A structural model for equilibrium swollen networks

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Abstract. – A tensile blob construction for branched structures is used to explain structural sizes larger than the strand length, as observed in neutron scattering data from equilibrium swollen networks. Under this model, equilibrium swollen networks display a base structural size, the "gel tensile blob" size, ξ, that follows the scaling relationship $\xi \sim l/(1/2 - \chi)^P$, where l is the monomer length, χ is the Flory interaction parameter and P is a power determined by the connectivity of the network and the degree of interpenetration. The gel tensile blobs compose a large-scale linear structure, whose length, L, follows the scaling relationship $L \sim Q^{1/2} N_{\text{avg}}$, where $1/N_{\text{avg}}^2 = ((1/f N_c^2) + (1/4 N_e^2))$, Q is the equilibrium swelling ratio, N_c is the strand length, N_e is the entanglement length and f is the functionality of the cross-links. The variation of the swelling ratio with molecular weight can now be expressed as $Q \sim N_{\text{avg}}^{3/5}$, which reduces to the correct expressions under the limits $N_e \gg N_c$ and $N_c \gg N_e$.

The microstructure of polymer gels and its relationship to swelling has been a source of controversy in the polymer literature [1–4]. It is well known that the microstructure of a polymer gel, in general, and the degree of topological constraint, in particular, depend on the preparation conditions, especially the polymer concentration in the solution in which the network is cross-linked [2, 4]. For networks prepared in solution with cross-links of identical functionality, the degree of topological constraint arising from trapped entanglements is expected to increase with the polymer concentration in the state of preparation and presumably reaches a maximum for networks prepared in the melt state. Trapped entanglements present in a network affect the modulus [5, 6] and possibly even the swelling behavior.

The equilibrium swelling of polymer gels is often described in terms of the Flory-Rehner theory [1], in which the free energy of the gel is written as the sum of an osmotic contribution, calculated using the Flory-Huggins free energy of mixing of a polymer and a solvent; and an elastic contribution, calculated assuming affine deformation of the network strands (*i.e.* the chains between cross-links) which exhibit Gaussian statistics. The equilibrium swollen state is calculated by minimizing the free energy with respect to the volume fraction of the gel [1] predicting that the equilibrium swelling ratio, $Q \sim N_c^{3/5}$, N_c being the strand length. The prediction seems to be reasonably confirmed by experiments, especially for highly cross-linked networks [7]. A polymer chain in a semi-dilute solution does not follow Gaussian statistics

but is expected to obey the concentration blob model [2]. Using the concentration blob model to describe the structure of the network strands in the Flory-Rehner theory does not alter the prediction for the swelling ratio [8].

On the other hand, de Gennes proposed that the polymer concentration in the gel at equilibrium swelling should be proportional to the overlap concentration of a linear polymer in solution, which yields $Q \sim N_c^{4/5}$. Although the c^* theorem was originally proposed to describe polymer networks prepared in dilute/semi-dilute solutions, most discussions of the c^* theorem in the polymer literature implicitly assume its validity even for melt cross-linked networks [9]. The c^* theorem implies sub-affine deformation for the network strands [2,9]. Benoit *et al.* [10] and others [11,12] observed that the chain extension in equilibrium swollen gels is always significantly lower than what would be expected from affine deformation of the cross-links. Further, Beltzung *et al.* [13] showed that the radius of gyration of the elastically effective chains, in networks prepared at several polymer concentrations in solution (including in the melt state) for a series of molecular weights between cross-links, is close to that for a linear chain in a dilute solution. The experimental observations in refs. [10–13] lend support to the c^* theorem.

Polymer chains in a melt are well described by random walk statistics [2]. The network strands in a dry network still exhibit Gaussian statistics as has been demonstrated for end-linked poly(dimethysiloxane) (PDMS) networks [14]. To reach the density of the dry network, the network webs must interpenetrate [15]. This lead Bastide *et al.* [16] to distinguish between the number of topological first neighbors for a given cross-link, which, if we consider a volume R^3, R being the strand length, is the cross-link functionality, f, and the number of spatial first neighbors in the volume R^3, n, determined by the number density of the cross-links in the dry network. In typical networks, n/f was calculated to be of the order 10 [16,17] which led Bastide *et al.* [16,18] to suggest that, in lightly cross-linked gels, equilibrium swelling involves, to a large extent, rearrangement of the network strands leading to reduction in the value of n, rather than the affine deformation of the individual chains between cross-links. This provided a plausible explanation for the experimentally observed excluded-volume expansion of the network strand during swelling and is in agreement with the c^* theorem. Bastide *et al.* [16] termed this expansion "disinterspersion".

Molecular-dynamics simulations [19] of perfect networks with cross-links of defined functionality prepared in the melt with strand lengths both above and below entanglement length (N_e) suggest several results, which both agree with and contradict parts of the Flory-Rehner theory [1]. The authors claim that for $N_c \gg N_e$, $Q \sim N_e^{3/5}$ implying that the swelling ratio saturates for high network strand lengths. Also, the end-to-end distance of the individual strands, $R \sim N_c^{7/10}$, *i.e.*, the network strands are stretched more than an excluded-volume chain in solution.

The structure of equilibrium swollen gels from small-angle neutron scattering measurements displays a good-solvent–like power law decay at high q ($q = (4\pi/\lambda)\sin(\theta/2)$ and θ is the scattering angle) [2,7,9]. At low q the scattered intensity follows a linear power law and terminates in a Guinier regime that reflects a structural size larger than the end-to-end distance of a strand. The large-scale structure is usually described as caused by static (quenched) heterogeneities induced during the cross-linking process [20–25] and a multitude of functions, mostly empirical, have been proposed to fit the scattering data [21–25]. This letter describes a potential model for this large-scale structure observed in neutron scattering from equilibrium swollen networks based on the concept of a tensile blob [26,27] for branched structures [27–29] and consideration of the forces acting on the tensile structure at large scales.

Swelling occurs when a polymer network is in contact with a good solvent. Swelling, in
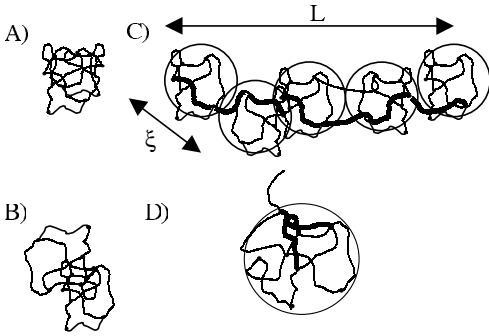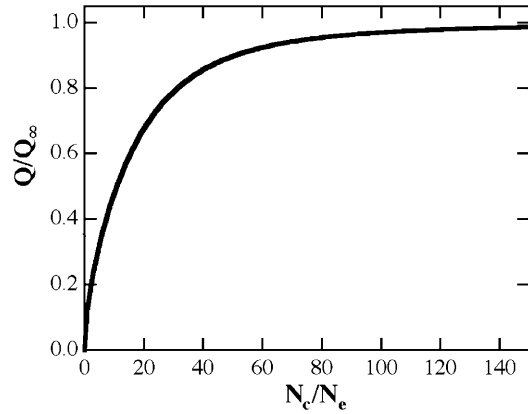
Fig. 1

Fig. 2

Fig. 1 – A) Interpenetration in the dry network. B) Disinterpenetration during swelling. The random knots, due to entanglements being trapped in the network during the cross-linking process, govern the extent of disinterpenetration. C) The extended tensile structure. Swelling can be viewed as a progression from A to C. D) Enlarged schematic of the tensile blob. The loop formed by the dark lines cannot disentangle during swelling without introducing another entanglement or the destruction of the network structure.

Fig. 2 – The dependence of the swelling ratio, Q, on the network strand length.

general, can be visualized as a combination of three distinct processes. Upon contact with the solvent, the chains in the network begin a process of disinterspersion [16, 17] accompanied by excluded-volume expansion of the individual chains in the network. Disinterspersion cannot occur uniformly in the network due to the presence of regions with high topological constraints (for, *e.g.*, random entanglements quenched in the structure). In these regions of high topological constraint, the network chains cannot fully disinterpenetrate, forcing these regions to move as a whole (instead of local disinterpenetration) and away from other such regions. The elastic stresses in the network due to the movement of the regions with high topological constraints are propagated along the topological minimum paths connecting these regions. The network chains that form these minimum paths are extended due to the stresses, as compared to the network chains that could comfortably disinterpenetrate, which leads to a contrast difference between these topologically connected minimum paths and neighboring regions. In this letter, we consider the large-scale element of the swollen network structure to be composed of a string of "gel tensile blobs" [26,27]. So the gel can be thought of as extended chains, connecting regions with high topological constraints, surrounded by a matrix of chains that are not extended. The chains that are not extended make no contribution to the total scattering above the corresponding concentration blob size. The large-scale structure seen in the scattering data arises completely due to the extended chains in the gel. The gel tensile blobs can be described as fractal structures whose connectivity is determined by the global topological constraints, like trapped entanglements, in addition to the constraints due to the network junctions. A sketch of the extended tensile structure and the swelling mechanism is shown in fig. 1.

Following Pincus [26] and Witten [27], one can consider a convoluted string drawn at the ends as a simple model for a tensile blob structure. Large-size scales of the string will straighten out first, while maintaining a convoluted or unperturbed structure at smaller scales.

For a polymer coil with tension applied to the ends, subject to thermal randomization [26], this behavior should manifest itself as a scaling transition at a size ξ. At scales larger than ξ linear scaling is observed and at smaller scales thermally determined scaling is observed. One prediction of the tensile blob model of use here is the tensile blob size, ξ, which is predicted to scale with temperature, T, and the imposed force, f_L [26],

$$\xi \sim kT/f_L, \tag{1}$$

where k is the Boltzmann constant, *i.e.* the energy stored in a tensile blob due to the deformation is of the order kT.

The following Flory-type free energy of a branched structure proposed by Vilgis [29] is used for the tensile blob of size ξ,

$$\frac{F}{kT} \sim \frac{n\xi^2}{l^2 N^{2-D}} + \frac{v(nN^D)^2}{\xi^d}, \tag{2}$$

where D is an internal dimension of the fractal structure, which has been identified with the spectral dimension or the chemical dimension in the literature [28–30], d is the spatial dimension and v is the excluded-volume parameter, $v = l^3(1 - 2\chi)$. N is the number of monomers along a minimum path on the fractal structure and n is the number of such interpenetrating fractal objects, both within the volume ξ^3. As the number of interpenetrating fractal objects in a volume ξ^3 can be expected to scale with ξ, and since ξ scales with N, we assume that $n \sim N^\alpha$. Our Flory analysis is similar to the one done in [19].

If we consider M_{dry} monomers in a volume ξ^3, then the density of the dry network $\rho_{\mathrm{dry}} \sim (M_{\mathrm{dry}}/\xi^3)$. The number of monomers within ξ^3, $M_{\mathrm{dry}} = nN^D$, implying $M_{\mathrm{dry}} \sim N^{D+\alpha}$. In the dry network, $\xi \sim N^{1/2}$ and ρ_{dry} is a constant, which leads to $M_{\mathrm{dry}} \sim N^{3/2}$ or $D + \alpha = 3/2$. For a linear chain, $D = 1$ and $\alpha = 1/2$. In a dilute solution of linear polymers, we expect no disinterpenetration and $\alpha = 0$. So, for $D = 1$, α is bounded by the inequality $0 \leq \alpha \leq 1/2$. α would decrease during swelling if disinterpenetration of the network strands occurs. The difference in α before and after swelling can be taken as a measure of the degree of disinterpenetration occurring in the network. The α used in eq. (2) is the value for the network after any possible disinterpenetration is complete.

Equation (2) can be minimized in ξ to obtain

$$N \sim \left(\frac{\xi}{l}\right)^{(2+d)/(2+D+\alpha)} (1 - 2\chi)^{-1/(2+D+\alpha)}. \tag{3}$$

By substituting (3) in (2),

$$\frac{F}{kT} \sim \left(\left(\frac{\xi}{l}\right)^{((D+\alpha)(4+d)-2d)} [1 - 2\chi]^{(2-(D+\alpha))}\right)^{\frac{1}{2+D+\alpha}}, \tag{4}$$

where k is the Boltzmann constant. From eq. (1), we can see that the energy stored in a tensile blob is of the order kT. Using this in eq. (4) yields an expression for ξ,

$$\xi \sim \frac{l}{(1 - 2\chi)^P}, \quad \text{where} \quad P = \frac{2 - (D+\alpha)}{((D+\alpha)(4+d) - 2d)}. \tag{5}$$

Equation (5) indicates that for a given solvent/temperature/α/D combination all equilibrium swollen gels of a polymer will display the same substructural size. The dependence of ξ on the

interaction parameter, eq. (5), is controlled by both the degree of interpenetration, α, and the degree of branching in the tensile blob, D. Even for linear chains, with $D = 1$, small changes in α will have large effects on the exponent, P, and consequently on the tensile blob size. For no interpenetration in linear chains, $\alpha = 0$, P is 1 while for maximal interpenetration, $\alpha = 1/2$, P is 1/9. Also, the higher the internal dimension, D, the weaker the dependence of the gel tensile blob size, ξ, on χ. ξ decreases in size with lower χ, as is expected from the tensile blob model of Pincus [26] and contrary to most current models for swelling such as the c^* theorem [2], where conditions of more favorable solvation (smaller χ) are expected to lead to larger ξ.

Equation (3) indicates that, due to the interpenetration of the chains, the scaling exponent is modified when compared to a dilute system. We can verify that for a dilute system given by $\alpha = 0$, the scaling exponent in eq. (3) reduces to the literature value, $(d+2)/(D+2)$ [29]. When the network chains are forced to remain interpenetrated in the swollen state due to the topological constraints, the number of monomers within a tensile blob, M, obeys $M \sim \xi^{(D+\alpha)(2+d)/(2+D+\alpha)}$. The proposed scaling exponent, α, could potentially explain variations in the mass fractal dimension at high-q values, seen in neutron scattering data from polymer gels prepared under different conditions which are expected to lead to the same D [9].

The size of the large-scale structures, L, as seen in neutron scattering data [9], is significantly larger than the distance between the cross-links. It is expected that the length of large-scale structures would maintain a functional relationship with the molecular weight between cross-links since the degree of topological constraint would increase with the cross-link density. The tensile-blob network model can be used to describe these equilibrium-swollen, large-scale structures. As mentioned before, the large-scale size in the system is thought to arise due to the minimum paths between regions of topological constraints being subjected to stretching due to a tensile force, f_L, at its ends. Using scaling arguments detailed in [26,27], the length of such an extended tensile structure, L, can be shown to obey $(L/\xi) \sim N_{\text{blob}}$, N_{blob} being the number of gel tensile blobs that make up L. This implies that the large-scale structure is linear/rod-like, of length, L, and the scattering function would be a power law with a slope -1 between the sizes ξ and L. The tensile force, f_L, is opposed by the elasticity of the network which can be quantified using a spring constant, k_L, associated with a number of cross-linked chains and entangled chains trapped by the network for high N_c networks,

$$f_L = k_L L. \tag{6}$$

The spring constant, k_L, associated with these chains must be approximated to obtain a relationship for L. We estimate the spring constant of the network strands, by considering the chains between "cross-links" as Gaussian springs, as originally done by Flory [1] and consistent with the level of approximation used here. The individual chains within the extended structure of length L oppose the chain extension due to the tensile force, f_L. We calculate the total spring constant by assuming that the individual springs act independently and that their angular relation to L is random. Additionally, it is assumed that all the chains contribute to the elasticity, *i.e.* there are no dangling ends, and that the density of entanglements remains unchanged due to cross-linking (all the entanglements in the melt are topologically trapped), and to a first approximation act as cross-links [19] with $f = 4$. Using these assumptions we write

$$k_L = \left\langle \cos^2 \theta \right\rangle^{1/2} \left\{ (\rho_{\text{c}}/N_{\text{c}} + \rho_{\text{e}}/N_{\text{e}})L\xi^2 \right\} \frac{3kT}{l^2}, \tag{7}$$

where N_{c} and N_{e} are the average number of monomers between cross-links and between entanglements, respectively. The $\langle \cos^2 \theta \rangle^{1/2}$ term reflects the probability that a given Gaussian

spring, arranged randomly, contributes to the elasticity of the tensile structure. The number density of the chemical cross-links/entanglements, ρ_x, can be calculated using,

$$\rho_x = \frac{2\phi}{f_x N_x l^3}, \tag{8}$$

where x stands for c or e, f_x, the functionality of the "cross-link" sites, equals f for the chemical cross-links and 4 for the entanglements, and $\phi = (1/Q)$ is the volume fraction of the polymer in the gel. k_L can then be approximated by

$$k_L = \frac{6\langle \cos^2 \theta \rangle^{1/2} kTL\phi\xi^2}{l^5} \left[\frac{1}{fN_c^2} + \frac{1}{4N_e^2} \right]. \tag{9}$$

By combining eqs. (1), (6) and (9),

$$f_L \sim \frac{kT}{\xi} \sim \frac{kTL^2\phi\xi^2}{l^5} \left[\frac{1}{fN_c^2} + \frac{1}{4N_e^2} \right]. \tag{10}$$

Using eq. (5) in eq. (10), we get

$$L \sim l(1 - 2\chi)^{\left(\frac{6 - 3(D+\alpha)}{14(D+\alpha) - 12} \right)} Q^{1/2} N_{avg}, \tag{11}$$

where $Q = 1/\phi$ and $\frac{1}{N_{avg}^2} = (\frac{1}{fN_c^2}) + (\frac{1}{4N_e^2})$.

A plot of L against $N_{avg}\sqrt{Q_{eq}}$ should be linear and pass through the origin in extrapolation. The other terms in (11) are constant for a given polymer/solvent/temperature/D/α system at equilibrium and form a prefactor for L. As $N_{avg} \sim N_c$, for $N_e \gg N_c$, and $N_{avg} \sim N_e$, for $N_c \gg N_e$, we are tempted to write

$$Q \sim N_{avg}^{3/5}. \tag{12}$$

It is easily verified that eq. (12) yields both the predictions of the classical theories [1,9,20] and the predictions of [19] as the limiting values. Figure 2 gives a plot of Q/Q_∞, where Q_∞ is the value of Q as $N_c \to \infty$, against N_c/N_e, and shows qualitative agreement with the simulation results in [19].

We have presented a structural model to explain the extended linear structures seen in neutron scattering data from polymer gels as arising due to the presence of regions of high topological constraint in the network. Trapped entanglements govern the swelling behavior for $N_c \gg N_e$. The main conclusions of our model include 1) the gel tensile blob is a fractal object of mass fractal dimension $(D + \alpha)(2 + d)/(2 + D + \alpha)$, whose size for a given polymer is determined only by the solvent used for swelling, the temperature, the internal dimension, D, the degree of interpenetration, α, and is independent of the molecular weight between cross-links; 2) the extended tensile structure displays a power law scattering, $I(q) \sim q^{-1}$ and obeys the scaling relationship $L \sim Q^{1/2}N_{avg}$, and 3) writing the scaling relationship for the swelling ratio, Q, as $Q \sim N_{avg}^{3/5}$, where N_{avg} is an "average" molecular weight that arises naturally out of the theory, can reproduce the appropriate scaling behavior for Q under the two limits $N_e \gg N_c$ and $N_c \gg N_e$. The predictions of our model should be verifiable with neutron scattering data.

REFERENCES

[1] FLORY P. J., *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY) 1953.
[2] DE GENNES P.-G., *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY) 1979.
[3] DEROSI D., KAJIWARA K., OSAKA Y. and YAMAUCHI A., *Polymer Gels* (Plenum Press, New York) 1991.
[4] COHEN ADDAD J. P., *Physical Properties of Polymeric Gels* (Wiley, New York) 1996.
[5] EDWARDS S. F. and VILGIS T. A., *Rep. Prog. Phys.*, **51** (1988) 243.
[6] DOSSIN L. M. and GRAESSLEY W. W., *Macromolecules*, **12** (1979) 123.
[7] HILD G., *Prog. Polym. Sci.*, **23** (1998) 1019.
[8] PANYUKOV S., *Sov. Phys. JETP*, **71** (1990) 372.
[9] BASTIDE J. and CANDAU S. J., in *Physical Properties of Polymeric Gels*, edited by COHEN ADDAD J. P. (Wiley, New York) 1996.
[10] BENOIT H. *et al.*, *J. Polym. Sci. Polym. Phys.*, **14** (1976) 2119.
[11] GEISSLER E., DUPLESSIX R. and HECHT A.-M., *Macromolecules*, **16** (1983) 712.
[12] BASTIDE J., PICOT C. and CANDAU S., *J. Macromol. Sci. Phys. B*, **19** (1981) 13.
[13] BELTZUNG M., HERTZ J. and PICOT C., *Macromolecules*, **16** (1983) 580.
[14] BELTZUNG M., PICOT C., REMPP P. and HERZ J., *Macromolecules*, **15** (1982) 1594.
[15] FLORY P. J., *Proc. R. Soc. London., Ser. A*, **351** (1976) 1666.
[16] BASTIDE J., PICOT C. and CANDAU S. J., *J. Macromol. Sci. Phys. B*, **19** (1981) 13.
[17] BELTZUNG M., PICOT C. and HERZ J., *Macromolecules*, **17** (1984) 663.
[18] CANDAU S., BASTIDE J. and DELSANTI M., *Adv. Polym. Sci.*, **44** (1982) 27.
[19] PUTZ M., KREMER K. and EVERAERS R., *Phys. Rev. Lett.*, **84** (2000) 298.
[20] MENDES E. *et al.*, *Phys. Rev. Lett.*, **66** (1991) 1595.
[21] ONUKI A., *J. Phys. II*, **2** (1992) 45.
[22] HORKAY F. *et al.*, *Macromolecules*, **24** (1985) 2896.
[23] BASTIDE J., LEIBLER L. and PROST J., *Macromolecules*, **23** (1990) 1821.
[24] FALCAO A. N., PEDERSEN J. S. and MORTENSEN K., *Macromolecules*, **26** (1993) 5350.
[25] PANYUKOV S. and RABIN Y., *Phys. Rep.*, **269** (1996) 1.
[26] PINCUS P., *Macromolecules*, **9** (1976) 386.
[27] WITTEN T. A., RUBINSTEIN M. and COLBY R. H., *J. Phys. II*, **3** (1993) 367.
[28] SOMMER J. U., VILGIS T. A. and HEINRICH G., *J. Chem. Phys.*, **100** (1994) 9181.
[29] VILGIS T. A., *Phys. Rep.*, **336** (2000) 167.
[30] LAY S., SOMMER J.-U. and BLUMEN A., *J. Chem. Phys.*, **110** (1999) 12173.