Nucleation near critical supersaturation

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Nuclei of a new phase are formed due to fluctuations. Small sub-critical nuclei have tendency to dissolve, but supercritical ones grow to microscopic sizes. The critical supersaturation is the threshold limit when no amount of new stable phase is detected. This quantity has important technological aspect. The critical supersaturation depends on the used detectable method, on the system under consideration, and on the volume of a parent phase (Kashchiev, 2011).

For the sake of simplicity we will consider homogeneous nucleation of vapor. (Nevertheless, our approach can be easily generalized to formation of crystallites from a liquid phase.) Katz (1970) introduced the critical supersaturation as the supersaturation at a rate of nucleation of one nucleus $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$. This is quite good approximation for nucleation of droplets from supersaturated vapor, but the use of this approximation to a liquid-solid phase transition is disputable. That is why we selected (Kožíšek *et al*, 2011) the critical supersaturation as the value at which one supercritical nucleus, formed by a certain number of molecules, is formed. The critical supersaturation was determined from $F_i = 1$, where F_i denotes the number of nuclei in unit volume formed by i molecules, and i was set to 1000. It is clear that the critical supersaturation depends on its definition (Kashchiev, 2000).

At supersaturation near its critical value a certain maximum nucleus size is reached and larger nuclei are not formed due to decreasing number density of nuclei as a function of size. The aim of this work is to determine how the maximum size of nuclei depends on the supersaturation.

We have numerically solved the kinetic equations describing homogeneous nucleation of ethanol droplets from supersaturated vapor – for details see Kožíšek and Demo (2009). In this work we have chosen the temperature T = 260 K. If we use the Katz definition $J^S = 1\ \mathrm{cm}^{-3}\mathrm{s}^{-1}$ (Katz, 1970), where J^S denotes the stationary nucleation rate, the critical supersaturation $S^* = 2.4249$, the critical size $i^* = 143$ and $F_{i^*} = 0.03$. The maximum size of formed nucleus is 80, *i.e.* $F_{80} = 1$ at the stationary state. No supercritical droplets are formed.

As the supersaturation increases, the maximum size of nuclei increases. We have determined the maximum radius of formed nucleus r_{max} (from the size distribution of nuclei F), for two cases: (i) one nucleus is formed within cubic meter (squares in Fig. 1) and (ii) cubic decimeter (circles in Fig. 1). Maximum radius of nucleus, r_{max}, increases with supersaturation, S, and at the same supersaturation r_{max} increases with the volume.

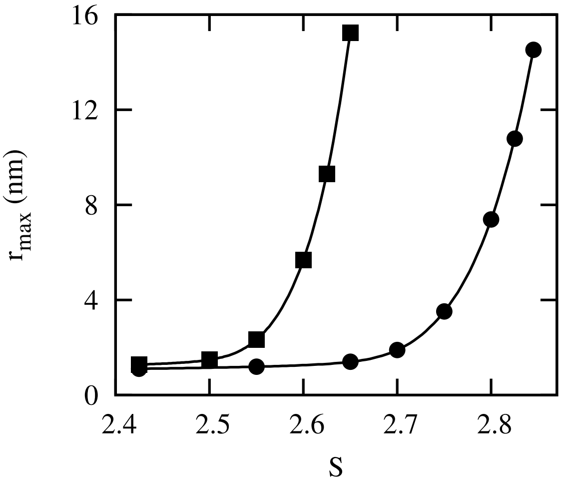

Figure 1: Maximum radius of nucleus, r_{max}, formed in cubic meter (squares) and cubic decimeter (circles) as a function of supersaturation S.

According to the Katz (1970) definition of critical supersaturation ($J^S = 1\ \mathrm{cm}^{-3}\ \mathrm{s}^{-1}$), S^* does not depend on the volume. On the other hand the highest supersaturation, at which the supersaturated vapor remains in metastable phase and no new phase evolves, depends on the volume of the system under consideration. As the supersaturation increases the growth of droplets up to microscopic sizes occurs after overcoming of some supersaturation level.

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