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INFLUENCE OF SIZE EFFECTS ON GAS ABSORPTION BY NANOPARTICLES

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The influence of size effects on gas absorption by small aerosol particles is studied theoretically.

In a number of cases nanoparticles are known to be building blocks for obtaining nanostructure materials [1, 2]. As noted in [3], the mechanism underlying the growth of particles is considerably important for understanding the formation of nanostructures. The production of nanoparticles by depositing a substance from a gas phase is related to such stages as homogeneous nucleation, growth of the particles formed, as well as their coagulation and coalescence. The size effects can significantly affect the processes mentioned. Some questions concerning the influence of the size effects and surface processes on the critical size of aerosol particles (clusters) and correspondingly on the process of homogeneous nucleation were considered in [4–6]. In some cases, of great interest are problems connected with the entry of molecules (atoms) of foreign gases into particles. This is due to the necessity of obtaining both rather clean nanoparticles and nanoparticles doped with different elements for various technological problems. It is common knowledge that even a very small concentration of an admixture in a basic substance can substantially change the physicochemical properties of the latter. Here a distinction needs to be drawn between the cases where an admixture component penetrates into nanoparticles during their growth and where admixture molecules are absorbed by the nanoparticles which have already been formed. The trapping of admixture molecules by growing particles was considered in [7]. Further we study the influence of the size effects on the trapping coefficient during gas absorption by the nanoparticles formed.

The size effects in absorption of gas molecules (atoms) by small (nanosized) particles are related both to the dependence of the probability of sticking of gas molecules to the surface of the particle on the size of the latter and to the mechanism of incorporation of molecules into the phase condensed. Moreover, the particle size affects also the supply of gas molecules to the particle surface (which manifests itself through the Knudsen number defined by the ratio of the mean free path of molecules to the particle radius). For simplicity's we consider the case of a free-molecular gas flow, where the Knudsen number greatly exceeds unity. Here, we suppose, following [8], that the concentration of absorbed gas molecules (atoms) in the particle is reasonably low, so that they do not influence the absorption of incident gas molecules. For simplicity's sake the inverse flow of molecules (atoms) from the stage of absorption into the adsorbed state is ignored by analogy with [8] (this is valid for the initial stage of the absorption process, when the flow of molecules into the particle is far in excess of the inverse flow). We shall analyze the influence of the surface and size effects on the trapping coefficient γ which characterizes the ratio of the flux density of the gas molecules falling on the particle and remaining in it to the flux density of fallen molecules. It should be noted that generally the coefficient γ is not equal to the sticking coefficient α defined as the probability that a gas molecule incident on the surface of the condensed phase is not reflected from the latter elastically (i.e., it is adsorbed on the particle surface). By analogy with [8], for a free-molecule regime of vapor flow we can write the following equations that connect the number densities of molecules respectively in the gas (n_g) and adsorbed (n_a) phases (further the degree of filling of the adsorbed layer is assumed for simplicity to be much less than unity):

$$\gamma n_g \left(\frac{kT}{2\pi m}\right)^{1/2} = \alpha n_g \left(\frac{kT}{2\pi m}\right)^{1/2} - n_a k_g \,, \tag{1}$$

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$$\gamma n_g \left(\frac{kT}{2\pi m}\right)^{1/2} = n_a k_c\,, \tag{2}$$

where k_g and k_c can be expressed as

$$k_g = k'_g \exp\left(-\frac{Q_g}{kT}\right), \tag{3}$$

$$k_c = k'_c \exp\left(-\frac{Q_c}{kT}\right). \tag{4}$$

The pre-exponential factors k'_g and k'_c are assumed to be constant. For the coefficient γ Eqs. (1)–(4) yield

$$\gamma = \frac{\alpha}{1 + \dfrac{k'_g}{k'_c}\exp\left(-\dfrac{Q_g - Q_c}{kT}\right)}. \tag{5}$$

We consider the case where $|Q_g - Q_c|/kT$ greatly exceeds unity. For simplicity we also assume that $k'_g \approx k'_c$. When $Q_g > Q_c$, the exponential term in the denominator of (5) can be ignored in comparison with unity, so that the quantity γ is approximately equal to the sticking coefficient α. When $Q_c > Q_g$ (an inequality such as this takes place, in particular, for desorption and dissolution of silver atoms on iridium [9]; here the activation energy of desorption of silver atoms from the (111)Ir surface for sufficiently small degrees of filling the surface by an adsorbate is equal to 3.7 eV, and the lower limit of the activation energy of dissolution of silver atoms in iridium can be estimated as 5 eV), unity in the denominator can be disregarded in comparison with the exponential term, and the quantity γ can be written as

$$\gamma = \alpha \exp\left(-\frac{Q_c - Q_g}{kT}\right). \tag{6}$$

It is known that nanosized particles are characterized by the melting temperature which is lower than that for massive samples of the same substance. We note that, according to [10], the activation energy for diffusion of atoms in a solid particle can be related to the melting temperature of the particle in the following way:

$$\frac{E_p}{E_\infty} = \frac{T_{m,p}}{T_{m\infty}}, \tag{7}$$

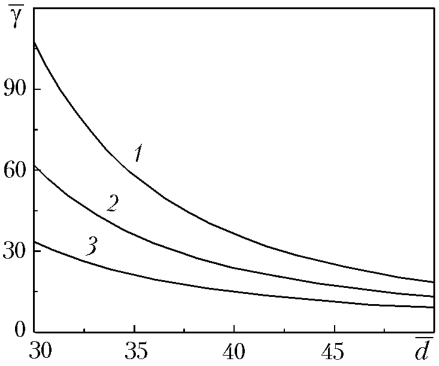
where E_p and $T_{m,p}$ are the activation energy for diffusion of atoms in the solid particle and the melting temperature of the particle with account for the dependence of the quantities mentioned on the particle size, respectively; E_∞ and $T_{m\infty}$ are the same characteristics for a massive sample.

Taking into account that for transition from the adsorbed state into the condensed phase an atom should overcome the potential barrier analogous to that for diffusion of atoms inside a condensed phase, we can write the following expression that connects the activation energies for transition of the atom from the stage of adsorption into the condensed phase respectively for a small particle $Q_{c,p}$ and a massive phase $Q_{c\infty}$:

$$\frac{Q_{c,p}}{Q_{c\infty}} = \frac{T_{m,p}}{T_{m\infty}}. \tag{8}$$

According to [11], the dependence of $T_{m,p}$ on the particle size can be presented as

$$T_{m,p} = T_{m\infty} \exp\left(-\frac{4\delta}{\delta + d}\right), \tag{9}$$



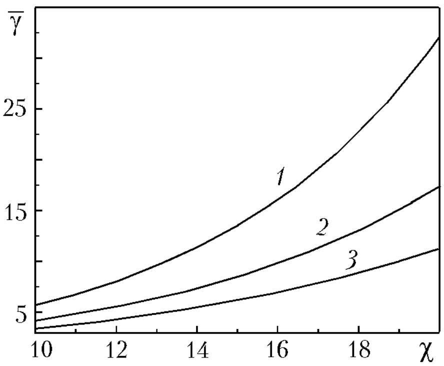


Fig. 1. Relative coefficient of the trapping of silver atoms by iridium nanoparticles $\bar{\gamma}$ vs. the dimensionless diameter $\bar{d}$: 1) T = 1500; 2) 1700; 3) 2000 K.

Fig. 2. Relative trapping coefficient $\bar{\gamma}$ vs. the dimensionless parameter $\chi = \frac{Q_{c\infty}}{kT}$: 1) $\bar{d}$ = 20, 2) 25; 3) 30.

where, according to [12], the Tolman length δ changes for different substances within 0.096–0.35 nm.

With allowance for the above, for γ from Eqs. (6), (8), and (9) we obtain

$$\gamma = \alpha \exp\left\{-\frac{Q_{c\infty}}{kT}\left[\exp\left(-\frac{4\delta}{\delta + d}\right)\right] + \frac{Q_g}{kT}\right\}. \tag{10}$$

Figure 1 shows the dependence of the relative coefficient of trapping of silver atoms by iridium nanoparticles $\bar{\gamma} = \frac{\gamma}{r|_{d\to\infty}}$ on the dimensionless particle diameter $\bar{d} = \frac{d}{\delta}$. This dependence has been calculated on the basis of relation (10) at different temperatures under the assumption of equality of the quantities α and Q_g for the nanoparticles and massive iridium sample. To estimate the influence of the size of the iridium particles on the coefficient of trapping of silver atoms, the energy value $Q_{c\infty}$ = 5 eV was taken. It follows from the figure that the trapping coefficient increases with a decreasing particle size.

The dependence of the coefficient $\bar{\gamma}$ on the dimensionless parameter $\chi = \frac{Q_{c\infty}}{kT}$ at different particle diameters is shown in Fig. 2. As is seen from the figure, the value of $\bar{\gamma}$ increases with χ, and the sharper the smaller the particles.

Generally the dependence of the trapping coefficient on the particle size and parameter χ will be more complex because the quantities α and Q_g, in principle, also depend on the size of the particles. We note that not only the effects related to the kinetics of the surface phenomena but also an increase in the diffusion coefficient of absorbed gases with a decrease in the size of nanoparticles lead to a faster transfer of gas atoms inside the particle (where the concentration of the atoms absorbed is lower). The process of outflow of the absorbed atoms form the particle can also be accelerated with a decrease in its size (here the concentration of gas atoms will be maximum in the particle center). Thus, the decrease in the activation energy for the processes of diffusion and absorption (dissolution) of atoms with a decreasing particle size can lead to a more intense course of the processes of absorption of gas atoms by the particle and its degassing. It should be noted that the decrease in the activation energy both for diffusion of atoms in the nanoparticle and for their transition from the adsorbed state to an absorbed state with a decreasing size of the particle can be due to the increase in the concentration of vacancies in it.

The increase in the diffusion coefficient of atoms in the nanoparticle can lead not only to the mentioned effect of the increase in the rate of absorption of atoms of a foreign substance by the nanoparticle but also to a more intense course of other processes related to the mobility of atoms. Thus, for example, the nucleation rate of a substance in a supersaturated solution increases with the density of the flux of atoms into the resulting cluster which, in turn, rises with the diffusion coefficient of atoms in the solution. In the case where nucleation takes place in nanoparticles, an increase in the diffusion coefficient of atoms with decreasing sizes of nanoparticles can lead to an increase in the nucleation rate.

Thus, the problem of trapping of admixture molecules by nanosized particles has been considered. It is shown that the trapping coefficient can increase with a decreasing size of particles. The possibility of a rise of the nucleation rate in nanoparticles is discussed, which is related to the increase in the mobility of atoms with a decreasing size of the particles.

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NOTATION

d, diameter of a particle; k, Boltzmann constant; k_g and k_c, constants of transition of molecules from the adsorbed state into a gas phase and into the absorbed state, respectively; m, mass of a gas molecule; Q_g and Q_c, activation energies for desorption of molecules into a gas phase and their transition from the adsorbed state into the condensed phase (particle); T, temperature; α, sticking coefficient; γ, coefficient of trapping of molecules (atoms) by a particle; δ, Tolman length. Subscripts: a, adsorption; c, condensed phase; g, gas; m, melting; p, particle; ∞, massive phase.

REFERENCES

1. T. Hawa and M. R. Zachariah, Coalescence kinetics of unequal sized nanoparticles, *J. Aerosol Sci.*, **37**, 1–15 (2006).
2. É. L. Nagaev, Small metal particles, *Usp. Fiz. Nauk*, **162**, No. 9, 49–124 (1992).
3. P. Cheyssac, M. Sacilotti, and G. Patriarche, Vapor–liquid–solid mechanisms: Challenges for nanosized quantum cluster/dot/wire materials, *J. Appl. Phys.*, **100**, 044315-1–044315-12 (2006).
4. V. V. Levdansky, J. Smolik, and P. Moravec, Critical size of aerosol particles in the resonance radiation field, *Int. Commun. Heat Mass Transfer*, **32**, 116–122 (2005).
5. V. V. Levdansky, J. Smolik, and P. Moravec, Influence of size effect and foreign gases on formation of nanoparticles, *Int. Commun. Heat Mass Transfer*, **33**, 56–60 (2006).
6. V. V. Levdansky, J. Smolik, V. Zdimal, and P. Moravec, Effect of surface processes on formation of aerosol particles, in: *Proc. 19th Int. Symp. on Gas Kinetics*, 22–27 July, 2006, Orleans, France (2006), pp. 189–190.
7. V. V. Levdansky, J. Smolik, and P. Moravec, Trapping of impurity molecules in condensation from mixtures of gases, *Int. J. Heat Mass Transfer*, **43**, 629–637 (2000).
8. G. M. Nathanson, P. Davidovits, D. R. Worsnop, and C. E. Kolb, Dynamics and kinetics at the gas–liquid interface, *J. Phys. Chem.*, **100**, 13007–13020 (1996).
9. N. R. Gall', E. V. Rut'kov, and A. Ya. Tontegode, Interaction of silver atoms with iridium and a two-dimensional graphite film on iridium: adsorption, desorption, solution, *Fiz. Tverd. Tela*, **46**, No. 2, 360–366 (2004).
10. Q. Jiang, S. H. Zhang, and J. C. Li, Grain size-dependent diffusion activation energy in nanomaterials, *Solid State Commun.*, **130**, 581–584 (2004).
11. S. Sh. Rekhviashvili and E. V. Kishtikova, On the melting temperature of nanoparticles and nanostructural substances, *Pis'ma Zh. Tekh. Fiz.*, **32**, Issue 10, 50–55 (2006).
12. R. C. Tolman, The effect of droplet size on surface tension, *J. Chem. Phys.*, **17**, 333–337 (1949).