Physics of the Solid State, 2024, Vol. 66, No. 1

12,08

Scaling Describtion of Network Structure of Gelatin Films

© D.V. Novikov

Kirov State Forest Technical University,
St. Petersburg, Russia

E-mail: dvnovikov65@mail.ru

Received October 17, 2023
Revised October 17, 2023
Accepted October 18, 2023

The structure of the physical network of macromolecules on the surface of thin films obtained from aqueous solutions of gelatin during cooling from 320 to 273 K have been studied with a resolution of 6−8 nm in the scale range of 8−80 nm using electron microscopy. The analysis of density-density correlation functions has shown that with an increase in the magnitude of the scale, there are structural transitions from coils of macromolecules to fractal aggregates of coils, and then to a homogeneous physical network of particle entanglements. The depth of the intramolecular transformation coil-helix determines the degree of interpenetration of coils and thereby the width of the scale interval of structural transitions. The unfolding of the coils increases the correlation length and spatial uniformity of the polymer network structure.

Keywords: thin polymer films, electron microscopy, density-density correlations, network structure, tangles of macromolecules.

DOI: 10.61011/PSS.2024.01.57864.228

1. Introduction

Special focus is made on the study of patterns of formation of film network structure from linear flexible polymers in three aspects. First, in terms of the effect of conformational [1] and phase [2,3] state of macromolecules on the density and spatial homogeneity of the formed particle fluctuation network. Second, due to the need to consider the history of interaction between the polymer and solvent, i. e. formation of macromolecule clusters in solution and cluster-cluster aggregation [4–6]. And finally, third, in terms of the possible use of fractal approach [7] to the scaling description of the polymer network structure, because the macromolecules and their aggregates are fractals [4,8,9].

Gel plays an important role among biopolymers used in the state-of-the art sol-gel transition technology [10], [3]. Typical properties of gel macromolecules include pronounced polymolecularity and quite high kinetic rigidity [11]. Therefore, the folded coil (FC) → helix type cooperative conformational transition implemented during gel aqueous solution cooling at $T = 313{-}293$ K is complicated and macromolecules generally proceed to the percolating coil (PC) state during gelling [9,12]. It has been shown earlier [13] that the main factor for the conformational transition is the configurational state of gel macromolecules or the defined amino-acid residue sequence. Two structural types of gel were detected — „non-helicalized“ (№ 1) and „helicalized“ (№ 2), respectively, with low and high FC → PC transition cooperativity and, thus, differing by almost factor of two in hydrodynamic volume of macromolecules at 293 K [12,14]. The general property of Gel № 1 and № 2 samples was their quite narrow molecular-mass distribution, they contained almost no oligopeptide fraction and had similar viscosity-average molecular weight $M \approx 10^5$ [13]. Such value of M corresponds to single co-called α-polypeptide chains [15].

Spatial correlations on the surface of films formed from aqueous solutions of Gel № 1 and № 2 samples during cooling from $T = 320$ to $T = 293$ K were studied in [16]. For visualization of the topological structure of films, gold surface decoration option of the electron-microscopic technique was used. The surface was preliminary activated by molecular bromine [17] to create nucleation centers of decorating nanoparticles in vacuum thermal gold plating. Resolution of this technique depends on the most probable interparticle distance and is equal to 6−8 nm depending on the type of Gel and concentration condition of film formation. In [16], „density-density“ type correlation functions $g(R)$ were obtained on scale $R < 15$ nm corresponding to the hydrodynamic radius of an individual macromolecule [14]. Therefore, the detected correlations [16] are actually related to the features of chain mass density distribution within a macromolecule and functions $g(R)$ on a larger scale shall be addressed to review the effect of the Gel type on the particle fluctuation network topology.

For this, electron-microscopic images of the gold decorated film surfaces of Gel № 1 and № 2 samples were examined herein in the scale interval 8−80 nm. To achieve the research objective, the computer image processing technique was improved to ensure digitizing of quite large arrays of decorating nanoparticle positions and to identify valid spatial correlations in the specified scale interval. Further to [16], new approaches to the calculation of density and degree of homogeneity of the polymer network structure through the analysis of discrete distribution patterns of the decorating gold nanoparticles were addressed.

2. Experimental procedure

Gel № 1 and № 2 samples with similar viscosity-average molecular weight ($\approx 10^5$), but with different unfolding capability of chains in aqueous solution. The hydrodynamic radius of macromolecules at $T = 293$ K was equal to 14.4 and 17.7 nm, respectively. 4−6 μm films were formed on glass at $T = 293$ K from 1.5 and 3 $\mathrm{g \cdot dl^{-1}}$ Gel aqueous solutions. The solutions were preliminary heated at $T = 320$ K during 30 min. Water content in vacuum treated (gold decorated) films was equal to 4% [16].

The density-density type spatial correlations on the „air" surface of films were studied using so-called „coarse-grained" radial functions $g(R)$ of decorating gold nanoparticle distribution. To obtain these functions, a computer step-scan technique was used to scan the particle distribution density ρ on two-dimensional images of the surface at δ interval corresponding to the most probable interparticle distance [18]. The correlation length was determined by the positions of singular points of functions $g(R)$. The area of the processed images was at least 0.5 $\mu\mathrm{m}^2$ and included more than 8000 nanoparticles. In contrast to [16], an additional grid was not applied to the decorating nanoparticle image herein, which significantly increased the calculation accuracy of functions $g(R)$.

The Gel network structure topology was studied be percolation on bound circles [19] with centers in gold nanoparticles. With gradually increasing circle radius R, the circles overlap and merge into clusters. At a certain value of R, a percolation cluster is formed to display the continuous fluctuation network of macromolecules. Formation of such cluster is recorded during the investigation of the dependence of a probability P of percolation on the bound circles on the degree ω surface filling by them. P was calculated as follows: $P = s_{max}/N$, where s_{max} is the maximum number of particles (circles) bound into a single cluster at a defined values of R or ω; N is the full number of particles on the gold decorated surface image. Inflection point of $P(\omega)$ meets the percolation threshold [8], and the critical value of ω^* characterizes the polymer network structure density.

The degree of spatial homogeneity of the macromolecule fluctuation network was assessed using the fluctuation scaling of the number of decorating nanoparticles. As known [20], particle number fluctuation FL in a two-dimensional space is expressed as follows

$$FL = 1 + 2\pi\rho \int_0^\infty \big(g(R) - 1\big) R dR, \qquad (1)$$

where ρ is the particle distribution density and $g(R)$ is the radial distribution function. When processing the final scale R images, equation (1) used the numerical correction ε [21]:

$$I(R) = 1 + 2\pi\rho \int_0^R \big(g(R) + \varepsilon - 1\big) R dR. \qquad (2)$$

By fitting of ε, $I(R)$ achieved the horizontal asymptote corresponding to FL [21,22]. Expression (2) was written as

$$I(R) = N(R) + (\varepsilon - 1)\pi\rho R^2, \qquad (3)$$

where $N(R)$ is the mean number of particles in the region with center in a particle and limited by the radius vector R. Equation (3) was used for computation and optimization of FL.

3. Findings and discussion

Decorating gold nanoparticle assembly (Figure 1) displays a continuous macromolecule fluctuation network in polymer films. The electron micrographs clearly show gold-free areas corresponding to the network cells. Computer-aided analysis of the decorated film sample surface images shows that the gold nanoparticle distribution density ρ increases in transition from sample № 1 to sample № 2. For example, in films produced from polymer solutions with a concentration of $c = 1.5\,\mathrm{g \cdot dl^{-1}}$ which is close to the threshold gelling concentration c_{thr} at $T = 293$ K [14], ρ is equal to $9.6 \cdot 10^3$ and $12.8 \cdot 10^3\,\mu\mathrm{m}^{-2}$ for samples № 1 and № 2, respectively. In this case, the most probable interparticle distance decreases (Figure 2). The obtained data indicates that the number of active centers of gold nanoparticle formation grows on the surface of sample № 2 compared with sample № 1 and is explained by unfolding of macromolecule coils.

„Coarse-grained" radial functions $g(R)$ of nanoparticle assembly density distribution demonstrate the network structure features of samples Gel № 1 and № 2 (Figure 3, a, b). Threshold polymer concentration c_{thr} in the solution corresponds to functions $g(R)$ with faint peak meeting the density alternation period L or the mean cell size of the polymer network structure (Figure 3, a). Periodical structure of the films indicates quite narrow cell distribution by size, which agrees with a relatively small interval of macromolecule cluster sizes in the solution near the gelling threshold measured by the viscosimetry and light scattering methods [12]. It is important that the effective hydrodynamic radius of clusters corresponds to L in films, which satisfies completely the cluster model of film superstructure formation [23].

The density of macromolecule fluctuation networks in films varies symbatically with c of Gel sample solutions, while with growth of c decrease in the correlation length ξ of the polymer network structure is observed and functions $g(R)$ approach 1.0 at $R = \xi$ (Figure 3, b).

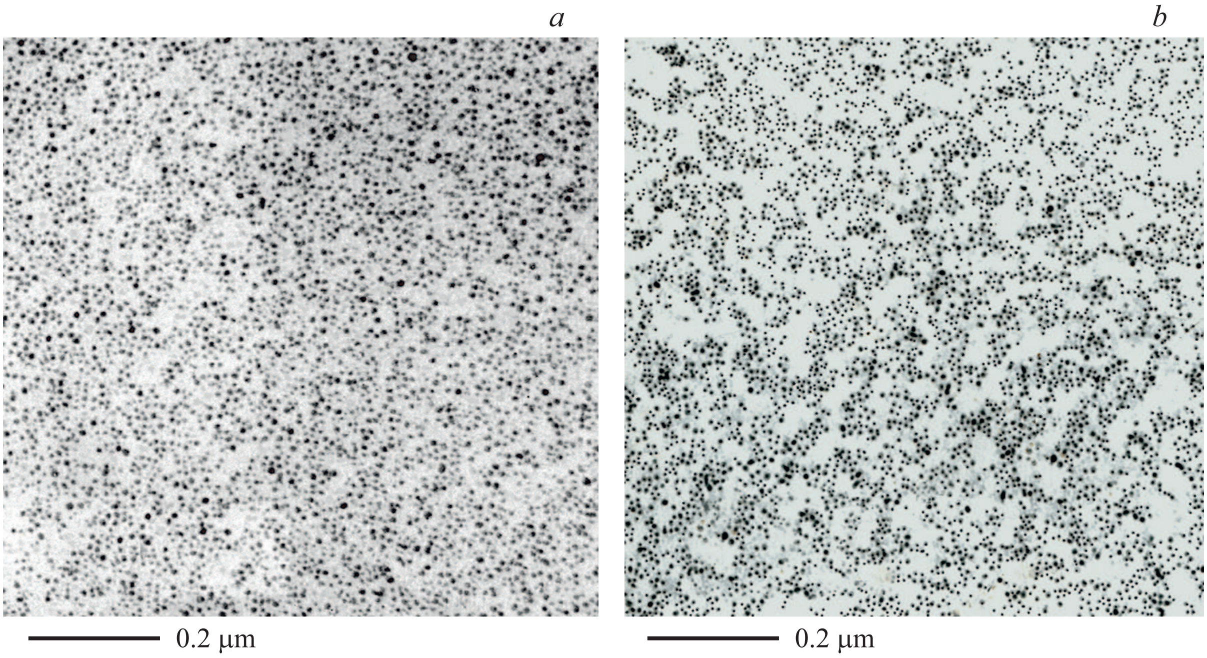

Figure 1. Electron micrographs of the gold decorated Gel films produced from $1.5\,\mathrm{g\cdot dl^{-1}}$ aqueous solutions. Samples: № 1 (a) and № 2 (b).

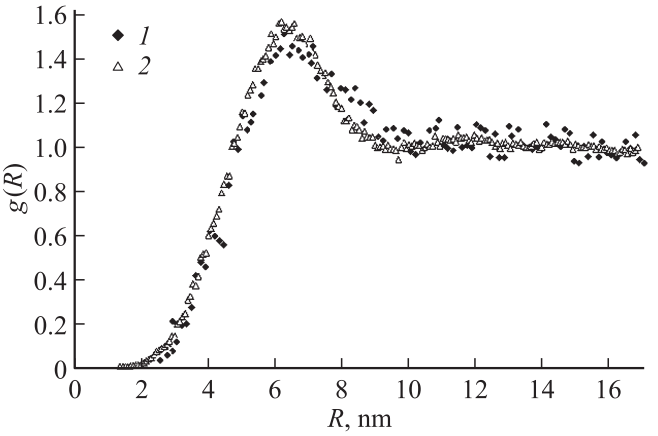

Figure 2. Functions $g(R)$ of distribution of individual gold nanoparticles on the Gel films produced from $1.5\,\mathrm{g\cdot dl^{-1}}$ aqueous solutions. Surface image scanning pitch is $\delta = 2\,\mathrm{nm}$. Samples: № 1 (curve *1*) and № 2 (curve *2*).

Local density fluctuations ρ result in a nonuniform variation of functions $g(R)$ with growth of R scale. In the initial section ($R < 15{-}25\,\mathrm{nm}$) the functions fall as a power function $g(R)\propto R^{D-2}$ valid for fractal objects with a fractal dimension D [4]. Moreover, two $g(R)$ variation regions are detected on the scale: the first corresponds to D 1.66 ± 0.01 (sample № 1) and 1.55 ± 0.02 (sample № 2), and the second corresponds to $D = 1.9 \pm 0.02$ for each of two samples. These scale regions in form of two linear sections are clearly identified by plotting log-log functions $g(R)$ (Figure 4). The first linear section corresponds to the macromolecule coils. Its boundary for sample № 1 is exactly equal to hydrodynamic radius $R_g = 14.4\,\mathrm{nm}$ [14] of the folded coil ($D = 5/3$ [9]), and for sample № 2 is lower than $R_g = 17.7\,\mathrm{nm}$ [14] of the percolating coil ($D = 3/2$ [9]). Thus, unfolding and overlapping of macromolecule coils due to FC → PC transition take place in sample № 2 compared with sample № 1. The second linear section of the curve in Figure 4 corresponds to the coil aggregate fragments for which $D = 1.9 \pm 0.02$. As known [7], $D = 1.9$ characterizes the topology of the internal percolation particle cluster in a two-dimensional space. Such macromolecule cluster is formed in the polymer solution at the gelling threshold at $c = c_{thr}$ [12,14]. The scale interval corresponding to the coil aggregates is also lower for sample № 2 compared with sample № 1 due to coil overlap.

The identified density-density type spatial correlations correspond to the multilayer cluster film structure and reflect structural transitions from macromolecule coils to fractal coil aggregates and then — on scale $R > L$ (or $R > \xi$), to a homogeneous particle fluctuation network.

Figure 5 shows the curves of the probability P of percolation cluster formation from the bound circles with centers in the decorating nanoparticles vs. the degree ω of filling with circles of the two-dimensional film surfaces of the given Gel samples. Inflection point of the curves meeting the critical percolation probability $P^* = 0.6$ defines the density ω^* of he polymer network structure. During unfolding of macromolecule coils, ω^* grows. For example, in the film formed from sample solution № 2 with $c \sim c_{thr}$,

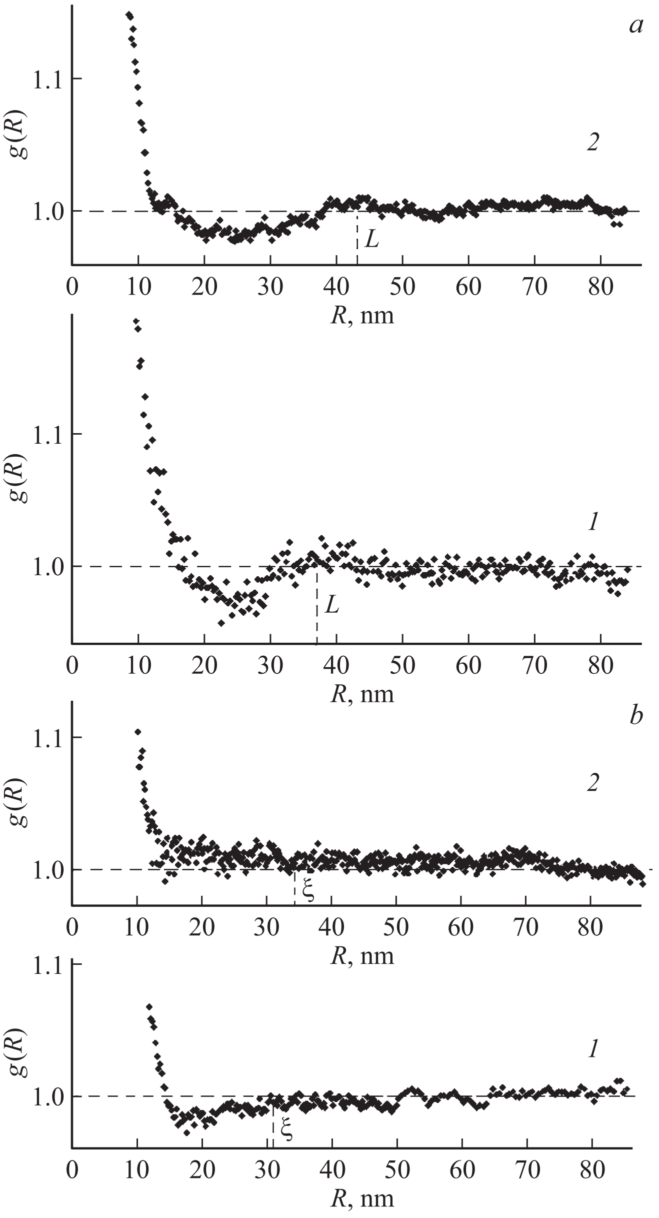

Figure 3. „Coarse-grained“ density-density type radial functions $g(R)$ for macromolecule fluctuation network. Surface image scanning pitch is $\delta = 8\,\mathrm{nm}$. Solution concentration $c = 1.5\,\mathrm{g \cdot dl^{-1}}$ (*a*) and $c = 3\,\mathrm{g \cdot dl^{-1}}$ (*b*). Samples: № 1 (curve *1*) and № 2 (curve *2*).

macromolecule fluctuation network resulting from FC → PC transition fills the space more densely by more than 10% compared with sample № 1 (Figure 5).

Decorating nanoparticle number fluctuations FL decrease with the growth of nanoparticle distribution density ρ on the film surface, while the values of FL for two Gel samples differ significantly. Thus, in films formed near the solution gelling threshold, FL for sample № 2 is twice lower than for sample № 1 (Figure 6). This indicates that the polymer network structure homogeneity increases with unfolding of macromolecule coils.

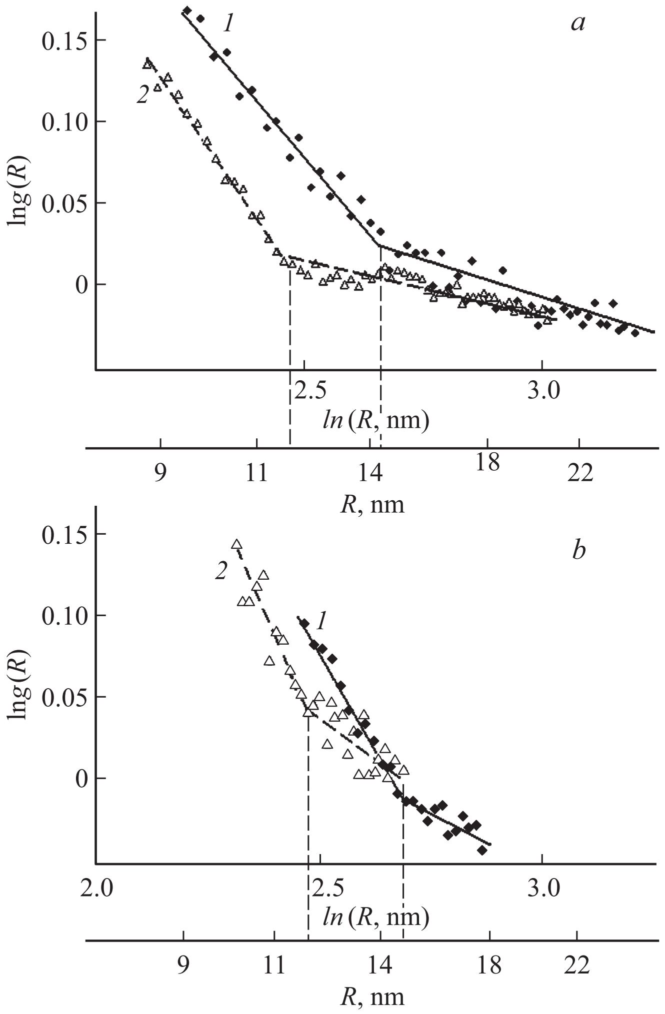

Figure 4. „Coarse-grained“ density-density type radial log-log functions $g(R)$. Solution concentration 1.5 (*a*) and $3\,\mathrm{g \cdot dl^{-1}}$ (*b*). Samples: № 1 (curve *1*) and № 2 (curve *2*).

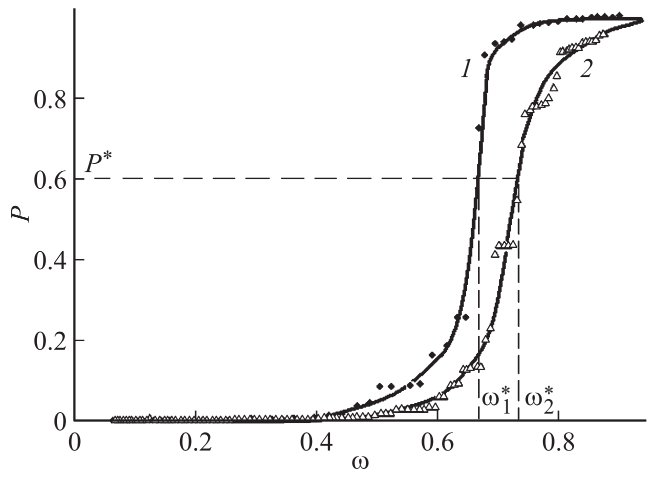

Figure 5. $P(\omega)$ curves for percolation on bound circles. Solution concentration $1.5\,\mathrm{g \cdot dl^{-1}}$. Samples: № 1 (curve *1*) and № 2 (curve *2*).

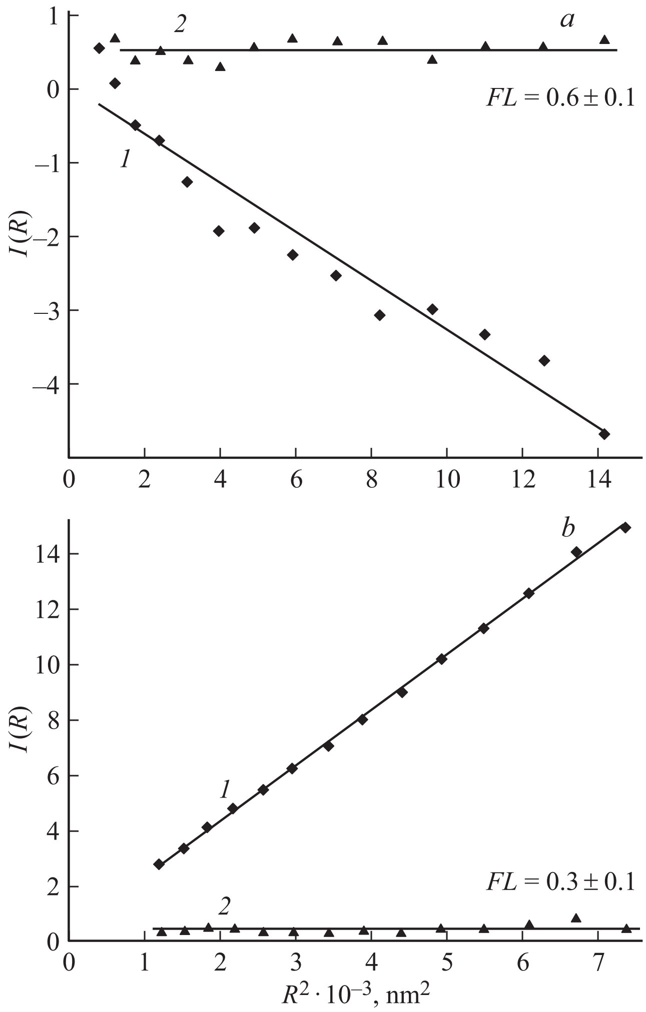

Figure 6. Calculation using equation (3) and optimization of the decorating nanoparticle number fluctuations FL. *a*) Sample № 1, numerical correction $\varepsilon = 0$ (curve *1*) and $\varepsilon = -0.031$ (curve *2*); *b*) Sample № 2, numerical correction $\varepsilon = 0$ (curve *1*) and $\varepsilon = 0.0006$ (curve 2). Solution concentration $1.5\,\text{g}\cdot\text{dl}^{-1}$.

4. Conclusion

Application of the fractal approach to the scaling description of the Gel film surface decorated with gold nanoparticles made it possible to display all structuring stages of the macromolecule fluctuation network — transition from macromolecule coils to coil aggregates and then — to the infinite particle cluster during the cluster-cluster aggregation. Geometrical dimensions of the multilayer Gel network cluster structure elements in films agree with the hydrodynamic dimensions of the particles in solution at the gelling threshold. Differences in dimensions are caused by coil interpenetration during macromolecule unfolding due to conformational transition FC (fractal dimension $D = 5/3) \rightarrow$ PC $(D = 3/2)$. Intramolecular cooperative transition FC → PC increases the correlation length and spatial homogeneity of the polymer network superstructure.

Conflict of interest

The author declares that he has no conflict of interest.

References

[1] T.M. Birshtein. Vysokomolekulyar. soyedinenya **61A**, 542 (2019). (in Russian).

[2] I.M. Lifshits, A.Yu Grosberg, A.R. Khokhlov. Uspekhi fiz. nauk, **127**, 353 (1979). (in Russian).

[3] G.M. Bartenev, S.Ya. Frenkel', Fizika polymerov. Khimiya, L. (1990). 432 p. (in Russian).

[4] D.V. Novikov, A.N. Krasovsky, N.A. Osmolovskaya, V.I. Efremov. FTT **49**, 364 (2007). (in Russian).

[5] H. Boediker, P. Doty. J. Phys. Chem. **58**, 968 (1954).

[6] S. Popa-Nita, P. Alcouffe, C. Rochas, L. David, A. Domard. Biomacromolecules **11**, 6 (2010).

[7] J. Feder. Fractals. Plenum Press, N.Y., London (1988). 260 p.

[8] J. Feder, T. Jossang, E. Rosenqvist. Phys. Rev. Lett. **53**, 1403 (1984).

[9] V.G. Baranov, S.Ya. Frenkel, Yu.V. Brestkin. Dokl. AN SSSR **290**, 369 (1986). (in Russian).

[10] V.N. Izmailova, S.R. Derkach, M.A. Sakvarelidze, S.M. Levachev, N.G. Voronko, G.P. Yampolskaya. Vysokomolekulyar. soyedinenya **46C**, 2216 (2004). (in Russian).

[11] A. Veis. The macromolecular chemistry of gelatin. Academic Press, N.Y. (1964). 433 p.

[12] A.N. Krasovsky, V.P. Nikolaev, A.M. Shlyakov, S.S. Mnatsakanov. Vysokomolekulyar. soyedinenya 37A. 273 (1995).

[13] A.N. Krasovsky, V.G. Baranov, E.P. Bochko, S.S. Mnatsakanov. ZhPKh **66**, 796 (1993). (in Russian).

[14] A.I. Andreeva. Sravnitelnoe izuchenie vyazkosti i struktura zhelatina v vodnykh i mitsellyarnykh rastvorakh v sisteme izooktan-voda-(bis-2-etilgeksil)sulfosuktsinat natriya. Avtoref. diss. kand. tekh. nauk. SPb., SPbGUKiT, 1998) 29 s. (in Russian).

[15] A. Rich, F.H.C. Krick. Nature **176**, 915 (1955).

[16] D.V. Novikov, A.N. Krasovsky. FTT **54**, 1582 (2012). (in Russian).

[17] D.V. Novikov, A.V. Varlamov, S.S. Mnatsakanov. Polymer Science **35B**, 1693 (1993). (in Russian).

[18] D.V. Novikov, FTT **63**, 146 (2021). (in Russian).

[19] A.L. Efros. Fizika i geometriya besporyadka. Nauka, M., (1982), 176 s. (in Russian).

[20] A. Ishara. Statistical Physics. Academic Press, N.Y. (1971). 450 p.].

[21] P. Wojtaszczyk, E.K. Mann, B. Senger, I.C. Voegel, P.J. Schaaf. J. Chem. Phys. **103**, 8285 (1995).

[22] D.V. Novikov, ZhPKh **81**, 157 (2007). (in Russian).

[23] B.M. Smirnov. Fizika fraktal'nykh klasterov. Nauka, M., (1991). 134 s. (in Russian).

Translated by E.Ilinskaya