

Effect of excluded volume on segmental orientation correlations in polymer chains

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We study the impact of excluded volume interactions on the orientation statistics of chain segments in polymer gels, and show that nuclear magnetic resonance (NMR) experiments provide a direct and unique measure of excluded-volume effects on the chain statistics. In particular we consider the tensor order parameter, which can be expressed as the second Legendre polynomial of the segment orientation with respect to a fixed end-to-end distance vector and which is directly related to the residual coupling constant obtained in NMR experiments. We provide analytical results for the case of single chains in a good solvent and for semidilute solutions. Computer simulations using the bond fluctuation model are applied to compare with the analytical predictions. Considering polymer gels at the equilibrium state of swelling we predict a unique relation between the tensor order parameter and the correlation length (blob size) of the gel. Experiments applying multiple-quantum NMR methods to both end-linked and randomly cross-linked polymer networks are in excellent agreement with this prediction. The initial decay of the tensor order parameter as observed in experiments at low and intermediate degrees of swelling can be explained as a solvent effect without making additional assumptions about constraint release processes during swelling.

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I. INTRODUCTION

The time-averaged (residual) orientation of fluctuating polymer chain segments reveals many details about the state of polymer systems, and is directly accessible in nuclear magnetic resonance (NMR) experiments [1–4]. Mostly, it is measured in the form of a partially averaged residual dipolar coupling constant (RDC), which is directly related to the second moment of the segmental orientation distribution. It depends in particular on restrictions imposed on the chain conformations, such as fixation of chain ends or entanglements.

Such restrictions are realized in polymer networks, where the ends of individual strands are chemically bound to cross-links and can be further restricted by entanglements. Therefore, NMR experiments have been used to characterize structural properties of polymer networks such as the density of cross-links. To achieve this goal, Gaussian statistics has been widely applied in the literature to calculate segmental order parameters for dry and swollen polymer networks in the context of NMR experiments [5–8]. For instance, Gaussian chain statistics predicts a strict increase of the RDC with the degree of swelling of networks. In many experiments on swollen networks, however, the opposite has been observed for low and intermediate degrees of swelling [9–11]. To explain these results, additional assumptions, such as release of entanglement constraints during swelling, have been made by regarding the principal relations provided by Gaussian chain statistics as invariant [9,10].

In this work we investigate the role of chain statistics (solvent effect) for the segmental orientation distribution, and we show that effects observed for swollen polymer networks must be reinterpreted due to the genuine influence of excluded volume interactions on segment orientation fluctuations. In particular we prove that dilution of polymer chains at constant end-to-end distance always decreases the value of the residual dipole coupling which is uniquely related to an order parameter characterizing the overall constraints on the orientation fluctuation of segments due to cross-linking and other restrictions [12].

Orientalional properties of chain segments are provided experimentally by the RDC associated with a pair of spins fixed to a given segment along the polymer chain [4]. The RDC and its distribution can be most reliably observed in multiple-quantum NMR experiments [3]. On the other hand, the RDC is directly related to the tensor order parameter s , an invariant of the averaged quadrupole tensor related to the segments' orientation vectors. This order parameter characterizes the disordered solid-state property of polymer networks and has been extensively discussed in our previous work [12]. A nonzero value of the order parameter indicates restricted orientation fluctuations of the segments irrespective of any local director. A finite value of s indicates the network (gel) phase, while a zero value is associated with the locally isotropic melt (solution) phase. It can be considered in analogy to order parameters defined for phase transitions in other disordered systems such as spin glasses [13]. For a general discussion of tensor and vector order parameters in polymers, the reader is referred to our previous work [12]. We note that a quasi-solid-like state (temporary network) can be caused by incomplete time averaging of the segment orientations. If the time of measurement in NMR, for instance, is short as compared to the relaxation time of the chains, residual orientational order can be observed even if the true

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equilibrium state is locally isotropic. This is possible for entangled polymer melts, where the (temporary) entanglement network only restricts orientation fluctuations on a sufficiently long time scale. The analytical treatment of such non-equilibrium states depends on whether the segment fluctuation in between the entanglement points (assumed as localized) can be considered in equilibrium. In the following we will only consider fluctuations in thermal equilibrium.

If the residual segment anisotropy originates from restrictions on the chain ends (cross-links, localized entanglements, forces), orientational order is uniaxial and the tensor order parameter is equivalent to the second Legendre polynomial of the segment orientation, l with respect to the end-to-end vector R . Given that the angle between R and l is θ , we obtain

$$s = \frac{1}{2}[(3\langle \cos^2(\theta) \rangle - 1)], \quad (1)$$

where $\langle \dots \rangle$ denotes the thermal average over all conformations of the polymer under the given restrictions, and $[\dots]$ denotes the structural average over all segments in the sample. A Gaussian chain at fixed end-to-end distance yields

$$s = \frac{3}{5} \left(\frac{R^2}{N^2 l^2} \right), \quad (2)$$

where l and N denote the length of a statistical segment and the number of such segments in a chain, respectively.

Polymer networks can take up large amounts of solvent, thus considerably diluting the polymer fraction. The degree of swelling shall be given by the swelling ratio

$$Q = V/V_0, \quad (3)$$

where V and V_0 are the volume of the network after and before swelling, respectively. The swelling ratio represents the inverse segment concentration. During swelling, the connectivity between chains remains invariant. The simplest model is to consider a deformation of individual network chains where end points are fixed and are displaced affinely with the macroscopic deformation [14]. Using Eq. (2), a strictly monotonic increase of the order parameter with respect to Q is predicted, $s \sim Q^{2/3}$.

In marked contrast, NMR experiments may display a much weaker increase or even a decrease of the order parameter at low and intermediate degrees of swelling. Examples are shown in Fig. 1. Up to now, this effect has been explained by the release of topological constraints (entanglements) during swelling [9,15]. In this work we show that excluded volume effects substantially influence the tensor order parameter and thus the RDC. We will derive expressions for the tensor order parameter for the cases of single chains in good solvent and for chains in semidilute solutions. Using these results we discuss the two classical models for equilibrium swelling of polymer networks, the Flory-Rehner model and the c^* model by de Gennes.

II. SINGLE CHAINS IN GOOD SOLVENT

Let us consider the extension of Eq. (2) to the case of good solvent conditions. We start with a single chain fixed at

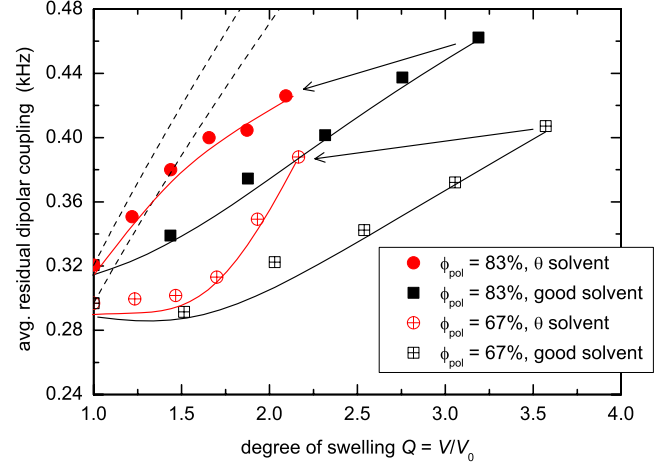


FIG. 1. (Color online) Experimental results for the averaged RDC $\sim s$ as a function of Q for two end-linked polydimethylsiloxane networks (linear precursor $M_n=5200$ g/mol), cross-linked in the presence of toluene at different polymer volume fractions ϕ_{pol} , swollen in good solvent (toluene) and θ solvent (styrene at 35°C [16]). The networks were prepared by a Pt-catalyzed end-linking reaction of vinyl-terminated chains and a tetrafunctional silane as cross-linker, as described in Ref. [17]. For details on the multiple-quantum experiments used to extract the RDC distributions and the averages, see Ref. [11]. Solid lines are a guide for the eye, and dashed lines are the affine predictions. Generally, the RDC is lower for good solvent conditions at the same degree of swelling. The arrows indicate the reduction of the equilibrium degree of swelling in θ solvent.

both ends at distance R . For large values of N and $R_0=ln^\nu \ll R \ll lN$, the distribution of the end-to-end vector in d dimensions is given by [18,19]

$$p(x) = Ax^\kappa \exp\{-Dx^\delta\} \quad \text{with } x^2 = \frac{dR^2}{N^2\nu^2}. \quad (4)$$

Here, the exponent δ is given by $\delta=1/(1-\nu)$, ν denotes the Flory exponent in d spatial dimensions (in the following we will only consider the case $d=3$), and D and A are some constants. The exponent κ is given by $(1-\gamma+\nu d-d/2)/(1-\nu)$, with γ being a second critical exponent for self-avoiding walks [20].

In order to calculate the order parameter according to Eq. (1), we consider a tagged segment located at the end of the chain with the end-to-end distance vector R . Given the probability $p(R'=R-l)$ by Eq. (4), we obtain the following distribution for $\cos \theta$ under the conditions of $R \gg l$ and $N \gg 1$:

$$p(\cos \theta; R) = A(R) \exp\{\beta \cos \theta\}, \quad (5)$$

and

$$\beta = \beta_0 \left(\frac{R}{Nl} \right)^{\nu(1-\nu)} f_\beta(R, N), \quad (6)$$

with $f_\beta = 1 - \frac{\kappa}{\beta_0} (R_0/R)^{1/(1-\nu)}$. Here, $\beta_0 = \delta D d^{\delta/2}$ is a numerical constant and $A(R)$ is a function of the end-to-end distance only. The properly normalized function $p(\cos \theta; R)$ gives the probability of $\cos \theta$ for a fixed value of R . This leads to the

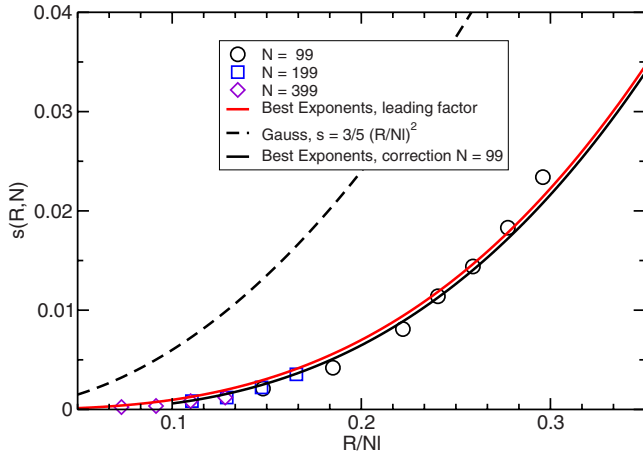


FIG. 2. (Color online) Comparison of simulation data with the analytic result for the tensor order parameter of end segments, using no fit parameters. The bond fluctuation model was used to simulate single chains (two lengths) with fixed ends in athermal (good) solvent. The numerical constant $D \approx 0.35$ in the definition of β_0 , see Eq. (6), was taken from a previous study [22]. For the critical exponents we used best estimates according to $\nu \approx 0.588$ and $\kappa \approx 0.25$. Results are also compared with the Gaussian model.

following generating function for the moments of $\cos \theta$:

$$Z(\beta) = \frac{1}{\beta} \sinh \beta \quad \text{with} \quad \langle \cos^n \theta \rangle = \frac{1}{Z} \frac{d^n}{d\beta^n} Z(\beta). \quad (7)$$

We note that β is related to the force exerted by the rest of the chain, which tends to orient the last segment in the direction of the end-to-end vector. Using Eq. (1) we obtain

$$s = \frac{1}{15} \beta^2 = \frac{1}{15} \beta_0^2 \left(\frac{R}{Nl} \right)^{2\nu/(1-\nu)} f_\beta^2(R, N). \quad (8)$$

In Fig. 2 we display simulation results for a single chain with fixed ends in athermal solvent using the bond fluctuation model (BMF) [12,21]. The result of Eq. (8) has been applied, using best estimates of the critical exponents in three dimensions (3D) (see figure caption). Furthermore, the only numerical constant left, D , was taken from a previous simulation study on the force-extension behavior using the same model [22], leaving no fit parameter for the comparison. Very good agreement between theory and simulations is already obtained by neglecting the correction due to f_β . Note that the scaling variable for s is R/Nl , i.e., the ratio between the end-to-end distance and the contour length of the chain. We call it the stretching ratio in the following.

The above analytical results have been obtained for end monomers only. In contrast to Gaussian chains, however, the order parameter in real chains is inhomogeneously distributed along the chain's contour displaying a maximum in the middle of the chain for good solvent conditions [12,23]. Since the order parameter averaged over the chain's contour is a primary result of NMR experiments we have investigated this property using Monte Carlo simulations in more detail.

In Fig. 3 we display our simulation results for the order parameter averaged over all bonds using three different chain

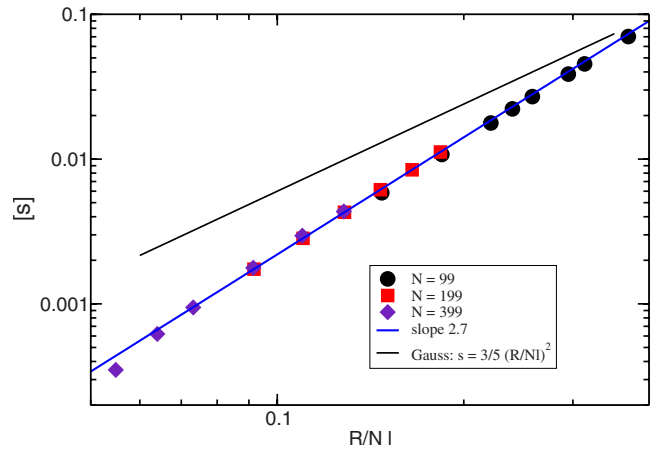


FIG. 3. (Color online) The chain-averaged tensor order parameter as a function of the stretching ratio for various chain lengths. The best fit is obtained for a slope of about 2.7. Results are compared with the Gaussian model.

lengths and various values of the end-to-end distance. Good scaling with respect to the stretching ratio R/Nl can be observed. The best fit to the data points leads to an exponent of about 2.7 which is close to $2\nu/(1-\nu) \approx 2.85$ and much larger than the Gaussian value of 2. The small deviation of the best-fitted exponent from the predicted value might be attributed to the corrections to scaling, as we have also seen for the chain ends given by the function $f_\beta(R, N)$; see Eq. (6) and below. It is interesting to note that these results are in marked contrast to the behavior of the first moment of the segmental orientation distribution, $m_1 = \langle \cos \theta \rangle$. For the end monomer using Eq. (7) one obtains $m_1 \sim (R/Nl)^{\nu/(1-\nu)}$. Since the sum over all segment vectors gives exactly the end-to-end vector, one obtains $[m_1] = R/N$, a result which has been recovered using renormalization group calculation for a freely fluctuating chain [24]. We conclude that the averaged tensor order parameter is strongly reduced by excluded volume effects and displays scaling with the stretching ratio following that obtained analytically for the end bonds, given by Eq. (8).

III. CHAINS IN SEMIDILUTE SOLUTION

We turn to the case of semidilute solutions, where the end-to-end vector distribution function in 3D takes the form

$$p(R) = A_0 \exp\left(-\frac{3R^2}{2R_0^2}\right), \quad (9)$$

with

$$R_0^2 = \frac{N}{g} \xi^2 = CNQ^{(2\nu-1)/(3\nu-1)}. \quad (10)$$

Here, ξ denotes the correlation length in the semidilute solution and g denotes the average number of monomers along the chain spanning the correlation length with the relation $\xi \sim g^\nu$; C being a numerical constant and A_0 is a normalization factor. Using Flory's value of the ν exponent ($\nu_F = 3/5$), we obtain $R_0^2 \sim NQ^{1/4}$. Along the same lines as above,

we obtain a similar relation as given by Eq. (5), with $\beta_{SD} = 3lR/R_0^2$. Using Eq. (8), we obtain

$$s = \frac{3l^2R^2}{5R_0^4}. \quad (11)$$

Here, R_0 is given by Eq. (10). Equation (11) predicts an overall reduction effect of the tensor order parameter with increasing solvent quality, which is fully supported by the experimental results shown in Fig. 1.

IV. NETWORKS AT EQUILIBRIUM SWELLING

We now apply our results to swollen polymer networks by considering two classical models for gels: The affine model as proposed by Flory and Rehner [25] and the c^* model as proposed by de Gennes [18]. For c^* -gels the equilibrium degree of swelling \bar{Q} corresponds to the overlap condition of the network strands given by $\bar{Q} = Q^* \sim N^{3\nu-1}$. Using the result of Eq. (8) with $R \sim N^\nu$, we obtain $\bar{s} \sim N^{-2\nu}$ which can be expressed in terms of the equilibrium swelling ratio as

$$\bar{s} \sim Q^{*-2\nu/(3\nu-1)}. \quad (12)$$

Using ν_F we obtain $\bar{s} \sim \bar{Q}^{-3/2}$.

Next, we consider the case of affine swelling, where the end-to-end distance follows directly the external deformation, $R = lN^{1/2}Q^{1/3}$. Using Eqs. (10) and (11), we obtain

$$s_{FR} \sim \frac{1}{N} Q^{2(2-3\nu)/(3\nu-1)}. \quad (13)$$

Using ν_F yields $s_{FR} \sim Q^{1/6}/N$. Generally, we have $2-3\nu > 0$. Thus, the affine swelling yields a monotonous increase of the order parameter, which is in contrast to the observed behavior at low and intermediate degrees of swelling; see Fig. 1 and Ref. [9]. However, the increase of the order parameter is much weaker than predicted upon ignoring the solvent effect (taking $R_0 = l^2N$). Under the assumption of affine deformation, Flory and Rehner [25] calculated the equilibrium degree of swelling. Using scaling arguments for the osmotic pressure and for the elastic free energy in the semidilute state, following Obukhov, Colby, and Rubinstein [26], one can generalize the original result by Flory and Rehner for the swelling equilibrium, $\bar{Q}_{FR} \sim N^{3(3\nu-1)/4}$ ($\bar{Q}_{FR} \sim N^{3/5}$ for ν_F). Using the result of Eq. (13) for the swelling equilibrium we obtain

$$\bar{s} \sim \bar{Q}_{FR}^{-2\nu/(3\nu-1)}. \quad (14)$$

Interestingly, both models yield the same relation between the segmental order parameter and degree of swelling under good solvent conditions regardless of the fact that both models predict very different properties of the gel at equilibrium: While for the c^* -model network chains just overlap and are not stretched with respect to their solvent state, in the FR-model network chains are under semidilute conditions and highly stretched due to the affine deformation.

In Fig. 4 we display experimental data for very different systems: Natural rubber and PDMS networks, both end-

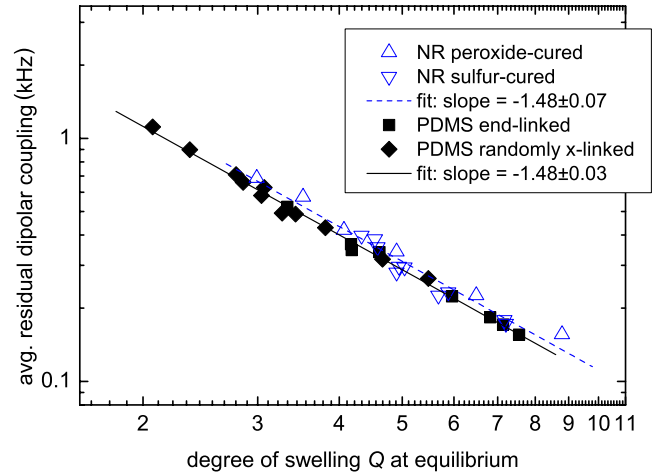


FIG. 4. (Color online) Average RDCs at swelling equilibrium vs the equilibrium degree of swelling in toluene (log-log plot) for different PDMS and natural rubber (NR) networks. The PDMS series includes networks that were synthesized at lower polymer volume fractions, down to $\phi_{\text{pol}} = 0.25$. Randomly cross-linked PDMS networks are based on multiply vinyl-functionalized chains and a difunctional cross-linker, using the same chemistry as in Ref. [17], and the NR samples are described in Ref. [27].

linked and randomly cross-linked in bulk and in solution. Excellent agreement between the theoretical prediction given by Eqs. (12) and (14) is obtained, and is in marked contrast to Gaussian statistics. The best fit to the data is obtained with a slope of -1.48 . We note that by taking into account the effective slope in Fig. 3 we arrive at a scaling relation of $\bar{s} \sim \bar{Q}^{-1.46}$. Cohen-Addad qualitatively observed the same correlation earlier in a single PDMS system, yet incorrectly interpreted it as a proof of the c^* theorem [28].

It is important to note that the predictions made in Eqs. (12) and (14) do not depend on the nature of the constraints at swelling equilibrium. Besides cross-links, also entanglements [29] might determine the equilibrium degree of swelling. This does not matter for the result of both equations because only directly measurable quantities (s and Q) are related, and the strand length (which can be either chain parts between cross-links or between entanglements) enters only implicitly.

In order to understand the coincidence of both models with respect to the tensor order parameter, we can rewrite Eqs. (12) and (14) in the following form:

$$\bar{s} \sim 1/\xi^2. \quad (15)$$

Thus, the tensor order parameter measures the blob size of the gel swollen at equilibrium. A close look at the Flory-Rehner model reveals the reason for this unexpected result. The mixing free energy is of order kT per segment while the elastic free energy is of order kT per chain only. Thus, elasticity is not an important contribution at the early stages of swelling. Due to the affine deformation of the network chains *a priori* assumed in the Flory-Rehner model, the swelling process stops only if the stretchability of the chains is reached. In the equilibrium state the chains form stretched

strings of blobs of size ξ . The chains' extension is given by $\bar{R} \sim (N/g)\xi \sim \bar{Q}^{(3\nu+1)/3(3\nu-1)} \sim N^{(3\nu+1)/4}$. The last relation leads to the well-known result of the FR model by using Flory's value of the ν exponent, $\bar{R} \sim N^{7/10}$. In this extended state, no orientation fluctuations occur on length scales larger than the blob size. The strong stretching force effectively fixes the concentration blobs as if they were cross-linked. Thus, the order parameter corresponds to that of a c^* gel at the corresponding swelling ratio.

As mentioned, the experimental observation of a nonmonotonic behavior of the segmental order parameter with respect to the degree of swelling (Fig. 1) suggests a two-stage swelling process. Let us consider a polymer chain in semidilute solution. Using Eqs. (10) and (11), we obtain $s \sim \frac{1}{R_0^2} \sim \frac{1}{N} Q^{-1/4}$. Thus, the order parameter decreases with the degree of swelling due to the decrease of excluded-volume screening despite the fact that the end-to-end distance is increasing with dilution due to coil expansion by excluded-volume forces. The experimental results (initial decrease or nonmonotonic increase of s at low swelling in good solvent) can therefore indeed be explained by a type of desinterspersation process that simply implies subaffine deformation of the end-to-end vector rather than a release of packing constraints [15]. This can be explained by a topological unfolding process [30]. In fact, excluded volume effects provide a decrease of the tensor order parameter as long as the following threshold for the deformation behavior $R(Q)$ is not exceeded:

$$R \sim Q^{1/4}. \quad (16)$$

In a second stage of swelling, constraints due to trapped entanglements can become localized [12] and finally contribute to the equilibrium state of gels [29]. However, the crucial role of trapped entanglements in understanding network swelling deserves further studies.

V. CONCLUSIONS

The directly observable residual dipole coupling from NMR experiments is related to the tensor order parameter of a polymer system and is therefore given by a second moment

of the orientation distribution function of the segments. As a consequence it is not directly related to static constraints such as cross-links or entanglements, but is strongly influenced by solvent conditions which determine the type of fluctuation statistics of the chains. Given the same end-to-end distance vector, the tensor order parameter is reduced if the solvent quality is changed from θ to good solvent. The key result of our calculations is given by Eq. (11). According to this result, the degree of tensorial order (for a certain extension R of the chain) is determined by the extension of the free chain under given solvent conditions, R_0 , and not *a priori* by the chain length N . Thus, the interplay between dilution and stretching can cause a complex behavior of the tensor order parameter.

We have shown that our results lead to a unique relation between the degree of equilibrium swelling and the residual dipole coupling which is in excellent agreement with the experimental data obtained in this work using multiple-quantum NMR techniques. The Flory-Rehner model yields to the same relation between the observable quantities as the c^* model, despite the fact that both models otherwise predict very different properties at equilibrium swelling. The network strands in the FR model at swelling equilibrium are stretched chains of concentration blobs and no contributions to the reorientation of segments emerge from larger scales. The equilibrium state of swelling is in fact given by the equivalence of concentration blobs and force (Pincus) blobs [31]. The concentration blobs might be considered as "pinned" at swelling equilibrium in the FR model. This is the consequence of two assumptions: First, individual chain deformation is affine. Second, no desinterspersation occurs during the swelling process (number of chains within the volume of gyration of a tagged chain is invariant).

To conclude, we have shown that NMR measurements on gels reveal solvent properties, which can be understood by using a general scaling relation between the distance between two constraints and the equilibrium length of the corresponding chain part under the given solvent conditions.

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