

 Open access • Journal Article • DOI:10.1051/JPHYSLET:01979004009019700

Incoherent scattering near a sol gel transition — [Source link](#)

P. G. de Gennes

Institutions: Collège de France

Published on: 01 May 1979 - Journal De Physique Lettres (Les Editions de Physique)

Topics: Debye–Waller factor, Correlation function (statistical mechanics) and Critical exponent

Related papers:

- [Mechanical measurements in the reaction bath during the polycondensation reaction, near the gelation threshold](#)
- [Frequency Dependence of Viscoelastic Properties of Branched Polymers near Gelation Threshold](#)
- [Gelation and critical phenomena](#)
- [Viscoelasticity of near-critical gels.](#)
- [Critical dynamics of the sol-gel transition.](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/incoherent-scattering-near-a-sol-gel-transition-4zf4dnuf8z>



HAL
open science

Incoherent scattering near a sol gel transition

P.-G. de Gennes

► **To cite this version:**

P.-G. de Gennes. Incoherent scattering near a sol gel transition. Journal de Physique Lettres, Edp sciences, 1979, 40 (9), pp.197-199. 10.1051/jphyslet:01979004009019700 . jpa-00231606

HAL Id: jpa-00231606

<https://hal.archives-ouvertes.fr/jpa-00231606>

Submitted on 1 Jan 1979

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

LE JOURNAL DE PHYSIQUE - LETTRES

Classification
Physics Abstracts
 66.10 — 82.35

Incoherent scattering near a sol gel transition

P. G. de Gennes

Collège de France, 75231 Paris Cedex 05, France

(Reçu le 9 janvier 1979, accepté le 13 mars 1979)

Résumé. — Nous calculons la fonction de self corrélation de van Hove pour un monomère marqué dans un système en cours de gélification. L'analyse est basée sur la distribution de Stauffer pour les tailles d'amas, plus une hypothèse de type loi d'échelle pour la viscosité à différentes échelles spatiales.

1) Dans la phase sol, la fonction intermédiaire $I_k(t)$ (k = vecteur d'onde, t = temps) doit décroître comme $t^{-\beta/(v+s)}$ où β , v et s sont les exposants critiques de la fraction gel, de la longueur de corrélation, et de la viscosité macroscopique.

2) En phase gel $I_k(t \rightarrow \infty)$ est fini et, pour $k \rightarrow 0$, est égal à la fraction gel.

Les propriétés 1) et 2) pourraient être testées par battement de photons avec un faible pourcentage de monomères marqués.

Abstract. — We consider the self correlation function for *one* monomer in a gelating system near the sol gel transition. Our analysis is based on the Stauffer distribution function for cluster sizes, plus a scaling ansatz for the viscosity at different spatial scales.

1) In the sol phase, the intermediate scattering function $I_k(t)$ (for wavevector k) is predicted to decrease like $t^{-\beta/(v+s)}$ where β , v , and s are critical exponents for the gel fraction, the correlation length, and the macroscopic viscosity (t being the time).

2) In the gel phase, $I_k(t \rightarrow \infty)$ is finite and defines a Debye Waller factor. Near $k = 0$, this is equal to the gel fraction. These properties might be checked by photon beat methods, using a dilute set of labelled monomers.

1. **Introduction.** — The *coherent* scattering of light by a (concentrated) gelating system is not large near the gel point : the important fluctuations are not in the concentration, but in the connectivity. The main aim of this note is to point out that the *incoherent* scattering is of greater interest. In principle, the effects which we have in mind could be probed by neutron scattering on the protons of the polymer, at small scattering wavevector \mathbf{k} , and at ultralow energy transfers $\hbar\omega$ [1]. However, the present set ups, even in their most sophisticated form [2] do not allow yet for the very low values of ω required here. A more accessible method is based on photon beats [3] using as scattering centres a *dilute* system of modified monomer (it may be feasible to match the refractive indices of the solvent and of the unmodified monomer). What is measured then is a correlation function of the form

$$\begin{aligned} I_k(\omega) &= (2\pi)^{-1} \int dt e^{i\omega t} \langle e^{i\mathbf{k} \cdot [\mathbf{r}(t) - \mathbf{r}(0)]} \rangle \\ &= (2\pi)^{-1} \int dt e^{i\omega t} I_k(t) \end{aligned} \quad (1)$$

where the bracket represents an average over all modified molecules, and \mathbf{r} is the position of *one* of them. We shall discuss here the function $I_k(t)$ in a chemically reacting system — e.g. a polycondensation of small, multifunctional units at rather high concentrations, in a good solvent. The fraction of reacted bonds will be denoted by p , and the gelation threshold by p_c . Near p_c , we expect to have large clusters described correctly by a percolation model [4], [5]. The geometrical properties of the clusters can be described in terms of critical exponents β , γ , and ν , defined as follows :

a) The gel fraction (S_∞) beyond threshold increases as $(\Delta p)^\beta$ where $\Delta p = p - p_c$ and $\beta \sim 0.4$.

b) The weight average molecular weight of the clusters in the sol phase ($p < p_c$) diverges by $|\Delta p|^{-\gamma}$, where $\gamma \sim 1.8$.

c) The spatial size of the largest clusters (below p_c) is called the correlation length ξ and diverges by $\Delta p^{-\nu} a$ where $\nu \sim 0.84$ and a is a monomer size.

As explained in ref. [4] the concentration of monomers belonging to n -mers decreases like

$$\varphi_n \cong n^{-(1+\beta/(\beta+\gamma))} \quad (2)$$

and the average size of an n -mer is

$$r_n \cong a n^{v/(\beta+\gamma)}. \quad (3)$$

The laws (2) and (3) hold for sizes below ξ , or for n smaller than a cut off value $N^* \cong (\Delta p)^{-(\beta+\gamma)}$.

Finally, the bulk viscosity of the sol phase $\bar{\eta}$ is expected to diverge by a certain power s of Δp

$$\bar{\eta} = \eta_0 (\Delta p)^{-s}. \quad (4)$$

A simple model [6] suggests that this exponent is also observed in conductance studies on random mixtures of normal and superconducting elements : for these systems, numerical calculations suggest $s \sim 0.7 - 0.8$ [7]. Here we shall keep s as an unknown exponent, separate from the geometrical exponents β, γ, v .

2. Brownian diffusion in the sol phase. — Let us first restrict our attention to the sol phase, and to wave vectors $k < 1/\xi$ so that all clusters may be considered as point scatterers. A labelled monomer belonging to a cluster of n units will then contribute to $I_k(t)$ a signal $\exp(-D_n k^2 t)$ where D_n is the diffusion constant of the cluster. We postulate for D_n a Stokes-Einstein form

$$D_n = \frac{k_B T}{6 \pi \eta(r) r} \quad (5)$$

where k_B is Boltzmann's constant and r is the radius of the cluster given by eq. (3). The delicate point in eq. (5) is the choice of the viscosity $\eta(r)$. This must be the viscosity of the sol for shears which are *not* uniform in space, but rather for shears which are modulated in space with a wavelength r . To construct $\eta(r)$ we start from three observations :

a) for $r > \xi$, the viscosity $\eta(r)$ must coincide with the macroscopic viscosity $\bar{\eta}$, given in eq. (4) ;

b) for r comparable to the monomer size a , the parameter $\eta(r)$ must become comparable to the viscosity η_0 of the original reaction bath (monomers + solvent, without any polymerization). The reason for this is that for $p = p_c$ most of the monomers are still engaged in small clusters (n of order of a few units) : a small molecule can move among them without serious hindrance ;

c) between the limits $r = \xi$ and $r = a$ we construct an interpolation which does not introduce any other characteristic length. It must then be a power law,

$$\eta(r) = \eta_0 \left(\frac{r}{a} \right)^{s/v} \quad (a < r < \xi). \quad (6)$$

The exponent in (6) ensures that condition a) is satisfied. From eqs. (4), (5), (6), we find a diffusion coefficient :

$$D_n = D_0 n^{-q} \quad (1 < n < N^*) \quad (7)$$

with

$$D_0 = k_B T / (6 \pi \eta_0 a) \quad \text{and} \quad q = (v + s) / (\beta + \gamma) \cong 0.8.$$

From (7) we arrive at an explicit form for the scattering function $I_k(t)$:

$$I_k = \sum_n \varphi_n e^{-D_n k^2 t} \cong \int_0^{N^*} dn n^{-[1+\beta/(\beta+\gamma)]} \exp(-n^{-q} \theta) \quad (8)$$

where $\theta = D_0 k^2 t$. The most important values of n in the integral (8) correspond to $D_n k^2 t \sim 1$ or $n = n_\theta = \theta^{1/q}$. We assume that the time t is not too large, so that $n_\theta < N^*$. (Physically, this means that, during an interval t , the largest clusters (of size ξ) have only moved over lengths smaller than k^{-1} .) Then the integral (8) can be safely extended to $n = \infty$, and the result is

$$I_k(t) = \text{const. } \theta^{\beta/(v+s)}. \quad (9)$$

Eq. (9) has some remarkable features :

1) it predicts a strongly non exponential relaxation (with an inverse power which is related to the viscosity exponent s) ;

2) in terms of the frequency shift ω , eq. (9) leads to a singular scattering function

$$I_k(\omega) \cong \omega^{-1+\beta/(v+s)} (D_0 k^2)^{-\beta/(v+s)} \quad (10)$$

(for $\omega > D_{N^*} k^2$) ;

3) both eqs. (9) and (10) are essentially independent of Δp : no special narrowing of the incoherent spectrum is expected at the gel point. (Critical narrowing occurs only for the fluctuations of an order parameter.) But, of course, the validity of eq. (9) is limited by the condition $n_\theta < N^*$. (In the opposite limit of very large times $I_k(t)$ decreases very fast towards zero.)

3. Debye Waller factor in the gel phase. — For $p > p_c$ the correlation function $I_k(t)$ has a finite limit at large times, reminiscent of the Debye Waller factor in crystals [8]

$$\begin{aligned} \text{Lim}_{t \rightarrow \infty} I_k(t) &= \langle e^{i\mathbf{k} \cdot \mathbf{r}(t)} \rangle \langle e^{-i\mathbf{k} \cdot \mathbf{r}(0)} \rangle \\ &= |f_k|^2 \end{aligned} \quad (11)$$

where f_k is a form factor for one labelled monomer attached to the infinite cluster. For $k \rightarrow 0$ we have $|f_k|^2 \rightarrow s_\infty$ (the gel fraction). In terms of the frequency distribution $I_k(\omega)$ eq. (11) leads to

$$I_k(\omega) = |f_k|^2 \delta(\omega) + I_k^1(\omega) \quad (12)$$

i.e. to the superposition of a strictly elastic peak and of an inelastic spectrum $I_k^1(\omega)$. For p not much larger than p_c , this inelastic part should be rather similar to eq. (10) : the motions of clusters smaller than ξ

inside the infinite network (of mesh size ξ) should not be affected very much by the presence of the network.

Eq. (12) suggests a determination of the gel fraction by optical methods. However, there are some complications :

a) Spurious scattering by dust particles or other defects may often dominate the elastic peak.

b) In the standard determination of S_∞ (washing out the finite clusters by a solvent flux) there is always an unwanted component due to the largest clusters, which move too slowly in the gel. The same difficulty is expected in the present method.

Another question of interest is related to the k dependence of the form factor f_k . It is plausible to assume that f_k is only a function of $k\xi$, and thus that the maximum excursion of a labelled monomer attached to the network is of the order ξ . But on the whole the experiments at $p < p_c$ appear more accessible.

Acknowledgments. — The author has benefitted from related discussions with M. Adam and F. Brochard.

Footnotes and References

- [1] MARSHALL, W., LOVESEY, S., *Theory of thermal neutron scattering* (Oxford) 1971.
- [2] See HAYTER, J. B., *Polarized neutrons in Neutron diffraction*, edited by H. Dachs (Springer, Berlin) 1978.
- [3] BENEDEK, G., in *Polarisation, Matière et Rayonnement* (Presses Universitaires, Paris) 1969, p. 49.
- [4] STAUFFER, D., *J. Chem. Soc., Faraday Trans. II* **72** (1976) 1354; see also *Phys. Rev. Lett.* **35** (1975) 74.
- [5] DE GENNES, P. G., *J. Physique Lett.* **37** (1976) L-61.
- [6] Note that the formula $s = 2\nu - \beta$ discussed in this note holds at high dimensionalities d (probably between $d = 4$ and $d = 6$) but not in the physical case $d = 3$.
- [7] STRALEY, J. P., *Phys. Rev.* **15B** (1977) 5733.
- [8] See for instance ABRAGAM, A., *L'effet Mössbauer* (Gordon and Breach, New York) 1964, p. 12-14.