Eur. Phys. J. B **11**, 439–444 (1999)

THE EUROPEAN PHYSICAL JOURNAL B
EDP Sciences

Homogeneous and inhomogenous polyacrylamide gels as observed by small angle neutron scattering: A connection with elastic properties

L. Benguigui[1,2,a] and F. Boué[1]

[1] Laboratoire Léon Brillouin, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France
[2] Solid State Institute, Technion-Israel Institute of Technology, 32000 Haifa, Israel

Received 30 December 1997 and Received in final form 26 June 1998

Abstract. Small angle neutron scattering of polyacrylamide solutions and gels is presented for different polymer and cross link concentrations. The gels are analyzed in connection with their elastic properties. For less than 11% of polymer concentration and for small cross link contents c_{x}, it was found that the gels are no more heterogeneous than the solutions. This corresponds to the range of c_{x} where the elastic modulus increases with c_{x}. For larger cross link contents when the elastic modulus decreases if c_{x} increases, the sample appears to be strongly heterogeneous with a large size distribution of the inhomogeneities. The results are compared with the recent model of Oshmyan and Benguigui of the elastic properties of the polyacrylamide gels. Thus a relation can be proposed between the observation of the inhomogeneities by scattering and the mechanical properties

PACS. 61.41.+e Polymers, elastomers, and plastics – 61.12.-q Neutron diffraction and scattering – 62.20.-x Mechanical properties of solids

1 Introduction

It is now well known that polymer gels exhibit important heterogeneities additional to those of polymer solutions *i.e.* the density of the cross linking has correlated spatial fluctuations, which are a memory of different processes occurring during one or another synthesis of the network [1]. We consider here polyacrylamide gels made from copolymerisation of monomers (acrylamide) and tetrafunctionnal agent (bisacrylamide). These gels have been widely studied and in particular their degree of heterogeneity was observed and studied by a variety of techniques [2–5]. A general study of the heterogeneities is not the aim of this paper but rather on the relation between the structure and the elastic behavior. Recently, a theoretical model of heterogeneity was proposed by Oshmyan and Benguigui[6] in order to explain the very particular elastic properties of these gels [7]. The basis of the model is that the formation of inhomogeneities is due to different kinetics of the polymer chains formation and of the cross linking process.

Let us recall the particular elastic properties: they lie in the dependence of the modulus (either the shear modulus G or the Young modulus Y, with $Y = 3G$ at small deformations) upon the density of the crosslinks. In general G is an increasing function of the relative amount of the cross linking agent c_{x} (c_{x} is defined as the ratio of the cross link agent weight to the weight of monomers). The rubber elasticity theory predicts a linear relation [8]. However, in the case of polyacrylamide gels, the elastic behavior is completely different, as seen in Figure 1. If

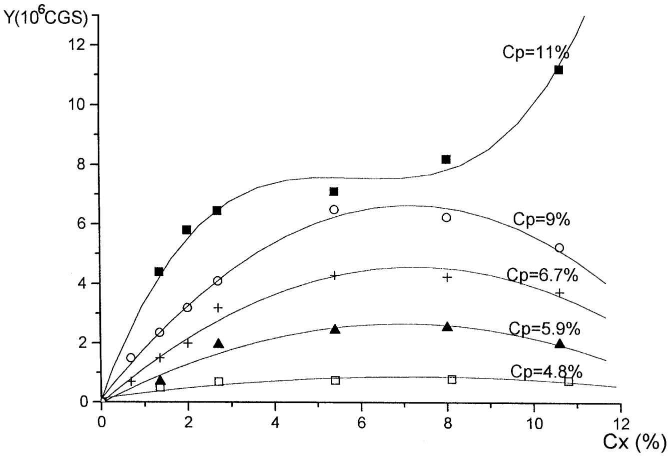

Fig. 1. Young modulus of polyacrylamide gels *versus* the cross link content on polymer content (w/w), c_{x}. The different curves are for different polymer concentration, c_{p}, as indicated near each curve. Note that for $c_{\mathrm{p}} < 11\%$, the $Y(c_{\mathrm{x}})$ curves begin by an increase and decrease after a maximum.

---

[a] e-mail: `ssgilles@techunix.technion.ac.il`

the concentration in monomers c_p (in weight per total weight of the sample) is less than 11%, Y as a function of c_x exhibits a maximum. Inside the range $c_p < 11\%$, the maximum is well pronounced for larger values of c_p.

One of the conclusions of the Oshmyan and Benguigui model (which is good only for samples exhibiting a maximum in Y) is that if $\mathrm{d}Y/\mathrm{d}c_x > 0$, the density fluctuations are weak such that the gel is practically homogeneous whereas if $\mathrm{d}Y/\mathrm{d}c_x < 0$, the gel is strongly heterogeneous. The goal of this work is to observe directly the degree of heterogeneity of the gels in the different regimes of $Y(c_x)$. This can be done by neutron scattering at small angles (SANS).

Before presenting our results, we recall that in the past, such degree of heterogeneity, which can be associated with the structure of the gels, has been studied by several teams. We mention the extended work of Hecht *et al.* [5] and a more recent by Cohen *et al.* [4] by X-rays. In the first case it was concluded that in the heterogeneous gels, the range of the size distribution is very large, from 5 to several thousands of Angstroms. In the second case, the X-ray scattering was interpreted on the basis of inhomogeneties having approximately the same radius of gyration R (considered by the authors of Ref. [4] as the mean radius of gyration). R was found to be of the order of several hundred of Angstroms and to decrease if the amount of the cross link agent c_x is increased.

2 Experimental

The gels were prepared as described in reference [7], by mixing the solvent (in the present case, heavy water to perform neutron scattering), the acrylamide monomers, the cross linking agent, N, N'-methylenebis acrylamide and adding ammonium persulfate and TEMED as catalysts. The values of the Young modulus displayed in Figure 1 were obtained with regular water as solvent and we checked that elastic modulus is not modified when using heavy water.

The SANS measurements were performed at the Laboratoire Léon Brillouin (LLB Saclay) using the spectrometer PACE. We use a neutron wavelength of 10 Å and the scattering vector varies from 0.003 to 0.12 Å^{-1}. For experimental details, see for example reference [9].

We selected three kinds of samples: samples A are the polymer solutions without cross linking molecules. Samples B are gels with $\mathrm{d}Y/\mathrm{d}c_x > 0$, with $c_x = 2.7\%$ and different c_p (from 5.6% to 11%). Samples C are gels $c_x = 8\%$ and different c_p, with $\mathrm{d}Y/\mathrm{d}c_x < 0$. For the samples with $c_p = 11\%$, $\mathrm{d}Y/\mathrm{d}c_x > 0$.

3 Results

We recall that our main interest is to follow the effect of cross linking density with respect to the different mechanical behavior. The measurements of the solutions were made only to check the quality of the polymer solutions.

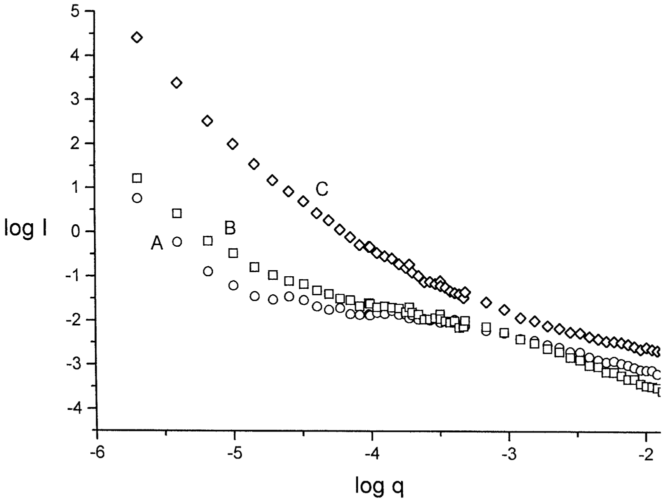

Fig. 2. Scattered intensity (arbitrary units) of a sample with polymer concentration of $c_p = 6.7\%$ for various cross link contents c_x: $c_x = 0\%$ (A), $c_x = 2.7\%$ (B), $c_x = 8\%$ (C).

We compare (in a log-log plot) the scattered intensity $I(q)$ *versus* the scattering vector q for three samples A ($c_x = 0\%$), B ($c_x = 2.7\%$) and C ($c_x = 8\%$) for $c_p = 6.7\%$ which is typical of the case $c_p < 11\%$ (Fig. 2), and for $c_p = 11\%$ (Fig. 3).

In Figure 2, we remark three features in the scattered intensity of the samples $c_p = 6.7\%$.

Firstly in the solution ($c_x = 0\%$), $I(q)$ increases strongly when q decreases. Such low up turns are not always observed in polymer semi dilute solutions but appears relatively frequently [1]. It is particularly visible by light scattering and often is called the Benoit-Picot effect. Its origin is still unclear. But it can be interpreted by either association between chains or unexplained long range density fluctuations in the solution. For larger q, the scattered intensity is as expected for a polymer semi-dilute solution: one has at intermediate q a "shoulder" and a decrease at large q (see below).

Secondly, the curve $I(q)$ of the sample B ($c_x = 2.7\%$) is almost identical with of the solution. We can already conclude that the gel process with low c_x does not introduce a noticeable amount of new heterogeneity.

Thirdly, for the sample C ($c_x = 8\%$), the intensity curve is now different from the two preceding cases. The intensity $I(q)$ increases continuously when q decreases. In particular the "plateau" or more precisely the "shoulder" is no longer visible. Our interpretation is that now the scattering is due to additional inhomogeneities produced by the cross linking procedure. The intensity of this scattering is so large that the thermal fluctuations (characteristic of the "plateau") are no longer visible. This scattering cannot be attributed to inhomogeneities with a well definite size but rather to a large range of sizes. In agreement with reference [5], the range is rather large: from our window of scattered wave vectors, it can be estimated from 10 to 1000 Å.

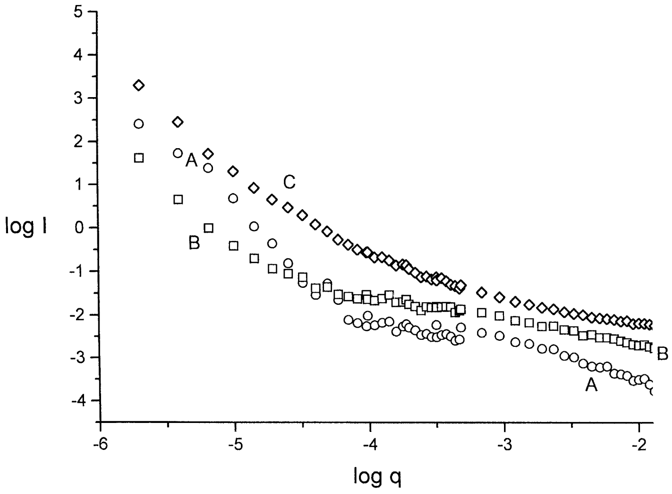

Fig. 3. As in Figure 2 for $c_{\mathrm{P}} = 11\%$.

In Figure 3, the $c_{\mathrm{P}} = 11\%$ samples are different from the other gels only when the cross link amount has the intermediate value 2.7%. The solution ($c_{\mathrm{x}} = 0\%$) is like the other solutions and for $c_{\mathrm{x}} = 8\%$, the gel is also similar to the other gels. The $c_{\mathrm{x}} = 2.7\%$ gel has a particular behavior: the plateau is still visible but the way $I(q)$ decreases at large q is intermediate between the solution and the completely heterogeneous gels. And at low q, the scattered intensity shows a unique dependence: it is lower than that of the solution suggesting a different structure.

4 Analysis and fit of the data

4.1 Samples A and B

We analyze together the solutions and the samples B since the scattering curves are very near. We suppose that we have two regimes. At low q, we can adopt the expression proposed by Koberstein *et al.* [10] for the Benoit-Picot effect. They use the so called Debye-Bueche expression which assumes an exponential correlation function for the density fluctuations and describes a two density random medium with sharp interface:

$$I(q) = \frac{a_1}{(1+\Xi^2 q^2)^2} \tag{1}$$

where Ξ is a characteristic length.

At larger q, we suppose that $I(q)$ is given by a Lorentzian function:

$$I(q) = \frac{a_2}{1+\xi^2 q^2} \tag{2}$$

where ξ is the correlation length, as for a semi-dilute solution [11]. At even larger q, for $\xi q > 1$, it is known that $I(q)$ is proportional to $q^{-5/3}$, so we do not use the last experimental points for the fit. The experimental curves were fitted only with the expression given by the sum of (1) and (2).

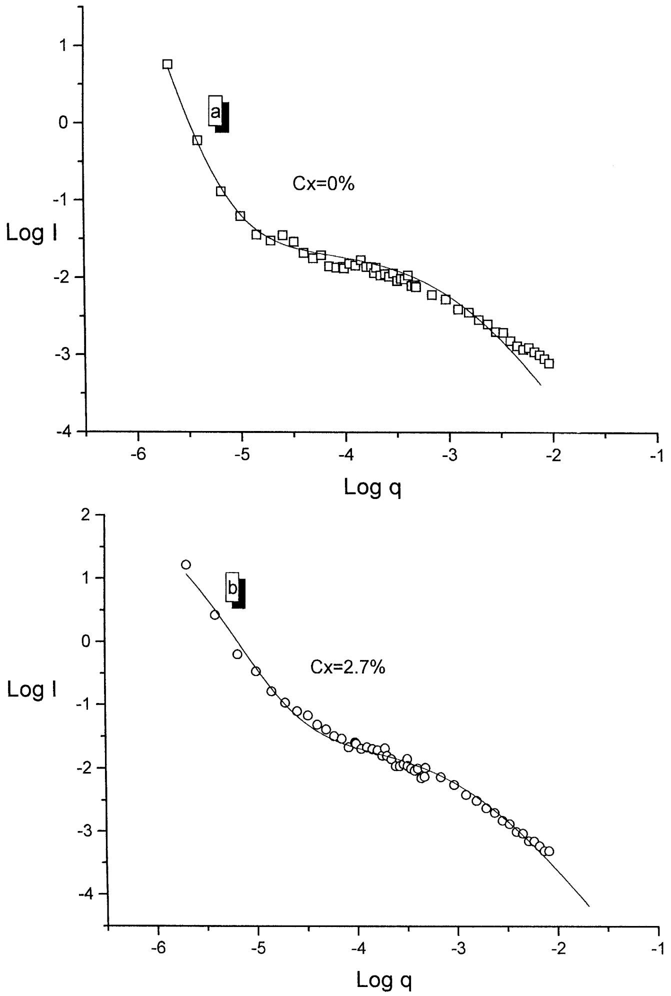

Fig. 4. (a) Fit of the scattered intensity of a solution ($c_{\mathrm{P}} = 6.7\%$) with $I(q) = (2.1 \times 10^{-10})/q^4 + 0.16/(1+400q^2)$. (b) Fit of the scattered intensity of a gel ($c_{\mathrm{P}} = 6.7\%$ and $c_{\mathrm{x}} = 2.7\%$) with $I(q) = 13/(1+(330q^2))^2 + 0.21/(1+484q^2)$.

For some of the samples, the fit gives values of the unknown parameters of (1), Ξ and a_1, with so large incertitude such that the values of the parameters have no meaning. This signals the fact that in the experimental range of q, a correct fit can be obtained only in the condition $q\Xi \gg 1$ such that in this range of low q, $I(q) \propto q^{-4}$. In such a case only the ratio a_1/Ξ^4 can be determined by the fit. In Figure 4a, we show the experimental results with the curve obtained from the fit for the solutions and in Figure 4b for a gel.

The values of Ξ that we succeeded to determined are around 300–500 Å. The correlation length ξ takes value between 25 and 12 Å and varies with the polymer concentration in agreement with the theoretical prevision [11] $\xi \propto c_{\mathrm{P}}^{-3/4}$.

In summary, the gels with low concentration of the cross link agent which corresponds to an increase of the Young modulus Y with c_{x}, are very similar to the solutions meaning that the cross linking process does not modify too

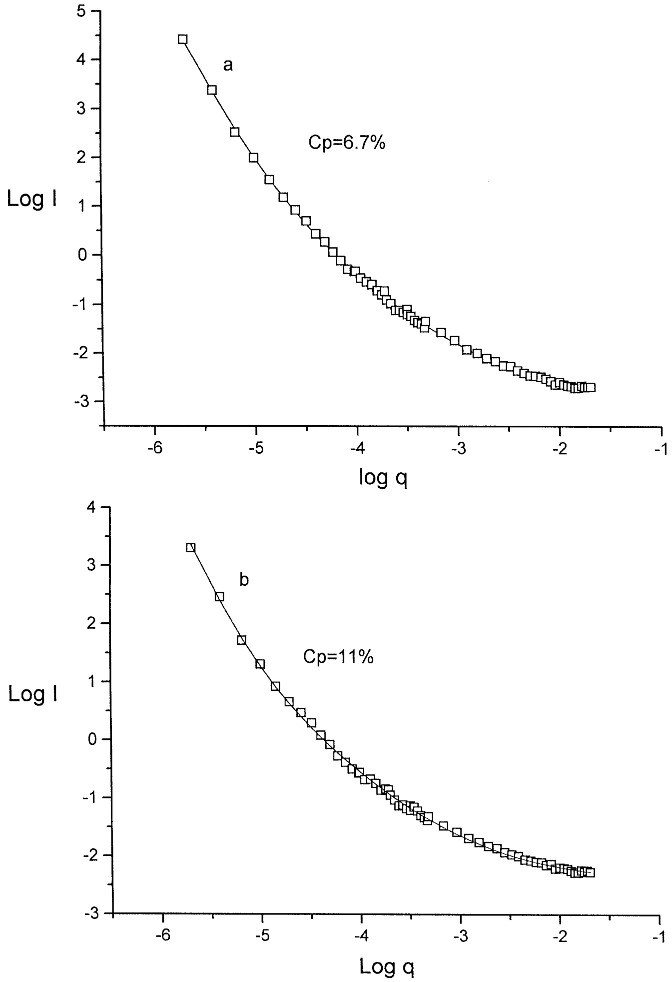

Fig. 5. Fit of the scattered intensity with equation (3) for two C gels with $c_x = 8\%$ (a) $c_p = 6.7\%$ (b) $c_p = 11\%$.

much their structure. However, there is an exception with the sample with $c_p = 11\%$ for which the behavior at large q is closer to that of the samples C.

4.2 Samples C ($c_x = 8\%$)

These samples are highly heterogeneous. At low q, it is difficult to decide whether the increase in $I(q)$ is a result of the Benoit-Picot effect as in the solutions (samples A) or is related to the gel formation. Here, we had to choose a new empirical expression in order to fit the results

$$I(q) = \frac{a_3}{q^{k_1}} + \frac{a_4}{q^{k_2}} + d. \tag{3}$$

This expression gives a very good fit for all gels (Fig. 5). First we took $k_1 = 4$ (we shall explain this choice below) and we found from the fit values of k_2 between 1.5 and 1.6 depending of c_p. If now k_1 is taken as a free parameter of the fit, we find $k_1 \cong 3.8$ and $k_2 \cong 1.4$ with only a small improvement in the quality of the fit. The coefficient a_3 is always much larger that the quantity a_1/Ξ^4 for the solutions; this gives ground to think that the low q scattering is not due to the Benoit-Picot effect but is characteristic of the gels. The constant d is very small and is probably the indication that the intensity scattered at large q's decreases very slowly when q increases. In the summary, the C gels with the unusual mechanical properties ($\mathrm{d}Y/\mathrm{d}c_x < 0$), behave differently than the gels of the B kind.

5 Interpretation

We can very tentatively interpret the preceding results concerning the samples C on the basis of the good fit of the experimental results with (3). We emphasis that the following analysis is only a first one and needs to receive confirmation. In particular, one has no precise model to explain the apparition of a polydisperse particle size distribution. The heterogeneous regions may be associated into two main groups. Those of the first group, have very large sizes (larger than the inverse of the smallest q vector of our window, $1/(3\times10^{-3})$ Å) and the second is responsible for the very long tail in $I(q)$ (second term in (3)). About the third term in (3), it corresponds to even smaller scale fluctuations or objects which can be nested in the inner structure of the large inhomogeneities.

About the first group of heterogeneous regions of very large sizes, it is known, from the theory of scattering by compact particles (Porod law [12]), that the scattered intensity decreases as q^{-4} for $qR_g \gg 1$ where R_g is the radius of gyration of the particles. Even when it is taken as a free parameter, k_1 remains near 4. This confirms the choice $k_1 = 4$.

The analysis of the properties of the second group of heterogeneities can be made only qualitatively. It would be very interesting to find the size distribution of the second group. But this does not seem possible to do quantitatively because the intensity scattered by one heterogeneous region depends not only on its size but also on its density.

Only for illustrative purposes, we calculate below the scattering of an hypothetical ensemble of regions with a distribution of size R

$$p(R) = AR^{-m} \tag{4}$$

where $p(R)$ is the number of regions with radius of gyration between R and $\mathrm{d}R$, and A is constant. If the regions are diluted enough, we can use a Guinier law [13] $\exp(-q^2R^2)$ for the scattering and if correlations are important, we can use a function $f(q^2R^2)$ which accounts for repulsion between regions. In both case

$$I(q) = A\int p(R)R^6 f(q^2R^2)\mathrm{d}R \tag{5}$$

giving

$$I(q) \propto \frac{A}{q^{7-m}}\cdot \tag{6}$$

If for the intermediate values of q (corresponding to the second term in (3)) we have an exponent $k_2 \cong 1.5$, this corresponds to $m \cong 5.5$. This simple argument shows that the exact size distribution is a very rapidly decreasing function of R and that if $I(q)$ is approximated by a power function the exponent might be rather large (between 5 and 7).

In conclusion of the analysis of the very heterogeneous samples (the C series), one can propose the tentative following picture. On the one hand, there is a group of very large heterogeneities (may be due to coalescence of smaller regions or like in other gels as a consequence of the gel formation) which gives the main contribution to the small q scattering. On the other hand, besides these large heterogeneities, the polyacrylamide gels of type C are also characterized by a very large distribution of smaller regions with strong increase towards the smallest size.

6 Comparison with a model

The final question we want to address is how the present results can be compared with the model of Oshmyan and Benguigui built initially to explain the elastic behavior. We recall that in a composite material with well separated spherical inclusions, as long as the total volume of the inclusion is smaller than say 20%, the effective elastic modulus is practically equal to that of the matrix. The purpose of the model was to explain the maximum in Y observed in Figure 1. The answer is given by competition between two processes: one giving an increase of Y when c_x as classically expected and the other producing a depletion of the matrix in polymer. Consequently, the matrix network cannot include all the cross linking molecules and this gives the decrease of the effective modulus. The model remains qualitatively valid whatever the real shape and size of the heterogeneous regions, at the condition that they do not touch and can be seen as independent.

In this model, it is assumed that the heterogeneous samples can be described by spheres of different sizes which fill all the volume. The type of filling is not important but each sphere is divided in two regions: an internal sphere of the stiff component and a surrounding shell of soft matter, and the volume ratio between the two components is the same for all the spheres. The size distribution does not need to be specified but the model implies necessarily a broad size distribution. This is effectively observed in the SANS, directly on the curves as well as via fitting. In the Appendix, we give an example of filling the space by spheres of decreasing radii and this gives an exponential size distribution with a large exponent, between 5 and 6. This is roughly in agreement with our qualitative discussion in the preceding section. In summary, direct observation as well fitting agree with the predictions of the model of composite material as used by Oshmyan and Benguigui for the effective modulus.

7 Conclusion

We measured the small angle neutron scattering of various poyacrylamide solutions and gels. It was found that the solutions have the expected behavior for the scattering intensity if one includes the Benoit-Picot effect. The discussion of this effect is not the scope of the paper and the data of the solutions have been given only for comparison with the gels. For gels (samples B) with a small amount of cross link (2.7%) there is almost no difference with the solutions, except for the largest amount of polymer (11%). But when the amount of cross link reaches 8%, the gels (samples C) appear to be more heterogeneous with a much large distribution of sizes. We proposed to classify the inhomogeneities into two groups: one with characteristic sizes above 300 Å and the other with a very broad size distribution until very small region of about 10 Å. Our main results are that the differences observed in the scattering of the two kinds of gels, B and C, coincide with the differences in their mechanical properties. Namely, for $c_p < 11\%$, the variation of the Young modulus with the cross link content is different being positive for B gels (the classical expectation) and the reverse negative for the C gels. This was explained by Oshmyan and Benguigui assuming that the matrix (the connected majority phase) is depleted from cross links which concentrate in clusters of all sizes. This agrees qualitatively well with the observations of the heterogeneous structure using scattering. We thus can relate the structure of the gel and its mechanical behavior.

One of us (L.B.) thanks V.Oshmyan for useful discussions and for his help in the calculation presented in the Appendix. He thanks also the fund for the Promotion of Research at Technion for support of this research.

Appendix: An example of space filling by spheres

In the first step of the filling, one puts spheres of radius unity, with their centers at the sites of a simple cubic lattice (lattice constant equal to 2). The filling coefficient is given by the volume of one sphere divided by the volume of one unit cell, *i.e.* $\alpha = \pi/6$. In the second step, one fills the space between the spheres by spheres with radius r_1, with $r_1 = 1/n$ and the volume of one of these spheres is $v_1 = 4\pi/3n^3$. The following steps are similar such that at the step k, one fills the residual space $(1-\alpha)^k$ by spheres with radius $r_k = 1/n^k$. The number of spheres introduced at the step k is $N_0(k)$, given by

$$N_0(k) = \frac{(1-\alpha)^k}{(4\pi/3)(1/n)^{3k}} \qquad \text{(A.1)}$$

or

$$N_0(k) = \frac{(1-\alpha)^k}{v_k} \qquad \text{(A.2)}$$

$N_0(k)$ is the discrete size distribution, giving the number of spheres with size v_k.

To replace this discrete distribution by a step distribution, one defines two volumes v_1 and v_2: $v_1 = (v_{k-1}+v_k)/2$ and $v_2 = (v_k+v_{k+1})/2$, such that $v_1 > v_k > v_2$. The number of spheres with volumes between v_1 and v_2 in the step distribution is

$$N(k) = \frac{N_0(k)}{v_2 - v_1} \tag{A.3}$$

or

$$N(k) = \frac{2(1-\alpha)^k n^3}{(n^6-1)(v_k)^2}\,\cdot \tag{A.4}$$

From the expression $v_k = (4\pi/3)n^{3k}$, one has

$$k = \frac{\ln(4\pi/3) - \ln(v_k)}{3\ln(n)}\,\cdot \tag{A.5}$$

Writing that $(1-\alpha)^k = \exp(k\ln(1-\alpha))$, one gets $(1-\alpha)^k$ proportional to $(v_k)^s$, where $s = -\ln(1-\alpha)/(3\ln(n))$. Finally it is found that $N(k)$ is proportional to $(v_k)^{-b}$ with

$$b = 2 + \frac{\ln(1-\alpha)}{3\ln(n)}\,\cdot \tag{A.6}$$

For k large enough, one can consider the step distribution as continuous with a distribution $N(r) \propto r^{-3b}$. Since $2 < n < \infty$, the exponent $3b$ is between 5 and 6.

References

1. J. Bastide, S.J. Candau, in *Physical Properties of Gels*, edited by J.P. Cohen-Addad (J. Wiley, 1996), chap. 5.
2. N. Weiss, T. van Vliet, S. Silberberg, J. Polymer Sci. Phys. **17**, 2228 (1979).
3. V.F. Janas, F. Rodriguez, C. Cohen, Macromolecules **13**, 977 (1980).
4. Y. Cohen, O. Ramon, I.L. Kopelman, S. Mizrahi, J. Pol. Sci. Pol. Phys. **30**, 1055 (1992).
5. A.M. Hecht, R. Duplessis, E. Geissler, Macromolecules **18**, 2167 (1985).
6. V.G. Oshmyan, L. Benguigui, J. Phys. II France **6**, 1585 (1996).
7. A.M. Hecht, J. Phys. France **39**, 631 (1978); L. Benguigui, J. Phys. II France **5**, 437 (1995).
8. L.R.G. Treloar, *The Physics of Rubber Elasticity* (Clarendon Press, 1976).
9. E. Mendes, P. Lutz, J. Bastide, F. Boué, Macromolecules **28**, 174 (1995).
10. J.T. Koberstein, C. Picot, H. Benoit, Polymer **26**, 673 (1985). The procedure adopted is very similar to that used by several authors (Mallam *et al.*, Macromolecules **22**, 3356 (1989); Shibayama *et al.*, J. Chem. Phys. **97**, 6829 (1992) and also Ref. [5]) which analyze the scattering curve $I(q)$ as the sum of a Gaussian $\exp(-q^2L^2)$ (instead of our Eq. (1)) and a Lorentzian. We tried also this method but the fit appears to be less good. The interesting point is that the values of L we found are very near those of the characteristic length Ξ.
11. P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, 1979).
12. A. Guinier, G. Fournet, *Small Angles Scattering of X-Rays* (John Wiley, 1955).
13. Although the Guinier law is rigorously valid only for $qR < 1$, for our qualitative approach, we can take it for all the q range. See also the Figure 6 of reference [12] and also the remark made by these authors in p. 27 about the Guinier law as being a surprisingly good approximation.