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EFFECTIVENESS OF BROWNIAN DEPOSITION OF NANOPARTICLES FROM A GAS FLOW IN A TUBE

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A comparison of experimental data, analytical results, and numerical calculations of the Brownian deposition of spherical nanoparticles is carried out. It is shown that for nanoparticles smaller than 10 nm and larger than 5 nm the relative discrepancy between experimental data and analytical results does not exceed 15%. In other radius ranges of nanoparticles the discrepancy is substantially smaller.

Keywords: *characteristic length of deposition, Brownian diffusion coefficient, tunneling probability.*

Introduction. The advances in nanotechnology have sustained the interest of engineers and research workers of various specialities in the problem of Brownian movement of nanoparticles in gas flows [1–4 and references therein]. However, there remains an important problem, not adequately studied, as to what extent theoretical calculations of the Brownian deposition of nanoparticles are close to experimental data. In this article we will consider this question on the example of deposition of nanoparticles from a gas flow moving in a laminar fashion in a cylindrical tube.

The equation describing the stationary Brownian diffusion of spherical nanoparticles in a laminar gas flow in a cylindrical tube has the form [2]

$$u(r)\,\partial_z n(r, z) = \frac{1}{r}\,\partial_r\left[Dr\partial_r n(r, z)\right], \tag{1}$$

where $u(r)$ is the Poiseuille profile of gas velocity in the tube; $n(r, z)$ is the numerical density of nanoparticles; D is the scalar coefficient of Brownian diffusion for spherical nanoparticles. The coordinate system has been selected so that the z axis is directed along the tube axis.

If an experiment on the Brownian deposition is carried out in a tube of length L and radius R_c, the qualitative estimation of Eq. (1) shows that the Brownian deposition is substantial if the dimensionless complex

$$\frac{DL}{u_0 R_c^2} \sim 1\,. \tag{2}$$

In particular, in the experiments described in [3, 4] a tube of length 1.1 m and radius 6.5 mm was used, with the characteristic velocity of the gas flow u_0 equal to 0.1 m/sec. The complex (2) for these experiments is of the order of unity, if $D \geq 4\cdot 10^{-7}$ m^2/sec. In isothermal experiments [3, 4] conducted at a temperature of 283 K in a nitrogen flow at atmospheric pressure, such a value of the Brownian diffusion coefficient was found for spherical nanoparticles of radius ≤ 2 nm. For particles whose radius is larger than 2 nm, the influence of Brownian diffusion is weaker, but, as is shown experimentally, it increases with decrease in the flow velocity [4].

The aim of the present work is to compare the theoretical results obtained in [2] with the high-quality experimental data of [3, 4], where the change in the average tube tunneling probability for a nanoparticle P on change in the flow rates of various gases, diameters of nanoparticles, and in the gas flow temperature was determined. Moreover, due to the calibration of nanoparticles in differential analyzers of mobility, monodisperse ensembles of nanoparticles of practically identical mobility were created.

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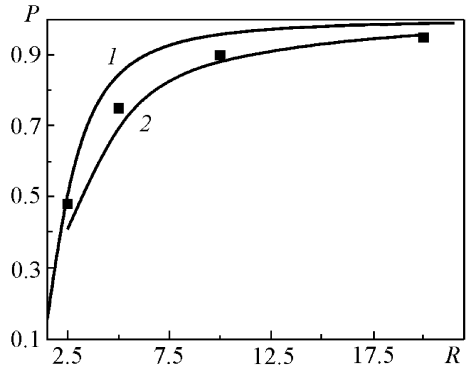

Fig. 1. Tunneling probability P vs. the nanoparticle radius R at T = 283 K, u_0 = 0.3 m/sec: 1) calculation on the basis of Eq. (4); 2) numerical solution of Eq. (1) at the initial distribution of particles being constant over the tube radius; points, experimental data. R, nm.

Elements of Theoretical Calculation. In what follows it is assumed that when a nanoparticle contacts the wall, it falls out of the gas flow. In the analytical solution of Eq. (1) by the Galerkin method [5] an expression was obtained in [2] for the characteristic length of the Brownian deposition l:

$$l = \frac{0.27 u_0 R_c^2}{D}. \tag{3}$$

For the experimental rig described in [3, 4], for nanoparticles of radius 2 nm l = 2.7 m, whereas for nanoparticles of radius 10 nm l = 63.3 m. It should be emphasized that the characteristic length decreases sharply on decrease in the channel radius. This fact should be allowed for in analyzing the medicinal consequences of the Brownian deposition of nanoparticles.

In [2] it was also shown that the fraction of nanoparticles that passes through a tube of length L is approximately assigned by the expression

$$P = \exp(-L/l) = \exp\left[-\frac{LD}{0.27 u_0 R_c^2}\right]. \tag{4}$$

Proceeding from Eq. (4), we will call the tubes used in the experiments on Brownian deposition short if the condition $L << l$ is fulfilled, and long if the condition $L > l$ is fulfilled.

If the Bessel function $J_0(br/R_c)$ exactly describes the initial distribution of nanoparticles over the radius, then expression (4) for the tunneling probability P is precise ($b \approx 2.4$ is the smallest positive value of the root of the equation $J_0 = 0$). It turned out that expression (4) describes the deposition of nanoparticles in long tubes with a high accuracy. In the experiments described in [3, 4] for nanoparticles whose radii exceeded 5–7 nm the tube used in the rig was short. As is seen from Fig. 1, expression (4) represents a useful analytical estimate in this case too.

Thus, the averaged probability that a nanoparticle will pass through the tube without being deposited is equal to P. Correspondingly, the fraction of nanoparticles F deposited on the walls of the channel of length L is defined by the following expression:

$$F = 1 - P.$$

A rigorous expression for F is assigned by the formula [2]

TABLE 1. Tunneling Probability for a Nanoparticle (numerator, experimental data; denumerator, predicted values for given experimental conditions)

R, nm	$P(N_2)$	P(He)	P(Ar)
5	0.78/0.904	0.75/0.767	0.825/0.919
6	0.863/0.933	0.775/0.831	0.863/0.943
10	0.913/0.975	0.863/0.936	0.9/0.979

$$F = \frac{\int_0^{R_c} [u(r,0)\, n(r,0) - u(r,L)\, n(r,L)]\, rdr}{\int_0^{R_c} [u(r,0)\, n(r,0)]\, rdr}. \tag{5}$$

It should be noted that both in the numerator and denominator of Eq. (5) the integrands at two points vanish. Thereby the integral quantity F and, consequently, $P = 1 - F$ do not depend on the fine details of the initial and final distributions of nanoparticles over the tube radius. It should be emphasized that Eq. (5) is valid also for nonisothermal gas flows. The definition adopted in [3, 4] for P as the ratio of the number densities of nanoparticles at the entrance and exit of the tube $n(0)/n(L)$ is valid only for isothermal flows.

To obtain a more precise analytical solution it is necessary to expand the initial radial distribution of nanoparticles into a Bessel function series. When the initial distribution of nanoparticles is uniform, for short tubes no less than two terms of the expansion in the Bessel functions should be kept [2]. Here, as can be easily shown, account for the second mode leads to a decrease in the tunneling probability calculated from Eq. (4). Since the characteristic length of the Brownian deposition for the second mode is approximately six times smaller than for the first mode (least eigenvalue), in long enough tubes the tunneling probability for a nanoparticle is determined by the first mode.

Comparison between the Results of Calculations and Experimental Data. In the free-molecular regime of interaction of a nanoparticle with a gaseous medium the Brownian diffusion coefficient D of a spherical nanoparticle depends on its radius and on the carrier gas temperature as follows [1, 6]:

$$D = \frac{3kT}{16\pi R^2 p}\sqrt{\frac{2\pi kT}{m}}, \tag{6}$$

where k is the Boltzmann constant, m is the mass of the carrier gas molecule, and p is the carrier gas pressure. To derive Eq. (6), the Einstein relationship between the mobility of the Brownian particle and the Brownian diffusion coefficient was used. It immediately follows from Eqs. (3)–(6) that with decrease in the mass of gas molecules the tunneling probability for nanoparticles in the tube decreases. The physical reason is that for lighter gas molecules the average thermal velocity of the chaotic motion of gas molecules increases, which at an identical gas pressure enhances the Brownian diffusion [5]. Experimental data confirm this conclusion. The generalization of Eq. (6) for a mixture of gases is done in [2]. From Eqs. (3) and (6) it also follows that the characteristic length of the Brownian deposition l depends strongly on the nanoparticle radius. For relatively small nanoparticles one and the same tube can be considered as long, whereas for larger nanoparticles — as short. Analogously, when using helium as a carrier gas instead of nitrogen, the characteristic length of the Brownian deposition decreases almost threefold. These facts should be kept in mind in analyzing experimental data.

Table 1 for three gases lists the values of the parameter P obtained in the experiments in [4] and calculated on the basis of expressions (4) and (6). It is seen that the computational formula (4) systematically overestimates the value of the parameter P. The main reason for the discrepancy is that the experiments were conducted with short tubes. In this case, the accuracy of formula (4) is worsened. Nevertheless for helium as a carrier gas and nanoparticles of radius 5 nm the correspondence between the experiment and calculation is rather good, with the relative discrepancy not exceeding 15%. The theoretical prediction that for large radii of nanoparticles the parameter P coincides for nitro-

gen and argon used as carrier gases is practically confirmed by the data of measurements. It is established experimentally and theoretically that in the case of helium the lowest tunneling probability for a nanoparticle is attained.

Figure 1 presents calculated dependences of the parameter P on the nanoparticle of radius R for the conditions of the experiment in [3]. Experimental results (points) from [3] are also given. The flow conditions are the same as in Fig. 3 of work [3] (the nitrogen flow rate is of 0.3 liter/min). The qualitative form of the dependence of the tunneling probability on the nanoparticle radius is the same as in [3, 4]. For small nanoparticles the correspondence between the theory and experiment is rather good, with the discrepancy not exceeding 15% on increase in the radius of nanoparticles.

The data presented in Fig. 1. confirm the above-made qualitative estimations that the Brownian diffusion substantially suppresses the transportation of nanoparticles through the tube if the radius of nanoparticles is smaller than 2.5 nm. It is seen from the figure that sufficiently large nanoparticles ($R > 10$ nm) pass with a high probability through the entire setup while they follow the streamlines of the isothermal laminar flow. The same conclusion follows from the experimental data of [3, 4].

The analysis of experimental results on the isothermal Brownian diffusion of nanoparticles [3] shows that the dependence of the tunneling probability P on the nanoparticle substance has not been revealed experimentally. This conclusion is in full accord with the theoretical result (see, e.g., [1]) form which it follows that the Brownian diffusion coefficient depends only on the squared radius of the nanoparticle (proportional to the surface area). In the experiments, nanoparticles from silver, titanium dioxide, and NaCl were used.

It is natural that an increase in the gas temperature in the channel enhances the deposition of particles under the action of intensified Brownian diffusion (see Eq. (6)).

Conclusions. A comparison of experimental and predicted results on the isothermal Brownian deposition of nanoparticles in a laminar gas flow in a tube has shown that the analytical expressions derived in [2] rather accurately describe integral experimental results for spherical nanoparticles.

It is shown that to calculate the Brownian diffusion coefficient one can use Eq. (6) for a solitary spherical nanoparticle. This equation rather accurately accounts for the influence of the carrier gas molecule mass. Simple estimation shows that the inequality should hold, according to which the average distance between nanoparticles is much greater than their radius: $n^{-1/3} >> \lambda$. In particular, for $\lambda = 1$ μm we have $n << 10^{18}$ nanoparticles/m^3. This condition was satisfied in the experiments in [3, 4] with great safety in the calculations.

The numerical calculation of the tunneling probability on the basis of Eqs. (1) and (5) makes it possible to increase the accuracy of calculation; however, this improvement is not of importance in practice. Indeed, the initial distribution profile of the nanoparticles at the tube inlet is usually unknown. Precisely for this reason it is useful to use Eq. (4), since it allows for the contribution of the most long-lived mode of the initial distribution. For long tubes the contribution of other modes can be neglected. For short tubes, independently of the initial distribution, the contribution of higher modes (corresponding to higher roots of the equation $J_0 = 0$, where J_0 is a Bessel function of zero order [2]) decays rather rapidly. Thus, the contribution of the first mode becomes the basic one.

The substantial contribution of the near-surface free energy for nanoparticles makes the existence of nanoparticles of nonspherical shape thermodynamically disadvantageous but possible. It is much more difficult to predict the rate of deposition of Brownian nanoparticles of complex shape. Note that drift motion of nanoparticles in a direction perpendicular to the tube axis may occur in this case. However, the rotational Brownian movement partially decreases the velocity of this drift motion. It is reasonable to expect that in this case the discrepancy between experimental and calculated results will be greater than for calibrated spherical nanoparticles.

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NOTATION

D, Brownian diffusion coefficient, m^2/sec; F, average probability of deposition; L, tube length; J_0, Bessel function of zero order; k, Boltzmann constant; l, characteristic length of Brownian deposition, m; m, mass of the carrier gas molecule, kg; $n(r, z)$, numerical density of nanoparticles, particles/m^3; P, average tunneling probability; p, gas

pressure, Pa; R, nanoparticle radius, nm; r, radial coordinate, m; T, gas temperature, K; $u(r)$, gas velocity profile, m/sec; λ, average free path of carrier gas molecules. Subscripts: c, channel; 0, average.

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