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Scaling approach to differential swelling of polymer solutions and gels

P. Pekarski (1), Y. Rabin (1,2) and M. Gottlieb (3,4)

(1) Department of Physics, Bar-Ilan University, Ramat-Gan 52900, Israel
(2) Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto 606, Japan
(3) Chemical Engineering Department, Ben-Gurion University, Beer Sheva 84105, Israel
(4) Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, NM 85445, U.S.A.

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Abstract. — The failure of the classical theories for swollen polymer networks was clearly demonstrated by recent differential swelling experiments of Gee, Eichinger and McKenna. We introduce a weaker form of the additivity assumption based on the separation of the gel into "solid"-like and "liquid"-like components. Using simple scaling arguments and the assumption that the effective solvent quality for a crosslinked polymer system is worse than for its uncrosslinked counterpart, we predict a similar anomaly of the swelling activity parameter (dilation modulus) in osmotic deswelling experiments in the semi-dilute range of concentration. The relevance to Eichinger's and McKenna's experiments on concentrated systems is discussed.

1. Introduction.

The classical theories of swelling in rubbers and gels postulate that, analogously to the case of a single macromolecule in a good solvent, the free energy of a swollen network can be represented as a sum of "solid" (elastic) and "liquid" contributions [1]. The elastic term originates in the entropy reduction associated with the deformation of the chains compared to their equilibrium dimensions. The "liquid" contribution is taken to be identical to the free energy of a solution of uncrosslinked polymers at the same monomer concentration.

In the absence of a more fundamental theory of polymer networks, the assumptions underlying these classical theories, i.e., the additivity of elastic and "liquid" effects, the use of linear-chain theory for the liquid contribution, and the affinity of the deformation down to polymer size, can only be justified on empirical grounds. Unfortunately, direct experimental tests are complicated by the difficulty to sort out the consequences of the different assumptions and different groups have chosen to uphold some of these assumptions while casting doubt on others. Thus, Eichinger and coworkers [2] following the pioneering work of Gee et al. [3],
assumed that the "liquid" free energy is the same in the gel and in solution and conclude that the difference between the chemical potentials of a solvent molecule in the two environments is of elastic origin. They measured the, so-called, "dilation modulus" (proportional to this chemical potential difference) by comparing the amount of solvent absorbed by the gel and by a solution of identical polymers and found that, depending on the solvent and temperature, it either goes through a maximum or decreases monotonically as a function of swelling (Fig. 1). They showed that this behavior can not be explained by the classical theories of rubber elasticity which predict a constant or a monotonically decreasing modulus and concluded that the additivity assumption is violated. A different approach was taken by McKenna et al. [4] who carried out similar measurements of the dilation modulus (which they call the "swelling activity parameter", a term we adopt in the following). They assumed that the additivity hypothesis is correct and, using the experimentally measured elastic contribution to the free energy associated with the deformation of the dry network, concluded that the effective Flory-Huggins (χ) parameter depends on the number density of cross-links (such dependence was predicted theoretically by Freed and coworkers [5]). While they still could not explain the anomalous behavior of the swelling activity parameter, they suggested that it may originate from the dependence of the "liquid" term on the state of deformation of the network (for large deformations, a similar effect was predicted by one of the present authors [6]).

![Swelling Activity Parameter Graph](image)

**Fig. 1.** — Plot of the measured swelling activity parameter $S$ as a function of the swelling stretch ratio $\lambda$ for PDMS networks ($c^0 = 1$) in 3 different solvents: TMP (squares), heptane (circles) and DMP (triangles). The corresponding $\chi$ parameters for the solutions are shown on the figure (from Zhao and Eichinger, Ref. [2]).

In this work we reconsider the problem by noticing that one has to distinguish between strong and weak additivity assumptions. **Strong additivity** means that (1) the free energy can be written as a sum of elastic and "liquid" contributions and that (2) the parameters entering the elastic contribution are independent of solvent and those entering the liquid contribution are independent of the preparation and state of deformation of the network. As demonstrated by the differential swelling experiments [2-4], strong additivity is clearly violated
in swollen polymer gels. However, as we will show in the following, the experimental results are consistent with the \textit{weak additivity} assumption which corresponds to upholding condition (1) while relaxing condition (2) (for example, by allowing the $\chi$ parameter to depend on the state of cross-linking). Although the weak additivity assumption can be treated as purely phenomenological, its deeper origins stem from the fact that the swollen gel can be considered as a two-component system in which one of the components is a "solid" (network) and the other a "liquid" [7] (solvent molecules and polymer chains between crosslinks). Recently we have shown [8] that the coupling between the solid and the liquid components results in violation of the affinity assumption on mesoscopic scales probed by small-angle neutron scattering (SANS) experiments and gives rise to the observed anomalous butterfly patterns [9]. Analogously to reference [8] in which we allowed the network moduli to depend on the composition of the "liquid" component, here we will allow the "liquid" interaction ($\chi$) parameter to depend on the "solid" component, i.e., on the concentration of crosslinks.

In section 2 we relate the swelling activity parameter (dilation modulus) to the partial pressures of the network and liquid components in the swollen gel and to the osmotic pressure in the polymer solution. Using simple scaling considerations we argue that the anomalous behavior of the swelling activity parameter is a consequence of worse solubility conditions for the gel compared to the corresponding polymer solution. Brief discussion of the results and their relevance to the experiments of references [2, 3 and 4] is given in section 3.

2. Scaling analysis of differential swelling.

In a typical differential swelling experiment one puts the same quantity of dry gel and polymer melt (i.e., identical crosslinked and uncrosslinked polymer chains) in a closed cell which contains solvent vapor at a given vapor pressure. Since the chemical potential of a solvent molecule is different in a gel and in solution, the gel and the solution swell to different volumes (in equilibrium with the vapor). One then repeats the experiment for different vapor pressures and compares the values of the vapor pressure $\Pi^g$ and $\Pi^v$ needed to maintain the gel and the solution, respectively, at the same polymer volume fraction $c$. The vapor pressure is related to the chemical potential $\mu$ of a solvent molecule in the corresponding system (solution or gel) by $\mu = \ln \Pi_v$. Here and in the following, the chemical potential is measured in units of $k_B T$, pressure is measured in units of $k_B T / v$ with $k_B$ the Boltzmann constant, $T$ the temperature and $v$ the molar volume of a solvent molecule. The \textit{swelling activity parameter} (or \textit{dilation modulus}) $S$ is defined as the product of the swelling stretch ratio $\lambda$, and the difference of chemical potentials of a solvent molecule in the solution and in the gel,

$$S = \lambda (\mu_v - \mu_g)$$  \hspace{1cm} (1)

The swelling stretch ratio $\lambda$ is defined as $(c^0 / c)^{1/3}$ or $(V/V^0)^{1/3}$ where $c^0$ is the polymer volume fraction during network formation (reference state), $V$ is the volume of the swollen polymer network and $V^0$ is the volume of the network in the reference state. It should be emphasized that $\lambda = 1$ corresponds to the undeformed network, i.e., $c = c^0$. For reasons which will become apparent in the following, this paper is concerned with networks formed in solution such that $c^0 \ll 1$ (and therefore our conclusions cannot be directly applied to the experiments of references [2] and [3] which used networks formed in the dry state). The chemical potential difference in equation (1) can be calculated from various free-energy models [2-4, 10]. Here we will take advantage of the fact that the dimensionless chemical potential of a solvent molecule and the dimensionless polymer osmotic pressure are related by [11] $\mu = -\Pi_{osm}$, and calculate
$S$ in terms of the difference between the osmotic pressure in the gel and in solution. In solution the osmotic pressure has only a "liquid" contribution

$$
\Pi_{\text{osm}}^G = \Pi_{\text{liq}}^G(c)
$$

(2a)

In the gel, the measured osmotic pressure is the difference of a "liquid" contribution $\Pi_{\text{liq}}^G$ which tends to expand the gel and an elastic "network" component $\Pi_{\text{net}}^G$ which tends to contract it (the two contributions balance exactly at equilibrium swelling in excess solvent),

$$
\Pi_{\text{osm}}^G = \Pi_{\text{liq}}^G(c) - \Pi_{\text{net}}^G(c)
$$

(2b)

Substitution into equation (1) yields

$$
S = \lambda(\Pi_{\text{net}}^G + \Pi_{\text{liq}}^G - \Pi_{\text{liq}}^G)
$$

(3)

where the various pressures are functions of the polymer volume fraction $c$ or, equivalently, of the swelling stretch ratio $\lambda$.

Notice that the swelling activity parameter is defined as the difference in the osmotic pressures needed to maintain the gel and the solution at the same volume fraction $c$. This suggests that the information content of experiments on differential swelling in equilibrium with solvent vapor is identical to that of osmotic deswelling experiments. The only difference is that while the former experiments are usually performed near the dry gel limit [2-4], the latter are done closer to equilibrium swelling in excess solvent [12] (saturation swelling). Since at present we have a better understanding of the physics of swollen gels than of that of dry rubber, we will calculate the swelling activity parameter for conditions corresponding to the semi-dilute regime of polymer concentration ($c \ll 1$).

We now proceed to estimate the concentration dependence of the various terms in equation (3). Osmotic deswelling and mechanical experiments on swollen gels formed in the diluted state [12] ($c^0 \ll 1$) show that in the vicinity of the swelling equilibrium, experimental observations are consistent with classical theories of gel elasticity. The classical expression for the network pressure is [1]

$$
\Pi_{\text{net}} = A c^{1/3}
$$

(4)

where $A$ is a constant which depends on network preparation. Although this scaling law appears to agree with experiments on both good and theta solvents, its validity for networks which contain a significant number of topological entanglements has been questioned and several modifications have been recently proposed [13]. For simplicity, we will only consider the case in which the elastic modulus is dominated by the contribution of permanent cross-links and assume that equation (4) holds independent of the quality of solvent.

The scaling exponents for the "liquid" contributions to the osmotic pressure depend on the quality of solvent. Both theory and experiments on semi-dilute solutions and swollen gels show that [11] in a good solvent,

$$
\Pi_{\text{liq}} = B_2 c^{9/4}
$$

(5a)

and in a $\Theta$-solvent

$$
\Pi_{\text{liq}} = B_3 c^{3}
$$

(5b)

where $B_2$ and $B_3$ are proportional to the second and third virial coefficients, respectively ($B_2 \to 0$ as $\Theta$-solvent conditions are approached). The quality of solvent depends on the thermodynamic conditions such as temperature, external pressure and, what is of great importance, on the polymer concentration and on the number density of the cross-link points. In general,
the solvent quality may be expected to be different for solutions and gels of identical chemical composition. Although we have limited knowledge about the form of this dependence, both experimental investigations [4] and model calculations [5] suggest that the quality of solvent diminishes with the degree of cross-linking (e.g., the difference between the $\chi$ parameters for the crosslinked and uncrosslinked systems is proportional to the density of crosslinks).

The possibility of a difference between the effective solvent qualities for the solution and for the gel suggests several possible scenarios. When the experiment is done under good solvent conditions for both the solution and the gel, the difference between the interaction parameters leads only to a difference between the second virial coefficients in the corresponding expressions for the osmotic pressures; the scaling exponents remain the same for the solution and for the network. A different situation occurs when conditions are such that the solvent is good for the solution and $B$-solvent for the gel. Such a situation can arise only in a narrow temperature interval and it may be related to the observed anomalous temperature dependence of the swelling activity parameter (Fig. 2).

![Graph showing swelling activity parameter versus swelling stretch ratio for polyisoprene in benzene at different temperatures.](image)

**Fig. 2.** — Plot of measured $S$ vs. $\lambda$ for polyisoprene in benzene, at 3 different temperatures (from Crissman and McKenna, Ref. [4]).

Using equations (3-5) and the geometric relation $\lambda = (c^0/c)^{1/3}$, we can obtain explicit expressions for the swelling activity parameter as a function of the swelling stretch ratio $\lambda$ in different regimes of solvent quality.

1) Identical solvent conditions for both the network and the solution during the entire swelling process. In this case the expressions for the swelling activity parameter are:

$$S = \begin{cases} A + (B_g^s - B_g^s)\lambda^{-23/4} & \text{good solvent;} \\ A + (B_g^s - B_g^s)\lambda^{-8} & \text{$B$-solvent.} \end{cases}$$  

(6)

where $A$ is the gel elasticity constant defined in equation (4), $B_g^s$ and $B_g^B$ are the coefficients in the scaling relations (Eqs. (5)) for the pressure of the "liquid" component in the gel and in the solution, respectively. Equation (6) predicts monotonic decrease of the swelling activity...
parameter as function of the swelling ratio (Fig. 3). Note that the coefficients $A$ and $B_2^g$ are related by the condition of equilibrium in excess solvent $\Pi^g_{\text{net}}(c^*) = \Pi^g_{\text{liq}}(c^*)$, which gives $A = B_2^g(c^*)^{23/12}$ (the $c^*$ theorem [11] is a special case of this more general relation).

ii) $\Theta$-solvent conditions for the gel and good solvent conditions for the solution. In this case the swelling activity parameter is given by:

$$S = A + B_2^g \lambda^{-23/4} - B_3^g \lambda^{-8}$$

(7)

and, for $B_3^g \geq (23/32)B_2^g$, has a maximum as a function of the swelling stretch ratio (see Fig. 4). Since $B_2 \gg B_3$ in a good solvent, the above condition is expected to be valid only when (a) $B_2^g \gg B_3^g$ and (b) the polymer solution is also not too far from its $\Theta$ point. Notice that the shape of the curves is very sensitive to the ratio $B_2^g / B_3^g$ when this ratio is of order unity and therefore a maximum may exist only in a limited range of temperatures.

iii) This regime arises if the solvent quality depends on polymer concentration. This would generally lead to deviations from simple scaling laws and to much stronger concentration dependence of the osmotic pressure than predicted by equations (5). However, the qualitative features of the expected behavior of the swelling activity parameter upon increase of concentration can be anticipated from the following argument: in the more concentrated regime (yet still dilute enough for Eq. (5b) to apply), we may expect $\Theta$-solvent conditions for both the network and the solution. In the intermediate concentration region there is a situation, analogous to that of case 2, i.e., $\Theta$-solvent conditions for the gel, and good solvent conditions for the solution. At even lower concentrations (larger swelling) the solvent conditions for the gel and the solution are both good. This produces monotonic decrease of $S$ with $\lambda$ for both high and low regimes of polymer concentration and a maximum or a plateau at intermediate degrees of swelling.

We would like to emphasize that although there appears to be a large number of parameters in equations (6) and (7), all these parameters have simple physical meaning and can be determined experimentally. Thus, all the parameters pertaining to the solution (i.e., $B_2^s$ and $B_3^s$)
are either well-known or can be determined independently. As already mentioned, the ratio \( A/B^g_2 \) can be determined from measurement of saturation equilibrium and therefore one has a single free parameter \( B^g_2 \) to fit the measured \( S \) vs. \( \lambda \) curve in the good solvent regime of equation (6). When the solvent quality is good for the solution but \( \Theta \) for the gel, \( B^g_3 \) can be determined from a single parameter fit to equation (7).

3. Conclusion.

We have shown that anomalous behavior of the swelling activity parameter may arise as a consequence of reduced solvent quality for a gel compared to that of a polymer solution. This result is consistent with the observation that the thermal fluctuation contribution to the intensity of SANS from a gel is larger than from a corresponding polymer solution [14]. This observation remains correct even upon subtracting the static component of SANS intensity, usually associated with frozen-in concentration inhomogeneities [15]. Our model predictions (Eqs. (6) and (7)) are in complete agreement with SANS measurements of osmotic moduli reported in reference [16].

We would like to comment on the relation of our approach to that of references [2, 3 and 4]. Similarly to McKenna [4] we attribute the observed anomaly to different solvent qualities for the solution and for the gel. However, instead of following his approach and considering the dry gel as a reference state for the calculation of the elastic contribution, we take as a reference the state of a well-diluted gel, close to saturation equilibrium. This choice is motivated by the observation that the elasticity of swollen gels is "simpler" than that of dry rubber, since the corrections [17] to the classical theories of rubber elasticity [1b], attributed to the effect of entanglements and chain-chain interactions in "real" networks are known to be negligible for networks formed in semi-dilute solution [12]. It is, of course, questionable whether such an approach can be extrapolated to the more concentrated regime in which most of the differential swelling experiments were performed (similar criticism pertains to the Flory-
Huggins theory used in references [2, 3 and 4]; a concentration-dependent \( \chi \) parameter has to be introduced to fit the high-concentration data. Indeed, measurements of the concentration dependence of osmotic pressures in this range [4c, 18] show that although this dependence can be fitted by a power law over a limited range of concentrations, the corresponding exponents are always considerably larger than those in equations (5). However, it is important to notice that even in this regime of intermediate concentrations one obtains a higher scaling exponent for a gel than for a solution [4c], indicating that solvent quality is indeed better for the latter. This suggests that one can attempt to describe the concentration dependence of the swelling activity parameter in the concentrated regime, equations (6) and (7), with exponents 23/4 and 8 replaced by empirical parameters \( \alpha \) and \( \beta \) which should be determined from fits to the osmotic pressure data. A more direct test of our scaling considerations can be obtained from differential osmotic deswelling experiments on networks formed at \( c^0 \ll 1 \), starting from saturation swelling for the gel and from identical initial concentration for the polymer solution. This can be done by re-analizing existing experimental data [12] (to the best of our knowledge, the dilation modulus was not calculated by these authors) and by new studies on different polymer-solvent systems.

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