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CURRENT VISION OF THE NUCLEATION RATE DESCRIPTION PROBLEM

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Abstract: *Theoretical description and/or an experimental research of new phase embryo formation kinetics are widely presented in a problem of Atmospheric Aerosol Dynamics. These problems involve the intensive heat-transfer devises; the natural deposits of methane or carbon dioxide, etc. Nucleation is arising at aerosol generation in the vapor turbines, at vapour cooling in the heat-exchangers or/and at vapour expansion to atmosphere (any injection through piston) and so on. Nucleation is common phenomenon for the broad spectrum of systems with phase transitions of the first order. Critical embryo of new phase is treated as small ball (droplet) with uniform density in the Classical Nucleation Theory (CNT) approximation. There is no warranty that the selected version of Nucleation Theory is good enough for the kinetics of hew phase embryos description. It is assumed that CNT has the best fit to the experimental data even CNT is distinguished among other "universal theories" by the internal consistency and simplicity of the axiomatic statements only. The experimental data are crossing usually the CNT predictions. Thermodynamics consideration comes to the formal corrections to make consistent the next theory version to the next set of experimental data. It is the ordinary event when statistical mechanics is applied unreasonable for nucleation phenomenon. Nucleation experiment accuracy has risen considerably during the last half of century, but it does not lead to consistent experimental results. Triple points (lines, volumes etc.) or/and partial solubility of components are producing the complicate topology of the nucleation rate surfaces. That result is not understood enough by the scientific community up to now. An idea of semiempirical design of the nucleation rate surfaces over diagram of phase equilibria is generated over 10 years. Phase equilibria lines are taken as a zero limit of nucleation rate. Simply to say the nucleation rate surfaces arise from the phase equilibria lines. I.e. topologies of zero limits of nucleation rate exist in multiple handbooks for phase equilibria. That idea can give a considerable effect for series of nucleation problems in Atmospheric Aerosol Dynamics. It is possible to conclude that the parametric versions of nucleation theory can be created for each set of scaled diagram of phase equilibria. Design of semiempirical presentations of nucleation rate surfaces permits to create some basic set of nucleation theories, which can be used for binary and higher dimension nucleation theories. More details of the semiempirical design of nucleation rate surfaces will be presented.*

Keywords: *atmospheric nucleation, nucleation rate surfaces.*

1. Introduction

Current theories correspond to various modifications of Classical Nucleation Theory that was completed in the 1940s (Frenkel, 1975). The theoretical results look quite reasonable for low vapor nucleation rates where the droplet approximation is applicable (Anisimov, 2003). 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.

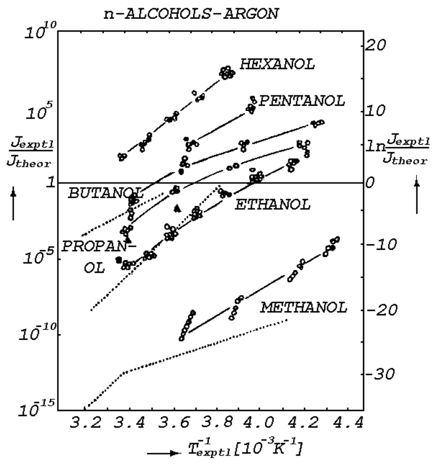

Figure 1. Ratio of the experimental nucleation rates (J_{expt}) and theoretical one (J_{theor}) versus reciprocal nucleation temperatures (*T*) for n-alcohol-argon systems (Strey et al., 1986).

Some researchers (Baydakov, 1995; Protsenko *et al.*, 2006) have expressed unreasonable optimism that nucleation theory and experiment are 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 (Fladerer and Strey, 2006; Brus *et al.*, 2005). Figure 1 illustrates the typical relation of theoretical and experimental values of the nucleation rates on example of n-alcohol – argon systems nucleation. 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 as a candidate for a nucleation standard (Anisimov et al., 2000c).

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 resutls.

2. Experimental detection of the nucleation rate surface singularities

Another aspect of the vapor nucleation theory is associated with the wrong theory using in the vicinity of condensate phase transition (p.t.) of the first order. It is easy to show that the resulting nucleation rate surface should have a broken first derivative at the p.t. conditions. That conclusion is appeared from consideration of Gibbs free energy of the critical embryo formation. Such transitions can exist in the vicinity of the triple point, when the probability exists for change in phase of the forming critical embryo.

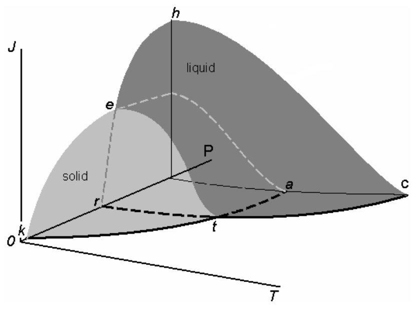

Figure 2. Nucleation rate (*J*) surfaces for solid (light grey) and liquid (dark grey) phases overpressure (*P*) – temperature (*T*) phase diagram (Anisimova *et al.*, 2001).

There could be a change in the dominant form of the forming embryo phase from one phase type to another such a liquid to a solid. The initial phase state of the critical embryo can exist over entire time of nucleation and embryo growth as was observed in the example of glycerin vapor nucleation and condensation (Anisimova *et al.*, 2001).

They suggested that there was a difference in accommodation of molecules on surface of the two different phase states of the condensing clusters. This difference in accommodation probability led to unequal growth rates of clusters for the different phases. Particle size measurements could then be used to detect the two separate phases. A clearly bimodal particle size distribution was found in the vicinity of glycerin triple point (Anisimova *et al.*, 2001). This result suggests two different embryo phases for the glycerin critical embryos and two nucleation rate surfaces simultaneously as it is shown in Fig. 2. If there were phase transitions in the growing clusters, the bimodal size distribution would have been smoothed into a continuum of sizes which is not what was observed in the experimental results (Anisimova *et al.*, 2001). The Gibbs free energy of the critical embryos governs the nucleation rate. In case of p.t. of condensate the first derivative of nucleation rate surface needs to split when nucleation occurs in the vicinity of phase transition of the first order in a condensed phase. In such circumstances, the conditions of continuity and monotony of the nucleation rate surface are simultaneously violated. These kinds of discontinuities have been found experimentally (Anisimov *et al.*, 1998a; 2000b).

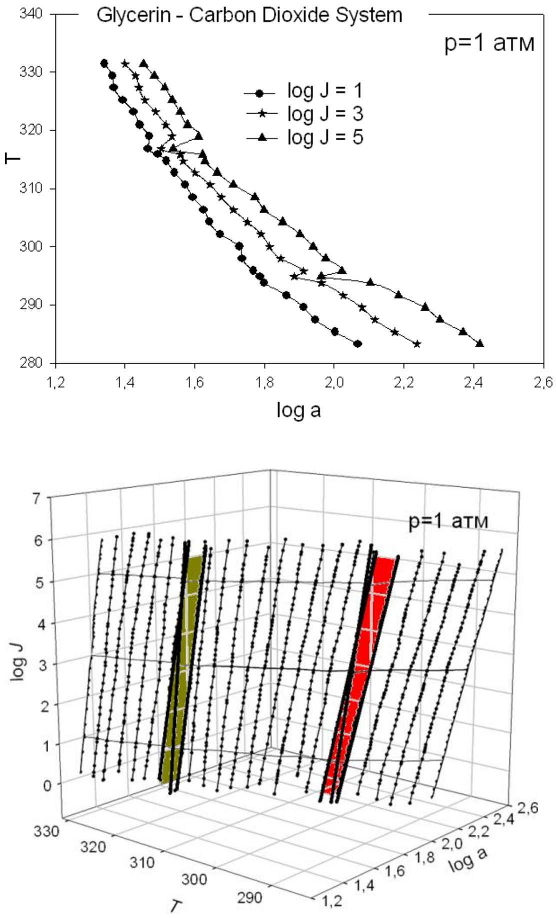

Figure 3. Nucleation rate surface levels (higher) in nucleation temperature (T) – logarithm vapor activity (log a) axis at log J = 1; 3; 5 (Anisimov *et al.*, 1998a) and Glycerin-Carbon Dioxide Nucleation rate surface with discontinuity initiated by glycerin melting (red) and unknown p.t. near the critical line (green).

The topology of nucleation rate surfaces near a triple point is illustrated in Fig. 2. The nucleation rate surface is hypothesized to arise from the *PT* phase equilibria. Two lines for phase equilibria with vapor exist in the triple point vicinity. Line, *et*, shows the equal nucleation rates for both phases. That line represents dynamic equilibria where a first derivative of a nucleation rate surface is broken. Lines *kt* and *tc* show the boundaries of single, i.e. solid or liquid phase embryo generation, respectively. Area *ket* illustrates nucleation rates when solid embryos prevail over droplet generation. Area *etch* is characterized by the higher rate of droplet formation. In common case a diagram of phase equilibria involves several lines of phase equilibria and several nucleation rate surfaces are appeared. That multifold nucleation rate surface did not have the adequate theoretical consideration. Multifold nucleation surface gets, as a rule, one-fold approximation of some version of nucleation theory. Theory has no chance to be proved by experiment in that way.

Clear discontinuities for nucleation rate surfaces for glycerin – carbon dioxide system can be seen for each data set (Anisimov *et al.*, 1998a) see, for example, Fig. 3. One discontinuity can be attributed to melting of glycerin–carbon dioxide binary system. The melting temperature (T_{melt}) clearly increases with a rise in carbon dioxide pressure from 0.1 to 0.3 MPa. Presumably the carbon dioxide concentration in solution increases proportional to the total pressure. The other disturbance is explained (Anisimov *et al.*, 1998a) by an unknown phase transition in critical embryos that appears near the critical line of the glycerine–carbon dioxide binary system. The origin of a nucleation rate surface discontinuity near critical conditions is not fully understood at this time because this type of phase transition has only been detected for the first time.

A conceptual problem in vapor-gas to liquid (or solid) nucleation is its treatment of the nucleation as a single component problem instead as a two component system. The impact of a critical embryo phase change on the nucleation rate surface topology has been reported by (Anisimov *et al.*, 1998a; 2000b; 2000c). A similar problem was found by Peeters *et al*. (2002). However, the observed jump in the water vapor nucleation rates was not reproduced in the next report from that group (Holten *et al.*, 2005). It may be that there is sufficient experimental variation in the nucleation rate measurements to prevent 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.

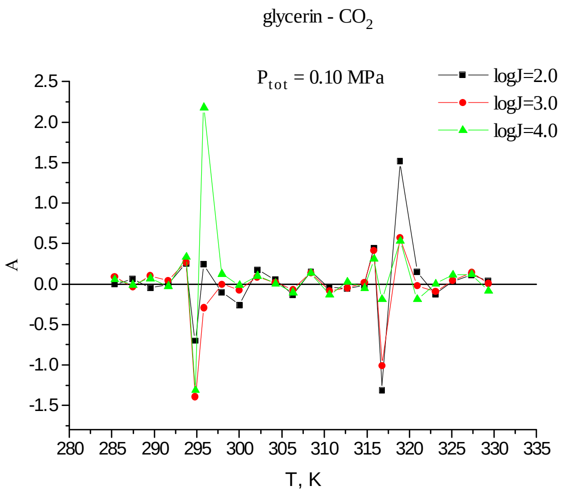

Figure 4. Distribution of average value of *A* and standard deviation, σ, on glycerine vapor nucleation in the vicinity of critical temperature of carbon dioxide such as $< A >= 0.01$, $\sigma=0.46$ and $< A >= 0.04$, $\sigma=0.16$ at total pressure $P_{tot}=0.1$ MPa for log *J*=3 with singularity and without it consequently (Anisimov et al., 2000c).

Anisimov *et al.* (2000c) have suggested using continuity and monotonic behavior in the data analysis to find the anomalies in the nucleation rate surfaces. This approach can be illustrated by defining the nucleation rate surface by the function, $F(x_1, x_2, ..., x_n)$, where $x_1, x_2, ..., x_n$ are independent variables such as pressure or temperature. When function *F* has continuous partial derivatives, the surface described by the function $F(x_1 , x_2 , . . . , x_n)$, is continuous and monotonic. For condition *F=constant, the* function, $F(x_1, . x_n)$ has *n*-1 independent variables.

The nucleation rate with two variables, such as temperature, *T*, and vapor supersaturation, *S*, and constant values of all other parameters $(P_1...P_n)$ can be considered. It is customary to present the nucleation rate experimental results with the A-criterion. A simple relation can be obtained along the surface section where $J(T,S) = constant$:

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

The criterion value, *A*, will be equal to zero if the vapor nucleation rate surface *J = J(T,S)* has no singularities. Because of experimental noise, the calculated values of *A* will include nonzero values that can be characterized by a non-dimensional standard deviation. The deviation of the *A* values from zero can characterize the quality of experimental results (if set of experimental values for *J* should represent a continuous and monotonous surface). A singularity in the nucleation rate surface (or surface for any other set of experimental results) breaks the local condition for surface continuity and monotony. Figure 4 presents the application of the A criterion for glycerin-carbon dioxide system (Anisimov *et al.*, 1998a). It can be seen that the *A*-criterion provides a sensitive tool for the detection of singularities in nucleation rate surfaces. Anisimov *et al.* (2000a) applied the *A*-criterion to data from Strey *et al.* (1995). The nucleation rate surface for pentanol-water vapor on the base of Strey *et al.* (1995) data shows the clear evidence of a nucleation rate surface singularity. This result is in contradiction to the conclusion that no effects on the nucleation rate surface topology is appeared for binary system with partial solubility of components (Strey *et al.*, 1995).

3. Total pressure and carrier gas nature effects

During the past two 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 (1956) made the first observations of a gas-pressure effect. They found that the nucleation rate decreased as the total system pressure increased. That effect is now called a negative gas-pressure effect. The result was reproduced in several other measurements (Katz *et al.* 1988; Brus and Zdimal, 2006). Katz *et al.* (1988) 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. Katz *et al.* (1988) suggested that the parameters for the heat and mass transfer calculations (diffusion coefficients, thermal conductivities, viscosities, *etc.*) are not sufficiently well defined and the variations of these parameters in terms of the error bars on the calculated nucleation rate values can dramatically change the gas-pressure effects.

Clear gas-pressure effects are discussed in several other publications. Anisimov and Vershinin (1988; 1990) experimentally found a positive gas-pressure effect and a gas-composition effect at gas pressures from 0.10 to 0.30 MPa. Fladerer and Strey (2006) 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 $J=10^{7(+/-2)}$ $cm^{-3}s^{-1}$ 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} $cm^{-3}s^{-1}$ for these conditions. Fladerer and

Strey (2006) suggested that calculations based on density functional theory can only partially explain the discrepancy of 20 orders of magnitude between the experimental and theoretical nucleation rates. Wedekind *et al.* (2008) take in to account the efficiency of thermalization and the additional work that a cluster has to spend for growing. These contributions produce the opposite trends in nucleation rates. Unfortunately a scale of these effects is located within two orders in nucleation rates when discrepancy of theoretical and experimental results is over 20 orders. Wedekind *et al.* (2008) consider their own result as qualitative because "we (Wedekind *et al.*, 2008) cannot discard the influence of other factors on the observed pressure effect." These experiments can be provided by molecular dynamics simulations as well or/and density functional theory calculations using a Lennard-Jones potential. Unfortunately these simulations and calculations usually fail for complex substances such as alcohols, water, *etc.* Experimental results of different experimental schemes used for nucleation rate measurements at cryogenic temperatures are still inconsistent (Fladerer and Strey, 2006) because of low accuracy of the experimental data.

4. The experimental nucleation rate data inconsistency

Several research groups have made comparative measurements of nucleation rates (Anisimov *et al.*, 1993; 1994; Wilck *et al.*, 1998; Brus *et al.*, 2005, *etc.*) The results of Brus *et al.* (2005) illustrate the inconsistency between the static diffusion chamber and an FDC for identical conditions of the same chemical system. The FDC values are higher than those from the static diffusion chamber results by three to four orders of magnitude. These examples illustrate the internal inconsistence of the experimental results that originate from different experimental systems. These inconsistencies generate the assumption that the typical nucleation vapor-gas experiments have an unrecognized and uncontrolled parameter.

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.* (1998a) and Anisimova *et al.* (2001) illustrate that high pressure measuring techniques need to be designed to study multi-channel nucleation.

5. 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.*, 2000c). 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.

6. Conclusions

Nucleation Theory has no chance to be proven when multifold nucleation surface gets interpretation by some version of nucleation theory using one-surface approximation. The present day Nucleation theory has no reliable experimental prove, because of the internal inconsistence of the experimental data. The pressure and carrier gas nature effects do not have reliable theoretical description and consistent experimental prove. 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. Because only dozens of molecules are involved in critical embryos formation for typical experimental conditions, the amount of vapor used to form the embryo is negligible compared to the total number of vapor-phase molecules and any vapor depletion problems within the nucleation volume are avoided.
- Decomposition of embryos should be evaluated when an adiabatic recompression (Allen & Kassner, 1969) 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 to be sure that heterogeneous seeds are activated (Anisimov and Cherevko, 1985).
- 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). This value is roughly the relative accuracy of modern nucleation rate measurements. Carrier gas purity of 99.995 % and higher is sufficient and available everywhere.
- 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 be considered as binary nucleation systems.
- Vapor-gas nucleation rate standards need to be developed to provide an absolute accuracy evaluation of experimental data. The problem of experimental data inconsistencies should be resolved to create a nucleation standard.
- Nucleation rate measurements of any single component systems such as noble gases or any other single vapor in a gas-free atmosphere are very attractive for research as examples of true single component systems.
- The critical embryo parameters such as number of molecules of each species, enthalpy of embryo formation, excess energy, *etc* can be estimated using experimental data for the nucleation rates (Anisimov and Cherevko, 1985; Anisimov *et al.*, 1987; Anisimov and Taylakov, 1989).

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