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INFLUENCE OF SIZE EFFECT ON EVAPORATION OF AEROSOL NANOPARTICLES

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INTRODUCTION

Evaporation of nanoscale particles plays a significant role in many branches of nanotechnology and also in the atmospheric physics and chemistry. The classical approach to the description of evaporation of small (nanoscale) aerosol particles is usually based on the Kelvin equation. The mentioned equation was used in (Nanda et al., 2003) to interpret the results of experiments related to evaporation of free Ag nanoparticles. The authors of the above-mentioned paper assume that the surface tension of free Ag nanoparticles can be significant greater than the mentioned value for bulk matter. It is worth noting that this assumption is in contradiction with the Tolman theory (Tolman, 1949). Below we consider the influence of the size dependence of the cohesive energy in the nanoparticle on its evaporation.

RESULTS AND DISCUSSION

Nanoparticle evaporation depends on the activation energy E_p needed to remove the atom from the nanoparticle. The value of E_p for the spherical nanoparticle is given by (Nanda et al., 2003)

$$E_p(d) = E_c - \frac{4\sigma V}{d}, \tag{1}$$

where d is the diameter of the nanoparticle, E_c is the cohesive energy per atom in the nanoparticle, σ is the surface energy, V is the volume per atom in the nanoparticle.

The value of E_c for the free Ag nanoparticle in (Nanda et al., 2003) is assumed to be equal to 2.95 eV (this is the value for bulk silver). It is worth noting that the value of E_c in the case of the nanoscale particle depends on its size. The size-dependent cohesive energy for the nanoparticle E_{cp} can be found from the equation (Yang and Li, 2007)

$$\frac{E_{cp}}{E_{c\infty}} = \frac{T_{mp}}{T_{m\infty}}. \tag{2}$$

Here $E_{c\infty}$, $T_{m\infty}$ are the cohesive energy and the melting temperature for bulk matter, T_{mp} is the size-dependent melting temperature of the nanoparticle. Let us consider the case when $\delta/d << 1$, where δ is the Tolman length. Taking into account the size dependence of the melting temperature and the surface energy for the nanoparticle (Rekhviashvili and Kishtikova, 2006), we can write the following equation for $E_p(d)$:

$$E_p(d) = E_{c\infty} - \frac{4\sigma_{eff} V}{d}, \tag{3}$$

where $\sigma_{eff} = \sigma_\infty[1+E_{c\infty}\delta/(\sigma_\infty V)-4\delta/d]$, σ_∞ is the surface energy for bulk matter (σ_{eff} is some effective value that has a dimension of σ).

According to (Nanda et al., 2003) the value of σ_∞ for Ag is in the range 1.065–1.54 J/m². In accordance with the results of (Calvo, 2012) the Tolman length for the composite Ag-Au nanoparticles (for arbitrary concentrations of components) is in the range 2–2.8 Å. Let us estimate the value of σ_{eff} at following values of parameters: σ_∞ = 1.065 J/m², δ = 2.3·Å, $E_{c\infty}$ = 2.95 eV, δ/d = 0.01. We obtain for these parameters the value of $\sigma_{eff} \approx 7.4$ J/m² that is close to the value 7.2 J/m² used in (Nanda et al., 2003) as the surface tension of the free Ag nanoparticle.

The critical diameter of the nanoscale particle (cluster) d_{cr}, neglecting the last term in the equation for σ_{eff}, can be written as

$$d_{cr} = \frac{4V\sigma_\infty}{kT\ln S}\left(1 + \frac{E_{c\infty}\delta}{\sigma_\infty V}\right), \quad (4)$$

where S is the saturation ratio.

The equation (4) shows that d_{cr} in the size dependence of the cohesive energy in the nanoparticle is greater than d_{cr} calculated on the basis of the Kelvin equation without considering the above-mentioned size effect. An increase in d_{cr} decreases the rate of homogeneous nucleation. It is also shown that the size dependence of the cohesive energy can affect the production of nanoparticles doped with different chemical elements.

CONCLUSIONS

Thus, it is shown that the experimental results on evaporation of free Ag nanoparticles can be interpreted on the basis of the size-dependent cohesive energy in the nanoscale particles. The influence of the size dependence of the cohesive energy in the nanoparticles on their critical size and on nanoparticle doping is discussed.

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