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Elastic energy in microscopically phase-separated swollen polymer networks

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Abstract

The paper analyzes a microscopic regime of strain, different from the one conventionally considered, that presumably takes place in swollen polymers showing strong microscopic phase separation, such as ion-exchange resins in water. Such systems show linear dependence of the elastic pressure on swelling in contrast to the Flory–Rehner theory and its modifications. The present work proposes a simple model that predicts this kind of behavior. Swelling is considered as a non-affine 'inflation' of the hydrophobic matrix by small aggregates of water molecules ('droplets') adsorbed by highly hydrophilic groups, whereas the macroscopic dimensions of the sample change as a result of the compression of the 'films' separating the droplets. This compression is then analyzed along the classical lines. In the case of the Dowex resins a partial test of the model based on the reported shear moduli showed reasonable agreement with experiment. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Non-affine model; Swelling; Elastic energy

1. Introduction

Swelling of a polymer network in a solvent is traditionally viewed as the balance between the osmotic and contractile (elastic) pressures. These are defined, respectively, as the derivatives of the free energies of mixing and network deformation with respect to the volume of the swollen network [1–3]. In many cases the Flory–Huggins theory provides a fairly good approximation for the free energy of mixing, while the Flory–Rehner theory is often used to calculate the elastic term [1,4]. These classical theories are based on the assumptions of random mixing (dilution) of solvent and monomers (the Bragg–Williams approximation [2]) and *affine*, i.e. linear in the macroscopic strain, deformation of the chains comprising the network.

The adequacy of these assumptions can be seriously questioned when a *macroscopically homogeneous* swelling is accompanied by a strong *microphase* separation. This may occur when a polymer matrix swells in a solvent, which is a very poor solvent for the matrix itself but is forced into it by strong interactions with some groups chemically attached to the polymer backbone. Limited swelling of many natural and synthetic hydrophilic polymers in polar solvents may follow this pattern. An almost ideal example of this behavior is the swelling of chemically crosslinked ion-exchange resins [5] or physically crosslinked (semicrystalline) ionomers [6] in very polar solvents, such as water or methanol. These materials possess a very hydrophobic hydrocarbon or fluorocarbon backbone with chemically bound highly hydrophilic ionic (e.g. sulfonic) groups. The groups themselves and the adsorbed water molecules strongly tend to associate and actually form a separate phase dispersed in the backbone polymer matrix, which always remains microscopic due to the constraints on association imposed by the martix. Although the recent theories [7,8] indicate that microphase separation may occur under certain conditions for many crosslinked polymer–solvent systems, the above case is unique in that such separation is, in fact, *always present*. In ionomers the evidence for aggregates comprising many groups and hundreds of water molecules has been conclusive, e.g. by X-ray scattering [6,9] or water diffusion studies [10]. For ion-exchange resins the constraints on association are seemingly more severe, yet evidence for the existence of 'water pools' as large as several nanometers has been recently reported [11].

Boyd and Soldano [12] and Glueckauf [13] determined the elastic pressure for a series of swollen polystyrene–divinylbenzene (PS–DVB) sulfonates from vapor sorption isotherms. The idea is schematically presented in Fig. 1.

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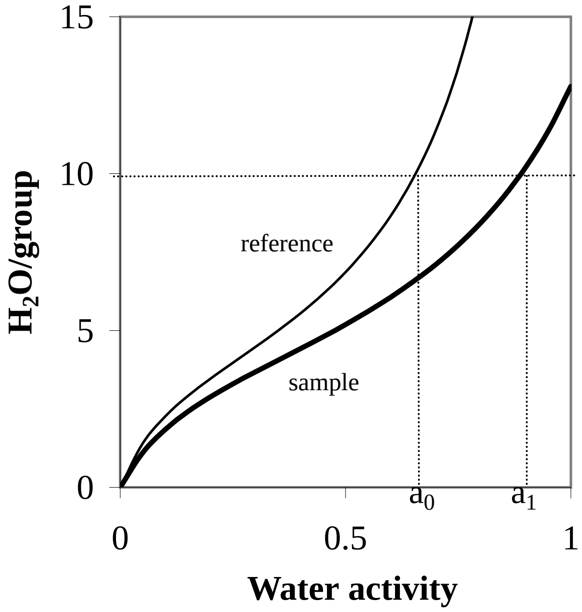

Fig. 1. The principle of measuring the elastic pressure in swollen ion-exchange resins of various crosslinking (differential swelling).

Solvent sorption by differently crosslinked resins of the same capacity and ionic form swollen to the same degree was analyzed at different water activities in relation to a reference polymer. An essentially identical method was later applied to non-polar polymer–solvent systems and was given a name 'differential swelling' [14–19]. Ideally, a non-crosslinked polymer (solution) should be used as a reference, as has been done in the case of non-polar system, but for technical reasons the use of a weakly crosslinked resin (0.5–1% DVB) was preferable. The swelling pressure at different degrees of swelling could be calculated as:

$$p_d = (RT/V_\mathrm{m})\ln(a_1/a_0), \tag{1}$$

where V_m is the molar volume of the solvent, a_1 the equilibrium water activity (relative humidity) at a given solvent content in a resin sample and a_0 is the water activity at the same solvent content in the reference resin (see Fig. 1). Since the content of the hydrophilic groups and, presumably, their distribution in the resin, are similar, all contributions, excluding only the elastic energy of the matrix, should effectively cancel out at the same water content. Importantly, so should, to a substantial degree, the electrostatic and interfacial effects, significant in such resins. For all resins the swelling pressure was found to be *zero* for the dry resin and was *proportional* to the swelling. This shows in the merge of the isotherms at low activities (Fig. 1) and may be expressed as follows [5,12]:

$$p_d = B\Delta V/V_0, \tag{2}$$

where ΔV is the change of the resin volume upon swelling, V_0 the volume of the resin at $p_d = 0$ and B is a parameter depending only on the degree of crosslinking (DVB content). Thus B was demonstrated to be independent of the ionic form of a resin. Using the same experimental method, Nandan and Gupta [20] confirmed this conclusion by measuring swelling of resins in various forms in water and methanol and also showed B to be independent of the solvent.

The classical theory and more recent developments are actually unable to predict the behavior given by Eq. (2). The extensive analysis presented by Gottlieb and Gaylord [21] demonstrate that all of them yield a *finite* elastic pressure at zero swelling, i.e. zero solvent content. Admittedly, these authors' analysis was in terms of a different parameter that nevertheless was related to the elastic pressure in a straightforward way. Despite some peculiarities that appeared quite difficult to explain theoretically, for *non-polar* polymers and solvents the measured elastic pressure *at zero swelling* was indeed found finite in good agreement with the theory.

In contrast, the behavior of the Dowex resins strongly deviates from this pattern. Our basic suggestion is that the discrepancy results from the assumption of affinity, i.e. essentially, *similarity of the macroscopic and microscopic strain*. This similarity is closely related to the approximation of random mixing, which is clearly incompatible with what is known about the microstructure of swollen resins and ionomers. Concerning the thermodynamics of mixing, it was realized long ago that, due to the too large enthalpic effects that destroy the random order, swelling of this type is more appropriately described in terms of *adsorption* of water by the ionic groups rather than dilution of the matrix of the Flory–Huggins type [22,23]. The inadequacy of the elastic term of the classical theory for calculating the contractile pressure in this case has drawn much less attention so far. Hsu and Girke [24] and Mauritz and Rogers [25] presented a new approach to calculating the elastic contribution in swollen Nafion ionomers. The elastic energy per aggregate was calculated as that of a spherical cavity expanding to an infinite elastic medium characterized by some effective modulus, constant or changing with total water content in yet undetermined manner. This phenomenological approach has the advantage of correctly predicting a linear change of the elastic pressure with the solvent content in the low swelling limit, an important fact that passed unnoticed by the authors. However, the neglect of the interaction of the aggregates upon expansion seems to be a too large simplification. In addition, the approximation of a Hookean medium used to calculate the elastic energy is not precise for a polymer as the bulk.

This paper presents a simple model where the interaction of aggregates embedded in a polymer bulk is explicitly considered. The elasticity calculations are based on the classical theory of polymer elasticity, although other models may also be readily incorporated. The microscopic picture of strain, however, is essentially *non-affine*, which removes the discrepancy obtained while applying the classical theory to such systems in a conventional way and leads to qualitatively correct results.

2. Theory

The Flory–Rehner [1,4] theory considers an affinely deformed network of N Gaussian chains and gives the following expression for the free energy of deformation per unit volume of undeformed network:

$$F_{\mathrm{el}} = 1/2G\sum_i (c\ln\lambda_i + \lambda_i^2 - 1), \tag{3}$$

where $G = NkT/V_0$, V_0 the volume of undeformed network and λ_i is the deformation ratio along the axis i. For isotropic swelling $\lambda_i = \phi_p^{-1/3}$ for all i, where ϕ_{p} is the volume fraction of the polymer, and the swelling pressure p_d is obtained from Eq. (3) by differentiating with respect to $1/\phi_{\mathrm{p}}$:

$$p_d = G(\phi_{\mathrm{p}}^{1/3} - c\phi_{\mathrm{p}}/2), \tag{4}$$

Flory [26] has argued that the constant c in the logarithmic term of Eq. (3) leading to the second term of Eq. (4) should vary between 0 (phantom limit) and 1 (affine limit). In either case the osmotic pressure always appears *finite* at zero swelling. At moderate degrees of swelling, it should remain *nearly constant* passing through a shallow maximum in the Flory–Rehner theory (affine limit) or even decrease in the phantom limit, in striking contradiction with the experimental results on swollen Dowex resins.

To understand what might be the cause, let us consider how a resin swells. The solvent phase in a swollen resin consists of microscopic 'droplets' that grow as the degree of swelling increases. The droplets are separated by 'films' of the polymer matrix. In the dry state the droplets are just the hydrophilic groups or their aggregates. In the swelling process the new water molecules increase the total volume of the resin by joining the existing aggregates (partial coalescence may also take place) but do not dilute matrix to maintain the affine deformation of each chain. This process resembles 'inflation' of the matrix rather than its dilution. To describe that, we propose to replace the affine deformation with the following (simplified) picture.

Starting from the dry state, we may subdivide the swollen matrix to polyhedral cells using the Voronoi tessellation (e.g. see Ref. [27]) with a droplet in the center of each cell, as shown in Fig. 2. The films (faces of the polyhedra) are thus assumed to look like flat and thick slabs. When the droplets grow, they squeeze the films causing changes in their dimensions, i.e. the surface area of the films grows and the thickness decreases. For flat films we may assume the strain in the films to be *uniaxial compression*. Under swelling, the idealized polyhedral cells are assumed to deform in such a way that their dimensions will change but not their shape (see Fig. 2). We have therefore replaced the affine deformation of each chain in the Flory–Rehner theory by the *affine deformation of the cells*. Finally, despite the fact that the films are microscopic objects, we assume that the volume of a film remains constant and apply Eq. (3), just as to macroscopic polymer samples [1,3]. We assume droplets to be large enough and the swelling not too high (say up to several tens percent, which is typical for resins and ionomers) so that the films are not reduced to separate chains.

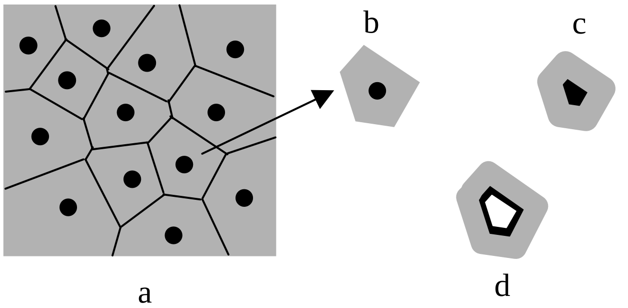

Fig. 2. The scheme of subdivision of the swollen material to polyhedral Voronoi cells. The bulk matrix is shown in gray, the hydrophilic groups in black and water in white; (a) Subdivision of a dry resin to polyhedral cells using the Voronoi tessellation (two-dimensional representation); (b) An imaginary single dry cell with an aggregate of dry hydrophilic groups in the center; (c) Idealized polyhedral structure of the dry cell (b); (d) Idealized structure of the cell (c) after swelling.

It may seem that spherical rather than polyhedral geometry of the droplets would be a more justified and natural choice. In this case, however, the model will loose all its simplicity since a non-uniform strain with non-zero shear components will have to be introduced and the model will be dependent on the size of the droplets and the coalescence effects, as the models of Refs. [24,25]. In contrast, the flat geometry has none of these complications while retaining most important qualitative features.

We may calculate now the elastic energy of the swollen sample. The changes of the macroscopic dimensions of the whole sample occur as a result of the changes of the dimensions of the films and cells under compression. The deformation ratios of a film along the axes parallel to the film (face) should be just the macroscopic swelling ratio $\lambda = \phi_{\mathrm{p}}^{-1/3}$, whereas the one along the axis normal to the film is λ^{-2}. By summation over all films we obtain from Eq. (3):

$$F_{\mathrm{el}} = 1/2G'(2\lambda^2 + \lambda^{-4}) \tag{5}$$

or, alternatively,

$$F_{\mathrm{el}} = 1/2G'(2\phi_{\mathrm{p}}^{-2/3} + \phi_{\mathrm{p}}^{4/3}), \tag{6}$$

where $G' = N'kT/V_0$ and N' may be interpreted as the effective number of the polymer chains in all films. It is expected to be somewhat lower than N due to the smaller strain in vertices and edges of the cells. Differentiating with respect to $1/\phi_{\mathrm{p}}$, we obtain the elastic pressure

$$p_d = 2/3G'(\phi_{\mathrm{p}}^{1/3} - \phi_{\mathrm{p}}^{7/3}). \tag{7}$$

Remarkably, the value of the parameter c in Eq. (3) does not affect this result due to the constancy of the volume occupied by the polymer, just as for deformed dry networks. The elastic pressure calculated using Eq. (7) (assuming

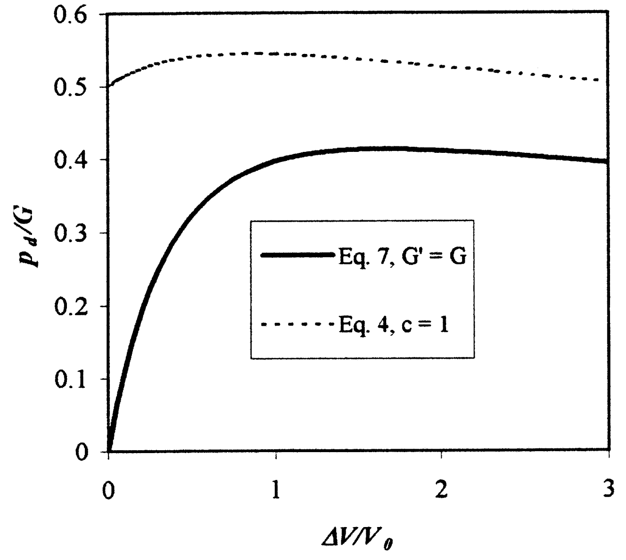

Fig. 3. The normalized swelling pressure calculated using the Flory–Rehner theory (Eq. (4) with $c = 1$) and the present model (Eq. (7)) vs. the degree of swelling.

$N' = N$) plotted against the relative volume change is shown in Fig. 3, the Flory–Rehner result (Eq. (4) with $c = 1$) being also presented for comparison. It is seen that, unlike the Flory–Rehner equation and in agreement with the empirical Eq. (1), the new equation predicts that the elastic pressure rises approximately linearly with the degree of swelling up to about $\phi = 1 - \phi_p = 0.2$. The leveling off for higher degrees of swelling is obviously due to the Gaussian approximation used to derive the expression for the elastic energy (Eq. (3)).

It is easy to show that for small $\phi (\phi \ll 1)$ the elastic pressure may be approximated by:

$$p_d \approx 4/3G'\phi \approx 4/3G'\Delta V/V_0. \tag{8}$$

This relation *coincides* with the functional form found experimentally for the swelling of ion-exchange resins (Eq. (2)).

It may be further assumed that N' is merely the total number of chains in the polymer phase, that is, $N' = N$. This *overestimate* of the elastic pressure should be reasonable in view of the crude model considered here. Comparing Eqs. (2) and (8) we obtain:

$$B = 4/3G. \tag{9}$$

We would like to note that the use of Eq. (3) as a starting point is not mandatory. Our main result is valid (up to a constant factor) for any expression of the elastic free energy of the type $F_{\mathrm{el}} = \sum \zeta(\lambda_i)$, where $\zeta(\lambda)$ is some function, in which case $B = 2/3[\zeta'(1) + \zeta''(1)]$, where prime denotes differentiation. For instance, assuming the matrix to be an incompressible linearly elastic continuum, i.e. $\zeta(\lambda) = G(\lambda - 1)^2$ [28], G being the shear modulus, Eq. (9) becomes exact for the whole range of swelling.

3. Comparison with experiment

We have seen, therefore, that, in contrast to the Flory–Rehner theory, our model predicts the correct *functional form* of the dependence of the swelling pressure on the volume change due to swelling (Eq. (2)). It would be also of interest to compare the experimental values of the parameter B to the ones calculated using the model. Unfortunately, suitable experimental data are very scarce, the main reason being that most data do not enable appropriate separation of different contributions to obtain the elastic energy or contractile pressure. We will therefore use the previously mentioned results for Dowex resins [10,11,18] and the data of Myers and Boyd [29]. Some of these results have been presented in the form of the empirical equation proposed by Gregor [30]: $V = ap_d + b$, which, in effect, coincides with Eq. (1) with $B = b/a$.

The principal problem arising with the Dowex-type resins is the degree of crossliking so high that the Gaussian statistics seems hardly applicable. Calculations of the average chain length based on the nominal DVB content and the additional factor 2/3 to convert the number of monomer units in a chain to the number of random links in polymethylene backbone show that the average chain between two crosslinks contains only 1.25 and 20 random links for the highest (25%) and lowest (2%) DVB contents, respectively. Gusler and Cohen [31] offered a non-Gaussian version of the classic model, but achieved only a moderate improvement for (non-sulfonated) PS–DVB resins. A non-uniform crosslinking in the course of copolymerization of PS and DVB during preparation of the resins [32] comes as an additional complication. As has been demonstrated both theoretically [8] and experimentally [33,34], swelling further enhances these static non-homogeneities resulting in films (in the present terminology) higher crosslinked and then more rigid than the matrix at average. We *cannot* therefore use the simple Gaussian formula $B = 4/3NkT/V_0$ (cf. Eqs. (3) and (9)) with N/V_0 based on the nominal DVB content. Apparently, *a full test* of the present model cannot be performed using the above data. We may suggest that such a test could be based on differential swelling experiments carried out using low-crosslinked resins swollen at very low water activities to avoid excessive swelling in order to stay within the range of applicability of the model.

Nevertheless, we may attempt a *partial* test by noting that it is the elastic component of the shear modulus G of the matrix that we actually need for comparison (see also the comment after Eq. (9)). Tiihonen et al. [35] have reported recently the shear moduli of some swollen resins. These data should be treated with some care since not readily separable electrostatic contributions may appreciably increase the mechanically measured modulus, particularly, in less polar solvents. Tiihonen et al. suggested to take as the closest estimates of G the values of moduli obtained for water-swollen samples, in which the electrostatic interactions are

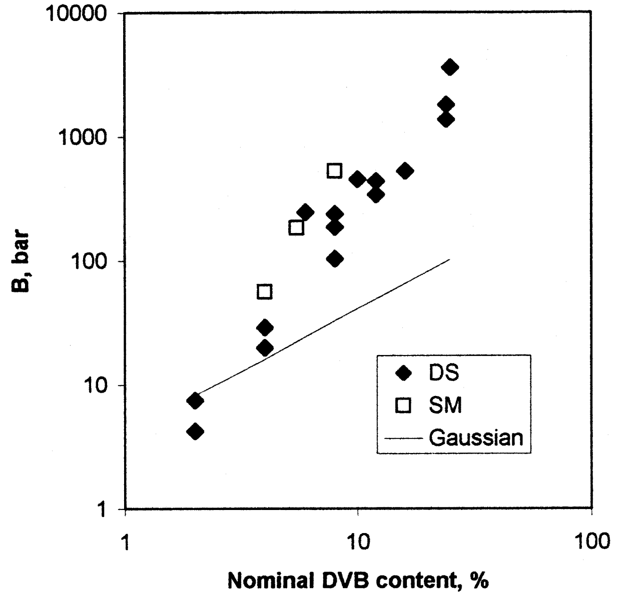

Fig. 4. The parameter B for some PS–DVB ion-exchange resins as a function of the nominal DVB content: DS — calculated from the differential swelling experiments [12,13,20,29]; SM — calculated from the experimentally measured shear moduli of the swollen resin normalized to the dry resin [35]; Gaussian — the estimates based on the nominal DVB content and Gaussian chains.

presumably minimized. They then used then the factor $\phi_p^{1/3}$ to get the modulus of the dry matrix G_0. We note, however, that this factor pertains to the classical model and follows from the fact that the deformation ratios in Eq. (3) change due to swelling by the same factor $\phi_p^{1/3}$ for all three dimensions and thus the modulus is reduced accordingly [1,3]. In the present model these ratios should differ for a given film. By averaging over all film orientations relative to a macroscopic strain we obtain for small strains the factor $1/3(\phi_p^{4/3} + 2\phi_p^{-2/3})$ (see Appendix). Although the legitimacy of using this factor for non-Gaussian networks is questionable, we preferred to use this (relatively small) correction to reevaluate G_0 based on the swelling reported in Ref. [35]. Fig. 4 shows the B values obtained from the differential swelling data of Refs. [12,13,20,29] (filled symbols) and the estimates of B based on Eq. (8) with $G = G_0$ (open symbols). The values based on G_0 seem to go somewhat higher, which can presumably be explained by the overestimate of the numerical coefficient in Eqs. (8) and (9) and possible increase of the measured modulus by the electrostatic and interfacial effects.

For comparison, Fig. 4 also shows the Gaussian prediction (solid line) calculated using Eq. (9) with $G = NkT/V_0$ based solely on the nominal DVB content. Expectedly, the results rapidly diverge as the degree of crosslinking increases and the deviations from the Gaussian behavior become stronger. It is worth noting that this rapid increase of B far beyond the Gaussian behavior provides justification for the use of weekly crosslinked resins as references.

4. Conclusions

We have seen therefore that the classical Flory–Rehner theory fails to describe the experimentally observed dependence of the elastic pressure on the volume of the system for swelling accompanied by microphase separation due to strong enthalpic effects. Thus it predicts for zero solvent content a finite elastic pressure that remains nearly constant as the solvent content increases, while experimental results show linear dependence with zero swelling pressure at zero solvent content. We proposed a picture of microscopic strain, different from the classical theory, by replacing the *affine deformation of the chains* assumed in the classical theory with the *affine deformation of the cells* enclosing the aggregated solvent molecules. The most important result was that we could obtain expressions for the elastic energy and contractile pressure that gave the *correct dependence* on the solvent content. The agreement was up to a constant parameter B that relates the elastic pressure to the relative volume change. This experimental parameter is predicted to be proportional to the elastic modulus of the matrix.

The values of B measured for differently crosslinked Dowex resins showed a fair agreement with the estimates based on the reported shear moduli. Some discrepancies could be explained by the approximations made in the model and the uncertainties of the elastic data resulting from the unaccounted for contributions. The estimates based merely on the number of chains per unit volume calculated from the nominal DVB content were found seriously in error, in particular, for highly crosslinked samples. This divergence was well expected in view of the strong deviations from the Gaussian statistics inevitable for a heterogeneous network of chains just a few random links long.

We would like to stress the approximate character of the present model. The complete model should give a better account for both the chain statistics (e.g. for short chains) and the non-uniformity of strain. We also emphasize that the model is limited to low and moderate swelling, where the amount of solvent adsorbed is comparable with that of the polymer. Thus it is not suitable for highly swollen gels, where the chains get completely separated by the solvent and the microphase separation disappears, in which case the assumption of affine deformation of the chains may be fully justified. Nevertheless, the model seems to give qualitatively correct results and might be a step towards a predictive theory for the swelling equilibria of the type considered here.

Appendix A. Elastic energy of a microscopically phase separated swollen network under mechanic deformation

We take the situation when a macroscopic sample is simultaneously swollen to a ratio $\lambda = \phi_p^{-1/3}$ and mechanically deformed. The principal extension ratios for the latter source of strain are given by a vector $\boldsymbol{\gamma} = (\gamma_x\gamma_y\gamma_z)$. The deformation of a microscopic film as a result of swelling is given by $\boldsymbol{\lambda} = (\lambda_1\lambda_2\lambda_3) = (\lambda^{-2}\lambda\lambda)$, where the microscopic axes 1, 2 and 3 are, in general, different from the macroscopic axes x, y and z and chosen so that axis 1 is normal to the film and axes 2 and 3 lie in the plane of the film. The total strain $\boldsymbol{\alpha} = (\alpha_x\alpha_y\alpha_z)$ of the film is superposition of the strains caused by swelling and mechanic deformation. Its components may be found as:

$$\alpha_i = \gamma_i\lambda_i, \tag{A1}$$

where i is x, y or z and λ_i are the components of the strain caused by swelling, which after transformation to the macroscopic coordinate system (x y z) will be given by:

$$\lambda_i^2 = \sum_j \lambda_j^2 \cos^2\beta_{ij}, \tag{A2}$$

where the summation is over the microscopic axes $j = 1, 2$ and 3 and β_{ij} is the angle between axes i and j.

The components of total strain α may be substituted to Eq. (3) to obtain the stored free energy of deformation. Since the derivation of the value of the modulus involves differentiation of Eq. (3), only the sum $\sum \alpha_i^2$ will be relevant, as the other terms will be constant assuming the polymer incompressible. Inspection of Eqs. (A1) and (A2) shows that this sum will contain terms of the type $\gamma_i^2\lambda_j^2\cos^2\beta_{ij}$. In order to obtain the macroscopic modulus we have to average the sum over all possible orientations of the film relative to the macroscopic coordinates. Under swelling alone the sample will remain macroscopically isotropic and the distribution of orientations will be *spherically symmetric*. We may assume the spherical symmetry be also approximately retained under *small* mechanical strains. Then, after averaging over all orientations, each term $\gamma_i^2\lambda_j^2\cos^2\beta_{ij}$ in the sum $\sum \alpha_i^2$ will be replaced with

$$\int_0^{\pi/2} \gamma_i^2\lambda_j^2\cos^2\beta_{ij}\sin\beta_{ij}\,\mathrm{d}\beta_{ij} = 1/3\gamma_i^2\lambda_j^2. \tag{A3}$$

From Eqs. (A1), (A2) and (A3) we easily conclude that for each i

$$\begin{aligned}\alpha_i^2 &= 1/3\gamma_i^2\sum\lambda_j^2 = 1/3\gamma_i^2(\lambda^{-4} + 2\lambda^2)\\ &= 1/3(\phi_\mathrm{p}^{4/3} + 2\phi_\mathrm{p}^{-2/3})\gamma_i^2.\end{aligned} \tag{A4}$$

The factor $1/3(\phi_\mathrm{p}^{4/3} + 2\phi_\mathrm{p}^{-2/3})$ is the same for all γ_i and constant for given λ or ϕ_p. While the free elastic energy (Eq. (3)) is expressed through the mechanical extension ratios for a given swelling, the above factor may formally relate the elastic energy of the *dry* network for swelling to that of a swollen network, just as the factor $\phi_\mathrm{p}^{1/3}$ in the classical model. Obviously, the same factor will apply for the *elastic moduli* in the limit of small strain. Of course, in general, the factor will be only approximate for large strains, when the spherical symmetry is violated.

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