



Identification of the Relation and Systematic Research of the Nature of Intermolecular Interactions and Acquired Physical Properties of Objects Formed

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ABSTRACT

The existing analytical mathematical models and numerical modeling work are not able to resolve a significant number of problems, known as the classical problems of the nucleation theory. The described research has revealed the main cause of these problems, the classical models correctly show the initial stages of the development of nanoparticles, where the use of traditional continuum approach and potentials, parameterized on the basis of macroscopic properties of liquids usually is ungrounded. This research is based on a more accurate representation of the nature of the small nano objects which is that of quantum.

Key words: Thermodynamic Stability, Entropy, Enthalpy, Gibbs Free Energy, Microphysical Nature, Nucleation.

INTRODUCTION

A numerical experiment to determine the structure, physical and chemical properties and the thermodynamic stability of multicomponent molecular clusters and complexes created in nucleating atmospheric systems. The importance of the presented studies is related to the complex physical and chemical nature of the atmospheric gas atmospheres and the presence of major difficulties

and contradictions concerning the nature of the mechanisms of atmospheric nucleation which is directly connected with global climate changes. Water is the dominant component of the condensable vapour in the atmosphere, and water is unable to autonomously nucleate under typical atmospheric conditions due to the very low supersaturation and, therefore, the clusters and particles nucleating in the atmosphere are multicomponent.

The main targets of research are neutral and charged binary and ternary clusters and complexes consisting of the main atmospheric nucleation agents (sulphuric acid, water and NH_3) and common organic compounds. Performed is a study of coexistence of various types of the afore-mentioned clusters, their structure, and thermochemical stability. The study of the 'preference mark' phenomenon in the case of a more complex binary system and the gas-cluster-liquid transition in multicomponent systems¹.

It is a common knowledge that it is exceptionally important to have a clear understanding of the new particle creation mechanisms to quantify a wide range of phenomena related to climate, health condition and environment of atmospheric aerosols.

Multicomponent nucleation models in the atmosphere

Nucleation is multicomponent in the atmosphere, and it occurs in a medium which contains the full range of various materials including sulphuric acid, ammonium, ions and organic substances. In the current period we identified several mechanisms that could serve as a source for the appearance of new particles in the atmosphere:

The binary homogeneous nucleation (BHN) H_2SO_4 and H_2O

One of the problems of classical BHN is the excessive sensitivity to hydration thermodynamics, the essence of which is not well described by classical methods. The homogeneous nucleation in water vapour is schematically described by the following equation:

$$J = N_1 \left(\sum_{i=1}^{\infty} \frac{1}{\beta_i f_i} \right)^{-1} \quad \dots(1)$$

where β - the speed of the collision of monomers with a cluster, N_1 is the concentration of monomers, and

$$f_i = \exp\left(-\frac{\Delta G_i(N_1, T)}{kT}\right) \quad \dots(2)$$

The equilibrium constant for the formation of the i -measure controlled by changes in the Gibbs free energy. Changes in the Gibbs free energy ΔG_i associated with the formation of i -measure described SCC by the following formula:

$$\Delta G_i^{SCC} = -(i-1)kT \ln S + 4\pi(r_i^2 - r_i^2)\sigma, \quad \dots(3)$$

where S - oversaturation, $\sigma = \sigma(T)$ - specific surface energy (surface tension).

Although the kinetic BHN model has been recently significantly upgraded and enhanced through the use of experimental data and quantum computing, errors still occur in the BHN calculations. Improving the BHN calculation accuracy is critical because the general theoretical formalism of BHN is widely used in other nucleation theories in multicomponent mixtures. At present, careful monitoring of existing BHN models is difficult because of the great complications in laboratory experiments due to difficulties in determining the H_2SO_4 concentration in the nucleation zone.

The three-component homogeneous nucleation (ÖHN) H_2SO_4 - H_2O - NH_3

For a long period BHN has been regarded as a dominant tool of nucleation in the atmosphere. However, BHN is not able to explain all of the observed phenomena of nucleation. In order to solve this problem, the THN theory was developed in which ammonia acted as a stabiliser of H_2SO_4 - H_2O clusters. Although THN is known as an effective neutraliser of sulphuric acid solutions, its beneficial effect in the neutralisation and stabilisation of small acid clusters is unknown until now. THN classical models predict that the NH_3 can increase the rate of nucleation H_2SO_4 - H_2O by ~ 30 orders of magnitude¹. Meanwhile, all the laboratory tests show that the presence of NH_3 at a much higher concentration at the nucleation ppm level increases the nucleation of H_2SO_4 - H_2O only by ~ 2 order of magnitude². Kinetic modelling using the THN model, which was parametrised with the experimental data, shows that the contribution of THN to the creation of new particles in the boundary layer is likely to be rather negligible².

The difference in the rate of nucleation is related to the dipole moment of the monomers, which

is a new parameter to control the ion nucleation process. Let us consider the creation of a molecular cluster consisting of molecules (i - measures) by sequential addition of monomers for i -meter. For this process, the nucleation rate is described by the following equation:

$$J = N \left[\sum_{i=n_0}^{i_{\max}-1} \left[\beta_i \exp \left(\frac{-(\Delta G_i - \Delta G_{n_0})}{k T} \right) \right] \right]^{-1} \quad \dots(4)$$

where J - the nucleation rate, k -Boltzmann constant, N - ion concentration.

The ionic nucleation (IMN) H_2SO_4 - H_2O - ion

The presence of ions, which are active catalysts, makes it possible to overcome the nucleation barrier leads to a significant increase in the rate of nucleation¹⁰. Strong interactions among ionic clusters and dipolar molecules of the most common pollutants, toxic and chemically active substances lead to the creation of ultrafine particles directly associated with adverse health effects⁶⁻⁸. It was shown, that IMN could be an important mechanism for the formation of particles². Quite recently a second generation of the IMN model has been developed, which is based on significant progress in understanding the molecular nature and thermodynamics of the charged and neutral clusters over the past few years. The simulation results show that IMN leads to significant nucleation in the lower atmosphere.

H_2SO_4 - H_2O - Organics

The experimental work¹¹ showed that the presence of organic acids may increase the rate of nucleation of H_2SO_4 and H_2O . Nadykto and Yu has proved that ammonia is absolutely not an exclusive stabiliser of H_2SO_4 - H_2O clusters in the atmosphere¹². The low-molecular formic and acetic acids, which are among the most common organic acids in the atmosphere, were at least as effective in stabilising H_2SO_4 and H_2O clusters as NH_3 .

Despite the fact that sulphuric acid is a key nucleation agent in the lower troposphere, its investment in the polar stratosphere chemistry is much more modest. Another strong acid, the nitric one plays an important role in the balance of ozone

in the lower and middle polar stratosphere. When in the gas phase, nitric acid hydrates, which are condensed and crystallised in the stratosphere, have an important function in the physics and chemistry of polar stratospheric clouds directly associated with the depletion of the ozone layer in the Arctic and Antarctic regions¹³.

The classical models of the homogeneous and ionic nucleation are quite sensitive to a number of key parameters, such as surface tension and vapour pressure, which are not determined for a number of important systems.

A simplified expression, according to the classical scenario, for the nucleation rate in the analytical form is as follows:

$$J = EF_n \cdot N \beta_n^{(c)} \exp \left(- \frac{(\Delta G_n^* - \Delta G_{n_0})}{k T} \right) \quad \dots(5)$$

Where n^* - the number of molecules in the critical nucleus.

In the classical theory, the thermochemistry of clusters and nanoparticles are determined on the basis of the liquid-drop approach, with the surface tension and density as the key parameters that determine the Gibbs free energy. The strong exponential dependence of the rate of nucleation on the Gibbs free energy explains the excessive nucleation rate sensitivity to the values of the input parameters.

Molecular methods, which have been repeatedly used as an alternative to the classical nucleation theory, do not use the approach of the fluid to calculate the rate of nucleation. However, communication is usually approximated by using empirical (particularly T1R4R, T1R5R, Dang-Chang) potentials parameterised for liquid. The above empirical potentials 'were never designed to be used with small clusters' and their applicability to molecular clusters/complexes raises doubts¹⁴. The existing molecular models of nucleation can be classified as quasi-classical because they implicitly use the capillary approach. It is very important to indicate that the above conclusion does not mean that the molecular methods based on the use of

empirical potentials are absolutely incorrect or defective. For all that, it is advisable to keep in mind that the rate of nucleation is excessively sensitive to the thermodynamics of the first steps of creating a cluster. This means that the empirical potentials used in the theory of nucleation should make sure to demonstrate the thermochemical properties of molecular clusters.

In contrast to the existing classical nucleation models, which are sensitive to poorly determined input parameters and empirical models of interaction, a quantum system can predetermine the properties of systems of the arbitrary chemical composition. The thermochemical information derived from the 'first principles' can be used in the kinetic modelling of nucleation, with adequate kinetics of collisions and thermodynamics determined by a change in the Gibbs free energy.

Nucleation in the atmosphere is multicomponent. However, the classical aspect used is usually not capable of providing a quantitative description of multicomponent systems due to:

- Excessive sensitivity to the inaccurately determined coefficients of activity, density and surface tension of the multicomponent solutions;
- Strong dependence of the nucleation rate on thermochemistry of the initial stages of growth, where the liquid drop model is inapplicable;
- The impossibility of using the scaling due to the lack of reliable experimental data.

The use of more complex molecular techniques based on empirical potentials that could improve the theoretical foundations of the theory of nucleation; in the meantime, they need reliable empirical potentials for multicomponent systems that are simply not available. Unlike some existing models of nucleation, the quantum theory can predict the properties of a system of arbitrary chemical composition based on its wave function and does not need any bulk properties of the liquid or spherically symmetric approximation.

It is extremely important to adequately display equilibrium geometry and vibrational spectra in order to calculate enthalpy, entropy and Gibbs

free energy. In comparing the equilibrium geometry of the sulphuric acid molecule and sulphuric acid monohydrate produced at various levels of the theory with the experimental data¹⁵, it can be seen that PW91PW91 in combination with the largest Poplovsky set of wave functions 6- 311 ++ G (3df, 3pd) reproduces the geometric properties of hydrates with high accuracy providing almost complete agreement with the experimental data.

We give a description of the PW91 method that is most commonly used in the study of atmospheric systems. The PW91 method consists of two parts, the exchange part which is very similar to the one proposed by Beck in 1988, known as V88 and is determined by the formula⁹:

$$\varepsilon_x^{PW91} = \varepsilon_x^{LDA} \left(\frac{1 + x_{a_1} \sinh^{-1}(x_{a_2}) + (a_3 + a_4 e^{-bx^2})x^2}{1 + x_{a_1} \sinh^{-1}(x_{a_2}) + a_3 x^2} \right) \quad \dots(6)$$

Evaluation of the sensitivity of incremental changes in the Gibbs free energy shows that in order to achieve a deviation of 1 kcal/mol, which is much lower than the typical experimental error, the value of the scaling factor should be either < 0.65 or > ~ 1.5. For all that, none of the existing quantum-chemical methods is capable of providing such rough prediction of the vibrational spectra. It is also quite important to indicate that the harmonic frequencies obtained using the density functional theory are usually closer to the experimental data than the harmonic frequencies obtained with Ab initio methods.

The structure and thermochemical properties (H₂SO₄)-(H₂O)-(NH₃) of clusters were reviewed in several publications^{5,7}. Currently, there are no structural or spectroscopic data for these experimental systems.

Nadykto and Yu came to the following conclusions concerning the thermochemistry of triple clusters^{5,12}:

- The stabilising effect of ammonia on the creation of small clusters (H₂SO₄)-(H₂O) increases with the number of sulphuric acid molecules in the cluster.
- The thermochemistry (NH₃) and (H₂SO₄) in small (NH₃)-(H₂SO₄)-(H₂O)_n clusters either

independent or weakly depends on the water content. This means that the stabilising effect of ammonia at the initial stages of growth of clusters is mainly due to the affinity of the sulphuric acid to the formed clusters.

The numerical experiments also confirmed that the contribution of NH_3 to the atmospheric nucleation is much weaker than that stated in the classical ternary nucleation theory (THN), it is also confirmed by laboratory tests⁶.

Using quantum chemical simulation methods can solve a number of practically important tasks. The contradictions concerning the preferences of charge in the nucleation of binary ions in the atmosphere were eliminated and explained. While laboratory experiments pointed to a stronger hydration of positive ions, atmospheric measurements have shown that negative ions are much more effective nucleation agents.

A numerical experiment to determine the structure and thermochemical properties⁶ showed that the similarity of negative ions/clusters to the sulphuric acid, which controls the flow of nucleation, is much higher than the positive ones thus explaining the greater dynamism of anions in the nucleation process.

The properties of a number of charged clusters were studied, and obtained was another confirmation of the rapid transition gas-cluster liquid in case of ions of the complex composition⁵.

The results⁵ virtually eliminate any stabilising effects of ammonia on the creation of negatively charged cluster hydrates and clearly show that the presence of the charge is generally not a sign of any increased stability in considering ionic and neutral clusters of any identical or very similar chemical composition. These materials lead us to the conclusion that not only a quantitative but also a qualitative analysis of the thermodynamic stability of the atmospheric clusters is possible without proper research with quantum methods.

Despite the fact that the hydrations (HSO_4^-) (NH_3) and (HSO_4^-)(NH_3)(H_2O) are stronger than the hydration (H_2SO_4) (NH_3) and (H_2SO_4) (NH_3) (H_2O) the difference in hydration at 2-3 kcal/mol per step is not high enough to offset the very large (>9 kcal/mol) difference in the change in the free energy between the (HSO_4^-)+(NH₃) <=> (HSO_4^-)(NH₃) and (H_2SO_4)+(NH₃) <=> (H_2SO_4)(NH₃) reactions. This virtually eliminates the stabilising effect of ammonia on the creation of negatively charged clusters (HSO_4^-) (H_2O)_n and shows that the common consideration of the charged clusters as a more stable against the neutral clusters of similar chemical composition do not apply to smaller Nano objects.

CONCLUSION AND RESULTS

The results of this study lead us to the following conclusions:

- The presence of NH_3 does not contribute to increasing in the thermochemical stability $\text{HSO}_4^-(\text{H}_2\text{O})_n$ and ammonia hardly participates in the gas-phase hydration of negative ions of the sulphuric acid in atmospheric conditions.
- The total change in free energy associated with the formation of charged (HSO_4^-)(NH_3) (H_2O)_n is less negative than the total free energy change associated with the formation of (H_2SO_4) (NH_3) (H_2O)_n in connection with the positive values of the affinity NH_3 to (HSO_4^-).
- Evaluation of the charged clusters in the classical theory of nucleation as thermodynamically more stable compared to the neutral one is not applicable to the nucleating atmospheric clusters. This means that not only quantitative but also qualitative evaluation of the thermodynamic stability of atmospheric clusters is impossible without the use of quantum chemical methods.

The stability of the positively charged clusters containing sulphuric acid, water and ammonia were studied using the density functional theory (DFT) in the work⁴. It is shown that under normal conditions of the boundary layer of the atmosphere a considerable part of the positive ions may include ammonia, while the majority of neutral and negative ions contain no ammonia.

REFERENCES

1. Napari, I.; Noppel, M.; Vehkamäki, H.; Kulmala, M. *J. Geo-phys. Res.* **2002**, *107*, 4381-4387. doi: 10.1029/2002JD002132
2. Yu, F. *J. Geophys. Res.* **2006**, *111*, D01204, doi:10.1029/2005JD005968
3. Xu, Y.; Nadykto, A. B.; Yu, F.; Jiang, L.; Wang, W. *J. Molec. Struct.* **2010**, *951*, 28-33. doi:10.1016/j.theochem.2010.04.004
4. Nadykto, A. B.; Herb, J.; Yu, F.; Xu, Y.; Nazarenko, E. S. *Entropy.* **2015**, *17*, 2764-2780. doi: 10.1021/jp9068575
5. Nadykto, A. B.; Yu, F.; Herb, J. *Chem. Phys.* **2009**, *360*, 67-73. doi:10.1016/j.chemphys.2009.04.007
6. Nadykto, A. B.; Yu, F.; Herb, J. *Phys. Chem. Chem. Phys.* **2008**, *10*, 7073-7078. doi: 10.1039/B807415A
7. Nadykto, A. B.; Yu, F.; Herb, J. *Int. J. Mol. Sc.* **2008**, *9*, 2184-2193. doi:10.3390/ijms9112184
8. Nadykto, A. B.; Yu, F. *J. Geo-phys. Res.* **2003**, *9*. doi: 10.1029/2003JD003664
9. Kurtén, T.; Torpo, L.; Ding, C. G.; Vehkamäki, H.; Sundberg, M.R.; Laasonen, K.; Kulmala, M. *J. Geo-phys. Res.* **2007**, *112*, doi:10.1029/2006JD007391
10. Lovejoy, E. R.; Curtius, J.; Froyd, K. D. *J. Geo-phys. Res.* **2004**, *109*. doi: 10.1029/2003JD004460
11. Arshadi, M.; Yamdagni, R.; Kebarle, p. *J. Phys. Chem.* **1970**, *74*, 1475-1489.
12. Nadykto, A. B.; Yu, F. *Chem. Phys. Lett.* **2007**, *435*, 14-18.
13. Al Natsheh, A.; Nadykto, A. B.; Mikkelsen, K. V.; Yu, F.; Ruuskanen, J. *Chem. Phys. Lett.* **2006**, *426*, 20-25. doi: 10.1016/j.cplett.2006.05.082
14. Valiev, M.; Garrett, B. C.; Tsai, M. K.; Kowalski, K.; Kathmann, S. M.; Schenter, G. K.; Dupuis, M. *J. Chem. Phys.* **2007**, *127*. doi: 10.1063/1.2768343
15. Fiocco, D. L.; Hunt, S. W.; Leopold, K. R. *J. Am. Chem. Soc.* **2002**, *124*, 4504-4511. doi: 10.1021/ja012724w