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Nucleation: theory and experiment

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Abstract. Various theoretical and experimental methods for studying nucleation are considered. Since theoretical methods have fundamental limitations, information is gained from experimental research. It is demonstrated that the nucleation theory is entering a new phase of development, which is going to be, in essence, semiempirical. A semiempirical method for constructing nucleation rate surfaces is described. The topology of these surfaces in the limit of the zero nucleation rate can be determined using phase equilibrium diagrams. This opens up possibilities for revising certain approximations employed in experiments and particular axiomatic statements of the classical nucleation theory. Examples of the practical use of nucleation essential for the development of modern technologies are given. The bibliography includes 396 references.

I. Introduction

In the last two decades, the problems of nucleation have attracted considerable interest. These problems are related to many disciplines and the vast majority of systems in which first-order phase transitions can occur. The available nucleation theories are arbitrarily divided into the so-called 'theories of original potential' and phenomenological theories. With the aim of simplifying the problem of determination of the nucleation rate, the authors who uphold the former line of investigation consider average fluctuations of a nucleating medium to find conditions under which the 'averaged' cluster evolves into a droplet.[1] The principle of detailed equilibrium is invoked to solve the kinetic problem of cluster growth. In doing so, one should specify the equilibrium distribution in such a way that the averaged clusters could, to a certain degree, simulate non-equilibrium clusters.[1]

Generally, a method for describing nucleation follows, with some delay, after the development of approximate methods in the many-body theory (see, for example, Ref. 2). The non-equilibrium state of a macroscopic system can be indirectly taken into account, using, in particular, the linear reaction theory. In this theory, the effects caused, for example, by thermal perturbations are expressed in terms of mechanical perturbations. Alternative methods employ the theory of stochastic processes and the Fokker – Planck equation or Onsager's hypothesis according to which the fluctuation damping follows the same law as the change in the corresponding macroscopic variables. There are also methods based on the use of a local-equilibrium distribution (*i.e.*, on the assumption that a near-equilibrium distribution occurs in small volumes in the case of moderate deviations from equilibrium) as the initial condition for the fulfilment of the Liouville equation. The methods of statistical Gibbs ensembles for non-equilibrium systems (for example, Zubarev's method of a non-equilibrium statistical operator based on the construction of local integrals of motion) as well as the method accounting for the effect of thermostating by considering non-potential forces find wide application.

In recent years, certain advances have been made in the study of non-equilibrium processes in dense multiparticle systems. Thus, the Vlasov equation was derived for a multiparticle system involving the field $U(r)$, which depends on the nature of particles

$$\frac{\partial f}{\partial t} + \boldsymbol{v}\,\mathrm{grad}_r f + \boldsymbol{a}\,\mathrm{grad}_r f = 0.$$

Here f is the distribution function of single-particle states in the phase space of coordinates (r) and rates ($\boldsymbol{v}$), $\boldsymbol{a} = -\mathrm{grad}_r U(r)/m$ (m is the particle mass). In the monograph,[3] this equation was considered as a special case of the more general Vlasov – Uehling – Uhlenbeck equation allowing for the formation of coupled states. The Vlasov equation results from the averaging of the generalised equation in the lowest approximation, where the energy of quasiparticles is calculated in the self-consistent Hartree – Fock approximation and collisions can be ignored. Vlasov deduced this equation by assuming that particles are not localised and their properties are responsible for the state of the system. This eliminates the problem of field averaging.

Vlasov reasoned that this equation does not follow from the Hartree – Fock or Liouville equations because of the presence of the property of branching of solutions, whereas neither processes of crystal formation nor crystal structures can be described using equations of classical statistics and quantum mechanics. Hence, the problem of allowing for collective interactions in a multiparticle system is replaced by the problem of finding an interaction potential of non-localised particles, including its functional dependence on the characteristics of the macroscopic state of the

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system (for example, on the temperature in the consideration of a crystallisation process). In other words, simplified relations were proposed for the description of physical systems, which allow one to obtain results consistent with experimental data. This is achieved due to the fact that many systems can be described in an approximation of noninteracting particles in a potential field.[2] Of methods employing this approximation, let us note first of all the effective (self-consistent) field methods. The idea is that a certain simplification is introduced, whereby the motion of a given particle can be considered as a motion in a potential field, which depends only on the coordinate of this particle and is independent of the coordinates of all other particles. If the properties of all particles in this effective field are known, the assumed potential can be calculated. If no consistence with the expected result is achieved, the effective field can be 'corrected' until the desired result is obtained.

In the approximation used in the classical nucleation theory, the cluster is considered as a liquid droplet of uniform density equal to the density of the macroscopic liquid; the droplet has a sharp boundary with the surrounding metastable phase. Using this model, one can calculate the free energies of real systems taking into account the translational degrees of freedom of the cluster.[4] The droplet model describes only some of the possible configurations of the cluster consisting of a particular number of molecules, and there is no assurance that it is one of these configurations that plays a decisive role in the dynamic process.[1]

The clusters under consideration can be divided into two types, *viz*., stable clusters whose configurations are determined by their own structures and clusters whose structures depend on the results obtained in the context of a particular theory (for example, the density functional theory). The former type of clusters corresponds to the approximation of noninteracting particles, whereas the latter type corresponds to the approximation of interacting particles, which is similar to the self-consistent field approximation. It should be noted that by specifying *a priori* the type of the cluster (rather than determining it by analysing intermolecular interactions), we actually go from analytical theories to phenomenological approaches.[1]

The best results, which are in quantitative or semiquantitative agreement with experimental data, were obtained using models based on the classical nucleation theory. In essence, such models are phenomenological rather than molecular.[1] The foundations of the classical nucleation theory were laid by Gibbs. In the 1940–1950s, this theory acquired its modern meaning after publications by Zeldovich [5] and Frenkel.[6]

In recent years, many studies have been devoted to the development of molecular theories of nucleation. However, the applications of certain relations of statistical mechanics to nucleation were not always justified.[2,3] The thermodynamic approach to the description of nucleation leads essentially to more than noting the introduction of additional terms to equations for the work of formation of critical nuclei of a new phase. For instance, Abraham [7] took into account characteristic features of dipole–dipole interactions. Dillmann and Meier [8,9] proposed various phenomenological coefficients. Overlapping of clusters was accounted for in the study.[10]

The correlation between the modern theoretical and experimental data can be judged from the curves shown in Fig. 1.[11] It should be noted that the agreement between the results can be substantially improved by varying a certain parameter of the theory, *e.g*., the surface tension, within its experimental error. At the same time, out of numerous theories one can always choose a theory, which is best suited for the description of a particular series of experimental results. Therefore, a good agreement between theoretical and experimental data does not evidence the predictive force of the theory.

In the last five decades, the accuracy of experimental methods was substantially improved. It was expected that the classical nucleation theory would be experimentally confirmed. Actually, abundant experimental data, which have been accumulated, are

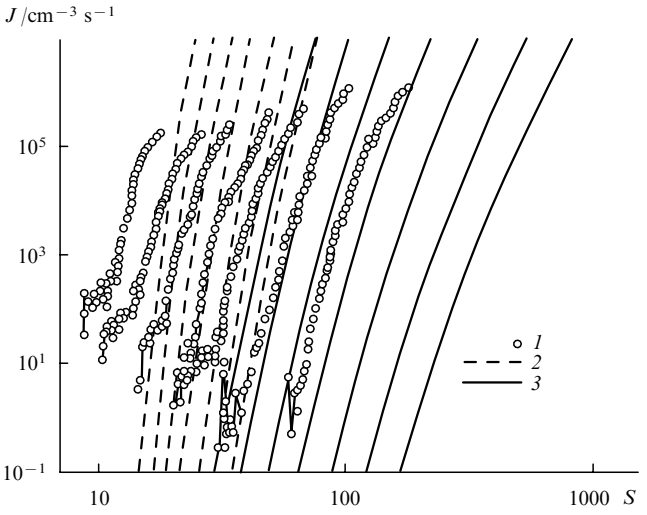


Figure 1. Experimental (*1*) plots of the nucleation rate J *vs*. supersaturation S of an octanol vapour in an octanol–sulfur hexafluoride system and analogous dependences calculated according to the classical theory (*2*) and the Dillmann–Meier theory (*3*).[11]
Nucleation temperatures for each series of experiments /°C (from right to left): 261.8, 266.3, 271.2, 276.4, 281.5, 286.6, 291.7.

not contradictory with this theory. However, taking into account the ever-increasing accuracy of experimental results, it becomes more and more evident that the classical nucleation theory has limits of applicability. Presently, there is a pressing need to reveal these limits and develop new nucleation models, which can predict nucleation rates in various systems.

Approximately 10 years ago, semiempirical methods were proposed for constructing nucleation rate surfaces based on phase equilibrium diagrams.[12,13] Based on this idea, nucleation rate surfaces were constructed for a series of simplest systems.[14] Assuming this rather evident concept, it is apparent that the multitude of nucleation rate surfaces can be constructed from the multitude of phase equilibrium lines. In other words, 'multiple' nucleation rate surfaces are a rule rather than an exception. Hence, scarce experimental data on nucleation rates need analysis for 'singularity'. A direct experiment on the detection of two rate surfaces upon glycerol nucleation in the vicinity of its triple point was described in study.[15] Each surface corresponds to its own nucleation channel. By contrast, the classical nucleation theory generally considers a singular nucleation rate surface. Of course, the multiplicity is implicitly embedded in the classical theory; however, no attention has been given to this fact until recently. Evidently, in the presence of many surfaces, attempts to describe the overall nucleation rate in the singular approximation of the classical theory are unjustified.

In the present review, attention is primarily given to studies published in the last 10–15 years. Earlier publications are considered, when the retrospective analysis of the problem is necessary. It may seem that the number of references relating to some problems, which have been covered in detail in scientific publications, is insufficient, whereas references relating to other problems, which are no less important but have not been adequately explored, are excessive. Some reviews devoted to rather narrow subject matters are mentioned with the aim of demonstrating the generality of approaches to the description of nucleation in different systems. The present review does not include particular details, for example, the preparation of sols for chemical syntheses in homogeneous solutions, micelles, vesicles, Langmuir–Blodgett films, polymers, glasses, zeolites, *etc*. Undoubtedly, the main conclusions are applicable to all systems in which nucleation takes place. The lines of investigation, which, in my opinion, show promise for the development of the

nucleation theory, are considered in most detail. Presently, is seems reasonable to focus efforts on developing individual parametric semiempirical theories for particular systems characterised by topologically similar (brought to a single topological form) phase equilibrium diagrams. Apparently, a combination of these theories based on the similarity criteria will be the next step in the development of concepts of nucleation. Progress in experimental methods gives promise that new unique results will be obtained in the nearest future, which will give impetus to further theoretical investigations of nucleation.

II. Nucleation theory

Nucleation accompanies first-order phase transitions. They occur in the initial metastable phase due to the fluctuation formation and nucleation (cluster formation) of a new phase.[16] The formation of a macroscopic nucleus requires energy for the formation of an interface between the old and newly formed phases. A need for an excess energy gives rise to hysteresis phenomena, such as supercooling (or superheating) of melts and solutions relative to the equilibrium melting point, supercooling of gases, overvoltage upon electrodeposition of films, *etc*.

In 1878, Gibbs was the first to describe theoretically the formation of a new phase.[17] He has provided a rigorous thermodynamic definition for critical nuclei of a new phase and laid foundations for the formalised description of nucleation rates. Almost five decades later, Volmer and Weber [18] elaborated the Gibbs model in a study devoted to nucleation kinetics. Volmer considered the nucleation work as the activation energy and described qualitatively the nucleation of a new phase in the course of crystallisation.[19] He also introduced the concept of three- and two-dimensional nuclei of a new phase and related their fluctuation appearance to the nucleation and crystallisation rates.

However, the proposed model has drawbacks. For example, the pre-exponential factor in the corresponding kinetic equations remains undetermined due to which the theory is only semiquantitative. Further efforts by researchers were directed at searching for more rigorous theoretical foundations of the kinetics of the process. Farkas [20] solved a system of Szilard kinetic equations describing the formation of droplets from a vapour. The nucleation theory as applied to the stationary kinetics of the droplet formation from a supersaturated vapour was elaborated in studies by Kaischew and Stranski.[21] Becker and Döring [22] completed the study aimed at determining the constants in equations considered by Farkas. They created a general picture of various molecular events proceeding upon the formation of a new phase.

Becker and Döring's statistical theory considers a simplified stationary model according to which the average number of nuclei consisting of 2, 3, 4, ... , n molecules remains constant with time, although depends on external conditions. Clusters whose sizes are larger than the critical value are withdrawn from the system, and the vapour pressure is maintained constant due to the introduction of monomers (molecules, atoms). For nuclei of each size, the evaporation and condensation rates are in balance. By going from a discrete to continual problem and using integration, the authors estimated the nucleation rate (J). The latter is equal to the number of clusters, which are capable of growing and are formed in a unit volume (generally, in cubic centimeter) in a unit time (1 s). It was assumed that clusters containing n molecules are formed from nuclei containing $(n-1)$ molecules.[22] This theory was completed in the above-mentioned studies by Zeldovich [5] and Frenkel.[6] The specificity of formation of crystalline nuclei from liquid and gas phases and the problem of heterogeneous nucleation were discussed in Refs 6, 23 and 24. The theory, as it formulated by Zeldovich and Frenkel, is called the 'classical nucleation theory'.

Up to the early 1960s, it was believed that this theory adequately described homogeneous condensation of a supersaturated vapour. The predictions based on this theory were in good agreement with results of experimental measurements of critical supersaturations using a Wilson chamber and studies of isentropic expansion of a gas in a nozzle or a turbulent vapour flow evaporated into a cold gas. However, in succeeding years, the determination of the dependence of the nucleation rate on supersaturation became possible and the principal foundations of the classical theory and its applicability to interpretation of experimental data were doubted. This gave rise to several tens of equations for the nucleation rate of a new phase.

1. Free energy of nucleation in the classical nucleation theory

For a metastable (according to the Gibbs definition [17]) system to become stable, energy sufficient for the creation of a phase interface is required. The free energy of cluster formation involved in a number of thermodynamic equations is one of the main parameters in the nucleation theory. The macroscopic approach, which employs concepts of thermodynamics and statistical physics developed for systems consisting of a large number of molecules, provides a quantitative description of nucleation. Below is given a brief derivation of the equation for the free energy of nucleation in approximations of the classical nucleation theory, which was described in detail in many publications (in particular, the latest versions were published in the book of collective works [25]).

In the droplet approximation, a change in the Gibbs free energy (ΔG) upon the formation of a cluster consisting of n molecules in a closed system, which contains a vapour at the temperature T and pressure p, can be written as follows

$$\Delta G = n(\mu_l - \mu_v) + 4\pi r^2\sigma, \tag{1}$$

where μ_l and μ_v are the chemical potentials of molecules in the liquid and vapour phases, respectively, r is the radius of the cluster and σ is the surface tension. Under isothermal conditions, the first component in the right-hand side of Eqn (1) can be estimated from the equation

$$\mathrm{d}(\mu_l - \mu_v) = (\upsilon_l - \upsilon_v)\mathrm{d}p_v, \tag{2}$$

where υ_l and υ_v are the specific volumes of molecules in the liquid and vapour phases, respectively, and p_v is the vapour pressure. If the vapour is considered as an ideal gas and the volume of the molecule in the condensed phase is ignored, the integration of Eqn (2) gives

$$\mu_l - \mu_v = -k_B T \ln S, \tag{3}$$

where k_B is the Boltzmann constant, $S = p_v/p_0$ is supersaturation (p_0 is an equilibrium vapour pressure over the planar interface at the temperature T). Assuming that nuclei of a new phase (clusters) retain the macroscopic physicochemical properties, the overall work of formation of rather large clusters in the droplet approximation can be expressed as a sum of surface ($4\pi r^2\sigma$) and volume ($nk_BT\ln S$) changes in the Gibbs free energy.† Then, the change in the free energy upon cluster formation is

$$\Delta G = 4\pi r^2\sigma - nk_BT\ln S, \tag{4}$$

where $n = (4/3)(\pi r^3/\upsilon_l)$. A liquid nucleus can grow to a droplet only when its size becomes larger than the critical radius r^*. The terms in Eqn (4) depend differently on r and have opposite signs at $S > 1$. Hence, the plot of ΔG *vs*. r passes through a maximum. The free energy of formation of a cluster with a critical size is

$$\Delta G^* = -\frac{4}{3}\pi(r^*)^3\frac{k_BT\ln S}{\upsilon_l} + 4\pi(r^*)^2\sigma. \tag{5}$$

† In the present review, the problem is considered in no more detail than follows from the early droplet model and determination of the surface and volume contributions. According to this model, a cluster is represented as an isotropic sphere covered with an infinitely thin film with a surface tension σ.

At a maximum, $r = r^*$ and $\mathrm{d}(\Delta G)/\mathrm{d}r = 0$. Hence, the radius of a critical nucleus can be easily determined as follows

$$r^* = \frac{2\sigma v_l}{k_B T \ln S}. \quad (6)$$

Equation (6) enables one to determine the equilibrium pressure of a saturated vapour over a droplet of radius r^* as a function of initial vapour supersaturation and cluster size. From Eqns (5) and (6), we have the following known equation

$$\Delta G^* = \frac{4}{3}\pi (r^*)^2 \sigma. \quad (7)$$

In the droplet approximation, ΔG^* is equal to one-third of the surface energy of the cluster. By excluding r^*, we obtain another form of the same equation

$$\Delta G^* = \frac{16}{3}\frac{\pi \sigma^3 v_l^2}{(k_B T \ln S)^2}. \quad (8)$$

The dynamics of droplet formation at pressures close to the equilibrium vapour pressure over the planar surface can be represented as follows. At $p < p_0$, the free energy of cluster formation rapidly increases as the cluster size increases. In the system occurring under these conditions, clusters of any sizes can, in principle, exist; however, the smallest clusters generally prevail in such systems. At $p > p_0$, the number of nuclei with a radius smaller than r^* undergoes random fluctuations. When the nucleus reaches a critical size, any favourable fluctuation leads to its infinite growth. Then the problem lies in estimating the rate (frequency) of formation of nuclei of the critical size.

The nucleation rate J is determined by the number of viable nuclei formed in a unit volume in a unit time. According to the classical theory,

$$J = \beta Z s^* c_{n^*} = 2 v_l \zeta_c \sqrt{\sigma}\frac{N^2}{\sqrt{2\pi m}}\exp\left(-\frac{\Delta G^*}{k_B T}\right), \quad (9)$$

where β is a flow of condensing monomers, Z is the Zeldovich non-equilibrium factor; s^* is the surface area of the critical nucleus, c_{n^*} is the concentration of the critical nuclei, ζ_c is the condensation coefficient determined by the ratio of the number of molecules condensed on the nucleus surface to the total number of collisions between the molecules, m is the mass of the monomer and N is the concentration of the monomers. The Zeldovich non-equilibrium factor is determined as follows

$$Z = \sqrt{\frac{1}{2\pi k_B T}\left(\frac{\partial^2 \Delta G}{\partial n^2}\right)_{n^*}}. \quad (10)$$

The flow of condensing monomers can be expressed by the equation

$$\beta = \zeta_c \frac{p}{\sqrt{2\pi m k_B T}}, \quad (11)$$

where p is the partial pressure of the monomer.

As a result, the stationary growth rates are identical for clusters of any sizes.[22, 25]

One of the most important problems of non-stationary nucleation kinetics is to determine the period (time) of non-stationarity. Zeldovich was the first to demonstrate that upon a sudden change in vapour supersaturation, a new stationary distribution of clusters follows the exponential law with a characteristic time constant τ called the time delay or relaxation time.[5]

According to the concepts proposed by Zeldovich, under conditions of a non-stationary process, the condensation rate is a function of time t (see Ref. 26)

$$J = J_s\left[1 - \exp\left(-\frac{t}{\tau}\right)\right],$$

where J_s is the stationary nucleation rate. Based on the results of the experimental investigation of the water vapour condensation in supersonic nozzles, Kantrowitz [27] found an empirical relationship between τ and vapour supercooling ΔT

$$\tau(\Delta T)^4 = 9.36 \times 10^3 \ (\mathrm{s\,K^4}).$$

The simplest approximation, which allows one to estimate the time required for the achievement of constant amount of nuclei, was proposed in the study [28]

$$\tau_s = \frac{25(n^*)^2(2\pi m_1 k_B T)^{1/2}}{4\pi p (r^*)^2},$$

where m_1 is the mass of the monomer. According to this approximation, the time τ under standard experimental conditions of vapour nucleation (at $\zeta_c = 1$) is 10^{-5}–10^{-7} s.

In the studies,[27–29] it was assumed that clusters whose sizes are similar to the size of the critical nucleus are of kinetic importance. The time required for the achievement of 95%–99% of the stationary nucleation rate is often taken as the period of non-stationarity.[30, 31] In principle, this level should be chosen depending on the accuracy of experimental measurements of the function $J(t)$ within the limits, where the change in the nucleation rate can be estimated. Knowing the dependence $J(t)$, the period of non-stationarity can be calculated.

In the investigation,[32] it was demonstrated that the period of non-stationarity depends on the value and shape of the energy barrier to nucleation. The formation of a cluster consisting of two atoms is the slowest step of nucleation. Kantrowitz [27] quantitatively estimated the influence of cluster heating through the latent condensation heat on the nucleation rate. In a typical case of nucleation of a 2% water vapour in air, this effect leads to a fivefold decrease in J_s. In the study,[33] it was hypothesised that corrections for a non-equilibrium state are generally of little importance in the classical nucleation theory. Hence, such corrections are introduced only in extreme cases.

The condition of consistency of supersaturation in the system is a substantial limitation, which hinders the application of theoretical conclusions to the solution of practical problems, because nucleation most often occurs at variable temperature and supersaturation. It was demonstrated [34] that the rate of nucleation, which proceeds under conditions of a slow increase in supersaturation of the system, is lower than the rate calculated provided that the process is stationary. A decrease in the nucleation rate is proportional to a change in supersaturation, the time of non-stationarity and the size of the critical nucleus. The macroscopic nucleation theory includes certain unjustified assumptions and mathematical approximations. For example, it is assumed that small clusters can be considered as small portions of a macroscopic phase.

In principle, nucleus formation and growth should occur at any vapour supersaturation. The critical supersaturation is arbitrarily determined as a condition for rather fast nucleation. The nucleation rate changes with a change in the degree of supersaturation so rapidly that no significance has been attached to an error of even several orders of magnitude in the estimation of the pre-exponential factor in Eqn (9) (see, for example, Ref. 35).

Lothe and Pound [36, 37] revised the classical nucleation theory and suggested an alternative scheme of condensation involving the following three steps:

(1) nN_n molecules of a vapour are condensed into a liquid through isothermal compression;

(2) this liquid is mechanically disintegrated giving rise to N_n droplets of equal size;

(3) translational and rotational motion is imparted to all the droplets formed.

The authors of the cited studies introduced two additional multipliers, which were found based on the concepts of quantum statistics. Taking into account these multipliers, the nucleation rate increases by a factor of 10^{17}–10^{20} (!). It should be noted that

the authors simply assumed that Eqn (8) is incomplete and should include a change in the translational and rotational entropy of the cluster. This question has been discussed in detail, for example, in Ref. 38. This problem was solved using statistical thermodynamic analysis. Finally, it was concluded that the correction for the translational and rotational motion of nuclei lacked experimental support (this problem was analysed in the review [39]). It should be noted that the concept of formation of a stationary droplet in a vapour is a principal drawback of the classical theory because clusters execute, for example, Brownian motion.

Critics of the foundations of the classical nucleation theory primarily note that the properties characteristic of a macroscopic droplet (density, surface tension, saturated vapour pressure) cannot be extended to clusters consisting of only several tens of molecules. Since the properties of small clusters cannot be divided into volume and surface characteristics, the concept of surface tension seems to be artificial as applied to these clusters. To eliminate this problem, the excess free energy of the cluster can be, for example, determined as the difference between its free energy and the free energy of the same number of molecules present in a macroscopic volume of the condensate.

In the studies,[40,41] the following dependence of the surface tension on the radius of the droplet was deduced:

$$\sigma(r) = \sigma_0\left(1 - \frac{2}{kr} + \frac{2}{k^2r^2}\right), \tag{12}$$

where σ_0 is the surface tension of the planar surface of the liquid, $1/k \approx (0.2-0.5)\times 10^{-7}$ cm.

When considering rather small clusters, not only the equation for σ but also the Kelvin equation [Eqn (6)] should be changed.[42] However, the authors of the studies [43,44] believed that the Kelvin equation is applicable to droplets of sizes $\geqslant 20$ Å. This is contradictory to the Tolman equation. The latter equation relates the surface tension to the droplet size. According to the Tolman thermodynamic theory,[45] in the case of high surface curvature, a change in the surface tension should be described by the equation

$$\frac{\sigma}{\sigma_0} = \frac{1}{1 + 2\delta/r}, \tag{13}$$

where δ is 0.25–0.6 of the diameter of the molecule.

Until recently, the efforts of many researchers were directed primarily towards the improvement of the classical model by making it consistent with thermodynamics by introducing additional correction coefficients, which take into account individual factors. However, the theory did not become universal.

2. Modifications of the classical nucleation theory

In recent years, one of the versions of the classical theory, the so-called self-consistent theory (SCT) of nucleation, has gained acceptance.[46–48]

From Eqn (1) describing the change in the free energy of a cluster in the classical nucleation theory, it follows that the work of formation of cluster consisting of one monomer is not equal to zero. By contrast, the change in the free energy of monomers in SCT is equal to zero due to the introduction of the corresponding corrections. According to this theory,

$$\Delta G = (4\pi r^2 - s)\sigma - (n-1)\,k_{\mathrm{B}}T\ln S, \tag{14}$$

where s is the area of monomer surface.

Using Eqn (14) written for the droplet approximation, we have a new equation for the nucleation rate

$$J_{\mathrm{SCT}} = \frac{\exp(\sigma s/k_{\mathrm{B}}T)}{S}J, \tag{15}$$

where J is the rate calculated in the context of the classical nucleation theory according to Eqn (9). It can be seen that this equation differs from the classical one by the presence of the coefficient e^{Θ}/S (here $\Theta = \sigma s/k_{\mathrm{B}}T$ is the surface energy of the monomer). The remaining physical assumptions in SCT are identical to those used in the classical nucleation theory.

The basis for the Dillmann–Meier theory is the semiphenomenological droplet model of the cluster formation.[8] In this case, the expression for the free energy includes such vapour parameters as virial coefficients, pressure and density at the critical point. The Dillmann–Meier theory takes into account all significant (in the author's opinion) contributions to the energy of cluster formation. The agreement between experimental results and data obtained in the context of the Dillmann–Meier theory was discussed in the studies.[8,49]

Dillmann and Meier modified Fisher's expression [50] for the free energy of cluster formation by adding the coefficient k_n, which reflects the difference between the surface energies of the cluster and macroscopic liquid droplet

$$\Delta G = k_n\sigma s n^{2/3} + \tau k_{\mathrm{B}}T\ln n - k_{\mathrm{B}}T\ln q_0 V - nk_{\mathrm{B}}T\ln S, \tag{16}$$

where k_n, τ and q_0 are parameters of the model and V is the volume of the system. The first term corresponds to the surface energy of the cluster and the last term takes into account relaxation of the metastable state. It should be noted that the authors did not discuss the question as to how the surface tension should be specified. The remaining two terms take into account the contributions of the translational, vibrational and rotational degrees of freedom to the free energy of the droplet. Unlike Lothe and Pound,[36,37] who calculated these contributions from the Boltzmann distribution, the authors of the cited study introduced the parameters τ and q_0 normalised to the experimental values. The configurational contribution to the overall sum is small and, hence, it is ignored.

The expression for the coefficient k_n was proposed by Tolman [45]

$$k_n = f\left(\frac{\delta}{r}\right),$$

where δ is the submolecular length, which is smaller than the radius of the monomer. Using the approximation of a spherical cluster, Dillmann and Meier [8] expressed the dependence of k_n on the cluster radius as the first terms of the power series

$$k_n = 1 + \alpha_1 n^{-1/3} + \alpha_2 n^{-2/3}, \tag{17}$$

where

$$\alpha_1 = \frac{(k_2-1) - (k_1-1)2^{-2/3}}{2^{-1/3} - 2^{-2/3}}, \tag{18}$$

$$\alpha_2 = -\frac{(k_2-1) - (k_1-1)2^{-1/3}}{2^{-1/3} - 2^{-2/3}}. \tag{19}$$

These authors obtained the expressions for k_1 and k_2 using the first two derivatives of the density with respect to pressure

$$k_1 = -\left(\frac{1}{\Theta}\right)\ln\left(\frac{p_{\mathrm{s}}}{q_0 k_{\mathrm{B}}T}\right), \tag{20}$$

$$k_2 = -\left(\frac{1}{2^{2/3}\Theta}\right)\ln\left[-\left(\frac{p_{\mathrm{s}}}{q_0 k_{\mathrm{B}}T}\right)^2 2^{\tau-1} q_0 B\right], \tag{21}$$

where B is the second virial coefficient. The parameters τ and q_0 are calculated with the use of experimental values characterising the state of the liquid at the critical point:

$$\begin{aligned} \rho_{\mathrm{c}} &= q_0\xi(\tau - 1), \\ p_{\mathrm{c}} &= q_0 k_{\mathrm{B}} T_{\mathrm{c}}\xi(\tau). \end{aligned} \tag{22}$$

Here, ρ_{c}, p_{c} and T_{c} are the critical density, pressure and temperature, respectively, and ξ is the Riemann function.

The nucleation rate in the Dillmann – Meier theory is calculated by the equation:

$$J_{\mathrm{DM}} = \frac{1}{3}\sqrt{\frac{\Theta}{\pi}\left[1+\alpha_1(n^*)^{-1/3}+\frac{9\tau}{2\Theta}(n^*)\right]^{-2/3}}\frac{s_1 p_{\mathrm{v}}}{\sqrt{2\pi m k_{\mathrm{B}}T}} \times \\ \times\, q_0 \exp[-k_{n^*}\Theta(n^*)^{-2/3}-\tau\ln n^*+n^*\ln S], \tag{23}$$

where p_{v} is the vapour partial pressure and m is the molecular mass.

The size of the critical nucleus (the number of atoms or molecules in this nucleus) n^* is determined by finding the real root of the cubic equation

$$\tau x^3 + \frac{1}{3}\alpha_1\Theta x^2 + \frac{2}{3}\Theta x - \ln S = 0.$$

Here

$$x = (n^*)^{-1/3},\ \Theta = \frac{\sigma s_1}{k_{\mathrm{B}}T}.$$

The Dillmann – Meier theory is consistent with the classical nucleation theory at $\tau = 0$, $q_0 = p/k_{\mathrm{B}}T$ and $k_n = 1$. The contradictions in the Dillmann – Meier theory were discussed in the study,[49] where corrections for the imperfectness of a vapour were introduced. However, the calculations performed with consideration for these corrections resulted in even poorer agreement with experimental observations.

Frenkel[6] introduced the concept of heterophase fluctuations in a vapour, which are small density fluctuations and do not disturb a particular aggregate state of the system. According to this concept, Frenkel assumed that the system is not quite homogeneous, *i.e.*, it contains prenuclei of a new phase already before the onset of the phase transformation.

The fluctuation mechanism of nucleation of a supersaturated vapour was developed in the publications.[51–53] It was suggested that in small subsystems isolated from a large system, fluctuations could occur such that their density reaches the value corresponding to conditions of spinodal decomposition, *i.e.*, of activationless nucleation of the condensate. The conditions of spinodal decomposition were considered using nonane as an example. For this purpose, the Peng – Robinson equation of state (see references in the study[51]) was rearranged to give

$$P = \frac{RT}{\upsilon - b} - \frac{a_T}{\upsilon(\upsilon+b)+b(\upsilon-b)} - \frac{\mathrm{d}(\sigma s/n)}{\mathrm{d}\upsilon}, \tag{24}$$

where P is the pressure in the subsystem, υ is the molar volume of the cluster consisting of n molecules, a_T is a temperature-dependent constant, b is a constant, s is the surface area of the fluctuating volume. In this case, the Gibbs potential takes the form

$$G = A + PV = A - \upsilon\left(\frac{\mathrm{d}A}{\mathrm{d}\upsilon}\right),$$

where A is the Helmholtz potential. The latter term in Eqn (24) describes the contribution of the bubble pressure within the microvolume.

A change in the Helmholtz potential due to a fluctuation of a small subsystem is described by the equation

$$\Delta A_{\mathrm{s}} = \upsilon_{\mathrm{s}}(P_{\mathrm{s}} - P_{\mathrm{p}}),$$

where the index s signifies the spinodal conditions and P_{p} is the pressure in the starting phase. Following the well-known Landau – Lifshits approximation, the frequency of cluster formation (J) was determined[51–53] as the density fluctuation

$$J = \Omega\exp\left(-\frac{\delta n_0 \Delta A_{\mathrm{s}}}{k_{\mathrm{B}}T}\right)\exp\left(-\frac{t}{\tau}\right),$$

where Ω is the coefficient corresponding to the number of fluctuations in the starting phase in a unit volume in a unit time; $\Omega = \Omega_0(1-T_{\mathrm{r}})^{3.57}$ ($\Omega_0 \approx 10^{23}$, $T_{\mathrm{r}} = T/T_{\mathrm{c}}$, T_{c} is the critical temperature); δn_0 is the fluctuation of the number of molecules in the cluster. The second exponent describes relaxation of fluctuation

$$\frac{t}{\tau} = \beta^{-1}(1-T_{\mathrm{r}})^3,$$

where β^{-1} is the constant associated with the diffusion coefficient within the fluctuating bulk. As a result, the expression for the nucleation rate takes the form

$$J = \Omega_0(1-T_{\mathrm{r}})^{3.57}\exp\left[-\alpha\frac{(1-T_{\mathrm{r}})^5}{T^4}(\ln S)^{-3}\right] \times \\ \times \exp[-\beta(1-T_{\mathrm{r}})^{-2}], \tag{25}$$

where α is a constant. It was assumed[51] that the nucleation begins when the size of the cluster reaches a size larger than the size of the classical critical nucleus. For such clusters, the condition of equality of the surface and volume contributions to the Gibbs free energy is fulfilled. The pre-critical nucleus has a lower density. At the pre-critical nucleus – vapour interface, the pressure jump is absent. Finally, as applied to the Peng – Robinson equation of state, nucleation is considered as local spinodal decomposition to give the Ostwald nucleus and supersaturated mother phase. In this case, the nucleation rate (like in the classical nucleation theory) is described by the exponential equation but with a different pre-exponential factor at the logarithm of supersaturation. According to the classical nucleation theory [see Eqn (8)], the logarithm of the nucleation rate should be a linear function of the value reciprocal to the square of the logarithm of supersaturation. By contrast, according to Eqn (25), this value is inverse to the cube of the logarithm of supersaturation. However, the linear regressions of the experimental nucleation rates both as the functions $(\ln S)^{-3}$ and $(\ln S)^{-2}$ give equally good approximations.

It was noted[52] that within the framework of the fluctuation model, the effect of the total pressure in the system on the nucleation rate, which is not predicted by the classical theory, can be attributed to compression of a nucleus under the action of a carrier gas. The limitation of the fluctuation model is that it assumes the independence of the density (or supersaturation) fluctuations. The fluctuation lifetime should be sufficient for spinodal decomposition giving rise to a pre-critical nucleus. At high temperatures and large supersaturations, the independence of fluctuations can be disrupted due to an increase in the coherence length. The above-considered approach has not been further developed, but can be mentioned as one of examples of possible theoretical models.

The theory of heteromolecular (binary) nucleation, as noted by Volmer,[54] began to be developed after the publication by Flood, who used the thermodynamic method, calculated the critical vapour supersaturation for aqueous-alcoholic mixtures and studied experimentally this supersaturation in a Wilson chamber. The experimental data were in qualitative agreement with the theoretical results. This theory was further elaborated in the investigation,[55] where the work of formation of two-component critical nuclei with different compositions and of different sizes was examined.

The solution of a differential equation describing the nucleation kinetics[56] made it possible to reveal the characteristic features of the free-energy surface of clusters as a function of the cluster composition, *viz.*, n_1 and n_2, where n is the number of molecules of the corresponding component (1 or 2) in the cluster. The equation for the homogeneous nucleation rate in a binary system is analogous to Eqn (9) for one-component nucleation

$$J = C\exp\left(-\frac{\Delta G}{k_{\mathrm{B}}T}\right), \tag{26}$$

where the pre-exponential coefficient C depends only slightly on the external conditions and ΔG is the energy of formation of a critical nucleus. For binary nucleation, the coefficient C was first determined by Reiss.[56] Stauffer [57] studied nucleation in an analogous system without considering the direction of nucleation in the bulk (like in the studies [56, 58, 59]) and obtained a self-consistent expression for the growth angle.

A quantitative simulation of vapour nucleation in a binary water–ethanol system,[60] which was carried out as a continuation of the study,[56] made it possible to calculate the critical supersaturations and achieve good qualitative agreement with experimental data.[18]

The correct determination of a saddle point on the free-energy surface of clusters is of great importance for an adequate prediction of the binary nucleation rate. This point can be determined by solving two equations:

$$\left(\frac{\partial \Delta G}{\partial n_1}\right)_{n_2} = 0,$$

$$\left(\frac{\partial \Delta G}{\partial n_2}\right)_{n_1} = 0.$$

Generally, it is assumed that the cluster retains a homogeneous composition throughout the bulk. The equations include the derivatives of the surface tension

$$\left(\frac{\partial \Delta G}{\partial n_1}\right)_{n_2} = \mu_{1l} - \mu_{1v} + \frac{2\sigma \upsilon_1}{r^*} - \frac{3X^* \upsilon}{r^*} \frac{\partial \sigma}{\partial X}\bigg|_{X=X^*} = 0, \quad (27)$$

$$\left(\frac{\partial \Delta G}{\partial n_2}\right)_{n_1} = \mu_{2l} - \mu_{2v} + \frac{2\sigma \upsilon_2}{r^*} - \frac{3\upsilon(1-X^*)}{r^*} \frac{\partial \sigma}{\partial X}\bigg|_{X=X^*} = 0, \quad (28)$$

where μ_l and μ_v are the chemical potentials of the liquid and vapour phases, respectively; υ_1 and υ_2 are the partial molar volumes of components 1 and 2, respectively; $\upsilon = (1-x)\upsilon_1 + x\upsilon_2$ is the molar volume of the solution; $X = n_2/(n_1 + n_2)$.

However, it was demonstrated [60–63] that the coordinates of the saddle point cannot precisely be determined using Eqns (27) and (28) because of the insufficiently correct description of the clusters. Various numerical methods have been proposed for calculating saddle points. In particular, it was postulated [64] that σ is constant at a particular composition of the nucleus. However, this assumption excludes, for example, the dependence of the excess energy on the cluster size and, hence, the coordinates of the saddle point cannot be accurately determined. An example of the practical use of these calculations is the study,[65] where the nucleation rate of a mixture of water and sulfuric-acid vapours was determined. More recently, analogous calculations were carried out at different supersaturations.[66]

A two-channel mechanism of nucleation in a binary system was considered in the study.[67] Two-channel nucleation occurs, when two saddle points appear on the surface of the Gibbs free energy. The relative contributions of individual channels to the nucleation process were estimated by thermodynamic methods.[68] Binuclear nucleation of vapours as liquids with limited mutual solubility was investigated.[69–71] Besides, binuclear nucleation of miscible liquids was also studied.[72]

A mixture of a vapour and a carrier gas is a special case of a binary system. Nucleation of propane-1,2- and -1,3-diols in carbon dioxide and sulfur hexafluoride was studied.[73] A phase transition in the condensate was observed for each propanediol–gas pair. An increase in the concentration (pressure) of the carrier gas was accompanied by a shift in the phase transition temperature toward the critical temperature of this gas. By changing the carrier gas (for example, from CO_2 to SF_6), the temperature of the phase transition in nuclei of the condensate can be changed by 15–20 °C. It should be noted that phase transitions in equilibrium propane-1,2- and -1,3-diols do not occur in the temperature range in which the nucleation rates were measured. The appearance of phase transitions in the condensate upon the addition of a carrier gas is indicative of the involvement of its molecules in the formation of critical nuclei of the condensate. The composition of the nuclei was determined from the slopes of isotherms of the nucleation rate and it was found that they contained up to 20% of carrier-gas molecules.

Experimental and theoretical studies often do not take into account the fact that a carrier gas can act as a nucleating component (see, for example, Refs 74 and 75), and vapour nucleation in a gas atmosphere is considered in the approximation of a one-component vapour. In this case, the gas is considered as a medium providing thermostatic control of nucleation. This assumption, which has been accepted in early experimental studies of vapour nucleation, should be revised.

It was demonstrated [76] that two different methods of calculations of nucleation rates in heteromolecular systems in a stationary state, which have been proposed in the studies,[57, 77] are virtually equivalent. One method [57] is based on the classical theory of binary nucleation, whereas an alternative method [77] is based on the solution of the Fokker–Planck equation. Although calculation by these two methods gave the same binary nucleation rates, the latter are inconsistent with the experimental data.[75] Analysis [77] of different conclusions [43] of the classical theory of binary nucleation [62, 78, 79] demonstrated that the methods under consideration give different estimates of the size and composition of critical nuclei. It should be noted that the solution of the Fokker–Planck equation requires the introduction of coefficients accounting for evaporation and accommodation of molecules in the cluster, and their uncertainty leads to a substantial decrease in the reliability of the results of calculations. The use of different values of these coefficients enables one to find numerical and sometimes even analytical solutions, which are nevertheless only of qualitative importance.

The parametric model considered in the study [80] was based on the equation reduced as applied to the nucleation rate of a one-component vapour (26) and the following assumptions were made: (1) the cluster grows (decreases) through condensation (evaporation) of monomers; (2) the probability of fixation of the molecule on the cluster surface upon collision is equal to unity; (3) clusters have a spherical shape; (4) interactions between clusters are absent. The authors of the cited study believed that incorrect results were obtained primarily because of the use of surface tensions measured for a planar interface. Hence, following Tolman,[45] the excess energy of clusters was calculated using expansion in a series

$$\sigma_{\text{micro}} = \sigma_0(1 + \alpha_\sigma n^{-1/3} + \alpha_\sigma^2 n^{-2/3} + ...),$$

where σ_0 is the surface tension coefficient for the planar interface; $\alpha_\sigma = 2\delta/r_1$ is the so-called Tolman length (δ is the length of the order of the molecular size; r_1 is determined from the equation $r_n = r_1 n^{1/3}$, r_n is the radius of the cluster consisting of n monomers). The work of formation of the cluster was determined using Eqn (16) converted to the parametric form

$$\beta\Omega_n = \beta\sigma_{\text{micro}} s n^{2/3} + \tau \ln n - \ln q_0 V_c.$$

The parameters of this equation are as follows: $\beta = (k_B T)^{-1}$, $2.1 < \tau < 2.2$, $q_0 \sim \rho_c/5$, where ρ_c is the density at the critical point.

The equilibrium density (ρ_n) of clusters is calculated assuming the Boltzmann distribution

$$\rho_n = \frac{1}{V_c} \exp(-\beta\Omega_n),$$

where V_c is the volume of integration for the determination of the configuration integral for the cluster. The parameters are normalised by extrapolation to the critical point.

A comparison of the nucleation rates calculated within the framework of the classical and parametric theories demonstrated

that the difference is very small in the case of water. In the study,[80] the nucleation rate predicted by different theories was compared with the published experimental data for vapours of different compounds. It appeared that the use of the parametric model gave the best results.

In the study,[81] the influence of an increase in the pressure of a carrier gas as a perturbing parameter was taken into account. The properties of the nucleating vapour vary depending on this parameter. The authors believed that this fact leads to reduction of binary nucleation to nucleation of a one-component vapour. The criterion characterising the perturbing action of the pressure of a carrier gas should meet the condition $x_g \ll (S-1)/S$, where x_g is the solubility of the carrier gas in the liquid phase at supersaturation S. Another parameter was introduced to compensate the effects of a decrease in the surface tension and an increase in the saturating vapour density. This modification of the nucleation theory is consistent with the model proposed in the study [80] as well as with the density functional theory.[82] Evidently, the introduction of additional parameters can lead to agreement between the theory and experiment. In the study,[83] multicomponent nucleation was described for a ternary system using a one-component model and introducing the effective parameters of the process.

Apparently, such approaches can be applied to the parametric description of practically important systems. However, these approaches seem to hold little promise from the viewpoint of the development of the theory because they have poor predictive ability even with respect to the model system under consideration. It is more correct to refer to this type of parametrisation as interpolation of experimental data. This parametrisation has no predictive potential outside the range of experimental characteristics parametrised and there is little likelihood that it will be correct even if only one family of nucleating systems is treated.

Below are considered models in which the intermolecular interaction potential is introduced in an explicit form, *i.e.*, through parameters determining the force interaction and geometric arrangement of molecules in the system. A simplified consideration of collective interactions can be, in particular, performed by introducing the dependence of the distribution function on a particular macroscopic parameter, for example, on the distribution density of molecules (density functional theory), which, in turn, includes the effect of collective interactions. The classical theory takes into consideration the fluctuation character of the exchange of substance between a nucleus and its environment. The number of molecules in the nucleus is a variable characterising the state of the system, all other parameters being equal to their average values.

In a number of studies (for example, in the study [84]), the influence of the pressure of a carrier gas on vapour nucleation was considered. It was demonstrated that the gas can either accelerate or decelerate the nucleation frequency. This depends on the sign of the second virial coefficient. If a carrier gas is absent, the different degrees of freedom of the cluster and particles forming the cluster can correspond to different temperatures.[85,86] This effect is observed in experiments with molecular beams expanding into vacuum. In experiments with a monosilane–argon mixture, nucleation was observed in a pulse supersonic jet.[87] In addition to clusters, mixed argon–silane complexes were detected for the first time and conditions for their formation in a flow were determined. The existence of mixed clusters is direct evidence for the involvement of the carrier gas in the nucleation of a new phase. The dependences of the concentrations of monomers and cluster ions on the stagnation pressure indicate that condensation in a flow at low stagnation pressure gives rise only to individual monosilane clusters, whereas condensation at high pressure affords monosilane–argon clusters. It is advantageous to analyse the nature of this phenomenon using phase diagrams of the system.

The determination of the nucleation rate by solving the one-dimensional Fokker–Planck equation for the probability density of the size distribution of nuclei is justified if rather rapid relaxation of all degrees of freedom takes place in the cluster. The necessity of taking into account relaxations and, correspondingly, using the multidimensional Fokker–Planck equation appears only when the above-mentioned condition is violated. Admittedly, the classical theory, which has made it possible to solve the fundamental problem of the formation of a new phase in the first approximation, is characterised by a high degree of completeness and can serve as an example of a reasonable combination of the approximations and the minimum necessary complexity of the mathematical apparatus used. At the same time, it is evident that the classical nucleation theory should give way to a theory possessing an essentially different axiomatic basis, whose foundations are already being developed.

The density functional theory holds considerable promise.‡ In this theory, only a part of collective interactions responsible for the attraction energy of molecules is taken into account in an explicit form. Short-range interactions are determined in the approximation of rigid spheres. This approach enables one to consider interactions between molecules in the pair-additive terms for which good approximations based on experimental data are available.

Oxtoby and co-workers [88–91] considered the nucleation process using the density functional theory. Unlike Vlasov,[3] who introduced the concept of a collective interaction from the very beginning (*i.e.*, he assumed that weak collective interactions between molecules lead to the existence of the system as an organic whole and cause a phase transition at particular parameters), Oxtoby believed that the presence of a gas–liquid interface is a manifestation of weak density inhomogeneity of the system. The profile of the equilibrium average density is determined from the condition of equality of the thermodynamic potential to zero. In this case, the expression for the free energy functional takes the form

$$\Omega_V(\rho) = \int \{f[\rho(\boldsymbol{r})] - \mu\rho(\boldsymbol{r})\}\mathrm{d}\boldsymbol{r} + \frac{1}{2}\int\int \varnothing(|\boldsymbol{r}-\boldsymbol{r}_1|)\rho(\boldsymbol{r})\rho(\boldsymbol{r}_1)\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}_1,$$

where f is the free energy of the unit volume of a liquid in the approximation of rigid spheres,[88] which was assumed to be known. Here, it is assumed that the potential of interactions can be represented as the sum of repulsion forces (in the approximation of rigid spheres) and attraction forces. This sum is denoted as ø. The functional derivative of this equation is an integral equation for the critical density profile.

In the study,[82] the pre-exponential factor used in the equation for the nucleation rate is identical to that in the classical nucleation theory. At the same time, it was noted that it is improper to use the classical pre-exponential factors in other theories. The description of the dynamics of the first-order phase transition presented in the study [92] is still of great interest.

The density functional theory was applied [93,94] to the investigation of gas–liquid nucleation in binary mixtures consisting of Lennard-Jones atoms in the approximation of one-point (monomers), two-point (dimers) and three-point (trimers) rigid spheres. The temperature dependence of the nucleation rate calculated within the framework of this theory is similar to the corresponding experimental dependence. At the same time, the results of calculations are not always consistent with the data obtained by other methods, for example, by numerical simulation. Numerical simulation (based on the Lennard-Jones potentials) was carried out for homogeneous gas–liquid nucleation in a binary mixture [95] and the dependences of the size and composition of critical nuclei on the composition and supersaturation of a vapour were studied. Growing nuclei are characterised by bifurcation of the composition. In the case of non-ideal systems, components cease to be soluble and droplets enriched with a particular component

‡ In 1998, W Kohn (Austria) was awarded the Nobel Prize in Chemistry for his development of the density functional theory.

appear. However, in studies using the density functional theory, the researchers did not reveal fractionation of phases within the critical nucleus.[96–98]

The theory of molecular homogeneous nucleation in a vapour phase [1] includes a minimum number of assumptions and parameters. Preliminary calculations carried out for argon by the Monte Carlo method [98] demonstrated that the free energy varies within two orders of magnitude. The authors of the cited study believe that areas of application of this method to the description of real processes of homogeneous nucleation in a vapour will be extended as the method is improved. One can partially agree with this statement, because it seems plausible that a reasonable simplification of the model of a nucleating system will allow one to obtain results, which can be verified experimentally.

The average values of the main parameters of an equilibrium system are determined by the conditions of its contact with the environment. To describe the non-equilibrium state, it is necessary to introduce additional parameters characterising the deviation of this system from equilibrium. The number and character of additional parameters required for the determination of the non-equilibrium state depend on a particular model.

The irreversibility can be described by equations for random processes, for example, by the Fokker–Planck kinetic equation or the Langevin equation. It should be noted that the area of application of such equations can be narrowed under certain conditions. As an example, let us consider the kinetic equation, which, on the one hand, serves for the description of transitions between the states of the system and, on the other hand, was derived using methods of non-equilibrium statistical mechanics in the approximation of noninteracting particles.[2,3] In the absence of memory effects, the time dependence of the probability $[p_n(t)]$ of the system occurring in the state n is determined by the frequency of its transitions (w_{nm}) from the state m

$$\frac{\mathrm{d}p_n(t)}{\mathrm{d}t} = \sum_m w_{nm}[p_m(t) - p_n(t)].$$

According to the principle of detailed equilibrium, the frequencies of direct transitions are equal to those of reverse transitions, *i.e.*, $w_{nm} = w_{mn}$. Taking into account the identical relation $\sum_n p_n(t) = 1$, we find the time derivative of entropy

$$\frac{\mathrm{d}S(t)}{\mathrm{d}t} = \frac{1}{2}k_\mathrm{B}\sum_n\sum_m w_{nm}[p_m(t) - p_n(t)]\,[\ln p_m(t) - \ln p_n(t)] \geqslant 0.$$

Therefore, if the states, between which transitions are allowable, are equiprobable, *i.e.*, $p_n(t) = p_m(t)$, the process under consideration is an equilibrium. The deviation from the identity of the conditions of stationarity and equilibrium of the process (which follows from the above-given equations) can take place only if the principle of detailed equilibrium breaks down. Consequently, if this principle is fulfilled, the kinetic equation in stationary conditions is inapplicable to the description of irreversible processes, in particular, of nucleation. It should be noted that the description of processes of the appearance and growth of clusters in a non-equilibrium system presents problems related to the non-equilibrium thermodynamics and the kinetic theory of rarefied gases (see, for example, the review [99]).

Roldugin [16] described the nucleation process in the context of concepts of non-equilibrium thermodynamics and analysed the symmetry of the diffusion tensor in the generalised parameter space of the process. He hypothesised that in the case of, for example, a one-dimensional system, the nucleation rate should be several orders of magnitude lower than that predicted by the classical theory. It should be noted that these conclusions may be influenced by a popular error in overestimating the reliability of experimental data. The above-discussed inconsistency between experimental data obtained by different researchers could be explained quite prosaically taking into account that many important problems associated with experimental procedures for performing nucleation remain to be solved. For example, there is a pressing need for the determination of an absolute error of experimental measurements.

In the classical kinetic theory of gases, collisions are taken into account only in short-range interactions. The question of whether it is possible to improve the description of long-range interactions in an ensemble of particles by successive inclusion of double, triple, quaternary, *etc*. collisions remains to be answered. Moreover, the kinetic equations include terms related to both the flow and collisions, which cannot be separated from each other.[99–101] An approach was developed as applied to non-equilibrium processes in non-ideal gases. This approach allows one, in principle, to derive closed kinetic equations provided that the initial correlations between two, three, *etc*. particles are weakened. However, it appeared that collision integrals, which determine dissipative processes in kinetic equations, become divergent when interactions of four and larger numbers of particles are taken into account [102] and only summation of the infinite number of multiparticle processes eliminates the divergence.

3. Use of the formal apparatus of quantum mechanics for the description of nucleation

First studies of nucleation at temperatures close to absolute zero using the formal apparatus of quantum mechanics were carried out as early as 1972.[103, 104] In these investigations, relaxation of a metastable state was associated with tunnelling of a nucleus of a new phase through a potential barrier in the configuration space. The nucleus passes through a series of local inhomogeneous states. In the phenomenological description of nucleation accepted in early studies, the problem of growth of a new phase was separated from the quasiclassical problem of the determination of a spectrum of cluster sizes. Later on, the quantum-mechanical description was proposed.[105] This approach includes quantum fluctuations, which lead to the tunnel transition of virtual clusters.

As an example, let us consider a brief scheme of quantum calculations of the nucleation rate.[16] A change in the nucleus radius r in the potential

$$V(r) = 4\pi r^2\sigma - \frac{2}{3}\frac{4\pi\sigma}{r}$$

can be described by the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(r) = E\psi(r),$$

where $\psi(r)$ is the wavefunction and E is the set of energies of quantum states.

Assuming spherical symmetry, the variables of the wavefunction $\psi(r) = [Z_n(r)/r)]Y(\theta,\varphi)$, where $Y(\theta,\varphi)$ is a spherical function, can be separated. Hence it follows that the motion equation can be deduced for $Z_n(r)$ in the potential

$$U(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2},$$

where l is the quantum number of the angular moment. At $l \neq 0$, there is an additional barrier, which noticeably decreases the probability of nucleation. Hence, the main contribution to nucleation is provided at $l = 0$. The probability of tunnelling P_t is determined by the equation

$$P_\mathrm{t} \propto \exp\left\{-\frac{2}{\hbar}\int_0^{r^+}[2m(r)V(r)]^{1/2}\mathrm{d}r\right\},$$

where $r^+ = (3/2)r^*$ (r^* is the radius of the critical nucleus) and $m(r)$ is the effective mass determined by the relation

$$m(r) = \frac{4\pi}{\rho_\mathrm{v}}(\rho_\mathrm{l} - \rho_\mathrm{v})^2 r^3,$$

where ρ_l and ρ_v are the liquid and vapour densities, respectively.

A somewhat different approach was used in the studies.[106, 107] According to the corrections[108, 109] to the Lifshits–Kagan theory,[103, 105] clusters are considered to be spherical and consist of an incompressible liquid whose energy depends on the cluster size. It is assumed that the centre of gravity of the clusters is at rest, whereas the surface layer and vapour environment move. The authors of the cited studies[106, 107] examined the possibility of tunnelling from all energy levels, except for the ground level.

To summarise, it should be noted that the quantum theory of nucleation is still being developed. However, this is the only theory, which may be useful for the interpretation of the results of experiments, for example, on binary nucleation in the ^{3}He–^{4}He system at temperatures close to 10^{-3} K,[110] from the quantum standpoint. The quantum-mechanical approach to the description of ion-induced nucleation was employed in the investigation,[111] where the nucleation rate of a water vapour on Na^+ ions was estimated. The results of this investigation are comparable with the results following from the classical nucleation theory. In particular, the free energy minima and the sizes of the corresponding clusters are identical to within experimental error. The free energy maxima are also virtually identical, but the size of the critical cluster evaluated by the classical theory is 20% larger.

A system of noninteracting particles can be considered with the use of conventional methods of statistical mechanics, where the Hamiltonian of the system is represented as a sum of the Hamiltonians of individual particles. The applicability of these methods is limited by the region, where the Boltzmann statistics is fulfilled. Systems consisting of many particles obey the Boltzmann statistics.§

In the classical nucleation theory, molecules of a metastable phase and the nuclei formed in this phase are also treated as a mixture of noninteracting particles. In the thermodynamic consideration, the frequency of collisions of molecules with the cluster consisting of n molecules is calculated in the ideal gas approximation, *i.e.*, without regard for their interactions. In the kinetic consideration, an analogous approach was used for determining the frequencies of transitions of nuclei from one size to another, *i.e.*, the dependence of these frequencies on interactions of a nucleus with other molecules and clusters of the mother phase are ignored.

Phenomenological theories describing states of solutions (for example, the theory of regular solutions), which employ equations for a particular average state of the system consisting of many particles, can be assigned to the same type of theories. Since these equations are, generally, empirical, it is more correct to refer to these theories as empirical theories. One of the simplest phenomenological theories of equilibrium phase transitions taking into account the co-operative effect is the van der Waals theory of condensation.[100] It should be noted that the Kac potential (as an effective potential) used in the study[100] is not a realistic value and the extension of the results thus obtained to real (in a physical sense) potentials is still an open problem. Certain progress in the use of the models under consideration is attributable not to the validity of their main concepts but to an appropriate choice of additional factors, which, in turn, allows one to consider these models as phenomenological.

III. Experimental methods for studying nucleation

Experimental studies of nucleation were carried out for various objects, *viz.*, from a mixture of the ^{3}He–^{4}He isotopes at temperatures of several thousandths of Kelvin up to a plasma. Complex processes, such as the formation of solid-phase nuclei from cooled molten metal and metal boiling upon superheating, formation of exciton drops and cavitation, for example, in a screw propeller or in the case of nuclear reactor accidents, *etc.*, were also investigated.

Experimental investigation of bulk nucleation is a complicated problem, because the parameters of the formation of a new phase rapidly vary with time and space, which substantially complicates their measurements. Hence, experimental publications on nucleation are scarcer than theoretical studies. Experiments on nucleation are hindered due to the lack of well-developed algorithms for the determination of parameters for many nucleating systems. Procedures for studying bubble frequencies in liquids and nucleation in a supersaturated vapour have been best elaborated. These methods can be extended to other systems.

1. Thermal effects of condensation

The non-isothermality of a real nucleation process is the subject of considerable attention. However, the classical theory assumes that nucleation is an isothermal process. In other words, a mixture of clusters and monomers is treated as if it were in a thermostat. In real systems, an inert gas, which is not condensed under the experimental conditions, plays a role of such a thermostat. The energy transfer occurs due to collisions of molecules of an inert gas with a vapour and clusters, and the final number of gas molecules as well as the final rate of this process are such that the system is transformed into the state in which the average temperature of clusters is higher than that of the vapour–gas mixture. This leads to a decrease in the efficiency of elementary events of the addition of vapour molecules to small clusters. According to an estimate made in the study,[39] the effect of non-isothermality should be manifested at nucleation rates higher than 10^2 cm^{-3} s^{-1}. More recent data obtained by methods of non-equilibrium thermodynamics[112] demonstrated that the influence of non-isothermality should decrease as the vapour supersaturation is increased, *i.e.*, at high nucleation rates.

The thermal effects of condensation were considered in a series of studies by Kuni and co-workers.[113–124] The data on a stationary flow and stationary distribution of near-critical droplets, their temperatures and characteristic sizes, rates of free-molecular and diffusion growth of overcritical droplets, the spectrum of their sizes and time of formation as well as information on the conditions of applicability of a macroscopic approach to the kinetics of condensation were surveyed in the study.[113] The final step of non-isothermal condensation was discussed in the publication.[114] Non-isothermal condensation at moderate concentrations of an inert gas was considered in the investigation.[115] A two-dimensional description of the material and heat balance of particles of a nucleating liquid phase in a vapour–gas medium was published and the effect of the quasi-isolated state of a nucleus of a liquid phase under non-isothermal conditions was examined in the studies.[116, 117] The two-dimensional Zeldovich–Frenkel equation in the kinetics of non-isothermal nucleation of a liquid phase was considered.[118] Problems of thermal relaxation of particles of a nucleating liquid phase were discussed in the study.[119] The effect of the temperature of particles of a liquid phase on the rate of non-isothermal nucleation and other effects associated with heat exchange were investigated in a series of studies.[120–124]

The theoretical problem of thermal effects of condensation seems to be solved, but the predictions of the theory remain to be experimentally confirmed.

2. Nucleation in electrochemical processes

Let us consider an electrochemical process as an example of practical application of the nucleation theory.¶

A substrate plays a very important role in such processes. The effect of the substrate state on the nucleation kinetics was

§ In this case, the motion of each particle in the field of surrounding particles is considered as a motion in the averaged field, which is independent of the local arrangement of the particles.

¶ Problems of nucleation in electrochemical processes were surveyed in detail in the review.[125]

studied.[126–129] In particular, chemical interactions upon adsorption and the role of the real surface in crystallisation of a new phase were discussed in detail.[127] The concept of nucleation on active centres of the substrate surface, which have a high free energy, was developed.[128, 129] If the effect of shielding zones occurring around growing nuclei is ignored,[130] the activity distribution function of the centres can be determined based on experimental dependences of the number of nuclei on supersaturation.[131]

When describing the nucleation in electrochemical systems, it is generally assumed that

— in the presence of a double electric layer and electric charges on particles that arrive at the electrode surface, it is necessary to take into account the kinetics of charge transfer at the electrode;

— adsorption of water molecules, cations, anions and organic compounds on the electrode leads to a change in the work of nucleation and influences the discharge kinetics of ions;

— diffusion is of importance: the lower is the activation energy of surface diffusion and the stronger are the interactions of the adsorbed atoms with the substrate, the higher is the nucleation rate on the electrode surface.

The heterogeneous nucleation theory assumes that a liquid nucleus on the surface of a solid substrate has a shape of a spherical segment. A change in the energy of the system upon the formation of a liquid nucleus is proportional to the work of homogeneous nucleation

$$\Delta G_{\text{het}} = \Phi \Delta G_{\text{hom}},$$

where Φ is the shape factor, which depends on the wetting angle and is equal to the ratio between the volume of the spherical segment of the liquid phase on the substrate surface and the volume of the sphere of the same radius.

In this case, the supersaturation can be characterised by the overvoltage at the cathode η. The dependence of the stationary nucleation rate J_0 on the work of nucleation has the form

$$J_0 = D_c Z(1) \exp\left(-\frac{\Delta G}{RT}\right) = K_1 \exp\left(-\frac{K_2}{\eta^2}\right), \qquad (29)$$

where D_c is the flow of atoms that add to the critical nucleus; $Z(1)$ is the concentration of individual atoms; K_1 and K_2 are constants. Equation (29) adequately describes experimental data within a narrow range of the overvoltage at the cathode.[125] This is not surprising because the use of the classical theory is most efficient for describing simple nucleation processes in electrochemical systems, *viz*., vapour nucleation or cavitation.

The experimental results obtained within narrow ranges of supersaturation were discussed in the publications.[126, 132–137] Analysis of the data obtained within the framework of thermodynamic and atomistic models led to virtually the same conclusions. In the model representations used in the cited studies, interactions between the nuclei formed are ignored.

In broad overvoltage ranges, the step of charge transfer assumes great importance. Hence, it is necessary to take into account the kinetics of ion discharge.[138–143] In this case, the $\ln J_0 - (1/\eta^2)$ or $\ln J_0 - \eta$ dependences are linear and the constant K_2 in Eqn (29) can be determined from their slopes. Experimental investigations of the nucleation kinetics within broad ranges of supersaturation present considerable problems. At high supersaturations, coalescence of nuclei giving rise to aggregates is highly probable. The surface curvature of nuclei influences the activation energies of both the cathodic and anodic processes.[142–144] The expressions for the stationary nucleation rate are deduced based on the Becker and Döring kinetic method.[22]

Nucleation requires an expenditure of work proportional to the electrochemical potential difference.[126, 132, 135, 140, 145, 146] This work characterises the deviation of the system from equilibrium (values with the subscript 0 belong to a stable state and the corresponding values without the subscript belong to a metastable state)

$$\Delta\bar{\mu} = \bar{\mu} - \bar{\mu}_0 = zF(\psi - \psi_0) = zF(E - E_0) = zF\eta,$$

where $\bar{\mu}$ is the thermodynamic potential, z is the ion charge, F is the Faraday number and E is the electrode potential. The potential of a metal nucleus is equal to the electrode potential E. The nucleus formation requires an expenditure of work

$$\Delta G = \Phi \frac{16\pi\sigma^3 V^2}{3(zF\eta)^2} = \frac{1}{2} n_c zF\eta.$$

In this case, Eqn (6) takes the form

$$r_c = \frac{2\sigma V}{zF\eta}.$$

It is assumed that the nucleation energy is determined by the amount of metal atoms deposited on the electrode surface rather than by the electrochemical potential difference.[138, 139, 147–150] This approach corresponds to the assumption that the ion discharge giving rise to adsorbed atoms is independent of nucleation in a medium of neutral atoms on the substrate surface.

In electrochemical nucleation processes, the nucleus formation proceeds most probably by the direct insertion mechanism.[151, 152] In the gas phase, heterogeneous nucleation through the direct insertion of atoms or molecules into a nucleus is highly improbable.[153] The concentration of surface atoms has an effect only on the pre-exponential coefficient in the equation for the rate of the process. The work of nucleation is determined by the cathode overvoltage.[154]

It should be noted that the work of nucleation is generally treated [141] as a continuous function of the number of atoms in the cluster n, although this function is actually discrete. It is assumed that the nucleus is in metastable equilibrium with the mother phase and has a size at which the probability of further growth is equal to the probability of dissolution. In the case of fluctuation formation, the maximum work corresponds to the critical nucleus. The nucleus size depends on the structure of the cluster and the interaction forces between the atom and substrate.

It was believed [125] that the changes in the surface energy and the kinetic factor can be ignored in the consideration of nucleation processes within narrow ranges of supersaturation. Hence, the number of molecules (atoms) in the critical nucleus can be determined from the slope of the experimental dependence of the nucleation rate on supersaturation according to the equation

$$n_c = RT \frac{d \ln J}{d\Delta\mu}.$$

This equation was first proposed in the study devoted to nucleation of supersaturated vapours. Below the deduction of this equation is considered in detail. It should be noted that this equation enables one to determine the critical nucleus size regardless of the nucleation model used as well as to find the dependence of this size on supersaturation $\Delta\mu$.

In the review,[125] it was stated that a decrease in the nucleation rate in an electrochemical process following the stationary region in a voltammogram is attributed to an exhaustive consumption of the active centres of the substrate, overlapping of shielding zones or coalescence of growing crystals. In the nucleation theory, it was assumed that in the case of electrodeposition, active centres of the substrate can appear during the action of a nucleation pulse, the rate of their formation being dependent on the degree of supersaturation. The nucleation kinetics in various systems can be studied experimentally, in particular, by determining the time of formation of the first nucleus. Methods for calculations of the space and time distributions of nucleation events upon electrodeposition, which have been developed in the studies,[126, 132, 151, 154] allow one to perform more detailed analysis of the mechanism of nucleation. The magnetic properties of electrodeposited amor-

phous Fe–Cr melts were investigated, for example, in the study.[155]

Adsorption of surfactants has an effect on the work of nucleation and the critical size of nuclei due to changes in the surface energy at nucleus–electrolyte and nucleus–substrate interfaces accompanied by changes in the wetting angle and shape factor.[156, 157] The effect of surfactants on the initial steps of electrocrystallisation is manifested in the redistribution of the rates of formation and growth of nuclei of a new phase due to blocking of active centres of the substrate and inhibition of ion discharge on the surface of growing crystallites. On the whole, the effect of surfactants on nucleation is poorly known. Experimental studies are generally aimed at solving applied problems. In these studies, the frequencies of nucleation of a new phase are, as a rule, not measured. Scarce data on the measured nucleation rates in the presence of surfactants cannot as yet be systematised. A more detailed discussion of this problem is beyond the scope of the present review.

The phase formation upon electrodeposition was studied by analysing the time dependences of the current under potentiostatic conditions. The theory of growth of two-dimensional layers and formation of three-dimensional crystals was developed in the investigations.[151, 158] In the last decade, the structures of various electrode materials, primarily, of atomic- and molecular-modified single-crystalline electrodes and electrodes including isolated nanoparticles have been established with very high accuracy by high-precision X-ray diffraction methods. These data enable one to reveal the characteristic features of a nucleation process giving rise to a particular structure. Evidently, coalescence and agglomeration, which accompany nucleus growth in the solid phase, hinder calculations of the number of nuclei of a newly formed phase.

Much less progress has been made in studying the structures of electrodes acting as catalysts, which are characterised by a large specific surface and a broad size distribution of particles (or blocks). Examples of such systems are electrolytic deposits of platinum metals on polycrystalline substrates. The dependence of the activity of platinum and palladium electrolytic deposits on the deposition potential is one of the prominent manifestations of the so-called 'structural effects' in electrocatalysis.[159, 160] Multilayer deposits, for example, of platinum metals on polycrystallines foils, are very complex systems characterised by a multi-level structural hierarchy. It is hardly probable that their structures could be established at the nanostructural level. However, it is of great interest to reveal factors responsible for the reproducible formation of nanostructural fragments and find reliable correlations between the macroscopic properties of materials and structural characteristics as the first step of such investigations.

Measurements of copper K X-ray radiation made it possible to observe co-deposition of copper and chloride ions from an electrolyte solution on the Au(111) surface. These results are indicative of a high degree of statistical disorder of molecules in the deposit, the Cu–Cl, Cu–Au and Cu–Cu bond lengths and the corresponding bond angles varying within narrow ranges. These data are very useful in simulating nucleation and subsequent film growth by molecular dynamics methods. Chronocoulometric measurements provided information on the film composition and the number of electrons crossing the interface per copper ion. Electrocrystallisation on dislocation-free faces of silver single crystals was studied experimentally.[151] The formation of anodic films was investigated.[161] The results of studies using mathematical simulation (see, for example, Refs 162 and 163) are consistent with the classical nucleation theory. A model of two-dimensional nucleation and subsequent three-dimensional crystal growth was proposed in the study.[164]

However, the seemingly good situation, which is manifested in the agreement between the results of theoretical studies of electrochemical nucleation and experimental data, resembles a situation, which has been observed in the field of investigation of vapour nucleation, when high-precision data have been lacking. Beginning in the 1980s, the necessity of developing a universal theory of vapour nucleation and a need for searching new ideas for the elaboration of this theory became evident because a rather large number of systems were studied and experimental data were obtained with a sufficiently high accuracy.

3. Nucleation in dense ion plasma

Atomic and molecular systems are traditionally studied by approximate methods based on expansion of a small parameter in a series (for example, virial expansions in statistical physics, the non-linear perturbation theory in non-equilibrium statistical mechanics, the perturbation theory in quantum mechanics, *etc.*). In the review,[165] it was emphasised that a small system follows the Gibbs distribution law provided that interactions with the environment are weak. Hence, the choice of such a system from a statistical ensemble should be the subject of the special consideration. There are different ways of isolating a small system from a macroscopic one.

It should be noted that the time it takes for the equilibrium to be established within a cluster is much shorter than the time interval between collisions of the cluster with gas particles. Hence, the cluster can be considered as an isolated system during a certain (short) period of time. The properties of the cluster as a small system influence the behaviour of the macrosystem as a whole. The thermodynamic properties of critical nuclei are resposible for the nucleation rate. A nonideal gas is considered as a mixture of clusters of different sizes, *viz.*, dimers, trimers, *etc.*

The description of clusters of charged particles in the region of a substantial deviation from the ideal state is hampered by the necessity of taking into account long-range Coulombic interactions. The collective effects are not weakened as the plasma density decreases. By contrast, this effect increases because the radius of the Debye shielding sphere increases. For ionic systems, the main results are obtained with the use of integral equations. A macrosystem is divided into clusters and the phase space of the system is divided into the corresponding regions. When estimating the equilibrium properties, the statistical integral reduces to the configuration integral over the coordinates of the molecules.

Nucleation in an ion plasma is associated with shielding of Coulombic interactions of ions in a liquid phase due to which the long-range Coulombic potential becomes an efficiently short-range potential. Investigations of the equilibrium properties of a model of charged spheres by the Monte Carlo method demonstrated that the shielding typical of a macrosystem is also observed in systems consisting of several tens of ions at the same temperatures as those in the macrosystem.

The fact that supersaturation cannot be attained in a cooled ionic system, *i.e.*, the fact that metastable thermodynamic states cannot occur, is associated with the absence of an energy barrier to the formation of microdroplets. The charge symmetry breaking in plasma causes a change in the nucleation mechanism. Of all possible orientations of triplets, only one type of orientation at which the symmetry axes of the triplets are mutually orthogonal leads to their mutual attraction. This result was obtained only by computer simulation.

The thermodynamic stability of a dense phase in ion plasma is determined by short-range attractions and medium-range repulsions between the molecules. Repulsions are changed to attractions as the temperature decreases. The formation of a stable dense phase is attributed to the appearance of a short-range orientational order. In a macroscopically homogeneous system, a short-range orientational order occurs at higher temperatures compared to those in a small system because surface particles in the former system are absent and the average number of the nearest neighbours in the former system is larger than that in the latter system. Mutual repulsions between ionic triplets can be interpreted as an additional internal pressure equilibrating the external pressure of the macrosystem. Hence, in the approximation of charged spheres microdroplets of a particular radius are formed at higher pressures and lower temperatures compared to

those in a neutral system. Due to a competition between Coulombic attraction and repulsion forces, emission of charged particles from the cluster can take place. The inhibition effect of microcondensation due to repulsions between ionic triplets is most pronounced in the case of microdroplets consisting of 10^2-10^3 ions. The mechanism of nucleation inhibition was studied by different methods, including numerical simulation by the Monte Carlo method, the lattice approximation and the approximation of physical groups.

4. Growth of critical nuclei in solid solutions

Coalescence in solid solutions is described using the Lifshits–Slezov theory,[166,167] which considers a change in the size of a spherical nucleus with time. It is assumed that there are weak interactions between nuclei and the nucleus size is a small fraction of the average distance between these nuclei. Based on this theory, spinodal decomposition of a binary system upon coalescence in solid solutions was studied.[168]

In the course of spinodal decomposition, it can happen that upon rapid removal of a system outside the spinodal, interactions between nuclei cannot be considered as weak. Using a nonlinear equation for the free energy of a two-component solution,[169] all steps of spinodal decomposition can be described. Nonlinear members of this equation take into account interactions between nuclei. The nonlinearity restricts the exponential growth of fluctuations in the region of thermodynamic instability and gives rise to the coalescence effect.

In the study,[168] a truncated equation for spinodal decomposition was used for estimating a change in the nucleus size in the ordered structure formed. The equation describing a change in the wavenumber as a characteristic of the structure was deduced using asymptotic methods. In the long-time limit, rather simple relationships were obtained, whose form depends on the size of the decomposition region d ($d = 1$ corresponds to coherent platelet-like structures, $d = 2$ corresponds to cylindrical structures and $d = 3$ corresponds to nearly spherical three-dimensional structures).

Upon nucleation and nucleus evolution of a new phase on solid substrate surfaces in closed multicomponent and multiphase systems, film formation proceeds through several steps.[170] First, dispersed particles appear on the substrate surface (generally, on its defects). Then the substance is redistributed between these particles. Evolution of ensembles of dispersed particles is accompanied by latent heat release and an increase in the temperature of the system. One mode of redistribution of the substance between dispersed particles involves coalescence.[171] Due to a decrease in the free energy upon interface reduction, the average particle size increases as a result of mass transfer from smaller to larger particles.

Interactions between dispersed particles upon crystallisation of one-component melts associated with the occurrence of a heat field is called 'heat coalescence'.[172,173] A consideration of the evolution processes occurring in multicomponent closed dispersed systems in the general form demonstrated that in the asymptotic limit, the concentrations of components and the equilibrium temperature on the particle surface are independent of the nature of the particles. The distribution functions of phases depend only on the heat and mass transfer. The types of phases formed are determined by the ratios between the amounts of compounds dissolved, temperature and rate constants of chemical reactions. The time dependence of the size distribution function of new phases was found.

Investigations of evolution processes in ensembles of multicomponent and multiphase dispersed particles were continued in the study.[174] The phase formation in closed systems has also been examined.[175] Real systems are open, and the heat and mass transfer can take place in such systems. Dispersed particles on a substrate, the generalised field of adsorbed atoms and mass and heat flows interact with each other.

The effect of heat, which is evolved in chemical reactions proceeding under adiabatic conditions, on the dynamics of decomposition and crystallisation of multicomponent multiphase solid solutions and melts was examined.[176] The final step of decomposition and crystallisation of solutions involves coalescence accompanied by heat evolution. Under adiabatic conditions, the temperature of the system increases and the equilibrium concentrations of the components change. As a result, some phases decompose. It should be noted that the phase co-existence regions differ from analogous regions occurring upon isothermal decomposition. The condensed phase grows as a result of two concerted processes, *viz*., diffusion and heat exchange. The system of equations proposed in the study [176] describes evolution of phase isolation in the step of coalescence in an N-component solid solution, where both the temperature and composition fluctuations can be ignored. This system consists of K continuity equations, N equations of the law of conservation of matter, $(N-K)$ stoichiometric relations for flows, K equations of the law of mass action, the heat balance equations and an equation relating the characteristic size of the phase deposited to the matter flow. The dependence of the equilibrium constants of chemical reactions on the temperature and sizes of the phases being deposited was taken into account and an additional equation for the rate of their growth was introduced. The asymptotic solution of the above-mentioned system of equations allows one to determine the boundaries of the co-existence regions of all possible K phases in the space of the initial amounts of components and temperature. The authors of the publications [174–176] believed that their results can be considered as laws, which can enable one to control evolution of ensembles of multicomponent dispersed particles in the course of the growing of films with desired structures and compositions.

5. Boiling of stretched liquids

An adequate theoretical description of the boiling process of the so-called stretched (superheated) liquids based on high-precision experimental studies was published in the studies.[177–179] Phase transitions in systems occurring in the vicinity of the boundary of thermodynamic stability (the so-called spinodal) were analysed in the review.[180] These transitions of the critical type are characterised by a strong space–time correlation of perturbations and a high degree of fluctuations. In the case of rapid liquid–vapour phase transitions, one or both co-existing phases are outside the region of stable states.

Spinodal decomposition is a special case of the initial step of a phase transition whose occurrence requires that the system be initially transformed into a labile state. The system relaxation is accompanied by an increase in the number of random inhomogeneities, which may give rise to modulated relaxation structures. Propagation of small perturbations is characteristic of a system occurring in an unstable state, whereas perturbations dissipate in the case of stable states.

At high supersaturations, metastable states occur at the boundary of the region of absolute instability. In rapid processes, a labile state can occur along with a metastable stable; the compound rapidly loses the spatial homogeneity and acquires a cellular granular structure. Unlike the phase transition from a metastable state, spinodal decomposition does not require activation. Nuclei of a new phase appear if a stable surface layer is formed. In this case, certain portions of the system can be located in a metastable region. If the stability condition is violated, a stable layer between two phases cannot occur. As the spinodal is approached, the mechanism of phase transition changes. Spinodal decomposition and nucleation are the initial and final steps of a continuous process of instability propagation.

In a one-component system, the rate of spinodal decomposition is limited by heat exchange between the contracting and expanding volume units.[181] The time of formation of an unstable state should be shorter than the characteristic time of spinodal decomposition.

In multicomponent systems, the region of unstable homogeneous states is limited by the critical liquid–vapour conditions. The diffusion instability is characterised by the negative diffusion coefficient (ascending diffusion). In the case of two-component systems, diffusion instability is preceded by mechanical instability.[182] The diffusion mass transfer is determined by the chemical potential gradient. In the case of stable states, the approach to the stability boundary is characterised by deceleration of the diffusion transfer (the diffusion coefficient D tends to zero). For unstable states, $D < 0$.

The phenomenological theory of spinodal decomposition was first presented in the study.[169] The use of the Fourier representation for analysis of the stability of a two-component isotropic solution made it possible to determine the critical wavenumber k_c and the critical wavelength $\lambda_c = 2\pi/k_c$. Within a spinodal, the solution is unstable with respect to relatively small fluctuations in composition with the wavelengths $\lambda > \lambda_c$. The plot of the amplification coefficient R, which characterises a change in the amplitude of the concentration wave, *vs*. the wavenumber k has a sharp maximum at

$$k = k_m = \frac{k_c}{\sqrt{2}}.$$

This indicates that all concentration waves, except for those characterised by the wavenumber k_m, can be ignored within a time interval after the onset of decomposition. At $k < k_c$ [$R(k) > 0$], the concentration waves are exponentially amplified. At $k > k_c$, these waves are exponentially attenuated [$R(k) < 0$]. The Cahn theory[169] is based on the self-consistent field theory. In the vicinity of a spinodal, there are strong interactions between fluctuations due to which the concept of the free energy may appear to be inapplicable. The usual linearised equation for diffusion is valid only in the initial steps of decomposition, when deviations of the composition from the average value are small.

The Cahn theory was further elaborated by Cook,[183] who considered thermal fluctuations in composition. This made it possible to explain the fact that the experimental critical wavevector k_c' is larger than the theoretically predicted wavevector k_c.

The work of formation of a near-critical bubble plays an important role in phase transitions to which decomposition of a gas-supersaturated solution belongs.[184] Under isothermal conditions, which occur at high thermal conductivity of a solution, two variables are required for the description of a nucleus of a stable phase. The work of formation of a near-critical bubble was approximated by the equation

$$F = F^* - x^2 + y^2,$$

where F^* is the work of formation of a critical bubble; $x = (V - V^*)/\Delta V^*$; $y = (P - P^*)/\Delta P^*$; V^* and P^* are the volume of the critical bubble and the pressure in this bubble, respectively.

The work of bubble formation includes the squares of variables with opposite signs. Hence, the activation barrier F has a saddle. The variable x is unstable (therefore, the bubble volume can increase infinitely), whereas the variable y is stable. On going from the variables x and y to variables characterising the bubble state, which are specified by the number of molecules in the bubble v and a series of critical parameters, the bilinear approximation is retained.

The intensity of the phase transfer is proportional to the normalising coefficient C corresponding to the equilibrium distribution of the clusters. After integration of a two-dimensional equilibrium distribution with respect to the stable variable v, we obtain a one-dimensional distribution of bubbles over this variable

$$g_e(v) = \frac{C\pi^{1/3}}{\Delta v_c}\exp[-F(v)],$$

where $F(v) = F_c - (v - v_c)^2/(\Delta v_c)$.[2] The correction ΔF for the work of accommodation of a gas molecule was found thermodynamically, which made it possible to refine the normalising coefficient

$$C = \frac{P_c[2v_c(1-\varepsilon^2)]^{1/2}}{\pi^{1/2}\varepsilon k_B T},$$

where $\varepsilon = [2\sigma/(3r^*p^*)]^{1/2}$ (r^* is the radius of the critical bubble).

The normalising coefficient in the thermodynamic equation was refined in the study.[185]

The above-considered theory can be applied to solutions supersaturated by an increase in their concentration by gas pumping or a decrease in the concentration upon a change in the temperature or pressure. The rate of formation of a metastable state in a gas-supersaturated solution influences all variables describing solution decomposition.[186] Conditions were found for attaining the maximum intensity of the formation of overcritical gas bubbles and supersaturation of a solution, and all characteristics of solution decomposition at this instant were studied. The size spectrum of overcritical bubbles in the stage of their formation was determined.

The work of formation of a critical bubble is a function of solution supersaturation. The metastability of a solution is described by the law of increase in ideal supersaturation with time, the time being measured from the instant when the ideal supersaturation is equal to zero. The coordinate z of the maximum of the overcritical bubble distribution over the excess free energy increases with time at a rate dependent on the supersaturation, temperature and some other parameters of the solution. The variable x, which is the deviation of the coordinate z from the size of the overcritical bubble, is introduced to characterise the size spectrum of overcritical bubbles $f(x)$. Throughout the growth process, each overcritical bubble is characterised by its own value of x. At $x = 0$, the spectrum $f(x)$ has a maximum. The material balance equation for a solution includes the function g corresponding to the difference between the ideal and real supersaturations. The dependence $g(x)$ and the related spectrum $f(x)$ are found by an iteration method.

Most researchers reasoned that the classical nucleation theory adequately describes experimental data on the frequency of formation of gas nuclei upon liquid boiling. Presumably, this is associated with rather large sizes of critical nuclei, although this assumption is evidently unjustified in the case of spinodal decomposition.

Skripov and co-workers[177–179] have achieved much success in experimental investigations on boiling of stretched (superheated) liquids. Since the elementary event of bubble formation can be observed experimentally, it is possible to demonstrate that the nucleation process is accidental. Thus, the expectation time cannot be predicted, and only the time of the elementary event of formation of the first bubble can be estimated at the probability level. Experimental studies showed that the expectation time is determined by the distribution of random values.

It should be noted that nucleation rates in any system are only certain average values. To determine these rates, it is necessary to carry out a statistically sufficient number of individual tests, like in studies of stretched liquids and investigations of the boiling of superheated metallic wires. Another way is to observe the appearance of numerous nuclei of a new phase. Apparently, the latter approach allows one to reduce the experimental time. Generally, researchers, who use this approach, do not measure elementary nucleation events and observe only average values. In the case of an insufficient number of parallel nucleation events, fluctuations of nucleation events can be observed. To obtain reliable average values, it is generally necessary to increase the time of observation. In the case of a statistically sufficient number of measurements (with the variance in average values of $\sim 1\%$) and a rather high relaxation rate, the experiment can be quasistationary, *i.e*., one of the parameters of the system can slowly (compared to the relaxation rate of the system) change. In this case, one can obtain

more experimental data than in the case of accumulation of the results of individual tests.

One of the main schemes used in experimental investigations of boiling of stretched liquids (in particular, of the cavitation phenomenon) involves stretching of a column of a temperature-controlled liquid by relieving pressure. Several tens of experiments are already sufficient for the determination of the average expectation time for the breaking (boiling) of a liquid (the value inverse to the expectation time normalised to the volume unit is the nucleation rate). Hence, it is necessary to carry out several hundreds of tests of the system to obtain 10–20 points for the construction of one isotherm.

In an alternative scheme, a metastable state is achieved by superheating, which is provided by passing an electric current through a conductor. This scheme allows one to attain high degrees of superheating when heterogeneous boiling centres no longer play an essential role. This way of performing experiments allows the use of electronic means of automatisation and control. If relaxation of a system is achieved in a short period of time, a statistically reliable data set can be collected in an automatic mode rather rapidly. For example, the bubble formation in liquid nitrogen on a conducting film surface was studied,[187] and the kinetics of bubble formation in glassy methyl methacrylate and polycarbonate containing dissolved carbon dioxide was investigated.[188] In the latter case, the bubbling was monitored using a light beam. The light-transmission factor served as a quantitative measure of the concentration of pores formed in the polymers. Pressure jumps and surface tension at the boundary of critical bubbles at different temperatures and concentrations of dissolved CO_2 were determined. In some cases, these values corresponded to parameters typical of homogeneous nucleation, otherwise they corresponded to those of heterogeneous nucleation. It should be noted that it is possible to carry out a more detailed interpretation of results. For this purpose, one should use phase diagrams of a polymer–gas system, because some characteristic features of nucleation rate surfaces may be associated with the characteristic features of phase equilibrium diagrams of the systems under study. Nevertheless, the conclusion that the nucleation properties of a polymer–gas solid solution vary with saturation with gas is beyond question. This result confirms the generality of the concept (which was considered using vapours as an example) that the nucleation rate depends on the total pressure in a medium.

The bubble nucleation can also be studied using a two-piston chamber.[189] A constant negative pressure pulse is applied to a liquid sample during several milliseconds after which stretching is decreased by 10%–20%. As a result, the formation of new nuclei ceases and the bubbles grow to sizes, which can be observed by an optical method. The advantage of this scheme is that several bubbles can be formed simultaneously, which allows one to obtain abundant data in a single experiment, thus accelerating measurements of elementary events of bubble formation a hundred times.

In a study of the boiling of polymers,[190] the thermal stability of a polymeric liquid was estimated using a controlled pulse heating technique. The average lifetime of the polymeric liquid before its boiling was determined from a temperature plateau in a thermogram of the process. A correlation was found between the thermal stability and the slope of the plot of the average lifetime of superheated liquids *vs.* the temperature. A distinct relationship between the average time of bubble nucleation and the total pressure was revealed.

Cavitation in binary systems has long attracted the attention of researchers. The kinetics of phase transitions in binary solutions of several systems based on hydrocarbons and water was examined [191] in the vicinity of critical stratification points. The stratification was detected by photomicrography. Corrections for the equations describing the growth of a new phase volume were found. It was demonstrated that at the late step of the process, the dependence of the reduced average radii of the droplets of a new phase on the reduced time is described by an exponential equation with the exponent of 0.81.

Achievements in the field of research of liquid boiling under the action of a current pulse have not gained wide acceptance. Some researchers concerned, for example, with the boiling of metallic wires, did not employ the concepts of the nucleation theory at all. For instance, in the study [192] devoted to the dynamics of microplasticity of whisker single crystals under the action of a current pulse, the nucleation of dislocations in single crystals and their propagation were investigated. However, the experimentally observed incubation period determined by the plasticity delay time of the initially dislocation-free silicon whisker crystal [192] is nothing else as the expectation time for nucleation of dislocations. The nucleation of dislocations is a nucleation process involving all inherent metastable states and accident events. The delay time should be a random value and be characterised by the distribution, which was not discussed in the cited study. The evident drawback of this study is that the authors did not use the formal apparatus of the nucleation theory, which could substantially change the direction of investigation and interpretation of the results.

To summarise, it should be noted that the methods for studying nucleation in vapours and cavitation in liquids have gained most acceptance. However, these methods are not rigorously justified and need a thorough validation of the assumptions used for the interpretation of experimental data. Thus, in spite of a rather reliable verification of the dependence of the vapour nucleation rates on the total pressure in a nucleating system (see, for example, Refs 73 and 81), some researchers traditionally, like a quarter of a century ago, reject the effect of gas pressure as such.[193] These researchers use a variable pressure in a two-piston chamber to maintain both the nucleation temperature and initial composition of the vapour–gas mixture constant. Undoubtedly, this makes experimental studies with adiabatic cooling easier, but leads to an error associated with the dependence of the nucleation rate on the total pressure in the nucleating system. In other words, experiments are carried out under isothermal conditions but at a variable total pressure. For the results to be interpreted correctly, the experimental data are necessary to recalculate as applied to the constancy of the total pressure. For example, such a procedure should be carried out in calculations of the compositions of critical nuclei from the slopes of nucleation isotherms. In the investigation,[193] one variable in the parameter space was ignored and, in actuality, a particular section from different subspaces was measured without an adequate description of the trajectory in this space.

The nucleation, for example, of a binary vapour can be described in a five-dimensional space including the nucleation rate, the composition of the initial vapour, the composition of the nuclei of the condensate, the total pressure in the system and the nucleation temperature. It should be noted that the level of description of the experimental processes is not sufficiently high to give an estimate of the changes in the state of a nucleating system in the above-mentioned space. Different trajectories in this space give different projections onto subspaces, which is one of the factors responsible for the disagreement in the results obtained by different methods. The common aim of researchers is to develop experimental techniques for obtaining more precise and reliable data in the well-determined conditions of nucleation.

6. Nucleation in condensed phases

Nucleation in condensed phases assumes the existence of transformations from one condensed phase to another. Experiments on crystallisation of supercooled liquids were surveyed in the review.[194] The rate of crystalline phase formation was estimated using the maximum supercooling with respect to the temperature of the equilibrium melting–crystallisation process. The nucleation begins to proceed at a substantial rate once a sufficiently high supersaturation is attained. Generally, the supercooling limit is determined by the rate of heterogeneous nucleation on the walls, the presence of a liquid surface and heterogeneous nuclei in this surface, *etc.*, rather than by a homogeneous process. In emulsions and on substrates, the liquid breaks into droplets. To weaken

interactions, droplets are coated with surfactants or salt melts. When droplets are rather large, many of them do not contain heterogeneous nuclei. The supercooling maximum is generally taken as a homogeneous limit. Container-free methods of investigations are of considerable interest. In the falling drop method, a molten drop falls in a tube, which is filled with an inert gas (or evacuated) and whose walls are cooled. By hanging a drop in an electromagnetic field, one can more easily control the phase state of a sample. In this case, observations can be more prolonged and measurements are more accurate. In the case of metals, the maximum supercooling is $\sim 20\%$ of the melting point.

In the study,[185] homogeneous nucleation was treated as a heterogeneous process in which individual molecules serve as nuclei. This approach enables one to introduce a correction in the equation for the work of nucleation under different conditions.[195–197] The type of the correction is determined by the presence or absence of a thermal equilibrium between the nucleus and the medium. The work of nucleation depends on the external conditions of the nucleation process. The equation was derived for the work of nucleation upon homogeneous nucleation in the absence of an equilibrium between the nucleus and the medium in the case of an isentropic isochoric process. Under other conditions, this work can be evaluated by removing the corresponding terms from the equation for the potential of a critical nucleus. In the case of a complete equilibrium between the nucleus and the medium, the results correspond to the classical theory. The Gibbs equation describing the work of nucleation in the case of a heterogeneous process includes the work of wetting. To determine the work of wetting, one should consider an ensemble of macroscopic nuclei, which are in equilibrium between the mother and new phases. Each nucleus is considered as a dispersed particle and its chemical potential is taken into account.[198]

Studies of glass relaxation are of great technological and scientific interest. Here the question arises as to the existence of the limit of liquid supercooling.[14] Liquid supercooling gives rise to an increase in viscosity, the possible spinodal transformation of the liquid to a crystalline state being 'diffused'. At the same time, it is common practice to treat a glass as a liquid occurring in a metastable state, which is reasonable to regard as one of the states of the supercooled liquid. In any case, investigations of glass relaxation rates provide a unique possibility to answer the above question. The maximum glass relaxation rate is observed at low temperatures. Samples are kept at a low temperature until nucleation of crystals starts and then the samples are annealed at higher temperatures. In this process, the rate of formation of new nuclei is low, whereas the rate of cluster growth is much higher compared to those under the conditions of nucleation. The clusters grow to sizes such that their amount can be measured by simple methods. In metallic glasses, nucleation and nucleus growth are often not separated. Investigations of metallic glasses did not provide new information compared to that obtained in studies of well-known silicate glasses. In studies of a series of metallic glasses, including Zr–Ti–transition metal, Al–Fe, Ni–rare-earth metal and Fe–Si–B systems, anomalously high nucleation rates (which sometimes approach 10^{17} cm^{-3} s^{-1}) were observed.[199–202]

Investigations of nucleation in condensed phases are of importance for both fundamental knowledge and the solution of applied problems. Tauer and Padtberg[203] devised a system for computer collection of data on conductivity and haziness (transmission of light) of aqueous solutions. The authors of the cited study believed that this system is a universal tool for investigating nucleation in such systems. The onset of nucleation in solutions is determined from the discontinuity of the first derivative of the conductivity and the appearance of a bend in the curve of the transmitted light intensity *vs*. the composition. These experiments closely resemble the initial stage of investigation of aerosol nucleation, in which aerosol was observed, whereas the nucleation rate has not been measured. Emulsion polymerisation was studied in a similar way.[203]

Nucleation in chemically reacting systems is of great interest. The theory of this process was developed within the framework of classical notions of nucleation as early as the 1980s. The effect of surfactants on nucleation was simulated in the study.[204] It was demonstrated that due to the presence of surfactants, clusters can occur before the onset of phase transition. The addition of surfactants is equivalent to an increase in the deviation from the equilibrium state because the term proportional to the concentrations of the introduced compounds is added to the equation for the thermodynamic potential. The energy of cluster formation passes through a minimum, which provides the occurrence of metastable states. Due to anisotropy of the surface energy, the adsorption pressure is different on different crystal faces and the latter grow at different rates. This fact can account for the formation of dendrites in the presence of surfactants.

Recently, a general model was proposed for nucleation in chemically reacting systems.[205] This model is based on the Becker–Döring kinetic scheme[22] according to which clusters grow and decompose due to one-step aggregation and fragmentation processes. The model takes into account the catalytic effect of the already formed clusters on the rate of appearance of other clusters. The role of precursors (or specific reagents), which spontaneously decompose to form relaxing metastable states, and inhibitors, which hinder the cluster growth to sizes larger than a particular value, was discussed. The model includes several key equations describing the experimentally observed macroscopic behaviour of a system. Based on these equations, the most important components of the reacting system can be revealed and the steps of the process dependent on the rate can be determined. One of the versions of this model was used for the description of cement hydration. The problem was solved in the asymptotic mode. The results of calculations were consistent with the experimental data.

In the scientific literature, the problem of spontaneous formation and the existence of dimers in a nucleating system is actively discussed. In the theoretical investigation of the drop growth in a medium of an inert gas containing monomers and dimers of the agent condensed,[206] analytical equations were proposed for estimating the effect of dimerisation of vapour molecules on the rate of growth in an isothermal approximation. The growth of cesium drops in a helium atmosphere was calculated as an example. At high supersaturations, the rate of drop growth increases substantially due to formation of dimers.

The kinetic molecular mechanism of the onset of snowballing condensation from a supersaturated vapour with a high concentration of dimers was described in the general form.[207] The possibility of cluster growth due to the presence of dimers was taken into account. The enthalpy effects were taken into consideration by fitting the parameters of the model to the experimental values. This model can be used for calculating the total entropy of the clusters. At high pressures, the rate constants of condensation are corrected for the restriction of diffusion of monomers and dimers involved in the growth process. The description of the nucleation process in the density functional approximation was extended to condensation in an associated liquid. The theory of associated liquids in a system of spherical molecules with one associated bond was used for this purpose. Calculations demonstrated that the use of the classical nucleation theory led to a substantial overestimation of the activation barrier to nucleation in these systems. This deviation can be to a large degree compensated using the model proposed in the study.[208]

The investigation of nucleation in a benzene vapour giving rise to dimers in the temperature range of 15–123 K is of obvious interest.[209] For the range of 15–88 K, the coefficient of the rate of dimer formation was calculated. The formation of benzene dimers was proved by studying the reactions of hydrocarbons with C_6H_6 and analysing the optical spectra of the products. Model calculations showed that the systematic error of measurements is low. The coefficients of the dimerisation rate calculated on the assumption of free rotation of dimers are in good agreement

with the experimental values for the temperatures above 30 K at which decomposition effects should be small.

Agglomeration of nanosols can be considered as a model of a phase transition without long-range interactions. The activation energy of restructurisation of agglomerates from nanoaerosols was determined *in situ*.[210] In experiments with agglomerates of silver and copper nanoparticles, the height of the activation barrier to the rearrangement of particles in the agglomerate was determined. Agglomerates are formed due to collisions of several tens of the initial nanoparticles. The structures of the agglomerates can be described by the exponential law relating the number of the initial nanoparticles to the radius of the agglomerate. The exponent including the radius is generally referred to as the fractal dimensionality. This exponent is determined from electron microscopic images.

Interactions between nanoparticles can be of a different nature from van der Waals forces to ionic or covalent bonds. Agglomeration in which strong bonds are formed gives rise to rigid (generally, porous) structures. Agglomeration characterised by weak bonds affords clusters with more compact structures, the number of nanoparticles involved in the clusters being increased. The temperature dependence of the restructuring rate is described by the Arrhenius equation whose exponent includes the activation energy of the process. The pre-exponential factor has the dimensionality of frequency. To estimate the bond energy of nanoparticles in an agglomerate, it is necessary to know how the coordination number of the nanoparticles changes with time and to determine the fractal dimensionality at a particular instant of time. The initial particles interact only with the adjacent closely located particles. The activation energy of this process is an order of magnitude lower than the bond energy calculated with the use of the Hamaker constant,[210] for example, for silver and copper. In the range of the nanosol sizes under study, the energy of activation for silver is similar to that for copper. The maximum activation energy corresponds to the particles with a diameter of $\sim$18 nm. This energy decreases as agglomerates grow. The addition of oxygen before the onset of agglomeration of the initial nanoparticles leads to a twofold increase in the activation energy, the maximum energy corresponding to the particles with a diameter of 15 nm.

In the review,[211] it was mentioned that the development of theories of solid-state nucleation allowing for the thermodynamic aspects of nucleation and cluster growth is presently underway. To detect nuclei and determine their phase states, Rayleigh scattering of Mössbauer radiation and Mössbauer spectroscopy are used. Diffusion of clusters in pores is investigated using the microprobe method. Generally, studies are accompanied by investigations of the catalytic activity of clusters.

7. Photonucleation

Based on the results of the investigation of photonucleation,† a new procedure was developed for the determination of ultralow concentrations of molecules.[212, 213] The high level of analytical sensitivity is attained by exciting molecules with UV radiation. Upon vapour supersaturation, particles of photonucleation products (radicals, ions, *etc*.) grow to sizes, which can be easily detected by simple methods. Due to high spectral sensitivity of photodetection, the desired compound can be selectively excited and detected. For example, resonant excitation made it possible to detect nitrotoluene vapours at such a low concentration that their pressure is 50 000 times lower than the saturated vapour pressure.[212, 213] As a result, the sensitivity with respect to the concentration of $\sim$10 particles per billion was achieved.

The explanation for the photoactivation effect was put forward, for example, in the publications,[214, 215] where the distribution of vibrational energy in a binary reacting gas mixture after optical excitation was theoretically analysed. Stationary optical pumping gives rise to a distortion of the equilibrium distribution function of molecules with resonant levels, the distribution of vibrational degrees of freedom of other molecules remaining unchanged. In a two-component system, the vibrational temperature of both components differs substantially from the translational one. These effects open up the possibility of performing experiments on nucleation upon relaxation of the levels preexcited with resonant electromagnetic radiation.

Advances in the studies of photographic processes were made largely due to intuition and practical skills of researchers and are to a lesser extent associated with theoretical studies. In studies of the mechanisms of spectral sensitisation of silver halides with dyes, it was concluded[216] that the primary event of electron transfer from the photoexcited dye and the secondary dark reactions involving an oxidiser (silver) play a decisive role. In these processes, numerous various nucleation phenomena take place. Unfortunately, these phenomena have not been considered in the context of the nucleation theory. For example, AgBr crystals are formed in an emulsion, and the sizes of these crystals influence the quality of photographs. The formation of aggregated cyanine dyes on the surface of silver halide crystals is also associated with nucleation. Such dyes are used for spectral sensitisation of photomaterials.

Knowing the mechanism of photoprocesses at the molecular and atomic levels, one can follow the dynamics of changes in the electron density and the course of chemical reactions associated with photoactivated electron jumps. In studies of the formation, for example, of photoaerosols, researchers often restrict themselves to the detection of the photoeffect with no investigation of its kinetics and mechanism. Among a few exceptions are the investigations,[217, 218] where the mechanism of atmospheric nucleation upon photoactivation of the simplest aldehydes was proposed. When studying the mechanism of formation and growth of an aerosol upon photolysis of tungsten hexacarbonyl, the authors gave particular attention to the time range during which vapours leave the irradiation zone. The generation of the condensed product was discontinued to measure the concentration and evaluate the size distribution of the aerosol formed. The kinetics of aerosol formation was simulated by numerical methods using the Smoluchowski equation. The rates of monomer formation were calculated at different photolysis rates, which were varied by changing the irradiation time. These calculated values were in good agreement with the measured photolysis rates. It should be noted that some methodological problems remain unresolved, which hinders the quantitative determination of the frequency of aerosol formation upon photoactivation.

The translational energy release upon multiphoton dissociation of organometallic compounds was studied.[219] The results were discussed from the viewpoint of expenditure of energy in aerosol formation from photolysis products of $W(CO)_6$. The processes of the preparation of aerosols and thin films were controlled by a laser. The properties of semiconducting CdSe nanoparticles with a diameter of 2–15 nm were examined.[220] It was assumed that the addition of butylamine to a colloidal solution of nanoparticles excludes the radiation path for their luminescence. An observation of interactions between nanoparticles and a hole acceptor (to which butylamine belongs) allows one to detect electron transitions in surface atoms of nanoparticles.

8. Search for similarity criteria

Many researchers are concerned with a search for similarity criteria allowing one to carry out rescaling of the results of studies of nucleation (see, for example, Ref. 221). The asymptotic limit of the activation energy on going from heterogeneous to homogeneous nucleation was determined depending on the contact angle.[222] This value is consistent with the results of numerical simulation. The possibilities of scaling as applied to the properties of molecules in the critical cluster and then to nucleation were

† Atmospheric nucleation giving rise to morning fog, which appears with the first sunbeam, is an example of photonucleation.

analysed.[223] The scaling properties of nuclei were treated based on the Kelvin equation. Analysis was carried out using the formal apparatus of the density functional theory and the molecular dynamics method. The concept of the reduced height of the barrier to nucleation was introduced. It was demonstrated that both modes of scaling are related to each other by the nucleation theorem and, hence, can be combined.

The model of scaling invariance for binary nucleation in ideal systems [35] was used for analysing experimental data on nucleation rates in a hexanol–ethanol system.[224] Nucleation in a water vapour was simulated by the Monte Carlo method [225] and the results were presented in a criteria form. The results of simulation are in agreement with the data from the experimental study.[226] Based on scaling, corrections applicable to the results obtained by other researchers were proposed.

9. Adiabatic expansion method

Homogeneous vapour nucleation can occur upon rapid adiabatic expansion of a vapour–gas mixture. First data on this type of nucleation were obtained already in the late 19th century. In early experiments (see, for example, Ref. 227), the critical supersaturation S_c, to which the nucleation rate $J = 1$ cm^{-3} s^{-1} corresponds, was determined. The construction of a Wilson chamber used for studying homogeneous nucleation has gradually been improved.[71, 228–231] Apparatus was devised to maintain a constant nucleation temperature over a long period of time, which made it possible to control the changes in the concentrations of the particles formed and their size distribution with time.[228, 232] The nucleation rates were measured with high accuracy in different systems using an adiabatic two-piston expansion chamber.[224, 233–235] Presently, a Wilson chamber is used most generally for studying different processes associated with volume nucleation.

In a number of studies (see, for example, Refs 236–238), condensation was examined in a shock tube. A shock tube is a device, where a vapour is heated and rapidly cooled due to generation of shock waves in a vapour–gas mixture. Generally, a tube consists of two cells separated by a diaphragm containing a vapour (gas) at high (driving chamber) and low (driven chamber) pressures. Once the diaphragm is broken, the shock wave propagates to the section containing the low-pressure vapour and rapidly heats the latter. The high-pressure gas is simultaneously cooled under the action of a rarefaction wave. Heating can cause decomposition of a chemical compound into non-volatile components,[236] while cooling leads to vapour supersaturation.[237]

The construction of a tube with two diaphragms made it possible to extend substantially the range of compounds under study.[239] In this tube, the vapour is compressed by a shock wave after breaking of the first diaphragm and then the vapour is expanded into vacuum after breaking of the second diaphragm. This tube can be used for studying compounds characterised by a high vapour pressure at room temperature (for this purpose, these compounds are mixed with an inert gas). Compounds occurring in the solid state at room temperature are introduced as aerosols. The shock wave causes evaporation of aerosols and the vapour formed is condensed in the expansion cycle.

The studies of nucleation of different systems at high pressures using a shock tube are of great interest.[240–242] The authors of the cited studies were among the first who concluded that nucleation under an atmosphere of a carrier gas should be considered as a binary process.[242]

A shock tube is extensively used in studies of nucleation at pressures of 70 atm.[243–245] The kinetics of formation of methane hydrates was the main subject of investigation. For example, nucleation of water in methane was studied at pressures up to 40 bar [243] and an *n*-nonane–methane system was investigated in the pressure range from 10 to 40 bar.[244] In the latter case, the dispersion in experimental measurements was much smaller than that achieved, for example, in the study.[245] The scheme was proposed for the use of a shock tube in studies at high temperatures.[246] The geometry of a shock tube was devised so that the reflected wave again increases the pressure after the expansion cycle, thus preventing the appearance of new nuclei and providing conditions for the growth of the already formed nuclei.

The processes occurring in the systems under consideration are non-stationary, which hinders interpretation of experimental results. A spontaneously formed aerosol can be prepared in experiments using a supersonic flow of a vapour or a vapour–gas mixture through Laval nozzles. The state of the gas throughout the length of the nozzle can be precisely determined with the use of the gas dynamics equations.[247–249]

Interesting results were obtained in the studies of nucleation of light and heavy water in nozzles.[250, 251] It appeared that the compositions of the aerosols thus prepared correspond to the initial compositions of the samples. These experiments were carried out with the use of computer simulation. The experimental results were more similar to the values calculated on the assumption of isothermal conditions of the process rather than non-isothermal conditions. Analogous results were obtained in parallel measurements in a two-piston chamber.[252]

Nucleation in Laval nozzles cannot be described on the basis of the isothermal theory because the process under consideration is non-isothermal. The nucleation theory at high supersaturations [39] (including the theory of processes occurring in nozzles) has not been developed in sufficient detail. The difference in the temperatures corresponding to different degrees of freedom was observed in experiments using high-intensity molecular beams.[253, 254] However, a theoretical description of these results is lacking. The developed methods for diagnostics of molecular beams enable one to study directly critical nuclei and distributions of clusters in a vapour expanded into a vacuum. These methods are very useful for quantitative studies of non-stationary non-isothermal nucleation.

10. Method for turbulent mixing

Studies of homogeneous condensation of a vapour by turbulent mixing of a hot vapour–gas mixture with a cold gas are of considerable interest.[255, 256] Up to the 1960s, qualitative studies were primarily carried out. The main results were systematised by Amelin in the monograph.[257] First data obtained by Friedlander were presented in the publications.[258, 259] The method under consideration was widely used in the investigations.[260–262] In spite of the simplicity, this method enables one to investigate nucleation processes in broad ranges of temperature, supersaturation and nucleation rate under stationary conditions due to which it has advantages over methods in which an adiabatic expansion chamber is used in a cyclic mode.

Similar apparatus were used in the studies [257–259] devoted to the determination of the critical vapour supersaturation at which the aerosol formation began. A gas flow heated to a particular temperature is ejected at high velocity through a nozzle into a surrounding atmosphere moving at a certain velocity [257] or into a resting gas.[258] The flow was initially saturated with a vapour of the compound under study and its cooling with the surrounding flow leads to vapour supersaturation to give an aerosol. To detect the aerosol, the flow is illuminated with a collimated light beam and photographed. A common drawback of the cited studies is that the presence of an aerosol is determined in an arbitrary way and the beginning of the particle detection depends on the point in time at which the critical vapour supersaturation is attained. However, these studies provided qualitative insight into the transformations that occur in this process.

In subsequent studies, the parameters of an aerosol formed in a turbulent flow were measured quantitatively. The aim of the study [263] was to validate the homogeneous nucleation theory proposed by Becker and Döring.[22] In the investigation,[263] the concentrations of particles formed in a generator were determined (unlike the above-considered studies) using a photoelectric counter.[264] A comparison of the calculated and measured concentrations of the particles demonstrated that the best agreement

between these values was achieved for dibutyl phthalate. There was a substantial discrepancy between the experimental and calculated concentrations of the particles of ethylene glycol, octadecane and sulfur.

A similar problem was solved in the studies.[265, 266] Octadecane and heneicosane were used as working compounds. At that time, the discrepancy between the calculated and experimental data of four orders of magnitude was considered to be satisfactory.

Procedures were developed for determining the concentrations and disperse compositions of aerosols formed by turbulent mixing of a vapour – gas mixture. The aerosol concentrations up to $10^7\,cm^{-3}$ can be measured using a flow-through ultramicroscope constructed by Deryagin and Vlasenko.[267] Besides, the concentration can be determined with lower accuracy but then rapidly from light scattering. After enlargement in a vapour of an organic compound, an aerosol can be considered as monodispersed and its concentration can be easily determined using a nephelometer.[260]

Time scales of nucleation under turbulent conditions were simulated by Barrett.[268] He studied the temperature and concentration distributions with no account for condensation. An increase in the rate as the nucleation peak is approached and a decrease in the rate after passing the peak were evaluated. The value inverse to time corresponds to the pulse rate. The number of the particles formed was estimated from the nucleation rate multiplied by the peak duration. The results of calculations were verified by comparing the results of more precise calculations performed on a computer and with the data obtained in a real turbulent flow containing water vapour. Under laboratory conditions at a temperature below 90 °C, condensation has only a slight effect on the number of droplets along the flow axis. However, condensation noticeably suppresses nucleation at temperatures above 95 °C. Barrett believed that the proposed model can be useful for the construction of systems in which nucleation and particle growth occur simultaneously.

In investigations of condensation under turbulent conditions, it is very important to estimate the amount of particles which are deposited on walls limiting the flow. Simulation of the particle motion in a near-wall turbulent layer [269] is based on analysis of the flow stability in a channel. The equation of motion includes the Stokes, gravitational and lifting forces. In the cited study,[269] the efficiency of particle deposition from a flow was analysed by considering trajectories ending in particle deposition. The precipitation rates predicted by the model were in good agreement with the available experimental data. Particle deposition on a small-disc target was studied.[270] The deposition effects associated with convection, diffusion, sedimentation, electrification and thermophoresis were investigated. It was found that thermophoretic purification from particles can be reduced to zero because of very weak attractions between charges.

The turbulence effect on the rate of particle formation in a vapour flow was studied experimentally.[271] The authors of the cited study investigated nucleation in a flow with the temperature of 400 K, which was injected into air at 298 K and 1 atm. To simplify calculations, the Levi number was taken equal to unity. The temperature fluctuations in an axis-symmetric flow were estimated and local rates of particle formation averaged over fluctuations were calculated. Turbulent pulsations substantially decrease the nucleation rates at local maxima and increase the nucleation volume. In the cited study, particle distribution fields were reported.

In the last two decades, the scheme using a turbulent flow was virtually not used for studying the rate of vapour nucleation because there was no assurance that homogenisation of a system occurs before nucleation. The data on nucleation at large temperature and concentration gradients remain to be adequately interpreted. However, it can be expected that this 'drawback' will soon become an advantage because this approach can be used for the quantitative determination of the delay times of nucleation under gradient conditions. This field of investigation is of importance because such processes often take place in practice.

11. Methods based on molecular diffusion

Of all the apparatus used for studying nucleation, a thermodiffusion chamber is of most interest from the viewpoint of accuracy of measurements, because only in this chamber (unlike a Wilson chamber, Laval nozzles and shock tubes), condensation proceeds in a stationary mode. This provides the possibility of measuring the parameters of the process with high accuracy. A thermodiffusion chamber was first proposed by Langsdorf.[272] The action of this chamber is based on the use of vertical diffusion of the vapour under study through a light carrier gas. A compound evaporates from a hot plate and diffuses through an inert carrier gas to a cold plate. The temperature and pressure of the vapour between the plates change approximately linearly, whereas the saturation pressure depends exponentially on the temperature which gives rise to supersaturation. At a supersaturation higher than the critical value, homogeneous condensation with the formation of droplets is observed.

There are two types of thermodiffusion chambers, which differ by the direction of vapour diffusion. Langsdorf evaporated the compound under study from an upper (hot) plate. However, this construction was rejected at a later time, and researchers used chambers in which the hot plate was located under the cold one.[273] The convenience of such chambers is that the condensate from the upper plate drains down and compensates the volume of the liquid that evaporates from the lower plate due to which the cycle becomes closed and the stationary mode is maintained during many hours. Due to the stationarity of the process, self-purification of the chamber from heterogeneous nucleation centres becomes possible. Relatively rare nucleation events caused by solar beams can be excluded from the statistics. A diffusion chamber was used for studying the dependence of the nucleation rate on supersaturation in different systems,[273–279] including those occurring at high pressures (up to 40 – 100 bar).[273–275]

In detailed studies of homogeneous nucleation of higher alkanes, critical supersaturations and nucleation rates were measured,[280] the relations between the corresponding states were found and the dependences of the critical supersaturation of hydrocarbons on the number of carbon atoms and the number of molecules in the critical nuclei were revealed.[281] In the investigation,[282] ion-induced nucleation of vapours of six compounds was examined in a thermodiffusion chamber. Ions were generated using an α emitter. Either positive or negative ions were generated by varying the electric field. Experiments were carried out both in the presence and absence of an electric field in the nucleation zone. In the presence of the field, nucleation on positive and negative ions proceeded differently.

Interesting experiments on nucleation were carried out using photoactivated ions.[212, 213, 283] Dose amounts of ions were produced with the use of small additives of 4-fluoroaniline or hexamethyldisilazane, which can be ionised upon resonance excitation. A resonance excitation pulse from a tunable UV laser initiated the generation of ions in the region below the point of maximum vapour supersaturation. Ions with the required sign were shifted to the nucleation zone by applying an electric field.

Diffusion chambers enable one to measure the frequencies of nucleus formation within 10^{-2} – $10^2\,cm^{-3}\,s^{-1}$. The lower limit is determined by the long expectation time for the appearance of a viable nucleus, whereas an upper limit is determined by the fact that at nucleation rates higher than $10^2\,cm^{-3}\,s^{-1}$ the droplets that appear substantially disturb the diffusion and heat flows. The dependences of the distribution of vapour and temperature in a thermodiffusion chamber as well as of the nucleation rates on both the stationary homogeneous vapour condensation on droplets and the release of the phase transition heat were examined, for example, in the study.[284] Moderate changes in supersaturation and temperature in a chamber caused by the release of phase transition heat and a decrease in the concentration of a vapour

upon its condensation on droplets lead to a substantial decrease in the nucleation rate as compared to the rate which should be observed (according to the nucleation theory) provided that the vapour is not consumed and the condensation heat is not released.

Distortions of the results obtained in flow diffusion chambers may be a consequence of particle deposition on walls. With the aim of estimating this effect experimentally, thermodiffusiophoresis of growing droplets of dioctyl phthalate formed in a supersaturated vapour upon homogeneous nucleation was studied.[285] It appeared that the thermodiffusiophoresis theory, which was developed as early as the 1970s, gives an adequate prediction of results obtained in real conditions. This theory allows one to estimate the effect of thermodiffusiophoresis on the overall nucleation rate in a flow diffusion chamber. The first experiments with the use of this chamber have already demonstrated [286] that an aerosol column formed along the flow axis does not virtually spread out during the period (several tenths of a second) of the presence of particles in the chamber. A noticeable (at the error threshold) effect can be observed if the number of particles decreases by a factor of 2–3 due to thermodiffusiophoresis. Such a decrease has not yet been observed in flow diffusion chambers. In investigations of nucleation of chemical compounds under conditions of a high vapour pressure (> 30 Torr), it is necessary to estimate additionally the effects under consideration.

In experiments on nucleation, there is a probability that aerosol particles undergo aggregation due to which their number and size distribution can change. This problem is most pressing in experiments with the use of adiabatic expansion methods, where high concentrations of aerosols are produced in the nucleation volume. This problem is rather easily solved based on the assumption that substantial coagulation cannot be observed in a fraction of a millisecond required for the particle detection. In studies with the use of a flow chamber, tenths of a second are required for the detection, the maximum concentrations of particles being four orders of magnitude lower than those in the case of adiabatic expansion methods, which also eliminates the problem of aggregation. In experiments with the use of a static diffusion chamber, this problem does not occur at all because the maximum concentrations of particles are too low to influence coagulation. A certain insight into the effect of aerosol aggregation on the nucleation rate was offered in the study.[287] A model of coagulation of a two-component aerosol was described in the investigation.[288] Coagulation occurring at different compositions and sizes of particles was examined in the publication.[289]

In experimental studies, the question as to the effect of vapour depletion on the nucleation rate is of importance. In a real system, only a limited amount of a vapour can be used and, hence, nucleation occurs inevitably on the background of a varying supersaturation. This fact is often ignored and the results of studies are related to average parameters of the system or conditions at which the maximum nucleation rate is achieved. In the study,[290] the nucleation rates and nucleus growth were examined under conditions of a limited amount of a vapour. The equations were derived for the particle growth and changes in the concentration of a vapour due to its condensation under conditions corresponding to a combination of continuous and free-molecular modes. The characteristic times for these modes were found depending on the particle sizes and these times were compared with the characteristic times of nucleation, coagulation and chemical reactions. The vapour concentration decreases as the number of particles in the system increases. The authors of the study [290] believed that an estimate of characteristic times is an efficient method for the determination of the relative importance of condensation compared to other competitive processes.

The idea of a thermodiffusion chamber was used in the study [286] of spontaneous vapour nucleation in a flow. A flow diffusion chamber was constructed such that two coaxial flows with different temperatures, *viz*., a heated gas saturated with the vapour of the compound under study and a cold blowing gas flow free from the vapour, move in a laminar mode. Supersaturation of the vapour of the condensed compound is achieved as a result of equalisation of the temperature and concentration through thermal conductivity and molecular diffusion. Under conditions of a laminar flow, the temperature and concentration distributions of a vapour in the bulk of a tube can be calculated using the standard heat-conduction and diffusion equations. Simplified examples of such calculations in vapour–gas laminar flows were given, for example, in the monograph. [257] The influence of perturbations occurring at the interface of hot and cold flows was studied in detail [286] and conditions at which these perturbations have virtually no effect on the nucleation rate were found experimentally.

In the study,[291] the nucleation and growth of aerosols in a laminar axis-symmetric flow were analysed theoretically, problems of heat and mass transfer were considered and the dynamics of the establishment of the size distribution of particles was investigated. Nucleation of one- and multicomponent condensation aerosols was studied using an experimental apparatus with a laminar axis-symmetric flow.[292] The measured aerosol concentrations were compared with those calculated within the framework of the classical nucleation theory. Nucleation of a dibutyl phthalate vapour as a function of temperature and supersaturation was studied in a flow diffusion chamber.[293, 294] An algorithm was proposed for solving the two-dimensional problem of heat and mass transfer.[295] It was demonstrated [296] that a carrier gas affects the nucleation rate of alcohols at atmospheric pressure. This result is of great importance because it provides independent evidence in support of the thesis about the influence of a carrier gas on nucleation, which I proposed earlier.[297]

In a modified version of a flow diffusion chamber,[297] a gas together with a vapour first go from a saturating reactor to a heated tube, where the flow becomes stationary and laminar, and then it passes to a condenser. Laminarisation of the starting vapour–gas flow facilitates substantially the specification of the boundary conditions for the flow rate distribution and vapour concentration distribution, which simplifies the solution of the stationary problem of heat and mass transfer in a chamber. Experience of the use of a flow diffusion chamber is being gradually accumulated. For example, reproduction [298] of earlier experiments [299] on nucleation of a dibutyl phthalate vapour gave results, which differ from the earlier data by a factor of 2–3. This is quite satisfactory for the initial stage of investigation.

Experimental methods for studying vapour nucleation are being extensively developed. Information on nucleation rates under precisely fixed conditions of nucleation can be gained in different ways. However, the method of a laminar axis-symmetric flow or a flow diffusion chamber holds, apparently, most promise. The simplicity of this method and the possibility of measuring a large number of experimental points in a rather short period of time enable one to observe, for example, a change in the phase state of critical nuclei.[73] Undoubtedly, this approach will be further elaborated and will find wide application in studies of processes of aerosol formation. It should be noted that different experimental methods complement each other. These methods can be arranged in the following order of increasing measured nucleation rates: a static diffusion chamber ($10^{-2 \div -3}$–10^{2} cm^{-3} s^{-1}), a flow diffusion chamber ($10^{0 \div 1}$–$10^{6 \div 7}$ cm^{-3} s^{-1}) and adiabatic expansion methods (10^{1}–10^{5} cm^{-3} s^{-1}). The employment of a flow diffusion chamber can be supplemented by the method for turbulent mixing ($10^{5 \div 7}$–$10^{9 \div 12}$ cm^{-3} s^{-1}). The adiabatic expansion methods assume the use of apparatus such as a Wilson chamber, shock tubes and nozzles.

IV. Excess energy of clusters. Experiment

It is known that the behaviour of a thin layer of a compound at the interface, in particular, at the vapour–condensate interface differs substantially from the behaviour of each of the homogeneous phases in the bulk. The theoretical representation of a surface layer as an inhomogeneous film, which separates homoge-

neous or virtually homogeneous substances, has been proposed already by Gibbs. The surface energy and, as a consequence, the surface tension are among the main thermodynamic characteristics of the surface layer. The available surface tension theories are far from being perfect and are, generally, applicable to only a narrow range of compounds (see, for example, Refs 8 and 80).

The excess (surface) energy of clusters plays a key role in the nucleation theory because it determines the activation energy of the nucleation process. Since our knowledge about complex systems are scarce, it is advantageous to use a simplified approach involving similarity methods and analysis of dimensionalities. The fundamental similarity criteria characterising microdisperse systems were found.[221] Calculations based on reference data for 38 liquids (condensed inert gases, alkanes, alkenes, dienes, aromatic hydrocarbons, alcohols, liquid metals) indicated that these criteria are temperature-dependent. The authors of the cited study believed that two systems are thermodynamically similar if their similarity numbers have (their pairs) close values. Presently, it is difficult to evaluate the importance of this approach for the nucleation theory because the proposed criteria need further verification with the use of a greater body of data for various chemical compounds. However, a search for similarity criteria undoubtedly belongs to classical problems of thermodynamics. It seems likely that the application of this or an analogous approach will pave the way to considerable progress in the development of the nucleation theory. It should be noted that a search for scale invariance requires that as much data should be used as possible and has need for intuition or research. Successive theoretical approaches are more unlikely to give a reasonable set of axiomatic statements favourable for the development of the parametric theory as compared to an essentially semiempirical search for scale invariants.

The importance of the determination of the excess energy of critical clusters was illustrated in the investigation,[300] where the size distribution of clusters was estimated in a broad range (from dimers to macroscopic drops). In the cited study, the ratios between the equilibrium constants of dimers and the surface tension coefficients were determined and the correction for the surface tension coefficient in the Frenkel equation was found. The chemical potential of a cluster is written as a linear function of the number of 'inner' and surface molecules. The author of the cited study believed that his semi-phenomenological model and data on the size distribution of clusters can explain, for example, the experimentally observed abnormally high nucleation rate of a mercury vapour.

In the study,[300] a vapour was treated as an ideal mixture of clusters with different sizes. The state of the atom in the cluster is characterised by the coordination number, which is similar to its value N for the corresponding condensed phase. The coordination number of the surface atoms is smaller than N. The surface tension of clusters can be described by the equation

$$\frac{\sigma}{\sigma_0} = 0.414(n-1)n^{-2/3},$$

where n is the number of molecules in an arbitrary cluster.

If the size of the critical nucleus $n^* < 30$, the surface tension of the cluster σ is much smaller than σ_0. Consequently, the Frenkel model substantially underestimates the nucleation rate as if nucleation had occurred at high supersaturation S. Nucleation of a mercury vapour proceeds, for example, at $S \approx 10^5$ at an abnormally high rate.[301]

The study[302] is yet another example of a search for an adequate description of the excess energy of critical nuclei. The authors introduced a correction to the equation for the surface tension and intermolecular interaction, which takes into account the second virial coefficient thus modifying the Fischer droplet model.[50] This leads to changes in the average area of the cluster surfaces and the number of molecules in the clusters. The authors of the cited study believed that their approach is applicable to any temperatures below the critical point, which was supported by the fact that the calculated values were consistent with experimental data.

The study[303] was concerned with nucleation in gases. The surface tension was described by modified McLeod's equation

$$\sigma(w_g, w_l, \theta) \simeq \Theta(\theta)(w_l^{-1} - w_g^{-1})^{\delta},$$

where $w_{g,l} = v_{g,l}/v_c$ is the ratio of the specific volume of gas (or liquid) molecules to the specific critical volume; $\Theta(\theta) = (A/v_c)^4(w_{leq}^{-1} - w_{geq}^{-1})^{4-\delta}$, where A is a constant, w_{leq} and w_{geq} are normalised specific volumes corresponding to bimodal conditions; $2 \leqslant \delta \leqslant 4$; in most calculations, it was taken that $\delta = 2.5$.

It is assumed that as the system approaches the conditions for spinodal decomposition, the work of formation of a critical cluster decreases more rapidly than is expected from the classical nucleation theory. The authors of the cited study reasoned that their approximation combines the simplicity of the classical theory and the ease of its use. In the region of small supersaturations (like in the limiting case), the results of the classical theory are reproduced. This is attributed to the fact that the surface tension of clusters in the case of slow nucleation is close to the equilibrium value corresponding to the planar surface and high supersaturation; the surface tension deviates from the reference data and approaches the dynamic values corresponding to the appearance of new interfaces. Therefore, the surface tension is inconsistent with its macroscopic value. Hence, the application of the classical theory to systems with high supersaturations leads to substantial errors. It can be readily seen that this approach includes a useful but rather trivial parametrisation, which is present in an indirect form as the consideration of the notion of dynamic surface tension. Hence, the calculation possibilities of this approach are no higher than those of other theories. The parametrisation enables one to describe correctly the behaviour of a series of nucleating systems. However, this parametrisation does not solve the problem of the development of a universal theory.

The drawbacks in the procedures for the determination of the excess energy of critical clusters were discussed in the study.[304] Concepts of statistical mechanics were employed for the development of the nucleation theory based on the determination of the potential energy of clusters, which is independent of the space distribution of molecules. It is assumed that the excess energy of the cluster consisting of one molecule should be equal to zero. Using the potential constants from models of macroscopic samples, one can calculate the latent heat and surface tension of clusters.

It was proposed to use a fractal model and the corresponding kinetic equations for the description of cluster formation.[305] Clusters formed due to coalescence can be characterised by a lognormal size distribution. The results obtained with the use of the Smoluchowski equation and different theories describing a cluster size spectrum are similar to those obtained in experiments with the use of molecular beam expansion into a vacuum and in the laser chemistry of organometallic compounds. The authors of the cited study believed that the model provides a statistically perfect basis for the interpretation of data on the distribution of clusters synthesised by different methods.

In the study,[306] a semi-phenomenological correction was proposed, which made it possible to refine the surface energy taking into account the curvature of a spherical drop known as the 'Tolman length'.[80] The following equation of state was derived with the use of Fischer's droplet model:[50]

$$\frac{P_{sat}}{q_0 k_B T} = \sum_{n=1}^{\infty} n^{-\tau} \exp[-\theta_0(1 + \alpha_\sigma n^{-1/3})n^{2/3}],$$

where P_{sat} is the saturated vapour pressure, $\theta_0 \equiv \sigma_0 s_1 / k_B T$ is the dimensionless surface tension at the planar interface and $\alpha_\sigma \equiv -2\delta_T / r_1$. At low temperatures, the surface tension is high and the Tolman length is, as expected, small ($|\alpha_\sigma| \ll 1$). In this case, the solution of the equation of state takes the form

$$\alpha_\sigma = -\frac{1}{\theta_0}\ln\left(\frac{P_{\rm sat}}{q_0 k_{\rm B} T}\right) - 1.$$

In the general case, the equation of state for different nonpolar compounds is solved by numerical methods. Away from the critical temperature, the Tolman length is positive and, according to the Dillmann – Meier model, is equal to ~20% of the surface tension of the droplet. The Tolman length becomes negative as the critical temperature is approached and its change is consistent with that predicted by the density functional theory.

The problem of the excess energy of clusters is closely related to the question about the limits of applicability of the droplet model to small clusters. A model, which is alternative to the droplet model used for small clusters, was suggested for the description of atomic chains spontaneously formed at rather high temperatures.[307] Analytical estimates were made on the assumption that the atom interacts only with the nearest neighbours. The interaction potential is additive and short-range. A model with a minimum number of bonds and a statistical model of a macroscopic droplet represented as many linked chains are two limiting models of the cluster. In the study,[307] the authors used both an analytical equation for the statistical sum of a gas-like cluster, which was derived within the framework of simplified model representations of the interaction potential of particles and the cluster structure, and numerical simulation of the cluster evolution in a supersaturated vapour by molecular dynamics.[308] The equilibrium size distribution of clusters was found by discrete methods. This distribution made it possible to calculate the homogeneous nucleation rate in a supersaturated vapour.

Studies by molecular dynamics and the Monte Carlo method demonstrated that in the first steps of cluster formation, the generation of branched chains (fractals) is energetically favourable. The latter are folded into a sphere as the size becomes rather large. A computer simulation showed [309] that the formation of chain clusters is typical of a polar Lennard-Jones liquid. The chain length increases with increasing number of dipoles in the cluster. As a particular size is reached, the fractal is broken to form a compact spherical cluster. At the boundary of spherical clusters, chain fragments still persist. The authors of the cited study stated that the interface of spherical clusters differs substantially from a planar boundary. Collapse of fractals occurs when the number of dipoles is as much as ~200.

The fact that atoms tend to be combined into clusters as energetically favourable structural units is evidenced by the results of mass spectrometric measurements. Dark-blue crystals of clusters with composition $Na_{48}[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]\cdot(\sim 1000\,H_2O)$ were prepared.[310] In these clusters, 368 molybdenum atoms form a virtually spherical shell with two open mouths on the opposite sides and the inner cavity of size ~2.5 × 4 nm. This structure was called a 'nanohedgehog' because of the presence of numerous protruding (like hedgehog hair) Mo=O bonds. The 'nanohedgehog' has a diameter of ~6 nm. Regions with both positive and negative curvatures are present on the cluster surface thus breaking the 'monotonicity' of symmetry within this nanoobject comparable in size to proteins. It is assumed that the nanocluster possesses catalytic properties. In addition to this surprising cluster, families of fullerenes and carbon nanotubes, huge nanoclusters, supramolecular compounds, *etc*. are known.

The idea that diamonds can be prepared by impact loading or rapid deposition of carbon onto a substrate followed by cooling was put forward rather long ago. Investigations of deposition on substrates have been successfully performed by Russian researchers. The results of these studies were generalised in papers and monographs.[311, 312] It was demonstrated [313] that meteorite diamonds are key objects, which can help in elucidating the nature of impact-wave cosmic phenomena. Studies of meteorite diamonds provided a reliable interpretation of impact recrystallisation of silicate minerals in meteorites.

Calculations by the Monte Carlo method [314] demonstrated that spheroidal silicon clusters consisting of more than 36 atoms are stable and showed that the bond energy rapidly increases as the cluster size increases. Such an increase in the bond energy is not observed if clusters are described in the droplet approximation. Calculations using the Hartree – Fock approximation for the icosahedral Si_{60} cluster gave similar results.[315 – 317] In the review [318] devoted to the computer simulation of nanotubes, it was noted that the synthesis of the first carbon nanomaterials was carried out virtually simultaneously with a series of studies on simulation of their electronic structures and almost all nanotube compounds and many of their properties were predicted based on the results of calculations. Due to the unique properties of nanomaterials, the latter attract great interest, which, in turn, causes an increase in the number of investigations.

Theoretical problems of nucleation as applied to nanotube materials remain to be solved. The practical realisation of the process has not yet sufficiently developed. Hence, the quantitative determination of the nucleation rate is not a problem to be solved. Nanostructures are prepared predominantly in an arc discharge using graphite electrodes. This method was used for the synthesis of structurally different clusters.

The results of the above-considered studies provide arguments in favour of the fractal model of critical nuclei. The formation of a nucleus of a new phase can be represented as a series of successive fluctuation transformations from one relatively stable configuration of the cluster to another one. Obviously, the problem of calculating the excess energy of clusters for the description of the nucleation kinetics without resorting to the droplet model becomes more complex. However, as will be demonstrated below, this problem can be resolved.

Presently, in spite of the complexity of the experimental determination of the size (and all the more, the shape) and the excess energy of critical nuclei, such attempts are made. The surface tension at the crystal – melt interface at atmospheric pressure was calculated based on experimental data on the kinetics of spontaneous crystallisation of a supercooled liquid.[319] The region where the surface tension was determined was extended beyond the triple point. Calculations were carried out with the use of a dimensionless parameter relating the surface tension, entropy of melting and specific volume of the crystal.

In the study,[320] the excess energy of the cluster formed upon crystallisation was determined using a computer experiment with the Lennard-Jones approximation, whereas other calculations were carried out using the density functional theory in the rigid-sphere approximation. In a parallel direct experiment, the nucleation and growth of crystalline nuclei was observed using a laser confocal microscope. The results of the study were compared with the results of computer simulation. Apparently, a combination of experimental investigations with theoretical methods has the most chance of making progress in studies of the nature of nucleation.

Based on generalisation of the results of experiments on nucleation, algorithms were developed for the determination of the numbers of molecules (atoms) in critical nuclei [228, 321 – 324] and evaluation of the surface tension.[323, 325 – 328]

It is known that the nucleation rate is expressed by an exponential relation analogous to Eqn (26). In the classical nucleation theory and its different modifications, the pre-exponential coefficient C is a weak function of supersaturation. In the general form, this factor can be written as

$$C = \frac{1}{\rho}\sqrt{\frac{2\sigma m}{\pi}}\left(\frac{p_0}{k_{\rm B} T}\right)^2 S^{n_0}, \qquad (30)$$

where ρ and σ are the density and surface tension of the condensed phase, respectively, m is the molecular mass, p_0 is the equilibrium vapour pressure under given conditions, n_0 is the exponent equal to 1 or 2. The size of the critical nucleus n^* can be calculated from the dependence of the nucleation rate on the supersaturation at constant temperature

$$\left(\frac{\mathrm{d}\ln J}{\mathrm{d}\ln S_i}\right)_T = \frac{\mathrm{d}\ln C}{\mathrm{d}\ln S_i} + n_i^* - \frac{\partial f(n,p)}{k_\mathrm{B}T\partial\ln S_i}, \quad (31)$$

where the subscript i is the ordering number of the component. In the study,[324] it was demonstrated that this equation is applicable to multicomponent nucleation. In the study,[320] the possibility of determining the size of a critical nucleus upon non-isothermal nucleation under conditions of crystallisation was substantiated. The assumption that there is a relationship between the nucleation rate J, supersaturation S_i and the nucleus size n^* was made, for example, in the publication.[228]

It should be noted that Eqn (31), which has gained wide acceptance, has one term less than the thermodynamically exact equation derived for one-component nucleation,[326, 327]

$$\left(\frac{\mathrm{d}\ln J}{\mathrm{d}\ln p}\right)_T = \frac{\mathrm{d}\ln C}{\mathrm{d}\ln p} + \frac{n_i^*}{k_\mathrm{B}T}(\upsilon_\mathrm{v} - \upsilon_\mathrm{l}) - \left.\frac{\partial f(n,p)}{k_\mathrm{B}T\partial\ln p}\right|_{n^*}, \quad (32)$$

where υ_v and υ_l are the molar volumes of the vapour and liquid, respectively. In the general case, υ_v and υ_l should be considered as the molar volumes of the initial and equilibrium phases, respectively. In the case of nucleation in a vapour, the vapour serves as the initial phase and the volume of the liquid away from conditions for spinodal decomposition and critical conditions can be ignored. In the case of cavitation, the volume of the initial liquid phase is ignored for the same reason, and the volume of the equilibrium phase, *viz*., the vapour, is considered.

Equation (31) for a one-component system was independently derived in the study,[323] where it was called the nucleation theorem. The difference between the chemical potentials of phases $\Delta\mu$ was used instead of the variable $\ln S_i$; however, judging from the estimate of the summands, this difference is described in the ideal gas approximation, *i.e*., $\Delta\mu \equiv k_\mathrm{B}T\log S$. This immediately excludes the term associated with the specific volume υ_v with the result that Eqn (31) becomes inapplicable in the region of critical and spinodal conditions, where these volumes are virtually identical. Oxtoby and Kashchiev [79] discussed the possibility of determining the number of molecules in a nucleus from the slopes of experimental isotherms of nucleation rates on the assumption that the first and third terms in Eqn (32) make only small corrections. In normal conditions, the situation is saved because the first and third terms have opposite signs, which provides their virtually complete compensation, and the specific volume of the vapour in the second term is three orders of magnitude larger than the specific volume of the condensate. However, in the case of transitions in condensed phases or in the vicinities of the critical or spinodal points, the difference between the specific volumes virtually vanishes and, hence, it is necessary to take into account all terms.

It should be noted that the exact solution of the problem of the determination of the critical nucleus size, *viz*., Eqn (32), exists only for a one-component system. Such a problem for multicomponent systems remains to be solved. As mentioned above, the use of the ideal gas approximation leads to a loss of significant terms. Hence, it is hardly probable that Eqn (31) can be considered as the nucleation theorem. The term 'nucleation theorem' has already gained acceptance. However, it should be remembered that this term is arbitrary. Presumably, this idea will be developed to the level of the theorem in the future.

Undoubtedly, the above-considered equations extend the possibilities of studying nucleation. However, the problem of the description of multicomponent nucleation calls for further analysis. This problem is being debated in scientific literature (see, for example, Ref. 79), which, undoubtedly, will help in gaining more precise insight into the fields of application of Eqns (31) and (32). These equations can be used for considering all first-order phase transitions. The specificity of the transition can be refined by calculating a change in the Gibbs thermodynamic potential corresponding to the formation of a critical nucleus of a new phase. The study of electrocrystallisation [125] provides an example. The usual error is to use these equations for the description of two-channel nucleation without separation of the channels. An example is the study,[193] where the estimation of the composition of critical nuclei from the slope of the nucleation rate surface in the case of two-channel nucleation was not substantiated.

Let us attempt to justify the possibility of determining the excess energy of clusters upon nucleation in a one-component system.

The necessity of taking into account such factors as the ambient pressure and, particularly, the radius of surface curvature in the deduction of an equation for the surface energy (or surface tension) requires a careful thermodynamic analysis. In the studies,[326–328] the method for the determination of the excess energy of critical nuclei in the case of homogeneous nucleation was theoretically validated. Let us consider the deduction of the corresponding equation.

The derivative of the change in the thermodynamic potential of nucleation ΔG takes the form [328]

$$\frac{\mathrm{d}\Delta G(n,T)}{\mathrm{d}T} = \left(\frac{\partial\Delta G}{\partial T}\right)_n + \left(\frac{\partial\Delta G}{\partial n}\right)_T \frac{\mathrm{d}n}{\mathrm{d}T}.$$

The condition for the formation of a critical nucleus is met when the second term in the right-hand side of the equation is equal to zero. At constant pressure,

$$\frac{\mathrm{d}\Delta\mu}{\mathrm{d}T} = -\Delta s,$$

where Δs is the difference between the entropies of the old and new phases per molecule. Without any assumptions about the shape of the cluster, the work of its formation ΔG can be written as follows

$$\Delta G(n, \Delta\mu, p, T) = n\Delta\mu + \Theta(n, \Delta\mu, p, T), \quad (33)$$

where $\Delta\mu$ is the difference between the chemical potentials in the macroscopic volume of the liquid and in the gas phase; p is the total pressure; T is the temperature; Θ is the energy of the cluster determined by the presence of the phase interface. Then the final equation for the surface (excess) energy of the critical nucleus Θ^* with consideration for Eqn (26) takes the following form:[70, 325, 326]

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(k_\mathrm{B}T\ln\frac{J}{C}\right) = n^*\Delta s - \left(\frac{\partial\Theta^*}{\partial T}\right)_n. \quad (34)$$

The solution of this equation includes the known values determined by the boundary conditions. An additional theoretical study is required to determine the multipliers in the expression for the pre-exponential coefficient C (which depends on the temperature).

Another way of estimating the surface (excess) energy of a critical nucleus was developed by Ford.[325, 329] The excess energy can be determined using critical supersaturation; however, another equation was also derived [325]

$$\left(\frac{\partial\ln J}{\partial T}\right)_S = \frac{\Delta H - k_\mathrm{B}T + \Theta^*}{k_\mathrm{B}T^2},$$

where ΔH is the heat of vapour formation per molecule. Ford did not report data sufficient for reproducing his results [in particular, it is necessary to know how the derivative of Θ in Eqn (34) was determined] and comparing these results with the data published in the literature. It should be noted that the monotonicity and continuity conditions of $J = J(S, T)$ as a function of independent variables, *viz*., the temperature T and supersaturation S, are not fulfilled in the vicinity of the phase transition temperature in the condensate

$$\left(\frac{\partial\ln J}{\partial\ln S}\right)_T\left(\frac{\partial\ln S}{\partial T}\right)_J\left(\frac{\partial T}{\partial\ln J}\right)_S = -1.$$

This can be attributed to the fact that the temperature dependence of the critical nucleus size in the nucleation isorate curve has a bend in the vicinities of the phase transition points.[330, 331] Evidently, the surface energy should also undergo certain changes. These changes can be found using the criteria for singularity of nucleation surfaces.

Let us consider the experimental method for the determination of the surface energy of a critical nucleus[332] with the constraint $p = \text{const}$. Assuming that the behaviour of a vapour is described by the equation of state of an ideal gas, *i.e.*,

$$\Delta\mu = -k_B T \ln S,$$

let us go to new independent variables in Eqn (33)

$$\Delta G(n, \ln S, T) = -n k_B T \ln S + \Theta(n, \ln S, T). \tag{35}$$

For a critical nucleus, the following equation is valid

$$\left(\frac{\partial \Delta G}{\partial n}\right)_{n=n^*,S,T} = 0\,.$$

The number of independent variables in Eqn (35) for the work of formation of a critical nucleus decreases by unity because the nucleus size is unambiguously determined at fixed temperature and supersaturation. Let us choose S and T as independent variables. Then

$$\Delta G^*(\ln S, T) = -n^*(\ln S, T) k_B T \ln S + \Theta(\ln S, T). \tag{36}$$

After differentiation of Eqn (36) with respect to T at a constant supersaturation, we obtain

$$\left(\frac{\partial \Delta G^*}{\partial T}\right)_S = -n^* k_B \ln S - k_B T \ln S \left(\frac{\partial n^*}{\partial T}\right)_S + \left(\frac{\partial \Theta^*}{\partial T}\right)_S.$$

Let us consider this equation as applied to nucleation. The exponential dependence of the rate of formation of a new phase J on the work of nucleus formation of this phase ΔG^* described by Eqn (26) is beyond question. However, the pre-exponential coefficient C was not unambiguously determined. According to the classical nucleation theory, the factor C is proportional to the square of supersaturation. However, in more recent studies (self-consistent theory),[46–48] this coefficient was reduced. While staying within the framework of the classical nucleation theory, the pre-exponential coefficient can, in the general case, be represented by Eqn (30).

By differentiating Eqn (26) with respect to T at a constant supersaturation, we have

$$\left(\frac{\partial \ln J}{\partial T}\right)_S = \left(\frac{\partial \ln C}{\partial T}\right)_S + \frac{\Delta G^*}{k_B T^2} - \frac{1}{k_B T}\left(\frac{\partial \Delta G^*}{\partial T}\right)_S. \tag{37}$$

Taking into account Eqn (30),

$$\left(\frac{\partial \ln C}{\partial T}\right)_S = \frac{1}{2}\frac{\partial \ln \sigma}{\partial T} - \frac{\partial \ln \rho}{\partial T} + 2\frac{\partial \ln p_0}{\partial T} - \frac{2}{T}. \tag{38}$$

In the analysis of the temperature dependences of the surface tension and density for a series of compounds (water, glycerol, pentanol, *etc.*), the first two terms in Eqn (38) are two orders of magnitude smaller than the third term and, hence, they can be ignored. Equation (37) can be rearranged to Eqn (39) using the Clausius–Clapeyron equation

$$\left(\frac{\partial \ln J}{\partial T}\right)_S = \frac{2(\Delta H - k_B T) + \Theta^*}{k_B T^2} + \ln S \left(\frac{\partial n^*}{\partial T}\right)_S - \frac{1}{k_B T}\left(\frac{\partial \Theta^*}{\partial T}\right)_S. \tag{39}$$

The latter equation reduces to the first-order linear differential equation

$$y' + f(x)y = g(x), \tag{40}$$

where $y = \Theta^*$, $x = T$. If the functions $f(x)$ and $g(x)$ are continuous, the integral curve passing through the point $(x,y) = (\xi,\eta)$, provided that $y(x) = \eta(\xi)$ is known, is described by the following equation

$$y = \mathrm{e}^{-F}\left(\eta + \int_\xi^x g(x)\mathrm{e}^F \mathrm{d}x\right), \qquad F(x) = \int_\xi^x f(x)\mathrm{d}x. \tag{41}$$

Therefore, to solve Eqn (40), it is necessary to know at least one point at which the required parameters of the system are determined. The dependence of $\ln p_0$ on the inverse temperature specified by the Clausius–Clapeyron equation can be considered to be linear at a vapour pressure corresponding to a constant supersaturation up to the conditions for spinodal decomposition.[333] At fixed supersaturations, an increase in the temperature of a system leads to the state at which the vapour pressure is equal to the pressure of spinodal decomposition. According to Eqn (36), the following equation should be fulfilled at the spinodal decomposition point

$$\Theta^*_{sp} = k_B T_{sp} n^* \ln S.$$

The use of this equation for solving Eqn (41) with consideration for Eqn (39) leads to the following expression for the surface energy of a critical nucleus:

$$\frac{\Theta^*}{k_B T} = n^* \ln S + 2\frac{\Delta H}{k_B T}\left(\frac{T}{T_{sp}} - 1\right) - 2\ln\frac{T}{T_{sp}} - \ln\frac{J}{J_{sp}}. \tag{42}$$

It can be seen that it is necessary to know the number of molecules in a critical nucleus n^* and the temperature T_{sp} at the spinodal decomposition point to determine the surface energy. The critical nucleus size is calculated from the slope of the curve of the isothermal nucleation rate in double logarithmic coordinates. The temperature of spinodal decomposition T_{sp} at a constant supersaturation is found from the equation of state for a one-component mixture on the condition that $(\partial P/\partial V)_T = 0$. The corresponding nucleation rate J_{sp} is determined by linearisation of experimental data followed by the linear extrapolation of the temperature dependence of the nucleation rate to the point T_{sp}.

The applicability of the method proposed for the determination of the surface energy of critical nuclei was tested using supersaturated vapours of polyhydric alcohols (propanediols and glycerol) under an atmosphere of carbon dioxide and sulfur hexafluoride.[332] These experiments were preceded by detailed investigations of the effect of the parameters of systems on the characteristics of critical nuclei.[73] For example, the phase transition was observed in critical nuclei in the investigation of nucleation of a supersaturated propane-1,3-diol vapour under an atmosphere of sulfur hexafluoride at different temperatures and pressures. The isotherms of nucleation rates at a total system pressure of 0.30 MPa are shown in Fig. 2. The isotherm measured at a nucleation temperature of 334 K corresponds to the transformation from one nucleation rate surface to another. At the temperature corresponding to a change in the phase state in critical nuclei, the isotherm of the nucleation rate becomes non-monotonic. The temperature dependence of the surface energy of nuclei should also have some characteristic features indicative of the discontinuity of the first derivative of the thermodynamic potential, which is a direct condition for the first-order phase transition.

The experimental investigation of nucleation of glycerol under an atmosphere of CO_2 in the temperature range of 310–320 K demonstrated that the parameters of critical nuclei undergo a jump caused by a first-order phase transition in the vicinity of the critical line of a binary glycerol–carbon dioxide system.[73] In the

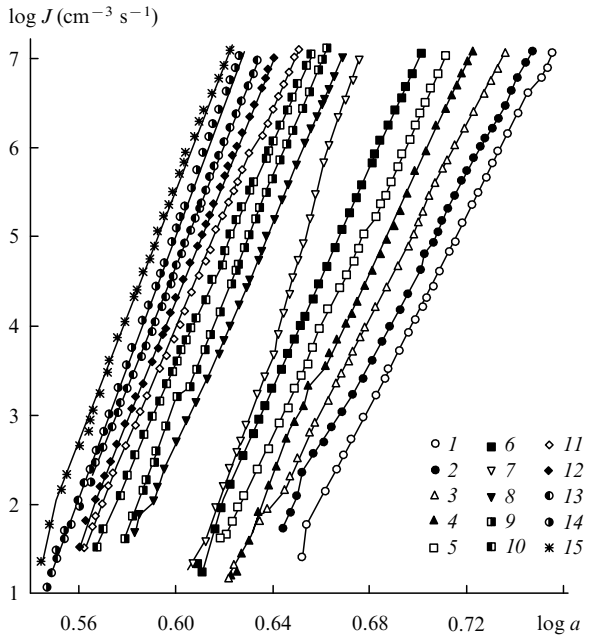


Figure 2. Nucleation rates *vs.* the activity of a propane-1,3-diol vapour under an atmosphere of sulfur hexafluoride at different nucleation temperatures.[73]
T/K: (*1*) 320.92, (*2*) 323.17, (*3*) 325.29, (*4*) 327.63, (*5*) 329.88, (*6*) 332.31, (*7*) 334.25, (*8*) 336.45, (*9*) 338.62, (*10*) 340.84, (*11*) 343.16, (*12*) 345.48, (*13*) 347.54, (*14*) 349.75, (*15*) 351.90.

melting-temperature range of glycerol (295 K), the cluster surface energy shows anomalous behaviour.

The temperature dependences of the size and surface energy of critical nuclei of propane-1,2-diol, propane-1,3-diol and glycerol under an atmosphere of carbon dioxide and sulfur hexafluoride were found.[332] The surface energy was calculated using Eqn (42) at a constant nucleation rate (10^3 cm^{-3} s^{-1}).

Figure 3 shows the experimental dependence of the excess energy on the nucleus size and presents the results of calculations of the surface energy of critical nuclei that appear (using the droplet model in a one-component approximation) in an octanol–sulfur hexafluoride system.[332] It can be seen that a decrease in the excess energy depending on the number of molecules in the nucleus is more rapid than that predicted according to the droplet model. Extrapolation to larger numbers allows one to estimate the critical nucleus size at the energies found according to the proposed algorithm which are identical with those determined using the droplet model. Beginning with this size, the droplet model of a nucleus becomes applicable. In the case under consideration, a nucleus should contain $\sim 100-140$ molecules.

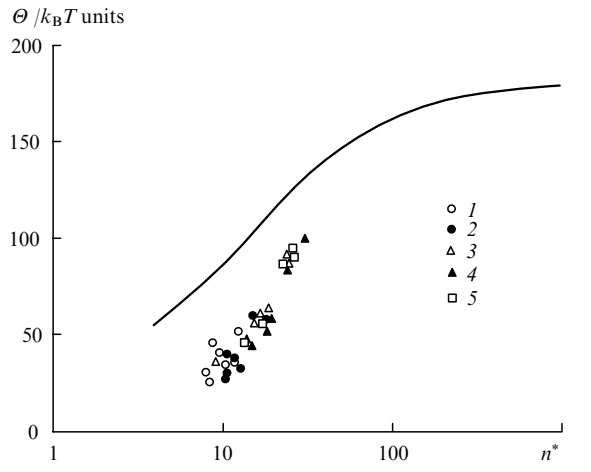


Figure 3. Surface energy *vs.* the critical nucleus size of octanol under an atmosphere of sulfur hexafluoride. Points correspond to the experimental data; the solid line indicates the data calculated using the droplet model. The total pressure in a vapour–gas system /MPa: (*1*) 0.10, (*2*) 0.15, (*3*) 0.20, (*4*) 0.25, (*5*) 0.30.

To extrapolate the dependence under consideration to the size of the nucleus consisting of one molecule (atom), it is necessary to define such a notion as the surface (excess) energy of the molecule. Langmuir proposed (using some simple compounds as examples) that the heat of evaporation of one molecule could be considered as an analogue of the surface energy.[334] This assumption is rather arbitrary in spite of the fact that the evaporation energy and surface energy depend on the same factors, *viz.*, intermolecular interactions. The inconsistency is attributed to the differences in the distribution of intermolecular bonds in the bulk of a macroscopic object and in the cluster.

The order of the dependence of the surface energy of critical nuclei on the cluster radius is higher than two.[335] This fact confirms the conclusion, which was made based on the results of computer simulation, that clusters have a fractal structure in the initial step of condensed phase growth. By extrapolating the logarithmic dependences of the energy on the nucleus size, the 'surface' energy of one molecule can be determined. A comparison of the surface energies of critical nuclei of polyhydric alcohols with the reference data[336] on the heats of evaporation of individual compounds demonstrated that, for instance, the heat of evaporation of the glycerol molecule is two times larger than its surface energy. Apparently, this difference can serve as the characteristic (in energy units) of the excess energy accumulated in the cluster. Another reason for this discrepancy is the presence of the dissolved gas in the cluster.

The method proposed for the determination of the surface energy of critical nuclei based on experimental results can, undoubtedly, be a convenient tool for the quantitative estimate of this very important physicochemical parameter. However, the incorrect interpretation can be made, for example, based on the results of measurements of the overall rates in the presence of two nucleation surfaces. A lack of reliable methods for the measurement of the nucleation rates corresponding to each individual surface hinders a comparison of theoretical and experimental data. The application of the theory developed for single-channel nucleation to the interpretation of the results of measurements of the overall rates in the presence of two (or more) nucleation surfaces leads to a deadlock situation. It becomes apparent that there is a need to elaborate on the experimental methods for separate measurements of nucleation rates for each surface.

The development of procedures for examining experimental methods is of great importance. An n-pentanol–helium mixture can be used as a testing system.[337] Evidently, the approximate dependence of the nucleation rate on the total pressure in this system has some errors, but the parameters of the approximation can be refined with more reliable data.

To test large sets of experimental data, it is advised to use differential values,[331] which formally characterise the conditions for monotonicity and continuity of the function. Therefore, one can achieve higher accuracy in the analysis of data and reveal inflections in the corresponding experimental curves.

The available analytical methods do not meet modern requirements. When performing theoretical analysis, one has to make initial assumptions about phase transitions and their kinetics rather than obtain the corresponding parameters based in more general laws. Experimental results often serve as a source of new theoretical ideas. For example, the possibility of using phase equilibrium diagrams for the development of the nucleation theory was not considered until recently. Taking into account that these diagrams (or their cross-sections) given in various

handbooks are lines of zero nucleation rates, the topology of the nucleation surface can be represented in the limit of its zero rates. By performing a few experimental measurements, one can determine the slope of the linearised nucleation rate surface thus estimating the rate with an accuracy, which is obviously higher than the accuracy of any theoretical calculations. This simple idea provided the basis for semiempirical methods for the construction of nucleation rate surfaces [14, 338] considered below.

V. Semiempirical methods for constructing nucleation rate surfaces

It is not always possible to determine nucleation rates in practically important systems using theoretical models. A method for the semiempirical construction of nucleation rate surfaces was described.[14]

It is known that the chemical potential surface of one phase as a function of temperature and pressure in a system can intersect the chemical potential surface of another phase. The intersection of these surfaces is a phase equilibrium line. If the first derivatives exhibit discontinuities along this line, the first-order phase transition occurs. In the case of the vapour–liquid equilibrium, the equilibrium line consists of numerous points of first-order phase transitions with the phase transition temperature T_p (Fig. 4). The critical point corresponding to the second-order phase transition with the temperature T_c is at the end of this line. At the critical point, the chemical potential and its first derivative for the liquid phase are identical with those for the vapour phase. An individual phase is 'insensitive' to the equilibrium line. The phase can cross this line and reach the region, where the chemical potential of this phase is higher than that of another phase. These metastable states are denoted by V_m and L_m for the vapour and liquid, respectively. The lines of spinodal decomposition serve as metastable state boundaries. Figure 4 gives the lines of spinodal decomposition having projections cs_1 and cs_2 onto the PT plane. The projection of the equilibrium line of chemical potentials forms a vapour–liquid equilibrium line T_pc. This pattern can be readily generalised to multicomponent systems.

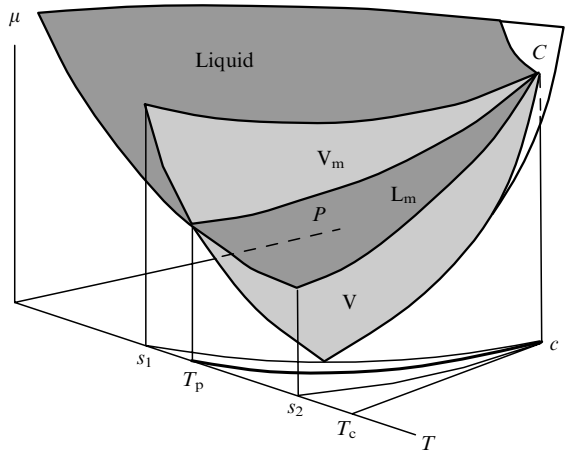


Figure 4. Chemical potential surface μ for the vapour–liquid equilibrium as a function of the pressure P and temperature T.[12, 14]

Metastable states appear upon first-order phase transitions due to the necessity of expending energy for the creation of the interface of critical nuclei. The lifetime of a metastable phase depends on the depth of penetration of one phase into the region of another co-existing stable phase, *i.e.*, on the degree of supersaturation of the initial phase. The diagrams of metastable states in processes of melting and cavitation have been discussed many times (see, for example, Refs 339–342). A diagram of a metastable state of a vapour and a nucleation rate surface were proposed and analysed in the study.[338]

1. Phase PT diagram of unstable equilibria

The basic knowledge about the topology of the nucleation rate surface can be gained by analysing a simplified PT diagram of a one-component system with a critical point.[14] Regions of metastable states, which exist for each phase, are shown in Fig. 5.

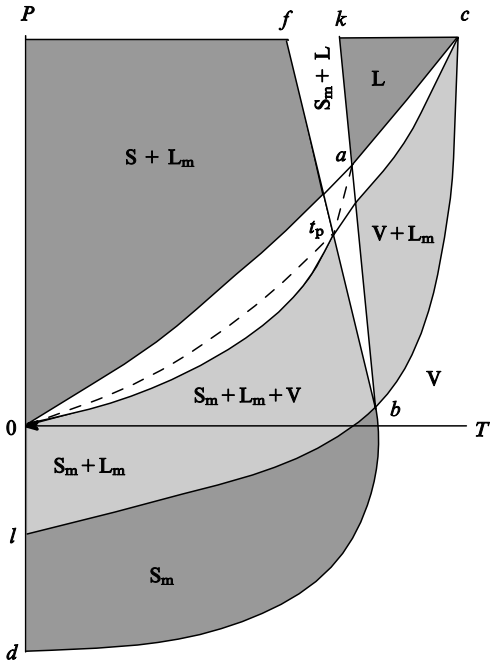


Figure 5. Simplified PT diagram of metastable states.[14] The zero temperature limit is indicated by an arrow; the liquid, solid and gas states are denoted by L, S and V, respectively; the subscript m signifies the metastable state.

It is known that the phase equilibrium lines never end in a triple point. For this reason, the S–L equilibrium line intersects with the line of spinodal decomposition (*kbd*) of a superheated (stretched) crystal and with the line of spinodal decomposition (*cbl*) of a stretched (supercooled) liquid. The point *b* is the point of critical instability [14] at which the S–L equilibrium line intersects with the spinodal for cavitation *cbl*. At the point *b*, the line of labile states of a liquid *cbl* intersects with both the line of labile states of a crystal *kbd* and the line of liquid–crystal unstable equilibrium ft_pb.

The viscosity of a supercooled liquid increases as the temperature decreases and this liquid can exist at as low temperatures as is wished,[14] the liquid being able to occur in the liquid or glassy state. The glassy state is not an independent phase because it has no equilibrium lines with other phases. In the degree of order, the glassy state is closer to the liquid in which the long-range order is absent. It seems reasonable to consider glassy states as metastable states of a liquid. However, glasses are sometimes (see, for example, Ref. 341) treated as individual phases and lines of spinodal decomposition of a liquid are passed to the region of existence of crystalline states. In this connection, it should be noted that the transformation of a liquid into the glassy state does not mean the glass–supercooled liquid equilibrium and it cannot be characterised by the equilibrium transition temperature. Hence, a glass cannot be considered as an individual phase. Nevertheless, the region of existence of a glass was approximated [341] by a line and it was assigned to conditions for spinodal decomposition of the liquid, the end of this line being called the critical point. In my opinion, the concept of the absence of a

temperature limit for spinodal decomposition of a liquid (see the line *cbl* in Fig. 5) up to the limiting temperature, *viz*., absolute zero, is preferable.

The S – V equilibrium line passes from the point *a* to the point 0. It is essential that this line begins at the point *a*, where the spinodal line for crystals *kb* intersects with the spinodal line for a vapour *ca*0. This indicates that the vapour – crystal equilibrium line extends upward to higher temperatures. The point *a* corresponds to the highest temperatures and pressure at which the solid – liquid – vapour metastable state can occur over a short period of time. The crystalline state is spontaneously transformed into the liquid state. It was stated that [14] the point *a* is not the crystal – vapour critical point, like the point *c*, because both phases at the point *a* occur at the same temperature and pressure, although they differ in density, structure and other properties and cannot be transformed into each other without activation. It should be noted that the difference in the density can be insignificant because the vapour supersaturation in an experiment can reach several hundred units. In the case of spinodal decomposition, it is reasonable to expect the vapour supersaturation to be as great as several thousand units, which is similar to the ratio between the densities of the condensed and vapour phases, *i.e*., the difference in the densities of the crystal and vapour can appear to be vanishingly small. The possibility of a continuous change in the order parameter when going round the point *a* remains an open question.

In experiments on the generation of aerosols, it is possible to produce crystalline particles at moderate supersaturations. At high supersaturations, particles with a non-crystalline structure, *i.e*., a supercooled liquid or an amorphous solid, are predominantly formed. Under the conditions for spinodal decomposition, the nucleation rate of a metastable liquid should be higher than the rate of crystal formation due to kinetic limitations. The above-mentioned limitations result from the fact that the formation of a nucleus with a crystalline structure requires that molecules (atoms) be able to migrate to sites of the crystal lattice formed. Evidently, in the case of a large flux of molecules that appears under conditions for spinodal decomposition, there can be not enough time for jumps of the molecules, which occupy crystal lattice sites and form a crystalline nucleus. Correspondingly, the probability (and the rate) of formation of droplets (or glasses) should be higher than the probability (and the rate) of formation of crystalline nuclei.

2. Examples of construction of nucleation rate surfaces

A nucleation rate surface can be constructed [14] above a simplified *PT* diagram with a triple point (see Fig. 5). Nucleation rates are considered to be steady. Transient phenomena upon the establishment of a stationary nucleation rate or effects of vapour depletion are ignored. Nucleation rate surfaces are constructed using the following assumptions.

1. An individual phase can exist behind the line of interphase equilibrium in a metastable state. The equilibrium line can be extended to the region of an equilibrium state of another phase as a line of unstable equilibrium.

2. Equilibrium lines in the phase diagram are lines of zero nucleation rate.

3. Under conditions for spinodal decomposition, the highest nucleation rate is achieved at a constant pressure or constant temperature.

4. Under conditions for spinodal decomposition, the nucleation rate giving rise to less stable states is higher than the rate of nucleus formation of a more ordered stable phase.

5. The nucleation rate at the critical point is equal to zero.

The first three assumptions correspond to known empirical results of studies of first-order phase transitions. The fourth assumption seems to be reasonable taking into account data on the kinetics of phase formation. Thus, under conditions for spinodal decomposition, molecules do not have time to be incorporated into crystal lattice sites and, hence, form amorphous particles with high probability. The fifth assumption is a consequence of the fact that the critical point corresponds to the second-order phase transition, where separation into phases is absent and, consequently, nucleation at the critical point cannot occur. It was noted [14] that the fifth assumption can follow from the second one.

Let us consider a fragment of the phase equilibrium diagram in the vicinity of the triple point *t* (Fig. 6). The vapour – crystal (*kt*) and vapour – liquid (*tm*) equilibrium lines are extended to the region of existence of the third equilibrium phases. The nucleation rate surface of liquid-droplet nuclei is pale-grey. The dark-grey surface corresponds to the nucleation rate of crystalline nuclei. The surfaces intersect in the line *et*. The intersection of the surfaces forms an ascending branch *ke* (and the dashed line is its extension to conditions for spinodal decomposition) corresponding to the nucleation rate of crystals. The nucleation rate of liquid-droplet nuclei is represented by the line *eh* (and its extension to zero rates). If a saturated vapour at the point *m* begins to be cooled at a constant pressure, a liquid-droplet aerosol can be prepared. At the temperature corresponding to the point *l* and below, the formation of crystalline nuclei starts. The nucleation rates of both phases increase as the temperature is decreased, but the nucleation rate of crystals increases faster. At the point *e*, the rates of formation of liquid-droplet and crystalline nuclei are equalised. It is easy to understand that if the phase state of nuclei is retained in the course of subsequent condensation growth, the sizes of aerosol particles are different due to the known nonequality of the accommodation coefficients of molecules on surfaces with different phase states. This conclusion was experimentally confirmed in the study.[15]

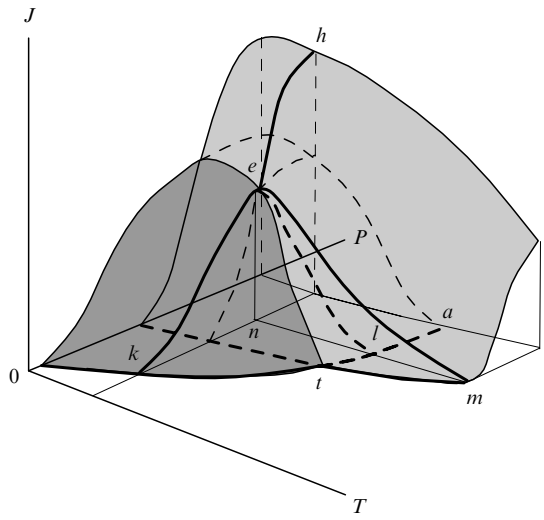


Figure 6. Nucleation rate surfaces for a one-component vapour.[15]

Surfaces of nucleation rates in superheated (or stretched) crystals, nucleation in a supercooled liquid and cavitation were constructed.[14] It should be noted that the assumption of a non-zero nucleation rate in the zero temperature limit [14] is, most likely, erroneous. Actually, the pressure vapour at absolute zero is also equal to zero and there is no question about nucleation in a vapour. Hence it follows that the nucleation rate in a vapour above the line of spinodal decomposition first increases as the temperature decreases from the critical one, then reaches a maximum and falls to zero in the zero temperature limit. Under conditions for spinodal decomposition, the nucleation rate is equal to the pre-exponential coefficient in the equation for the nucleation rate. In the case of a vapour, this coefficient increases from zero to a maximum and then again decreases to zero as the temperature decreases from the critical value to absolute zero. By contrast, in the case of nucleation in condensed phases, the pre-exponential coefficient, apparently, only increases with decreasing

temperature. However, this assumption needs further verification. Such a verification can be performed in the case of simultaneous homogeneous and heterogeneous nucleation, as was demonstrated using ion-induced nucleation as an example.[333]

Nucleation rate surfaces of binary vapours can be represented in the four-dimensional surface JTa_1a_2, where J is the nucleation rate, T is the temperature and a_1 and a_2 are the activities of the vapours of the components. Let us consider the simplified PX diagram of a binary solution at the fixed temperature T, total pressure in the system P and composition x. In this case, the phase diagram is cigar-like in shape (lines *mfn* and *nrgm* in Fig. 7).

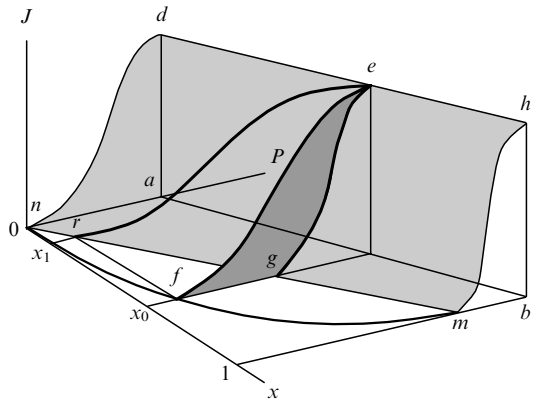


Figure 7. Nucleation rate surface (J) for ideal solutions (P is the total pressure, x is the composition of a binary solution).[14]

The nucleation rates of individual components are represented by the curves *nd* and *mh*. At the point of vapour equilibrium (n, m), the nucleation rates of the vapour are equal to zero. The nucleation rates of the components have maximum values above the spinodal decomposition points a and b. These maximum rates in a simplified form can be related by the line *deh* corresponding to maxima of the binary nucleation rate. The nucleation of a binary vapour with composition x_0 starts at the point f.

A condensed phase has the composition x_1 at the point r. Each point on the line *nfm* corresponds to a point on the line *nrgm*. The latter line, which is an equilibrium line between a liquid and two-phase states, is the trajectory of points of the zero nucleation rate and forms a surface boundary of the nucleation rates. The nucleation rate surface is contoured by *hednrgm*. Above the spinodal, the composition of a vapour is identical with those of condensed phases due to the absence of the barrier to transformation into the condensed phase. The line *re* describes the nucleation rate of a vapour (with the known composition of critical nuclei) in the course of an increase in the pressure from the point r to the point e at the constant nucleation temperature T and the initial composition of the vapour x_1. The curve *fe* is a projection of the curve *re* onto the plane corresponding to the composition x_0. No information on the composition of critical nuclei can be extracted from the curve *fe*.

In the case of an unknown composition of critical nuclei, a nucleation rate surface can be constructed if all experimental nucleation rates (analogous to the curve *re*) correspond to the initial composition of the vapour in the phase diagram (for example, the line *fe* for the composition x_0). In this case, the points of the zero rate of vapour nucleation are located on the lower line of the cigar-like diagram. The rate surface under consideration is presented in the JxP coordinates. Apparently, the mode of representation of binary nucleation rates of a vapour depends on whether or not the composition of critical nuclei is known. If the composition of critical nuclei is unknown, a nucleation rate surface for an ideal binary solution is contoured by *hednfm* (see Fig. 7). In experiments, the composition of nuclei is usually unknown and the measured nucleation rate in a binary system is assigned to its initial composition. Thereafter, the composition of nuclei of the condensate can be determined from the slopes of nucleation rate isotherms.[324, 343]

The nucleation in a binary system with partial mutual solubility of the components was discussed in the study.[344] Earlier, it was demonstrated [69] that in this case, two-channel nucleation takes place. In the publication,[344] a new assumption was made according to which each channel is characterised by its own nucleation rate surface for ideal solutions. The authors of the cited study used the rule of summation of nucleation rates for both channels in the linear approximation analogous to the lever rule for solutions. The validity of assumming linear summation of nucleation rates calls for experimental verification. However, an essential advantage of this approach is that it substantiates the possibility of the presence of local maxima in a nucleation rate isotherm, which does not follow from the classical theory. This result can be illustrated by the experimental dependence of the nucleation rates on the activity of an alcohol vapour in n-pentanol–argon (Fig. 8) and n-pentanol–sulfur hexafluoride systems.[344]

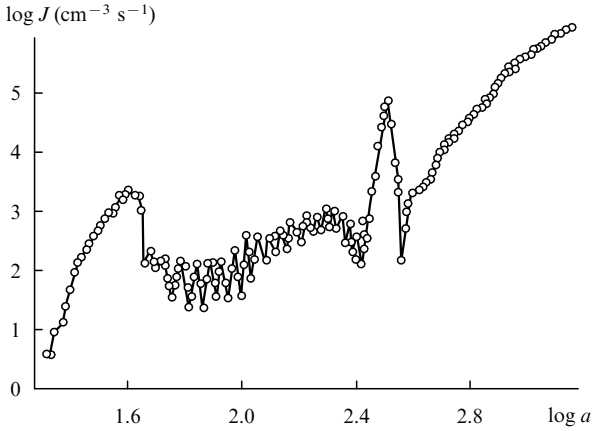


Figure 8. Nucleation rate in an n-pentanol–argon system *vs.* the activity of an n-pentanol vapour.[338]

The pressure in the system influences the course of nucleation. However, this fact has not been noted in early experiments performed by Wilson and other researchers. Examples of the pronounced effect of the pressure in the course of boiling water, ethanol, acetone and their solutions were given in the studies.[345, 346] Noteworthy is the idea of bond percolation used by the authors of these studies. However, this idea was not confirmed experimentally and, hence, the assumption about the continuity threshold of unbroken intermolecular bonds in a liquid in the metastable region was made. The authors of the study [347] and their colleagues [233, 348–350] still attributed the pronounced effect of the total pressure on the nucleation rate in vapours of a number of chemical compounds to other factors by referring to corrections for non-ideality of a vapour, compressibility of a critical cluster and the Poynting effect. Undoubtedly, all these factors should be taken into account, but there is one more important factor as well. Thus, direct experiments demonstrated (see, for example, Ref. 73) that a gas and a vapour form a binary system in which phase transitions take place in critical nuclei due to the presence of a carrier gas.

VI. Nucleation in binary systems

The nucleation in a binary solution in which a chemical reaction proceeds (see, for example, Ref. 351) has distinguishing features. In this case, the phase diagram consists of the phase diagrams of two individual binary systems and a newly formed compound is considered as a limiting compound in each of these diagrams.

None of the available nucleation theories can predict nucleation rate surfaces resulting from interactions. Many problems remain to be solved among which is the problem of the rates of non-stoichiometric chemical reactions, which are determined by extension of the nucleation rate surface to the non-stoichiometric region. It is not inconceivable that in further studies, approaches of chemical kinetics will be combined with nucleation kinetics.

1. Phenomenological consideration of intermolecular interactions

A semiempirical approach to the construction of nucleation surfaces [12–14] is based on the relationship between nucleation rates and phase diagrams. This relationship is evident in the case of stationary dynamic systems, which occur close to the equilibrium. However, a more careful examination should be carried out for systems existing far from equilibrium. For example, large flows of matter occur upon the formation of a cloud layer in the atmosphere or upon atmospheric precipitation. It is known that a strong dynamic response is characteristic of flow systems.[182] This dynamic response is manifested in the transformation of the system to another dynamic mode (hydrodynamic or thermodynamic crisis, autowave mode). The effect of this type, which was studied first, is called the Benard (convective) instability. This effect is manifested in the appearance and rearrangement of convective cells in a liquid layer heated from below. Under conditions far from equilibrium, instabilities are responsible for the long-range order and, as a result, the system acts as an organic whole.[182] Besides, in the case of a non-equilibrium first-order phase transition, a compound goes through a metastable state (supersaturated vapour, superheated or supercooled liquid). As a result, the metastable phase by itself becomes a flow system, which can produce a stationary flow of nuclei of a new phase at a given temperature, pressure and composition. The study [352] examined the evolution of dynamic phase diagrams of a binary system as the flow J (nucleation rate) increases on the assumption that the latter plays a dominant role compared to other types of flows (for example, a hydrodynamic flow). The deviations of the nucleating system from equilibrium are characterised by the flow of nuclei of a new phase. Hence, nucleation isorates (J = const) can be treated in the corresponding coordinates as dynamic phase diagrams.

Experimental data on nucleation rates were compared with empirical phase diagrams of binary systems using a water–propan-1-ol system with an azeotropic point as an example.[353] Figure 9 shows static ($J = 0$ at $T = 298$ K) and dynamic ($J = 1$ cm^{-3} s^{-1} at $T = 298$ K and $J = 10^7$ cm^{-3} s^{-1} at $T = 260$ K) phase diagrams of a water–propan-1-ol system in the coordinates of the mole fraction of alcohol *vs.* the reduced pressure (the total pressure related to the pressure of the saturated propan-1-ol vapour in an ideal solution $P_{298} = 2700$ Pa at $T = 298$ K and $P_{260} = 125$ Pa at $T = 260$ K). The line *5* for a liquid in the dynamic phase diagram is constructed based on the data on the molar composition of critical nuclei (see references cited in the study [353]).

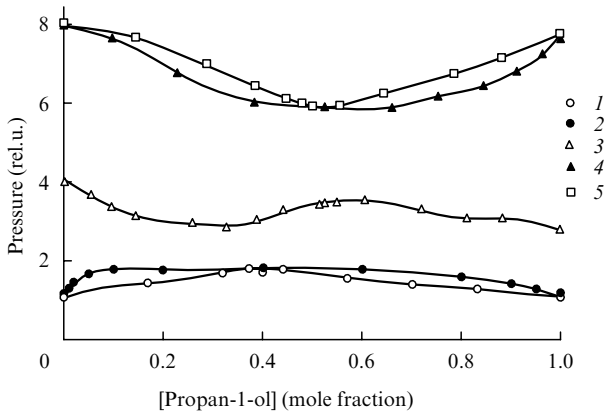


Figure 9. Phase diagrams of a water–propan-1-ol system at nucleation rates $J = 0$ [(*1*) vapour, (*2*) liquid]; $J = 1$ [(*3*) vapour] and $J = 10^7$ cm^{-3} s^{-1} [(*4*) vapour, (*5*) liquid].[353]

In the case of large deviations from an ideal solution, dynamic phase diagrams are transformed as the nucleation rate increases. As can be seen from Fig. 9, this transformation is accompanied by a shift of the azeotropic point of a water–propan-1-ol system along the axis of composition. An analogous change from a convex diagram to a concave one was observed for a water–ethanol system.[335] In Fig. 10, the spinodal is schematically represented by the line *be*. It was taken into account that the convexity of the diagrams changes for concavity as the nucleation rate increases and it was also considered that the lines for a vapour and a liquid should coincide under conditions of spinodal decomposition. The dynamic diagrams corresponding to $\log J = 0$, 4, 7 and 10 (cm^{-3} s^{-1}) are schematically represented by the corresponding contours (the nucleation rate surface shown in grey colour passes through the vapour lines). The spinodal *be* has a concave shape, *i.e.*, the vapour pressure of the mixture at the end of the line of azeotropic solutions is lower than the vapour pressures of the pure components. By contrast, the equilibrium diagram (*ad*) is convex (the pressure reaches the maximum values at the azeotropic point in the phase equilibrium diagram). Deviation of dynamic diagrams from the equilibrium diagram should primarily be observed upon enrichment of the mixture with water, which takes place in the experiment (see Fig. 9). A change in the shape of the spinodal curve can lead to another transformation of dynamic diagrams.

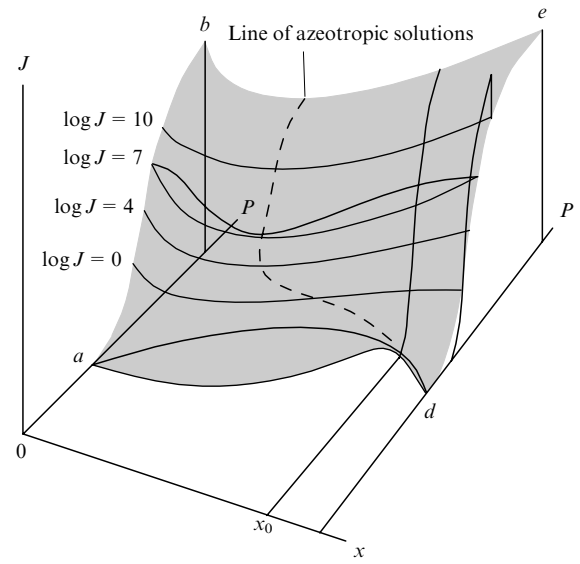


Figure 10. Schematic representation of the nucleation rate surface in a binary system constructed on the basis of experimental data for a water–ethanol system.

As a binary system moves away from the equilibrium, small contributions of binary interactions between the molecules can, on the contrary, appear to be prevailing. In such nonlinear systems, components lose their individuality (typical of an equilibrium state) and the mixture behaves as a whole, *i.e.*, in the case of substantial deviations from equilibrium, intermolecular interactions are collective in character. A strengthening of intermolecular interactions, as applied to static phase diagrams of binary systems, is manifested in an increase in the negative deviation of the system from an ideal solution (the total vapour pressure is lower than the additive value). The evolution of the phase diagrams presented in Figs 9 and 10 is also accompanied by a decrease in the total

pressure as the system moves away from the equilibrium (as J increases). In other words, the changes in dynamic phase diagrams are analogous to the changes in usual phase diagrams as intermolecular interactions are strengthened.

In calculations of phase diagrams of a binary system within the framework of a single-liquid model (homogeneous liquid), the correction parameter k, which takes into account binary interactions and determines mutual attractions between molecules of different components, was entered into the equation of state (for example, into the van der Waals equation).[353] Therefore, the nucleation isorates of a vapour can be interpreted as phase diagrams corresponding to the parameters of the binary interactions k. For a metastable state, the boundary of a stable homogeneity of a phase is determined by the condition of vanishing vapour tension $(\partial P/\partial V)$ in an isotherm of state, *i.e.*, by a spinodal.

A choice of an algorithm for calculating a spinodal is governed by the condition for stability of a binary solution. As the system moves deep inside the metastable region, it retains the fixed entropy S, volume V and amount of matter at a constant internal energy $\mathrm{d}U = 0$. Instability of relatively continuous changes in the parameters of state is initially manifested in the vanishing of the diffusion coefficient of stability

$$\left(\frac{\partial \Delta\mu}{\partial x}\right)_{P,T} = 0, \tag{43}$$

where x is the composition of the binary system. Then the necessary and sufficient conditions for stability of a binary solution are expressed by the inequality

$$\left(\frac{\partial \Delta\mu}{\partial x}\right)_{P,T} > 0 \tag{44}$$

or a system of inequalities

$$-\left(\frac{\partial P}{\partial V}\right)_{T,x} > 0, \tag{45}$$

$$\left(\frac{\partial T}{\partial S}\right)_{V,x} > 0. \tag{46}$$

In the van der Waals single-liquid model, a binary solution at fixed x is considered as an efficient one-component fluid obeying the equation of state in the above-mentioned variables

$$\pi = \frac{8\tau}{\varphi - b(x)/b_{11}} - \frac{27a(x)/a_{11}}{\varphi^2}, \tag{47}$$

where $\pi = P/P_{c1}$, $\tau = T/T_{c1}$ (P_{c1} and T_{c1} are the pressure and temperature, respectively, at the critical point of the low-temperature component 1); $\varphi = V/b_{11}$; the coefficients $a(x)$ and $b(x)$ depend on the concentration of the second component and are calculated by the equations

$$a(x) = (1-x)^2 a_{11} + 2(1-x)x a_{12} + x^2 a_{22}, \tag{48}$$

$$b(x) = (1-x)b_{11} + x b_{22}, \tag{49}$$

the constants a_{11} and a_{22} characterise the intensity of intermolecular attractions in the components 1 and 2, respectively; the constant a_{12} characterises the intensity of attractions between the molecules of different components; the parameters b_{11} and b_{22} are determined by the sizes of the molecules of the solution. According to the combination rule, the constant a_{12} can be written through the binary interaction parameter k^*

$$a_{12} = k^*(a_{11}a_{22})^{1/2}. \tag{50}$$

Taking into account Eqn (47), Eqn (46) is fulfilled. The condition (45) goes to zero at the spinodal line. Considering Eqn (47), we obtain the equation for the diffusion spinodal

$$\varphi^3 - \left[\varphi - \frac{b(x)}{b_{11}}\right]^2 \frac{a(x)}{a_{11}} \frac{27}{4\tau} = 0. \tag{51}$$

The constants in the equation of state can be determined using the critical parameters

$$a_{11} = \frac{27}{64}\frac{(RT_{c1})^2}{P_{c1}}; \qquad a_{22} = \frac{27}{64}\frac{(RT_{c2})^2}{P_{c2}};$$

$$b_{11} = \frac{RT_{c1}}{8P_{c1}}; \qquad b_{22} = \frac{RT_{c2}}{8P_{c2}}.$$

Figure 11 shows the calculated spinodal curves for a water – propan-1-ol system at 260 K and different values of the parameter k^* in the coordinates of the mole fraction of propan-1-ol *vs.* the reduced pressure (the total pressure related to the critical pressure of the alcohol). It can be seen [352, 353] that the asymmetry associated with the difference in the individual properties of the components decreases as the binary interaction is strengthened. At high k^*, the spinodal curve becomes symmetric with respect to an equimolar composition. This fact can be attributed to a loss of individuality of the components of the system as the latter moves away from equilibrium. Apparently, this situation is something common to the phenomenon mentioned in the review: [354] '...a loss of individuality of a substance appears as the system approaches the critical conditions. The character of the properties is determined by the degree of approach to the critical conditions rather than by the individuality of substances and even rather than by the type of phase equilibrium'. As the system approaches the conditions for spinodal decomposition, the free energy of formation of critical nuclei decreases. The vanishing of this energy is the condition for spinodal decomposition. This superficially resembles a continuum of liquid – vapour phase transitions ending in the critical point. It should be noted that under normal conditions of vapour nucleation, vapour supersaturation is as great as a thousand units. This indicates that the density of a supersaturated vapour approaches the density of a condensate thus providing conditions for a phase change with a low enthalpy of transition. Here one can speak about a first-order phase transition similar to a second-order phase transition. Hence, there are certain grounds to assume that a substance can lose individuality as it approaches the spinodal curve.

Dynamic phase diagrams become similar to a spinodal curve as J increases. It is assumed that the parameter k^* in the equation of state for a metastable phase can be substantially larger than that allowable in the equation of state for an equilibrium phase. In other words, the equations of states for equilibrium and metastable phases can differ in the parameters determining intermolecular interactions in a binary system. For example, according to the above-considered calculations [see Eqns (43) – (51)], the pres-

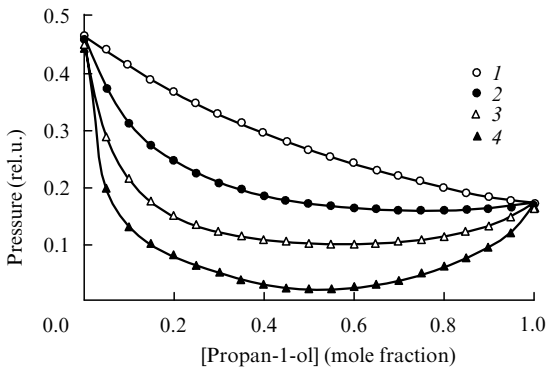


Figure 11. Spinodals of a water – propan-1-ol system at 260 K for various parameters of binary interactions.
k^*: (*1*) 1, (*2*) 2, (*3*) 4, (*4*) 8.

sure in the spinodal corresponds to the binary interaction parameter $k^* = 5.65$.

Based on a spinodal curve for which the binary interaction parameter k^* is close to unity, the transformation of phase diagrams shown in Fig. 9 becomes impossible. Therefore, the behaviour of a binary system as it moves away from equilibrium is determined by the spinodal. It was assumed [353] that the deviation of the system from linearity characterises a change in intermolecular interactions as the system moves away from equilibrium. Knowing the parameter k^* in a metastable state, one can determine the limiting values J thus finding the stability boundary of the state under consideration. As the system moves further away from equilibrium, it should go to another mode, which is, as a rule, accompanied by an organisation of a new structure.[182]

2. Bimodal distribution of aerosols

The well-known effect of the bimodal distribution of an atmospheric aerosol remains to be adequately explained. Attempts to attribute this effect to fluctuations of the parameters of atmosphere with time and space seem to be artificial, because the time interval of averaging is generally equal to a few minutes. As a result, the conditions of growth of all heterogeneous nuclei are statistically equalised giving rise to a broad unimodal distribution. Actually, the use of time-averaged values cannot lead to a bimodal distribution because the nucleation time is several orders of magnitude smaller than a hundredth of a second, *i.e.*, the nucleation has time to proceed and nuclei have time to grow within one fluctuation cycle.

The bimodal distribution of aerosols can be reasonably explained assuming the existence of two independent surfaces (channels) of nucleation for the separate formation of crystals and liquid nuclei. Evidently, the accommodation coefficients of molecules on nuclei occurring in different phase states differ from each other. The difference in the growth rates of liquid and crystalline aerosol particles can lead to a bimodal distribution of particles in the atmosphere, where nucleation of a water vapour generally occurs in the vicinity of the triple point. A direct experiment on nucleation of glycerol in the vicinity of the triple point [15] demonstrated that the presence of condensation nuclei is not required for the occurrence of the bimodal distribution of particles. It should be noted that in a real atmosphere, condensation nuclei undoubtedly make an additional contribution to the size distribution of particles.

The above-mentioned experiment [15] is of fundamental importance for testing the semiempirical procedure for the construction of nucleation rate surfaces above phase equilibrium diagrams. The problem of the order of phase formation upon vapour nucleation below the triple point was easily solved. Crystalline and liquid-droplet nuclei appear simultaneously in ratios determined by the arrangement of the rate surfaces of formation of each phase relative to one another. Evidently, supercooled droplets can adopt a crystal or amorphous structure with certain probability. Apparently, the initial phase states of nuclei were retained in the study [15] due to the use of a high-viscosity sample. Undoubtedly, such experiments give a clue to the separation of nucleation channels, which is of fundamental importance for the estimation of the agreement between theory and experiment. Actually, researchers had no possibilities to test the validity of a particular theory because theoretical results obtained in the one-channel approximation were generally compared with the characteristics corresponding in reality to two-channel nucleation.

3. Ion-induced nucleation

In the present review, the problem of heterogeneous nucleation is not discussed in detail. The detailed description of this process under conditions of a slowly changing supersaturation was given in the study.[120]

Under conditions of ion-induced nucleation, the following rules are fulfilled.[352]

1. The energy of ion-induced vapour nucleation is always lower than the energy of homogeneous nucleation. Compared to homogeneous nucleation, lines (or in the case of a multicomponent system, a subspace) of ion-induced nucleation rates correspond to lower supersaturations (activities) of a vapour or, in the case of isobaric nucleation, to higher nucleation temperatures.

Let us note the well-known fact [326, 327] that the lines of ion-induced nucleation rates coincide with the line of homogeneous nucleation rate when all ions pass into a condensed phase. The properties of a nucleating substance (for example, polarisability) can influence the relative intensity of heterogeneous nucleation of various vapours. This parameter depends on the differences in the vapour activity and temperature in the case of isothermal and isobaric nucleation, respectively.[333]

2. At a constant vapour supersaturation, the rate of heterogeneous isothermal (or isobaric) vapour nucleation is proportional to the concentration of ions. If the concentration of ions is nearly equal to or higher than the concentration of nucleating molecules, the heterogeneous nucleation rate reaches its upper limit. This limit determines the envelope curve (or a multidimensional surface), which corresponds to the limiting rate of ion-induced nucleation as a function of vapour activity. The lines of the highest and zero rates of heterogeneous nucleation are located on the surface of homogeneous nucleation rates.

3. Surfaces of homogeneous and heterogeneous vapour nucleation intersect at high temperatures in the line of spinodal decomposition.

Examples of the qualitative construction of nucleation rate surfaces describing phase transformations of various initial phases were given in the study.[14]

4. Experimental determination of conditions for spinodal decomposition

The experimental method for the determination of conditions for spinodal decomposition was developed in the study.[333] The lines ct_p and mt_p in Fig. 12 correspond to vapour – liquid and vapour – solid equilibria. For simplicity, the spinodal line sc is considered to be common to the liquid and solid states. The isorates of homogeneous and heterogeneous nucleation of a liquid can be measured at moderate supersaturations. The extrapolation of both lines gives an intersection w belonging to the spinodal line for a liquid as follows from the third rule for ion-induced nucleation. An analogous extrapolation can be carried out also in the case of the crystalline state (point r in Fig. 12). The results of measurements of the supersaturation as a function of the nucleation temperature of n-butanol [352] are presented in Fig. 13. For homogeneous nucleation, the linear regression of the logarithm of the vapour pressure on the inverse temperature is described by the equation

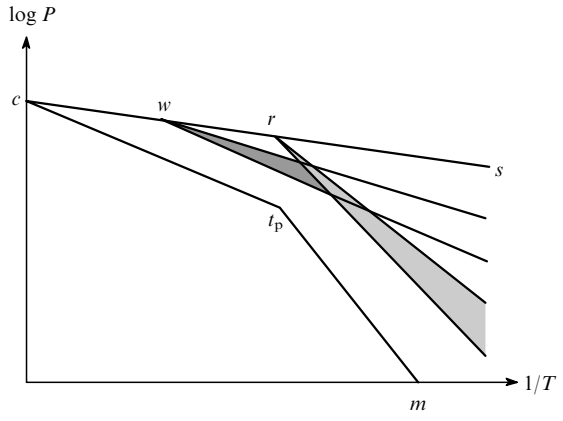


Figure 12. Schematic representation of vapour – liquid and vapour – solid equilibria for log$P$ *vs.* $1/T$.[333]

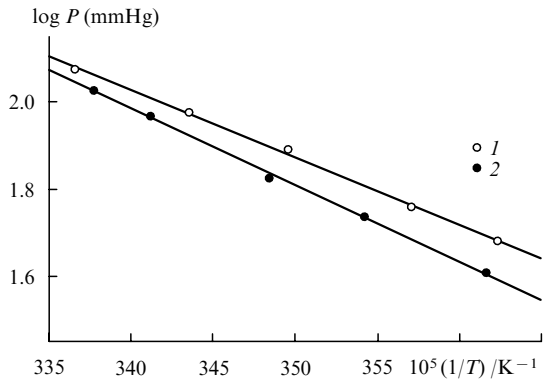


Figure 13. Experimental data on critical supersaturations of n-butanol for log$P$ *vs.* $1/T$.[333]
(*1*) Homogeneous nucleation, (*2*) ion-induced nucleation.

$$\log P_{\text{hom}} = 7.4076 - \frac{1582}{T}\,.$$

For ion-induced nucleation, this regression is described by the equation

$$\log P_{\text{het}} = 8.0728 - \frac{1791}{T}\,.$$

The extrapolation allows one to determine the pressure (230 mmHg) and temperature (310 K) of spinodal decomposition. This pressure corresponds to a reasonable estimate of the vapour supersaturation in the spinodal ($\log S = 2.6$). In other words, studies of heterogeneous and homogeneous nucleation enable one to estimate experimentally the conditions for spinodal decomposition, which makes it possible to find the temperature dependence of the pre-exponential coefficient in the equation for the nucleation rate in the classical theory. Evidently, in the case of spinodal, the exponential multiplier becomes equal to unity and, hence, the only remaining multiplier is pre-exponential. Generally, this multiplier is considered to be constant. Taking into account that the nucleation rate at the critical point of a liquid–vapour system is equal to zero, it is easily understood that the pre-exponential coefficient increases from zero at the critical point to a maximum value and then again decreases and goes to zero at absolute zero of temperature.

The studies by Fuks ‡ and Sutugin [355] have made an impact on the development of concepts of aerosol mechanics and the application of these concepts to the description of cluster growth.

VII. Use of nucleation in scientific studies and some technological processes

Nucleation is used in one way or another in many scientific studies and in a number of technological processes. This phenomenon is so widespread that researchers are often not aware that they deal with nucleation.

Aerosols are used for visualisation of particle motions, which occur upon nuclear decay, in a Wilson chamber. The latter is extensively employed for studying nucleation of supersaturated vapours. More than a half-century ago, Sinclair and La Mer designed a generator of monodispersed particles, which was described, for example, in Ref. 356. In different laboratories throughout the world, researchers extensively used a particle condensation counter, which is based on the Sinclair–La Mer scheme. A lack of theoretical support for the principles of its action stimulated experimental and theoretical investigations. In the study,[357] a theoretical model of the counter was proposed and the results of its tests at different pressures, nucleation temperatures and amounts of the gas to be analysed were reported. A condensation counter was used as a detector for capillary chromatography.[358] Initially, the sensitivity has been 100 ng ml^{-1}, but then this limit was improved by two orders of magnitude.[347, 359] Being an instrument for research, a condensation counter by itself was also the object of an individual study.[360] The construction of a counter of aerosol particles is gradually improved. Thus, the schemes have already been developed,[361, 362] which enable one to detect particles with sizes of 3 nm with an efficiency of almost 100%.

Nanoparticles are used for creating quantum points, luminescent materials, gas sensors, resistors, conducting and capacitive films, high-temperature superconductors, thermoelectric, optical, magnetic, laser materials, *etc*. Methods for the synthesis of such particles were surveyed in the study.[363]

The generation of nanoparticles in plasma holds promise. Powders formed by evaporation and condensation of various materials in a plasma were studied experimentally and their numerical simulation was carried out.[364] The theoretical consideration of the processes occurring in an inductively coupled plasma made it possible to give recommendations on the construction of apparatus for the production of nanoparticles.[365] In the investigation on simulation of nucleation and growth of iron particles in a plasma reactor, a parametric equation was derived for the description of a spectrum of sizes and number of the particles formed.[366] These parameters depend substantially on the rate of cooling and the initial concentration of monomers. A mathematical model was proposed for the formation of metal powders and ceramics of high purity.[367, 368] Experimental methods for the preparation and simple models of generation of metal clusters were surveyed in the review.[369] An experimental apparatus for the generation of ultradispersed titanium oxide, which is used as a pigment, catalyst, for the construction of electronic devices, *etc*., was described in the study.[370] It was noted that the nanoparticles thus formed have a high mechanical strength and low sintering temperatures.

High-temperature chemical reactors, in which materials are oxidised under an oxygen atmosphere and conditions are provided for the generation of ultradispersed particles, are characterised by high performance and relative simplicity. The scheme was elaborated for the production of ultradispersed powders (with particle sizes of < 100 nm) of titanium oxide.[371] Experimental investigations of metal evaporation under the action of electrical pulses followed by the formation of ultradispersed metallic powders in a medium of various gases at different temperatures and pressures were carried out in Russia as early as the 1960s. The results of these studies were analysed in the review.[372] It was noted that the nucleation processes depend on the nature of the gas and the total pressure.

Advances in the new line of research, *viz*., nanochemistry, demonstrated that the classical equations of chemical kinetics are inapplicable to nanosized particles. The excess energy of surface atoms whose percentage with respect to internal atoms is high has a substantial effect on the temperature of phase transitions in nanoparticles. If their sizes are comparable, for example, to the radius of delocalisation of charge carriers, nonlinear optical and electrical phenomena take place. This fact gives rise to the development of new original methods for the preparation of nanoparticles.

It was proposed to prepare nanoparticles by metal evaporation in a static diffusion chamber under the action of pulse laser radiation.[373–375] The desired compound is formed by the chemical reaction of heated metal atoms with a gas reagent (for example,

‡ The monograph by N A Fuks 'The Mechanics of Aerosols' (Moscow: Academy of Sciences of the USSR, 1955), which the author wrote in Stalin's camps, is still extensively cited. The contribution of N A Fuks to the development of the science of aerosols was recognised by establishing the prize in his memory. This prize is awarded at International Conferences on Problems of Aerosols.

O_2, N_2, NH_3, *etc*.) in a medium of an inert gas (Ne or Ar) at a pressure of 1–0.01 Torr. The molecules thus formed and the unconsumed metal atoms deposit on the cold upper surface of a diffusion chamber. By varying the gas composition, temperature gradient and laser pulse power, one can control the chemical composition and size of nanoclusters.

The size of a nanocluster influences, for example, the gap width in semiconductors,[376] which, in turn, has a strong effect on the rate of luminescence quenching. It was noted [377] that the rate of luminescence quenching by oxygen molecules depends on the size of light-irradiated MoS_2 nanoparticles. Therefore, nanoparticles can influence redox processes, which is of importance for solving a number of practical problems. Examples of such a 'size' influence on the gap width, in particular, upon photoreduction of methyl viologen on nanoparticle surfaces of metal chalcogenides can be cited.[378, 379] The use of nanoparticles in photocatalysis opens up considerable possibilities. Metals deposited onto nanoparticle surfaces can serve as catalysts. For instance, platinum deposited onto TiO_2 nanoparticles catalyses the liberation of hydrogen from water.[380]

The kinetics of formation of a metal-polymer material was studied.[381] Metal polymers are composite materials whose properties depend on the composition and size of dispersed particles distributed in a polymer matrix. The widely used methods for their preparation were surveyed in the publications.[382, 383] The simplified scheme of the thermal synthesis involves three steps, *viz*., decomposition of a metal-containing compound, the nucleus growth of a metal phase and the formation of a volatile compound, which is then removed from the reaction zone. Real processes occurring in the course of formation of a composite are much more complicated.

Industrial technologies are devised using numerical simulation of the kinetics of growth of metal clusters. The reaction space is divided into cubic cells in which only one nucleus can form. It is assumed that the appearance of a new phase results from homogeneous nucleation. The probability of nucleus formation is calculated within the framework of the classical theory.[384] Nuclei grow due to diffusion of the substance from the bulk of the solution to the phase formed. It is believed that nuclei do not decompose and do not migrate due to high viscosity of polymer melts. Two models of the substance exchange between the adjacent cells were considered. In a model with stirring, a change in the concentration in one cell leads to instantaneous changes in the concentrations in other cells. In a model without stirring, the substance exchange between the adjacent cells takes place. In the latter case, the average particle size first increases with time and then remains virtually constant. The number of particles also sharply increases until the nucleation rate reaches a maximum after which it ceases to change. In a system with stirring, larger particles are formed, but their number is smaller than that observed in a system without stirring. The calculated size distributions of particles are in agreement with experimental values.[385] If a reagent is added dropwise, a model with stirring is characterised by a polymodal distribution. In the absence of stirring, the modes overlap.

Nucleation processes are used for the preparation of metallic ultradispersed powders serving as catalysts. Studies of such catalysts contribute to the development of scientific fundamentals of catalysis and corresponding technologies. For example, the use of ultradispersed powders, which are prepared using an electrical explosion of conductors, instead of usual silver powders made it possible to extend substantially the temperature range of selective oxidation of ethanol to acetaldehyde.[386] It appeared that ultradispersed metals are essentially non-equilibrium systems whose relaxation gives rise to particles of the same type exhibiting high catalytic activity.

Van der Waals interactions play a decisive role in the formation of such compounds.[387] In the mid-1930s, Nikitin formulated the analogy rule: 'If two substances have similar van der Waals forces and their molecules are similar in size and shape, they should form analogous compounds with a third substance, and the resulting compounds should exhibit similar stability and can form mixed crystals with each other'. Nikitin has forestalled one of the main concepts of supramolecular chemistry, *viz*., spatial complementarity, and its decisive role in the formation of supramolecular compounds.

A radically new organisation of a chemical material at a higher level has been discovered and described.[388] In this case, the compatibility of sizes and shapes of one type of molecule, the so-called guests, with the cavities of the framework consisting of molecules of another type, the so-called hosts (or a cavity of another larger host molecule), rather then their reactivities plays a decisive role in the formation of particular compounds from components. This principle of organisation of compounds allows one to combine coordinatively saturated molecules, which are not involved in chemical interactions with each other, into supramolecules or supramolecular crystalline phases, which are thermodynamically more stable than mixtures of the starting components. From the viewpoint of traditional chemistry, it is difficult to imagine that compounds of different chemical nature, such as Xe, SO_2, H_2S, HBr, CH_4, CO, HCOOH, *etc*., can react in a similar way, for instance, with hydroquinone to form isostructural clathrate compounds. However, these compounds are analogous from the viewpoint of clathrate chemistry. At the same time, of two chemical analogues, *viz*., CH_3OH and C_2H_5OH, only methanol forms a clathrate with hydroquinone because the ethanol molecule is too large to be located in the cavity of the hydroquinone framework.

The main concepts of clathrate chemistry stated by Powell [388] stimulated studies in this field and gave impetus to a target search for supramolecular substances. A number of discoveries were made. Statistical thermodynamic studies of clathrates [389, 390] provided an explanation why the initial components can be combined to form a thermodynamically stable phase in the case of the absence of chemical valence bonds between the molecules.

The French chemist Lehn has emphasised an important role of nonbonded interactions in the formation of such compounds.§ He introduced a new concept 'supramolecular chemistry', which he defined as the 'chemistry beyond the molecule', the 'chemistry of molecular ensembles and intermolecular bonds'.[391, 392]

The discovery of clathrate-forming metal complexes gave rise to the preparation of numerous new compounds and offered inexhaustible possibilities for the rapid and target construction or modification of host molecules. The discovery of supramolecular compounds made it possible to reveal yet another mechanism of nucleus formation of a new phase. This mechanism is thermodynamically favourable to an extent that it enables one to solve a complex problem of preparing high-purity gases (gaseous hydrates were recognised as a new class of impurities in high-purity gases and gas mixtures).[393]

In 1970, deposits of methane hydrates were discovered in Yakutiya,[394] after which it was found that huge deposits of fossil methane are available in the world. Presumably, methane will be the main fuel in the future. However, safe conditions of its recovery is a limiting factor. This problem is directly associated with nucleation. Actually, the equilibrium of methane hydrate can be easily disturbed after drilling operations. Upon decompression, methane hydrate becomes unstable and decomposes to eliminate methane, which can give rise to a substantial volume of metastable water ice. Since the thermodynamic potential of the metastable state is higher than the corresponding potential of the stable state, relaxation can assume a character of explosion in the case of a large volume of ice, and the energy of such an explosion can be higher than the energy of a powerful hydrogen bomb.[395] The frequencies of the 'boiling' of methane hydrates remain to be studied. The seemingly special problem of estimating the rates of

§ In 1987, J-M Lehn (France), C J Pedersen and D J Cram (USA) were awarded the Nobel Prize in Chemistry.

formation of gas bubbles in gas-hydrate systems becomes one of the key current problems. The possible schemes of experimental investigations of the frequencies of gas nucleation in metastable gas hydrates were analysed in the publication.[395]

Intercalation compounds of graphite and fullerene belong to an important class of clathrates.[396] The specific chemical and physical properties of intercalation compounds offer considerable possibilities for their use in different fields among which heterogeneous catalysis and electrochemistry are of the most importance. These compounds are also used in analytical chemistry and pharmacology.

* * *

Theoretical methods for studying nucleation have some fundamental limitations. Hence, experimental investigations are of great importance, because they provide information, which cannot be obtained by theoretical methods. By analogy with classical mechanics, it can be stated that the classical stage of nucleation theory has come to an end. However, in the nucleation theory there are no analogues equivalent to quantum mechanics.

The present-day situation can be characterised as 'pre-revolutionary' when the stage was set for the development of a semiempirical nucleation theory because all drawbacks of the theory become increasingly evident, nucleation models become increasingly complicated and theorists have high skills. However, a new key idea is required, whose appearance can be facilitated by an original experiment in combination with a critical review of the axiomatic concepts of the theory. One of the steps involves a semiempirical method for the construction of nucleation rate surfaces. Actually, this seemingly simple approach based on the use of phase equilibrium diagrams enables one to determine the topology of the nucleation rate surfaces in the zero limit. This is already sufficient for revision of certain approximations employed in experiments and particular axioms of the nucleation theory.

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References

1. B Senger, P Schaaf, D S Corti, R Bowles, J-C Voegel, H Reiss *J. Chem. Phys.* **110** 6421 (1999)
2. D N Zubarev *Neravnovesnaya Statisticheskaya Termodinamika* (Non-equilibrium Statistical Thermodynamics) (Moscow: Izd. Fiz.-Mat. Lit., 1972)
3. G Röpke *Statistishe Mechanik für das Nichtgleichgewicht* (Berlin: Doutscher Verlag der Wissenschaften, 1987)
4. J Lothe, G Pound *J. Chem. Phys.* **36** 2080 (1962)
5. Ya B Zel'dovich *Zh. Eksp. Teor. Fiz.* **12** 525 (1942)
6. Ya I Frenkel' *Kineticheskaya Teoriya Zhidkostei* (Kinetic Theory of Liquids) (Moscow, Leningrad: Izd. Akad. Nauk SSSR, 1945)
7. F F Abraham *J. Chem. Phys.* **50** 3977 (1969)
8. A Dillmann, G E A Meier *Chem. Phys. Lett.* **160** 71 (1989)
9. A Dillmann, G E A Meier *J. Chem. Phys.* **94** 3872 (1991)
10. H Reiss, R Bowles *J. Chem. Phys.* **112** 1390 (2000)
11. M Anisimov, P Hopke, I Shalmordanov, S Shandakov, L E Magnusson *J. Chem. Phys.* **115** 810 (2001)
12. M P Anisimov *J. Aerosol Sci.* **21** (Suppl. 1) 23 (1990)
13. M P Anisimov *Dokl. Akad. Nauk* **352** 816 (1997) [a]
14. M P Anisimov, P K Hopke, D H Rasmussen, S D Shandakov, V A Pinaev *J. Chem. Phys.* **109** 1435 (1998)
15. L Anisimova, P K Hopke, J Terry *J. Chem. Phys.* **114** 9852 (2001)
16. V I Roldugin *Russ. J. Phys. Chem.* **74** (Suppl. 3) 522 (2000)
17. J W Gibbs *The Collected Works* (New York: Longmans, Green, 1928)
18. M Volmer, A Weber *Z. Phys. Chem. A* **119** 277 (1926)
19. M Volmer *Kinetik der Phasenbildung* (Dresden, Leipzig: Steinkopf Verlag, 1926)
20. L Farkas *Z. Phys. Chem.* **125** 236 (1927)
21. R Kaischew, I N Stranski *Z. Phys. Chem.* **26** 317 (1934)
22. R Becker, W Döring *Ann. Phys. (Leipzig)* **24** 712 (1935)
23. N O Fuks *Usp. Fiz. Nauk* **15** 496 (1935)
24. V Danning, in *Khimiya Tverdogo Sostoyaniya* (The Chemistry of Solid State) (Translated into Russian; Moscow: Izd. Inostr. Lit., 1961) p. 213
25. J W S Schmelzer, G Röpke, V Priezzhev (Eds) *Nucleation Theory and Applications* (Dubna: JINR, 1999 – 2002)
26. G S Springer *Adv. Heat Transf.* **14** 281 (1978)
27. A Kantrowitz *J. Chem. Phys.* **19** 1097 (1951)
28. F Farley *Proc. R. Soc. London, Ser. A* **212** 530 (1952)
29. H Wakeshima *J. Chem. Phys.* **22** 1614 (1954)
30. V S Gerasimenko, B Ya Lyubov, in *Mekhanizm i Kinetika Kristallizatsii* (Mechanism and Kinetics of Crystallisation) (Minsk: Nauka i Tekhnika, 1969) p. 80
31. W G Courtney *J. Chem. Phys.* **36** 2009 (1962)
32. B I Kidyarov *Kinetika Obrazovaniya Kristallov iz Zhidkoi Fazy* (Kinetics of Formation of Crystals from Liquid Phase) (Novosibirsk: Nauka, 1979)
33. Yu I Petrov *Klastery i Malye Chastitsy* (Clusters and Small Particulars) (Moscow: Nauka, 1986)
34. D Kashchiev *J. Surf. Sci.* **14** 209 (1969)
35. B Hale, D DiMatto, in *Nucleation and Atmospheric Aerosols 2000* (Eds B Hale, M Kulmala) (Melville, NY: AIP, 2000) p. 31
36. J Lothe, G Pound *J. Chem. Phys.* **45** 630 (1966)
37. J Lothe, G Pound *J. Chem. Phys.* **48** 1849 (1968)
38. R A Oriany, B E Sandquist *J. Chem. Phys.* **38** 2082 (1963)
39. A A Lushnikov, A G Sutugin *Usp. Khim.* **45** 385 (1976) [*Russ. Chem. Rev.* **45** 197 (1976)]
40. L M Shcherbakov *Kolloid. Zh.* **14** 379 (1952) [b]
41. L M Shcherbakov, P P Ryazantsev, N P Filippov *Kolloid. Zh.* **23** 338 (1961) [b]
42. L M Shcherbakov *Kolloid. Zh.* **24** 502 (1962) [b]
43. O Sinanoğlu *J. Chem. Phys.* **75** 463 (1981)
44. A W Sun, J M Shik, P Hyungsuk, C Seihum *J. Colloid Interface Sci.* **38** 605 (1972)
45. R C Tolman *J. Chem. Phys.* **17** 333 (1949)
46. S Girshick, C-P Chiu *J. Chem. Phys.* **931273** (1990)
47. S Girshick, C-P Chiu, P McMurry *Aerosol Sci. Technol.* **13** 465 (1982)
48. S Girshick *J. Chem. Phys.* **94** 826 (1991)
49. A Laaksonen, I J Ford, M Kulmala *Phys. Rev. E* **49** 5517 (1994)
50. M Fisher *Physics* **3** 255 (1967)
51. D H Rasmussen, M Liang, E Esen, M R Appleby *Langmuir* **8** 1868 (1992)
52. D H Rasmussen *Aerosol Sci. Technol.* **5** 438 (1996)
53. D H Rasmussen *J. Cryst. Growth* **56** 45 (1982)
54. M Volmer *Kinetik der Phasenbildung* (Drezden: Th Steinkopff, 1939)
55. K Neuman, W Döring *Z. Phys. Chem. A* **186** 203 (1940)
56. H Reiss *J. Chem. Phys.* **18** 840 (1950)
57. D Stauffer *J. Aerosol Sci.* **7** 319 (1976)
58. J O Hirchfelder *J. Chem. Phys.* **61** 2690 (1974)
59. P Mirabel, J L Katz *J. Chem. Phys.* **60** 1138 (1974)
60. G Wilemski *J. Chem. Phys.* **62** 3763 (1975)
61. R Renninger, F Hiller, R Bone *J. Chem. Phys.* **75** 1584 (1981)
62. G Wilemski *J. Chem. Phys.* **80** 1370 (1984)
63. P Mirabel, H Reiss *Langmuir* **3** 228 (1987)
64. N Robinson *J. Aerosol Sci.* **12** 75 (1981)
65. G Doyle *J. Chem. Phys.* **35** 795 (1961)
66. C S Kiang, D Stauffer *Faraday Symp. Chem. Soc.* **7** 26 (1973)
67. D E Temkin, in *Rost Kristallov* (Growth of Crystals) (Moscow: Nauka, 1983) p. 71
68. A A Melikhov, V B Kurasov, Yu Sh Dzhikaev, F M Kuni, in *Aktual'nye Voprosy Fiziki Aerodispersnykh Sistem (Tez. Dokl. XV Vsesoyuzn. Konf.), Odessa, 1989* [Topical Questions of Physics of Aerodispersed Systems (Abstracts of Reports of XVth All-Union Conference), Odessa, 1989] Vol. 1, p. 39
69. A K Ray, M Chalam, L K Peters *J. Chem. Phys.* **85** 2161 (1986)
70. M P Anisimov *K Voprosu ob Eksperimental'nom Issledovanii Ob'emnoi Nukleatsii Para. Preprint INKH Sib. Otd. Akad. Nauk SSSR, (12), Novosibirsk, 1981* [On the Problem of Experimental Investigation of Volume Nucleation of the Vapour. Preprint of the Institute of Inorganic Chemistry, Siberian Branch of Academy of Sciences of the USSR, (12), Novosibirsk, 1981]
71. R Strei, P E Wagner *J. Aerosol Sci.* **19** 813 (1988)

72. B E Wyslouzil, C H Heath, J L Cheung, G Wilemski *J. Chem. Phys.* **113** 7317 (2000)
73. M P Anisimov, J A Koropchak, A G Nasibulin, L V Timoshina *J. Chem. Phys.* **112** 9917 (1998)
74. P Mirabel, J Katz *J. Chem. Phys.*, **67** 1697 (1977)
75. A Grassmann, F Peters *J. Chem. Phys.* **113** 6774 (2000)
76. P G Kevrekidis, M Lazaridis, P G Georgopoulos *J. Chem. Phys.* **111** 8010 (1999)
77. A Laaksonen, R McGraw, H Vehkamaki *J. Chem. Phys.* **111** 2019 (1999)
78. P G Debenetty *Metastable Liquids: Concepts and Principles* (Prinston: Prinston University Press, 1996)
79. D W Oxtoby, D Kashchiev *J. Chem. Phys.* **100** 7665 (1994)
80. V Kalikmanov, M van Dongen *J. Chem. Phys.* **103** 4250 (1995)
81. C C M Luijten, M E H van Dongen *J. Chem. Phys.* **111** 8524 (1999)
82. X C Zeng, D W Oxtoby *J. Chem. Phys.* **95** 5940 (1991)
83. P Peeters, J Hruby, M E H van Dongen *J. Phys. Chem. B* **105** 11763 (2001)
84. D Kashchiev *J. Chem. Phys.* **104** 8671 (1996)
85. A V Bogdanov, N R Zainalov, V A Pavlov *Khim. Fiz.* **10** 1 (1991) [c]
86. A E Belikov, G V Dubrovskii, A E Zarvin, N N Karelov *Chislennye Metody v Kineticheskoi Teorii Gazov* (Numerical Methods for Kinetic Theory of Gases) (Novosibirsk: Nauka, 1986)
87. R G Sharafutdinov, A E Zarvin, N G Korobeishchikov, V Zh Madirbaev, S Ya Khmel' *Pis'ma Zh. Tekh. Fiz.* **25** 47 (1999) [d]
88. D W Oxtoby *J. Phys.: Condens. Matter* **4** 7627 (1992)
89. X C Zeng, D W Oxtoby *J. Chem. Phys.* **94** 4472 (1990)
90. V Talanquer, D W Oxtoby *J. Chem. Phys.* **100** 5190 (1993)
91. A Laaksonen, D W Oxtoby *J. Chem. Phys.* **102** 5803 (1995)
92. N N Tunitskii *Zh. Fiz. Khim.* **15** 41 (1941) [e]
93. I Napari, A Laaksonen, R Strey *J. Chem. Phys.* **113** 4476 (2000)
94. I Napari, A Laaksonen, R Strey *J. Chem. Phys.* **113** 4480 (2000)
95. P R Wolde, D Frenkel *J. Chem. Phys.* **109** 9919 (1998)
96. V Talanquer, D W Oxtoby *J. Chem. Phys.* **104** 1993 (1996)
97. I Napari, A Laaksonen *J. Chem. Phys.* **111** 5485 (1999)
98. B Senger, P Schaaf, D S Corti, R Bowles, D Pointu, J-C Voegel, H Reiss *J. Chem. Phys.* **110** 6438 (1999)
99. V M Zhdanov, V I Roldugin *Usp. Fiz. Nauk* **168** 408 (1998) [*Physics-Uspekhi* **41** 349 (1998)]
100. M Kats *Neskol'ko Veroyatnostnykh Zadach Fiziki i Matematiki* (Some Probabilistic Problems of Physics and Mathematics) (Moscow: Nauka, 1987)
101. Yu L Klimontovich *Statisticheskaya Fizika* (Statistical Physics) (Moscow: Nauka, 1982)
102. E M Lifshits, L P Pitaevskii *Fizicheskaya Kinetika* (Physical Kinetics) (Moscow: Nauka, 1979)
103. I M Lifshits, Yu M Kagan *Zh. Eksp. Teor. Fiz.* **62** 385 (1972) [f]
104. S V Iordanskii, A M Finkel'shtein *Zh. Eksp. Teor. Fiz.* **62** 403 (1972) [f]
105. Yu M Kagan, L A Maksimov *Zh. Eksp. Teor. Fiz.* **76** 687 (1979) [f]
106. I K Robinson, D J Tweer *Rep. Prog. Phys.* **55** 599 (1992)
107. S Godoy, L S Garcia-Golin *Phys. Rev. E* **53** 5779 (1996)
108. T Nakamura, Y Kanno, S Takagy *Phys. Rev. B* **51** 8446 (1995)
109. J C Martinez *J. Colloid Interface Sci.* **205** 476 (1998)
110. T Satoh, M Morishita, S Katoh *Physica B (Amsterdam)* **197** 397 (1994)
111. K Sakiyama, H Takano, H Tomida, M Itoh, in *Nucleation and Atmospheric Aerosols 2000* (Eds B Hale, M Kulmala) (Melville, NY: AIP, 2000) p. 225
112. I V Skutova, S P Fisenko, S I Shabunya *Matematicheskoe Modelirovanie Kinetiki Neizotermicheskoi Nukleatsii v Paro-Gazovykh Smesyakh. Preprint Inst. Teplo- i Massoobmena, Akad. Nauk Bel.SSR, (3), Minsk, 1986* [Mathematical Modelling of the Kinetics of Nonisothermal Nucleation in Gas-Vapour Mixtures. Preprint of the Institute of the Heat and Mass Exchange, Academy of Sciences of Bel.SSR, (3), Minsk, 1986]
113. F M Kuni, A A Melikhov, K V Kopeikin *Kolloid. Zh.* **48** 270 (1986) [b]
114. F M Kuni, I A Terent'ev, A A Melikhov *Kolloid. Zh.* **48** 474 (1986) [b]
115. A P Grinin, F M Kuni *Kolloid. Zh.* **52** 21 (1990) [b]
116. A P Grinin, F M Kuni *Vestn. Mosk. Univ., Ser. 4, Geologiya* **2** 91 (1989)
117. F M Kuni, A P Grinin *Kolloid. Zh.* **52** 54 (1990) [b]
118. A P Grinin, F M Kuni *Kolloid. Zh.* **52** 227 (1990) [b]
119. F M Kuni, A P Grinin *Kolloid. Zh.* **52** 351 (1990) [b]
120. F M Kuni, A K Shchekin, A P Grinin *Usp. Fiz. Nauk* **171** 345 (2001) [*Physics-Uspekhi* **44** 331 (2001)]
121. F M Kuni *Kolloid. Zh.* **47** 39 (1985) [b]
122. F M Kuni *Kolloid. Zh.* **47** 284 (1985) [b]
123. F M Kuni *Kolloid. Zh.* **47** 497 (1985) [b]
124. F M Kuni *Kolloid. Zh.* **47** 698 (1985) [b]
125. A I Danilov, Yu M Polukarov *Usp. Khim.* **56** 1082 (1987) [*Russ. Chem. Rev.* **56** 619 (1987)]
126. S Wu, Z Shi, J Lipkowski, A P Hitchcock, T Tyliszczak *J. Phys. Chem. B* **101** 10310 (1997)
127. L Ickert *Z. Phys. Chem.* **221** 328 (1962)
128. I Markov, D Kashchiev *Thin Solid Films* **15** 181 (1973)
129. W Obretenov, I Petrov, I Nachev, G Staikov *J. Electroanal. Chem.* **109** 195 (1980)
130. I Markov, S Toschev *Electrodepos. Surf. Treat.* **3** 385 (1975)
131. V V Trofimenko, V P Zhitnik, Yu M Loshkarev *Elektrokhimiya* **17** 1644 (1981) [g]
132. A N Baraboshkin *Elektrokristallizatsiya Metallov iz Rasplavlennykh Solei* (Electrocrystallisation of Metals from Molten salts) (Moscow: Nauka, 1976)
133. S Stoyanov *Curr. Top. Mater. Sci.* **3** 422 (1979)
134. D Kashchiev *Surf. Sci.* **86** 14 (1979)
135. R Kaishev *Izbrani Trudove* (Selected Works) (Sofia: Bulgarian Academy of Sciences, 1980)
136. S Stoyanov, D Kashchiev *Curr. Top. Mater. Sci.* **7** 69 (1981)
137. R Kaischew, S Stoyanov, D Kashchiev *J. Cryst. Growth* **52** 3 (1981)
138. V V Trofimenko, Yu M Loshkarev, V S Kovalenko *Dokl. Akad. Nauk SSSR* **227** 45 (1976) [a]
139. V V Trofimenko, V S Kovalenko, Yu M Loshkarev, V P Artemenko, A T Zamulyukin *Ukr. Khim. Zh.* **43** 152 (1977)
140. R Kaishev *Godishn. Sofiisk. Univ., Fiz.-Mat. Fak. (Khim.)* **43** 53 (1946/1947)
141. A Milchev, S Stoyanov, R Kaishev *Elektrokhimiya* **13** 855 (1977) [g]
142. V A Isaev, V N Chebotin, in *Ionnye Rasplavy i Tverdye Elektrolity. Trudy Inst. Elektrokhimii UNTs Akad. Nauk SSSR, Sverdlovsk, 1978* (Ionic Melts and Solid Electrolytes. Proceedings of the Institute of Electrochemistry of Urals Scientific Centre, Academy of Sciences of the USSR, Sverdlovsk, 1978) No. 27, p. 46
143. A I Danilov, Yu M Polukarov *Elektrokhimiya* **17** 1883 (1981) [g]
144. G J Hills, D J Schiffrin, J Thompson *Electrochim. Acta* **10** 671 (1974)
145. J O'M Bockris, B E Conway (Eds) *Modern Aspects of Electrochemistry* (London: Butterworths, 1964)
146. G Tohmfor, M Volmer *Ann. Phys. B* **33** 109 (1938)
147. W F Schottky *Z. Phys. Chem., Neue Folge* **31** 40 (1962)
148. G Mierke, W F Schottky *Ber. Bunsen-Ges. Phys. Chem. B* **71** 516 (1967)
149. I Gutsov *Izv. Inst. Fiz. Khim. Bolg. Akad. Nauk* **4** 69 (1964)
150. N Pangarov *Electrochim. Acta* **28** 763 (1983)
151. E Budevski, V Bostanov, G Staikov *Annu. Rev. Mater. Sci.* **10** 85 (1980)
152. T Vitanov, A Popov, E Budevski *J. Electrochem. Soc.* **121** 207 (1974)
153. R L Deutsher, S J Fletcher *J. Electroanal. Chem.* **164** 1 (1984)
154. A I Danilov, Yu M Polukarov *Elektrokhimiya* **19** 1427 (1983) [g]
155. S D Antipov, G E Goryunov, A A Edigaryan, Yu M Polukarov, P N Stetsenko, in *Sbornik Trudov XVIII Mezhdunarodnoi Shkoly-Seminara 'Novye Magnitnye Materialy Mikroelektroniki', Moskva, 2000* (Collection of Works of XVIIth International School-Seminar 'New Magnetic Materials of Microelectronics', Moscow, 2000) p. 172
156. G Bliznikov *Izv. Bolg. Akad. Nauk, Ser. Fiz.* **6** 301 (1956)
157. R Kaishev *Izv. Khim. Inst. Bolg. Akad. Nauk* **7** 145 (1959)

158. S Fletcher, R G Barradas, J D Porter *J. Electrtochem. Soc.* **125** 1960 (1978)
159. B I Podlovchenko, R P Petukhova *Poluchenie i Svoistva Dispersnykh Elektroliticheskikh Osadkov Metallov Gruppy Platiny* (Production and Properties of Dispersed Electrolytic Deposits of Platinum Group Metals) (Moscow: Moscow State University, 1988)
160. M Yu Rusanova, G A Tsirlina, O A Petrii, T Ya Safonova, S Yu Vasil'ev *Elektrokhimiya* **36** 517 (2000) [g]
161. R G Barradas, J D Porter *J. Electroanal. Chem.* **110** 159 (1980)
162. G Staikov, J A Harrison *J. Electroanal. Chem.* **77** 187 (1977)
163. R G Barradas, S Fletcher, J D Porter *Can. J. Chem.* **56** 336 (1978)
164. M Y Abyaneh, M Fleischmann *J. Electroanal. Chem.* **119** 187 (1981)
165. S V Shevkunov *Zh. Eksp. Teor. Fiz.* **104** 3032 (1993) [f]
166. I M Lifshits, V V Slezov *Zh. Eksp. Teor. Fiz.* **55** 479 (1958)
167. V V Slezov, E F Tikhonov *Dokl. Akad. Nauk SSSR* **266** 619 (1982) [a]
168. V S Mitlin *Zh. Eksp. Teor. Fiz.* **95** 1826 (1989) [f]
169. J W Cahn, J E Hillard *J. Chem. Phys.* **31** 688 (1959)
170. S A Kukushkin *Fiz. Tv. Tela* **35** 1582 (1993) [h]
171. Ya E Geguzin, Yu S Kaganovskii *Usp. Fiz. Nauk* **125** 489 (1978) [i]
172. S A Kukushkin *Fiz. Tv. Tela* **27** 2987 (1985) [h]
173. S A Kukushkin *Poverkhnost* **10** 53 (1986)
174. S A Kukushkin *Fiz. Tv. Tela* **35** 1597 (1993) [h]
175. A L Fradkov, P Y Guzenko, S A Kukushkin, A V Osipov *J. Phys. D* **30** 2794 (1997)
176. S A Kukushkin, V V Slezov *Khim. Fiz.* **9** 563 (1990) [c]
177. V P Skripov *Metastabil'naya Zhidkost'* (Metastable Liquid) (Moscow: Nauka, 1972)
178. V P Skripov, E N Sinitsyn, P A Pavlov, G V Ermakov, G N Muratov, N V Bulanov, V G Baidakov *Teplofizicheskie Svoistva Zhidkostei v Metastabil'noi Oblasti* (Thermophysical Properties of Liquids in the Metastable Region) (Moscow: Atomizdat, 1980)
179. V G Baidakov, V P Skripov *Termodinamicheskie Svoistva Zhidkogo Argona v Metastabil'nom (Peregretom) Sostoyanii* [Thermodynamic Properties of Liquid Argon in Metastable (Overheated) State] (Sverdlovsk: Urals Scientific Centre, Academy of Sciences of the USSR, 1978)
180. V P Skripov, A V Skripov *Usp. Fiz. Nauk* **128** 193 (1979) [i]
181. Ya B Zel'dovich, O M Todes *Zh. Eksp. Teor. Fiz.* **10** 1441 (1940)
182. I Prigozhin, R Defei *Khimicheskaya Termodinamika* (Chemical Thermodynamics) (Novosibirsk: Nauka, 1966)
183. H E Cook *Acta Met.* **18** 297 (1970)
184. F M Kuni, V M Ogenko, L N Ganyuk, L G Grechko *Kolloid. Zh.* **55** 22 (1993) [b]
185. A I Rusanov, F M Kuni, A K Shchekin *Kolloid. Zh.* **49** 309 (1987) [b]
186. A A Melikhov, Yu V Trofimov, F M Kuni *Kolloid. Zh.* **56** 201 (1994) [b]
187. V N Skokov, V P Koverda, V P Skripov, V B Ivakin, N M Semenova *Dokl. Akad. Nauk* **333** 614 (1993) [a]
188. E I Blednykh, V P Skripov *Colloid J.* **58** 15 (1996)
189. B Rathke, H Boumgartl, R Strey, in *Nucleation and Atmospheric Aerosols 2000* (Eds B Hale, M Kulmala) (Melville, NY: AIP, 2000) p. 414
190. P V Skripov, A A Starostin, D V Volosnikov *Zh. Tekh. Fiz.* **69** 92 (1999) [j]
191. O M Lapteva, G I Pozharskaya, Y D Kolpakov, S P Samokhin, V P Skripov *Colloid J.* **56** 717 (1994)
192. A I Drozhzhin, F P Ermakov, S N Yatsenko *Kondens. Sred. Mezhfazn. Gran.* **3** 194 (2001)
193. P E Wagner, R Strey *J. Phys. Chem. B* **105** 11 656 (2001)
194. K F Kelton, in *Nucleation and Atmospheric Aerosols 2000* (Eds B Hale, M Kulmala) (Melville, NY: AIP, 2000) p. 386
195. D Kashchiev *Nucleation: Basic Theory with Applications* (Oxford: Butterworth-Heinemann , 2000)
196. H Reiss, J L Katz, E R Cohen *J. Chem. Phys.* **48** 5553 (1968)
197. R J Kikuchi *Stat. Phys.* **1** 351 (1969)
198. A I Rusanov, F M Kuni, E D Shchukin, P A Rebinder *Kolloid. Zh.* **30** 744 (1968) [b]
199. Y H Kim, A Inoue, T Masumoto *Mater. Trans., JIM,* **31** 747 (1990)
200. S Schneider, P Thiyagarajan, W L Johnson *Appl. Phys. Lett.* **68** 493 (1996)
201. D R Allen, J C Foley, J H Perepezhko *Acta Mater.* **46** 431 (1998)
202. S Omata, Y Tanaka, T Ishida, A Sato, A Inoue *Philos. Mag. A* **76** 397 (1997)
203. K Tauer, K Padtberg, in *Nucleation and Atmospheric Aerosols 2000* (Eds B Hale, M Kulmala) (Melville, NY: AIP, 2000) p. 432
204. V B Fedorov, E G Kalashnikov, M Kh Shorshorov *Fiz. Khim. Obrab. Mater.* **1** 65 (1981)
205. H A D Wattis, P V Coveney *J. Chem. Phys.* **106** 9122 (1997)
206. J Smolik, B Triska *J. Aerosol Sci.* **24** 737 (1993)
207. S H Bauer, Y-X Zhang, C F Wilcox *J. Chem. Phys.* **110** 7926 (1999)
208. J L Katz, H Saltsburg, H Reiss *J. Colloid Interface Sci.* **21** 560 (1966)
209. S Hamon, S D LePicard, A Canosa, B R Rowe, I W M Smith *J. Chem. Phys.* **112** 4506 (2000)
210. A Weber, S Friedlander *J. Aerosol Sci.* **28** 179 (1997)
211. I P Suzdalev, V N Buravtsev, Yu V Maksimov, V K Imshennik, S V Povichikhin, V V Matveev, A S Plachinda *Ros. Khim. Zh.* **45** 66 (2001) [k]
212. J Katz, B Johnson, H Lihavainen, M Rudek, B Salter, in *Nucleation and Atmospheric Aerosols 2000* (Eds B Hale, M Kulmala) (Melville, NY: AIP, 2000) p. 284
213. J Katz, H Lihavainen M Rudek, B Salter *J. Chem. Phys.* **112** 8363 (2000)
214. T Z Kalanov, A I Osipov, V Ya Panchenko *Pis'ma Zh. Tekh. Fiz.* **4** 3 (1977) [d]
215. B I Shapiro *Usp. Khim.* **63** 243 (1994) [*Russ. Chem. Rev.* **63** 231 (1994)]
216. B I Shapiro *Usp. Khim.* **66** 278 (1997) [*Russ. Chem. Rev.* **66** 255 (1997)]
217. G I Skubnevskaya, G G Dul'tseva, S N Dubtsov *Opt. Atmos. Okeana* **13** 562 (2000)
218. S N Dubtsov, A I Levykin, K K Sabelfeld *J. Aerosol Sci.* **31** 509 (2000)
219. R M Villarica, B Samoriski, J Chaiken, S E Novick *Appl. Surf. Sci.* **106** 99 (1996)
220. C F Landes, M Braun, M A El-Sayed *J. Phys. Chem. B* **105** 10 554 (2001)
221. L M Shcherbakov, V M Samsonov, V A Lavrov, O A Rybal'chenko *Kolloid. Zh.* **61** 128 (1999) [b]
222. V Shneydman, M Weinberg *J. Chem. Phys.* **95** 9146 (1991)
223. R McGraw, in *Nucleation and Atmospheric Aerosols 2000* (Eds B Hale, M Kulmala) (Melville, NY: AIP, 2000) p. 373
224. R Strey, Y Viisanen *J. Chem. Phys.* **99** 4693 (1993)
225. B Hale, G Wilemski *Chem. Phys. Lett.* **305** 263 (1999)
226. Y Viisanen, R Strey, H Reiss *J. Chem. Phys.* **112** 8205 (2000)
227. R T Helmholz *Wied. Ann.* **27** 508 (1896)
228. L B Allen, J L Kassner *J. Colloid Interface Sci.* **30** 81 (1969)
229. M A Sharaf, R A Dobbins *J. Phys. Chem.* **77** 1517 (1982)
230. P E Wagner, R Strey *J. Chem. Phys.* **85** 2694 (1981)
231. R Strey, P E Wagner, Y Viisanen *J. Phys. Chem.* **98** 7748 (1994)
232. D E Hagen, J L Kassner *J. Chem. Phys.* **81** 1416 (1984)
233. Y Viisanen, R Strey, H Reiss *J. Chem. Phys.* **99** 4680 (1993)
234. R Strey, P E Wagner, T Schmeling *J. Chem. Phys.* **84** 2325 (1986)
235. J Hrubý, Y Viisanen, R Strey *J. Chem. Phys.* **104** 5181 (1995)
236. P Wegener, G Lundquist *J. Appl. Phys.* **22** 233 (1951)
237. J B Homer, I R Hurle *Proc. R. Soc. London, Ser. A* **327** 61 (1972)
238. R A Zahoransky, F Peters *J. Chem. Phys.* **83** 6425 (1985)
239. A W Hodgson, J C Mackie *J. Colloid Interface Sci.* **83** 547 (1981)
240. C C M Luijten, O D E Baas, M E H van Dongen *J. Chem. Phys.* **106** 4152 (1997)
241. C C M Luijten, K J Bosschaart, M E H van Dongen *J. Chem. Phys.* **106** 8116 (1997)
242. K N H Looijmans, J F H Willems, M E H van Dongen, in *Shock Waves @ Marseille I* (Eds R Brun, L Z Dumitrescu) (Berlin, Heidelberg, New York: Springer, 1997) p. 215

243. P Peeters, M E H van Dongen, in *Nucleation and Atmospheric Aerosols 2000* (Eds B Hale, M Kulmala) (Melville, NY: AIP, 2000) p. 67
244. K N H Looijmans, C C M Luijten, M E H van Dongen *J. Chem. Phys.* **103** 1714 (1995)
245. C C M Luijten, O D E Baas, M E H van Dongen *J. Chem. Phys.* **106** 4152 (1997)
246. J Hruby, J Hosek, J Blaha, F Marsik, in *Nucleation and Atmospheric Aerosols 2000* (Eds B Hale, M Kulmala) (Melville, NY: AIP, 2000) p. 237
247. B J C Wu, G A Lagune *J. Chem. Phys.* **71** 2991 (1979)
248. P Wegener, G Stein *J. Chem. Phys.* **46** 3685 (1967)
249. P Wegener, A Pouring *Phys. Fluids* **7** 348 (1965)
250. C H Heath, K A Streletzky, J Wolk, B E Wyslouzil, R Strey, in *Nucleation and Atmospheric Aerosols 2000* (Eds B Hale, M Kulmala) (Melville, NY: AIP, 2000) p. 57
251. C H Heath, K A Streletzky, B E Wyslouzil, G Wilemski, in *Nucleation and Atmospheric Aerosols 2000* (Eds B Hale, M Kulmala) (Melville, NY: AIP, 2000) p. 63
252. J Wolk, R Strey *J. Phys. Chem. B* **105** 11 683 (2001)
253. A Kantrowitz, J Grey *Rev. Sci. Instrum.* **22** 328 (1951)
254. A K Rebrov, in *6-ya Vsesoyuznaya Konferentsiya po Dinamike Razrezhennykh Gazov. Rasshirennye Tezisy Dokladov, Novosibirsk, 1979* (The 6th All-Union Conference on Dynamics of Rarefied Gases. Expanded Abstracts of Reports, Novosibirsk, 1979) p. 165
255. A G Amelin *Kolloid. Zh.* **10** 169 (1948)
256. A G Amelin *Novye Idei v Oblasti Izucheniya Aerozolei* (New Ideas for Investigation of Aerosols) (Moscow: Academy of Sciences of the USSR, 1949)
257. A G Amelin *Teoreticheskie Osnovy Obrazovaniya Tumana pri Kondensatsii Para* (Theoretical Foundations of the Formation of Fog at Vapour Condensation) (Moscow: Khimiya, 1972)
258. G M Hidy, S K Friedlander *AJCHE J.* **10** 115 (1964)
259. D G Levine, S K Friedlander *Chem. Eng. Sci.* **13** 49 (1960)
260. Ya I Kogan, Z A Burnysheva *Zh. Fiz. Khim.* **34** 2631 (1960) [e]
261. A G Sutugin, N A Fuks *Kolloid. Zh.* **32** 255 (1970) [b]
262. A G Sutugin, A A Lushnikov *J. Aerosol Sci.* **47** 295 (1973)
263. W J Higuchi, C T O'Konski *J. Colloid Sci.* **15** 14 (1960)
264. C T O'Konski, G T Doyle *Anal. Chem.* **27** 694 (1955)
265. A S Puchkov, A G Sutugin *Dokl. Akad. Nauk SSSR* **224** 1418 (1979) [a]
266. A G Sutugin, A S Puchkov, A A Lushnikov *Kolloid. Zh.* **40** 285 (1978) [b]
267. B V Deryagin, G Ya Vlasenko *Dokl. Akad. Nauk SSSR* **63** 155 (1948) [a]
268. J C Barrett *J. Aerosol Sci.* **31** 51 (2000)
269. F-G Fan, G Ahmady *J. Colloid Interface Sci.* **172** 263 (1995)
270. T W Peterson, F Stratmann, H Fissan *J. Aerosol Sci.* **20** 683 (1989)
271. T Leniewski, S K Friedlander *Aerosol Sci. Technol.* **23** 174 (1995)
272. A Langsdorf *Rev. Sci. Instrum.* **10** 91 (1939)
273. V N Chukanov, B A Korobitsyn *Zh. Fiz. Khim.* **63** 1970 (1989) [e]
274. J L Katz, H Cheng-Hung, M J Krasnopoler *Lect. Notes Phys.* **309** 356 (1988)
275. H Cheng-Hung, M J Krasnopoler, J L Katz *J. Chem. Phys.* **90** 1856 (1989)
276. L D Stulov, A N Grimberg, A G Sutugin *Kolloid. Zh.* **50** 313 (1988) [b]
277. J Smolik, V Zdimal *Aerosol Sci. Technol.* **20** 127 (1994)
278. R H Heist, J Ahmed, M Janjua *J. Phys. Chem.* **99** 375 (1995)
279. A Bertelsmann, R Stuczynski, R H Heist *J. Phys. Chem.* **100** 9762 (1996)
280. M Rusyniak, V Addelsayed, J Campbell, M Samy El-Shall *J. Phys. Chem. B* **105** 11 866 (2001)
281. M Rusyniak, M S El-Shall *J. Phys. Chem. B* **105** 11 873 (2001)
282. H Rabeony, P Mirabel *J. Phys. Chem.* **91** 1815 (1987)
283. J L Katz, J A Fisk, V M Chakarov *J. Chem. Phys.* **101** 2309 (1994)
284. A P Grinin, P S Avtonomov *Zh. Tekh. Fiz.* **66** 55 (1996) [j]
285. J Smolik, J Vasakova *Colloid Surf., A* **78** 85 (1993)
286. M P Anisimov, V G Kostrovskii, M S Shtein *Kolloid. Zh.* **40** 116 (1978) [b]
287. Z Alexandrowicz *J. Phys. A* **26** L655 (1993)
288. Y Efendiev, M R Zachariah *Chem. Eng. Sci.* **56** 5763 (2001)
289. M Z Jacobson, R P Turco, E J Jensen, O B Toon *Atmos. Environ.* **28** 1327 (1994)
290. C-Y Wu, P Biswas *Aerosol Sci. Technol.* **28** 1 (1998)
291. A J Peshty, R C Flagan, J H Seinfeld *J. Colloid Interface Sci.* **91** 525 (1983)
292. J R Brock, P J Kuhn, D Zenavi *J. Aerosol Sci.* **17** 11 (1986)
293. K Hämeri, M Kulmala *J. Chem. Phys.* **105** 7696 (1996)
294. M Wilck, K Hämeri, F Stratmann, M Kulmala *J. Aerosol Sci.* **28** (Suppl. 1) 171 (1997)
295. M Wilck, K Hämeri, F Stratmann, M Kulmala *J. Aerosol Sci.* **29** 899 (1998)
296. H Lihavainen, Y Viisanen *J. Phys. Chem. B* **105** 11 619 (2001)
297. M P Anisimov, S N Vershinin, in *Proceedings of 3rd International Aerosol Conference, Kyoto, 1990* Vol. 1, p. 205
298. V Mikheev, N Laulainen, S Barlow, M Knott, I Ford *J. Chem. Phys.* **113** 3704 (2000)
299. K Hämeri, M Kulmala, E Krissenel, G Kodenev *J. Chem. Phys.* **105** 7683 (1996)
300. D I Zhukhovitskii *Zh. Fiz. Khim.* **67** 1962 (1993) [e]
301. J Martens, H Uchtmann, F Hensel *J. Phys. Chem.* **91** 2489 (1987)
302. C F Delale, G E A Meier *J. Chem. Phys.* **98** 9850 (1993)
303. J W P Schmelzer, J Schmelzer Jr *J. Chem. Phys.* **114** 5180 (2001)
304. I Ford, J Barrett, M Lazaridis *J. Aerosol Sci.* **24** 581 (1993)
305. M Villarica, M J Casey, J Goodisman, J Chalken *J. Chem. Phys.* **98** 4610 (1993)
306. V Kalikmanov *Phys. Rev. E* **55** 3068 (1997)
307. D I Zhukhovitskii *Zh. Eksp. Teor. Fiz.* **113** 181 (1998) [f]
308. D I Zhukhovitskii *Zh. Eksp. Teor. Fiz.* **109** 1 (1996) [f]
309. P ReintenWolde, D W Oxtoby, D Frenkel *J. Chem. Phys.* **111** 4762 (1999)
310. A Muller *Angew. Chem.* **114** 1210 (2002)
311. D V Fedoseev, B V Deryagin, I G Varshavskaya, A S Semenova-Tyan-Shanskaya *Kristallizatsiya Almaza* (Crystalisation of Diamond) (Moscow: Nauka, 1984)
312. D V Fedoseev *Almaz v Elektronnoi Tekhnike* (Diamond in Electronics) (Moscow: Energoatomizdat, 1990)
313. G P Vdovykin *Byull. Mosk. O-va Isp. Prir., Otd. Geol.* **66** (2) 87 (1991)
314. V P Meleshko *Zh. Strukt. Khim.* **40** 21 (1999) [l]
315. H Boukari, M E Briggs, J N Shaumeyer, R W Gamman *Phys. Rev. Lett.* **65** 2654 (1990)
316. F Zhong, H Meyer *Phys. Rev. E* **51** 3223 (1995)
317. J Straub, L Eicher, A Haupt *Phys. Rev. E* **51** 5556 (1995)
318. A L Ivanovskii *Usp. Khim.* **68** 119 (1999) [*Russ. Chem. Rev.* **68** 103 (1999)]
319. V P Skripov, M Z Faisullin *Zh. Fiz. Khim.* **75** 670 (2001) [e]
320. U Gasser *Science* **292** 258 (2001)
321. M P Anisimov, V G Kostrovskii, M S Shtein *Kolloid. Zh.* **40** 317 (1978) [b]
322. V G Baidakov, A M Kaverin, V P Skripov *Kolloid. Zh.* **42** 314 (1980) [b]
323. D Kashchiev *J. Chem. Phys.* **76** 5098 (1982)
324. M P Anisimov, S N Vershinin, A A Aksenov, A M Sgonnov, G L Semin *Kolloid. Zh.* **49** 842 (1987) [b]
325. I J Ford *Phys. Rev. E* **56** 5615 (1997)
326. M P Anisimov, A G Cherevko *J. Aerosol Sci.* **16** 97 (1985)
327. M P Anisimov, A G Cherevko *Izv. Sib. Otd. Akad. Nauk SSSR* **4** (2) 15 (1982)
328. M P Anisimov, A V Taylakov *J. Aerosol Sci.* **20** 1063 (1989)
329. I J Ford *J. Chem. Phys.* **105** 8324 (1996)
330. M P Anisimov, A G Nasibulin, I N Shaimordanov *J. Aerosol Sci.* **30** (Suppl. 1) 315 (1999)
331. M P Anisimov, A G Nasibulin, S D Shandakov *J. Chem. Phys.* **112** 2348 (2000)
332. M P Anisimov, A G Nasibulin, S D Shandakov, I N Shaimordanov *Kolloid. Zh.* **63** 149 (2001) [b]
333. M P Anisimov, P K Hopke, J Terry, S Shandakov, V A Pinaev *Aerosol Sci. Technol.* **29** 547 (1998)
334. I Langmuir *Chem. Rev.* **13** 147 (1933)

335. M P Anisimov, I N Shaimordanov, S D Shandakov, in *Abstracts of Reports of the 19th Annual AAAR Conference, St. Louis, MO, 2000* 11P03
336. R C Reid, J M Prausnitz, T K Sherwood *The Properties of Gases and Liquids* (New York: McGraw Hill, 1977)
337. M P Anisimov, P K Hopke, S D Shandakov, I I Shvets *J. Chem. Phys.* **113** 1971 (2000)
338. M P Anisimov, A G Nasibulin, S D Shandakov, I I Shvets, L V Timoshina *Opt. Atmos. Okeana* **9** 1573 (1996)
339. V P Skripov *High Temp.* **31** 448 (1993)
340. V P Skripov *Zh. Fiz. Khim.* **68** 1382 (1994) [e]
341. P G Debenedetti, in *Physical Chemistry of Aqueous Systems* (Eds H J White Jr, J V Sengers, D B Neuron, J C Bellows) (New York: Wallingford, 1995) p. 339
342. P G Debenedetti, M C D Antonio *AIChE J.* **34** 447 (1988)
343. M P Anisimov, A G Nasibulin, L V Timoshina *Kolloid. Zh.* **59** 437 (1997) [b]
344. M Anisimov, P Hopke *J. Phys. Chem. B* **105** 11683 (2001)
345. V N Chukanov, A P Kuligin *Teplofiz. Vys. Temp.* **25** (1) 70 (1987) [m]
346. V Chukanov, B Korobitsyn, A Zvir *Kinetika Nukleatsii v Rastvorakh $LiClO_4$ v Vode, Etanole i Atsetone* (Kinetics of Nucleation in $LiClO_4$ Solutions in Water, Ethanol and Acetone), Sverdlovsk, 1987; article deposited in the VINITI, No 2172-V87 (Moscow, 1987)
347. J Koropchak, S Sadain, X H Yang, L-E Magnusson, M Heybroek, M P Anisimov, S Kaufman *Anal. Chem.* **71** 386A (1999)
348. G Wilemsky, B E Wyslouzil, M Gauthier, M B Frish, in *Nucleation and Atmospheric Aerosols* (Eds N Fukuta, P E Wagner) (Hampton, VA: Deepak, 1992) p. 11
349. P E Wagner, R Strey, Y Viisanen, in *Nucleation and Atmospheric Aerosols* (Eds N Fukuta, P E Wagner) (Hampton, VA: Deepak, 1992) p. 27
350. J A Fisk, J L Katz *J. Chem. Phys.* **104** 8649 (1996)
351. A Nasibulin, E Kaupinen, D Brown, J Jokiniemi *J. Phys. Chem. B* **105** 11 067 (2001)
352. M Anisimov, S Shandakov, V Pinaev, I Shvets, P Hopke, in *Nucleation and Atmospheric Aerosols 2000* (Eds B Hale, M Kulmala) (Melville, NY: AIP, 2000) p. 315
353. M Anisimov, P Hopke, S Shandakov, P Seraphimov In *Abstracts of Reports of the 20th Annual AAAR Conference, Portland, OR, 2001* p. 133
354. V G Yurkin *Usp. Khim.* **64** 237 (1995) [*Russ. Chem. Rev.* **64** 223 (1995)]
355. N A Fuks, A G Sutugin *Usp. Khim.* **37** 1965 (1968) [*Russ. Chem. Rev.* **37** 855 (1968)]
356. K-W Tu *J. Aerosol Sci.* **13** 363 (1982)
357. Z Q Zhang, B Y H Liu *Aerosol Sci. Technol.* **13** 493 (1990)
358. J A Koropchak, C L Heenan, L B Allen *J. Chromatogr., A* **736** 11 (1996)
359. J Koropchak, L-E Magnusson, M Heybroek, S Sadain, X Yang, M P Anisimov *Adv. Chromatogr.* **40** 275 (2000)
360. W T McDermott, R C Octovic, M R Stolzenburg *Aerosol Sci. Technol.* **14** 278 (1991)
361. K-H Ahn, B Y H Liu *J. Aerosol Sci.* **21** 263 (1990)
362. A Rebours, D Boulaud, A Renoux *J. Aerosol Sci.* **27** 1227 (1996)
363. F E Kruis, G Fissan, A Peled *J. Aerosol Sci.* **29** 511 (1998)
364. M Vardelle, A Vardelle, P Fauchais, C Trassy, P Proulx *Colloq. Phys.* **51** (C5) 171 (1990)
365. J-F Bilodeau, P Proulx *J. High Temp. Chem. Proc. (Colloq., Suppl. 3)* **1** 141 (1992)
366. S L Girshik, C-P Chiu *Plasma Chem. Plasma Process* **9** 355 (1989)
367. J F Bilodeau, P Proulx *Aerosol Sci. Technol.* **24** 175 (1996)
368. S V Joshi, Q Liang, J Y Park, J A Batdorf *Plasma Chem. Plasma Process.* **10** 339 (1990)
369. W A de Heer *Rev. Mod. Phys.* **65** 611 (1993)
370. T Seto, M Shimada, K Okuyama *Aerosol Sci. Technol.* **23** 183 (1995)
371. H D Jang, J Jeong *Aerosol Sci. Technol.* **23** 553 (1995)
372. M Ya Gen, Yu I Petrov *Usp. Khim.* **38** 2249 (1969) [*Russ. Chem. Rev.* **38** (1969)]
373. M S El-Shall, W Slack, W Vann, D Kane, D Hanley *J. Phys. Chem.* **98** 3067 (1994)
374. M S El-Shall, S Li, D Graiver, U Pernisz *Nanotechnology, Mol. Des. Mater.* (*ACS Symp. Ser.*) **622** 79 (1996)
375. M S El-Shall, D Graiver, U Pernisz, M I Baraton *Nanostruct. Mater.* **6** 297 (1995)
376. T Rajh, O I Micic, A J Nozik *J. Phys. Chem.* **97** 11999 (1993)
377. R F Khairutdinov, N A Rubtzova, S M B Costa *J. Lumin.* **68** 293 (1996)
378. P V Kamat, N M Dmitrijevic *Proc.-Electrochem. Soc.* **6** 90 (1988)
379. A Green, A Mills *J. Photochem. Photobiol., A* **64** 211 (1992)
380. R Palmans, A J Frank *J. Phys. Chem.* **95** 9438 (1991)
381. N D Zhuravlev, V I Roldugin, A P Tikhonov *Kolloid. Zh.* **61** 322 (1999) [b]
382. S P Gubin, I D Kosobudskii *Usp. Khim.* **52** 1350 (1983) [*Russ. Chem. Rev.* **52** 766 (1983)]
383. S P Kozinkin, S P Gubin *Neorg. Mater.* **30** 678 (1994) [n]
384. B V Derjagin *J. Chem. Phys.* **61** 3665 (1974)
385. S P Pogorelova, G M Plavnik, A P Tikhonov, T P Pudryaeva *Kolloid. Zh.* **61** 100 (1999) [b]
386. B S Bal'zhinimaev *Ros. Khim. Zh.* **45** 59 (2001) [k]
387. B A Nikitin *Izbrannye Trudy. Issledovaniya po Khimii Blagorodnykh Gazov* (Selected Works. Investigations on the Chemistry of Noble Gases) (Moscow, Leningrad: Academy of Sciences of the USSR, 1956)
388. H M Powell, in *Inclusion Compounds* (Eds J L Atwood, J E D Davies, D D MacNicol) (London: Academic Press, 1984) p. 1
389. J H Van der Waals, J C Platteuw *Adv. Chem. Phys.* **2** 1 (1959)
390. R-M Barrer, W I Stuart *Proc. R. Soc. London, Ser. A* **243** 172 (1957)
391. J-M Lehn *Supramolecular Chemistry. Concepts and Perspectives* (Weinheim: VCH, 1995)
392. C J Pedersen, J-M Lehn, D J Cram *J. Inclusion Phenom.* **6** 337 (1988)
393. V M Vorotyntsev, V M Malyshev *Usp. Khim.* **67** 87 (1998) [*Russ. Chem. Rev.* **67** 81 (1998)]
394. Yu F Makagon, A A Trofimuk, V P Tsarev, N V Cherskii *Geolog. Geofiz.* **4** 3 (1973)
395. M P Anisimov, S D Shandakov, A G Nasibulin, Yu I Polygalov *Khim. Inter. Ustoich. Razvitiya* **8** 465 (2000) [o]
396. F Okino, H Touhara *Comprehensive Supramolecular Chemistry* Vol. 7 (Eds J L Atwood, J E D Davies, D D MacNicol, F Vögtle) (Oxford: Pergamon Press, 1996) p. 5

[a] — *Dokl. Chem. (Engl. Transl.)*
[b] — *Colloid J. (Engl. Transl.)*
[c] — *Chem. Phys. Rep. (Engl. Transl.)*
[d] — *Tech. Phys. Lett. (Engl. Transl.)*
[e] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[f] — *J. Exp. Theor. Phys. (Engl. Transl.)*
[g] — *Russ. J. Electrochem. (Engl. Transl.)*
[h] — *Phys. Solid State (Engl. Transl.)*
[i] — *Physics-Uspekhi (Engl. Transl.)*
[j] — *Tech. Phys. (Engl. Transl.)*
[k] — *Mendeleev J. (Engl. Transl.)*
[l] — *Russ. J. Struct. Chem. (Engl. Transl.)*
[m] — *High Temp. (Engl. Transl.)*
[n] — *Inorg. Mater. (Engl. Transl.)*
[o] — *Chem. Sust. Develop. (Engl. Transl.)*