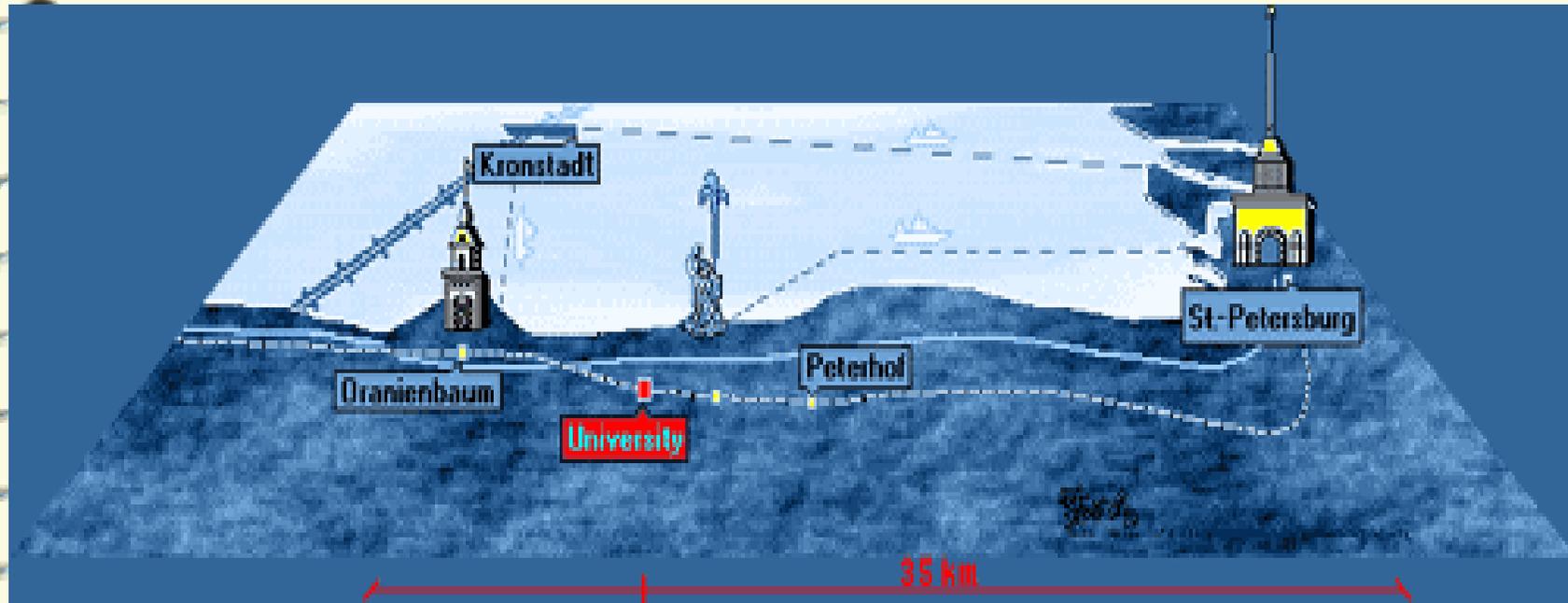


A spiral-bound notebook with a brown cover and a cream-colored page. The spiral binding is on the left side. The text is centered on the page.

**Mechanisms of Heterogeneous Nucleation on Wettable Particles:  
the Electric Polarization, Osmotic Pressure, Disjoining Pressure,  
and Micellization Effects**



# INSTITUTE OF PHISICS



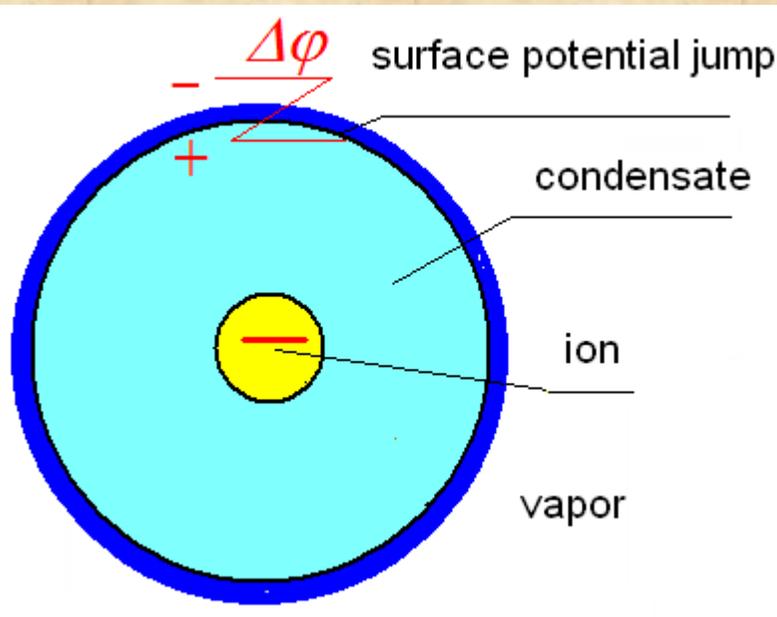
# Outline

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- ☞ The electric effects and sign preference in ion-induced nucleation
- ☞ The atmospheric electricity and small nanosized droplets
- ☞ Nucleation on soluble particles and the osmotic pressure
- ☞ Nucleation on wettable insoluble condensation nuclei and the disjoining pressure
- ☞ The general mechanism of heterogeneous nucleation
- ☞ Joint effects of the osmotic and disjoining pressures: deliquescence and efflorescence
- ☞ Joint effects of the electric field and the disjoining pressure: charge and sign preference in nucleation on nanosized charged particles

# The electric effects and sign preference in ion-induced nucleation

Experiment shows that nucleation in water vapor begins on negative ions at smaller supersaturation ratios than on positive ions, since C.T.R. Wilson (1899).



A strong electric field of the central ion brings nonlinear surface polarization of a nucleating nanodroplet. As a result, the saturation vapor pressure depends on ion charge value and its sign as  $\sim q^3$ . It also depends on the value and sign of the spontaneous potential jump at the vapor-liquid interface.

F.M.Kuni, A.K.Shchekin, A.I.Rusanov. Expansion in the curvature parameter of a drop in a strong field of charged nucleus. *Colloid Journal*. 1983. V.45 (4), pp. 598-604.

F.M.Kuni, A.K.Shchekin, A.I.Rusanov. Calculation of the work of formation for a droplet in the strong field of a charged nucleus. *Colloid Journal*. 1983. v.45 (5), pp. 801-807.

F.M.Kuni, A.K.Shchekin, A.I.Rusanov. Chemical potential of vapor on threshold of barrierless nucleation, and asymmetry of chemical potential relative to sign of nuclear charge. *Colloid Journal*. 1983. v.45 (6), pp. 951-957.

A.K.Shchekin, A.I.Rusanov, F.M.Kuni. Barrierless nucleation in vapors of organic liquids. *Colloid Journal*. 1984. V. 46 (3), pp. 474-481

Confirmed within the density functional approach — Kusaka I., Wang Z.G., Seinfeld J.H. *J. Chem.Phys.* 1995. v.109, n.2, p.913.

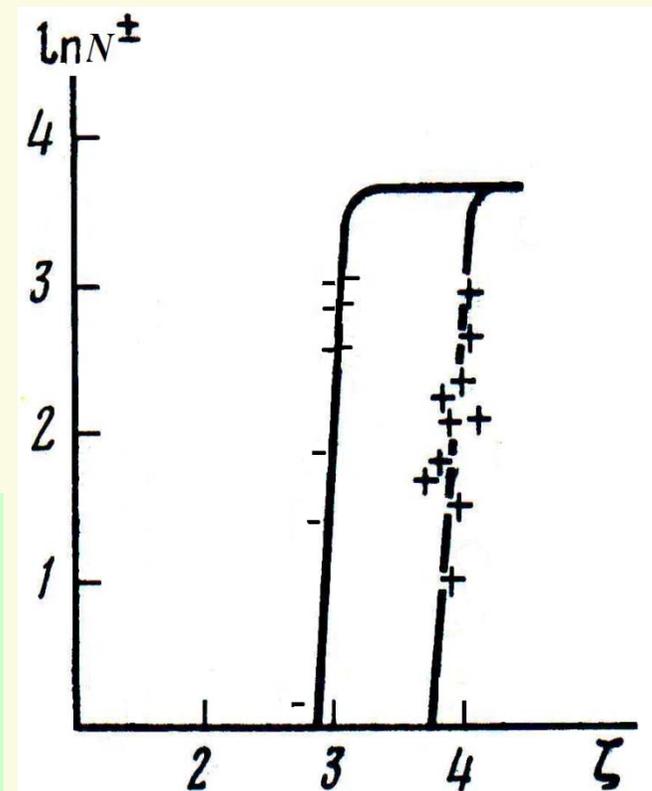
## The effect of sign preference in nucleation of water on ions

Theory of non-steady state kinetics of ion-induced nucleation kinetics under conditions in the Wilson chamber is formulated with account of the sign preference effect

F.M.Kuni, A.K.Shchekin, K.V.Kopeikin. Kinetics of heterogeneous condensation. Condensation on charged nuclei and asymmetry of condensation relative to sign of charge on nucleus. Colloid Journal. 1985. v. 47 (2), pp. 247-253.

Experimental data on the number  $N^\pm$  of nucleating droplets on positive and negative ions as a function of critical vapor supersaturation ratio  $\zeta$  were compared with the theoretical predictions.

D.R.White and J.L.Kassner, Jr., J.Aerosol Sci. 1971, v.2 (2), p.201



# The atmospheric electricity and small nanosized droplets

In order to explain the atmospheric electricity, about 20 theoretical approaches had been proposed, but they did not stay on thermodynamic ground.

Due to the electric structure of water molecule (its dipole and quadrupole moments), the electric potential jumps at the interface (even in the absence of an external electric field).

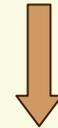
**Separation of charges in the atmosphere**



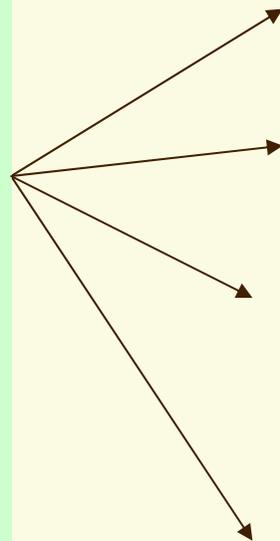
**Anomalous polarization of clouds**



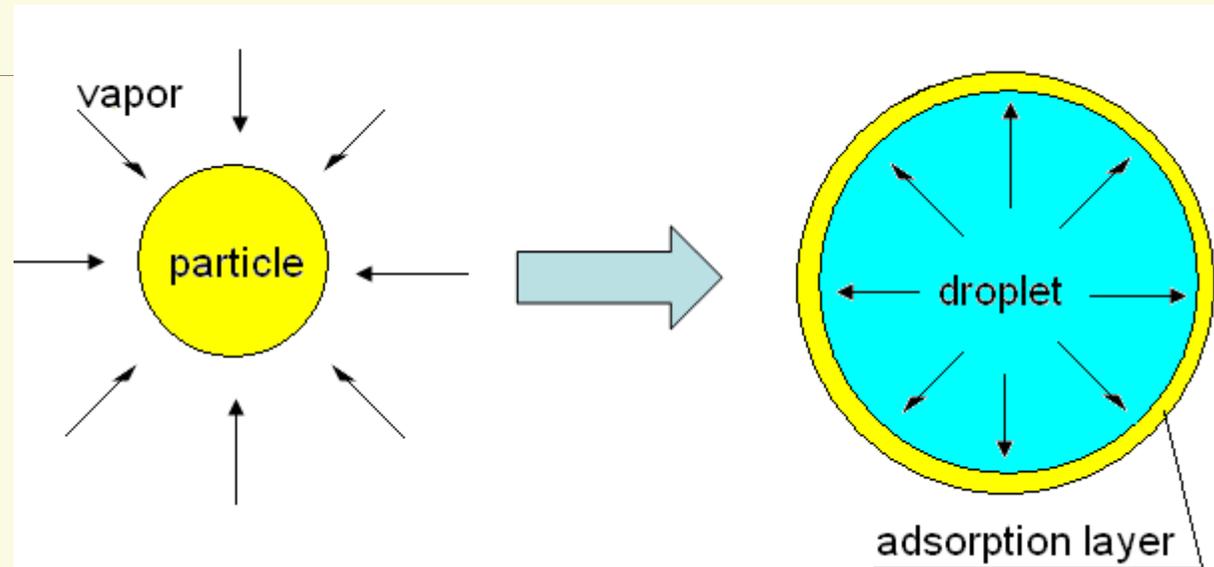
**Negative charge of rain**



**Negative charge of the Earth**

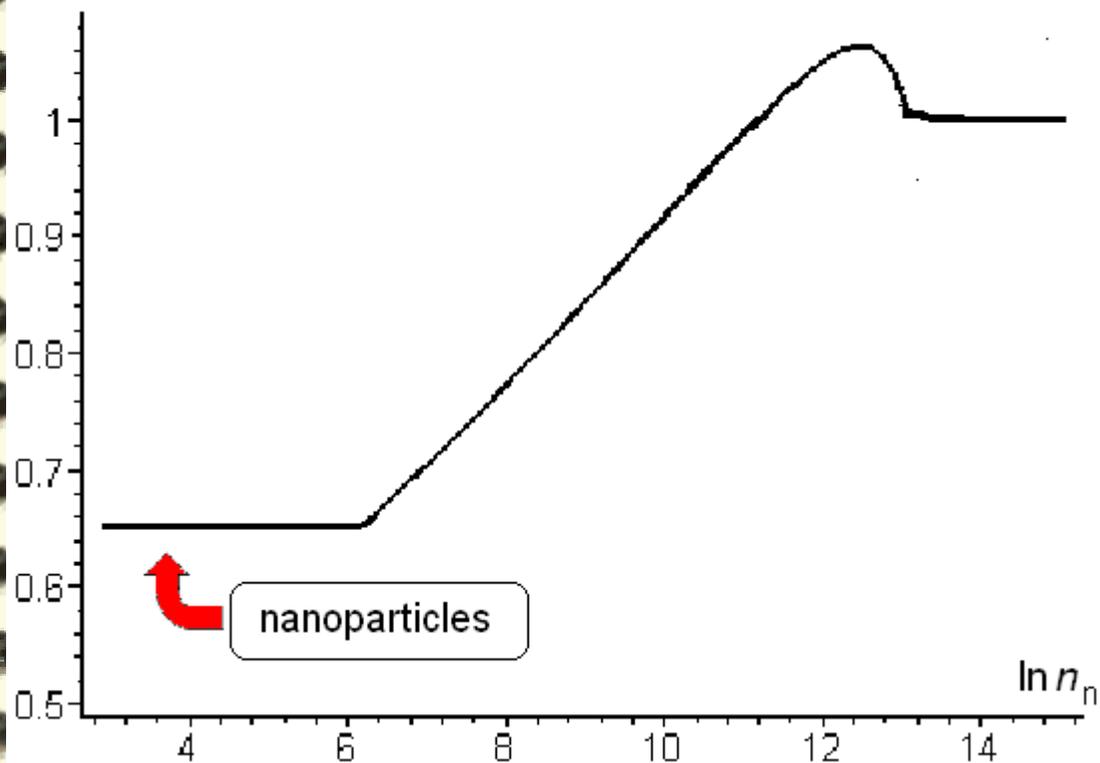


# Nucleation on soluble particles and the osmotic pressure



**Soluble particles may consist of salt or soluble organics. Surface active organic compounds can be accumulate at solution at the droplet surface and form an adsorption monolayer. If the volume concentration of the surfactant exceeds the critical micelle concentration, the substance can be in the solution within the droplet in the form of small stable aggregates – micelles. Even though the classical Köhler theory takes into account the osmotic pressure effects, it does not consider adsorption and micellization effects.**

the threshold vapor supersaturation



The theory can now predict the threshold vapor supersaturation as a function of the initial particle size ( $n_n$  is the number of molecules in the soluble particle). For very small particles, the threshold vapor supersaturation can be considerably below than that predicted by the Köhler theory. Thus, if the surfactant has a high solubility in the condensate, the adsorption can stimulate heterogeneous nucleation.

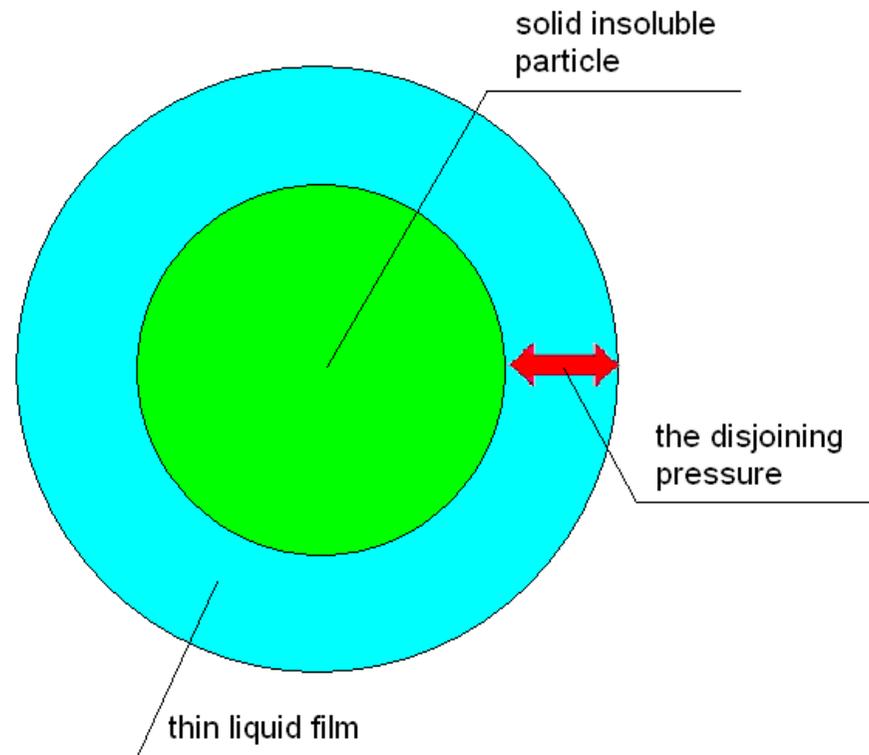
A.I.Rusanov, F.M. Kuni, A.K.Shchekin. Principles of thermodynamics of condensation on soluble nuclei of surface-active substances. Colloid Journal. 1993. V. 55 (2), pp. 193-201.

A.K.Shchekin, F.M.Kuni, T.M.Yakovenko, A.I.Rusanov. Thermodynamic principles of condensation kinetics on the soluble surfactant nuclei. Colloid Journal. 1995. V.57 (1), pp. 93-101.

A.K.Shchekin, F.M.Kuni, T.M.Yakovenko, A.I.Rusanov. Calculation and analysis of thermodynamic characteristics of condensation kinetics on the soluble surfactant nuclei. Colloid Journal. 1995. V.57 (2) pp.242-248.

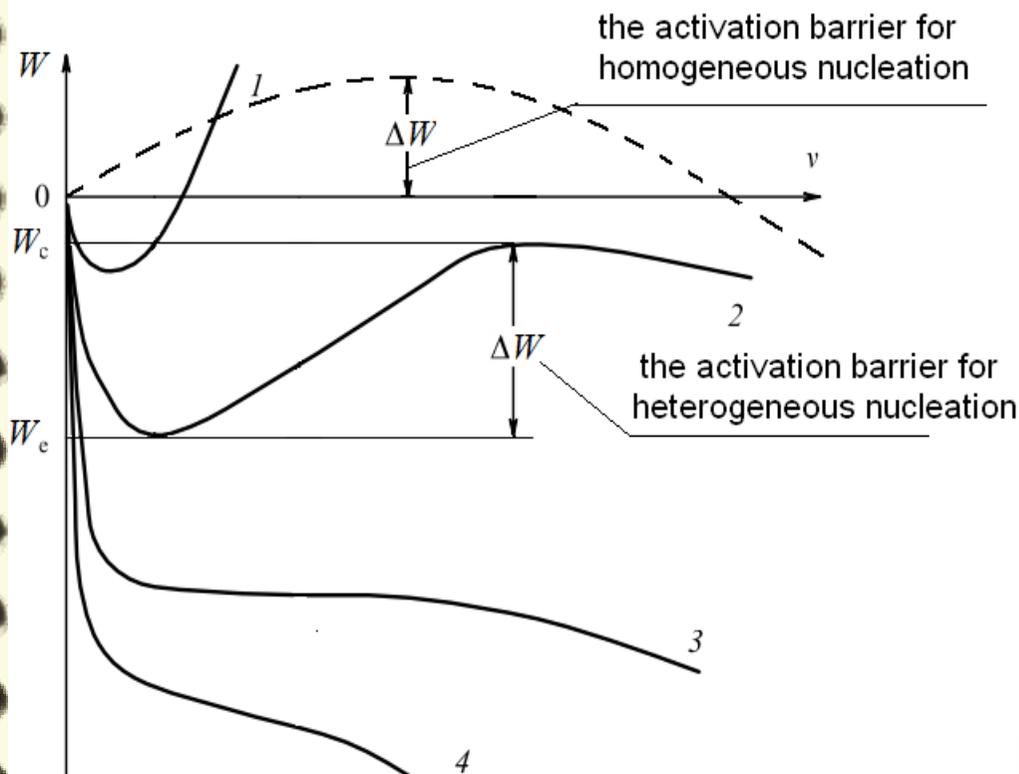
# Nucleation on wettable insoluble condensation nuclei and the disjoining pressure

Nucleation on small insoluble particles is usually considered in the frameworks of the Volmer-Fletcher theory. It was assumed in the Krastanov theory that activity of such particles can be explained by the fact that droplet growth starts from the size of the particle and requires smaller activation energy. Such approach could not explain the existence of ultra-small critical vapor supersaturations for this type of nucleation.



F.M.Kuni, A.K.Shchekin, A.I.Rusanov, B.Widom. Role of surface forces in heterogeneous nucleation on wettable nuclei. *Advances in Colloid and Interface Science*, 1996, v.65, p.71-124.

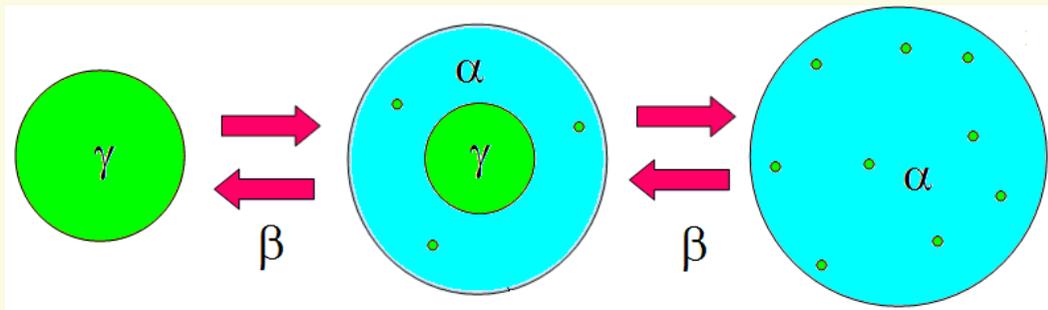
# The general mechanism of heterogeneous nucleation



The typical behavior of the work  $W$  of droplet formation as a function of the number  $v$  of condensate molecules in the droplet for homogeneous and heterogeneous nucleation. Curves 1, 2, 3 and 4 illustrate the influence of vapor supersaturation  $\zeta$  : 1 – undersaturated vapor, 2 – barrier nucleation in supersaturated vapor, 3 and 4 – barrierless nucleation in supersaturated vapor.

F.M. Kuni, A.K. Shchekin, A.P. Grinin. Theory of heterogeneous nucleation for vapor undergoing a gradual metastable state formation process. Physics Uspekhi, 2001, vol.44, no. 4, pp.331-370.

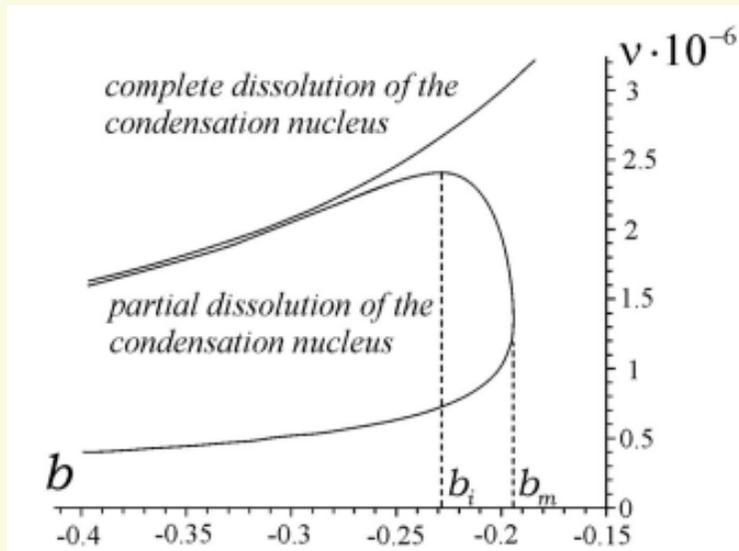
# Joint effects of the osmotic and disjoining pressures: deliquescence and efflorescence



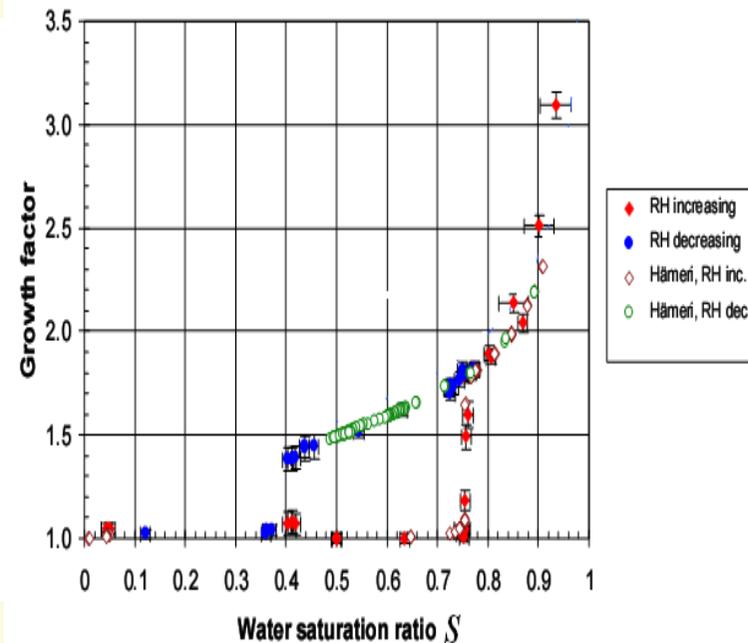
Core-shell aggregate in an ambient vapour: phase  $\gamma$ =soluble core; phase  $\alpha$ =enveloping liquid film (solvent shell); phase  $\beta$ =solvent vapour.

The initial stage of nucleation on soluble solid particles in the atmosphere of a solvent vapor with formation of droplets consisting of the liquid solution film around incompletely dissolved particles (the deliquescence stage) attracts now a considerable attention due to abilities of obtaining a stable droplet distribution at aggregative equilibrium in undersaturated vapor. The reversal process (the efflorescence stage) gives a possibility to modify the size and initial composition of aerosol particles.

# Theory and experiment



$$b = \ln S$$



The deliquescence stage illustrates the significance of the disjoining pressure in film nucleation.

# Two dimensional theory of deliquescence

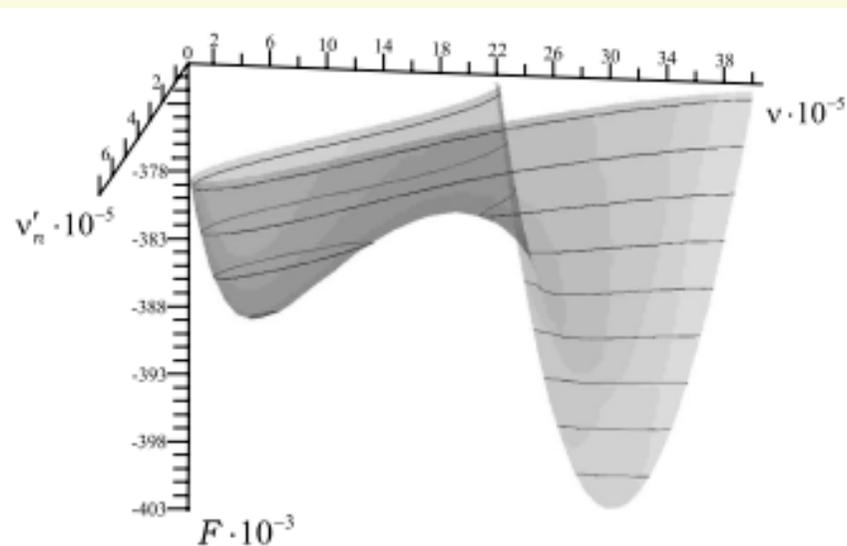


FIG. 1. The two-dimensional work  $F$  of the droplet formation on a soluble nucleus in an undersaturated vapor at the vapor chemical potential  $b=-0.2$ .

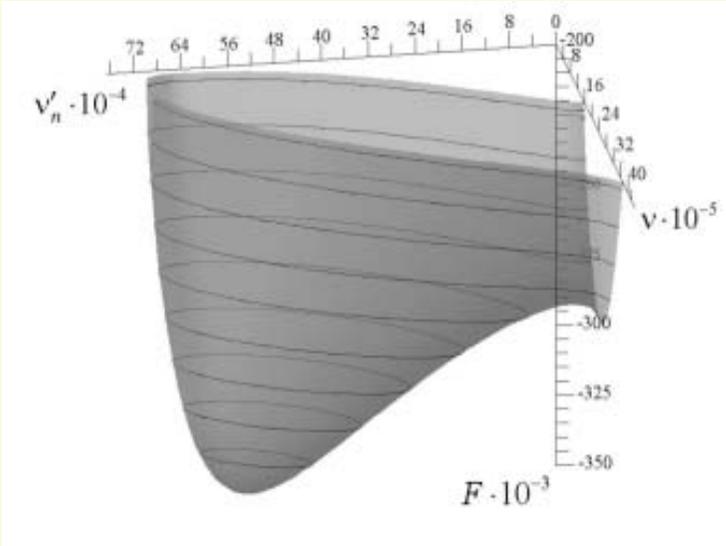
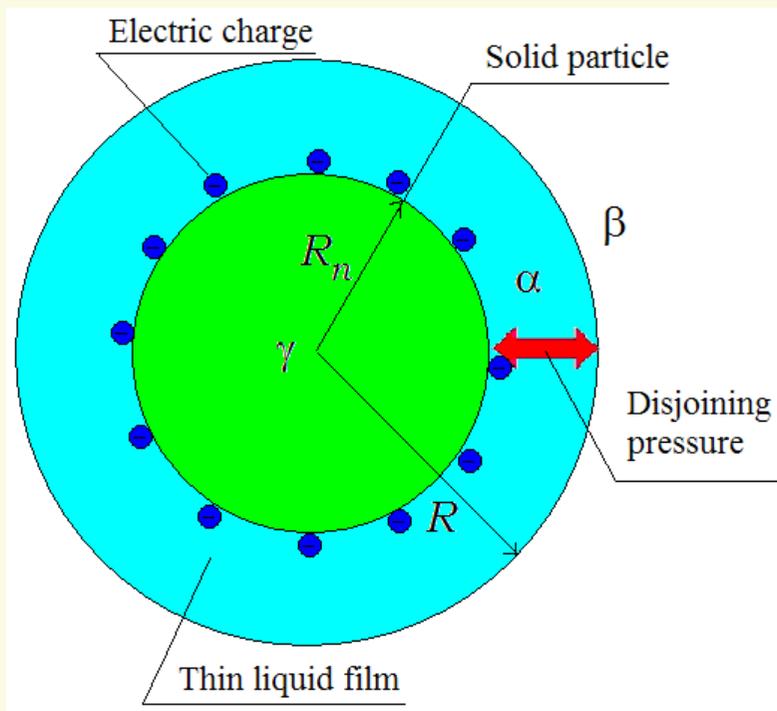


FIG. 2. The two-dimensional work  $F$  of the droplet formation on a soluble nucleus in an undersaturated vapor at the vapor chemical potential  $b=-0.25$ .

A.K Shchekin, A.I. Rusanov. Generalization of the Gibbs–Kelvin–Köhler and Ostwald–Freundlich equations for a liquid film on a soluble nanoparticle. *Journal of Chemical Physics*. 2008. v. 129, 154116.

A.K. Shchekin, I.V. Shabaev, A.I. Rusanov. “Thermodynamics of droplet formation around a soluble condensation nucleus in the atmosphere of a solvent vapor”. *Journal of Chemical Physics*. 2008, v. 129, 214111.

## Joint effects of the electric field and the disjoining pressure: charge and sign preference in nucleation on nanosized charged particles



The initial stage of the formation of a droplet around the charged solid particle.

- Do the properties of bulk liquid phase be achieved within a film around the solid particle?
- What is the role of hydrophobicity or hydrophilicity of the particle surface?
- How the joint description of the effects of electric field and the disjoining pressure can be incorporated?