Swelling of network structures

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Rubber swelling theory is revisited in an attempt to derive consistent thermodynamic expressions for the elastic free energy valid for the swelling of a crosslinked polymer by liquids, gases or supercritical fluids. In this approach, evaluation of solvent properties in a hypothetical reference state is not needed. An equation of state for the crosslinked polymer is presented which may be used for the evaluation of its internal pressure. Model calculations are compared with experimental data on the swelling of crosslinked poly(dimethylsiloxane) by benzene and supercritical carbon dioxide.

(Keywords: rubber elasticity; swelling; supercritical fluids; lattice fluid model; equation of state; chemical potential)

Introduction

The statistical mechanical developments on rubber elasticity 50 years ago[1–4], were one of the major breakthroughs in polymer science. In recent years, the rubber elasticity and in particular the swelling of network structures has attracted considerable attention in the context of emerging new technological applications such as the development of thermoreversible hydrogels[5,6], the swelling of rubbers by liquid crystals[7,8] and the use of supercritical fluid mixtures for the impregnation of polymers and rubbers[9,10].

The main objective of this communication is to present a general framework for the consistent and unified treatment of the above diverse cases of rubber swelling. For this purpose an expression for the Gibbs free energy of the swollen rubber is formulated that reduces, under appropriate conditions, to a free energy expression for mixtures of liquids or gases. The very same framework has been used recently for the description of hydrogen-bonded fluids such as water and polyalcohols[11], and for the description of nematic liquid crystals[12]. There are no new concepts involved in this development. The unifying character of the Lattice–Fluid theory of mixtures[13–15], is simply pursued one step further.

Theory

Consider a mixture of N_2 polymer chains with N_1 solvent molecules at temperature T and external pressure P. Polymer chain and solvent molecules are assumed divided into r_2 and r_1 segments, respectively, and are arranged on a quasi-lattice of N_r sites, N_0 of which are empty. The arrangement is such that for f chain ends within a small volume $\Delta\tau$, the chains are interconnected through f functional crosslinks. In the enumeration of the system configurations care must be exercised to properly account for the fact that the set of f chain ends of a given crosslinkage are always the same regardless of any external conditions.

In spite of the above over-simplistic formulation, an attractive solution to the problem calls for further assumptions and approximations. Thus, the central approximation is now made that the total Gibbs free energy of the system can be factored into two terms:

$$G = -RT\ln Q_{\mathrm{LF}} - RT\ln Q_{\mathrm{el}} \qquad (1)$$

The first term in equation (1) is the Gibbs free energy of the corresponding uncrosslinked system at the same external conditions. The second term is a correction term which takes into account the chain connectivity and the assumed affine geometry of the network expansivity. In this communication, and for the clarity of the argument, two simple expressions will be used for both terms in equation (1). Thus, for the first term, the Lattice–Fluid configurational partition function[13–15] will be chosen, namely

$$Q_{\mathrm{LF}} = \left(\frac{1}{f_0}\right)^{N_0}\left(\frac{\omega_1}{f_1}\right)^{N_1}\left(\frac{\omega_2}{f_2}\right)^{N_2}\exp\left(-\frac{E+PV}{RT}\right) \qquad (2)$$

where

$$f_i = \frac{r_i N_i}{N_r} \qquad (i=0,1,2) \qquad (3)$$

ω_1 and ω_2 in equation (2) are constants characteristic of components 1 and 2 that can be ignored in all applications of interest here, and E is the total intermolecular interaction energy of the system.

The second term in equation (1) depends on the crosslinking conditions or on the amount of solvent present during crosslinking. Let V be the volume of the expanded polymer when crosslinks are introduced. The degree of swelling of the crosslinked network is then:

$$\alpha_s^3 = \frac{V}{V_0} \qquad (4)$$

It will be assumed here that the distribution of chain displacement lengths is undistorted by dilution with the solvent. One of the simplest available expressions for Q_{el}

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and which we will adopt here is that of Flory[16], namely

$$Q_{\mathrm{el}} = \left\{ \alpha_{\mathrm{s}}^3 \exp\left[-\frac{3}{2}(\alpha_{\mathrm{s}}^2 - 1) \right] \right\}^{N_2} \left(\frac{2N_2 \Delta\tau}{Ve} \right)^{\frac{2(f-1)}{f} N_2} \qquad (5)$$

where e is the usual transcendental number. In deriving this expression Flory has assumed that the process of going from the system of dissolved uncrosslinked chains to the final state of the swollen network can be accomplished in two steps: dilation of the most probable chain displacement length distribution by the factor α_{s} followed by the assemblage of the chain elements in $2N_2/f$ groups of f ends each[16]. The first bracketed term in equation (5) is the contribution of the first step by assuming Gaussian distribution of chain displacement lengths. The second bracketed term in equation (5) is the contribution of the second step.

Having formulated an expression for the total free enthalpy of the system we may now proceed with the derivation of expressions of the basic thermodynamic quantities.

In the Lattice–Fluid theory[13–15] each fluid i is characterized by three scaling constants, namely, a number of segments per molecule, r_i, a hard core volume per segment, v_i^*, and an average segment–segment interaction energy, ε_i^*. If s_i is the average number of external contacts per segment i it is convenient to define ε_i^* by:

$$\varepsilon_i^* = \frac{s_i}{2} \varepsilon_i \qquad (6)$$

On the basis of these scaling constants other characteristic parameters for the fluid may be defined. Thus the characteristic temperature and pressure of the fluid are obtained from:

$$\varepsilon_i^* = RT_i^* = P_i^* v_i^* \qquad (7)$$

If M_i is the molar mass of fluid i, the close-packed density ρ_i^* of the fluid is given by:

$$\frac{M_i}{\rho_i^*} = r_i v_i^* \qquad (8)$$

In mixtures, besides mole fractions x_i [$= \mathrm{N}_i/(\mathrm{N}_1 + \mathrm{N}_2)$], segment fractions

$$\varphi_i = \frac{x_i r_i}{x_1 r_1 + x_2 r_2} = \frac{x_i r_i}{r} \qquad (9)$$

and surface fractions

$$\theta_i = \frac{x_i r_i s_i}{x_1 r_1 s_1 + x_2 r_2 s_2} = \frac{x_i r_i s_i}{rs} = f_i \frac{s_i}{s} \qquad (10)$$

will be used.

The Lattice–Fluid characteristic quantities in mixtures are given by the following mixing and combining rules:

$$\varepsilon^* = \varphi_1 \varepsilon_1^* + \varphi_2 \varepsilon_2^* - \varphi_1 \theta_2 RTX_{12} \qquad (11)$$

where

$$X_{12} = \frac{\varepsilon_1^* + \frac{s_1}{s_2} \varepsilon_2^* - 2\sqrt{\frac{s_1}{s_2}}\, \varepsilon_{12}^*}{RT} \qquad (12)$$

and

$$\varepsilon_{12}^* = \zeta_{12} \sqrt{\varepsilon_1^* \varepsilon_2^*} \qquad (13)$$

ζ_{12} is a dimensionless binary parameter expected to have values close to unity.

The hard core volume v^* is given by:

$$v^* = \varphi_1^2 v_1^* + \varphi_2^2 v_2^* + 2\varphi_1 \varphi_2 v_{12}^* \qquad (14)$$

By assuming the simple mixing rule:

$$v_{12}^* = \frac{v_1^* + v_2^*}{2} \qquad (15)$$

equation (14) reduces to the simple combining rule:

$$v^* = \varphi_1 v_1^* + \varphi_2 v_2^* \qquad (14a)$$

In the general case we set

$$v_{12}^* = \xi_{12} \left(\frac{v_1^{*1/3} + v_2^{*1/3}}{2} \right) \qquad (15a)$$

Once again, the dimensionless binary parameter ξ_{12} is expected to have values close to unity.

With these definitions, the total interactional potential energy of the system is given by:

$$E = -rN\tilde{\rho}\varepsilon^* \qquad (16)$$

The reduced density $\tilde{\rho}$ in equation (16) is obtained from the equation of state which we will derive subsequently. For the total volume of the system we may write:

$$V = rN \frac{v^*}{\tilde{\rho}} = rN\tilde{v}v^* \qquad (17)$$

Two other useful reduced quantities are the reduced temperature, $\tilde{T}$, and the reduced pressure, $\tilde{P}$, given by:

$$\tilde{T} = \frac{T}{T^*} = \frac{RT}{\varepsilon^*} \quad \text{and} \quad \tilde{P} = \frac{P}{P^*} = \frac{Pv^*}{\varepsilon^*} \qquad (18)$$

The equation of state of the system will be obtained by minimizing the total free energy, equation (1), with respect to $\tilde{\rho}$ (or $\tilde{v}$). The resulting equation is:

$$\tilde{P} + \tilde{\rho}^2 + \tilde{T}\left[\ln(1-\tilde{\rho}) + \tilde{\rho}\left(1 - \frac{\varphi_1}{r_1}\right) + \frac{\varphi_2}{r_2}\tilde{\rho}\left(\alpha_{\mathrm{s}}^2 - \frac{2}{f}\right) \right] = 0 \qquad (19)$$

The last term in the bracket is the elastic contribution to the equation of state. Note that the volume element $\Delta\tau$ does not contribute to the equation of state. If no solvent is present during crosslinking, the swelling ratio α_{s}^3 is given by:

$$\alpha_{\mathrm{s}}^3 = \frac{V}{V_0} = \frac{rN\tilde{v}v^*}{r_2 N_2 \tilde{v}_2 v_2^*} = \frac{\tilde{v}v^*}{\varphi_2 \tilde{v}_2 v_2^*} \qquad (20)$$

where the reduced volume $\tilde{v}_2$ ($= 1/\tilde{\rho}_2$) for the pure polymer 2 is given by the Lattice–Fluid analogue of equation (19), namely

$$\tilde{P}_2 + \tilde{\rho}_2^2 + \tilde{T}_2[\ln(1-\tilde{\rho}_2) + \tilde{\rho}_2] = 0 \quad \text{(pure polymer)} \qquad (19a)$$

This equation should not be confused with the equation of state for the pure crosslinked rubber obtained from equation (19) by setting $\varphi_1 = 0$:

$$\tilde{P}_2 + \tilde{\rho}_2^2 + \tilde{T}_2\left[\ln(1-\tilde{\rho}_2) + \tilde{\rho}_2 + \frac{\tilde{\rho}_2}{r_2}\left(\alpha_{\mathrm{s}}^2 - \frac{2}{f}\right) \right] = 0 \quad \text{(rubber)} \qquad (19b)$$

This equation is useful for deriving equations for the expansivity, compressibility and internal pressure of the rubber.

Swelling equilibria will be calculated by equating the chemical potentials of the solvent in the pure state and in the swollen rubber. The equation for the chemical potential of the solvent obtained from equation (1) is:

$$\frac{\mu_1}{RT}=\frac{\mu_{1,\mathrm{LF}}}{RT}+\frac{r_1}{r_2}\phi_2\left[\alpha_s^2-1+\frac{2(f-1)}{f}\right]\times\left[\frac{2(\varphi_1 v_1^*+\varphi_2 v_{12}^*)}{v^*}-1\right] \tag{21}$$

where the Lattice–Fluid contribution is given by[13–15]:

$$\frac{\mu_{1,\mathrm{LF}}}{RT}=\ln\varphi_1+\varphi_2\left(1-\frac{r_1}{r_2}\right)+r_1\tilde{\rho}\theta_2^2X_{12}+\ln\frac{\tilde{\rho}}{\omega_1}+r_1(\tilde{v}-1)\ln(1-\tilde{\rho})-\frac{r_1\tilde{\rho}}{\tilde{T}_1}+r_1\frac{\tilde{P}\tilde{v}}{\tilde{T}}\left[\frac{2(\varphi_1 v_1^*+\varphi_2 v_{12}^*)}{v^*}-1\right] \tag{22}$$

The corresponding expression for the pure solvent is:

$$\frac{\mu_1^0}{RT}=r_1(\tilde{v}_1-1)\ln(1-\tilde{\rho}_1)+\ln\frac{\tilde{\rho}_1}{\omega_1}-\frac{r_1\tilde{\rho}_1}{\tilde{T}_1}+r_1\frac{\tilde{P}_1\tilde{v}_1}{\tilde{T}_1} \tag{23}$$

$\tilde{\rho}_1$ is obtained again from equation (19) by setting $\varphi_2=0$. At ordinary pressures the pressure-explicit terms in equations (22) and (23) can be ignored.

Applications

The essential feature of the present model is that it provides the volume of the system over an extended range of external conditions. Thus, it is suited for studying cases where there is a substantial volume change upon mixing. In this section we will apply the formalism of the preceding section to two representative cases: swelling with a liquid solvent and swelling with a supercritical fluid.

In a comparative study Yen and Eichinger[17] carefully measured the solvent volume fraction difference in a swollen rubber and in its uncrosslinked polymer counterpart under the same external conditions. In particular, they presented data for the systems benzene and poly(dimethylsiloxane) (PDMS)—crosslinked and uncrosslinked. (As expected, the uncrosslinked polymer absorbs more solvent.) We have studied recently[15] the system benzene and uncrosslinked PDMS with the Lattice–Fluid theory. This system exhibits a relatively large negative volume of mixing at ambient conditions. Since the Lattice–Fluid binary parameters are available from our previous work[13,14] it is worth comparing the predictions of the present model with the experimental data for the swollen crosslinked PDMS. This comparison is shown in *Figure 1*. The experimental volume fraction, Φ, in *Figure 1* is defined by:

$$\Phi_1=\frac{\varphi_1 v_1^*\tilde{v}_1}{\varphi_1 v_1^*\tilde{v}_1+\varphi_2 v_2^*\tilde{v}_2} \tag{24}$$

In these calculations, and for simplicity, we have neglected the effect of side chains. An average molecular weight of 3000 for the chains between two crosslinks has been used. As observed, the model predicts in a qualitatively correct manner the effect of crosslinking on the solvent activity.

Shim and Johnston[18] have recently reported experimental data for the swelling of crosslinked PDMS by supercritical CO_2. Their rubber was lightly crosslinked (average molecular weight of 11 000 for the chains between two crosslinks). The interesting feature of their experimental data at 35°C was the S-shaped behaviour of the degree of swelling *versus* pressure in the range from 1 to 300 bar. The present model can be applied to this system since it allows for the straightforward calculation of the chemical potential of CO_2 in both the pure supercritical state and in the mixture swollen rubber. The Lattice–Fluid scaling constants for CO_2 reported in *Table 1* have been obtained on the basis of data for vapour pressures, orthobaric densities, supercritical densities and heats of vaporization from the IUPAC compilation[19]. As observed in *Figure 2*, the model is able to reproduce semiquantitatively the experimentally observed degrees of swelling with varying pressure. For these calculations only the energetic binary parameter ζ_{12} was adjusted to 1.08. For simplicity both ξ_{12} and s_1/s_2 were set equal to one.

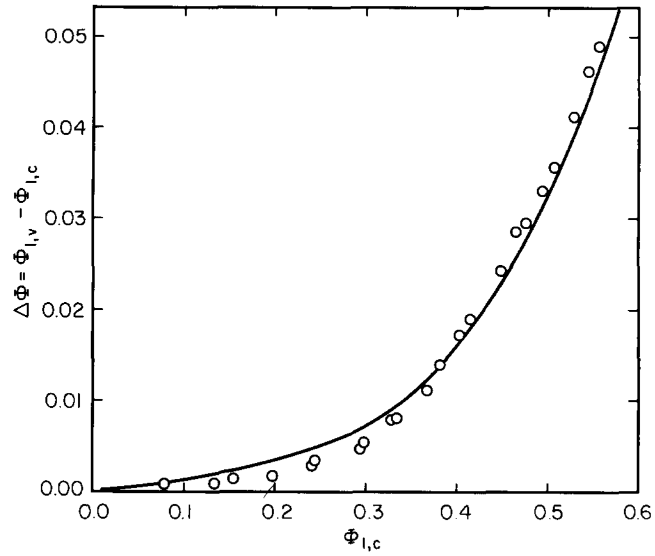

Figure 1 Solvent volume fraction difference (solvent in uncrosslinked–crosslinked) *versus* solvent fraction in crosslinked PDMS at 25°C. Experimental data (○) by Yen and Eichinger[17]. Solid line calculated by the present model. Crosslinking reduces solvent uptake

Table 1 Lattice–Fluid scaling constants of fluids

Fluid	ε^* (J mol^{-1})	v^* (cm^3 mol^{-1})	ρ^* (g cm^{-3})
CO_2	2566	4.47	1.505
Benzene	4348	9.80	0.994
PDMS	3957	13.10	1.104

Discussion

In this communication we have confined ourselves to the study of rubber swelling in systems without specific interactions or orientational order. Hydrogen-bonded systems and in particular hydrogels can be studied with the present framework by properly modifying Q_{LF} for hydrogen-bonded systems[11]. Swelling by liquid crystals can be dealt with in an analogous manner. A form of Q_{LF} for the case of liquid crystals exhibiting a nematic–isotropic transition is under development[12].

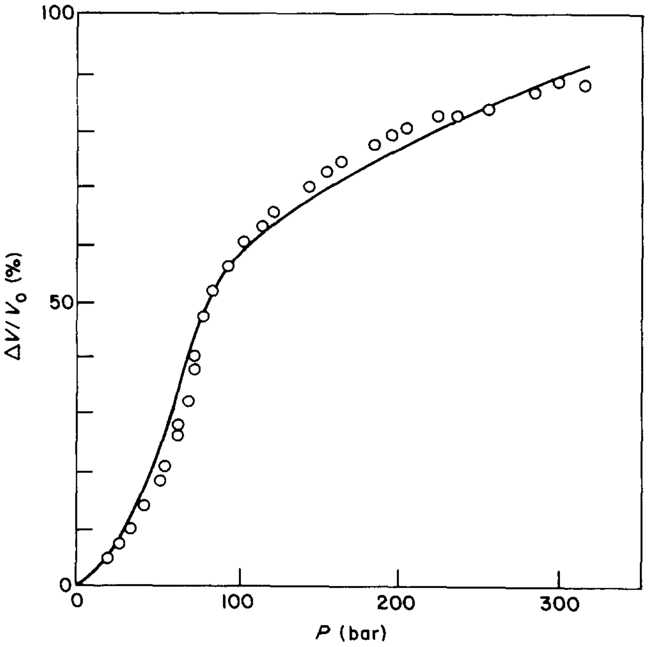

Figure 2. Fractional swelling of PDMS rubber with supercritical CO_2 at 35°C. Experimental data (○) by Shim and Johnston[18]. Solid line calculated by the present model

One particular feature of the model in this communication is the derivation of an equation of state for the rubber—swollen or unswollen. This equation may form the basis for a number of systematic studies such as the effect of the degree of crosslinking on the volumetric properties of the rubber and its internal pressure. It is also of interest to examine the validity of the usual assumption that the equation of state scaling constants of a rubber are the same as those of the uncrosslinked polymer counterpart.

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References

1 Guth, E. and Mark, H. *Monatsh.* 1934, **65**, 93
2 Kuhn, W. *Kolloid Z.* 1936, **76**, 258
3 Flory, P. J. and Rehner Jr, J. *J. Chem. Phys.* 1943, **11**, 521
4 Hermans, J. J. *Trans. Faraday Soc.* 1947, **43**, 591
5 Kramer, O. (Ed.) 'Biological and Synthetic Polymer Networks', Elsevier, London, 1988
6 Burchard, W. and Ross-Murphy, S. B. (Eds), 'Physical Networks Polymers and Gels', Elsevier, London, 1990
7 Brochard, F. *J. Physique* 1979, **40**, 1049
8 Orendi, H. and Ballauff, M. *Mol. Cryst. Liq. Cryst. Lett.* 1991, **7**, 185
9 Wissinger, R. A. and Paulaitis, M. E. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 2497
10 King, J. W., Eissler, B. L. and Friedrich, J. P. in 'Supercritical Fluid Extraction and Chromatography: Techniques and Applications' (Eds B. A. Charpentier and M. R. Sevenants), American Chemical Society, Washington DC, 1988
11 Panayiotou, C. and Sanchez, I. C. *J. Phys. Chem.* 1991, **95**, 10090
12 Panayiotou, C. and Sanchez, I. C. unpublished calculations
13 Sanchez, I. C. and Lacombe, R. *J. Phys. Chem.* 1976, **80**, 2352, 2568
14 Sanchez, I. C. and Lacombe, R. *Macromolecules* 1978, **11**, 1145
15 Panayiotou, C. *Macromolecules* 1987, **20**, 861
16 Flory, P. J. *J. Chem. Phys.* 1950, **18**, 108
17 Yen, L. Y. and Eichinger, B. E. *J. Polym. Sci., Polym. Phys. Edn* 1978, **16**, 121
18 Shim, J. and Johnston, K. P. *AIChE J.* 1989, **35**, 1097
19 Angus, S., Armstrong, B. and de Reuck, K. M. 'International Thermodynamic Tables of the Fluid State: Carbon Dioxide', Vol. 3, Pergamon Press, Oxford, 1976