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INFLUENCE OF SIZE EFFECTS ON HOMOGENEOUS NUCLEATION INSIDE NANOPARTICLES

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INTRODUCTION

It is known that many physicochemical processes in aerosol systems with nanoscale particles and in nanoparticles themselves depend on the particle size. The influence of size dependence of the condensation coefficient on gas-phase nucleation was discussed in (Levdansky et al., 2010). Some problems related to nucleation in confined space, in particular the depletion effect of the ambient phase, were considered in (Kožíšek et al., 2011; Schmelzer and Abyzov, 2011). Here we study the size effects in homogeneous nucleation inside nanoparticles related to size dependence of the effective rate constant for the attachment of monomers to the critical cluster.

RESULTS AND DISCUSSION

Let us consider the situation when supersaturation of one component in the two-component nanoparticle takes place that can lead to nucleation of this component. The nucleation rate J_n by analogy with (Ring, 2001) can be written as

$$J_n = k_Z k_{eff} n N_c = k_Z k_{eff} n^2 \exp\left(-\frac{W}{kT}\right), \qquad (1)$$

where k is the Boltzmann constant, T is the temperature, k_{eff} is the effective rate constant for the attachment of monomers to the critical cluster allowing for both diffusion of monomers to the critical cluster and their incorporation into the cluster, k_Z is the Zeldovich factor, n is the number density of monomers, N_c is the number density of critical clusters, W is the work of critical cluster formation.

Taking into account both the diffusion and kinetic resistance in respect to the attachment of monomers to the critical cluster, the value of k_{eff} in view of (Vorob'ev, 2003) can be written as

$$k_{eff} = \frac{2\pi d_c D_m}{1 + \dfrac{2D_m}{k_s d_c}}, \qquad (2)$$

where d_c is the diameter of the critical cluster, D_m is the diffusion coefficient of monomers in the nanoparticle (further for simplicity diffusion of clusters is neglected), k_s is the rate constant of the heterogeneous process related to the incorporation of monomers located in the vicinity of the critical cluster into the cluster. The value of k_s and D_m are given by

$$k_s = k_{s0} \exp\left(-\frac{Q_c}{kT}\right), \qquad (3)$$

$$D_m = D_{m0} \exp\left(-\frac{Q_p}{kT}\right). \qquad (4)$$

Here Q_c and Q_p are the activation energies accordingly for the incorporation of monomers into the critical cluster and for diffusion of monomers in the nanoparticle, the pre-exponencial factors k_{s0} and D_{m0} are assumed further to be constant for simplicity.

Taking into account Eqs. (2)-(4), in view of (Vanithakumari and Nanda, 2008; Rekhviashvili and Kishtikova, 2006) we can write for the value of k_{eff} the following equation:

$$k_{eff} = \frac{2\pi d_c D_{m0} \exp\left(-\frac{\beta_p Q_{d\infty}}{kT}\right)}{1 + 2k_{s0}^{-1} d_c^{-1} D_{m0} \exp\left(\frac{\beta_c Q_{c\infty} - \beta_p Q_{d\infty}}{kT}\right)}, \tag{5}$$

where $\beta_p = \exp[-4/(1+d_{p0})]$, $\beta_c = \exp[-4/(1+d_{c0})]$, $d_{c0} = d_c/\delta_c$, $d_{p0} = d_p/\delta_p$, d_p is the nanoparticle diameter, δ_c is the Tolman length for the critical cluster, δ_p is the Tolman length for the nanoparticle, $Q_{c\infty}$ and $Q_{p\infty}$ are the values of Q_c and Q_p for a bulk matter.

In the case when the second term in the denominator of Eq. (5) is much less than unity the diffusion controlled regime for nucleation takes place. In the opposite case, the kinetic controlled regime of nucleation is realized. The size dependence of the activation energies for diffusion of monomers in the nanoparticle and their incorporation into the critical cluster leads to the size dependence of the effective rate constant for the attachment of monomers to the critical cluster.

CONCLUSIONS

Thus, it is shown that the influence of the size effect on the rate of homogeneous nucleation in nanoscale particles can be related to size dependence of activation energies for diffusion of monomers in the nanoparticle and their incorporation into the critical cluster.

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