On kinetic theory of diffusion of nanoparticles in a rarefied gas

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We propose to describe the diffusion of nanoparticles in a rarefied gas using kinetic theory. For this purpose, we use the interaction potential between a disperse particle and a carrier gas molecule we have constructed ourselves. The dependence of the diffusion coefficient on the radius of a particle and temperature of the carrier gas is studied. The theoretical results are compared with experimental data in detail. It has been established that the commonly used Cunningham—Millikan—Davies (CMD) correlation is inapplicable to small particles (less than 10 nm in diameter). Hence, any measurement method measuring mobility of particles or the diffusion coefficient to determine the particle size using the CMD correlation leads to a large systematic error (up to 100% and even more) in the region of small particle size. Furthermore, the CMD correlation is shown to apply adequately only in a narrow range of near-room temperatures, for which the parameters of this correlation were determined.

Diffusion of aerosol particles, being an important factor of their evolution, has been intensely studied in the second half of the 20th century. A number of experimental methods (diffusion batteries, differential analyzers of electric mobility, etc.) have been developed by now, and these methods have shown their efficiency in measurements of, at least, rather large aerosol particles. In fact, the theoretical basis for most measuring methods is the Einstein formula for the diffusion coefficient of Brownian particles

$$D_E = kT/\gamma_S, \ \gamma_S = 6\pi\eta R, \quad (1)$$

where η and T are the viscosity coefficient of the carrier medium and its temperature; R is the characteristic particle radius.

The coefficient of resistance entering the Eq. (1) corresponds to the Stokes resistance force acting on a spherical particle in an incompressible fluid. To extend the applicability of Eq. (1) and make it applicable to description of diffusion of disperse particles in a rarefied gas, the experimental Cunningham—Millikan—Davies (CMD) correlation is usually used[1,2]:

$$D_k = kT/\gamma_k,$$

$$\gamma_k = 6\pi\eta R[1 + 1.257\,\mathrm{Kn} + 0.4\,\mathrm{Kn}\exp(-1.1/\mathrm{Kn})]^{-1} =$$

$$= 6\pi\eta R/C, \quad (2)$$

where $\mathrm{Kn} = l/R$ is the Knudsen number of a particle with radius R; l is the mean free path of carrier gas molecules.

The correlation (2) is widely used in various applications. In fact, some methods for measurement of the size of aerosol particles and their diffusion coefficients are instrumentally based on the correlation (2) (Refs. 3 and 4). It is clear that this correlation should have a rather limited domain of applicability. This is connected with the facts that, first, the parameters entering Eq. (2) were determined in a very narrow temperature range and, second, it is based on the Stokes hydrodynamic resistance force. However, for nanoparticles, whose characteristic size is about $10^{-9}-5\cdot10^{-8}$ m, hydrodynamic consideration of their interaction with the carrier medium is incorrect. An alternative approach is needed. Development of such an approach based of the Boltzmann kinetic theory and its testing are just the objectives of this paper.

As shown in Refs. 5 and 6 the dynamics of particulate matter suspended in an even rarefied gas is, in the general case, described by a system of kinetic equations, which include multiparticle collision integrals. However, to describe ultradisperse matters suspended in a gas, it is quite possible to use the system of Boltzmann kinetic equations. The similarity parameter here is the Knudsen number, and the condition of applicability of the Boltzmann kinetic theory has the form Kn ≫ 1. In particular, at the atmospheric pressure this range includes nanoparticles, so the dynamics of nanoaerosols (that is, aerosols, whose disperse component is presented by nanoparticles) can be described with the system of Boltzmann kinetic equations. For this description to be closed, it is needed to specify the law of interaction of a nanoparticle with the carrier gas molecules. In Ref. 7 (see also Ref. 8) it was proposed to use for this purpose the potential

$$\Phi(r) = \Phi_9(r) - \Phi_3(r), \quad (3)$$

$$\Phi_i(r) = C_i\{[(r-R)^{-i} - (r+R)^{-i}] -$$

$$- a_i[(r-R)^{-(i-1)} - (r+R)^{-(i-1)}]\},$$

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where $C_9 = 4\pi\varepsilon_{ij}\,\sigma_{ij}^{12}/45V$, $C_3 = 2\pi\varepsilon_{ij}\,\sigma_{ij}^{6}/3V$; $a_9 = 9/8r$, $a_3 = 3/2r$, V is the effective volume per one molecule of a particle; ε_{ij} and σ_{ij} are the parameters of the Lennard–Jones potential of interaction of carrier gas molecules with atoms (molecules) of the particle; r is the distance between the carrier gas molecule and the center of the particle.

As a result, it can be shown that the diffusion coefficient of a nanoparticle is described by the following equation (see, for example, Ref. 9):

$$D = \frac{3}{16}\frac{\sqrt{2\pi\mu kT}}{n\mu\pi R^2 \Omega_{ij}^{(1,1)*}(T^*,\sigma_{ij}/R)}, \qquad (4)$$

where $\mu = mM/(m + M)$, m and M are the mass of the carrier gas molecule and the mass of the particle; $T^* = T/\varepsilon_{ij}$; $\Omega_{ij}^{(l,\,m)*}$ are the so-called reduced omega-integrals.[9]

The study presented in this paper was aimed at calculating diffusion of nanoparticles in rarefied gases using potential (3) and obtaining the experimental dependence of the mobility on the nanoparticle diameter in order to reveal the adequacy of using correlation (2) and the kinetic theory for interpretation of the experimental data.

For calculation of the omega-integrals with potential (3), we have developed a computer program, which was tested using the available literature data for mixtures of rarefied gases and the tests made have shown quite good accuracy of the calculations.

The dependence of the diffusion coefficient on the particle radius at a fixed temperature ($T = 288$ K) is illustrated in Fig. 1. As an example, we consider here the diffusion of condensation nuclei in air at atmospheric pressure.
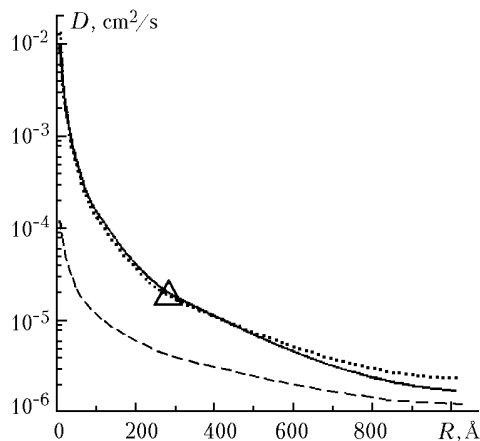
Fig. 1. Diffusion coefficient D vs. particle radius R: calculations with potential (3) (solid line), calculation by CMD equation (2) (dotted line); calculation by the Einstein formula (dashed line), and experimental data[10] ($\triangle$).

The diffusion coefficient was obtained using the kinetic theory [Eqs. (3) and (4)]. The experimental

CMD correlation (2) agrees well with our data in the most part of the considered range. At large particle diameters ($R > 8\cdot10^{-8}$ m), the agreement between the calculated and experimental data worsens (though the discrepancy here turns out to be about $5-10\%$). This is not surprising, since for quite large particles the character of their interaction with molecules becomes more complicated and potential (3) can be only the first approximation. On the other hand, in the range of small particles, where the applicability of the kinetic theory is undoubted, the discrepancy between the CMD correlation and the kinetic theory turns out to be significant.

To reveal the adequacy of application of the kinetic theory (or CMD correlation) in the region of small particle radii, the measurements of particle size and diffusion coefficients were carried out.[11] To obtain objective experimental data, the particle mobility was measured with a differential analyzer of electric mobility (DAEM), and the particle diameter was measured using electron microscopy (EM). Then the diffusion coefficients of the particles used in the experiment were calculated using the kinetic theory, and the obtained experimental and theoretical data were compared.

In the experiment described in Ref. 12 Cu_2O nanoparticles were used. Particles were synthesized through thermal decomposition of the metalorganic precursor of copper acetylacetonate. The experimental investigations were carried out in a vertical laminary flow-through reactor, which is described thoroughly in Ref. 12. Nitrogen with the volume concentration of 99.999% was used as a carrier gas.

The mobility distribution of particles in the size range of $2-200$ nm was measured with a DAEM consisting of a radioactive ionizer, a classifier,[12] and a condensation particle counter TSI 3027. An ESP InTox electric filter was used to collect particles on a carbonated copper grid (SPI). The particle size and crystal properties were studied with a transmission electron microscope (Philips CM200 FEG).

The DAEM operating principle is based on separation of charged particles according to their mobility. Charged (in our case, Cu_2O) particles, moving in the field of electric potentials applied to DAEM plates, deflect and penetrate through a narrow slit in the internal plate. The electrical mobility of particles Z is measured experimentally and then used to determine the diffusion coefficient of the particles

$$D_e = ZkT/ne, \qquad (5)$$

where n is the number of elementary charges on a particle; e is the elementary charge.

The measured mobility is then assigned to the particle diameter obtained using the electron microscope. Thus, the experimental dependence of the diffusion coefficient D_e on the nanoparticle diameter can be found. The results obtained are shown in Fig. 2. In the range of small particle sizes the diffusion coefficients differ widely.
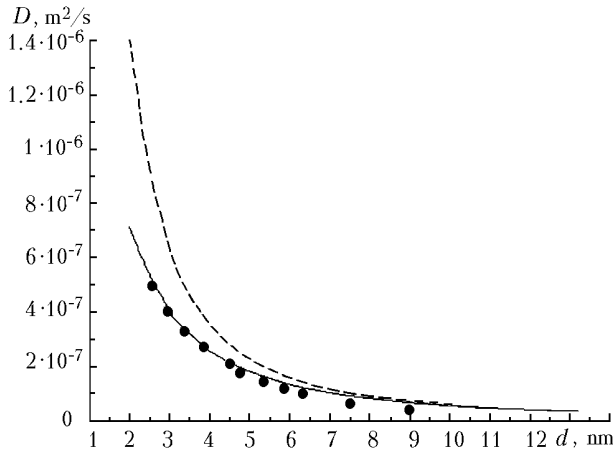
$D, \text{m}^2/\text{s}$

Fig. 2. Diffusion coefficient D vs. particle diameter d: calculations with potential (3) (solid line), calculation by CMD equation (2) (dashed line), experimental data ($\bullet$).

To obtain the theoretical dependence, we used the kinetic theory of rarefied gases. To calculate the diffusion coefficient of Cu_2O particles in N_2 at the atmospheric pressure and temperature $T = 21°C$, it is necessary to know the constants of the Lennard–Jones 6–12 potential of interaction of the carrier gas molecule with the atom (molecule) of the nanoparticle. For this purpose, we used the following combination relations: $\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}}$ and $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$. For nitrogen molecules $\varepsilon_{jj} = 71.4$ K and $\sigma_{jj} = 3.798$ Å (Ref. 13).

The Cu_2O potential parameters were determined using the law of corresponding states. In describing the interaction of Cu_2O molecules by the Lennard–Jones 6–12 potential, it was assumed that $\varepsilon_{ii} = 1.92kT_m$ (T_m is the melting point) and $\sigma_{ii} = \sqrt[3]{1.8v_m}$ (v_m is the volume per one solid-phase molecule at the melting point[14]). For calculation we used the following reference data for Cu_2O: $T_m = 1242°C$, $\rho = 6.1$ g/cm^3. As a result, we obtained $\varepsilon_{ii} = 2909$ K and $\sigma_{ii} = 4.124$ Å. Hence, using the above combination relations we can find the constants of the potential of interaction between the nitrogen molecule and the Cu_2O molecule: $\varepsilon_{ij} = 455.8$ K and $\sigma_{ij} = 3.957$ Å.

The dependence of the diffusion coefficient on the diameter of a nanoparticle obtained using the kinetic theory (that is, using Eqs. (3) and (4)) is also shown in Fig. 2 by solid line.

The discrepancy between the diffusion coefficients is especially large for small particles. The theoretical curve agrees well with the experimental data down to the particle size of about 1 nm. As the particle diameter decreases, the discrepancy between diffusion coefficient (2) and that calculated by Eqs. (3) and (4), as well as the deviation from the experimental data increase considerably. The detailed data on the calculated diffusion coefficient are summarized below.

Here the values of the diffusion coefficients D_k were obtained using correlation (2), D — through

the use of the proposed kinetic theory, D_e are the experimental data. In the range of small radii, CMD correlation (2) gives strongly overestimated values of the diffusion coefficient. Thus, for example, for the particles with the characteristic size of about 2 nm diffusion coefficient (2) more than twice exceeds both the experimental (obtained using EM for determination of the particle diameter) and calculated data.

Dependence of the diffusion coefficient D (m^2/s) on the particle diameter d (nm)

d	D_k	D_e	D
8.94	$6.701 \cdot 10^{-8}$	$4.373 \cdot 10^{-8}$	$6.694 \cdot 10^{-8}$
7.54	$9.385 \cdot 10^{-8}$	$6.543 \cdot 10^{-8}$	$9.044 \cdot 10^{-8}$
6.32	$1.331 \cdot 10^{-7}$	$9.810 \cdot 10^{-8}$	$1.215 \cdot 10^{-7}$
5.84	$1.557 \cdot 10^{-7}$	$1.202 \cdot 10^{-7}$	$1.397 \cdot 10^{-7}$
5.35	$1.853 \cdot 10^{-7}$	$1.470 \cdot 10^{-7}$	$1.601 \cdot 10^{-7}$
4.79	$2.308 \cdot 10^{-7}$	$1.798 \cdot 10^{-7}$	$1.932 \cdot 10^{-7}$
4.51	$2.602 \cdot 10^{-7}$	$2.198 \cdot 10^{-7}$	$2.118 \cdot 10^{-7}$
3.87	$3.528 \cdot 10^{-7}$	$2.689 \cdot 10^{-7}$	$2.678 \cdot 10^{-7}$
3.33	$4.758 \cdot 10^{-7}$	$3.299 \cdot 10^{-7}$	$3.418 \cdot 10^{-7}$
2.94	$6.097 \cdot 10^{-7}$	$4.034 \cdot 10^{-7}$	$4.102 \cdot 10^{-7}$
2.55	$8.097 \cdot 10^{-7}$	$4.925 \cdot 10^{-7}$	$5.063 \cdot 10^{-7}$

Finally, it should be noted that the diffusion coefficient of nanoparticles, as in the case of diffusion of molecules and Brownian particles, significantly depends on the medium temperature. The temperature dependence of the diffusion coefficient at atmospheric pressure for particles with the fixed radius R ($R = 3 \cdot 10^{-8}$ m) is depicted in Fig. 3.
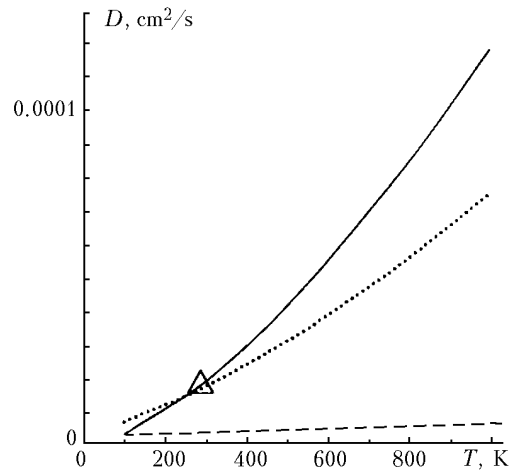

$D, \text{cm}^2/\text{s}$

Fig. 3. Temperature dependence of diffusion coefficient D. Calculations with potential (3) (solid line); calculation by CMD equation (2) (dotted line); calculation by the Einstein formula (1) (dashed line), and experimental data[10] (Δ).

Diffusion of condensation nuclei in air at atmospheric pressure is again considered as an example. To determine the temperature dependence of the air viscosity coefficient, tabulated data were used.

Analysis of Fig. 3 shows that as the temperature changes from 100 to 1000 K, the diffusion coefficient of the aerosol particle changes by tens times. On the

other hand, the Einstein formula gives the diffusion coefficient only slightly varying with temperature. Equation (2) has a rather narrow domain of applicability regarding the temperature variation. It agrees with our data within the accuracy of 15% only at the temperature from 100 to 300 K. At high temperatures CMD equation (2) leads to strongly underestimated values of the diffusion coefficient and becomes inapplicable.

Summarizing the above said, we can draw the following three main conclusions.

First, any method for determination of the particle diameter d from mobility using CMD correlation (2):

$$d = neC/3\pi\eta Z, \qquad (6)$$

and, in particular, DAEM and diffusion batteries, includes a systematic error in determination of the size of ultradisperse (smaller than 10 nm) particles, since they assign incorrect value of the particle diameter to the obtained value of mobility. As was shown, these errors may exceed 100%. Equations (2) and (6) work well for a rather large particles, but cannot be applied to nanoparticles.

The second circumstance to be noted is that the kinetic theory proposed here rather well describes diffusion of nanoparticles, including the range of small radii, where correlation (2) is inapplicable. Besides, it should be emphasized that the diffusion coefficient and mobility of nanoparticles in the general case depend not only on the particle diameter, but also on the type of the carrier gas and the material of disperse particles. The kinetic theory developed here takes this into account through the parameters of the interaction of carrier gas molecules with the particles of disperse matter.

Finally, unlike correlation (2), the proposed kinetic theory can be used to describe diffusion in a wide temperature range, while experimental CMD correlation (2) can be applied only in the range of near-room temperatures, for which its parameters were determined.

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