Phase state features of non-equilibrium thermodynamic polymer-solvent systems

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Abstract. A boundary between the regions of labile and metastable phases of non-equilibrium thermodynamic polymer-solvent systems is determined as applied to the synthesis products of the sol-gel technology. Models that qualitatively and quantitatively predict properties and morphology of nanostructured composites, obtained on the basis of the analyzed systems, have been developed. The simulation results were verified using experimental data of atomic force microscopy.

At present, both 3D materials and thin nanostructured films are nanotechnology products [1–2]. A wide variety of film surface morphologies is required for using in various fields. As The results of experiments on the synthesis of sol-gel composites have shown that it is possible to obtain three-dimensional reticulated composites, a periodic system of pores on the surface, and a system of spherical fractal clusters by varying the technological conditions [3]. The first two types of morphology of composites are the product of spinodal decomposition of the polymer-solvent system, and the latter is realized during decomposition of the system in the region of metastable states, namely, between the spinodal and binodal curves. The aim of this work is to analyze the phase state of non-equilibrium thermodynamic systems obtained using the sol-gel technology.

All potential products of the sol-gel technology are widely used in nanoelectronics. Thus, an ordered system of pores on the surface can be used as containers for bio-nanomaterials, and a system of spherical clusters can be used as a matrix realizing a multiple-barrier quantum structure [4]. However, the most widespread application is found for three-dimensional mesh composites, which are sensitive elements of new generation gas and vacuum sensors.

To create a controlled technology for the synthesis of self-organizing fractal systems, it is necessary to find a boundary between the regions of labile and metastable phases, i.e., to find the locus of points on the phase diagram that satisfy the condition:

\[
\left[ \frac{\partial^2 \Delta G^m}{\partial X^2} \right]_{p,T} = 0,
\]

where \(\Delta G^m\) is the Gibbs energy of the polymer-solvent system; \(X\) is the mole fraction of the system component. Let us find the spinodal equation. To do this, we use the ratio:

\[
\Delta G^m = \Delta G^m(X, T, p) = \frac{\partial^2 \Delta G^m}{\partial X^2} X = X^2
\]
\[ \Delta G^m = \Delta H^m - T \Delta S^m, \quad (2) \]

where \( \Delta H^m \) and \( \Delta S^m \) are the enthalpy and entropy of mixing, respectively; \( T \) is the temperature.

In the isothermal approximation, the enthalpy of mixing will not depend on the concentration of the polymer in the solution; therefore, its concentration derivative will be equal to zero. Then the equation to the locus of the spinodal points will correspond to the equation:

\[ -T \frac{\partial^2 S^m}{\partial X^2} = 0. \quad (3) \]

We find the configuration entropy from the Boltzmann relation \( S = k \ln W \), where \( k \) is the Boltzmann constant; \( W \) is thermodynamic probability determined by the number of microstates that can realize a given macrostate of the system. Let us assume that \( N \) is the number of solvent molecules and \( n \) is the number of polymer molecules in the polymer solution at the time \( \tau = 0 \), and the evolution of the number of polymer molecules being determined by solving the Smoluchowski equation:

\[ \tau \frac{\partial}{\partial \tau} n + \nu \frac{\partial}{\partial s} n = K \nu n c_0, \quad (4) \]

where \( \nu \) is the volume of sol; \( c_0 \) is the initial concentration of molecules in the sol; \( K \) is the constant defined as:

\[ K = \zeta \frac{4kT}{3\eta}. \quad (5) \]

where \( \zeta \) is effective collision probability of colloidal particles in the sol; \( \eta \) is the viscosity of sol.

Then the thermodynamic probability \( W \) is determined at any time moment \( \tau \) as:

\[ W = \frac{(N + n(\tau))!}{N! n(\tau)!}. \quad (6) \]

Using Stirlin’s ratio \( \ln X! = X (\ln X - 1) \), we obtain:

\[ \ln W = (N + n(\tau)) \ln(N + n(\tau)) - N \ln(N) - n(\tau) \ln(n(\tau)). \quad (7) \]

Let us find the molar fraction of the polymer in the sol solution at the moment of time \( \tau \). It is defined by the following equality:

\[ X = \frac{n(\tau)}{N + n(\tau)}. \quad (8) \]

Equation (8) implies that:

\[ n(\tau) = \frac{NX}{1 - X}, \quad (9) \]

\[ \frac{\partial n(\tau)}{\partial X} = \frac{N}{(1 - X)^2}. \quad (10) \]

Then, taking into account (9) and (10), the first derivative of the entropy with respect to the molar fraction of the polymer will be expressed in the form:

\[ \frac{\partial S^m}{\partial X} = \frac{\partial S^m}{\partial n(\tau)} \frac{\partial n(\tau)}{\partial X}. \quad (11) \]

In this case, the first derivative of the entropy with respect to \( n(\tau) \) is defined as:
\[
\frac{\partial S^m}{\partial n(\tau)} = k \left[ \ln(N + n(\tau)) - \ln(n(\tau)) \right].
\]  

(12)

Transforming (10) taking into account (11), we obtain:

\[
\frac{\delta S^m}{\delta X} = k \ln(1/X) \frac{N}{(1 - X)^2}.
\]

(13)

The second derivative of the entropy with respect to the molar fraction of the polymer will have the form:

\[
\frac{\partial^2 S^m}{\partial X^2} = kN \left[ \frac{X}{(1 - X)^2} - \frac{\ln(1/X)^2}{(1 - X)^3} \right].
\]

(14)

Then the spinodal equation can be written implicitly as:

\[
\ln \left( \frac{1}{X} \right)^{2T} = X^2T - XT,
\]

(15)

Graphically, dependence (15) is shown in figure 1.

**Figure 1.** The locus of the spinodal points of a non-equilibrium thermodynamic system obtained using the sol-gel technology.

Thus, by varying modes for obtaining sol-gel materials, it is possible to get a wide variety of types of film surfaces. Besides, due to the application of the theory of fractals and the theory of coagulation, the average value of the composite cluster diameter or the thickness of the percolation network branches can be determined.

To study the effect of the preparation conditions, a number of samples with the most typical properties of sol-gel composites were obtained: 1) \(T = 340\, K, \; X = 0.185, \; \tau = 5\, h\); 2) \(T = 340\, K, \; X = 0.208, \; \tau = 1\, h\); 3) \(T = 310\, K, \; X = 0.208, \; \tau = 1\, h\); 4) \(T = 310\, K, \; X = 0.185, \; \tau = 5\, h\); 5) \(T = 310\, K, \; X = 0.125, \; \tau = 15\, h\).
According to the constructed theoretical models, samples 1, 2, and 3 are in the region of metastable states, i.e., a system of spherical fractal-like clusters should be the coagulation product. This assumption was justified by the results of studies of the morphostructure of the corresponding films. Research into the morphology of the film nanostructures, obtained in this work, was carried out using atomic force microscopy. The research results of the first three samples are shown in figure 2.

![Figure 2](image1.png)

**Figure 2.** Morphostructures of samples obtained by decomposition in the region of metastable phases.

The results obtained indicate good agreement between model concepts of decomposition of polymer solutions and experimental data. However, it is necessary to estimate the diametrical sizes of the resulting clusters as well. For this, we will use the Smoluchowski model of fast coagulation under the assumption that Julien’s mathematical fractal is its product. Then the radius of the colloidal particle $R$ at time $\tau$ will be:

$$R(\tau) = \xi \ln((1+KC/\tau)/\ln(\xi)), \quad (16)$$

where $\gamma$ is the coefficient reflecting an increase of the aggregate radius during the next iteration; $\xi$ is the coefficient equal to the number of particles in a fractal aggregate.

Figure 3 shows the dependences reflecting the relationship (16). The dots on the graphs mark the experimental data of atomic force microscopy for the samples under study. It can be seen that, with the introduction of a correction for the effective collision probability, the kinetics of the evolution of sol-gel systems obeys the Smoluchowski theory of fast coagulation, and Julien’s fractal aggregate being the selected coagulation product, adequately describes real composites.

![Figure 3](image2.png)

**Figure 3.** Dependence of the cluster radius on the sol maturation time.

Let us consider typical samples obtained in the region of labile phases. According to the constructed models, the configurational entropy of the polymer-solvent solution decreases with time due to the growth of fractal aggregates, which leads to a decrease in the thermodynamic probability $W$. At some point in time, the product $T\Delta S^m$ becomes larger than $\Delta H^o$. This leads to the fact that the Gibbs free energy of mixing becomes a positive value. It follows from the general laws of thermodynamics that
in this case, a transition from a single-phase system to a two-phase system, namely, spinodal decomposition should begin. The system is decomposed into a solvent and a polymer. Due to the principle of minimum energy, being the surface one in this case, the liquid phase aggregates fractal spherical polymer particles around itself. When this system is annealed, the liquid phase of the solvent is removed, leaving a three-dimensional framework of the composite branches [5]. The resulting branches are not continuous, but arranged in hierarchical structures. The average branch diameter is determined by the average size of the cluster formed during coagulation.

According to atomic force microscopy data (figure 4), sample 4 has an average branch thickness of about 300 nm, and the proposed coagulation model determines the branch thickness of 400 nm. Sample 5 matured for 15 hours, and according to theoretical models, there was the process of fractal coagulation for the first 3 hours in the sol. Apparently, in the next 12 hours, two main processes (fractal coagulation, which caused a large distance between the pores on the surface, up to the elimination of the 3D system, and spinodal decomposition, which determines the resulting picture of the pore system) took place.

Thus, the constructed models make it possible to qualitatively and quantitatively predict the properties and morphology of nanostructured composites obtained using the sol-gel technology. They can find application in the development and production of sensitive elements for highly efficient gas and vacuum sensors.

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References
[1] Chen X, Put B, Sagara A, Gandrud K, Murata M, Steele J A, Yabe H, Hantschel T, Roelfaers M, Tomiyama M, Arase H, Kaneko Y, Shimada M, Mees M and Vereecken P M 2020 Science Advances 6(2) eaav3400
[2] Komolov A S, Lazneva E F, Gerasimova N B, Sobolev V S, Panina Yu A, Pshenichnyuk S A and Asfandiarov N L 2019 Physics of Solid State 61(3) 468–73
[3] Pronin I A, Averin I A, Yakushova N D, Karmanov A A, Moshnikov V A, Ham M-H, Cho B K and Korotcenkov G 2017 Arabian Journal for Science and Engineering 42(10) 4299–305
[4] Igoshina S E, Averin I A, Karmanov A A, Pronin I A, Yakushova N D and Moshnikov V A 2018 IOP Conference Series: Materials Science and Engineering 012062
[5] Li X, Nakagawa S, Tsuji Y, Watanabe N and Shibayama M 2019 Science Advances 5(12) eaax8647