

***Interactive comment on* “Formation of binary ion clusters from polar vapours: Effect of the dipole-charge interaction” by A. B. Nadykto and F. Yu**

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1. We agree that the applicability of the present nucleation model, which is derived assuming the bulk surface tension, density and dielectric constants of the condensed matter, might be generally limited when the critical cluster is composed of $n \ll 1000$ molecules. The discussion is included in the revised paper. However, the quality of the measurements of the bulk surface tension applied in the nucleation models is another problem. It is well known that the values of the surface tension given by different methods such as capillary rise, maximum bubble pressure and Vilgelmi plate (or other contact methods) often deviates by several dynes. Unfortunately, in studies concerning the surface tension very important data such as isotherms of the contact angles or control of the bubble shape are often absent. Since the cluster thermodynamics depend strongly on the surface tension of the nucleating substance, it is difficult to fig-

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ure out whether the capillary approximation is imperfect or the bulk surface tension is measured (or maybe defined) inaccurately.

2. Comparison of the new model predictions with the available experimental data on the thermodynamics of binary clusters/particles would be useful indeed. However, at this point we found in the literature just few experimental studies concerning single-component the charged water clusters and sulfuric acid clusters. We would like to emphasize that the paper is focused on the thermodynamics of the binary clusters while the available the experimental studies consider the single-component ones. On the other hand, for the single-component clusters the validity of the thermodynamical model applied in the present theory has likely been justified through the comparison made in the recently published Nadykto et al. Chem.Phys. Lett. (Vol 382/1-2 pp 6-11, 2003). Running a binary model to get the results for a single-component case is not practical because the models of the activity coefficients are valid over limited range of the ambient concentration of sulfuric acid ($1E7 - 1E10 \text{ cm}^{-3}$) and water vapour molecules ($1E16 - 1E18 \text{ cm}^{-3}$) and they fail at low (or very high) concentrations.

3. The nature of the effect of the dipole-charge interaction is different from that of the Thomson effect. The Thomson effect relates to the condensed phase while the dipole-charge interaction modifies the chemical potential of the condensing monomers in the electrical field of the charged particle/cluster. The classical IIN model is derived assuming a flat monomer concentration profile in the vicinity of the nucleating cluster, which a good approximation for non-polar vapours. The interaction of polar monomers with the electrical field of the charged particle leads to the enhancement in the monomer concentration near the particle surface (Nadykto et al. (2003)).

4. We included a brief discussion on the sign preference in the paper. Although the present theory is not focused on the sign effect, it possesses some potential for explaining the sign preference because both the enhancement factor for the condensation rate (Nadykto & Yu. JGR, 108, 4717, 2003) and correction to the chemical potential of the condensable vapour molecules strongly depend on the stretch of electrical field and

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the mean cluster density, which may be different for positive and negative ions due to different geometry and charge distribution.

5. The method used Nadykto et al. (2003) is different from that given in publication by Korshunov. Korshunov's study is based on the comparison of the chemical potentials and it does not give any information about the Gibbs free energy of the cluster formation. We will include the reference to the Korshunov's study concerning the calculation of vapour pressure in the vicinity of the particle. (The explanation about the difference in the computation techniques is given in Nadykto et al. (2003)).

6. Ions influence the nucleation rates through both the reduction of change in the Gibbs free energy (evaporation) and enhancement of the growth rates (condensation). Hence, both effects have to be taken into account simultaneously. The contribution of the dipole-charge interaction to the growth kinetics may be very big (Nadykto & Yu. JGR, 108, 4717, (2003)) and, thus, the derivation of the nucleation rates is not as straightforward as it could be expected. We do not include the comparison of the changes in the Gibbs free energy in the paper purposely, because the presentation of the change in the Gibbs free energy only may make wrong impression about the charge effect on the nucleation rates. For the general audience difference in the change of the Gibbs free energy is associated directly with the difference in the nucleation rates that is not always the case. In the case studied in the paper, there does exist another important factor-enhancement of the condensational growth due to the dipole-charge interaction that can affect strongly the nucleation rates. The complete theory of the nucleation rates requires corrections to both the Gibbs free energy and forward (condensation) rate, as well as the other related effects such as hydration and possibly change in the dielectrical properties of the condensed phase due to the electrical field applied, to be accounted for simultaneously. The work on the detailed model of the nucleation rates is in progress and we plan to publish it elsewhere.

Technical corrections: Corrected accordingly.

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