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Computation of the Cross-Link Dependence of the Effective Flory Interaction Parameter χ for Polymer Networks

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ABSTRACT: The application of the Frenkel–Flory–Rehner hypothesis to elastic energy measurements has been shown by McKenna and co-workers to produce a cross-link dependence of the effective interaction parameter χ for swollen rubber networks, while solvent activity measurements by Neuburger and Eichinger demonstrate the presence of a solvent dependence to the deduced elastic properties. We address a portion of the question by computing the cross-link dependence of χ for polymer networks using the traditional lattice model of polymers and our general theory for systematically evaluating the corrections to the Flory–Huggins approximation, which must be the source of any cross-link dependence, because the Flory–Huggins approximation cannot describe a cross-link dependence of χ.

Introduction

A description of the swelling of networks and gels in solution requires simultaneously a theory of the elastic free energy changes upon swelling and of the mixing free energy for the polymer network and the solvent. Because of our poor understanding of the former theory, a common assumption in dealing with these systems is the Frenkel[1]–Flory–Rehner[2] hypothesis that at equilibrium the elastic free energy is balanced by the mixing free energy. This assumption ignores any differences in the elastic free energy change between the dry and swollen network.

Recenty, McKenna and co-workers[3] have studied the Frenkel–Flory–Rehner hypothesis by performing mechanical measurements of the elastic energy of natural rubber networks and by using this elastic energy to compute the free energy of mixing of the equilibrium swollen network. Thus, if ΔA is the elastic free energy per unit volume of the dry rubber, v_2 is the volume fraction of rubber in the swollen state, $\lambda = (v_2)^{-1/3}$ is the stretch ratio of the swollen rubber, V_1 is the molal volume of the solvent, and RT is the thermal energy, the Frenkel–Flory–Rehner hypothesis yields[1,2]

$$-RT[\ln(1 - v_2) + v_2 + \chi v_2^2] = (V_1/\lambda^2)(\partial\Delta A/\partial\lambda) \qquad (1)$$

where the left-hand side of (1) is the change in chemical potential of the solvent relative to its pure state and where the quantity χ is the phenomenological Flory–Huggins polymer–solvent interaction parameter.[4,5] McKenna and co-workers[3] measure $\partial\Delta A/\partial\lambda$ for the networks in the dry state and use eq 1 to determine the χ parameter as a function of cross-link density ρ_x and solvent. They find a linear relation between χ_{net} for the network and ρ_x for low to moderate cross-link densities ρ_x

$$\chi_{net} = \chi_0 + \alpha'\rho_x \qquad (2)$$

where χ_0 is the independently measurable Flory–Huggins interaction parameter for the un-cross-linked rubber–solvent system. One importance of the experiments lies in establishing the dependence of χ_{net} on ρ_x, but this result is based upon the hypothesis (1), which remains to be independently tested.

Neuburger and Eichinger take the alternative approach of experimentally determining[6] the change in chemical potential upon mixing, which is on the left-hand side of (1), and of using (1) to test whether a reduced dilation modulus, as calculated from the right-hand side of eq 1, is dependent on solvent. They observe solvent dependences, which they call nonadditivity effects, that appear to conflict with the Frenkel–Flory–Rehner hypothesis and that suggest the existence of different swelling energies for the dry and solvated networks. Nonadditivity effects of this type are intuitively reasonable and are also present in the theory of Edwards and co-workers.[7] We note, however, that eq 2 and the well-known solvent dependence of χ_0 and the solvent dependence of α' implied by the analysis of McKenna et al. combine to show that nonadditivity effects [i.e., a solvent dependence of the right-hand side of (1) divided by V_1] are to be expected and therefore that the observations of ref 3 and 6 may not be in conflict. We discuss the physical origins of the cross-link dependence in eq 2 of the effective polymer network–solvent interaction parameter.

An alternative to the experimental test of the hypothesis (1) could involve the theoretical computation of the cross-link dependence of χ_{net} for comparison with the values deduced from the experimental[3] mechanical data. Such a theory would have the added utility of perhaps explaining the observed dependence of the slope α' in (2) upon the nature of the solvent and of explaining the nonadditivity effects observed by Neuburger and Eichinger. However, the traditional Flory–Huggins theory does not depend on the topology of the polymer system; it effectively describes a random mixture of solvent, monomers, and uncorrelated bonds between the monomers and cannot distinguish between a single long polymer chain and a highly branched network.

In order to introduce such a distinction, it is necessary for a theory to describe correlations between at least three bonds that are connected to a network junction. The situation can be understood by reference to the arguments of Guggenheim[8] and of Koningsveld and Kleintjens[9] for linear polymers in concentrated solutions. They argue that interior (or mid) chain segments have different interaction energies with the solvent than do end segments because the former *must* have at least two polymer segments as nearest neighbors while the latter *must* only have at least one. Similarly, the junction points in tetrafunctional networks *must* have at least *four* polymer segments as neighbors and *must* therefore have different average interaction energies with the solvent than do interior strand polymer segments or end chain segments. Recent Monte Carlo simulations of the mixing energies of polymer–solvent systems by Madden[10] verify the accuracy of the Guggenheim counting[8] of interaction energies in the athermal limit and thereby support our contention that a similar physical reasoning can partially explain the cross-link dependence of χ_{net} observed by McKenna and co-workers.[3] An argument of this type has previously been attempted by Dusek and Prins.[11] However, their computations do not produce the linear cross-link dependence

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of eq 2 and instead yield an effect that is far too small to explain the experiments of McKenna and co-workers. The difficulty lies in the highly nontrivial complexity of systematically computing the requisite averages.

The computations of Guggenheim and of Koningsveld and Kleintjens do not incorporate the three-bond correlations that are necessary to distinguish between linear and branched polymer systems. However, we have recently developed a systematic lattice theory that is capable of treating these and higher bond correlations.[12-16] Our theory is based on the traditional lattice model of polymers,[4,5] in which each lattice site is occupied either by a monomer or by a solvent molecule and in which there are van der Waals energies between nonbonded nearest neighbors. The theory includes bond correlations in a systematic cluster expansion of the mixing free energy in inverse powers of the lattice coordination number z (the number of nearest neighbors to a lattice site). Moreover, our approach is capable of distinguishing the properties of linear and branched chains as well as of treating solvent molecules and monomers that have internal structure and therefore cover several lattice sites.[12,13] Some important results from our cluster calculations are a molecular computation of the previously enigmatic entropic contribution to the χ parameter[15] and a determination of the monomer structure, composition, and temperature dependence of the free energy of mixing of polymer blends.[12] Here, we consider the application of this cluster theory to the computation of χ_{net} for a swollen polymer network.

The cluster calculations are rather lengthy and are described elsewhere.[13] Computations for a binary system,[13] in principle, apply to the swollen network. However, the general treatment of binary systems, presented by us elsewhere,[13] neglects corrections proportional to the inverse number of polymer chains, whereas the network case corresponds to a situation in which there is but a single polymer network. Hence, these correction terms are important. It has, therefore, been necessary for us to extract the single network contribution from the previous computations. We follow standard principles of statistical mechanics for evaluating the average properties of an ensemble of networks with the anticipation that they adequately represents the average properties of several experimental samples.

Theory and Comparison with Experiment

The computations are specialized to the case of tetrafunctional junctions and flexible solvent molecules that each have N_s flexible bonds and therefore occupy $N_s + 1$ lattice sites. Otherwise, the precise structure of the monomers or solvent molecules does not enter into predictions of α' in (3) to the order (z^{-2}) of the computations. The remaining parameters of the theory are the polymer volume fraction φ_p, the cross-link volume fraction ψ_x, and the dimensionless interaction parameter

$$\epsilon = (\epsilon_{pp} + \epsilon_{ss} - 2\epsilon_{ps})/kT \tag{3}$$

where the subscripts p and s refer to polymer and solvent, respectively. The detailed computations[16] produce the effective interaction parameter (as defined through the chemical potential in eq 1)

$$\chi_{\text{net}} = \chi_0 + \{(12\epsilon/z) + [8N_s/z^2\varphi_p(N_s + 1)] + O(z^{-3})\}\varphi_x + O(z^{-4}\varphi_x{}^2) \tag{4}$$

where corrections in the square of the cross-link density can be shown to enter in the indicated order. These corrections are, therefore, expected to be negligible under the conditions of low to moderate cross-link density in the experiments of McKenna and co-workers.[3] The quantity χ_0 in (4) is the effective interaction parameter (defined in terms of the chemical potential) that is presented in the Appendix as a function of the structure of the monomers and solvent molecules. χ_0 has both entropic and enthalpic components, as is generally observed for effective interaction parameters. Given our expansion in powers of z^{-1}, the leading order in χ_0 is the Flory value of $\chi^F = \epsilon z/2$. Hence, maintaining strict orders in the expansion converts (4) into

$$(\chi_{\text{net}} - \chi_0)/\chi_0 = \{(24/z^2) + [16N_s/z^3\epsilon\varphi_p(N_s + 1)] + O(z^{-4})\}\varphi_x \tag{5}$$

However,, in some polymer systems the entropic portion of χ_0 may exceed χ^F, and then (4) is the more appropriate equation.

There are several difficulties in the quantitative comparison of either (4) or (5) with experiment due to the lack of knowledge about the parameters z, ϵ, and N_s for the systems considered by McKenna and co-workers. Some assistance with this problem could be obtained from temperature-dependent studies of χ_0 to separate the entropic from enthalpic contributions. The theory of χ_0 in the Appendix can then be used to extract from such data reasonable values of z, ϵ, and N_s for insertion into (4) or (5) as is appropriate. This theory of χ_0 is, in fact, in general qualitative accord with the data of Neuburger and Eichinger in predicting a roughly linear dependence of both the entropic and enthalpic portions of χ_0 on φ_p for $\varphi_p >$ 0.4. However, in the absence of similar information for the rubber networks of ref 3, we analyze the qualitative predictions of the theory and compare these with the experimental data of McKenna and co-workers.[3] Perhaps lattice theory predictions should generally be used only in this qualitative sense, but this point must be addressed by further comparisons of theory with experiment.

Let us now consider the form of (5). The first term on the right-hand side arises from the differences in average polymer–solvent interaction energies at the junctions and at the polymer strand interiors, while the next term arises from the differences in excess (noncombinatorial) entropy of mixing of junctions and solvent molecules.[16] The latter entropic part is proportional to temperature (cf. eq 3) and inversely proportional to polymer volume fraction. Hence, temperature-dependent studies might be used to separate these two contributions for a more direct comparison with experiment. The entropic portion also depends on the flexibility of the solvent molecules, and this can be varied by a change in solvents. However, the interaction parameter ϵ in (3) is also altered when changing solvents, because in reality, differing functional groups in the solvent molecules have different interaction energies with a given functional group in the polymer. (It is possible to perform lattice model computations with group–group energies[16] ϵ_{ij}, but without some means of specifying the ϵ_{ij}, this leads to rather unwieldy expressions with too many adjustable parameters.)

In order to evaluate the predicted slopes $\partial\chi_{\text{net}}/\partial\varphi_x$ from eq 4, we introduce the rough estimate of $\epsilon \sim z^{-1}$, nothing that ϵ must actually vary with solvent and temperature. An optimistic value of $z = 4$ is used to obtain the results in Table I for φ_p in the range of 0.5–0.9 and for N_s from 0 to 5. In order to compare with experimental data, it is necessary to convert between the experimental cross-link density in mol/cm^3 and our dimensionless variable φ_x. The monomer molecular weight is 58, and it takes two monomers to form a cross-link. If the junction site is taken as composed of $2y$ monomers, the conversion factor is $116y$

Table I
Values of the Slope $\partial\chi_{\mathrm{net}}/\partial\varphi_x$ As Computed from Equation 4 with $z = 4$ and $\epsilon \sim z^{-1}$ and Various Values of N_s and φ_p As Indicated

	N_s					
φ_p	0	1	2	3	4	5
0.5	0.75	1.25	1.41	1.50	1.55	1.58
0.6	0.75	1.17	1.31	1.37	1.42	1.44
0.7	0.75	1.11	1.23	1.29	1.32	1.35
0.8	0.75	1.06	1.17	1.22	1.25	1.27
0.9	0.75	1.03	1.12	1.17	1.19	1.21

cm^3/mol. The predicted slopes, $\partial\chi_{\mathrm{net}}/\partial\varphi_x$, in Table I may be compared with the experimental one (solvents in parentheses) of $5.1/y$ (benzene), $7.8/y$ (ethyl acetate), $9.5/y$ (methyl ethyl ketone), and $25/y$ (acetone). A value of y of about 4 brings the theoretical predictions in line with experimental data, but the values of z and y are probably overly optimistic. It thus appears that the theory somewhat over estmates $\partial\chi_{\mathrm{net}}/\partial\varphi_x$, but the qualitative solvent and temperature dependences might be well represented. An analysis[18] of data of Gnanou et al.[19] for poly(ethylene oxide) networks yields slopes similar to those for the rubber networks. It will be useful to analyze the temperature and polymer volume fraction dependence of χ_0 from the appendix to help pin down some of the parameters (namely, z, ϵ, and N_s) of the theory for substitution in eq 4 to provide more stringent tests of the theory.

It should be noted that entanglements figure prominently into interpretations of the elastic modulus of rubbers.[20] Thus, the measured elastic energies contain significant contributions from entanglements since the higher experimental cross-link densities yield average strand molecular weights that are less than the entanglement molecular weight. However, our computations of the free energy of mixing apply to a hypothetical network having an equilibrium structure for the swollen state. This may differ from the actual structure of the experimental gels because of the presence of entanglements during swelling and deswelling. Additional discrepancies between theory and experiment may arise from inadequacies in the lattice model computations, from deficiencies in the hypothesis (1), from differences in ϵ between the saturated junctions and the unsaturated midchain segments, or from a combination of these. Our lattice model computations should aid in further understanding the thermodynamic properties of swollen networks. Further experimental analysis of χ_0 should aid in empirically determining some of the parameters that should enter into eq 4.

Appendix: Lattice Model Computations of χ_0

The network is taken to be a single highly branched polymer chain in which the individual monomers may cover several lattice sites. Solvent molecules may occupy M_s lattice sites, with flexible bonds connecting these sites. The effective χ parameter appropriate to eq 1 and 2 depends on a set of structural indices. For instance, let $N_i^{(s)}$ be the number of different sequences of i consecutive bonds that may be formed in a single solvent molecule, and let $N_i^{(p)}$ be the corresponding quantity for the polymer network. Similarly, $N_{i,j}^{(p)}$ is the number of ways of selecting i and j consecutive bonds on the polymer that are separated by at least a single polymer bond, and M_p is the total number of sites occupied by the polymer network. Examples of these counting indices for a variety of monomer structures are given in ref 13 and 14. If φ_s designates the volume fraction of solvent, the lattice computations through order z^{-2} and ϵ/z yield the lengthy expression[17]

$$\begin{aligned}\chi_0 = {}& \epsilon z/2 + 2/z - (\epsilon^2 z/4)\varphi_p(\varphi_s - \varphi_p) + \\ & (\epsilon/zM_p)(1 + 3\varphi_p)(2N_2^{(p)} + 3N_3^{(p)}) + \\ & (\epsilon/zM_s)(1 + 3\varphi_s)(2N_2^{(s)} + 3N_3^{(s)}) - \epsilon[(N_1^{(p)}/M_p)(1 + \\ & 3\varphi_p) + (N_1^{(s)}/M_s)(1 + 3\varphi_s)] + z^{-2}\{-(N_1^{(s)}/M_pM_s) \times \\ & (4N_2^{(p)} - 2N_1^{(s)}N_2^{(p)} + N_{1,2}^{(p)} + 2N_3^{(p)}) - \\ & (8N_1^{(s)}N_1^{(p)}/3M_s^2M_p)(2 + 3\varphi_p) - (N_1^{(s)}/M_s^2)(4N_2^{(s)} - \\ & 2N_1^{(s)}N_2^{(s)} + N_{1,2}^{(s)} + 2N_3^{(s)}) - (16N_1^{(s)3}\varphi_s/3M_s^3) + \\ & (2N_1^{(s)4}/M_s^4)\varphi_s(1 - 3\varphi_p)\} - (4\epsilon N_1^{(s)}/zM_pM_s) \times \\ & (N_1^{(p)} + 3N_2^{(p)} + N_{1,1}^{(p)} - N^{(p)2})\varphi_p(\varphi_s - \varphi_p) + \\ & (4\epsilon N_1^{(s)}/zM_s^2)(N_1^{(s)} + 3N_2^{(s)} + N_{1,1}^{(s)} - \\ & N_1^{(s)2})\varphi_p(\varphi_s - \varphi_p) + (12\epsilon/z)\{(N_1^{(s)3}/M_s^3) - \\ & 3(N_1^{(p)}N_1^{(s)}/M_s^2M_p)\}\varphi_p^2(3\varphi_s - \varphi_p) \qquad (6)\end{aligned}$$

which contains both entropic (ϵ-independent) and enthalpic (ϵ-dependent) contributions and which is primarily a linear function of polymer volume fraction φ_p with some slight curvature emerging for $\varphi_p < 0.4$. Both of these features are in qualitative accord with the experiments of Neuburger and Eichinger on poly(dimethylsiloxane) networks. The computation of (4) and (6) applies strictly only to the "equilibrium" network structure appropriate to a network formed at equilibrium in the solvent at polymer volume φ_p. A network formed in one solvent, dried, and then swollen in a different solvent, in principle, does not have such an equilibrium structure because of the influence of entanglements during drying and swelling.

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