По результатам компьютерного моделирования методом молекулярной динамики процессов плавления и кристаллизации нанокластеров серебра, состоящего из 561 атома, показана зависимость перехода от ГЦК структуры к икосаэдрической структуре от скорости нагревания и охлаждения кластера. На основе проведенного компьютерного анализа можно сделать вывод, что при нагревании кластера переход от ГЦК структуры к икосаэдрической происходит при медленном нагревании, в то же время для формирования икосаэдрической структуры при охлаждении кластера необходима высокая скорость охлаждения

#### Литература

1. Iijima S. and Ichihashi T. Structural instability of ultrafine particles of metals // J. Phys. Rev. Lett. 56, 617, 1986.

2.Гафнер С.Л., Редель Л.В., Головенько Ж.В., Гафнер Ю.Я., Самсонов В.М., Харечкин С.С. Структурные переходы в малых кластерах никеля // Письма в ЖЭТФ. 2009. Т. 89. Вып. 7. С. 425-431.

3.Plimpton S.J. Fast Parallel Algorithms for Short-Range Molecular Dynamics // J. Comp. Phys. 117, 1-19 (1995).

4.Daw M. S. and Baskes M. I. Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals // Phys. Rev. B, 29(12):6443-6453, 1984.

5.Daw M. S., Foiles S. M., and Baskes M. I. The embedded atom method: a review of theory and applications, materials science reports // Materials Science Reports, 9 (7,8):251–310, 1993.

6.Mei J., Davenport J. W., and Fernando G. W. Analytic embedded-atom potentials for FCC metals: Application to liquid and solid copper // Phys. Rev. B, 43(6):4653-4658, 1991

7.Belonoshko A. B., Ahuja R., Eriksson O., and Johansson B. Quasi ab initio molecular dynamic study of Cu melting // Phys. Rev. B, 61(6):3838–3844, 2000.

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## Modern State of Nucleation Theory and the Advantages Review of Nucleation Rate Surfaces Semiempirical Design for Materials Science

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To academician Howard Reiss memory is devoted

# Современное состояние теории нуклеации и обзор достижений в полуэмпирическом построении поверхностей скорости зародышеобразования для материаловедения

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#### Аннотация

Технологическая цепочка обычно предполагает сложную последовательность физико- химических трансформаций, сопровождаемых фазовыми переходами и химическими преобразованиями. Эти явления могут быть описаны теорией зародышеобразования. В обзоре делается краткий обзор современного состояния теоретических и экспериментальных исследований по кинетике зародышеобразования в метастабильных системах. Обсуждается набор аксиоматических утверждений, позволяющий выполнять полуэмпирические построения поверхностей скорости зародышеобразования над классами диаграмм равновесий фаз. Приводятся экспериментальные результаты, подтверждающие топологию поверхностей скорости зародышеобразования, построенных над диаграммой с тройной точкой.

Ключевые слова: материаловедение; нуклеация; скорости зародышеобразования; методы исследований; построение поверхностей зародышеобразования

### 1. Introduction

The vapor nucleation rate measurements data have the key impotence for a material production. The first nucleation experiment can be considered to be associated with measurements of liquid and crystals supercooling done by Fahrenheit [1]. The nucleation of bubbles in gas saturated solutions was observed and the concept of critical embryos of a new phase was introduced in nucleation science during the second half of 19<sup>th</sup> century [2]. The quality of vapor/liquid nucleation rate results has improved substantially beginning in 1980s because of the development of new measurement systems. For example, the first prototype Flow Diffusion Chamber for vapor nucleation rate measurements was developed by Anisimov *et al.* [3, 4]. Currently, the most significant problem in nucleation is the correspondence between experimental data and theoretical predictions of nucleation rate values. As a rule, theoretical and experimental data on nucleation rate are not in a good agreement over a range of temperatures and/or pressures. It appears that there may be problems in both the experiments and theory and deficiencies can be identified in all versions of nucleation theories and practically all of the reported experimental results.

Current theories correspond mostly to various modifications of Classical Nucleation Theory that was completed in the 1940s [5]. The theoretical results look quite reasonable for sufficiently low vapor nucleation rates where the droplet approximation is applicable [6]. However, these approaches have problems at the nanometer scale when the critical embryos contain of the order of 200 or less molecules (atoms). It appears that this quantity of molecules is near the threshold for the droplet critical embryo approximation, at least for organic vapors. Some researchers [7, 8 *et al.*] have expressed unreasonable optimism that nucleation theory and experiment were in agreement for the case of bubble generation from the superheated liquids.

At the present time, vapor-gas nucleation theory can produce values that deviate from the experimental results by up to several orders of magnitude [9, 10]. However, nucleation experiments using different devises also show significant inconsistencies in the measured rates, for example [10]. Both problems produce difficulties in establishing one or more standard vapor/liquid nucleation systems that could be used to test vapor-gas nucleation rate measurement systems. The problem of the nucleation rate standard is more complex than simply using the n-pentanol-helium system as was suggested by the International Workshop on Nucleation in the Czech Republic, Prague in 1995 [11] as a candidate for a nucleation standard. The n-pentanol-helium system has unfortunately not produced sufficiently consistent data to date. The advantages and current problems of the vapor-gas nucleation experiments are discussed below and a view of the future studies is presented based on the assessment of vapor-gas/liquid nucleation experimental results.

One can find in scientific literature a pretty fresh idea of the nucleation rate surfaces design over the diagrams of phase equilibria. That idea looks like profitable for the nucleation theory development and for various practical applications where predictions of theory have no high enough accuracy for today. The common thermodynamics has no real ability to predict parameters of the first order phase transitions. Kinetics description of these transitions is complicate problem as well. It is known widely that many-body problem has no exact solution. The usual way of any theory is to reduce the many-body problem to one body in some field. The features of one body and the field are adjusted usually to get the reasonable compliance to the empirical results. Relation of the theoretical and empirical results is not good enough in case of the Nucleation Theory.

#### 2. The Empirical Methods

Initial measurements of vapor nucleation were made by Aitken [12] and Coulier [13, 14] using the rapid adiabatic expansion of air saturated with water vapor to provide the necessary supersaturation. Allen and Kassner [15] modified the experimental procedure by using an expansion/compression cycle in a Wilson-type chamber where compression is introduced after the adiabatic expansion of a vapor-gas mixture. The compression stops the nucleation and initiates growth of the generated clusters to optically detectable sizes in an atmosphere of low supersaturated vapor. This key idea has been the basis for quantitative optical measurements of nucleation rate up to the present time.

This expansion/compression cycle of Allen and Kassner [15] was applied in the two-piston expansion chamber such as that described by Strey *et al.* [16]. The expansion chamber is filled with a vapor-gas mixture at pressure,  $p_o$ , and temperature,  $T_o$ . The mixture is then expanded adiabatically. The pressure drops to  $p_{exp}$  resulting in a temperature drop to  $T_{exp}$ . The temperature drop causes supersaturation, S, of the vapor that drives the formation of critical embryos, which are containing  $n^*$  molecules (or atoms), of new phase at temperature  $T_{exp}$ . The compression of the mixture raises the temperature and reduces the vapor supersaturation such that further new particle formation is negligible. However, the resulting vapor supersaturation permits the growth of the nucleated clusters to optically detectable sizes. Nucleation pulse experiments yield the number density of droplets,  $N_d$ , that can be measured using the first Mie maximum of

scattered laser light. The nucleation rate, J, is described by the ratio  $J = N_d/\Delta t_{exp}$ , where  $\Delta t_{exp}$  is the duration of the vapor-gas expansion [17]. Precise determination of the vapor/carrier gas ratio is important for accurate measurements of the nucleation rate. These studies employ high purity materials and clean systems that are created using vacuum cleaning technologies. The pressure change, intensity of transmitted/scattered laser light, and other parameters are recorded. Temperatures are measured with uncertainties of the order of several tenths of a degree Kelvin.

The shock tube as a version of the expansion technique has recently shown considerable improvements in the quality of nucleation rate data (for example, Peters & Paikert [18]). A shock tube (or wave tube) is a tube that is initially divided by diaphragm with at a much higher pressure at one side than the other one. An adiabatic expansion occurs when a diaphragm is broken and the vapor-gas mixture becomes supersaturated. Nucleation then occurs. It has been thought that wave tube measurements are less accurate "because pressure pulses cannot always be accurately reproduced" in comparison with two-piston chamber (Holten *et al.* [19]). Supersonic jets have recently been used to produce the same adiabatic expansion scheme where cluster generation and growth are decoupled (Kim *et al.* [20]). The shock tube and supersonic jets provide the opportunity to measure high nucleation rates with values up to  $10^{17}$  cm<sup>-3</sup>s<sup>-1</sup> even if it may not yet provide as high accuracy as other measurement systems. The nucleation temperature for adiabatic expansion techniques ranges from 30 to 370 K. Nucleation rates can be measured over an interval of up to five orders of magnitude in one system under investigation. The expansion techniques cover a total nucleation rate interval from  $10^3$  up to  $10^{17}$  cm<sup>-3</sup>s<sup>-1</sup>. The total nucleation pressures involve interval from approximately 100 kPa to 7 MPa.

## **3. Diffusion Chambers**

Langsdorf [21] created the first static diffusion chamber (SDC). The SDC is described in detail by Katz [22], Kacker and Heist [23], *etc.* The static diffusion chamber consists of two wet plates maintained at different temperatures. Vapor diffusion and temperature gradient produce vapor supersaturation and nucleation in the space between the plates such that clusters of the new phase are formed. Clusters then grow. Particles can move toward the cold plate direction by temperature and vapor concentration gradients. A particle drops when its mass gets sufficiently large. A special SDC design was used for vapor-gas nucleation measurements at elevated pressures up to 4.0 MPa (Heist *et al.*[24]).

The temperature and mole fraction distributions over the chamber volume need to be calculated using a transport process model. Heist and coworkers have reported results of careful analysis of the SDC heat-mass transfer problem (Heist *et al.*, 2003). The key problem is to achieve operational stability of the vapor-gas mixture in SDC with respect to convective flows. Important conditions such as "the total pressure must remain below a limiting value that depends on temperature, condensable vapor, and background gas" needs to be recognized (Heist *et al.*[24]). Total nucleation temperatures for SDC range from 240 to 370 K so that nucleation rates can be measured over four orders of magnitude in one measuring system. The total nucleation rates span the range of  $10^{-2}$  up to  $10^2$  cm<sup>-3</sup>s<sup>-1</sup>. The total nucleation pressures span the interval from near 30 kPa to 4 MPa.

Another system is the Flow Diffusion Chamber (FDC). Initial versions of the FDC were described by Anisimov *et al.* [3, 4]. The FDC scheme uses a hot laminar vapor-gas flow within cold boundary conditions. Hot vapor-gas flow enters the chilled tube (condenser). The vapor-gas velocity distribution at the beginning of the tube is parabolic one. The distributions of temperature, T, vapor supersaturation ratio, S, and nucleation rate, J, along the tube axis can be revealed as the result of the Navier-Stokes equations solution. Embryos form in the nucleation volume and subsequently grow in the supersaturated vapor. A flow laminator is used to produce fully developed initial laminar flow. Parameters of that flow are used as boundary conditions for the stationary heat-mass transfer problem. It is assumed that the boundary vapor pressure near the tube wall is at equilibrium at the wall temperature. The vapor concentration at the beginning of tube is defined by vapor saturator design. Nucleation occurs in the condenser. The particle concentration and size distribution are measured with an aerosol counter that is placed before pressure controller to avoid the nucleation in the controller resulting from a decrease in the exhaust pressure.

An algorithm for estimation of the average nucleation rate over FDC nucleation volume was suggested by Anisimov *et al.* [25]. The maximum experimental value of the nucleation rate,  $J_{max}$ , in diffusion chambers can be measured using an obvious relation  $J_{theor}/N_{theor}=J_{max}/N_{exp}$ , where  $J_{theor}$  is maximum theoretical nucleation rate;  $N_{theor}$  and  $N_{exp}$  are the theoretical and experimental FDC particle concentrations respectively (Hyvarinen *et al.* [26]; Wagner and Anisimov [27]). That relationship can also be used for  $J_{max}$ measurements using a supersonic nozzle (Streletzky *et al.* [28]). The current FDC scheme has been used for vapor nucleation rate measurements at total pressures from 0.03 to 0.50 MPa. The FDC data span over six orders of magnitude in nucleation rate that can be measured in a single experimental system. Nucleation temperatures from 230 to 400 K can be obtained in these systems now. Versions of FDC have built in Finland (Anisimov *et al.* [29]; Lihavainen & Viisanen [30]), the USA (Mikheev *et al.* [31]), the Czech Republic (Brus *et al.* [10]), *etc.* Brock and co-authors built laminar flow systems to study single (Brock *et al.* [31]) and multicomponent (Brock *et al.* [32]) nucleation kinetics and properties of condensational aerosols.

Several groups have used rapid turbulent mixing to measure nucleation rates of the single and binary vapors (Kogan & Burnasheva [33]; Sutugin & Fuchs [34]; Okuyama *et al.* [35]; Wyslouzil *et al.* [36], *etc*). Most studies have only measured the critical supersaturation for two-component vapor systems. Nguyen *et al.* [37] have studied homogeneous and heterogeneous nucleation of a single vapor in a laminar flow aerosol generator. The Thomson equation was considered empirically for small clusters using an FDC in article [38]. The nucleation theorem (Anisimov & Cherevko [4]; Anisimov *et al.* [25, 39]; Kashchiev [40]) is presenting the theoretical relationship between the nucleation rates and the number of molecules in the critical embryos of condensate for vapor-gas measurements. It has been suggested in some articles, that single condensable vapor nucleation in the gaseous media should be considered as binary systems because of clear influence of carrier gas (CO<sub>2</sub>, SF<sub>6</sub>) on critical embryo phase transitions (Anisimov *et al.*[41, 42]).

The problem of a turbulent mixing scheme is associated with wide spectrum of nucleation conditions. Fluctuations of vapor supersaturation and temperature can be large enough in the pre-nucleation zone to generate some pre-particles before system achieves homogeneity. These pre-particles initiate heterogeneous nucleation. Thus, turbulent flow systems are rarely used for homogeneous nucleation measurements. However, they have proved useful for heterogeneous (Lee *et al.* [43]; Mavliev *et al.* [44]) and ion-induced (Seto *et al.* [45]; Gamero-Castano, *et al.* [46]; *etc.*) nucleation measurements.

During the past three decades, several research groups have examined the effects of pressure and carrier gas composition on homogeneous nucleation to better understand the experimental data describing vapor to condensed phase nucleation. Classical nucleation theory assumes that the only role of the carrier gas is to maintain the temperature equilibrium of the clusters with the ambient media. Frank and Hertz [47] made the first observations of a gas-pressure effect. The result was reproduced in several other measurements (Katz *et al.* [48]; Brus and Zdimal [49], *etc*).

Katz *et al.* [48] found experimental variation from negative to positive gas-pressure effects. Nevertheless these authors concluded that the effect is not significantly larger than the changes in nucleation rate that occur due to other uncertainties such as in thermal conductivity of the mixture. That conclusion is unsatisfied as it follows from other empirical results. Clear gas-pressure effects were found in several publications. For example, Anisimov and Vershinin [50, *etc*] experimentally found a positive gas-pressure effect and a gas-composition effect at gas pressures from 0.10 to 0.30 MPa. They concluded on the basis of the ideal solution approximation (known now as the nucleation theorem) that carrier gas molecules were involved in the critical embryos. Heist and co-workers [51, 52] have reported effects of pressure and carrier gas composition on the nucleation rates for a series of short-chain alcohols. Other experimental results have supported a dependence of the nucleation rate on the nature and total pressure of the carrier gas (Luijten and van Dongen [53]; Luijten *et al.* [54]; Anisimov *et al.* [42]; Lihavainen and Viisanen [55]. Gas-pressure effects were detected by van Remoortere *et al.* [56] although most of the measurements from this research group (i.e., Viisanen *et al.* [57]; Viisanen and Strey [58]) did not observe carrier gas influences on nucleation rate.

Fladerer and Strey [9] did attempt to measure supersaturated argon nucleation using a cryogenic nucleation pulse chamber. They concluded that growth rate of the nucleated argon droplets was too high to make permit decoupled nucleation and embryo growth. Nevertheless the onset of nucleation corresponding to a nucleation rate of  $J=10^{7(+/-2)}$  cm<sup>-3</sup>s<sup>-1</sup> at temperatures 52 < T(K) < 59 and argon vapor supersaturation value near 10 was estimated. Classical theory predicts nucleation rates of the order of  $10^{-28} - 10^{-13}$  cm<sup>-3</sup>s<sup>-1</sup> for these conditions. Experimental results of different experimental schemes used for nucleation rate measurements at cryogenic temperatures are still inconsistent (Fladerer and Strey [9]) because of low accuracy of the experimental data.

Several research groups have made comparative measurements of nucleation rates (Anisimov *et al.*, [29, 59]; Wilck *et al.* [60]; Brus *et al.* [10], *etc.*) The nucleation rates of n-butanol in helium using both an FDC (Hyvarinen *et al.* [61]) and an expansion chamber (Strey *et al.* [16]) illustrate the data sets deviation on 4-5 orders of magnitude. It can be seen that the data from the different systems can cross each other. However, the slopes of the nucleation rate isotherms for the two measurement systems are nearly the same.

The origin of these data discrepancies can be better understood through the consideration of nucleation rate surfaces (Anisimov *et al.* [62, 63]). In the most events, the vapor-gas nucleation temperature is higher than the critical temperature of gas. In that case, nucleation rate surface extends over a drop-shaped region as it is by Anisimov *et al.* [62].

In the most cases, the gas is treated as an inert media to absorb the heat released from the phase transitions. Inconsistencies among the experimentally measured values from the different experimental schemes are a major problem for current vapor-gas nucleation experiments. Consideration of vapor-gas

nucleation as a binary system is a reasonable way to resolve the data inconsistencies. It is plausible to think that different experimental systems have the inconsistent trajectories along the nucleation rate surface when the vapor-gas system is treated as binary system. Several results, for example, Anisimov *et al.* [41, 63] illustrate that high pressure measuring techniques need to be designed to study multi-channel nucleation.

## 4. Reference system for nucleation rate measurements

In order to test the accuracy of an experimental system, it is important to have a standard system that can be measured over a range of nucleation conditions. The n-pentanol-helium system was proposed in Prague, 1995 for such measurements. The available results from several research groups were collected and compared (Anisimov *et al.* [11]). They proposed a reference equation for nucleation rates of n-pentanol-helium as a practical test of any experimental measurement system for total pressures from 0.10 to 0.30 MPa. Although the equation does not reproduce all of the results, the approximation is useful in its present form to provide a relative view of the different results up to time when a more accurate approximation can be generated. The problem of a nucleation standard can only be solved when consistent results have been obtained by independent groups that use the different experimental schemes. It is believed that the vapor-gas nucleation rates should be represented by a surface instead of the single line that is used for most current presentations of the isothermal nucleation rate data in vapor-gas systems.

#### 5. Nucleation rate surfaces design

Nucleation experiment can be provided in very local nucleation conditions even the nucleation takes place from the critical conditions down to the absolute zero temperature limit and from zero nucleation rates at phase equilibria up to the spinodal conditions. Theory predictions have low reliability as a rule. It is well known that any phase diagram has several lines of phase equilibria. It is easy to show that each line of phase equilibria generates the nucleation rate surface in space of nucleation process parameters. It means that one has multi sheet nucleation rate surfaces in the common case. Each nucleation rate surface is related to one phase state generation, or it is related to a single channel of nucleation. Semiempirical design of the nucleation rate surfaces over diagrams of phase equilibria have a potential ability to provide a reasonable quality information on nucleation rate for each channel of nucleation. Consideration and using of the nucleation rate surface topologies to optimize synthesis of a given phase of the target material can be available when data base on nucleation rates over diagrams of phase equilibria will be created.

One reason for nucleation theory problem is the application of inconsistent assumptions that are used to interpret the experimental results. The most experimental data on vapor nucleation are interpreted as a one-surface (one nucleation channel) approximation of a nucleation theory. However, two or more nucleation channels are really present in most systems as it was recently reported by Anisimov *et al* [6, 68].

We need to admit now that agreement between experimentally measured vapor nucleation rates and current theoretical predictions exists for only a limited number of systems. It was found long ago that the lines of phase equilibria are continued by line of unstable equilibria for metastable systems. Vortisch et al. concluded [64] retrospectively that "the temperatures and compositions leading to a given nucleation rate roughly follow the melting curve." That kind of empirical result initiated the two-sheet vapor nucleation rate surface design (Figure 1) twenty years ago in the vicinity of the triple point [65].



**Figure 1.** Nucleation rate, *J*, surface topology for triple point vicinity. Vapor-solid (light grey) and vapor-liquid (dark grey) nucleation separately. *T* is temperature; *P* is pressure; *kta* is line of vapour-solid and *rtc* is vapour-liquid equilibria; *t* is triple point; *c* is critical one

To empirically detect a single nucleation channel one needs to have the appropriate measuring system, but these kinds of systems are not currently under active development. The semiempirical approach permits the prediction of a realistic topology for the nucleation rate surface. That topology can be designed over the phase equilibria diagrams [62, 66]. One needs at least several experimental points on the nucleation rate

surface and the phase diagram to effectively develop these surfaces [66].

A short history of semiempirical design of the nucleation rate surfaces over phase equilibrium diagrams will be presented. This approach involves a simple idea developed by Anisimov et al. [65], that nucleation rate surfaces arise up from the phase equilibria lines. It means that each line of the real and metastable phase equilibria produces two nucleation rate surfaces (for two are Both surfaces reflect the nucleation kinetics for each of two metastable phases that can be jointed by an equilibrium line.



Figure. 2. Sulfur hexafluoride – 1,3- propanediol nucleation at pressure of 0.30 MPa.

Experimental detection of nucleation rate for each of two individual vapor nucleation rate channels, which are generating two single nucleation rate surfaces for vicinity of the triple point, one can see in article [67]. That result is unique to the present time. However, the most experimental data are interpreted in the one-surface (one channel) approximation. The theory not yet adequately developed to accurately predict two-channel nucleation unfortunately.

Empirical studies of vapor nucleation are of significant interest as this is a fundamentally important problem of the first-order phase formation kinetics description. The current technical level of research for the study of aerosol formation is of fairly high quality, but there is no theory that is suitable for quantitative prediction of the experimental vapor nucleation rates. In the common case, the theory of phase transitions cannot predict the phase transition parameters such as pressure and temperature for nowadays as of the adjacent metastable states.

Theory involves a number of assumptions to describe small clusters [68]. Further, when the size dependencies of the surface tension and density of nuclei were taken into account [6] and the inherent degrees of freedom were used to calculate the statistical sum for a nascent cluster [69], agreement between theoretical and experimental results get worse. Semiempirical design over diagram of phase equilibria is applied for metastable volume construction [65-68]. That way has a considerable potential in the nucleation rate description.



Figure 3. Sulfur hexafluoride – 1,2- propanediol nucleation rates at total pressures of 0.10 and 0.20 MPa.

A Laminar Flow Diffusion Chamber [41] is widely used for nucleation rate measurements of vapor-gas systems. A simple relation [63] can be used as criterion, A, to detect a nucleation rate surface singularity which is initiated by phase transitions of the first order for the surface section at J(T,S) = constant:

$$\left(\frac{\partial \ln J}{\partial T}\right)_{S,P_1\dots P_n} + \left(\frac{\partial \ln J}{\partial \ln S}\right)_{T,P_1\dots P_n} \left(\frac{\partial \ln S}{\partial T}\right)_{J,P_1\dots P_n} = A$$

The criterion value, A, is equal to zero if the vapor nucleation rate surface J = J(T,S) has no singularities. Here S and  $P_i$  are vapor supersaturation and partial pressure of component *i* at temperature T of system respectively. Singularity in the nucleation rate surface breaks the local condition for surface continuity and monotony. Criterion, A, is deviating from zero value in that case. The A-criterion provides a sensitive tool for the detection of singularities in nucleation rate surfaces.

Clear singularities presence was found for data in Figures 2&3. These singularities can be attributed to unknown earlier phase transitions of the first order in the vicinity of critical line of binary (vapor-gas) systems. The phase transition temperature clearly decreases with a rise in sulfur hexafluoride pressure (P). Presumably the sulfur hexafluoride concentration in a condensed solutions increases proportionally to the total pressure. Mole fraction of sulfur hexafluoride grows up in a critical embryo composition. Naturally for that trend that phase transitions in subcritical conditions, which are higher a sulfur hexafluoride critical temperature, are shifting down to critical point temperature. New phase transitions of the first order probably produce surface. It needs to get more data to reveal the real topology of the phase transition surface.

That surface involves critical points of gas and vapor, jointed by critical line for sulfur hexafluoride and propanediol system in the present case. A vapor-gas as binary system has a three dimensional volume of metastable states, which is bounded by surfaces of phase equilibria and spinodal conditions. These surfaces are jointed along the critical line of binary system which can be calculated using one of the correlations [70]. The glycerine vapor activities (a) on nucleation temperatures (T) for two levels of the nucleation rates (J) are presented in article [9] for a total pressure 0.10 MPa. The same shapes are appeared for total pressure of 0.20 MPa. The clear discontinuities, which are produced by melting points, can be seen for all cases.

Let look the reasons for these discontinuities. In our experiments we have transition from a nucleation rate surface of one phase to other. In common case nucleation rates can be expressed such as  $J = B \exp(-\Delta G/kT)$ . In that equation  $\Delta G = n^*(\mu_{cond} - \mu_{vapor}) + f$ ; where  $n^*$  is number of molecules in the critical embryos;  $\mu_{cond} - \mu_{vapor}$  is a chemical potential difference for the condensed phases and vapor for the macroscale samples; f is an excess energy of a critical embryo comparing with  $n^*$  molecules in a bulk condensed phase (presumably  $\delta T$  has a discontinuity at conditions of the phase transition); Partial derivative  $\delta T$  is broken at conditions for a phase transition of the first order;  $\mu_{vapor}$  is a continuous and monotonous function of temperature. The partial derivatives  $\delta T$  and  $\delta T$  are negative and positive quantities. In some cases their difference  $\left( \delta T - \delta T \right)$  as well as A criterion can be equal to zero. It means that a nucleation rate surface has

difference ( $\delta T = \delta T$ ) as well as *A*-criterion can be equal to zero. It means that a nucleation rate surface has a local continuity and monotony in that case.



Figure 4. Schematic presentation of a chemical potentials,  $\mu$ , on vapor activity (a) for the condensed phases of 1 and 2 (left panel) and Pressure (*P*) -Temperature (*T*) – partial volume ( $\nu$ ) diagram for a single component system with the metastable areas colored by gray

Figures 2&3 illustrate an impact of a critical embryo phase change on the nucleation rate surface topolo-

gy. Partial derivative  $\partial T$  is broken at conditions for a phase transition of the first order;  $\mu_{vapor}$  is a continuous and monotonous function of temperature. The partial derivatives  $\partial T$  and  $\partial T$  are negative and positive quantities. In some cases their difference  $(\partial T - \partial T)$  as well as A-criterion can be equal to zero. It means that a nucleation rate surface has a local continuity and monotony in that case. Figures 2&3 illustrate an impact of a critical embryo phase change on the nucleation rate surface topology.

It may be that there is a sufficient experimental variation in the nucleation rate measurements which is preventing the detection of this kind of nucleation event. A major problem in detection of the nucleation rate surface singularities is the random error inherent in any experimental data. This problem exists even one has experimental results of relatively high accuracy as it is shown by Anisimov [6]. A conceptual problem in vapor-gas to liquid (or solid phase) nucleation is its treatment of the nucleation as a single component problem instead as a two component system.(s'a) of the triple points. Lines  $mac_1$  and  $sac_2$  are the vapour-liquid and vapour-solid binodals.  $c_1$  and  $c_2$  are critical points (right panel).

Results of the present research illustrate clearly that gases can generate a phase transitions in a condensed state of matter. It has led conclusion that gas can be involved in the critical embryos and any vapor-gas system nucleation should be considered in an approximation of binary solution. A direct mass spectrometric measurements show the presence of the carrier gas in the critical cluster under some nucleation conditions for example in a monosilane-argon system [71].

## 6. Conclusions

In the present review, advantages and problems related to aerosol generation experiments are discussed. Adiabatic expansion and gas-jet techniques, diffusion chambers, turbulent mixing apparatus were considered. It can be concluded that the development of accurate experimental techniques for vapor-gas nucleation research are still in progress. Measurable nucleation rates for the available experimental techniques span up to 19 orders of magnitude ranging from  $10^{-2}$  cm<sup>-3</sup>s<sup>-1</sup> up to  $10^{17}$  cm<sup>-3</sup>s<sup>-1</sup> and nucleation temperatures from cryogenic around 30 K to near 1300 K. Pressures in vapor-gas systems have been achieved within the interval from 30 kPa to 10 MPa. The current recommendations for vapor-gas nucleation rate measurements can be summarized such as: Vapor nucleation and cluster growth volumes should be decoupled to allow the embryos to grow before light scattering detection. Decomposition of embryos should be evaluated when an adiabatic recompression (Allen & Kassner [15]) is applied to interrupt nucleation.

Theory independent algorithms are needed to estimate experimental nucleation rates based on FDC and others flow systems experimental data. Homogeneous nucleation rates should be measured for sufficiently high supersaturation values (Anisimov and Cherevko [4]). Impurities in the vapor substance must not exceed 0.2% for the present time. This level of impurities shifts the nucleation rate values within one order of magnitude as shown by Anisimov *et al.* (1987) and Strey *et al.* (1995). Aerosol size distribution measurements are strongly recommended to identify the possibility of two and more channels for homogeneous and heterogeneous nucleation. Continuity and monotony criteria should be applied for the detection of nucleation rate surface singularities and data quality characterization. Vapor-gas systems are strongly recommended to create a nucleation systems. The problem of experimental data inconsistencies should be resolved to create a nucleation standard. It can be hoped that the uncontrolled parameter(s) will be identified in the near future and permit consistent nucleation rate data to be derived from different research methods. The introduction of one or several nucleation standard(s) is a major current problem. Success in the nucleation standard development and its introduction in nucleation research practice is a key issue for current nucleation experiments.

It can be concluded that a conceptual problem in vapor-gas to liquid (or solid phase) nucleation is its treatment of the nucleation as a single component problem instead of a two component approximation. Results of the present research illustrate clearly that gases can generate a phase transitions in a condensed state of matter in the critical line vicinity. Gas can be involved in the critical embryos and any vapor-gas system nucleation should be considered in an approximation of binary solutions. A direct mass spectrometric measurements show the presence of the carrier gas in the critical cluster under some nucleation conditions, for example, in a monosilane – argon system [12]. Several contemporary achievements are collected in the present review. It is clear that idea of a semiempirical design of the nucleation rate surfaces is promising tool for the advanced material synthesis. One can easily see that idea of semiempirical design of the nucleation rate surfaces will get development in the nearest future. The data base file of the algorithms of that kind of activities, the digital information on nucleation rates, equations of states, phase equilibria diagrams, binodal

and spinodal conditions, *etc* will be intensively collected without doubt. Time when soft to the nucleation rate surface design will be available for each scientist and engineer is approaching. It means that knowledge on nucleation will get position of powerful tool which is effective in scientific research and industrial applications.

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#### References

1. Ostwald, W. (1896-1903). Lehrbuch der Allgemeinen Chemie. W. Engelmann: Leipzig.

2. Volmer, M. (1939). Kinetik der Phasenbildung. T. Steinkopf: Dresden-Leipzig.

3. Anisimov, M.P., Costrovskii, V.G., & Shtein, M.S. (1978) A supersaturated vapor and a dibutilphtalate aerosol receipt by a diffusion mixturing of the different temperature vapor-gas flows. Colloidniy Journal (Russian), 40 (1) 116-121.

4. Anisimov M.P. and Cherevko A.G. (1985) Gas-flow diffusion chamber for vapor nucleation studies. Relations between nucleation rate, critical nucleus size and entropy of transition from a metastable into a stable state. J.Aerosol Sci., 16(2), 97-107.

5. Frenkel, Ja.I. (1975). Kinetic theory of liquids. Nauka: Leningrad.

6. Anisimov, M.P. (2003). Russian Chemical Reviews, Nucleation: Theory and Experiment 72, 591-628.

- 7.Baydakov, V.G. (1995) Superheating of cryogenics liquids. Ural Branch RAS: Ekaterinburg.
- 8. Protsenko, S.P., Baydakov, V.G., Zhdanov, E.D., & Teterin, A.S. (2006). In. Metastable States and Phase Transitions. Vol. 8, Ural Branch RAS, Ekaterinburg, 171 202.
  - 9. Fladerer, A. and Strey, R. (2006). Journal of Chemical Physics, 124, 164710 164715.
  - 10. Brus, D., Hyvarinen, A.. Zdimal, V., & Lihavainen H. (2005). JCP, 122, 214506 21514.
  - 11. Anisimov, M.P., Hopke, P.K., & Shvets, I. (2000). Journal of Chemical Physics, 113, 1971 1975.
  - 12. Aitken, J. (1888) Transactions of the Royal Society of Edinburgh, 35, 1-9.
  - 13. Coulier, P. J. (1875). J. de Pharmacie et de Chimie, Paris, Ser. 4, 22:165-173.
  - 14. Coulier, P. J. (1875). J. de Pharmacie et de Chimie, Paris, Ser. 4, 22:254-255.
  - 15. Allen, L.B. & Kassner, J.L., Jr. (1969) Journal of Colloid and Interface Science, 30, 81 93.
  - 16. Strey, R., Wagner, P.E., & Schmeling, T. (1986). Journal of Chemical Physics, 84(4), 2325 2335.
  - 17. Strey, R., Wagner, P. & Viisanen, Y. (1994). Journal of Physical Chemistry, 98, 7748 7758.
  - 18. Peters F. & Paikert B. (1989). Journal of Chemical Physics, 91, 5672 5678.
  - 19. Holten, V., Labetski, D., & van Dongen, M.E. (2005). Journal of Chemical Physics, 123, 104505 104509.
  - 20. Kim, Y.J., Wislouzil, B.E., Strey, R. Et al. (2004). Journal of Physical Chemistry, 108(A), 4365 4377.
  - 21. Langsdorf, A. (1939). Review of Scientific Instruments, 10, 91 103.
  - 22. Katz, J.L. (1970). Journal of Chemical Physics, 52, 4733 4748.
  - 23. Kacker A. & Heist, R.H. (1985). Journal of Chemical Physics, 82, 2734 2744.
  - 24. Heist, R.H., Bertelsmann, A., Martinez, D., & Chan, Y.F. (2003). Atmospheric Research, 65, 189 209.
  - 25. Anisimov, M.P., Costrovskii, V.G., Shtein, M.S, & Mikheev, V.B. (1980) Colloid J. (Russian), 42, 941 945.
  - 26. Hyvarinen, A.P., Brus, D., Zdimal, V., et al. (2006). Journal of Chemical Physics, 124, 224304 224311.
  - 27. Wagner, P.E. & Anisimov, M.P. (1993). Journal of Aerosol Science, 24, Suppl.1., 103 104.
  - 28. Streletzky, K.A., Wyslouzil, & Strey, R. (2002). Journal of Chemical Physics, 116, 4058 4070.
  - 29. Anisimov, M. P., Hameri, K., Kulmala, M. (1993). Report Series in Aerosol Scince, 23, 19 24.

30. Lihavainen, H., & Viisanen, Y. (1998). Report series in aerosol science No. 41, Eds by J.Hienola and K.Hameri (pp. 381 – 382). Helsinki.

- 31. Brock, J.R., Kuhn, P.J. & Zenavi, D. (1986). Journal of Aerosol Science, 17, 11 22.
- 32. Brock, J.R., Kuhn, P.J. & Zenavi, D. (1988). Journal of Aerosol Science, 19, 413 424.
- 33. Kogan, Ja. I. & Burnasheva, Z.A. (1960). Journal of Physical Chemistry (Russian), 34, 2630 2639.
- 34. Sutugin, A.G. and Fuchs, N.A. (1970). Colloidniy Journal (Russian), 32, 255 260.
- 35. Okuyama, K., Kousaka, Y., Flagan, R.C., & Seinfeld, J.H. (1988). JCP, 89, 6442 6453.

36. 36. Wyslouzil, B.E., Seinfeld, J.H., Flagan, R.C., & Ocuyama, K. (1991 Journal of Chemical Physics, 94, 6827 - 6841.

37. Nguyen, H. V., Okuyama, K., Mimura, T., Kousaka, Y., Flagan, R.C., & Seinfeld, J. H. (1987). Journal of Colloid and Interface Science, 119, 491 – 504.

38. Kodenev, G.G., Baldin, M.N. & Vaganov, V.S. (1987). Cluster Physics, Eds A. A. Vostrikiv and A. K. Rebrov, (pp.110 – 115). ITP Novosibirsk.

- 39. Anisimov, M.P., et al. (1987). Colloidniy Journal (Russian), 49, 842 846.
- 40. Kashchiev, D. (1982). Journal of Chemical Physics, 76, 5098 5102.
- 41. Anisimov, M.P., Koropchak, J.A., Nasibulin, A.G., & Timoshina, L.V. (1998). JCP, 109, 10004 10010.
- 42. Anisimov, M.P., Koropchak, J.A., & Timoshina, L.V. (2000). Journal of Chemical Physics, 112, 9917 9928.
- 43. Lee, D.-W., Hopke, P.K., Rasmussen, D.H., Mavliev, R. (2003) J. Phys. Chem. B 107, 13813-13822.
- 44. Mavliev, R., Hopke, P.K., Wang, H.-C., Lee, D.-W. (2004) J. Phys. Chem. B 108, 4558-4564.
- 45. Seto, T., Okuyama, K., de Juan, L., Fernández de la Mora, J. (1997) JCP 107, 1576-1585.
- 46. Gamero-Castano, M., Fernández de la Mora, J. (2002) Journal of Chemical Physics 117, 3345-3353.
- 47. Frank, J. & Hertz, H. (1956). Zeitschrift fur physik, 143, 559 590.
- 48. Katz, J. L. Hung, C. H. & Krasnopoler, M. (1988). Proceedings of the 12-th ICNAA (pp. 356 359). Vienna (Lecture Notes in Physics V.309. Springer-Verlag, Berlin, 1988), 356 359.
  - 49. Brus, D., Zdimal, V., & Stratmann, F. (2006). Journal of Chemical Physics, 124, 164306 1634310.
  - 50. Anisimov, M.P. & Vershinin, S.N. (1990) Journal of Aerosol Science, 21 (1), 11-14.

51. Heist R.H., Ahmed, J. & Janujua, M. (1994). Journal of Physical Chemistry, 98, 4443 - 4453.

52. Heist R.H., Ahmed, J. & Janujua, M. (1995). Journal of Physical Chemistry, 99, 375 - 383.

53. Luijten, C.C.M, & van-Dongen, M.E.H. (1999). Journal of Physical Chemistry, 111, 8524 - 8534.

54. Luijten, C.C.M, Peeters, P. & van-Dongen, M.E.H. (1999). Journal of Chemical Physics, 111, 8535 - 8544.

55. Lihavainen, H. & Viisanen, Y. (2001). Journal of Physical Chemistry, 105, 11619-11629.

56. van Remoortere, P., Heath, C., Wagner, P., & Strey, R. (1996). Proceedings of the 14-th ICNAA, Helsinki, Eds by M. Kulmala and P. Wagner (pp. 256 – 259). Pergamon: Oxford.

57. Viisanen, Y., Strey, R., & Reiss, H. (1993). Journal of Chemical Physics, 99, 4680 – 4692.

58. Viisanen, Y. & Strey, R. (1994). Journal of Chemical Physics, 101, 7835 - 7843.

59. Anisimov, M.P., Hameri, K., & Kulmala, M. (1994). Journal of Aerosol Science, 25 (1), 23 – 32.

60. Wilck, M., Stratmann, F., & Kulmala, M. (1998). Journal of Aerosol Science, 29, 899 – 911.

61. Hyvarinen, A.-P., Lihavainen, H., & Kulmala, M. (2004). Journal of Chemical Physics, 120, 11621 – 11633.

62. Anisimov, M.P., Hopke, P.K; Rasmussen, D.H., & Pinaev, V.A. (1998). JCP, 109, 1435-1444.

63. Anisimov, M.P. Nasibulin, A.G., & Shandakov, S.D. (2000). Journal of Chemical Physics, 112, 2348 - 2354.

64. Vortisch H., Kramer B., et. al., "Homogeneous freezing nucleation rates and crystallization dynamics of single levitated sulfuric acid solution droplets Phys. Chem. Chem. Phys. 2000, 2, 1407-1413.

65. Anisimov M. P., J. Aerosol Sci. Metastable vapor states diagram. 1990, 21, suppl.1, 23-25.

66. Anisimova L., Hopke, P. K., et al. An Algorithm for Semi-Empirical Design of Nucleation Rate Surface, J. Colloid Interface Sci., 2005, 290, 107-116.

67. Anisimova L., Hopke P. K., and Terry J., Two Channel Vapor Nucleation in the Vicinity of the Triple Point, J. Chem. Phys. 2001, 114(22), 9852-9855.

68. Anisimov M. P., Hopke, P. K., et al., Vapor-Gas/Liquid Nucleation Experiments: A Review of the Challenges. J. Aerosol Sci., 2009, 40, 733-746.

69. Lothe J.and Pound G., On the statistical mechanics of nucleation theory. J. Chem. Phys., 1966, 45, 630-634.

70. Reid R. C., Prausnitz J. M., and Sherwood T. K., The Properties of Gases and Liquids (McGraw-Hill, New York, 1977). 71. Sharafutdinov R. G., Zarvin A. E., at al., Clusters in a pulsed free jet of a monosilane–argon mixture. Technical Physics Letters, 1999, 25(21), 47.