core under both compressive and expansion conditions, and the extension ratios along all principle axes within the core will be equal. Here,  $v_{2,s}^A$  and  $\lambda_i^A$  are the polymer volume fraction and extension ratio in the inner domain, A.

$$\lambda_1^A = \lambda_2^A = \lambda_3^A = \frac{1}{(v_{2,s}^A)^{1/3}} \quad (14)$$

### Cylindrical Analysis

For cylindrical systems the force balance derived by Rivlin<sup>22</sup> (where the  $r$ ,  $\theta$ , and  $z$  directions are identified by the subscripts 1, 2, and 3, respectively) is

$$\frac{d\sigma_1}{dr} = \frac{1}{r} (\sigma_2 - \sigma_1) \quad (15)$$

The extension ratios for each of the three principle directions are derived with the added geometric constraint that the swelling in the  $z$  direction is restricted. Therefore, the extension ratios may be written

$$\lambda_1 = \frac{dr}{dr'} \quad (16)$$

$$\lambda_2 = \frac{r}{r'} \frac{d\theta}{d\theta'} = \frac{r}{r'} \quad (17)$$

$$\lambda_3 = \frac{dz}{dz'} = 1 \quad (18)$$

where

$$(r'_B)^2 = 2 \int_0^{r_B} r v(r)_{2,s} dr \quad (19)$$

Here  $r$  is the radial position of interest in the swollen polymer.  $r_B$  and  $r'_B$  are the radii of the swollen and unswollen networks respectively at the solvent/polymer interface.

The extension ratios may be expressed as

$$\lambda_1 = \frac{1}{v_{2,s} \lambda_2} \quad (20)$$

and

$$\lambda_2 = \frac{r}{r'} = r \left[ r_A^2 v_{2,s}^A + 2 \int_{r_A}^r r v_{2,s}(r) dr \right]^{-1/2} \quad (21)$$

The stresses in the  $r$  and  $\theta$  directions will be identical within the inner core under both compressive and expansion conditions. The extension ratios for the inner core are written as

$$\lambda_1^A = \lambda_2^A = \frac{1}{(v_{2,s}^A)^{1/2}} \quad (22)$$

within the core.

### Equilibrium Swelling Model

The generalized equation of stress proposed by Treloar<sup>16</sup> and Erman<sup>17</sup> is used to derive the relationship between stress and swelling. The expression for stress,  $\sigma_i$ , is given as

$$\sigma_i = \lambda_i v_{2,s} w'(\lambda_i) + \frac{N}{\bar{V}_1} \frac{\partial \Delta A_{\text{mix}}}{\partial n_1} \quad (23)$$

Here the first combination of terms on the right-hand side of eq. (23) is the contribution due to the elastic free energy of the system,  $\Delta A_{\text{mix}}$  is the free energy of mixing,  $\bar{V}_1$  is the molar volume of the solvent;  $n_1$  is the number of solvent molecules, and  $N$  is the Avogadro number.

Eq. (23) is used in the force balances to formulate generalized equations for the equilibrium swollen polymer volume fraction,  $v_{2,s}$ , as a function of position. The boundary conditions at the A/B interface are considered, and conservation equations for each geometry are developed.

For the planar systems, eq. (23), leads to the following expression:

$$\sigma_1 = \lambda_1 v_{2,s} w'(\lambda_1) + \frac{N}{\bar{V}_1} \frac{\partial \Delta A_{\text{mix}}}{\partial n_1} = 0 \quad (24)$$

This equation may be used to solve for the equilibrium swollen polymer volume fraction,  $v_{2,s}$ . Coupled with eq. (23), the stresses,  $\sigma_2$  and  $\sigma_3$ , in the other two principle directions can also be calculated. For the planar geometry presented, the extension ratios in the  $y$  and  $z$  directions are equal in each phase.

The A/B interface is now considered in order to formulate the boundary conditions used to translate from phase to phase for the solution of problems in spherical and cylindrical geometry. Two boundary conditions apply in this approach. The first boundary condition is

$$\begin{aligned} \lambda_3^A &= \lambda_3^B \\ \lambda_2^A &= \lambda_2^B \end{aligned} \quad (25)$$

The extension ratios in both phases in the angular directions are equal at the A/B interface. The second boundary condition is the continuity of radial stress at the A/B interface. This condition is expressed as

$$\sigma_1^A = \sigma_1^B \tag{26}$$

evaluated at the polymer/polymer interface.

To simplify the analysis the outer interface of phase B in the unswollen, nondeformed network is normalized to unity for every geometry. The ratio of the location of the outer interface of phase A relative to phase B is expressed by the parameter  $H$ .

$$H = \frac{r'_A}{r'_B} \tag{27}$$

Further analysis is needed to express the force balance in terms of more recognizable parameters for spherical systems. By incorporating eq. (23) in eq. (5), the following extended equation is derived:

$$\begin{aligned} \lambda_1 w'(\lambda_1) \frac{dv_{2,s}}{dr} + v_{2,s} w'(\lambda_1) \frac{d\lambda_1}{dr} + v_{2,s} \lambda_1 \frac{dw'(\lambda_1)}{dr} + \frac{N}{\bar{V}_1} \frac{d\Delta\bar{A}_{\text{mix}}}{dr} \\ = \frac{2}{r} v_{2,s} [\lambda_2 w'(\lambda_2) - \lambda_1 w'(\lambda_1)] \end{aligned} \tag{28}$$

Here,  $\Delta\bar{A}_{\text{mix}}$  is the mixing free energy per solvent molecule given by the second term in eq. (23). Differentiating eq. (12) and substituting in to eq. (28) results in the following expression for the gradient of the equilibrium swollen polymer volume fraction,  $v_{2,s}$

$$\frac{dv_{2,s}}{dr} = \frac{\frac{2v_{2,s}}{r} [\lambda_2 w'(\lambda_2) + \lambda_1^2 w''(\lambda_1)] - \frac{2v_{2,s}}{r'} [w'(\lambda_1) + \lambda_1 w''(\lambda_1)]}{\frac{N}{\bar{V}_1} \frac{d\Delta\bar{A}_{\text{mix}}}{dv_{2,s}} - \lambda_1^2 w''(\lambda_1)} \tag{29}$$

where  $w'(\lambda_i)$  and  $w''(\lambda_i)$  are the first and second derivative of the  $i$ th component of the work function with respect to the  $i$ th extension ratio, respectively.

Continuity of the  $\theta$  extension ratios,  $\lambda_2$ , in each phase at the interface leads to the following equation

$$\lambda_1^B = \frac{(v_{2,s}^A)^{2/3}}{v_{2,s}^B} \tag{30}$$

Furthermore, the continuity of radial stress at the A/B interface is written by incorporating eqs. (30) and (23) into eq. (26)

$$(v_{2,s}^A)^{2/3} w'(\lambda_1^A) + \frac{N}{\bar{V}_1} \Delta\bar{A}_{\text{mix}}^A = (v_{2,s}^A)^{2/3} w'(\lambda_1^B) + \frac{N}{\bar{V}_1} \Delta\bar{A}_{\text{mix}}^B \tag{31}$$

Therefore, eq. (31) establishes the criterion to relate conditions on either side of the A/B interface.

The conservation equation for the spherical geometry is derived using eq. (9).

$$\int_{r_A}^{r_B} v_{2,s}(r)r^2 dr = (1/3)[r_B'^3 - r_A'^3] \quad (32)$$

Here  $r_A$  and  $r_B$  are the radii of the outer interface of phases A and B in the equilibrium swollen network, respectively, and  $r_A'$  and  $r_B'$  are the radii of the outer interface of phases A and B in the unswollen, nondeformed network.

An analysis similar to the one presented for the spherical system is used for cylindrical systems. The following equation was derived in the same manner as eq. (28) for the spherical system by incorporating eq. (23) into eq. (15)

$$\begin{aligned} \lambda_1 w'(\lambda_1) \frac{dv_{2,s}}{dr} + v_{2,s} w'(\lambda_1) \frac{d\lambda_1}{dr} + v_{2,s} \lambda_1 \frac{dw'(\lambda_1)}{dr} + \frac{N}{\bar{V}_1} \frac{d\Delta\bar{A}_{\text{mix}}}{dr} \\ = \frac{1}{r} v_{2,s} [\lambda_2 w'(\lambda_2) - \lambda_1 w'(\lambda_1)] \quad (33) \end{aligned}$$

Differentiation of eq. (20) and substitution into eq. (33) results in an expression for the gradient of the equilibrium swollen polymer volume fraction,  $v_{2,s}$ , in the cylindrical system

$$\frac{dv_{2,s}}{dr} = \frac{\frac{v_{2,s}}{r} [\lambda_2 w'(\lambda_2) + \lambda_1^2 w''(\lambda_1)] - \frac{v_{2,s}}{r'} [w'(\lambda_1) + \lambda_1 w''(\lambda_1)]}{\frac{N}{\bar{V}_1} \frac{d\Delta\bar{A}_{\text{mix}}}{dv_{2,s}} - \lambda_1^2 w''(\lambda_1)} \quad (34)$$

From continuity of the  $\theta$  extension ratios,  $\lambda_2$ , in each phase at the interface, the following relationship is obtained

$$\lambda_1^B = \frac{(v_{2,s}^A)^{1/2}}{v_{2,s}^B} \quad (35)$$

The continuity of radial stress at the A/B interface is then written as follows by incorporating eqs. (35) and (23) into eq. (26)

$$(v_{2,s}^A)^{1/2} w'(\lambda_1^A) + \frac{N}{\bar{V}_1} \Delta\bar{A}_{\text{mix}}^A = (v_{2,s}^B)^{1/2} w'(\lambda_1^B) + \frac{N}{\bar{V}_1} \Delta\bar{A}_{\text{mix}}^B \quad (36)$$

The conservation equation for the cylindrical geometry is written as

$$\int_{r_A}^{r_B} v_{2,s}(r)r dr = (1/2)[r_B'^2 - r_A'^2] \quad (37)$$



where the terms have been previously defined. The system is normalized with respect to the unswollen, nondeformed network dimension as in the case of the spherical networks.

The following methodology is a summary of the steps applied in order to solve the previous equations:

1. Select a geometry which best describes the system; this geometrical shape sets the value of the parameter  $H$  in the analysis.
2. Select the polymers/solvent combination; this selection fixes the parameters required in the work function and thermodynamic expression for the free energy of mixing.
3. Select an arbitrary value for the equilibrium polymer volume fraction in the internal phase,  $v_{2,s}^A$ , where  $0 < v_{2,s}^A < 1$ .
4. Solve for the equilibrium polymer volume fraction in the external phase at the A/B interface,  $v_{2,s}^B$ , from the continuity of interfacial stress boundary condition.
5. Calculate the equilibrium polymer volume fraction as a function of position; i.e., the term  $v_{2,s}(\xi)$ , from the modified force balance; a finite forward difference procedure is used where, at each incremental step, the extension ratios along the principle axes are updated.
6. Apply the polymer conservation equation at each step to determine if an additional step is required.
7. Once the polymer/solvent interface is reached; check the interfacial boundary condition to verify if the primary stress at the interface is equal to the predetermined constant. If this condition holds, the equilibrium values of the polymer volume fraction, stresses, extension ratios, and gradients of these parameters are the correct ones. If the boundary condition is not satisfied, return to step three and increment the selection of the equilibrium polymer volume fraction in the internal phase,  $v_{2,s}^A$ , and repeat the procedure until a satisfactory solution is reached.

The models have been developed in a general manner so that they may be applied with or without a network theory for polymeric systems. In further development, knowledge of the work function and free energy of mixing is required. As presented thus far, this knowledge is not required since the information can be acquired from experiments with homogeneous materials.

In subsequent analysis, well known forms of the work function and mixing free energy will be used. The work function may be expressed by the phantom network expression<sup>23,24</sup> where

$$w(\lambda_i)_{ph} = \frac{1}{2}G(\lambda_i^2 - 1) \quad (38)$$

and the derivative term is defined as

$$w'(\lambda_i)_{ph} = G\lambda_i \quad (39)$$

Of course,  $G$  is the elastic modulus of the elastomer.

The free energy of mixing for a polymer/solvent swollen network will be expressed using the statistical mean field theory of Flory and Huggins<sup>8,9</sup>

$$\Delta\bar{A}_{\text{mix}} = \frac{\partial\Delta A_{\text{mix}}}{\partial n_1} = kT[\ln(1 - v_{2,s}) + v_{2,s} + \chi_{1,2}v_{2,s}^2] \quad (40)$$

Here  $n_1$  is the number of solvent molecules,  $k$  is Boltzman's constant and  $\chi_{1,2}$  is the solvent/polymer interaction parameter, representing the mixing enthalpy. Positive values of  $\chi_{1,2}$  represent an unfavorable change in mixing enthalpy. Both  $\chi_{1,2}$  and  $v_{2,s}$  are chosen to approximate conditions of commonly found polymer networks reported in the literature.

## DISCUSSION

### Model Predictions

Solutions of the models presented in the preceding section give values of the equilibrium polymer volume fraction as a function of position,  $v_{2,s}(\xi)$ , in a two-phase equilibrium swollen polymer network. Knowledge of the equilibrium swollen polymer volume fraction enables the stresses throughout the system to be computed.

The equilibrium polymer volume fraction and the stress profiles throughout the network are effected by the chemical composition of the polymeric materials and the physical arrangement of the network phases. The network parameters required for the determination of these quantities include the solvent/polymer interaction parameter,  $\chi_{1,2}$ , and the elastic modulus,  $G$ , of the polymers in each phase. In addition, the dimensions of the confined (inner) phase influence both the equilibrium swollen polymer volume fraction and stress profiles.

The first case examined is a spherical heterogeneous system with a confined phase that swells to a lesser degree than the surrounding phase. The arguments presented here are also applicable to cylindrical and planar geometries. The distribution of stress causes the equilibrium swollen polymer volume fraction near the polymer-polymer interface to be larger than in homogeneously swollen systems. The radial stresses in the surrounding phase will be tensile in nature, while the stresses in the  $\theta$  and  $\phi$  directions are compressive in nature. The radial stress diminishes with increasing radius and approaches the boundary condition value at the outer surface. However, the  $\theta$  and  $\phi$  stresses remain finite at the outer surface since these stresses are a result of the constraining nature of the confined phase. In the second case the confined phase swells to a larger degree than the surrounding phase. The analysis is similar, but the signs on the stresses will be opposite to those discussed previously.

In the following analysis the examples are restricted to the spherical geometry due to the excessive number of parameters (five) and of geometries (three) involved. However, information from the cylindrical and planar geometric systems may be of equal importance. In all cases, the methodology and models required have been presented in previous sections of this text.

### Influence of the Elastic Modulus, $G$

Mechanical and swelling properties of polymer networks are affected by their structure. Network characteristics, such as the number average molecular

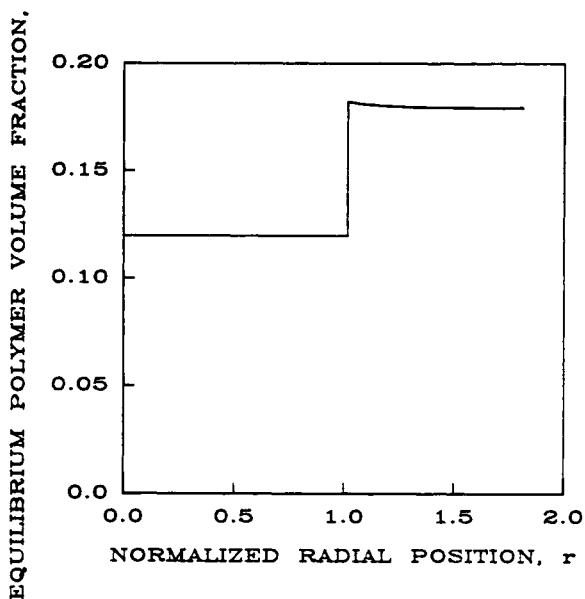


Fig. 2. Equilibrium polymer volume fraction,  $v_{2,s}$ , as a function of normalized radial position,  $r$ , for a heterogeneous two-phase system. The solvent/polymer interaction parameters are  $\chi_A = 0.0$  and  $\chi_B = 0.0$ . The elastic moduli are  $G_A = 0.05 \text{ Nmm}^{-2}$  and  $G_B = 5.0 \text{ Nmm}^{-2}$ . The  $H$ -factor is  $H = 0.5$ .

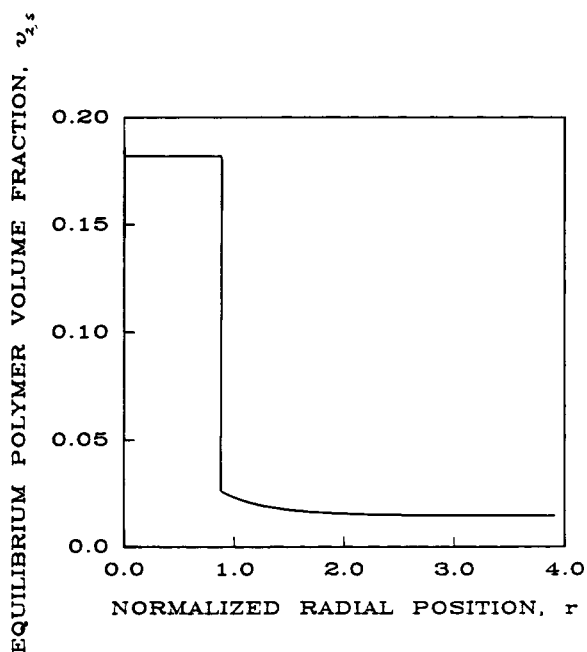


Fig. 3. Equilibrium polymer volume fraction,  $v_{2,s}$ , as a function of normalized radial position,  $r$ , for a heterogeneous two-phase system. The solvent/polymer interaction parameters are  $\chi_A = 0.0$  and  $\chi_B = 0.0$ . The elastic moduli are  $G_A = 5.0 \text{ Nmm}^{-2}$  and  $G_B = 0.05 \text{ Nmm}^{-2}$ . The  $H$ -factor is  $H = 0.5$ .

weight,  $\bar{M}_n$ ; the number average molecular weight between crosslinks,  $\bar{M}_c$ ; and the number of entangled and complexed chains, influence the type of structure formed and the resistance of the network to deformations. Here networks swollen to equilibrium are described by the elastic modulus,  $G$ , of the material. The elastic modulus is defined as

$$G = \frac{\xi kT}{V_0} \quad (41)$$

where  $\xi$  is the cycle rank of the network;  $k$  is the Boltzman constant;  $T$  is the absolute temperature; and  $V_0$  is the molar volume of the unswollen, undeformed network.

For networks with tetrafunctional crosslinks, Flory<sup>23,24</sup> has shown the cycle rank is a function of the number average molecular weight between crosslinks,  $\bar{M}_c$ . The following expression for the elastic modulus,  $G$ , results from incorporating the expression for  $\xi$  in eq. (41)

$$G = \frac{\rho RT}{\bar{M}_c} \left( 1 - \frac{2\bar{M}_c}{\bar{M}_n} \right) \quad (42)$$

In the above equation  $\rho$  is the density of the network in the unswollen state,  $R$  is the universal gas constant, and  $\bar{M}_n$  is the number average molecular weight of the original uncrosslinked polymer.

Figures 2 and 3 represent two-phase spherical networks swollen to equilibrium conditions. The values of the elastic modulus,  $G$ , used in the calculations ranged from 0.05 N/mm<sup>2</sup> to 5.0 N/mm<sup>2</sup>—a common range for most polymers. The equilibrium swollen polymer volume fraction,  $v_{2,s}$ , is plotted for systems encompassing a range of solvent compatibility,

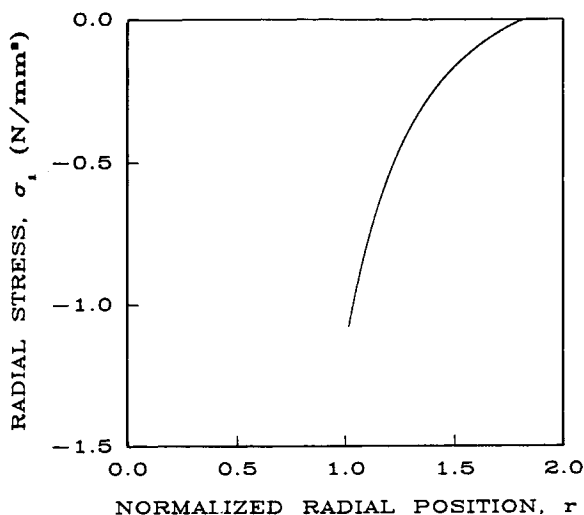


Fig. 4. Radial stress,  $\sigma_1$  (Nmm<sup>-2</sup>), as a function of normalized radial position,  $r$ , for a heterogeneous two-phase sphere. The solvent/polymer interaction parameters are  $\chi_A = 0.0$ , and  $\chi_B = 0.0$ .

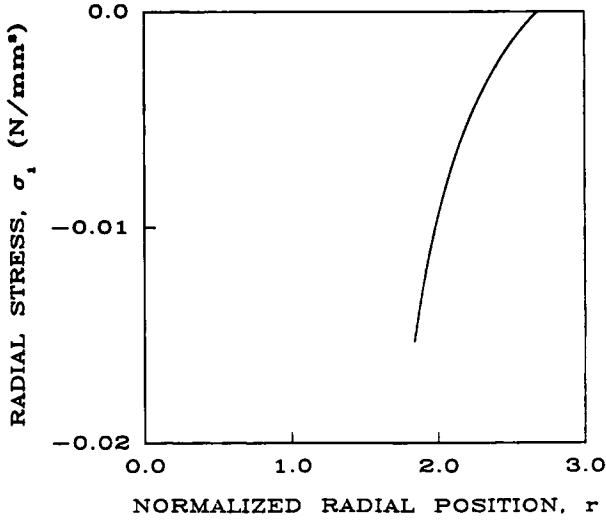


Fig. 5. Radial stress,  $\sigma_1$  ( $\text{Nmm}^{-2}$ ), as a function of normalized radial position,  $r$ , for a heterogeneous two-phase sphere. The solvent/polymer interaction parameters are  $\chi_A = 0.25$ , and  $\chi_B = 0.25$ . The elastic moduli are  $G_A = 0.05 \text{ Nmm}^{-2}$  and  $G_B = 5.0 \text{ Nmm}^{-2}$ . The  $H$ -factor is  $H = 0.5$ .

and either the inner or outer phase is chosen as the “stiffer” phase in these examples.

The magnitude of stress is greatest in systems with phases that differ widely with respect to their network structure and compatibility with the solvent.

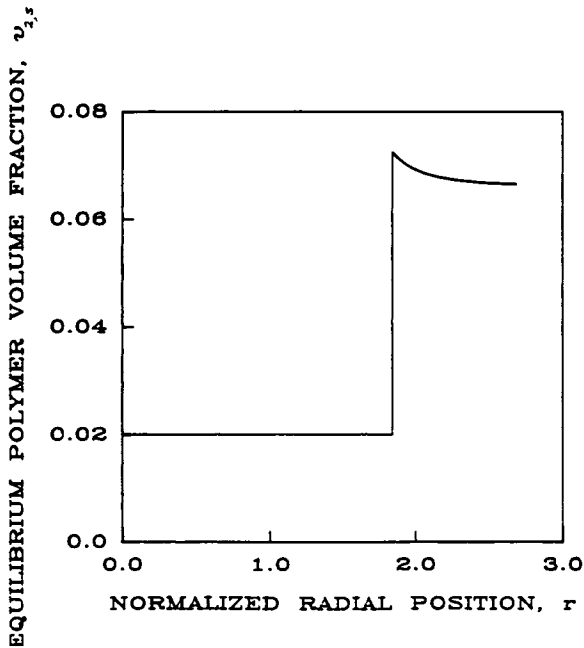


Fig. 6. Equilibrium polymer volume fraction,  $v_{2,s}$ , as a function of normalized radial position,  $r$ , for a heterogeneous two-phase sphere. The solvent/polymer interaction parameters are  $\chi_A = 0.0$  and  $\chi_B = 0.5$ . The elastic moduli are  $G_A = 0.05 \text{ Nmm}^{-2}$  and  $G_B = 0.05 \text{ Nmm}^{-2}$ . The  $H$ -factor is  $H = 0.5$ .

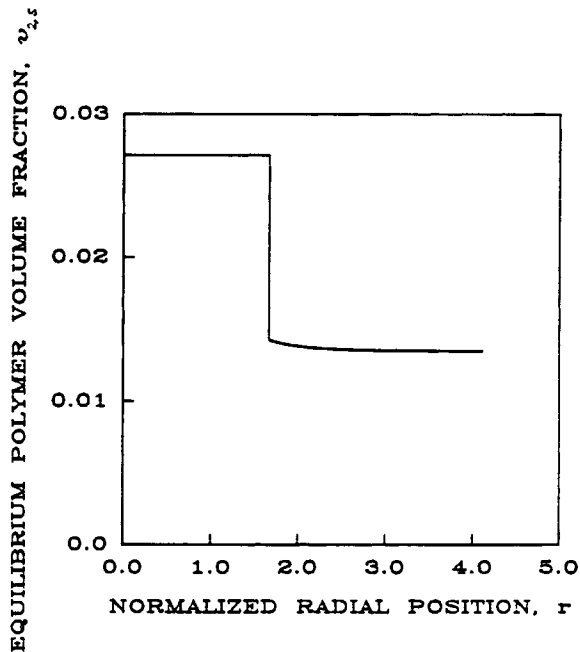


Fig. 7. Equilibrium polymer volume fraction,  $v_{2,s}$ , as a function of normalized radial position,  $r$ , for a heterogeneous two-phase sphere. The solvent/polymer interaction parameters are  $\chi_A = 0.5$  and  $\chi_B = 0.0$ . The elastic moduli are  $G_A = 0.05 \text{ Nmm}^{-2}$  and  $G_B = 0.05 \text{ Nmm}^{-2}$ . The  $H$ -factor is  $H = 0.5$ .

Figures 4 and 5 are presented to demonstrate the effect of the elastic modulus on the stresses in these systems.

#### Influence of Solvent/Polymer Interaction Parameter, $\chi_{1,2}$

The solvent/polymer interaction was accounted for using the Flory-Huggins theory. In this development the solvent/polymer interaction parameter,  $\chi_{1,2}$ , was used as a measure of the extent of these interactions. Values of  $\chi$  ranged from 0.0 to 0.5—commonly reported values for many solvent/polymer systems.

Figures 6 and 7 represent the equilibrium conditions of a swollen two-phase spherical system. The networks with lower (more favorable) solvent/polymer interaction parameters,  $\chi_{1,2}$ , are swollen to a greater extent. The response of the system indicates that as  $\chi_{1,2}$  decreases the interaction of the solvent with the polymer becomes more favorable, causing the polymer concentration, as expressed by the  $v_{2,s}$ , to decrease.

Figures 8 and 9 are plots of stresses as a function of position in the two-phase polymer networks. The stresses and stress differences are most pronounced in systems where unlike networks are in contact. Also, as the equilibrium swollen polymer volume fraction,  $v_{2,s}$ , decreases, the difference of the stresses becomes larger due to the larger deformation of the swollen polymers.

#### Influence of the Parameter $H$

The relative size of the inner to outer phases is expressed by the parameter,  $H$ . In a system with a small value of  $H$ , and an inner phase, A, with a high

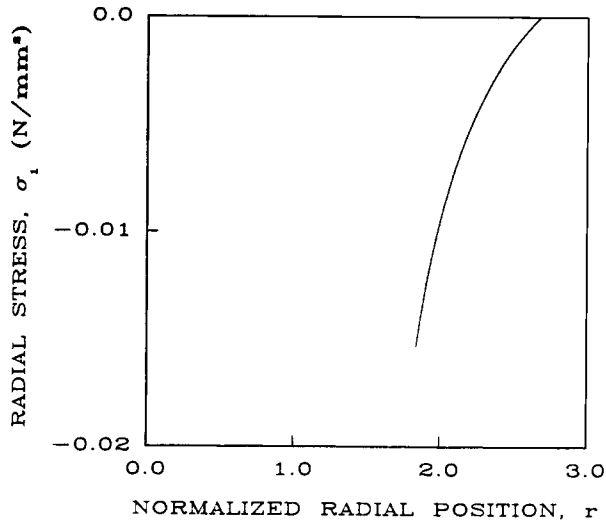


Fig. 8. Radial stress,  $\sigma_1$  ( $\text{Nmm}^{-2}$ ), as a function of normalized radial position,  $r$ , for a heterogeneous two-phase sphere. The solvent/polymer interaction parameters are  $\chi_A = 0.0$ , and  $\chi_B = 0.5$ . The elastic moduli are  $G_A = 0.05 \text{ Nmm}^{-2}$  and  $G_B = 0.05 \text{ Nmm}^{-2}$ . The  $H$ -factor is  $H = 0.5$ .

polymer volume fraction (low degree of swelling), the equilibrium swollen polymer volume fraction in the outer phase, B, will be greater than in homogeneously swollen networks composed of material B. This effect is due to constraints the inner phase places on the outer phase.

Figure 10 is provided to demonstrate the effect of the parameter,  $H$ , on the two systems. The first system considered consists of two phases that interact with the solvent differently, and the second system is composed of two phases that vary in structure. The effect of the  $H$ -factor on the stresses in both systems are shown in Figure 11.

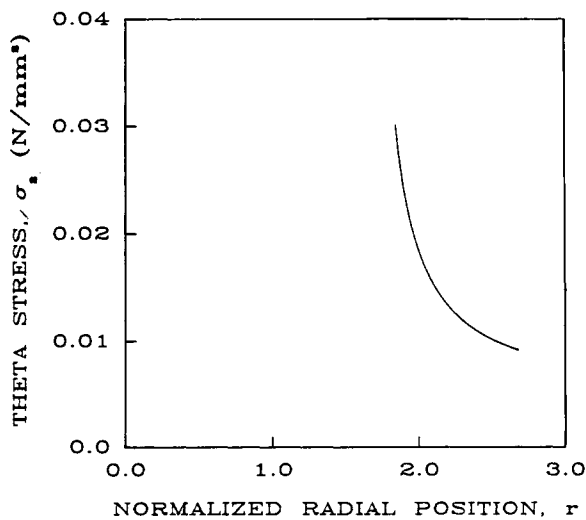


Fig. 9. Theta stress,  $\sigma_2$  ( $\text{Nmm}^{-2}$ ), as a function of normalized radial position,  $r$ , for a heterogeneous two-phase sphere. The solvent/polymer interaction parameters are  $\chi_A = 0.0$  and  $\chi_B = 0.5$ . The elastic moduli are  $G_A = 0.05 \text{ Nmm}^{-2}$  and  $G_B = 0.05 \text{ Nmm}^{-2}$ . The  $H$ -factor is  $H = 0.5$ .

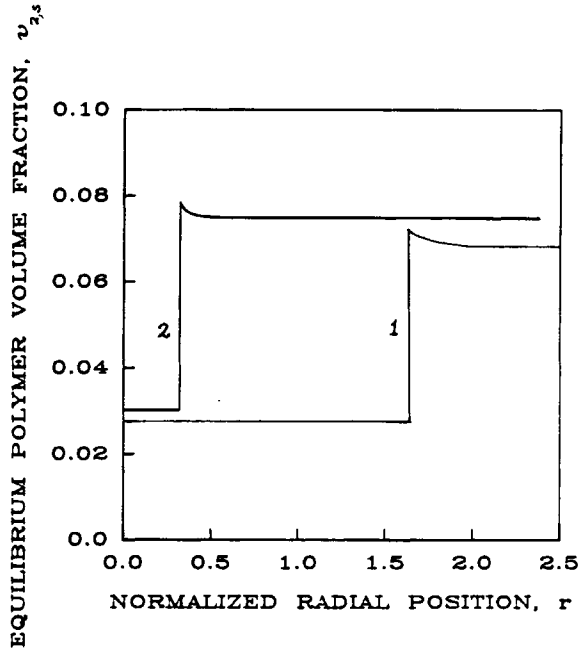


Fig. 10. Equilibrium polymer volume fraction,  $v_{2,s}$ , as a function of normalized radial position,  $r$ , for a heterogeneous two-phase sphere. The solvent/polymer interaction parameters are  $\chi_A = 0.25$  and  $\chi_B = 0.5$ . The elastic moduli are  $G_A = 0.05 \text{ Nmm}^{-2}$  and  $G_B = 0.05 \text{ Nmm}^{-2}$ . The  $H$ -factors are  $H = 0.5$  (curve 1) and  $0.1$  (curve 2).

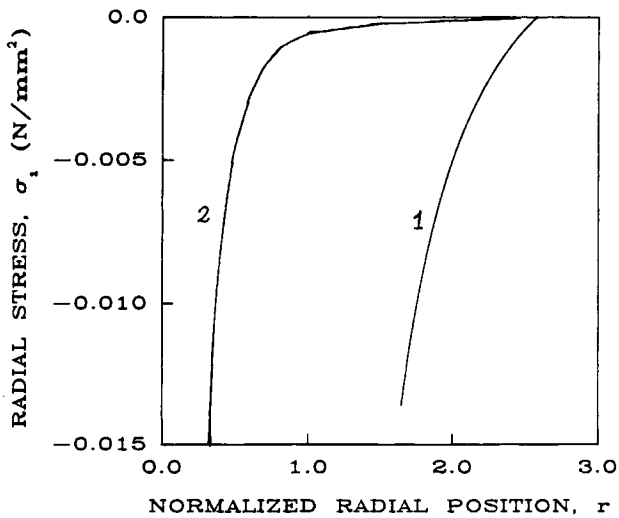


Fig. 11. Radial stress,  $\sigma_1$  ( $\text{Nmm}^{-2}$ ) as a function of normalized radial position,  $r$ , for a heterogeneous two-phase sphere. The solvent/polymer interaction parameters are  $\chi_A = 0.25$ , and  $\chi_B = 0.5$ . The elastic moduli are  $G_A = 0.05 \text{ Nmm}^{-2}$  and  $G_B = 0.05 \text{ Nmm}^{-2}$ . The  $H$ -factors are  $H = 0.5$  (curve 1) and  $0.1$  (curve 2).



## CONCLUSIONS

The development of models to predict the concentration of polymer and stresses in two-phase heterogeneous networks was shown. A generalized approach to the problem was presented to allow extension of the models to practical systems. The relationship between stress and equilibrium swelling enabled the equilibrium swollen polymer volume fraction profile to be calculated. Variations in stress and equilibrium swollen polymer volume fraction with changes in the relative radius of the inner phase, solvent-polymer interactions, and elastic modulus in each phase was demonstrated. Gradients of stress and equilibrium swollen polymer volume fraction resulted from the nonhomogeneity of the system. Since transport and mechanical properties of polymer networks may depend strongly on degrees of swelling and deformation, the results presented above may be used to help describe transport and mechanical properties of heterogeneous systems.

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