New results in the theory of binary condensation of a supercritical droplet

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The formation and growth of droplets in binary vapours is a common phenomenon, the understanding of which is very important in the theory of phase transitions and physics of aerosols as well as in many branches of technological applications and chemical engineering. Several analytical and numerical models for the growth of a single binary supercritical droplet under isothermal and non-isothermal conditions had been proposed by Kulmala et al (1993), Vesala and Kulmala (1993), and Vesala et al (1997). It was numerically found that, if the vapour pressures of condensing species and the temperature far from the droplet do not change in time, the mole fractions of the species within the droplet and the droplet temperature settle to stationary values (independent of the droplet radius) after a certain onset stage.

Usually this onset stage is not mentioned in applications to specific aerosol systems, and using stationary regimes for binary droplet growth is common. However, this stage can be important if the establishing of a stationary composition is not fast. Recently the problem of the onset nonstationary stage of the binary droplet growth had been analytically studied by Kuni et al (2009) in diffusion-controlled and free-molecular regimes under isothermal conditions. This analysis assumed small (linear) initial deviations of the solution concentration within a growing droplet from the stationary concentration. It permitted using the steady rate of the droplet growth at finding relaxation of the droplet composition. The analysis revealed exponential and power-law relaxation to the stationary composition in time.

This communication is devoted to extension of the above analysis of the onset stage at condensation of a binary supercritical droplet in the diffusion-controlled or free-molecular regimes at arbitrary initial conditions, i.e., at arbitrary initial composition of the droplet immersed in the vapour mixture. It means that the deviations of droplet concentration from the stationary one can be large and nonlinear, and we need now to take account of non-steady effects in the growth rate of the square of the droplet radius.

To simplify the problem, we will assume that condensational growth of the droplet is isothermal and of non-Stefan type due to the presence of a large amount of carrier gas. Speaking about a supercritical droplet, we mean that the growth of the droplet is regular one, and the fluctuation, the capillarity (Kelvin) and adsorption effects can be neglected for such supercritical droplets. We will not consider here the transitional growth regime for a binary droplet, for which a simple interpolation model in the Knudsen number (Kulmala et al, 1993) can be used, because the stationary composition of the droplet in this regime depends on the droplet radius and is not a constant.

As a result, we have found an analytical solution of the problem which establishes two integral relations between square of the droplet radius and solution concentration, and between square droplet radius and time. These relations refer to a droplet which isothermally grows or evaporates in the diffusion-controlled or free-molecular regimes in the atmosphere of binary mixture of vapours and gas-carrier. It is not restricted by the approximation of an ideal solution in the droplet, but neglects the dependence of the partial molecular volumes in the droplet solution on concentration. In the case of the ideal solution, the integration in the solution can performed in the explicit form.

The solution found describes in a general form the dynamics of establishing of the stationary regime of condensation of a binary droplet at arbitrary initial conditions. In the case of small deviations from the stationary composition of the droplet, the solution can be reduced to the results obtained by Kuni et al (2009). It is shown now that using stationary rate of droplet growth at description of chemical relaxation of the droplet in time is no longer justified at nonlinear deviations from the stationary composition.

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