Nucleation research progress for description of atmospheric aerosol dynamics. 1. Experiment and semiempirical approaches

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Using the experimental and semiempirical approaches, the topology of the nucleation rate surface near the triple point is determined. Some general requirements to the vapor nucleation experiments are formulated. The most important problem is now the measurement of a single-channel nucleation rate for two- and higher channel nucleation. Measurements of the single-channel nucleation rate are of key importance as compared with the experimental data on the nucleation rate and single-channel nucleation theory.

Introduction

The agreement between the experimentally measured nucleation rates in the supersaturated vapor and predictions by modern theories is observed only for a limited number of experimental data.[1] It should be noted that now it is possible to obtain quite close tilts of experimental isotherms of nucleation rates in the range of experimentally achievable conditions, but the temperature trends of these results are usually different. Therefore, to reach an agreement between the theory and experiment, linear corrections have recently been introduced into the theoretical equation for the nucleation rate.[2] Such corrections make theories essentially parametric and do not guarantee their correspondence to the reality beyond the range of experimental data, to which the theory has been normalized. Note that the linearity of corrections to the nucleation rate was not checked in a rather wide (wider then 100 degrees) range of nucleation temperatures. The possibility of a rather simple parameterization gives the impression that the modern theory is close to completeness, that is, it is necessary to focus efforts on the determination of a "final" correction to the theory, after which the harmony will be achieved between the nucleation theory and experiment. By now, only first attempts have been undertaken to take into account the effect of the total pressure and properties of an individual carrier gas on the nucleation rate. Obviously, the consideration of these effects makes the problem of corrections more complicated, at least, multidimensional.

Within a close consideration, to get the agreement between the theory and experiment, it is still necessary to overcome some basic problems, unsolved as yet. Actually, it is quite obvious that zero limits for the nucleation rates are the phase equilibrium lines in the corresponding diagrams. In other words, nucleation rate surfaces of new phases originate from the phase equilibrium lines. Hence, it is clear that the success in the development of the nucleation theory certainly depends on advances in the development of the phase equilibrium theory from the first principles. The prediction (drawing) of qualitative equilibrium diagrams from the first principles remains an unsolved problem yet. From this it follows that the development of the general theory of nucleation should be expected only after a significant progress in the theoretical description of the dynamics of multiple bodies and the construction of the general (nonparametric) theory of the equilibrium diagrams. The approximation of the average field and the currently popular approximation of the density functional do not provide a sufficient basis for construction of the nucleation theory.[1]

Now we can hope only for the creation of parameterizations for the classes of systems having reducible equilibrium diagrams.[1] By this we mean the topologically homotypic diagrams, reducible to the same universal diagram through re-scaling. However, this condition is necessary but, with a high probability, not sufficient. It remains unclear, for example, whether there is universal equation for nucleation rates or, rather, universal equations for the exponent factor and the exponent itself in the equation for the nucleation rate. Formally, there are some universal equations, but the practice shows that their universality is limited and does not allow obtaining rather accurate values for the nucleation rates in practically significant cases.

One of the most serious problems is now the critical analysis of the most axiomatic statements, used to interpret experimental data and to obtain theoretical constructions. However, today there are only some prerequisites for such analysis. The compilation of the complete set of axiomatic

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statements, sufficient for the development of the closed nucleation theory, will remain an urgent problem for a rather long time.

This paper analyzes the adequacy of some axiomatic statements, used by now to construct new versions of the nucleation theory and to interpret experimental data. Obviously, the critical update of these statements will facilitate the simulation of atmospheric aerosol dynamics. In addition, this paper discusses some details of the nucleation model, which are already out-dates, and shows new approaches of the adequate (up to date) theoretical description of atmospheric nucleation, as well as presents the requirements to modern nucleation experiments.

Change of the phase state in critical nuclei

The current sensitivity of the most experimental devices, intended for measurements of the nucleation rates in supersaturated vapor, is sufficient for detecting the change of the phase state in condensate critical nuclei. Let us justify such measurements briefly. Actually, according to the definition of the first-order phase transition, the first temperature derivative of the chemical potential undergoes a discontinuity at the transition temperature. The difference of the chemical potentials of the initial and new phases enters the equation for the nucleation rate, along with the contribution from the condensate/vapor interface. From this it follows that the free energy of formation of a condensate critical nucleus has a discontinuity of the first derivative, and, correspondingly, the nucleation rate surface for condensate nuclei near the phase transition must lose its monotonicity and continuity.

The opposite signs of the volume and surface terms of the free energy of a critical nucleus may lead to the situation when the discontinuities of the first derivatives of these terms may appear to have same absolute values. This equality means that non-monotonicity of the nucleation rate surface is not fulfilled at only one point. Hence it follows that the detection of singularity on the nucleation rate surface allows the change of the phase state in critical nuclei to be identified, but it is necessary to take into account the probability of hitting a single point (in the case of the two-channel nucleation), where the discontinuities of the derivatives compensate for each other.

It is obvious that it is possible to detect the alternation of the phase state of critical clusters, rather than the phase transition itself. Since the nucleation conditions overlap because of the possible appearance of metastable states of every condensate phase, then there is some range of parameters, in which the nucleation rate is irregular due to the competition between probabilities of appearance of both of the condensate phases.

The experimental results, illustrating the above-said, are presented below. Figure 1 shows the isotherms of the nucleation rates of 1,3 propanediol in the SF_6 medium.[3]

Isotherms, following with the interval of 2 to 3 degrees, clearly separate into two series with respect to an isotherm with the nucleation temperature at 334.2 K. This isotherm passes through the break in the monotonicity and continuity of the nucleation rate surface.
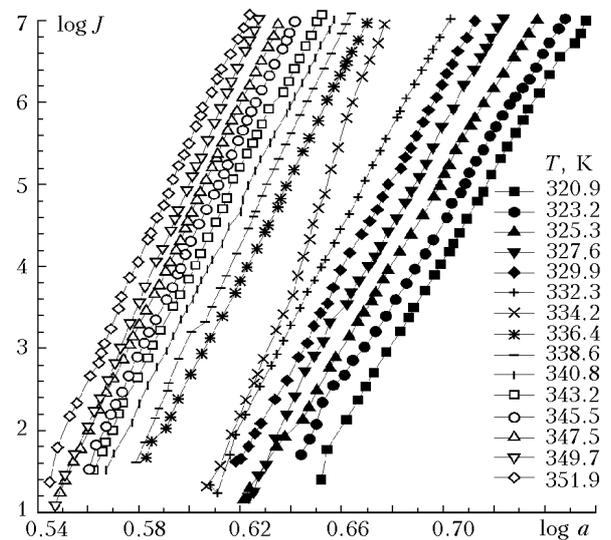

Fig. 1. Nucleation rates (J) of 1,3 propanediol in the SF_6 medium as functions of the vapor activity a at the total pressure $P = 0.30$ MPa.

Figure 2 shows the cross section of experimental isotherms at two constant values of the rate. One can clearly see two breaks in the monotonicity of the nucleation rate surface. The cross sections are shown for two values of the total pressure. The shift in the temperatures of phase transitions at different pressure illustrates the effect of the carrier gas pressure. It is worthy to note that if the step of the nucleation temperature exceeds 5 degrees, the break in monotonicity can be missed or excluded from a series as a mistake in the general temperature behavior. The measurement of less than five to six points per a decimal exponent in the nucleation rate also may lead to an unjustified wish to exclude one or two points, "falling out from regular behavior for unknown reasons."

Nonobservance of recommendations mentioned above will lead to the loss of data on physical effect and, obviously, decrease the reliability of conclusions. The detection of phase transitions in critical nuclei becomes technically simpler in the case of isobaric measurement of the nucleation rate. The most reliable way of detecting the change in the phase state of nuclei can be the scanning of a system at a constant partial vapor pressure with the nucleation temperature drift of about tenths of a degree per minute. However, it is worth conducting a real experiment in the range of easily detectable aerosol concentrations, as in Ref. 4. The range of

detectable concentrations expands continuously, which allows us to hope for an increase in the efficiency of the isobaric measurements of the nucleation rate. It is expected that, after the first studies[3,6,9,12,etc.] of the determination of the influence of a phase transition in the condensed phase on the topology of nucleation rate surface, new results will be reported. This phenomenon obviously calls for a more detailed investigation.
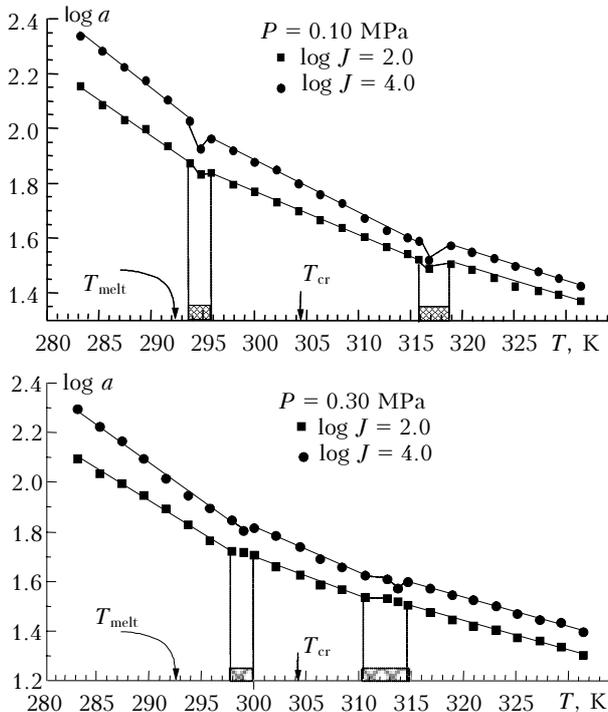

Fig. 2. Shifts of two-phase transitions with respect to the melting point T_{melt} and the critical temperature T_{cr} on the cross sections of the nucleation rate surface of glycerin vapor for different vapor activity at the total pressure of 0.10 and 0.30 MPa.

Note that the visual analysis of experimental data may miss a singularity. It is commonly known that the application of differential characteristics increases the sensitivity of the surface analysis. The main problem is the presence of random errors, which are inevitable companions of even very accurate measurements, as for example, in the paper by Strey, Viisanen, and Wagner.[5] For a more accurate analysis of the data, it is possible to use the condition of continuity and monotonicity of functions, known from the mathematical analysis. For the surface, corresponding to a function of two variables $F(x_1, x_2)$, at $F(x_1, x_2) = $ const this condition has the form

$$\left(\frac{dF}{dx_1}\right)_{x_2} = \left(\frac{\partial F}{\partial x_1}\right)_{x_2} + \left(\frac{\partial F}{\partial x_2}\right)_{x_1}\left(\frac{\partial x_2}{\partial x_1}\right)_F = 0.$$

This equation can be presented in the form

$$\left(\frac{dF}{dx_1}\right)_{x_2} = \left(\frac{\partial F}{\partial x_1}\right)_{x_2} + \left(\frac{\partial F}{\partial x_2}\right)_{x_1}\left(\frac{\partial x_2}{\partial x_1}\right)_F = A,$$

where A is introduced as a criterion of monotonicity and continuity of the function. The criterion A will have a nonzero value along the singularity line on the surface. It can be shown quite easily that for $F(x_1, x_2, \ldots, x_n)$ the criterion can be presented in the matrix form.[6] For any set of experimental data, the criterion value, exceeding the triple standard deviation (the triple value of the standard deviation is accepted as a minimum value of a reliable signal, as follows from the principles of signal and noise analysis), can be used as a proof of the presence of the surface singularity or an uncontrollably varying parameter in the measuring device.

Figure 3 shows the values of the criterion A for the n-pentanol–water binary system obtained using the data from Ref. 5.
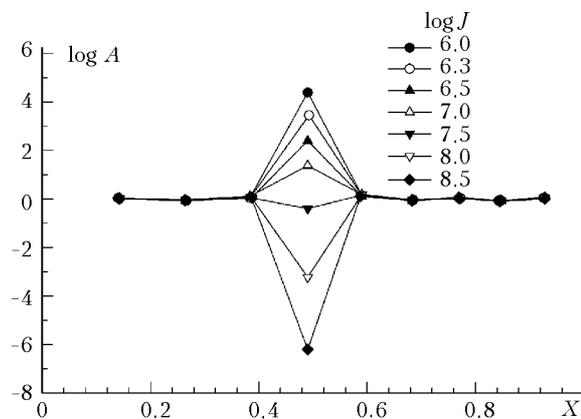

Fig. 3. Criterion A as a function of the mole fraction X obtained using the results from Ref. 5.

In Ref. 5, the average value of the criterion $\langle A \rangle$ is equal to 0.01 at the rms deviation of the experimental values equal to 0.06. At the mixture composition $X \approx 0.5$, pronounced deviations from the zero value of A are clearly seen. They are indicative of the nonmonotonic nucleation rate surface in a system with limited solubility of components in the condensed state. This singularity was missed in Ref. 5, where the experimental values were mistakenly approximated by a smooth curve. The criterion A may take positive and negative values. This indicates that, at some constant value of the nucleation rate, the criterion can have a local zero value. Obviously, to avoid a wrong conclusion on monotonicity and continuity of a function, it is needed to check the criterion at several (no less than two) constant values of the nucleation rate or two different directions in the space of parameters for a given point.

It should be emphasized that the criterion proposed in Ref. 6 can be used for analysis of data with any number of variables (at any dimensionality of the space of parameters). The criterion provides for the dimensionless estimate of noise in experimental data and the estimate of the dimensionless standard deviation.

Test on checking the experimental nucleation systems and the effect of total pressure in a nucleation medium

Until recently, no reference systems have existed for test measurements with the experimental devices intended for measuring the nucleation rate. The reference system to test experimental devices for measurement of the nucleation rate in supersaturated vapor was selected at the International Seminar "Nucleation Experiments — State of the Art and Future Development," held in Prague (1995, Czech Republic).[7]

The n-pentanol–helium mixture was selected as a test system at the Seminar. But the existing measurements of this system were insufficient to be used as calibrating values; therefore, the nucleation rates of n-pentanol and helium were measured in several laboratories. A sample of n-pentanol from the same vessel with n-pentanol, bought in Germany,[8] was used for all measurements. All the results measured were approximated by a classical formula with a linear correction for the total pressure in the nucleating system.[8] The approximating dependence was recommended for practical tests of the measuring devices. With time the approximating equations will, certainly, be refined, but already now this equation can give an idea on the relation between data obtained by different authors with the use of different measurement systems under different nucleation conditions.

Note that the effect of the total pressure on the nucleation rate and the effects from the presence of a gas in the system are not still recognized by some investigators (see, for example, Refs. 2 and 5). But the effect was certainly observed by several independent teams (for example, Refs. 9 and 10), and most investigators already have no doubts that the carrier gas should be considered as a second component, affecting the nucleation rate.

For example, the nucleation of glycerin vapor in the carbon dioxide medium was considered in Ref. 9. Two phase transitions in condensate critical nuclei were used as markers (see Fig. 2). as a result, it was found that the glycerin melting temperature increases with the increase of pressure, and this was reasonable from the viewpoint of theory of binary solutions. The temperature of the second phase transition approached the temperature of the critical point of the pure carrier gas, that is, decreased. The opposite trend of the temperatures of phase transitions indicates that the inevitable error of experimental determination of the temperatures in the system was much smaller than the effect of the total pressure, generated by the second component — carbon dioxide, in these experiments. This result is a direct proof of the effect of the total pressure in the nucleating system on the nucleation rate. Hence it follows that the nucleation rate of water vapor, for example, in the stratosphere, must differ significantly from that at the normal atmospheric pressure with the identical values of the water vapor partial pressure and nucleation temperature.

Sharafutdinov with co-workers[10] observed mixed argon–silane complexes in a pulsed supersonic jet, which confirms the participation of the gas in formation of nuclei of the new phase and transfers the gas from the role of a thermostat, as was believed earlier, to the role of a full participant of the nucleation process. This, naturally, leads to the dependence on the gas concentration (partial pressure), as should follow from the theory of nucleation of a binary mixture. In this case, we have to establish that the problem referred to as the gas pressure effect arose, because the role of the gas, accompanying the aerosol formation, was reduced, without any justified grounds, to the role of a thermostat medium. Because of the wrong assumption about the role of the carrier gas in nucleation, one should carefully consider the conclusions of works based on the old axiomatic basis.

Summing up these results, we can conclude that today the use of the nucleation theory in the one-component approximation to describe the vapor nucleation in a gas medium already requires special justification and additional estimates in order to determine the range of parameters, within which this approximation is applicable satisfactorily accurate.

Multichannel nucleation in vapor

It is obvious that it will be a mistake to use the single-channel approximation for description of the multichannel nucleation (nucleation through several saddle-points on the free energy surface of critical nuclei of a new phase). The ideas of multichannel nucleation are not still widely used in practice of aerosol formation studies; therefore, let us consider briefly the preconditions for its appearance. Turn our attention to the concept of semiempirical construction of nucleation rate surfaces using the equilibrium diagrams.[11] It is easy to understand that the nucleation rate surfaces, rising, usually, from several phase equilibrium lines, form multilayer constructions. This situation takes place in many cases, because practically significant investigations of nucleation are carried out near triple points, at which a two-layer nucleation rate surface realizes.

The two-layer rate surface near a triple point was constructed in Ref. 12 for the first time. Its existence was confirmed experimentally in Ref. 13, whose authors used the measurements of the aerosol disperse composition. The main idea assumed the consideration of the widely known difference in the probability of accommodation of a molecule upon the collision with surfaces of particles of the same substance, but being in different phase states. It inevitably follows from here that the rate of growth of particles having different phase states will be different, which must lead to formation of particles of different size. That is, simple measurements of the disperse composition on completion of the condensation growth of particles should allow one to

judge on the difference in the initial phase state of particles. The pronounced bimodal distribution of glycerin particles, obtained in Ref. 13, indicates that the initial phase state of particles remained the same by the completion of the condensation growth, because the change of the phase state would inevitably lead to the coalescence of both peaks (or, what is the same, to filling the dip between the peaks). The measurement of the aerosol disperse composition is promising for the measurement of nucleation rates in an individual nucleation channel. This allows one to determine the average numbers of molecules in critical nuclei in one- and multi-component systems, as was proposed earlier.[14,15]

The determination of singularities on the nucleation rate surface is of principal significance, because they are indicators of two-channel nucleation, for which the single-channel approximation can be used only after identification of individual surfaces for each nucleation channel. However, it should be recognized that the methods of separation of the nucleation channels are still in the embryo state. The only promising method now is that based on measurement of the aerosol disperse composition, as in Ref. 13. Ideally, it seems promising to separate aerosol in different phase states based on the difference in the refractive index. The difference in the refractive index introduces changes into the signal of Rayleigh scattering from particles and, correspondingly, can be used for a separate measurement of particles being in different phase states, but this approach was not applied to practical measurements yet.

It should be emphasized that an up-to-date experimental device, intended for the measurements of nucleation rates in a vapor, should meet certain requirements, namely:

1) it should be checked with measurements of a test system (now, n-pentanol in helium);

2) it should have sensors and algorithms for separation of each of the nucleation channel;

3) it should have a short (1–2 min) measurement cycle for data corresponding to one experimental point;

4) it should be sensitive enough for detection of a phase transition or incomplete solubility of components in the condensed state;

5) it should have the software for data processing in order:

a) to determine empirically the composition of critical nuclei;

b) to detect a singularity on the nucleation rate surface, etc.

More results, confirming the existence of two nucleation channels near triple points, are presented below.

Experimental proof of the two-channel nucleation near the triple point

The idea of semiempirical construction of nucleation rate surfaces using the equilbrium diagrams leads to the existence of two nucleation rate surfaces near the triple point.[12] Actually, in the case of water everybody knows that the vapor–liquid equilibrium line continues after the triple point as the temperature decreases. This is known as an unstable equilibrium of vapor with overcooled liquid. It is obvious that the triple point is indistinguishable (in the thermodynamic sense) and is only an interception of binary phase equilibrium lines (in the one-component case) and a point corresponding to the conditions of co-existence of three phases. It is logical to assume that the vapor–crystal equilibrium can also be continued after the triple point. In this case, an unstable equilibrium of vapor with an overheated crystal takes place.
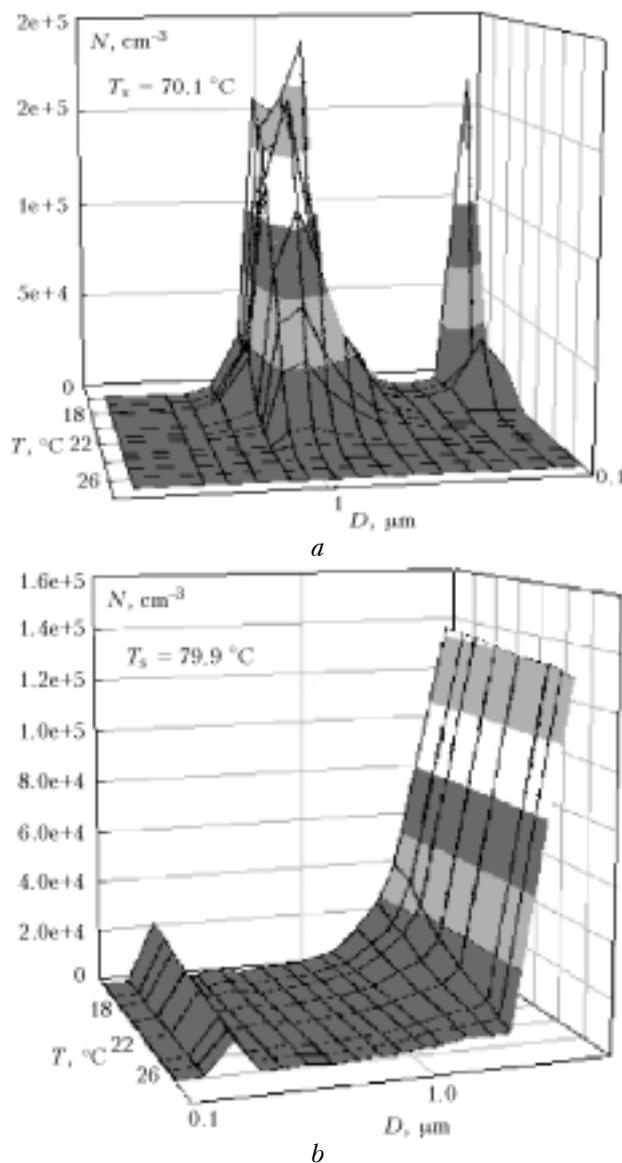

a

b

Fig. 4. Size distribution of glycerin particles as a function of nucleation temperature T for partial pressures at the glycerin vapor saturation temperature $T_s = (70.1 \pm 0.2)$ and (79.9 ± 0.2)°C; D is the particle diameter; N is the relative content of particles.

As was already mentioned, the nucleation rate surfaces are formed by the phase equilibrium lines (including unstable equilibriums). Two equilibrium lines give rise to two rate nucleation surfaces, that is, the nucleation rate surface is two-layer near the triple point. In the general case, the surface is also two-layer in the far vicinity of the triple point, but at the current state of the experimental technology the two-layer character of the surface can be detected only near the intersection line of the surfaces, corresponding to nucleation of nuclei, being in different phase states. This consideration is valid for all triple points, that is, melting points and points of crystal–crystal transition. Each rate surface corresponds to one independent nucleation channel. In Ref. 13 this result was confirmed experimentally. The existence of two independent nucleation channels was shown for glycerin, nucleating near the triple point. In Ref. 16 this result was repeated and extended.

References 13 and 16 are of principle importance for this discussion; therefore, let us mention their basic ideas. As was mentioned above, the probability of attachment is different for vapor molecules (atoms) colliding with particles (in our case, with nuclei), being in different phase states. This leads to different cluster growth rates and the resultant sizes of particles, having different phase state.[13] The existence of two well separated peaks in the size spectrum suggests that the nuclei keep their initial phase state. Figure 4a demonstrates the repeated results of Ref. 13, in which the bimodal spectrum of aerosol was obtained for the glycerin vapor saturated at the temperature of (70.1 ± 0.2)°C.

The saturation temperature of (79.9 ± 0.2)°C (Fig. 4b) causes significantly unequal peaks, which, in combination with the results shown in Fig. 4a, suggest that the isotherms of crystal nucleation rates have a maximum as approaching the conditions of vapor–crystal spinodal decomposition. The topology of nucleation rate surfaces for this case is shown schematically in Fig. 5.

The laminar flow was established at the temperature of 91.2°C in all the experiments, which made the vapor unsaturated. The range of variation of condenser temperatures was 15–28°C with a step of 1°C for each individual measurement of the aerosol size spectrum. At a condensation temperature of 60°C, detected particles were absent (see Ref. 16).

In the analysis of this experiment, the influence of the carrier gas on nucleation was believed constant and did not determined. The results of Ref. 16 confirm that simple measurements of the aerosol disperse composition allow detecting the existence of two phase states of critical nuclei of the condensate, produced from the vapor near the triple point. Earlier, the bimodal aerosol distribution, for example during the nucleation in magnesium vapor near the triple point, was found in Ref. 17, but the authors did not attribute the obtained result to the existence of two rate nucleation surfaces, arising near the triple point.

Fig. 5. Nucleation rate surface for drops (gray color) and crystal particles (dark-gray), shown schematically based on the data of Fig. 4; t is the triple point.

Continuum of topologies of nucleation rate surfaces

It is obvious that the consideration of a multilayer nucleation rate surface in the approximation of one-layer (single-channel) nucleation is absolutely incorrect, that is, it gives rise to large problems and does not solve the problem of agreement between theory and experiment. Let us consider the topology of the rate surface near the triple point.

Consider a fragment of the equilibrium diagram near the triple point t, shown in Fig. 6.
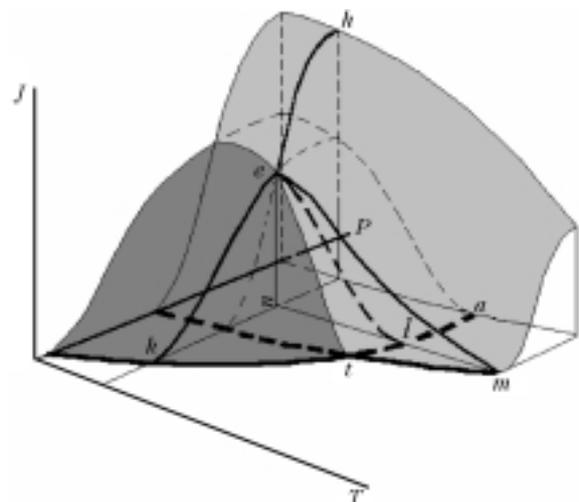

Fig. 6. Nucleation rate surfaces of one-component vapor. Vapor–crystal (kt) and vapor–liquid (km) equilibrium lines.

The vapor–crystal (kt) and vapor–liquid (km) equilibrium lines are continued to the range of existence of third equilibrium phases (Fig. 6). The light-gray surface is the nucleation rate surface for liquid-droplet nuclei. The dark-gray surface corresponds to the nucleation rate of crystal nuclei. The surfaces intersect along the et line. The cross section of the surfaces gives the upward going branch ke (and its dashed continuation up to the conditions of spinodal decomposition) for the crystal nucleation rate. The nucleation rate of liquid-droplet nuclei is shown by the eh line (and its continuation to the zero rates). If the saturated vapor at the point m is cooled at a constant pressure, then it is possible to obtain a liquid-droplet aerosol. At a temperature corresponding to the point l and below, the formation of crystal nuclei begins. With the decrease of temperature, the nucleation rates of both phases increase, but for crystals this increase is faster, and therefore at the point e the rates of formation of liquid-droplet and crystal nuclei become equal. If the phase state of nuclei keeps during the following condensation growth, then it is easy to understand that the size of aerosol particles will be different, as was already mentioned above, due to the known difference in the coefficients of accommodation of molecules on surfaces with different phase states.

In the zero temperature limit the vapor pressure becomes zero, and the question about nucleation in vapor disappears. Hence, it follows that the nucleation rate in the vapor above the spinodal decomposition line increase with the temperature decrease from the critical one, achieves the maximum, and again decreases to zero in the zero temperature limit. If we take into account that the nucleation rate under conditions of spinodal decomposition is equal to the exponent in the equation for the nucleation rate, then for the nucleation in vapor the exponent varies from zero to the maximum and then to zero at the temperature trend from the critical point to zero thermodynamic temperature, while for the nucleation in condensed phases the exponent, probably, only increases with the temperature decrease. However, this statement is still to be checked. The possibility of checking this appears at simultaneous measurements of the homogeneous and heterogeneous nucleation, as was shown for the ion-induced nucleation in Ref. 18.

The nucleation rate surface of a binary vapor can be drawn in the four-dimensional space JTa_1a_2, where J is the nucleation rate; T is temperature; a_1 and a_2 are the activities of the component vapor. Consider a PX-diagram of a binary solution at a fixed temperature T, the total pressure P in the system, and the composition X. In the simplified case, we have a cigar-shaped phase diagram (curves mfn and $nrgm$ in Fig. 7).

The nucleation rates of individual components can be shown by the curves nd and mh. At the vapor equilibrium points (n, m), the vapor nucleation rates are zero. The nucleation rates of the components have

the maximum values above the spinodal decomposition points a and b. The points of the maximum nucleation rate of individual components are connected simplistically by the deh straight line, showing the maximum rate of the binary nucleation. The nucleation of the binary vapor with the composition X_0 starts at the point f.

The condensed phase has the composition X_1 at the point r. Every point of the nfm line corresponds to a point on the $nrgm$ line. The $nrgm$ line — equilibrium line of a liquid and two-phase states — is the trajectory of points with the zero nucleation rate, and it must be the boundary of the nucleation rate surface. The nucleation rate surface is bounded by the $hednrgm$ outline (light gray color). Above the spinodal, the composition of the vapor and the condensed phases coincides due to the barrierless transition to the condensed phase. The pressure increase from the point r to the point e gives the vapor nucleation rate line re (this line corresponds to the known composition of critical nuclei) at the constant nucleation temperature T and the vapor initial state X_1. The curve fe is a projection of the curve re in the equilibrium diagram at the composition X_0. The curve fe already bears no information about the state of critical nuclei.
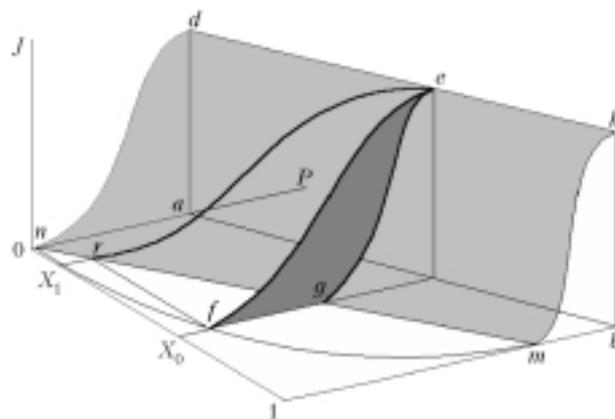

Fig. 7. Nucleation rate surface J for ideal binary solutions: P is the total pressure; X is composition of binary solution.

The construction of the nucleation rate surface in the case of unknown critical nuclei becomes possible, if all the experimental nucleation rates (like the curve re) correspond to the initial composition of the vapor in the equilibrium diagram (for example, fe for the composition X_0). In this case, the points with zero vapor nucleation rate belong to the bottom line of the cigar-shaped diagram. This surface is shown in the JXP coordinates. Obviously, in the JPX coordinates there are two methods of representation of the vapor binary nucleation rates, namely the one, which requires the composition of critical nuclei to be known and the other that deals with unknown composition. The nucleation rate surface with unknown composition of the critical nuclei is shown in the $hednfm$ outline (see Fig. 7) for the ideal

binary solution. In the experiment, the composition of nuclei is usually unknown and the resulting nucleation rate of a binary system is assigned to the initial composition of the system.

The nucleation of a binary system with partial mutual solubility of components was discussed in Ref. 19. The authors showed that in this case the two-channel nucleation takes place, as was shown earlier in Ref. 20. A novelty here is the assumption that each of the nucleation channel corresponds to a rate surface for solutions with a cigar-shaped diagram taken as an example. In the linear approximation, the authors assume the rule of addition of the nucleation rates of both channels, similar to the lever rule for solutions. The linearity of addition of the nucleation rates is not proved and thus it is to be checked experimentally. A significant result here is justification of the possibility of obtaining the isotherm of the nucleation rate with local maxima, which in no ways follows from the classical theory of nucleation. This result can be illustrated by the experimental dependence of the nucleation in the n-pentanol–argon system on the activity of the n-pentanol (Fig. 8) or pentanol–SF_6 vapor.[19]
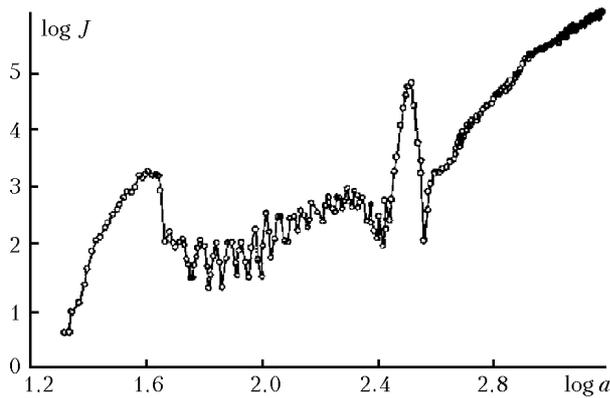
At the temperature, intermediate between the critical temperatures of components, the equilibrium diagram becomes drop-shaped, which again corresponds to the single-channel nucleation. Then the nucleation remains single-channel up to the highest temperature of the critical line.

From the above simplified example, it is seen that with the increasing temperature the continuum of nucleation rates is observed, in which the single-channel variant of nucleation should be connected with the two-channel one and pass from the two-channel to the single-channel nucleation again. In any handbook on equilibrium diagrams, it is stated that the practically significant systems usually have several peritectic or eutectic points. Moreover, this may be complicated by formation of new stable structures (for example, clathrates) or chemical compounds. As seen from this example the modern practice of using the single-channel version of the nucleation theory is wrong in the most cases. Obviously, it is necessary to develop the versions allowing the equations for nucleation rates of systems to be connected with the variable number of nucleation channels.
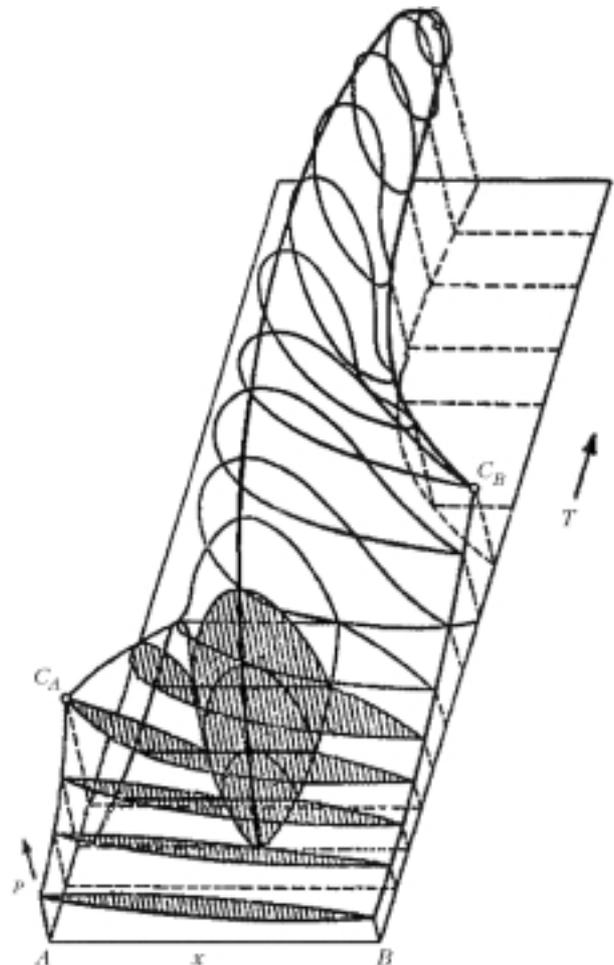

Fig. 8. Nucleation rate (J, cm^{-3}·s^{-1}) in the n-pentanol–argon system vs. the activity a of n-pentanol vapor.

Figure 9 shows schematically the spectrum of binary equilibrium diagrams from the critical line to some temperature in the region of liquid states of the condensed phase. It can be seen that the cigar-shaped equilibrium diagrams transform into the diagrams with a peritectic point.

As known from theory of solutions, a cigar-shaped diagram is indicative of the unlimited mutual solubility of components of a solution, while the presence of a peritectic (or eutectic) point is indicative of the limited solubility of the components. As follows from Ref. 19, the cigar-shaped diagram corresponds to one nucleation channel (see, for example, Fig. 7). In the case of a system with the limited solubility of components of the condensed phase, the two-channel nucleation with two-layer nucleation rate surface takes place. This region corresponds to the vicinity of a critical point (point C_A in Fig. 9) of one of the components.

Fig. 9. Example of binary equilibrium diagrams.

Note that the above approach to the study of topology of nucleation rate surfaces is already quite well developed to be applied to any, arbitrarily complex equilibrium diagrams. Emphasize, apart from the problems of the single-channel nucleation theory, that recent advances in the semiempirical analysis of topology of nucleation rate surfaces allow the number of nucleation channels, occurring in a nucleating system, to be found from the equilibrium diagrams.

The state of the art of the theory and experiment on equilibrium diagrams gives a sufficient basis for analysis of the topology of nucleation rate surfaces. Certainly, the consideration of the topology of rate surfaces complicates the study. However, its ignorance leads investigators to a deadlock, because the application of single-channel version of the nucleation theory for interpretation of multi-channel nucleation without separation into individual channels is an absolute nonsense. For a more detailed description of the problems in description of atmospheric nucleation, see the reviews by K.Ya. Kondratyev [Refs. 21 and 22].

Conclusions

Summarizing the above discussion, we note that by now there already exists the first version of the test system[8] to check the experimental nucleation systems. As was noted in Ref. 8, the next test for measuring systems may be the detection of changes in the phase state of critical nuclei, for example, in melting glycerin. A series of experiments with glycerin was carried out by only one research team (see Ref. 9 etc.). With the development of the general level of nucleation rate measurements, the detection of changes in the phase state of critical clusters will become a routine procedure and then it will be needed to introduce the corresponding test. The effect of the total pressure of the nucleating system and the influence of the carrier gas properties on the nucleation rate should be considered as established facts, and these dependences can be used in practical models of nucleation, including the atmospheric one.

The change of the phase state of the critical nuclei corresponds to the triple point in the equilibrium diagram. It gives rise to a two-layer rate surface or the two-channel nucleation process. The experimental measurement of nucleation rates separately for each of the channels remains an urgent problem now. The problem of separating the channels existing near the triple point is of principal importance for further progress in the development of the nucleation theory. The investigators should be prepared to study multi-channel (more than two channels) nucleation.

Today it is obvious that the continuum of topologies of nucleation rate surfaces should be parameterized by the version (versions) of the nucleation theory, allowing the variable number of nucleation channels. By now the experimental measurements of nucleation rates remain the most reliable source of information on the nucleation. The reliability of experimental results will increase, when it will become possible to measure rates for each of the nucleation channel separately.

It should be recognized that the experimentally achievable region of nucleation parameters makes up only a very small (10–15 orders of magnitude smaller) fraction of the possible nucleation rate surface. Thus, it is clear that computer methods for constructing nucleation rate surfaces should necessarily be developed. The semiempirical approach based on the use of equilibrium diagrams and some experimental measurements for each nucleation rate surface seems to be the most reliable. The atmospheric nucleation is known to occur in the close (about 100 degrees) vicinity of the water triple point, and therefore the consideration of two nucleation channels (two-layer nucleation rate surface) is necessary in this case.

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