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Spinodal Decomposition in Polymeric Systems

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The characteristics of the phase separation in multicomponent systems in the region of unstable states are considered using the formal treatment of Cahn and Hilliard. The general theories of spinodal decomposition developed recently are briefly discussed. The characteristic features of systems based on high-molecular-weight components are analysed from the standpoint of phase separation using the Debye-van Aartsen relations. The theory of spinodal decomposition developed by de Gennes and Pincus for mixtures based on two homopolymers is examined in detail. The principal results obtained in experimental studies of phase separation of the liquid-liquid type in polymer-solvent and polymer-polymer systems are presented. The possibilities in the application of the concept of spinodal decomposition to a wider range of complex multicomponent systems as well as the results obtained recently by the authors of the review in the study of phase separation in systems of this kind are discussed. The attempts at the analysis of the spinodal decomposition phenomena within the framework of the non-linear thermodynamics of irreversible processes developed by Prigogine are considered.
The bibliography includes 89 references.

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I. INTRODUCTION

It is known that, depending on the character of the interaction of the components, binary systems can consist of one or two phases. If a system of this kind consists of only one phase, microregions with a non-homogeneous decomposition of the components, namely composition fluctuations, exist in it. After time intervals of the order of magnitude of the duration of diffusional jumps, such fluctuations are spontaneously generated or dissipated. A characteristic feature on the basis of which a particular system can be classified as a one-phase system, is the presence of an equilibrium distribution of fluctuations.[1] Such a distribution is fully controlled by external conditions and the composition of the system and is independent of time. At the same time, there exist two-phase systems with a high degree of dispersion which are outwardly similar to the one-phase systems. The principal difference between the former systems and one-phase systems is the absence of an equilibrium distribution of microregions of inhomogeneity.

An important difference between one- and two-phase systems also consists in the fact that in the latter systems the microregions of inhomogeneity consist of microvolumes with the properties of pure phases. In principle, the size of such microregions can increase with time until the complete separation of the system into layers. The transition from a one-phase system to a two-phase system is attributed to an enhancement of the intensity of the composition fluctuations and the development of their basis of microregions of new phases. This takes place when the system is in a metastable region (between the binodal and the spinodal) or in an unstable region (within the spinodal) of the phase diagram.

The classical approach to the problem of the stability of phases has been developed by Gibbs.[2] According to Gibbs, the most characteristic points on the free energy—concentration relation $G(c)$ are points of inflexion at which the sign of the second derivative changes. When the condition $\partial^2 G/\partial c^2 > 0$ holds, the diffusion fluxes of the components are directed towards a diminution of the composition fluctuations, while under the condition $\partial^2 G/\partial c^2 < 0$ the directions of the diffusion fluxes are reversed. In this case the intensity of the composition fluctuations in the system increases—as a one-phase system it becomes unstable and should decompose spontaneously into regions with equilibrium compositions. The region of unstable states is bounded on the phase diagram by a curve called the spinodal. On the "outer" side, the region of metastable states bounded by the binodal adjoins the spinodal. In this region, as in the case of a one-phase binary system, the diffusion fluxes of the components are directed towards the diminution of the composition fluctuations. Nevertheless, the segregation of a new phase begins precisely in this part of the diagram. Under these conditions, the occurrence of the energetically unfavourable effect involving the formation of an interface makes the system unstable only in relation to fluctuations whose dimensions are greater than the critical value and the fluctuations themselves have a composition similar to that of the new phase. Such fluctuations are called critical nuclei.

The appearance of such critical nuclei in an A + B mixture, for example nuclei based on component A, leads to the formation around the nucleus of a zone depleted in component A. The diffusion fluxes tend to make good the resulting deficiency and at the same time feed the nucleus which has been formed. This is responsible for the continuous growth of the microvolumes of the new phase. In this

case phase separation proceeds via a mechanism involving nucleation and growth. A characteristic feature of the "classical" theories of nucleation is that the critical nucleus is regarded as a microscopic drop of a pure new phase. The treatment of the kinetic aspects of the appearance, growth, and coalescence of the microregions of the segregated phase within the bulk of the homogeneous solution in the region of metastable states is based on this hypothesis.[3]

A general approach to phase separation in inhomogeneous systems has been developed in the studies of van der Waals, Hart, Cahn and Hilliard.[4-11] The theory of spinodal decomposition in solution developed by Cahn and Hilliard has proved particularly fruitful[7-11] and has been confirmed experimentally by numerous data on phase separation in metallic alloys and inorganic glasses.[12,13] In particular, Cahn and Hilliard have established that the critical nuclei formed on nucleation in the metastable state can differ significantly in their composition from the particles of the new phase.[8] In the immediate vicinity of the binodal, critical nuclei are formed whose composition, radii, and interfaces are indeed close to the characteristics of the classical nuclei of the new phase. However, as the spinodal is approached, the deviations of the concentration in the nuclei from that in the initial solution become smaller to an increasing extent, the radii of the nuclei become increasingly larger, and the work of their formation approaches zero.

II. THEORETICAL IDEAS CONCERNING PHASE SEPARATION IN BINARY SYSTEMS VIA THE SPINODAL MECHANISM

According to the ideas developed by Cahn and Hilliard,[6-8] the free energy of a binary system with small composition fluctuations can be formulated as follows in terms of a linear approximation:

$$F = \int_v [f(c) + k(\nabla c^2)]\,dv \,, \qquad (1)$$

where $f(c)$ is the density of the free energy of the homogeneous system in which the concentration of component A is c and $k(\nabla c)^2$ is the "gradient energy", which represents the first term in the expansion of the free energy, describing its increase as a result of the appearance of the concentration (composition) gradient. Taking into account the expansion of $f(c)$ in terms of the average concentration c_0, the difference between the free energies of the inhomogeneous system and the initial homogeneous solution is

$$\Delta F = \int_v \left[\frac{1}{2}\left(\frac{\partial^2 f}{\partial c^2}\right)_{c_0}(c - c_0)^2 + k(\nabla c)^2\right] dv \,. \qquad (2)$$

Bearing in mind that the quantity $k(\nabla c)^2$ is always positive, the condition for the instability of the system in relation to small composition fluctuations can be written as follows.

$$\partial^2 f/\partial c^2 < 0 \,. \qquad (3)$$

For composition fluctuations corresponding to a periodic variation of the density along the coordinate x, we have

$$c - c_0 = A\cos(qx) \,, \qquad (4)$$

where A is a constant factor and q the wave vector. The sum of such fluctuations for different periods, representing the sum of the Fourier components in the expansion of the concentration, can be regarded as the local difference between the concentrations. The contribution of the component with the wavelength $2\pi/q$ in the relation for the free energy change as a result of composition fluctuations is

$$\frac{1}{4}VA^2\left[\left(\frac{\partial^2 f}{\partial c^2}\right) + 2kq^2\right] , \qquad (5)$$

where V is the volume of the system.

When condition (3) holds, the contribution of an expression of type (5) to ΔF becomes negative if the wavelength of the Fourier component reaches the critical value λ_c defined by the expression

$$q_c = \left(-\frac{\partial^2 f}{\partial c^2}\cdot\frac{1}{2k}\right) . \qquad (6)$$

In the initial stages of spinodal decomposition, where the linear approximation of the Cahn–Hilliard theory [Eqn.(1)] is valid, the difference between the local chemical potentials of the components can be represented in the form[9]

$$\mu_A - \mu_B = \left(\frac{\partial F}{\delta C_A}\right) - \left(\frac{\partial f}{\partial c_A}\right) - 2k\nabla^2 c_A \,. \qquad (7)$$

In this case the diffusion fluxes of the components are expressed by the relation

$$J_A = -J_B = M\nabla(\mu_A - \mu_B) \,, \qquad (8)$$

where M is a phenomenological coefficient characterising the diffusional mobility of the components. Using the relations presented, the diffusion equation can be reduced to the form

$$\partial c/\partial t = M(\partial^2 f/\partial c^2)\nabla^2 c - 2Mk\nabla^4 c \,. \qquad (9)$$

The coefficient of $\nabla^2 c$ is the diffusion coefficient.

Thus, in contrast to Fick's Second Law, Eqn.(9) contains a term proportional to $\nabla^4 c$. On the spinodal, the diffusion coefficient changes sign, which leads to an enhancement of the composition fluctuations characteristic of spinodal decomposition. Under these conditions, phase separation is initiated by the selective growth of sinusoidal composition fluctuations and takes place on the basis of microregions with small deviations from the composition of the equilibrium solution. The solution of the diffusion equation yields the time variation of the local concentration difference $c - c_0$:

$$c - c_0 = \exp[R(q)t]\cdot\cos(qx) \,, \qquad (10)$$

where $R(q)$ in the exponent represents the so-called amplification factor:

$$R(q) = -Mq^2(1 + 2q^2) . \qquad (11)$$

It is seen from Eqn.(5) that, when $q > q_c$, we have the factor $R(q) < 0$ and consequently the concentration difference diminishes with time. This corresponds to the decay of the composition fluctuations. On the other hand, when $q < q_c$, the quantity $R(q)$ becomes positive and the concentration difference increases with time. The amplification factor has a maximum when

$$q_m = \frac{1}{2}\left[-\left(\frac{\partial^2 f}{\partial c^2}\right)/k\right]^{1/2} \,. \qquad (12)$$

For the maximum value of $R(q)$, a sharp maximum is obtained in the quantity $c - c_0$ specified by Eqn.(10). In the general solution of the diffusion equation one can therefore neglect all the components of the Fourier expansion of the difference $c - c_0$ except that which corresponds to q_m.

Thus in the initial stages of the spinodal decomposition, an exponential increase of the intensity of the composition fluctuations, whose wavelength is defined by Eqn.(12), is observed. The following equation holds between the optimum and critical wavelengths of spinodal decomposition:[9]

$$\lambda_m = \sqrt{2}\lambda_c \,. \qquad (13)$$

For later stages of the spinodal decomposition, i.e. with increase of $c - c_0$, Eqn.(1) becomes a rough approximation, since a continuous increase of $c - c_0$ with time follows from it. In fact the concentration difference cannot exceed a limiting value corresponding to the segregation of microregions of the pure components.

It has been shown[14] that the diffusion equation for later stages of spinodal decomposition becomes

$$\partial c/\partial t = D_1\nabla^2 c - D_2\nabla^4 c + D_1'(\nabla c)^2 + D_n \quad (14)$$

where

$$D_1 = \frac{M}{N_v}\left[-\frac{\partial^2 f}{\partial c^2}\right]; \; D_2 = 2Mk/N_v; \; D_1' = \partial D_1/\partial c$$

(N_v is the number of atoms per unit volume) and D_n is a higher-order non-linear expression.

In those cases where the volume of the system depends on its composition, the sequence of infinitesimal composition fluctuations in the solid should lead to the appearance of elastic deformations.[11] It has been shown that this results in the appearance of an additional contribution to the free energy of the system described by the expression[10,11]

$$\eta^2 E(c - c_0)^2/(1-\nu) \quad (15)$$

where E is Young's modulus, ν the Poisson coefficient, and η the linear expansion corresponding to a unit change in the composition. When account is taken of this relation, the contribution of the Fourier component with a wavelength $2\pi/q_m$ to ΔF can be represented by the expression

$$\frac{1}{2}VA^2\left[\left(\frac{\partial^2 f}{\partial c^2}\right) + \frac{2\eta^2 E}{1-\nu} + 2kq^2\right] \quad (16)$$

Consequently, for a system with elastic deformations resulting from the local change in composition, the limit of stability is defined by the condition

$$\partial^2 f/\partial c^2 + Y = 0 \quad (17)$$

where $Y = 2\eta^2 E/(1 - \nu)$.

Thus elastic stresses stabilise the system. Eqn.(17) yields the position of the so-called coherent spinodal, in contrast to the "chemical" spinodal determined solely by the chemical nature of the components and expressed by the conditions $\partial^2 f/\partial c^2 = 0$.

Cahn's theory nowadays continues to be the main one employed in the study of the kinetics of phase separation via the spinodal mechanism in ageing metallic alloys,[12] in inorganic glasses,[13] etc. The corresponding experiments are based on the application of methods of the low-angle scattering of X-rays.

The application of the Cahn–Hilliard theory to the interpretation of experimental data for the scattering of radiation makes it possible to obtain characteristics such as the optimum and critical wavelengths of the spinodal decomposition, the second derivative of the free energy with respect to composition, the quantities $\eta^2 E/(1 - \nu)$ (if elastic stresses arise in the system), and k in Eqn.(1). The calculations carried out for this purpose are based on the analysis of the time variation of the intensity of X-ray scattering in the region of the diffraction maximum. It has been shown[15] that this variation is defined by the relation

$$I(q, t) = I(q, 0)\exp[2R(q)t] \quad (18)$$

where

$$R(q) = -(D/f'')(f'' + 2\eta^2 E/(1-\nu) + 2kq^2)q^2 \quad (19)$$

(D is the mutual diffusion coefficient for the components). It follows from the theory that the following main features of spinodal decomposition can be isolated: (1) the linear dependence of the logarithm of the intensity of the scattered radiation on time; (2) the linear dependence of $R(q)/q^2$ on q^2; (3) the presence of an interference maximum in the relation between the intensity of the scattered radiation and the angle. The manifestation of these effects makes it possible to reach a qualitative conclusion concerning the presence or absence of spinodal decomposition and analysis of the corresponding relations permits the determination of the most important characteristics.

It follows from Eqn.(18) that the slope of the linear relation $\ln[I(q, t)] = \phi(t)$ yields $R(q)$. It it is positive, the composition fluctuations in the system are enhanced, i.e. separation via the spinodal mechanism takes place. The quantity $(-2kD/f'')$ can be determined from the slope of the plot of $R(q)/q^2$ against q^2 and $\{-D[1 + 2\eta^2 E/(1-\nu)f'']\}$ can be estimated from the intercept which the straight line makes on the ordinate axis. Thus all the quantities characterising the phase separation can be obtained for the initial stages of spinodal decomposition.

In the determination of the most characteristic features of spinodal decomposition, studies on the mathematical modelling of phase separation in the region of unstable states on the phase diagram have played a major role. Despite the comparatively small number of such investigations, their results have proved extremely instructive, because they make it possible to follow the appearance, enrichment, and in certain individual instances also the coalescence of the microregions of the heterogeneous structure as a function of time.[16,17] In particular, it has been shown[17] that, for a definite composition of the system, there is a temperature corresponding to the maximum rate of formation of interrelated microregions of the phase separation. In this case the formation of modulated structures in spinodal decomposition corresponds to a comparatively brief period of the development of interacting nuclei. In the course of later stages of the decomposition, hydrodynamically initiated coalescence begins to play an important role. The possibility of modelling the process of phase separation in both the metastable and unstable regions of the phase diagram and also the possibility of obtaining information about the coalescence of the microregions at later stages of the decomposition[17] must be regarded as a significant characteristic of the results obtained in the numerical soluton of a diffusion equation of type (14).

A series of theoretical studies whose aim was a more general description of the phenomenon of spinodal decomposition than had been achieved on the basis of the Cahn–Hilliard theory have appeared recently. The necessity for a more general approach to the analysis of phenomena arising in spinodal decomposition is associated primarily with the fact that the fundamental equation in the given theory [an equation of type (1)] is inapplicable in the general case because, for reasons involving symmetry considerations, it does not take into account contributions proportional to ∇c. A theory[18] based on a set of phenomenological coefficients determined from the conditions for correlation with experimental data has been proposed as one of the alternative formulations of the theory for the description of phase separation in the region of unstable states on the phase diagram.

Another approach developed recently is based on the extension of the perturbation theory for the liquid state to the case of inhomogeneous liquids.[19] The numerical solution of the corresponding diffusion equation, this time for the one-dimensional case, reveals appreciable deviations from the Cahn–Hilliard theory outside the linear regime.

One of the most rigorous versions of the modern theory of phase separation, including the description of nucleation and spinodal decomposition processes, has been developed

by Metiu et al.[20] and Varea and Rodledo.[21] It is based on the consideration of these processes as relaxation phenomena obeying the Markov equation. For a thermodynamic system with such a relaxation process (for example for a liquid in a specified state), the rate of change of the local density $\rho(r, t)$ is defined by the following evolution equation:

$$\frac{\partial \rho(r, t)}{\partial t} = -K\left[1 - \exp\left(\lambda^2\nabla^2/r\right)\frac{\partial\Omega}{\delta\rho(r)}\Big|_{\rho(r,t)}\right], \qquad (20)$$

where K is a constant related to temperature and to the characteristic time of the transitions, Ω the grand thermodynamic potential, and λ the distance traversed by the molecule of the liquid during the characteristic time.

Eqn.(20) describes the rate of the most probable evolution of density fluctuations. In terms of the approximation assuming a small variation in $\rho(r, t)$ compared with λ, the equation first obtained by Cahn[10] is valid:

$$\frac{\partial\rho}{\partial t} = K'\nabla^2\frac{\delta\Omega}{\delta\rho(r)}\Big|_{\rho(r,t)}. \qquad (20')$$

Analysis of Eqns.(20) and (20') shows that $\Omega[\rho(r)]$ can be identified with Lyapunov's function. Here the study of the number and properties of the corresponding stationary solutions is of special interest. The direction of the most probable evolution of this system is defined by the condition

$$\frac{d}{dt}\Omega[\rho(r, t)] \leqslant 0 .$$

In particular, if we have two stationary states $\rho_1(r)$ and $\rho_2(r)$, then on the path from the first to the second, the following condition is valid for the $\Delta\rho(r)$ fluctuation:

$$\Omega[\rho_1(r) + \Delta\rho(r)] > \Omega[\rho_2(r)] .$$

The stationary states are then defined by the condition:

$$\frac{\delta\Omega}{\delta\rho(r)} = \frac{\delta\Omega}{\delta\rho(r)} - \mu = 0 . \qquad (21)$$

Homogeneous states correspond to the trivial solution $\rho(r) = \rho$ of Eqn.(21). At the point where the trivial solution becomes unstable, a branching or bifurcation takes place.

Eqn.(21) yields the condition for the instability of each homogeneous solution in the spinodal region, i.e. an infinite family of inhomogeneous stationary states branches out from each point within the spinodal. The instabilities of the homogeneous solutions are determined either in terms of a mechanical analogy (a large response to an external influence) or in terms of a thermodynamic analogy {the absence of an unambiguously defined minimum in $\Omega[\rho(r)]$}. It has been established that periodic stationary states branch with a specific initial wavelength λ_c. A series of spontaneous fluctuations can cause a transition of the system from the homogeneous state which has become unstable, via the periodic states indicated, to a metastable state. Subsequently there is a possibility of a transition via nucleation from the metastable state to an equilibrium homogeneous state. Regarded as the Lyapunov function (20), the property $\Omega[\rho(r)]$ defines the direction in the sequence of stationary states traversed along the most probable path after the transition to the spinodal region of the phase diagram.

Thus the phenomenon of spinodal decomposition is associated with a large number of pathways whereby the system relaxes to equilibrium. In all cases, after quenching the system develops a periodic inhomogeneity, whose wave vector corresponds to the initial state; after a time, this inhomogeneity increases in amplitude and in wavelength until nucleation begins following the attainment of the metastable state. It has been shown[21] that in this state the fluctuations in different regions of space are independent. Such fluctuations lead to the development of a nucleation process which cannot be described within the framework of the local Cahn–Hilliard approximation.

III. APPLICATION OF THE THEORY OF SPINODAL DECOMPOSITION TO SYSTEMS BASED ON HIGH-MOLECULAR-WEIGHT COMPONENTS

The majority of investigations of phase separation in systems based on high-molecular-weight components are themselves based on the familiar study by Debye[22] devoted to critical opalescence. The relations obtained by Debye for a few systems are in essence analogous to the results of the studies of Cahn and Hilliard examined above. Debye used the following expression for the free energy of a binary system:

$$F = k_BT\int_v d\upsilon\left[\left\{\frac{\varphi_A^0}{\omega_A}\ln\varphi_A^0 + \frac{(1-\varphi_A^0)}{\omega_B}\ln(1-\varphi_A^0) + \right.\right.$$
$$\left.\left. + \frac{\Omega}{2k_BT}\varphi_A^0(1-\varphi_A^0)\right\} + \left(\frac{1}{\omega_A\varphi_A^0} + \frac{1}{\omega_B\varphi_B^0} - \frac{\Omega}{k_BT}\right)\frac{\eta^2}{2} + \frac{H}{2k_BT}(\nabla\eta)^2\right], \qquad (22)$$

where ϕ_A^0 is the volume fraction of component A, ω_A the volume occupied by the molecule of A, ϕ_A the local value of ϕ, $\eta = \phi_A - \phi_A^0$, and

$$\Omega = W_{AA}\,|\,\omega_A^2 + W_{BB}\,|\,\omega_B^2 - 2W_{AB}\,|\,\omega_A\omega_B ,$$
$$H = \frac{1}{6}\left[\frac{W_{AA}}{\omega_A^2}\,l_{AA}^2 + \frac{W_{BB}}{\omega_B^2}\,l_{BB}^2 - 2\frac{W_{AB}}{\omega_A\omega_B}\,l_{AB}^2\right] .$$

The quantities Ω and H are the interaction parameters. Here we have

$$W_{AA} = \int\varepsilon_{AA}d\upsilon,\ W_{AA}l_{AA}^2 = \int r^2\varepsilon_{AA}d\upsilon,$$
$$l_{AA}^2 = \int r^2\varepsilon_{AA}d\upsilon\Big/\int\varepsilon_{AA}d\upsilon$$

where $-\varepsilon_{AA}$ is the energy of the A–A interaction between the molecules and l_{AA} the characteristic distance of the interaction between these molecules.

On the basis of the relations presented above, the contribution to the free energy of the system associated with the inhomogeneous distribution of the components can be represented in the form

$$\Delta F = \int d\upsilon\left[\frac{1}{2}\left\{\frac{\partial^2F_m/V}{\partial^2\varphi_A^2}\right\}_{\varphi_A^0}\eta^2 + \frac{1}{2}H(\nabla\eta)^2\right], \qquad (23)$$

where F_m is the free energy of mixing for a homogeneous solution. It is seen that Eqns.(2) and (23) for the free energy of mixing are almost identical.

Van Aartsen applied the Debye relations to systems based on high-molecular-weight components.[23] He began with the assumption that the Flory–Huggins expression is valid for ΔF_m in the case of a homogeneous solution:[24]

$$\frac{\Delta F_m}{V} = RT\left[\frac{\varphi_A}{\bar{V}_A}\ln\varphi_A + \frac{1-\varphi_A}{\bar{V}_B}\ln(1-\varphi_A) + \frac{\chi}{\bar{V}_A}\varphi_A(1-\varphi_A)\right], \qquad (24)$$

where $\bar{V}_A$ and $\bar{V}_B$ are the molar volumes of the solvent and the polymer respectively.

In this case one can write for the second derivative of the free energy with respect to composition

$$\left\{\frac{\partial^2(\Delta F_m/V)}{\partial\varphi_A^2}\right\}_{\varphi_A^0} = \left[\frac{1}{\bar{V}\varphi_A^0} + \frac{1}{\bar{V}_B(1-\varphi_A^0)} - \frac{2\chi}{\bar{V}_A}\right] \qquad (25)$$

If the relation

$$\chi = A + (B\bar{V}_A/RT) \qquad (26)$$

is valid for the Flory–Huggins parameter χ, Eqn.(25) can be transformed into

$$\left\{\frac{\partial^2(\Delta F_m/V)}{\partial \varphi_A^2}\right\}_{\varphi_A^0} = \frac{2RT}{\bar{V}_A}(\chi_{T_s} - \chi_T) = 2B\left(\frac{T - T_s}{T_s}\right), \qquad (27)$$

where χ_{T_S} is the interaction parameter corresponding to the temperature of the spinodal. It follows from the relations presented that the expression

$$\lambda_m = 2\pi l\,[3(1 - T/T_s)]^{-1/2} \qquad (28)$$

can be written for the optimum wavelength of spinodal decomposition.

Thus the most "critical" parameter for the determination of the dimensional characteristics of the microregions of phase separation in the given instance is the characteristic distance for the interaction of the molecules. Debye assumed that

$$l = 0.5\text{–}2 \text{ nm} \qquad (29)$$

for low-molecular-weight components and

$$l = R/\sqrt{6} \qquad (30)$$

for polymer–solvent systems. Here R^2 is the mean square of the distance between the ends of the polymer chain. For polymer–polymer systems, McMaster[25] suggested that l be determined from the relation

$$l = R/\sqrt{3} \quad . \qquad (31)$$

The most complete treatment of the phenomenon of spinodal decomposition in systems based on two high-molecular-weight components has been carried out in the theoretical studies of de Gennes[26] and Pincus.[27] An extension of the corresponding Flory–Huggins expression for an inhomogeneous system[28] was used in the above studies to formulate the free energy of the system:

$$\frac{F}{k_BT} = \frac{\varphi_A}{N_A}\ln\varphi_A + \frac{(1-\varphi_A)}{N_B}\ln(1-\varphi_A) + \frac{a^2}{36\varphi_A(1-\varphi_A)}(\nabla\varphi_A)^2, \qquad (32)$$

where a is the size of the monomeric unit and N_A and N_B are the degrees of polymerisation of components A and B respectively.

In the de Gennes theory account is taken of the fact that the main mechanism of the movement of molecular chains in polmer–polymer systems involves their reputation or "creep" in a tube formed by the labile nodes of the entanglement network.[29–31]

The time variation of the local composition of the system ϕ_A is related to the flux J_A of component A by the continuity equation

$$\partial\varphi_A/\partial t + \operatorname{div} J_A = 0 \quad . \qquad (33)$$

The Fourier component of the flux for the wave vector J_A is determined on the basis of the corresponding Fourier component of the chemical potential gradient of the given component $\nabla\mu(q)$ by means of the relation

$$J_A(q) = -[\Lambda(q)/k_BT](\nabla\mu(q)), \qquad (34)$$

where $\Lambda(q)$ is the Onsager coefficient. Having found $\nabla\mu$ and leaving in the expression for this quantity only terms linear in $\delta\phi(r)$, we have

$$\frac{\nabla\mu}{k_BT} = \nabla(\delta\varphi_A)\left(\frac{1}{N\varphi_A(1-\varphi_A)} - 2\chi\right) - \frac{a^2}{36\varphi_A(1-\varphi_A)}\nabla^3(\delta\varphi_A) \quad . \qquad (35)$$

Eqns.(33)–(35) have been used to obtain the so-called central relaxation formula:

$$\frac{1}{\tau_q} \equiv \frac{1}{\delta\varphi_q}\frac{\partial(\delta\varphi_q)}{\partial t} = q^2\Lambda(q)\left(\frac{1}{N\varphi_A(1-\varphi_A)} - 2\chi + \frac{a^2q^2}{36\varphi_A(1-\varphi_A)}\right). \qquad (36)$$

The relaxation spectrum, found on the basis of Eqn.(36), defines the initial unstable mode in the binary system and the rate of growth of this mode. Assuming a unique relaxation time for the mode of the wave vector q in a melt of two polymers, the Onsager coefficient obtained by de Gennes assumes the following form:

$$\Lambda(q) \simeq \varphi_A(1-\varphi_A)N_eD_1(qa)^2, \qquad (37)$$

where N_e is the number of monomeric units between the sites where the chains are hooked to one another and D_1 is the coefficient of microscopic diffusion. It follows from Eqn.(37) that the Onsager coefficient is proportional to the square of the wave vector, i.e. increases sharply with decrease of wavelength.

Subject to the condition $\chi \gg \chi_{T_1}$, i.e. after the instantaneous transfer of the system to a region lying within the spinodal on the phase diagram, we have from the central relaxation formula

$$-1/\tau_q = \chi\Lambda(q)q^2(2 - q^2l^2) \qquad (38)$$

where $l = 1/3a\chi^{-1/2}$ is the thickness of the interfacial transitional layer determined on the basis of the Helfand theory for polymer–polymer mixtures.[32,33]

Eqn.(38) shows that, when $ql < \sqrt{2}$, the composition fluctuations are enhanced, i.e. the system passes to the regime of spinodal decomposition. The greatest enhancement is characteristic of the optimum wavelength corresponding to the following wave vector:

$$q_m = 2\sqrt{3}a^{-1}\chi^{1/2} \quad . \qquad (39)$$

It is seen from Eqn.(39) that the optimum wavelength of spinodal decomposition is slightly smaller than the mean square radius of the molecular coil. In principle, this conclusion is inconsistent with the theoretical predictions based on the Debye–van Aartsen theory.

When account is taken of Eqn.(39), the rate of relaxation to the equilibrium two-phase state for the optimum wavelength is defined by the relation

$$-1/\tau_q = D_1N_e\chi a^2l^{-4} \equiv (N_e/\tau_1)\chi^3, \qquad (40)$$

where τ_1 is the time of the microscopic diffusion of a chain segment.

On the basis of the de Gennes central relaxation formula, Pincus[27] amended de Gennes' conclusion concerning the magnitude of the optimum wavelengths of spinodal decomposition. In particular, Pincus took into account the fact that, for the wave vector of non-interacting chains in the melt, there is not one but at least two independent relaxation modes.[34] As a result, we have for the Onsager coefficient when $qR_0 \gg 1$

$$\Lambda(q) = 2T\mu_1(ql)^{-2}[1 - \exp(-q^2R_0^2/6)]\varphi_A(1-\varphi_A), \qquad (41)$$

where μ_1 is the mobility of the monomeric unit.

Thus the Onsager coefficient proves to be proportional to the reciprocal of the square of the wave vector. On combining Eqns.(36) and (41), we obtain the following expression for the rate of relaxation of the system to the state of equilibrium:

$$\frac{1}{\tau_q} = \frac{1}{2}(T\mu_1/L^2)[1 - \exp(-q^2R_0^2/6)][N^{-1} + 2\chi\varphi_A(1-\varphi_A) + (qa)^2/36], \qquad (42)$$

where L is the contour length of the macromolecule. When $\tau_q < 0$, an exponential growth of the intensity of composition fluctuations is observed. The sharp transition from $\chi < 0$

to $\chi > \chi_{T_S}$ corresponds to the fact that the initial unstable mode q_m is specified by the extremum in Eqn.(42), i.e.

$$q_m^{-1} \simeq (R_0/6)\,[\ln(6\chi/\chi_{T_S})]^{-1}, \quad \chi > \chi_{T_S} \qquad (43)$$

when the system passes rapidly from the one-phase state for into the region bounded by the spinodal. In the unstable region of the phase diagram near the spinodal, we have

$$q_m^{-1} \simeq (R_0/6\sqrt{3})\,(\chi/\chi_{T_S} - 1)^{-1/2}, \quad (\chi - \chi_{T_S})/\chi_{T_S} \ll 1 \ . \qquad (44)$$

For the optimum rate of growth of fluctuations in the former case, we obtain

$$1/\tau_{q_m} \simeq T_{rep}^{-1}(\chi/\chi_{T_S}), \quad \chi \gg \chi_{T_S} \ . \qquad (45)$$

In the second case we have correspondingly

$$\frac{1}{\tau_{q_m}} \simeq T_{rep}^{-1}\,(\chi/\chi_{T_S} - 1), \quad (\chi - \chi_{T_S})/\chi_{T_S} \ll 1 \ , \qquad (46)$$

where T_{rep} is the time required for the molecular chain to emerge from the entanglements tube.

We shall note the most important features of Pincus' study, which constitutes a further development of the ideas of de Gennes.

1. The unstable mode has a wavelength comparable to the radius of the molecular coil and hence varies in proportion to $N^{1/2}$.

2. The rate of increase of the intensity of the composition fluctuations corresponding to the given mode is proportional to the reputation diffusion constant in the melt, varies as N^{-2}, and its concentration dependence is represented by a curve having the same form as the spinodal.

Thus Pincus' analysis of the phenomenon of spinodal composition in mixtures of homopolymers shows that microphase separation on the scale of distances of the order of magnitude of N_e is possible only for very intense cooling of the one-phase mixture of polymers. This case has been considered by de Gennes[35] in relation to cross-linked polymer blends. Quenching of this extent is equivalent to the fulfilment of the condition $\chi/\chi_{T_S} \gg N/N_e$. This is unlikely in blends of homopolymers under real experimental conditions. It is seen from the foregoing that, in the entire set of multicomponent polymer systems, only polymer–solvent and homopolymer–homopolymer systems have so far been analysed as regards spinodal decomposition in the region of unstable states on the phase diagram; more complex systems have been scarcely considered.

IV. EXPERIMENTAL STUDIES OF SPINODAL DECOMPOSITION IN SYSTEMS BASED ON HIGH-MOLECULAR-WEIGHT COMPONENTS

In the first study of the phase separation of polymer systems in the region of an unstable state, the poly-2,6-dimethyl-1,4-phenyl ether (PDMPE)–caprolactam system was investigated.[36] By measuring the scattered light intensity, it was established that cooling drives the solution to the region of unstable states on the phase diagram and phase separation then occurs via the spinodal decomposition mechanism. Microscopic observations on the phase separation processes have been made in the same system[37] and it was found that the size of the microdrops of the phase enriched in the polymer increases with time.

Phase separation in the PDMPE–toluene system has also been studied,[38] the increase in turbidity being recorded visually, while in another investigation[39] the same system was studied by electron microscopy. In those cases where homogeneous PDMPE–toluene mixtures were cooled to a temperature below T_S, two characteristic phenomena were observed. At a quenching temperature differing only slightly from the spinodal temperature, there is sufficient time for the formation of many nuclei in the system during the passage through the metastable region of the phase diagram. Cooling to a temperature somewhere above T_S gives rise to a pattern typical for phase separation via the nucleation and growth mechanism. On the other hand, if the system is cooled to a temperature somewhat lower than T_S, the electron microscopic patterns reveal the formation of two interlinked structures (structural networks) together with the nuclei.

Thus the rate at which the system passes through the metastable region on the phase diagram determines to a large extent the structure of the liquid mixture. On the other hand, if the homogeneous solutions are cooled to temperatures appreciably lower than T_S, the system passes rapidly through the metastable region and the electron micrographs show mainly interlinked structures characteristic of phase separation via the spinodal mechanism.

Phase separation in the polystyrene–decalin system has been investigated[40] and the dimensions of the regions corresponding to phase separation via the spinodal mechanism have been determined from light scattering data using the fundamental relations of Cahn's theory. The phenomenon of spinodal decomposition also proved to be typical for certain polymeric gels. Thus a diffraction maximum has been observed on the light scattering intensity curves for hydrogels and agarose, which is associated with the formation of regularly arranged phase separation regions.[41] A detailed investigation of phase separation in the sol–gel transition in the given system, occurring when it is cooled, was subsequently carried out.[42]

In conformity with Cahn's theory, in the majority of the studies considered the fulfilment of all the main criteria for the occurrence of spinodal decomposition mentioned above was assessed. It was shown that the occurrence of spinodal decomposition depends in many respects on the rate of transition of the system to an unstable state and, for solutions, also on the concentration, since in highly dilute systems the formation of modulated structures is altogether difficult.[9] In many instances the criteria of spinodal decomposition in solutions at a concentration above the critical value are fulfilled only in the initial stages of phase separation. In later stages nucleation apparently occurs.

A detailed study has been made[43] of phase separation in solutions of gel-forming atactic and isotactic polystyrenes, poly(phenylene oxide) and their mixtures in various solvents.[43] It was observed that the formation of a gel is not associated with crystallisation but is due to the transition of the system to the region of an unstable state on the phase diagram and the formation (as a result of fine dispersion) of microregions enriched in the polymer, the glass points of which are sufficient for the fixation of the ends of various polymer chains in a single vitrified region. The small size of the microregions (approximately 1000 Å) and the high rate of their formation are considered as evidence for the spinodal mechanism of phase separation of the liquid–liquid type. Fusion of the gel is attributed to the fact that, when the microregions are devitrified, the sections of the polymer chains bound by them are liberated. McMaster[25,44] investigated the system comprising the styrene–acrylonitrile copolymer and poly(methyl methacrylate). This system is characterised by a phase diagram with a lower consolute temperature. The interaction parameter can be represented as the sum of the enthalpy and entropy contributions, i.e.

$$\chi = \chi_h + \chi_s \qquad (47)$$

(χ_h and χ_s are the enthalpy and entropy components of the interaction parameter) and Eqn.(27) can be written as follows:

$$\frac{\partial^2 f}{\partial c^2} = \frac{2R\chi_h}{V_1}\left(\frac{T-T_s}{T_s}\right) . \quad (48)$$

The expression for k can be formulated thus:

$$k = \left(\frac{RT\chi}{V_1}\right) l^2/6 . \quad (49)$$

In this case the optimum wavelength of the spinodal decomposition is given by the relation

$$\lambda_m = 2\pi l \left(\frac{3\chi_h}{\chi T} \cdot \frac{T_s - T}{T_s}\right)^{-1/2} . \quad (50)$$

Thus, by neglecting the entropy contribution to the interaction parameter, it is possible to obtain Eqn.(28).[23] The development of phase separation microregions in time has been observed experimentally by transmission electron microscopy.[43] It is significant that, with increase of the heat treatment time, there was a gradual increase of the content of one of the components in the developing microregions. The diffuse interfacial layers then gradually became sharper and it was actually possible to observe the early stages of the coalescence of the microregions. The size of the microregions in the given stages of phase separation is approximately 50–100 nm. The interlinking of various microregions is characteristic of the early stages of the decomposition. For a composition remote from the critical composition, a very slow coalescence process, controlled by the Ostwald ripening mechanism, takes place after the attainment of equilibrium phase compositions.[45] Accordingly, the increase of the volume of the microregions of the disperse phase as a function of time is expressed by the relation

$$d^3 = d_0^3 + 64\tau (x_c V_m) Dt/9RT , \quad (51)$$

where d_0 is the diameter of the microregions after they have attained the composition of the equilibrium phases, x_c the mole fraction of the component entering into the composition of the disperse phase, V_m the molar volume of the given component, τ the disperse phase–matrix interfacial tension, and D the diffusion coefficient for the matrix phase. Using Eqn.(51), McMaster estimated the diffusion coefficient, which proved to be 9×10^{-16} m^2 s^{-1} for 538 K.

The data obtained for the phase separation of mixtures having the critical composition show that a relation of type (1) is applicable only to the description of the earliest stages of decomposition. In particular, as a result of heat treatment at 453 K, it is possible to observe in the course of only 4.4 min the simultaneous increase of the difference between the compositions of the microregions and the size of the latter. Thus, the use of the non-linear version of the Cahn–Hilliard relation of type (14) is now necessary for the description of the kinetics of phase separation.

McMaster[44] estimated the diffusion coefficient in mixtures having the critical composition by means of the relation

$$R(\lambda_m) = \left(-\Omega \frac{\partial^2 f}{\partial c^2}\right) \frac{2\pi^3}{\lambda_m^2} , \quad (52)$$

which follows from the Cahn–Hilliard theory. Accordingly it was found that the diffusion coefficients at 453 and 483 K are 2.6×10^{-18} and 3.3×10^{-17} m^2 s^{-1} respectively.

Thus McMaster was able to explain on the basis of the Cahn–Hilliard theory the most characteristic features of the early stages of the spinodal decomposition of a polymer–polymer system. He predicted correctly the scale level of the separation, which proved to be greater than in systems based on low-molecular-weight components.

In particular, the experimental determination of the diffusion coefficients in the early stages of the decomposition of a system having the critical composition and in the Ostwald ripening of the disperse phase in a system whose composition is remote from the critical composition must be recognised as specially important. A virtually new feature of the interpretation of the phase separation phenomena in polymer systems involves the explanation of the increased rate of growth of the phase separation microregions owing to coalescence due to the viscous flow of the components in "channels" formed by the interlinked structures. The appropriate analysis based on the use of a modified form of the relations for the stability of anisodiametric inclusions[46] yields a satisfactory agreement with experiment.

Nishi et al.[47] investigated the phase separation in the polystyrene (PS)–poly(methyl vinyl ether) (PMVE) system by NMR, light transmission, and optical microscopic methods. This system is also characterised by the presence of a lower consolute temperature. On the basis of morphological observations, the authors noted two types of phase separation in the systems investigated. Phase separation either proceeds at a high rate, giving rise to a characteristic network of interlinked microregions of approximately identical size, or, during slow phase separation, the microregions are spherical in shape from the very beginning. In the former case the microphase structure becomes finer as the temperature increases and in the last stage of the phase separation the microregions grow rapidly, remaining interlinked, and then either break up into small spheres or merge into macrospheres. In the latter case the dimensions of the microregions are small compared with the periods of interlinked structures.

Data obtained by pulse NMR confirmed the continuous variation of the composition of the microregions with time, which agrees with the hypothesis of the spinodal mechanism of the phase separation. Another piece of evidence for the spinodal mechanism is provided by the estimate of the quantity $R(q_m)$ in the Cahn–Hilliard equations, according to which the kinetics of the variation of the composition of the phase separation microregions can be described by the relation

$$c - c_0 = A(q_m) \exp[R(q_m)t] \cos q_m x \quad (53)$$

when

$$R(q_m) = \frac{1}{2} q_m^2 D \quad (54)$$

In the present case the quantity c represents the concentration of PMVE in the phase enriched in polystyrene. On this basis, it follows from Eqn.(53) that the total decrease of Q (of the content of PMVE) in the given phase during phase separation is described by the expression

$$Q = \left[\int_{\pi/2q_m}^{3\pi/2q_m} (c - c_0)\, dx\right]^3 = \left[\frac{2}{q_m} A(q_m)\right]^3 \exp(3R(q_m)t) . \quad (55)$$

We have the following time variation of $\ln Q$:

$$\ln Q = 3 \ln\left[\frac{2}{q_m} A(q_m)\right] + 3R(q_m)t \quad (56)$$

whose slope is $3R(q_m)$. The quantity $\ln Q$ is estimated from NMR data. The positive value of $R(q)$ shows that the concentration fluctuations become more intense with time, i.e. in the system containing 50% PMVE at 403 K spinodal decomposition takes place. If q_m is estimated from morphological data, we have for the diffusion coefficient

$$D = -2R(q_m)/q_m^2 = -2.8 \cdot 10^{-17} \text{ m}^2 \text{ s}^{-1} \quad (57)$$

when

$$R(q_m) = 3.82 \cdot 10^{-4} \text{ c}^{-1};\ q_m = 5.24 \cdot 10^{6} \text{ m}^{-1}. \quad (58)$$

A negative value of D indicates active transport in the system which is in the region of unstable states on the phase diagram.

The quantity χ, found on the basis of the Debye–van Aartsen theory, is −0.42 at 373 K, $k = 37 \times 10^{-13}$ J m^{-2} (in 1 m^3 of PMVE), and $f'' = -4.1 \times 10^6$ (in 1 m^3 of PMVE). The temperature of the spinodal for the given composition is 391 K and $l \cong 58$ nm.

Thus, on the basis of rigorous quantitative data, the spinodal mechanism of the phase separation in the PS–PMVE system has been demonstrated[47] and the principal characteristics of the phase separation process have been determined. As in the study of the phase separation in the system comprising the styrene–acrylonitrile copolymer and poly(methyl methacrylate) examined above, the periodicity of the modulated structure is much greater than in systems based on low-molecular-weight components. In particular the value of $\langle R^2 \rangle^{1/2}$ found by Nishi et al.[47] is very close to the radius of an unperturbed Gaussian coil. This is in full agreement with the de Gennes–Pincus theory.

The influence of particular factors, which determine the characteristic features of spinodal decomposition, has been examined in a number of studies. In particular, a study[48] has been devoted to phase separation in thin films of the PS–PMVE system. The authors showed that the conditions for spinodal decomposition then depend on the chemical nature of the support and on the thickness of the film. The influence of vitrification and of the presence of a low-molecular-weight component on the phase separation processes in the poly(phenylene oxide)–(*p*-chlorostyrene–*o*-chlorostyrene) copolymer system has been investigated.[49] A very sophisticated low angle technique for the investigation of the X-ray emission spectrum, involving the application of a position-sensitive detector, was used.

V. CHARACTERISTIC FEATURES OF PHASE SEPARATION IN BLOCK SYSTEMS

The results of a large number of theoretical[50–54] and experimental[55–60] studies show that phase separation is observed under certain conditions in high-molecular-weight compounds whose molecular chains consist of an alternation of blocks of different nature. As a result, microregions with equilibrium composition, whose size and shape depend on the "architecture" of the molecular chains and on the volume fraction of each block, are segregated. Since block polymers can be usefully treated as multicomponent polymer systems as regards phase separation, the same conditions for phase separation (based on the existence of binodals and spinodals) are valid for them as for the systems based on chains of different types not linked chemically. At the same time the results of theoretical and experimental studies have shown that the appearance of differences from traditional multicomponent systems is to be expected for polymeric materials of this kind. It must be assumed that such differences are capable of influencing significantly the phase separation processes and the final structure of multiphase systems.

Evidently, in those cases where the block copolymer relaxes fairly slowly from the spatially homogeneous state, the formation of a microphase structure can take place via the spinodal decomposition mechanism. This problem was considered for the first time with adequate rigour in two investigations[59,60], where it was shown that, whereas the condition for instability in homopolymer blends is considered only as regards instability with respect to separation into infinite homogeneous phases (with a wavenumber $q = 0$), for block copolymers it is considered as regards instability with respect to separation into microphases with a characteristic period of spatial inhomogeneity defined by the wavenumber $q = q_0 \neq 0$.

In the region of stability of a spatially homogeneous state, any small inhomogeneity decays exponeitially with a characteristic relaxation time. As the spinodal is approached, the relaxation times increase and on the spinodal become infinite. In the region of unstable states the amplitude of the inhomogeneities to which correspond negative eigenvalues of the matrix G_q^{-1} (the inverse matrix of the pair correlation functions in q-space) increases exponentially, resulting in the breakdown of the spatially inhomogeneous state. The periodic inhomogeneities with wavenumbers in the specific range $q_1 < q < q_2$ then grow, while the fluctuations with $q < q_1$ and $q > q_2$ again dissipate. After a time, the above range of wavenumbers becomes narrower until the formation of a heterogeneous structure with a characteristic period d_0 and the amplitude of the inhomogeneity increases exponentially. For "highly blended" heteropolymers, the period of the heterogeneous structure is of the order of magnitude of the correlation radius in the system of ruptured units. An increase of the average length of the chemically homogeneous sections results in an increase of the equilibrium values of the periodicity.

In connection with the characteristic features of the equilibrium microwave structure of block polymers, an interesting analogy, observed, on the one hand, in the behaviour of the block copolymers and, on the other hand, in that of multicomponent systems which decompose in the region of unstable states of the phase diagram, merits mention.[61] The point is that the transition from a one-phase solution of the blocks to the state of microphase separation is observed for block copolymers of the styrene–butadiene and styrene–butadiene–styrene systems as the temperature is reduced. A higher degree of microphase separation corresponded to a lower temperature. This was manifested by a gradual increase of the intensity of the low-angle X-ray scattering maxima with decrease of temperature. As shown previously, such phenomena characterise the spinodal decomposition of binary systems.[15] The analogy in the changes in the low-angle scattering curves proved extremely close; together with the characteristic increase of the intensity of the maxima, a decrease of the intensity in the "tail" section of the scattering curve and the presence of a common point of intersection of all the curves (cross-over) have been observed. Taking this factor into account, by analogy with Eqn.(18), Roe et al.[61] proposed the following expression for the intensity of the low-angle scattering in block systems in a state of equilibrium at different temperatures:

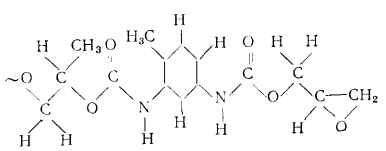
$$I(q, \chi) = I(q, 0) \exp(\alpha(q)\chi) . \quad (59)$$

Here the multiplier $\alpha(q)$ corresponds to the amplification factor used to describe the spinodal decomposition process and it is assumed that the thermodynamic interaction parameter varies with temperature in accordance with Eqn.(26). The multiplier $\alpha(q)$ has a maximum at $q = q_m$ and is zero at $q = q_c$. The ratio q_c/q_m is close to 1.5 (in the case of spinodal decomposition $q_c/q_m = \sqrt{2}$).

The temperature variation of the logarithm of the intensity of the low-angle scattering for two- and three-block copolymers of the type investigated is linear. This makes the analogy with the changes in the intensity of the low-angle scattering in spinodal decomposition quite unambiguous.

It seems natural to examine the question whether this analogy in the behaviour of block copolymers in equilibrium at different temperatures and blends in significantly non-equilibrium states in the course of spinodal decomposition is fortuitous. It is known that the increase of the period of the inhomogeneous distribution of the components in spinodal decomposition is limited by the finite rate of their diffusion. The latter is determined by the multiplier Dq^2 in Eqn.(11). The possibility of a decrease in the wavelength of the spinodal decomposition is limited by the increase of the free energy of the system [the term $2kq^2$ in Eqn.(11)]. An expression analogous to Eqn.(11), which determines the stability of the periodic microphase structure of systems of the same kind, is also valid for block copolymers at different temperatures. Taking into account the above analogy with the phenomenon of spinodal decomposition, in the case of block copolymers a multiplier similar to Dq^2 should reflect the fact that the microregions based on blocks of any kind are limited in size from below by the size of the corresponding molecular coils. Since the shape of the latter can be represented by the diffusion equation, it is quite possible that the geometrical effect indicated is associated with a multiplier proportional to q^2. On the other hand, the multiplier $f'' - 2kq^2$, which determines the increase of the size of the phase separation microregions, usually occurs in the thermodynamics of inhomogeneous liquid mixtures[8] and is therefore applicable to the description of block copolymers.

It is noteworthy that the phenomena examined above, associated with the microphase separation in block copolymers, have been observed[61] in relation to two- and three-block copolymers with a comparatively high molecular weight. It is all the more interesting that we observed a similar temperature variation of the intensity of the low-angle X-ray scattering for oligomers consisting of a single flexible small block (a butadiene–isoprene copolymer with a molecular weight of 4500) and two quite small terminal rigid blocks,[89]



each of which has a molecular weight of approximately 300. At 433 K this oligomer is characterised by such a weak level of low-angle scattering that it can be regarded as "transparent" in the X-ray emission spectrum. With decrease of temperature, the intensity of the low-angle scattering increases and a distinct maximum (Bragg period 8.3 nm) gradually appears on the intensity curve. In the temperature range up to 293 K its positions remains unaltered.

Thus, when the temperature is varied from 433 to 293 K, a microphase structure is formed in the given oligomer. It follows from the results obtained that the degree of enrichment of the phase separation microregions in a particular component increases under these conditions. This shows that a phase diagram with an upper consolute temperature is characteristic of a block copolymer treated as a binary system. Analysis of the dependence of the logarithm of the scattering intensity on the reciprocal of temperature shows that it is linear. Thus, on the basis of the characteristic features of the low-angle scattering curve and the validity of the Eqn.(59), one may conclude that the temperature variation of the changes in the microphase structure of the given oligomer is analogous, as in the study of Roe et al.,[61] to the structural changes observed in spinodal decomposition.

VI. PHASE TRANSFORMATIONS IN MULTICOMPONENT POLYMER SYSTEMS OCCURRING AS A RESULT OF CHEMICAL REACTIONS

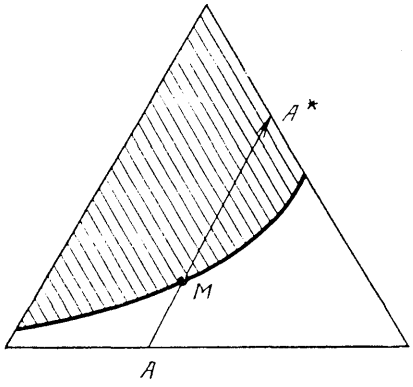
The systems examined above by no means exhaust all the versions of polymer systems potentially capable of undergoing phase separation in the region of unstable states on the phase diagram. It is known that phase separation can occur for reasons other than a change in temperature, pressure, or composition. There is an extremely wide range of systems (particular for high-molecular-weight compounds) for which phase separation is induced by chemical processes: degradation, polymerisation, depolymerisation, etc. In this case the systems can be of the simplest type (the monomer–polymer type) or can be very complex (for example, interpenetrating polymer networks based on several network polymers). The cases where the partial polymerisation of the monomer leads to the phase separation of the system into microregions enriched in the polymer and monomer are particularly widely known. The same is possible also in the partial depolymerisation of a macromolecular polymer.

The phase separation processes occurring on formation of carbon fibres as a result of the high-temperature treatment of polyacrylonitrile or cellulose hydrate fibres (carbonisation or graphitisation) are extremely characteristic and of practical importance.[62] This is known to entail the formation of a microporous structure characteristic of hydrocarbons with a pore size of the order of several nanometers.[63–66] The volume fraction of such micropores can reach 10%. Thus, as a result of carbonisation (heat treatment at approximately 1300 K) or graphitisation (heat treatment at approximately 2300–2800 K), a comparatively homogeneous polymeric material is converted into a heterogeneous carbon–micropores system. This can be explained by the fact that, in the course of the high-temperature treatment, the polymer is converted by chemical reactions into a carbonaceous material and gaseous product dissolved in the latter. At a specific stage of the transformations, phase separation takes place with segregation of liquid and gaseous phases, the latter forming the micropores. The very small sizes of the micropores and their comparatively narrow distribution can be regarded as a consequence of the fact that phase separation takes place via the spinodal decomposition mechanism and not via nucleation and growth.

The phase separation processes in the formation of a network polymer in an oligomer–solvent system have been investigated in relation to the polymerisation of oligoacrylate esters. The initial system consisted of a solution of αω-dimethacrylatebis(diethylene glycol phthalate) in tetrahydrofuran or in its mixtures with toluene or hexane. The polymerisation was carried out via an anionic mechanism. It was shown that the polymerisation of the oligomer leads to a sharp increase of the intensity of the low-angle X-ray diffraction. The cause of such appearance of "turbidity" is microphase separation of the system at the level of approximately 1–100 nm. The characteristics of the microphase structure, estimated from structural data, proved to depend on the type of the low-molecular-weight solvent. This is manifested by the fact that the curves for the distribution of the microheterogeneous regions with respect to size are characterised by different widths.

Since the microheterogeneity thus produced is a result of phase separation in the oligomer–solvent–network polymer system, we shall consider a hypothetical phase diagram for such a system (see Figure). The shaded part of the diagram represents a two-phase region and the unshaded part a one-phase region. The sequence of states occurring in the

system during the polymerisation of the oligomer is indicated by the $A-A^*$ straight line. In the initial state the solution of the oligomer in the solvent constitutes a one-phase system. As the oligomer is consumed, the system intersects the binodal at point M and enters the region of two-phase states. It then tends to separate into phases enriched in the polymer and the solvent. Bearing in mind the traditionally small extent of the region of metastable states in systems based on high-molecular-weight components, one may expect that the nucleation processes play an insignificant role and, after a short time has elapsed following the transition through the binodal, the system enters the region of unstable states on the phase diagram where its separation takes place via the spinodal decomposition mechanism. This is confirmed by the small sizes of the phase separation microregions and their comparatively narrow distribution.



Phase diagram for a polymerising polymer–oligomer–solvent network system. Initial state (A): oligomer–solvent; final state (A^*): network polymer–solvent. During the polymerisation process, the system passes through a sequence of states corresponding to the AA^* straight line. The region of two-phase states is shaded.

Together with phase separation processes, a three-dimensional network of chemical bonds is formed in the system. The cross-linking establishes a definite inhomogeneity in the distribution of the components and hence hinders the further occurrence of the phase separation processes required for the attainment of the state of equilibrium. This leads to the formation, in a system undergoing polymerisation, of a non-equilibrium microphase structure which is a result of incomplete phase separation. For systems containing different solvents, the phase diagrams are characterised by different positions of the phase equilibrium curves. Accordingly the system begins to separate at different times, i.e. for different compositions. Consequently cross-linking leads to different instants of phase separation and different levels of heterogeneity.

The gel produced as a result of polymerisation is a system with alternation of microregions enriched in the network polymer or the solvent. The absence of interference maxima from the low-angle scattering curves shows that polymerisation results in the fixation not of the initial stages of the spinodal decomposition, characterised by a regular alternation of microregions, but of later stages in which this periodicity has already disappeared. The latter may be a consequence of the polydispersity of the microregions formed during later stages of decomposition owing to coalescence.

We believe that such treatment of the appearance of heterogeneity in network polymers formed in the presence of a solvent is more constructive and more general compared with the ideas concerning the appearance of heterogeneity owing to microsyneresis used for purposes of this kind.[67] In this connection it is noteworthy that the thermodynamics of chemical reactions is in essence the non-linear thermodynamics of irreversible processes. The appearance of heterogeneity in reacting systems is therefore the rule rather than the exception. In those cases where diffusion fluxes of the components in systems of this kind are directed along the concentration gradient, diffusion smooths out the local inhomogeneity induced by the occurrence of the reaction. However, if the system is in the region within the spinodal as a result of polymerisation, the diffusion fluxes change direction and do not lead to the smoothing out of the local inhomogeneities. Thus the heterogeneity observed in cross-linked gels can be explained as a result of the formation of dissipative structures (see below), which become fixed as a result of cross-linking.

The kinetics of phase separation in the formation of network block copolymers have been studied in relation to a system whose initial components are oligoisoprene dihydrazide with a molecular weight of 3100 and the diglycidyl ether of di(4-hydroxyphenyl)propane (DGEHP).[68] The system was hardened at a temperature above the point corresponding to the appearance of turbidity (at 383 K). Throughout the hardening process, the scattering of X-rays in the reaction mixture was recorded continuously. The system was initially completely "transparent", but, after a definite polymerisation time had elapsed, a gradual appearance of turbidity was observed. The angular dependence of the X-ray scattering intensity then showed an interference maximum whose magnitude increased with time.

Thus the blend of the initial oligomers is a one-phase system and the formation of a system of chemical bonds between them leads to microphase separation at the level of several nanometers. The time dependence of the logarithm of the scattering intensity in the initial stages of the polymerisation obtained from diffraction data is linear. This shows that in the initial stages of phase separation the rules governing spinodal decomposition are fulfilled in the case considered. This effect, which has not been observed hitherto in systems of the block copolymer type, permits the conclusion that the kinetics of the phase separation of block systems do not differ fundamentally (at least in the early stages) from those of the phase separation of the usual binary systems in the region of unstable states on the phase diagram and involving the spinodal decomposition mechanism.

Studies of the above network polymer over a wide range of temperature have shown that, in the range from 293 to 533 K, the state of microphase separation is maintained. However, the characteristic features of the diffraction patterns discussed in the previous section, which are characteristic of linear block polymers and oligomers, are not then observed. This fact probably indicates significant deviations of the microphase structure of the network polymer from the state of equilibrium at different temperatures. It is to be supposed that this deviation is determined to a large extent by the presence of a three-dimensional network of chemical bonds, which limits the mobility of blocks of different nature and leads to the appearance of non-equilibrium structures. As a result of this, the state of the system can no longer be described from the standpoint of equilibrium thermodynamics.

Microphase separation is a typical process, which occurs also in the formation of interpenetrating polymer networks (IPN).[69,70] In particular, this has been convincingly demonstrated for IPN based on polyurethane and the styrene–divinylbenzene copolymer. It follows from the low-angle scattering data obtained for the above system that the formation of the IPN leads to a significant alteration of the profile of the low-angle scattering curves. Consequently, the formation of microregions enriched in the matrix and penetrated by networks is characteristic of such IPN. Between the regions indicated, there are transitional zones with a smooth profile of the variation of concentration. This picture of the microphase structure indicates the formation of the IPN of "diffuse" microphase regions characteristic of the early stages of the spinodal decomposition. The absence of the interference maxima characteristic of the spinodal decomposition of the system from the low-angle scattering curves for the IPN considered shows that partial coalescence of the segregated microregions has taken place in the system, as a result of which the periodicity in their disposition has been significantly impaired.

Thus network polyblock polymers and IPN are characterised by the presence of stable "diffuse" phase separation microregions, i.e. the degree of segregation of the components in such microregions can be extremely remote from equilibrium values. This quantity is defined by the expression[71,72]

$$\alpha = \overline{\Delta\rho^2} \Big/ \overline{\Delta\rho_c^2} = \overline{\Delta\rho^2} \Big/ [\varphi(1-\varphi)(\rho_1-\rho_2)^2] \quad , \qquad (60)$$

where $\overline{\Delta\rho^2}$ is the average square of the electron density fluctuation calculated from the absolute low-angle scattering intensity, $\Delta\rho_c^2$ the theoretical estimate of the average square of the electron density fluctuation obtained on the assumption of microphase separation at the level of the pure components, ϕ the volume fraction of one of the components, and ρ_1 and ρ_2 are the electron densities of components A and B respectively. A detailed analysis of data on the relation between phase separation and the degree of segregation in various multicomponent systems undergoing phase separation has been carried out in a monograph.[72] We shall consider the question of the relation between two-phase systems and systems with a comparatively high but nevertheless remote from unity degree of segregation of the components.

Numerous experimental data[72] show that the degree of segregation of the system components in microphase separation depends on many factors: the presence or absence of transverse chemical bonds in the system, the cross-linking density, composition, etc. Evidently in the phase separation beginning after the system has passed from the one-phase state to the region of unstable states, the stable entanglement nodes prevent the separation of fragments of different chemical nature, as a consequence of which the system is held in a state of "enforced" blending. This should lead to an additional contribution to the free energy of the system.

Thus the situation is to some extent similar to the phenomenon of the stabilisation of metallic alloys within the region bounded by the limited chemical spinodal. However, for polymer systems, it is at present impossible to obtain an exact estimate of the contribution of the elastic energy arising under these conditions. Even for much simpler systems of the type of low-molecular-weight glasses, it has been shown[16] that the spinodal decomposition is complicated as a result of the possibility of the relaxation of stresses leading to a time variation of the elastic energy. In order to take it into account, the elastic energy at time t can be converted into the elastic energy at time $t + \Delta t$ in accordance with the equation

$$E_{rel}(t+\Delta t) = E_{unrel}(t)\exp(-2\Delta t/S), \qquad (61)$$

where $S = \nu_\nu \Theta M^0/\lambda^2 G_S$, ν_ν is the shear viscosity, G_S the modulus of shear, M^0 the mobility of the molecules, and Θ the thermal energy per molecule.

It is quite evident that the contribution of the elastic energy in complex multicomponent systems is minimal at the beginning of the phase separation process and should increase with increase of the difference between the compositions of the microregions. As a result, when the thermodynamic driving force of the phase separation is balanced by the contribution due to elastic stresses caused by the entanglements of fragments of the network structure, the system is stabilised in a state of partial separation of the components.

The limit of the stability of the stressed state of a polymer system is in this case characterised by the position of the curves located below the chemical spinodal. This curve reflects the real condition governing the transition to the two-phase state. We have called it the lower real spinodal. We note yet again the significant difference between the concept of the coherent spinodal introduced by Cahn and the concept of the real spinodal which we have resorted to in order to describe the limit of stability in the transition to the two-phase state of polymer systems.[73] The coherent spinodal is known[9,10] to be a curve outside which no processes involving the decomposition of the one-phase solution are possible. The real spinodal is a curve separating the state of partial phase separation from the two-phase state. It follows from Eqn.(17) that, for systems with an upper consolute temperature (UCT), the real spinodal passes below the corresponding chemical spinodal. It must be assumed that for certain systems, such as polyblock network polymers or interpenetrating polymer networks, the region of unstable states within the lower real spinodal lies far below the chemical spinodal and may be altogether inaccessible.

The results of temperature studies of the epoxydiene networks examined above have shown that systems of this kind can be not only in a state of enforced blending but also in a state of enforced microphase separation of the components. If the presence of a UCT is characteristic of systems of this kind, then completion of the transition to the state of a one-phase solution corresponds to a curve lying above the chemical spinodal. This curve can be called the upper real spinodal. Its position is determined by the elastic stresses, which are necessary, in the absence of free migration of blocks of different chemical nature, for the transition of the system with microphase separation to the one-phase state by heating.

Thus, depending on the previous history, multicomponent polymer systems with a three-dimensional network of chemical bonds can possess a more or less extensive region in the vicinity of the chemical spinodal in which states with partial phase separation of the components are realised. Evidently, in the transition from the one-phase state to the two-phase state, one-phase systems with an equilibrium distribution of composition fluctuations exist above the chemical spinodal. Below the real spinodal, there are two-phase systems with a definite degree of dispersion.

In the system between the chemical and real spinodals, there are also microregions with an inhomogeneous distribution of the components. However, they can no longer be regarded as equilibrium composition fluctuations, because thermodynamic forces, tending to cause phase separation, displace the system from the state of equilibrium towards an approach to the two-phase state. Despite the failure of the phase separation process to reach completion, the region of states between the chemical and real spinodals is relatively stable. However, in terms of the concept of "one-phase–two-phase system", within the framework of which we operate

in considering binary systems, there are no analogues of such intermediate states.

Systems of this kind can be usefully segregated from the set of one- and two-phase systems. The expression "concentration fluctuation" really has no bearing on the microregions (states) in the system located in the region of the phase diagram between the chemical and real spinodals, because it is applicable only to one-phase systems. Nor can they be called microphase regions, because the latter are characteristic only of two-phase systems. Bearing in mind that the microregions of inhomogeneity in systems intermediate between one- and two-phase systems are in principle capable of passing into microphase regions, they can be regarded as virtual microphase regions and can be referred to accordingly as phasons.[73] The system located in the region of states between the chemical and real spinodals is a system of the phason type.

We shall consider how such a system differs from the "classical systems" undergoing spinodal decomposition in the Cahn–Hilliard theory. According to the conditions in the phase separation mechanism, the term Y in Eqn.(17), which defines the limit of instability (i.e. the onset of spinodal decomposition), can be a function of time, temperature, the degree of segregation attained at the given instant, etc. After the system has reached the region of the chemical spinodal and, following the loss of stability, processes increasing the contribution of Y develop in it in the course of time, after which, following the attainment of a particular instant (as a consequence of relaxation processes or chemical reactions), they diminish this contribution. Therefore, having begun to decompose, the system can be additionally stabilised at some stage or the stabilisation effect vanishes completely. If this condition did not obtain, then, on transition through the chemical spinodal, the system would have undergone no changes whatever. This factor actually determines the appearance of phason systems, the main characteristic of which is the degree of separation into phases. Specific dimensions of the order of magnitude of tens of nanometers are characteristic of the corresponding microregions of heterogeneity.

VII. EXAMINATION OF SPINODAL DECOMPOSITION WITHIN THE FRAMEWORK OF THE FORMALISM OF THE NON-LINEAR THERMODYNAMICS OF IRREVERSIBLE PROCESSES

The conditions for thermodynamic equilibrium in isolated systems is an entropy maximum, while for systems at a fixed temperature it is a minimum in the Helmholtz free energy. When these requirements are taken into account, the corresponding systems can be described by equations whose solution corresponds to the so-called thermodynamic branch. If the action on the system is varied in such a way that the latter moves further and further away from equilibrium, non-equilibrium thermodynamics makes it possible to formulate an adequate condition for the stability of the thermodynamic branch.[74,75] On the other hand, if this condition is not fulfilled, then the thermodynamic branch can become unstable and the appearance of a new structure characterised by coherent behaviour will become possible in the system.

Thus a new type of organisation, linking the coherent space–time behaviour of the system to dynamic processes within it, can arise outside the region of stability of the thermodynamic branch. In the studies of Prigogine and co-workers,[74,75] it has been shown that the so-called dissipative structures appearing under these conditions differ significantly from the "equilibrium structure" studied by classical thermodynamics. An analogy has been noted,[76,78] between the alternation of low- and high-energy regions, characteristic of the dissipative structures, and the appearance of modulated structures as a result of spinodal decomposition. Having expressed the thermodynamic forces and fluxes in terms of concentration gradients, Prigogine showed that the following relation is valid for the increment in the generation of entropy near the stationary state of the system:

$$\Delta P = \int_V \left[\frac{1}{2} \delta^2 P + \sum_{kl}' R_{kl} \nabla c_k \nabla c_l + \ldots \right] , \qquad (62)$$

where

$$R_{kl} = D_{kl} \left(\frac{1}{T} \frac{\partial \mu_l}{\partial c_k} \right) .$$

For a binary system, the last term of Eqn.(62) is analogous to the term $k(\nabla c)^2$ in Eqn.(2) and $\frac{1}{2}(\partial^2 f/\partial c^2)(c - c_0)^2$ corresponds to $\frac{1}{2}\delta^2 P$ in the expansion of the increment of the generation of entropy. Thus the spinodal can be regarded as representing the condition for the equality of the excess generation of entropy to zero. Comparison of the above relations makes it possible to express the wavelengths of the modulated structure in spinodal decomposition in the following form

$$\lambda_m = \left[-8\pi (c - c_0)^2 \sum_{kl}' R_{kl} + \ldots \Big/ \sum_k \delta J_k \delta X_k \right] , \qquad (63)$$

where J_k and X_k are the generalised flux and force. Consequently the formation, as a result of phase separation, of diffuse microregions intermediate between the initial one-phase and the resulting two-phase systems can be regarded as a result of the breakdown of the stability of the phase separation process within the spinodal. The thermodynamic forces then tend to a minimum and the kinetic fluxes can increase in one part of the system and decrease in another, leading to the formation of dissipative structures.

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As already mentioned, the theory of spinodal decomposition was developed approximately 20 years ago by Cahn, Hilliard, Hillert and their successors to describe the processes occurring in metallic alloys. In the thermodynamics of polymers this period has been characterised by an intense development of a general theory of polymer solutions. During the last 20 years, much attention has been devoted to the application of the Flory–Huggins theory of solutions to the description of polymer blends and their thermodynamic compatibility has come to be regarded as one of the most important factors determining the operational properties of polymeric materials. Studies on spinodal decomposition in polymer system began to develop only in the last 10 years. We believe that this has been due to the increasing practical application of polymer blends, as shown, in particular, by the publication of a number of large monographs on these questions.[79–82]

The data which we have considered show that the spinodal mechanism of phase separation in polymer blends is the decisive factor in structure formation in such blends and hence in establishing the entire set of the physicomechanical properties of these materials. In the first place one should note polymeric composite materials and the clear tendency to employ in the latter second generation binders. Such binders may be either alloys and blends of thermoplastic polymers or systems of the type of interpenetrating, half-interpenetrating, and segregated networks,[83] which should

be regarded as hybrid binders.[88] A characteristic feature of second generation binders is that in essence they are themselves composite materials whose properties are determined to a large extent by their phase state and, as can be seen from the foregoing, by the character and the degree of completion of the phase separation in hybrid binders during their formation. An important task in the thermodynamics of polymer–polymer blends is therefore the accumulation of experimental data and the determination of the fundamental characteristics of the phase separation via the spinodal mechanism as a function of the parameters of the thermodynamic interactions of the components, the conditions in their polymerisation or polycondensation, the cooling regimes, and similar factors.

Only the main theoretical postulates have now been formulated and the applicability of the theory to the description of the experimental data has been demonstrated in relation to what are so far limited instances. The question of the relation between the phase separation conditions and the conditions for the interaction of binary polymer systems with fillers is important for the creation of composite materials based on second generation binders. Only a limited number of experimental data are so far available on this question.[84–87] At the same time one may claim that the introduction of a filler into the system can exert at least two different effects on the spinodal decomposition. If one of the components of the binary system interacts preferentially with the surface, the filler should promote an increase of the rate of phase separation. If the energies of the interaction of the components with the surface are approximately the same, then, as a consequence of the adsorption effects and the overall decrease of molecular mobility near the interface, phase separation processes may be inhibited. It can be shown that, under certain conditions, there is also a possibility of a change in the positions of the phase equilibrium curves (binodal and spinodal) under the influence of the surface of the solid.

The data presented in this review show that the structures arising as a result of spinodal decomposition in polymer–polymer systems then remain in a metastable state, i.e. as a rule the spinodal decomposition does not reach the stage where the system is fully separated into two coexisting phases. Otherwise studies on these lines would have been only of purely theoretical interest. However, it follows from this that evidently the most adequate description of the structures produced can be achieved using the principles of irreversible thermodynamics and the concept of dissipative structures. We believe that studies on polymer–polymer systems within the framework of the formalism of irreversible thermodynamics should have priority in the future over studies based on the apparatus of the classical thermodynamics of phase equilibria.

REFERENCES

1. L.D.Landau and E.M.Lifshits, "Statisticheskaya Fizika" (Statistical Physics), Izd.Nauka, Moscow, 1964, p.405.
2. J.W.Gibbs, "Collected Works", Yale Univ.Press, Yale, 1948, Vol.1, p.360.
3. E.M.Lifshits and L.P.Pitaevskii, "Fizicheskaya Kinetika" (Physical Kinetics), Izd.Nauka, Moscow, 1979, p.503.
4. J.D.van der Waals, Verhandel.Koninkl.Akad. Wetenschap.Amsterdam, Afdeel.Naturk.Sect.1, 1893.
5. E.W.Hart, Phys.Rev., 1959, **113**, 412.
6. J.W.Cahn and J.E.Hilliard, J.Chem.Phys., 1958, **28**, 238.
7. J.W.Cahn, J.Chem.Phys., 1959, **30**, 1121.
8. J.W.Cahn and J.E.Hilliard, J.Chem.Phys., 1959, **31**, 688.
9. J.W.Cahn, J.Chem.Phys., 1965, **42**, 93.
10. J.W.Cahn, Trans.Metallurg.Soc.AIME, 1968, **242**(2), 166.
11. J.W.Cahn, Acta Metallurg., 1961, **9**, 795.
12. K.V.Chuistov, "Modulirovannye Struktury v Stareyushchikh Splavakh" (Modulated Structures in Ageing Alloys), Izd.Naukova Dumka, Kiev, 1975.
13. N.S.Andreev, O.V.Mazurin, E.A.Porai-Koshits, G.P.Raskova, and V.N.Filipovich, "Yavleniya Likvatsii v Steklakh" (Liquation Phenomena in Glasses), Izd.Nauka, Leningrad, 1974.
14. J.W.Cahn, Acta Metallurg., 1966, **14**, 1685.
15. K.B.Rundman and J.E.Hilliard, Acta Metallurg., 1967, **15**, 1035.
16. L.A.Swanger, P.K.Gupta, and A.R.Cooper, Acta Metallurg., 1970, **18**, 9.
17. L.H.Shendelman and J.T.O'Toole, J.Colloid Interface Sci., 1968, **27**, 145.
18. W.A.Tiller, G.M.Pound, and J.P.Hirth, Acta Metallurg., 1970, **18**, 225.
19. W.E.Lanclois and F.F.Abraham, Chem.Phys.Letters, 1977, **52**, 129.
20. H.Metiu, K.Kitahara, and Y.Ross, J.Chem.Phys., 1976, **65**, 393.
21. C.Varea and A.Rodledo, J.Chem.Phys., 1981, **75**, 5080.
22. P.Debye, J.Chem.Phys., 1959, **31**, 680.
23. J.J.van Aartsen, Europ.Polymer J., 1970, **6**, 919.
24. P.J.Flory, "Principles of Polymer Chemistry", Cornell Univ.Press, Ithaca, 1953, p.495.
25. L.P.McMaster, Adv.Chem.Ser., 1975, **142**, 43.
26. P.G.de Gennes, J.Chem.Phys., 1980, **72**, 4756.
27. P.Pincus, J.Chem.Phys., 1981, **75**, 1996.
28. P.G.de Gennes, J.Phys.(Paris) Letters, 1977, **38L**, 441.
29. M.Doud and P.G.de Gennes, J.Chem.Sci., Polymer Phys.Ed., 1979, **17**, 1971.
30. J.Klein, Macromolecules, 1978, **11**, 852.
31. P.G.de Gennes, "Scaling Concepts in Polymer Physics", Cornell Univ.Press, Ithaca, 1979, Chapter 4.
32. E.Helfand and Y.Tagami, J.Polymer Sci., Polymer Letters, 1971, **9**, 741.
33. E.Helfand and A.M.Sapse, J.Polymer Sci., Polymer Symp., 1954(54), 289.
34. P.G.de Gennes, J.Phys.(Paris), 1981, **42**, 735.
35. P.G.de Gennes, J.Phys.(Paris), Letters, 1979, **40**, 69.
36. J.J.van Aartsen and C.A.Smolders, Europ. Polymer J., 1970, **6**, 1105.
37. C.A.Smolders, J.J.van Aartsen, and A.Steenbergen, Kolloid Z.–Z.Polymere, 1971, **243**, 14.
38. P.T.van Emmerik and C.A.Smolders, J.Polymer Sci.C, 1972(38), 73.
39. P.T.van Emmerik, C.A.Smolders, and W.Geymaer, Europ.Polymer J., 1973, **8**, 309.
40. V.M.Andreeva, A.A.Tager, I.S.Tyukova, and L.F.Golenkova, Vysokomol.Soed., 1977, **19A**, 2604.
41. E.Pines and W.Prins, Macromolecules, 1973, **6**, 888.
42. G.T.Feke and W.Prins, Macromolecules, 1974, **7**, 527.
43. S.Wellinghoff, J.Shaw, and E.Baer, Macromolecules, 1979, **12**, 932.
44. L.P.McMaster, Amer.Chem.Soc.Polymer Prepr., 1974, **15**, 254.

45. I.M.Lifshitz and V.V.Slyozov, J.Phys.Chem.Solids, 1961, **19**, 35.
46. S.Tomotika, Proc.Roy.Soc., 1935, **150**, 322.
47. T.Nishi, T.T.Wang, and T.K.Kwei, Macromolecules, 1975, **8**, 227.
48. S.Reich and Y.Cohen, J.Polymer Sci., Polymer Symp.Ed., 1981, **19**, 1255.
49. F.P.Price, J.Polymer Sci., Polymer Symp., 1978, **63**, 13.
50. D.J.Meier, J.Polymer Sci.C, 1969(26), 81.
51. D.F.Leary and M.C.Williams, J.Polymer Sci., Polymer Phys.Ed., 1973, **11**, 960.
52. S.Krause, Macromolecules, 1970, **3**, 84.
53. E.Helfand and Z.R.Wasserman, Macromolecules, 1976, **9**, 879.
54. L.Leibler, Macromolecules, 1980, **13**, 1602.
55. A.Keller, E.Pedemonte, and F.M.Willnouth, Kolloid.Z.–Z.Polymere, 1970, **238**(1/2), 385.
56. P.R.Lewis and C.Price, Polymer, 1971, **12**, 258.
57. G.Hadziioannou, A.Mathis, and A.Skoulios, Coll. Polymer Sci., 1979, **257**, 136.
58. J.V.Dawkins, in "Block Copolymers" (Edited by D.C.Allport and W.H.Janes), Wiley, New York, 1973.
59. I.Ya.Erukhimovich, Vysokomol.Soed., 1982, **24A**, 1942.
60. I.Ya.Erukhimovich, Vysokomol.Soed., 1982, **24A**, 1950.
61. R.Roe, M.Fishkis, and J.C.Chang, Macromolecules, 1981, **14**, 1091.
62. A.A.Konkin, in "Uglerodnye i Drugie Zharostoikie Voloknistye Materialy" (Carbonaceous and Other Heat Resistant Fibrous Materials), Izd.Khimiya, Moscow, 1974.
63. W.Ruland, J.Polymer Sci.C, 1969(28), 143.
64. R.Perret and W.Ruland, J.Appl.Cryst., 1970, **3**(6), 525.
65. A.Fourdeux, R.Perret, and W.Ruland, "International Conference on Carbon Fibres, Their Composites and Applications", London, 1971, Paper No.9.
66. Yu.S.Lipatov and V.V.Shilov, "Preprinty II Mezhdunarodnogo Simpoziuma po Khimicheskim Voloknam" (Preprints at the IInd International Symposium on Chemical Fibres, Kalinin, 1981, Vol.5, p.49.
67. S.P.Popkov, "Studneobraznoe Sostoyanie Polimerov" The Gel-Like State of Polymers), Izd.Khimiya, Moscow, 1974.
68. Yu.S.Lipatov, V.V.Shilov, V.A.Bogdanovich, D.P.Kochetov, and V.K.Grishchenko, Dokl.Akad. Nauk Ukrain.SSR, Ser.B, 1981(7), 50.
69. V.V.Shilov, Yu.S.Lipatov, L.V.Karabanova, and L.M.Sergeeva, J.Polymer Sci., Polymer Chem.Ed., 1979, **17**, 3083.
70. V.V.Shilov, L.V.Karabanova, Yu.S.Lipatov, V.A.Bogdanovich, and L.M.Sergeeva, Vysokomol. Soed., 1980, **22A**, 1354.
71. R.Bonart and E.H.Müller, J.Macromol.Sci.(Phys.), 1974, **10**, 177.
72. Yu.S.Lipatov, V.V.Shilov, Yu.P.Gomza, and N.A.Kruglyak, "Rentgenograficheskie Metody Izucheniya Polimernykh Sistem" (X-Ray Diffraction Methods for the Investigation of Polymer Systems), Izd.Naukova Dumka, Kiev, 1982, p.135.
73. Yu.S.Lipatov and V.V.Shilov, Kompozitsionnye Polimernye Materialy, 1981(11), 55.
74. P.Glansdorff and I.Prigogine, "Thermodynamic Theory of Structure, Stability, and Fluctuations" (Translated into Russian), Izd.Mir, Moscow, 1973.
75. G.Nicolis and I.Prigogine, "Self-Organisation in Non-Equilibrium Systems" (Translated into Russian), Izd.Mir, Moscow, 1979, p.66.
76. P.H.Lindenmeyer, Polymer J., 1979, **11**, 677.
77. P.H.Lindenmeyer, J.Polymer Sci., Polymer Phys.Ed., 1979, **17**, 1965.
78. P.H.Lindenmeyer, Textile Res.J., 1980, **50**, 395.
79. Yu.S.Lipatov, "Fizicheskaya Khimiya Napolnennykh Polimerov" (Physical Chemistry of Filled Polymers), Izd.Khimiya, Moscow, 1977.
80. V.N.Kuleznev, "Smesi Polimerov" (Polymer Blends), Izd.Khimiya, Moscow, 1980.
81. Yu.S.Lipatov and L.M.Sergeeva, "Vzaimopronikayushchie Polimernye Setki" (Interpenetrating Polymer Networks), Izd.Naukova Dumka, Kiev, 1979.
82. D.R.Paul and S.Newman (Editors), "Polymer Blends" (Translated into Russian), Izd.Mir, Moscow, 1981.
83. Yu.S.Lipatov, V.F.Rosovizky, and Yu.Masliuk, J.Appl.Polymer Sci., 1982, **27**, 455.
84. Yu.S.Lipatov, V.V.Shifrin, and F.G.Fabulyak, Vysokomol.Soed., 1976, **18A**, 767.
85. Yu.S.Lipatov, A.E.Fainerman, and V.V.Shifrin, Dokl.Akad.Nauk SSSR, 1977, **234**, 596.
86. V.V.Shifrin, F.G.Fabulyak, and Yu.S.Lipatov, Vysokomol.Soed., 1978, **20B**, 87.
87. Yu.S.Lipatov, in "Adhesion and Adsorption of Polymers", Vol.12B (Edited by L.-H.Lee), Plenum Press, New York, 1980, p.601.
88. Yu.S.Lipatov, "Mekhanika Kompizitnykh Materialov" (The Mechanics of Composite Materials), 1983, p.771.
89. V.V.Shilov, Doctoral Thesis in Chemical Sciences, Institute of the Chemistry of Macromolecular Compounds, Academy of Sciences of the Ukrainian SSR, Kiev, 1983.

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