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# INFLUENCE OF THE PHYSICAL PROPERTIES OF THE MATERIAL OF NANOPARTICLES ON THEIR DIFFUSION IN RAREFIED GASES

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*The influence of the physical properties of nanoparticle materials and the parameters of the molecule–particle-interaction potential on the diffusion of nanoparticles has been studied on the basis of kinetic theory. It has been established that unlike Brownian particles, the diffusion of fairly small nanoparticles is substantially dependent on their material. This effect becomes stronger with growth in the carrier-gas temperature. In all cases the use of the well-known Cunningham–Milliken–Davies correlation brings about considerable errors in determining the diffusion coefficient of nanoparticles.*

Today's development of nanotechnologies intended for various purposes requires, in particular, that the intrinsic dynamics of nanoparticles in gases be investigated. Usually, in studying the diffusion of nanoparticles in gases, one employs the experimental technique and corresponding procedures used for investigation of macroscopic aerosols (see, e.g., [1]). Actually, the theoretical foundation of these procedures is the Cunningham–Milliken–Davies (CMD) correlation [2, 3]

$$D_k = \frac{kT}{\gamma_k}\,, \quad \gamma_k = \frac{6\pi\eta R}{C} = \frac{\gamma_{\text{S}}}{C}\,, \tag{1}$$

$$C = 6\pi\eta R \left[1 + 1.257\ \text{Kn} + 0.4\ \text{Kn}\ \exp\left(-1.1\right)/\text{Kn}\right]\,,$$

which is based on the Einstein formula for the diffusion coefficient of Brownian particles

$$D_{\text{E}} = \frac{kT}{\gamma_{\text{S}}}\,. \tag{2}$$

The parameter $\gamma_{\text{S}}$ in formula (1) is the drag coefficient corresponding to the Stokes drag force acting on a spherical particle in an incompressible fluid. However, for carrier-gas nanoparticles whose characteristic dimension is of the order of the hydrodynamic physically infinitesimal scale, hydrodynamic consideration of their interaction with the medium is not valid. An alternative approach is required. The development of such an approach on the basis of the kinetic Boltzmann theory has been the focus of [4, 5] (see also [6]). It has been shown that the dynamics of even a finely divided rarefied gas suspension is generally described by a system of kinetic equations that contain many-particle collision integrals. However, one can safely apply a system of kinetic Boltzmann equations to the description of ultradivided gas suspensions, among which are gas nanosuspensions.

It has been established in [7, 8] with the kinetic theory developed there and the specially conducted experiment that correlation (1) (and hence the procedures using it) unsatisfactorily describes the diffusion of fairly small nanoparticles and is applicable in a very narrow temperature range.

Kinetic theory [6–8] yields, for the diffusion coefficient of nanoparticles, the following formula:

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TABLE 1. Values of the Parameters of the Interaction Potential, Density, and Molecular Weight of Gas Molecules

| Parameters | Li | Zn | U | $H_2$ | Ne | $UF_6$ |
|---|---|---|---|---|---|---|
| $\varepsilon_{ij}/k$, K | 500.0 [12] | 1040.0 [12] | 2703.6 [13] | 2.968 [14] | 35.7 [14] | 236.8 [15] |
| $\sigma_{ij}$, Å | 3.95 [12] | 2.46 [12] | 3.343 [13] | 33.3 [14] | 2.789 [14] | 5.967 [15] |
| $\rho$, g/cm$^3$ | 0.534 | 7.133 | 19.04 | 0.09 | 0.9 | 15.7 |
| $\mu$, amu | 6.939 | 65.39 | 238.029 | 2.016 | 20.179 | 352.019 |

TABLE 2. Values of the Particle–Molecule Interaction Potential

| Parameters | $H_2$ | | | Ne | | | $UF_6$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | Li | U | Zn | Li | U | Zn | Li | U | Zn |
| $\varepsilon_{ij}/k$, $10^2$ K | 1.29 | 3.00 | 1.86 | 1.34 | 3.11 | 1.93 | 3.44 | 8.00 | 4.96 |
| $\sigma_{ij}$, Å | 3.42 | 3.15 | 2.70 | 3.33 | 3.06 | 2.62 | 4.86 | 4.47 | 3.83 |
| $C_3$, $10^4$ K·Å$^3$ | 2.00 | 2.95 | 1.00 | 1.74 | 2.56 | 0.87 | 43.32 | 63.82 | 21.69 |

$$D = \frac{3}{16} \frac{\sqrt{2\pi\mu kT}}{n\mu\pi R^2 \Omega_{ij}^{(1.1)^*}}, \tag{3}$$

which is fundamentally different from the Einstein relation (2). The diffusion of Brownian particles (formula (2)) is dependent just on their size and on the viscosity of the carrier medium. Meanwhile, the diffusion of nanoparticles, in accordance with (3), too, must be determined by the relation of the particle and molecular masses and by the parameters of the law of particle–molecule interaction. This work seeks to study the influence of these factors on the diffusion of nanoparticles. The diffusion of nanoparticles is studied with kinetic theory [6–8].

To calculate the diffusion coefficient of nanoparticles according to (3) we must calculate Ω integrals. To do this in turn requires that the molecule–particle interaction potential be prescribed. Such a potential has specially been constructed in [10] (see also [6]):

$$\Phi (r) = \Phi_9 (r) - \Phi_3 (r) , \tag{4}$$

$$\Phi_i (r) = C_i \left\{ \left[ (r-R)^{-i} - (r+R)^{-i} \right] - a_i \left[ (r-R)^{-(i-1)} - (r+R)^{-(i-1)} \right] \right\} , \quad i = 9, 3 ,$$

where $C_9 = 4\pi\varepsilon_{ij}\sigma_{ij}^{12}/45V$, $C_3 = 2\pi\varepsilon_{ij}\sigma_{ij}^{6}/3V$, $a_9 = 9/8r$, $a_3 = 3/2r$, and $V = \nu/\rho N_A$ is the effective volume per dispersed-particle molecule.

The potential (4) has been constructed under the assumption that the interaction of the molecules of the carrier gas with the atoms (molecules) of a dispersed particle is described by the Lennard–Jones potential 6–12 $\Phi_{ij} = 4\varepsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6}]$. The subsequent use of kinetic theory with the potential (4) and a comparison of the results obtained to numerous experiments have revealed its adequacy in the description of the processes of transfer of nanoparticles in gases (see [6]).

In the present work, we have calculated, on the basis of the kinetic theory (3) and (4), the diffusion coefficients and corresponding reduced Ω integrals for lithium, zinc, and uranium nanoparticles in hydrogen, neon, and uranium hexafluoride in a wide range of nanoparticle radii $R$ = 5–500 Å and gas temperatures $T$ = 200–1000 K. These carrier gases and nanoparticle materials were selected to consider all possible limiting cases of greatest interest.

To compute Ω integrals we used the specially created software package [11] tested on the data on calculation of the corresponding integrals for mixtures of rarefied gases. In calculating Ω integrals, we had to precompute the parameters of the particle–molecule potential $\sigma_{ij}$ and $\varepsilon_{ij}$. They were determined from the parameters of the interaction potential of the molecules of one-component gases $\sigma_{ij}$ and $\varepsilon_{ij}$ (Table 1) using combination relations (see [6]):

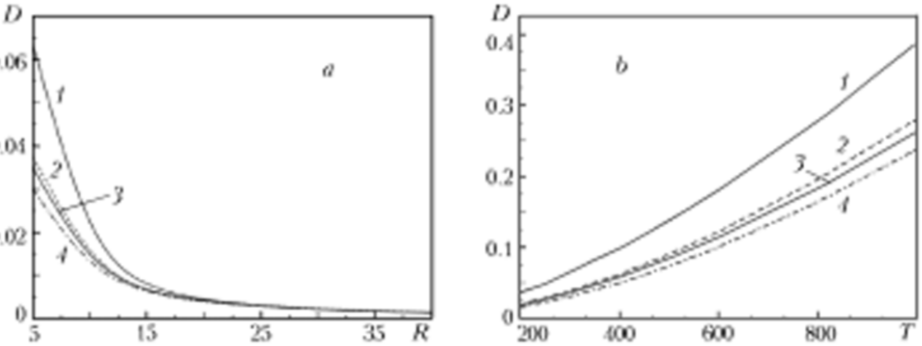


Fig. 1. Diffusion coefficient of nanoparticles in neon vs.: a) nanoparticle radius; b) gas temperature at $R = 5$ Å: 1) CMD correlation; 2) lithium; 3) zinc; 4) uranium. $D$, cm$^2$/sec; $R$, Å; $T$, K.

$$\sigma_{ij} = \sqrt{\sigma_{ii}\varepsilon_{jj}}\,, \quad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}\,.$$

The resulting values for different combinations of substances used are given in Table 2.

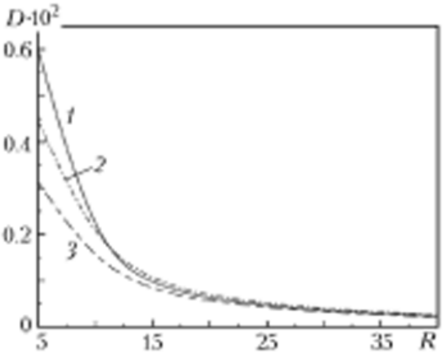
A typical calculation of the diffusion coefficients of these nanoparticles as functions of their radii in neon at a fixed value of the temperature $T = 300$ K is given in Fig. 1a. The CMD correlation is in good agreement with the data of calculations from the kinetic theory (3) and (4) for $R > 25$ Å. However, in the region of small nanoparticle size, the CMD correlation yields substantially overstated values of the diffusion coefficient. For example, this difference amounts to 80% for uranium particles of diameter 2 nm.

The second important fact is that the CMD correlation, just as Einstein's theory, yields the same values of the diffusion coefficient for nanoparticles of different substances, whereas in fact these values are different for fairly small nanoparticles. As is shown in Fig. 1b, the above differences grow with carrier-gas temperature. Here the temperature dependence of the diffusion coefficient at atmospheric pressure is presented for the same nanoparticles in neon. The nanoparticle diameter is fixed and equal to 1 nm. At a temperature of 500 K, the value of the diffusion coefficient of uranium is nearly 60% lower than the diffusion coefficient of zinc, whereas at a temperature of 300 K, it is nearly 7% lower.

The temperature dependence of the Einstein diffusion coefficient (2) is determined by the temperature dependence of the viscosity of the carrier gas and, as has been shown in [6], it is fairly weak: $D_{\mathrm{E}} \sim T^{0.35}$. The relationship is much more complex for the CMD correlation (1), since the mean free path (and hence the Knudsen number) is temperature-dependent at a prescribed pressure. Indeed, we have $l \sim 1/n \sim T$. Thus, we obtain $D_k \sim T^{0.35}(1 + a\mathrm{Kn}T)$, where $a$ is a certain constant of the order of unity. For very small nanoparticles, the Knudsen number involved here is large and evaluation is simplified: $D_k \sim T^{1.35}\mathrm{Kn}$. At the same time, the kinetic theory yields a more rapid increase in the diffusion coefficient with temperature than the CMD correlation.

We note that the CMD correlation leads to highly overstated values of the diffusion coefficients of small nanoparticles. This is due to the strong influence of the free molecular asymptotics used in constructing the CMD correlation even for comparatively small local Knudsen numbers. However, the CMD correlation yields, conversely, understated values of the self-diffusion coefficient for fairly large nanoparticles (see examples in [6, 7]). Also, it is noteworthy that the kinetic theory yields a much more rapid increase in the diffusion coefficient with temperature than the CMD correlation.

The regularities of the diffusion of nanoparticles from the same materials in hydrogen turn out to to be qualitatively the same as those presented in Fig. 1. At the same time, the diffusion of the same nanoparticles in uranium hexafluoride presented in Fig. 2 is qualitatively different. Here, for large and moderate nanoparticle size, the situation is the same as that in Fig. 1. However, in the region of small size ($R \leq 1.2$ nm), lithium (and then, in descending order, zinc and uranium) nanoparticles have the highest value of the diffusion coefficient. The situation observed in Fig. 3 seems quite natural: the diffusion coefficient of nanoparticles at the prescribed radius and temperature is the higher, the lower the molecular weight of the molecules making up a nanoparticle. This is in agreement with formula



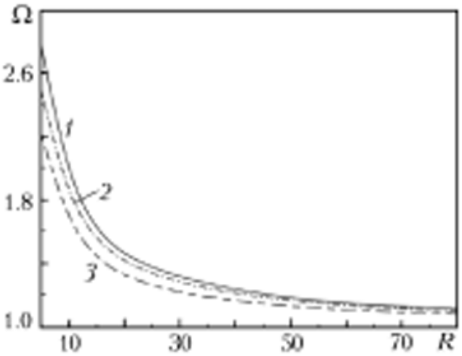


Fig. 2. Diffusion coefficient of nanoparticles in uranium hexafluoride vs. their radius. $D$, $\text{cm}^2/\text{sec}$; $R$, Å.

Fig. 3. Dependence of the Ω integral $\Omega_{ij}^{(1,1)*} = \Omega$ on the radius of nanoparticles in neon for temperature $T = 300$ K. $R$, Å.

(3), too, since we have $D \sim R^{-2}$, and for particles of prescribed composition and fixed radius, their mass is in proportion to the radius cubed. Therefore, we can easily see that $R^2 \sim \nu^{2/3}$. However, the case presented in Fig. 1 does not fit into this logic. In this connection, we must unravel the character of the dependence of the diffusion coefficient (3) on the parameters of nanoparticles. We note primarily that for fairly massive nanoparticles, when $M >> m$, diffusion is virtually independent of the nanoparticle mass. It is precisely such a situation that is realized in U–Ne and Zn–Ne and U–$H_2$ and Zn–$H_2$ gas nanosuspensions; the situation realized in Li–$H_2$ and Li–Ne is virtually the same. In such cases the power of the diffusion effect will be determined mainly by the value of the Ω integrals which in turn is determined by the value of the constant $C_3$ responsible for the attractive forces in the potential (4), i.e., $\Omega \sim C_3$. Table 2 gives the values of this constant for the metals under study. The quantity $C_3$ has the highest value for uranium and the lowest value for zinc. In accordance with this, the Ω integral has its maximum precisely for uranium (see Fig. 3) and its minimum for zinc. Since the diffusion coefficient is in inverse proportion to the Ω integral, we obtain the situation presented in Fig. 1. The values of the Ω integrals for small nanoparticles may be two times different; the differences in the diffusion coefficients will be equally significant.

On the other hand, in gas nanosuspensions where $M \sim m$ or even $M < m$, the diffusion coefficient of nanoparticles begins to be substantially dependent on the relation of the masses of a nanoparticle and the molecules of the carrier gas. The reduced mass no longer turns out to be of the order of $m$. Therefore, if we consider the diffusion of light-weight nanoparticles in the gas of heavy-weight molecules, we have the situation where $D \sim \sqrt{M}$. If, conversely, $M \sim m$, we have $D \sim \sqrt{A/m}$ $(A > 1)$, whereas for $M >> m$ the diffusion coefficient of nanoparticles is $D \sim \sqrt{1/m}$. This explains the character of the dependence of the diffusion coefficient of nanoparticles in uranium hexafluoride. Since a lithium nanoparticle of radius $R = 0.5$ nm has a mass of 168.38 amu, i.e., half as large as a uranium-hexafluoride molecule, we can easily see that $D_{\text{Li}} \sim \sqrt{3.09/m}$ in this case. As a consequence, the diffusion coefficient of lithium nanoparticles of supersmall radius (less than 1 nm) exceeds the diffusion coefficient of zinc nanoparticles.

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## NOTATION

$D$, diffusion coefficient, $\text{cm}^2/\text{sec}$; Kn, Knudsen number; $l$, mean free path of carrier-gas molecules, m; $m$ and $M$, masses of carrier-gas molecules and a dispersed particle, g; $N_A$, Avogadro number; $R$, particle radius, Å; $T$, temperature of the carrier medium, K; $\eta$, coefficient of viscosity of the carrier medium, $\text{N} \cdot \text{sec}/\text{m}^2$; $\mu = mM/(m + M)$, reduced mass; $\nu$, molecular weight of the molecules making up a particle; $\rho$, density of the material of a dispersed particle, $\text{g}/\text{cm}^3$; $\Omega_{ij}^{(l,m)*}$, reduced Ω integrals (see, e.g., [9]); $\sigma_{ij}$ and $\varepsilon_{ij}$, parameters of the Lennard–Jones potential.

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