A First Order Phase Transition: Aerosol Formation

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Abstract

A computational model has been developed to simulate heterogeneous nucleation on different conditions with different vapours. In this study the model has been applied for two cases: binary water – n-propanol vapour mixture and binary water – sulphuric acid vapour mixture.

1 Introduction

The word aerosol is used for small solid or liquid particles suspended in gas. The size of these particles varies from 1 nm to 100 μm. Some common examples of aerosols are clouds, water droplets and smoke.

Aerosol formation is due to primary and secondary sources. Primary sources like trees, volcanoes and automobiles emit aerosols directly to the atmosphere. Secondary paths of aerosol formation include several gas-to-particle conversion processes (e.g. condensation). Nucleation is the first step of secondary aerosol formation.

2 Nucleation

Nucleation initiates a first order phase transition, which can be connected e.g. to atmospheric processes and aerosol formation. There are a few types of different nucleation processes. Homogeneous nucleation means the formation of droplets from pure vapour (figure 1 a) and heterogeneous nucleation the formation of particles on pre-existing nuclei or ions (figure 1 b). Nucleation can be homomolecular (only one vapour species) or heteromolecular (two or more vapour species). Nucleation plays a fundamental role in many everyday processes like boiling and freezing.

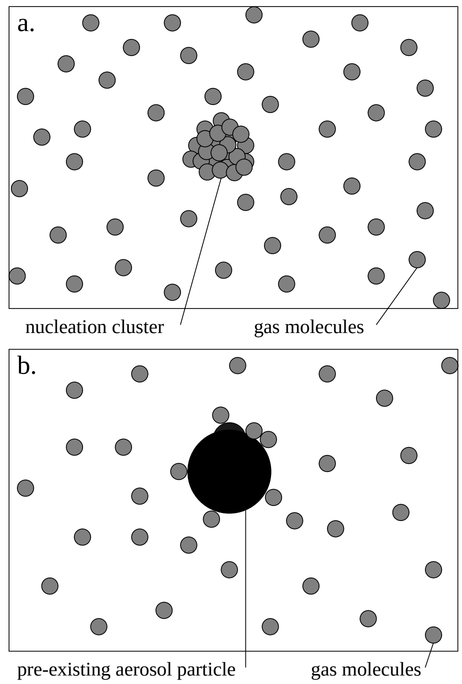

Figure 1: Homogeneous (a) and heterogeneous (b) nucleation

In a binary system the Gibbs free energy of formation of a liquid drop is [1]

$$\Delta G = n_1 \Delta\mu_1 + n_2 \Delta\mu_2 + 4\pi r^2 \sigma, \qquad (1)$$

where n_a is the number of species a molecules, r the radius of a critical cluster and $\Delta\mu_a$ the chemical potential of species a:

$$\Delta\mu_i = -kT \ln \frac{p_i}{p_{i\infty}}, \qquad (2)$$

where p_i is the vapour pressure of species i and $p_{i\infty}$ is the saturation vapour pressure of species i.

There is a saddle point, which corresponds to the minimum height of the Gibbs free energy [2] (figure 2). When a cluster reaches this point, nucleation occurs. At the saddle point the following conditions must be satisfied:

$$(\frac{\partial \Delta G}{\partial n_1})_{n_2} = (\frac{\partial \Delta G}{\partial n_2})_{n_1} = 0. \qquad (3)$$

From equations (1), (2) and (3) it can be concluded that for every saturation ratio $S = \frac{p_i}{p_{i\infty}}$ of the gas

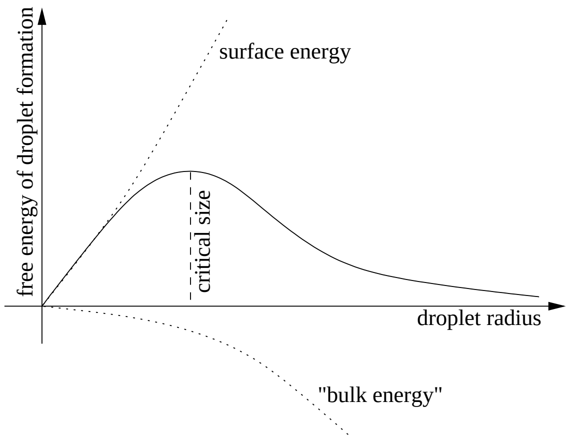

Figure 2: Change of Gibbs free energy as a function of droplet radius

phase of the compounds there exists a corresponding radius giving the smallest stable size of a droplet.

Using the capillarity approximation (surface tension σ taken as that of the bulk liquid monomer) [3] and the droplet volume

$$V = \frac{4}{3}\pi r^3 = n_1 v_1 + n_2 v_2 \tag{4}$$

the critical value of the Gibbs free energy can be calculated [4]:

$$\Delta G^* = \frac{\partial \Delta\mu_1}{\partial n_1} + \frac{\partial \Delta\mu_2}{\partial n_2} + \frac{4}{3}\pi\sigma r^2. \tag{5}$$

Using the generalized Kelvin equations [5] the critical value of the Gibbs free energy can be written as

$$\Delta G^* = \frac{4\pi r^2 \sigma}{3}, \tag{6}$$

where σ is the surface tension.

Furthermore, the formation rate of critical embryos (nucleation rate) is given by

$$I_0 = C \exp(\frac{-\Delta G^*}{kT}), \tag{7}$$

where C is (mainly) a kinetic factor.

The first theory of heterogeneous nucleation was introduced by Volmer [6] in 1939. Fletcher [5] extended the theory in 1958 to include the effects of particle size. Hamill et al [1] showed that the contact angle and the radius of curvature of the pre-existing particles have a great effect on the nucleation rate.

On figure 3 a picture of the embryo formation mechanism in heterogeneous nucleation can be seen. An embryo (2) of radius r starts forming on an existing aerosol particle of radius R_p (3) with contact angle θ in parent phase (1). The nucleating particle is considered to be a sphere and the embryo is assumed to be a part of a sphere [4].

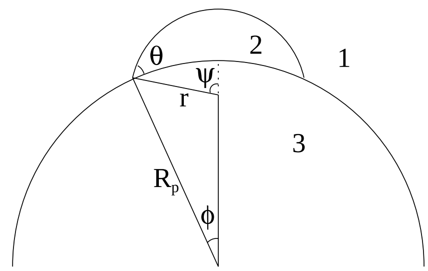

Figure 3: Embryo 2 on particle 3 in parent phase 1

Using the generalized Kelvin equation [5] and simple geometry it is quite straightforward to calculate the critical radius of the embryo:

$$r^* = -\frac{2\sigma_{12}}{\Delta G_v}, \tag{8}$$

where σ_{12} is the surface tension of the compound 2 in parent phase 1.

Furthermore, the free energy of the critical embryo formation can be calculated from [7]

$$\Delta G^* = \frac{2}{3}\pi r^{*2}\sigma_{12} f(m,x), \tag{9}$$

where

$$\begin{aligned} f(m,x) &= 1 + (\frac{1-mx}{g})^3 \\ &+ x^3[2 - 3(\frac{x-m}{g}) + (\frac{x-m}{g})^3] \\ &+ 3mx^2(\frac{x-m}{g} - 1), \end{aligned} \tag{10}$$

$$g = (1 + x^2 - 2mx)^{1/2}, \tag{11}$$

$$m = \cos\theta, \tag{12}$$

and

$$x = \frac{R_p}{r^*} \tag{13}$$

following from the geometry of the system.

The nucleation rate is given by [1]

$$I_0 = N^{ads} Z R_{av} \exp(-\frac{\Delta G^*}{kT}), \qquad (14)$$

where N^{ads} is the number of molecules adsorbed per unit area on the solid nuclei [7], Z is the Zeldovich non-equilibrium factor [4] and R_{av} the average condensation rate [8].

Finally, under the assumption that the active site is uniform and covers the whole surface of the aerosol particle, the probability of an embryo appearance on an aerosol particle (nucleation probability) is given by [9]

$$P = 1 - \exp(-4\pi R_p^2 I_0 \tau), \qquad (15)$$

where τ is the duration of the experiment.

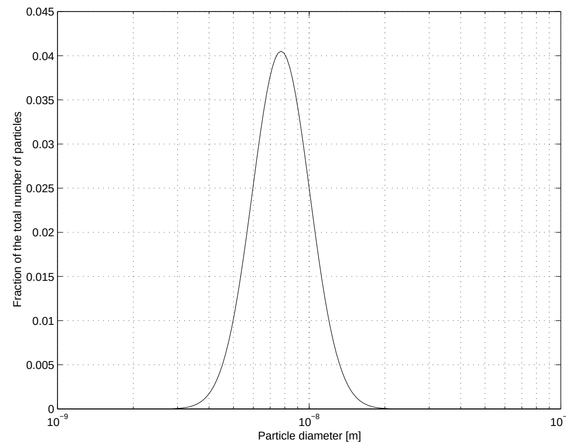

Figure 4: A typical lognormal particle size distribution with a mean diameter of 8 nm

3 The model

A computational model has been built to simulate the heteromolecular heterogeneous nucleation for binary vapour mixtures. In this study it has been applied for two kinds of mixtures: water – n-propanol and water – sulphuric acid mixtures. Especially sulphate aerosols play an important role in the Earth's climate system and in atmospheric chemistry.

The model calculates the nucleation probability from various input values (temperature, saturation ratios/activities of both substants, size distribution of aerosol particles, duration of the experiment etc.).

The size distributions used in the model are lognormal, with mean diameter varying from 8 nm to 100 nm (figure 4).

4 Results and discussion

Heterogeneous nucleation takes place on much smaller vapour concentration than homogeneous nucleation. It is suggested that small, undetectable particles (size under 3 nm) are formed by homogeneous nucleation [10], while bigger particles are formed mainly by heterogeneous nucleation – the atmosphere is full of small particles onto which vapour molecules can nucleate.

In the case of water – sulphuric acid binary system the number of adsorbed water molecules represents the number of all adsorbed molecules rather well, because the number of sulphuric acid molecules is usually very small compared to the number of water molecules. This is not the case in the water – n-propanol system, however. When comparing the results gained using the model with the measurement data, it can be seen that the results improve dramatically when the influence of adsorbed n-propanol molecules is included. The upper curve in figure 5 is calculated without taking adsorbed n-propanol molecules into account. The lower curve includes adsorbed n-propanol molecules. The stars represent measured values [11].

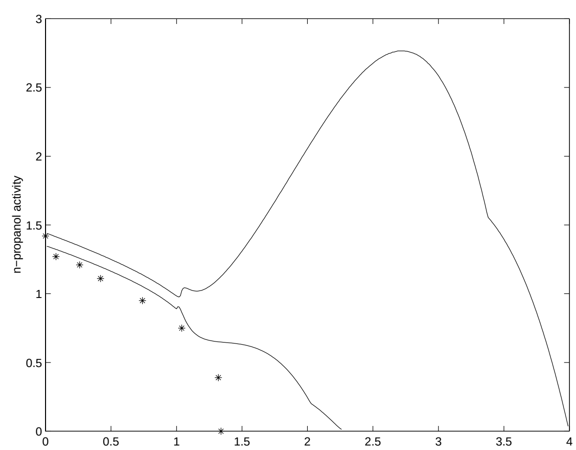

Figure 5: Calculated and measured activities for n-propanol and water in heterogeneous nucleation

The presence of hydrates tends to decrease the nucleation rate, because they stabilize the vapour by reducing the number of sulphuric acid monomers (single molecules). The hydration in water – sulphuric acid nucleation process affects the nucleation probability remarkably as can be seen in figure 6. The lower curve is calculated including the effect of hydration and the upper curve without hydration.

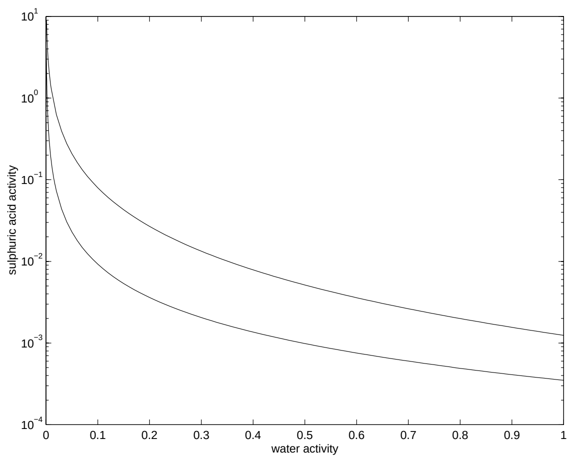

Figure 6: Calculated activities for sulphuric acid and water in heterogeneous nucleation

The results from the heterogeneous nucleation model are going to be used in a large atmospheric physico-chemical model (AEROFOR) [12].

Acknowledgements

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