

# About Nanoparticle Friction Force in Gases and Liquids

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**Abstract.** The nanoparticle drag force in dense gases and liquids is calculated by the molecular dynamics method. Dependences of this force on nanoparticle radius and mass are presented. The drag coefficient in rarefied gases is calculated using kinetic theory with the nanoparticle–molecule interaction potential developed by the authors. The values of the drag force are shown to differ from the Stokes results.

**Keywords:** nanoparticle, drag force, rarefied gas, dense gas, liquid, kinetic theory, molecular dynamics method.

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## INTRODUCTION

Today it is clear that nanoparticles are a unique physical object and the transport processes of nanoparticles are not adequately described by traditional models. The nanoparticle size is on the order of the hydrodynamic, physically infinitesimal size for the carrier medium. Therefore, the fluid dynamics approach and the Stokes–Einstein (SE) formula, in particular, are not suitable for predicting the nanoparticle drag force. Neither is it appropriate to use the ordinary intermolecular potential to describe the nanoparticle–molecule interaction in rarefied gases, and a correct application of kinetic theory requires special interaction potentials.

The mechanisms of nanoparticle interaction with carrier gases and carrier liquids differ significantly; therefore, there are no universal methods for determining the interaction force. In the study described here, kinetic theory with the nanoparticle–molecule interaction potential [1, 2] was used to describe nanoparticle diffusion and relaxation in rarefied gases and the molecular dynamics (MD) method with the smooth hard-sphere potential was employed to describe these processes in dense gases and liquids.

A difficulty that arises in specifying the nanoparticle–molecule potential is that the interaction of a nanoparticle with solvent molecules is a collective interaction. In a dense medium, many collisions occur during the time when the particle interacts with a molecule. Moreover, even if the carrier gas is sufficiently rarefied, a gas molecule interacts simultaneously with all molecules contained in the particle. Therefore, we propose to treat a nanoparticle as a solid particle and model it by a set of molecules enclosed in a sphere of radius  $R$ .

We used the smooth hard-sphere model for MD simulation of the interaction of a nanoparticle with carrier fluid molecules. The nanoparticle radius  $R$  was varied from  $r$  to  $5r$  and the nanoparticle mass  $M$  from  $m$  to  $300m$  (here  $r$  is the radius of the carrier fluid molecule and  $m$  is its mass).

Calculated values of the drag force were compared with the values obtained by the Stokes formula

$$F = 6\pi\eta RU = \gamma_s U. \quad (1)$$

Here  $U$  is the particle velocity and  $\eta$  is the viscosity of the carrier medium. This formula describes the motion of both Brownian particles and macroscopic particles. For a long time, researches have believed that the Stokes law can be applied to the calculation of the nanoparticle drag force. However, studies of the diffusion of macromolecules and fullerenes have shown that there are differences between the Stokes values and experimental results [3–5]. The purpose of this paper is to examine the features of nanoparticle relaxation, diffusion, and interaction with solvents.

## FORCE ACTING ON NANOPARTICLE IN LIQUIDS AND DENSE GASES

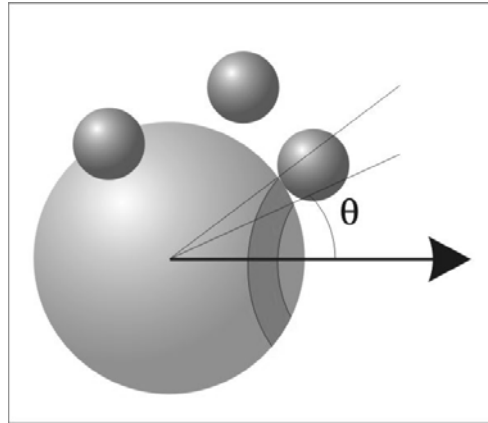
The MD method can be used to predict the average force acting on each surface element of a nanoparticle and the total drag force due to the carrier medium. The ordinary MD algorithm was applied. The cubic cell contained  $N = 1000 \div 4000$  molecules and one nanoparticle. Periodic boundary conditions were used to compensate for the finite number of molecules. The density of this medium was defined by the parameter  $\alpha = (V - V_p)/V_0$ , where  $V$  is the cell volume,  $V_p$  is the nanoparticle volume,  $V_0 = 8N r^3 / \sqrt{2}$  is the close-packed volume of molecules. Two values of the parameter  $\alpha$  were considered:  $\alpha = 2$  and  $\alpha = 5$ .

To determine the force  $F$  acting on a particle surface element, we initialized the particle velocity by the value of the mean-square velocity of the molecules at thermal equilibrium. The particle surface was then divided into rings, each of them being defined by the angle  $\vartheta$  (see Fig. 1). When there was a collision of any molecule with the particle, the corresponding angle  $\vartheta$  was determined and the momentum transfer was calculated. This procedure was repeated after each collision during the velocity relaxation process. Then, we used ensemble averaging to calculate the regular values of the force  $\mathbf{p}(\theta, t)$  acting on the unit surface element of the nanoparticle. The projection of this force onto the particle velocity direction is given by

$$p_U(\theta, t) = \frac{\mathbf{p}(\theta, t) \cdot \mathbf{U}_0}{U_0}, \quad (2)$$

where  $\mathbf{U}_0$  is the initial nanoparticle velocity. The total force acting on the nanoparticle is obtained by integrating (2) over the total surface

$$F(t) = \int p_U(\vartheta, t) dS. \quad (3)$$



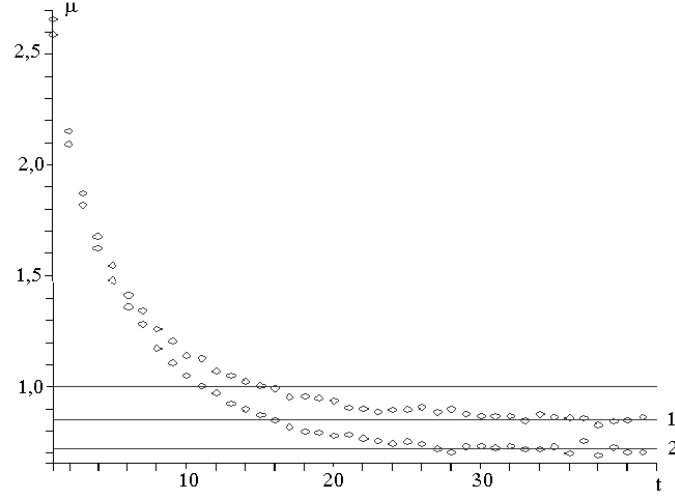
**FIGURE 1.** Particle surface partition. The direction of the arrow shows the direction of the initial particle velocity

It is convenient to represent the force (3) in the form

$$F(t) = k(t)U, \quad (4)$$

where  $k(t)$  is the time-dependent drag coefficient. Figure 2 gives the time dependences of this coefficient normalized to the Stokes value  $\mu = k / 6\pi\eta R$  for  $R = 3r$ ,  $M = 50m$  and  $100m$ , and  $\alpha = 2$ . In both cases, the drag coefficient is nonstationary, and at the beginning of the relaxation process, it is much higher than the Stokes value. The mass dependence of the initial values of the drag coefficient is negligibly small. From a certain time on, this coefficient is saturated, reaching an asymptotic value. This value corresponds to the Stokes coefficient only for a

massive particle. The force acting on less massive particles turns out to be weaker than the Stokes force. This difference is higher the lower the mass ratio of the molecule and nanoparticle. These features are valid for different particle sizes and densities of the medium.



**FIGURE 2.** Time dependence of the nanoparticles drag force for  $R/r = 3$ ,  $M/m = 100$  (curve 1), and  $M/m = 50$  (curve 2). Time is measured in units of the mean free time of the molecules.

This behaviour of the drag force is due to the existence of two mechanisms of nanoparticle relaxation. The velocity autocorrelation function  $\chi_{vv}$  of a nanoparticle in dense gases and liquids has the following form [6, 7]:

$$\chi_{vv} = b_1 \exp(-t / \tau_1) + b_2 \exp(-t / \tau_2), \quad (5)$$

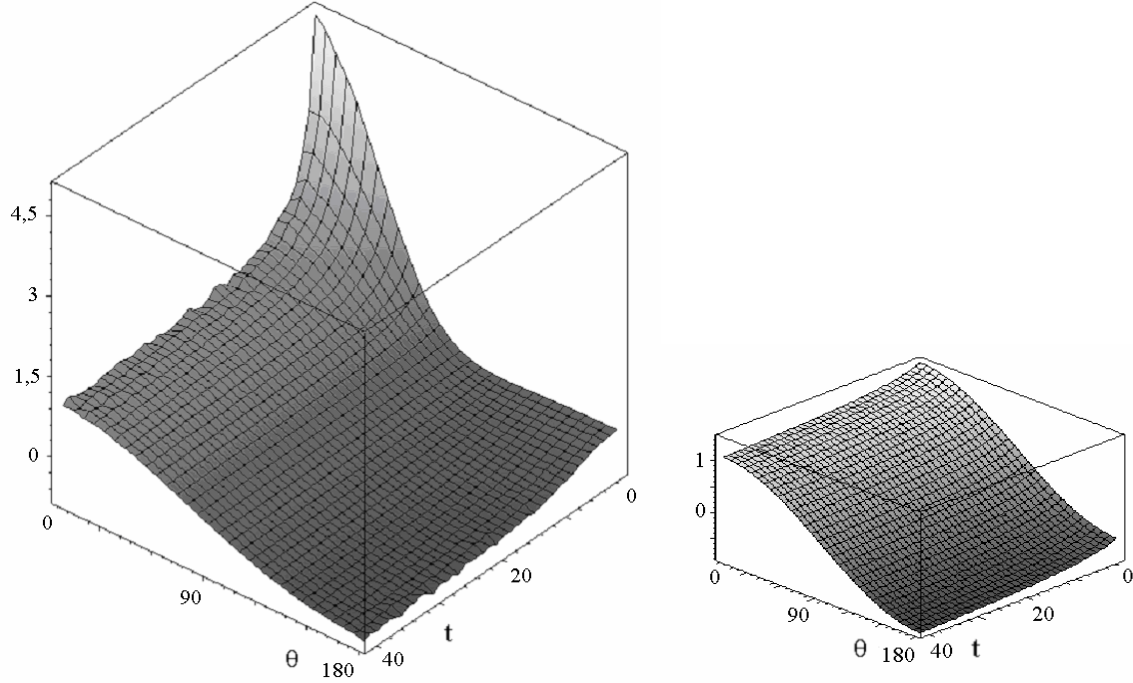
The first term is due to a kinetic mechanism, which is characterized by the small relaxation time  $\tau_1$ . In this stage of relaxation, interactions of carrier-fluid molecules with the nanoparticle are individual. This stage is characterized by microfluctuations in the density and velocity fields of the fluid molecules and a decrease in the drag coefficient [7]. Long-time values of the drag force are related to interactions of the nanoparticle with the microfluctuations; this stage has the relaxation time  $\tau_2$  in formula (2). In this stage, the drag force has a quasihydrodynamic nature. Figure 2 shows data for the drag force acting on a comparatively small particle. As the radius ratio increases, the initial value of the drag force ratio also increases (see Table 1). However, the dependence of the asymptotic force value on the radius ratio is weak one.

**TABLE 1.** Initial values of the normalized drag force.

$R/r$	2	3	4
$M/m=100$	2,07	2,66	3,16
$M/m=50$	2,03	2,59	3,22
$M/m=25$	1.95	—	—

Fig. 3 shows the time dependence of the calculated pressure force  $p_U(\theta, t)$  (2). One can see that the drag force is strongly anisotropic whereas the Stokes theory predicts isotropic behaviour (the angle dependence on the right picture with the Stokes values is caused only by the hydrostatic pressure force). At the initial time, the force acting on the frontal area of the surface exceeds the values predicted by the Stokes theory by a factor of more than five. This large difference leads to the conclusion that the description of nanoparticle interaction with the carrier media using the traditional hydrodynamic approach gives unrealistic results even when ensemble-averaged values of the

drag forces are studied. It is important to emphasize that the Knudsen number constructed with respect to the nanoparticle diameter is of the order of  $10^{-2}$ .



**FIGURE 3.** Pressure on different parts of the nanoparticle surface. The left picture shows the calculated data, the right picture illustrates the values corresponding to the Stokes law.

## NANOPARTICLE FRICTION COEFFICIENT IN RAREFIED GASES

The applicability of the Stokes formula (1) can be extended to the diffusion of dispersed particles in rarefied gases through the use of the experimental Cunningham–Millikan–Davies (CMD) correlation [8]

$$F = \gamma_{CMD} U, \quad \gamma_{CMD} = 6\pi\eta R [1 + 1.257 Kn_R + 0.4 Kn_R \exp(-1.1 / Kn_R)]^{-1}, \quad (6)$$

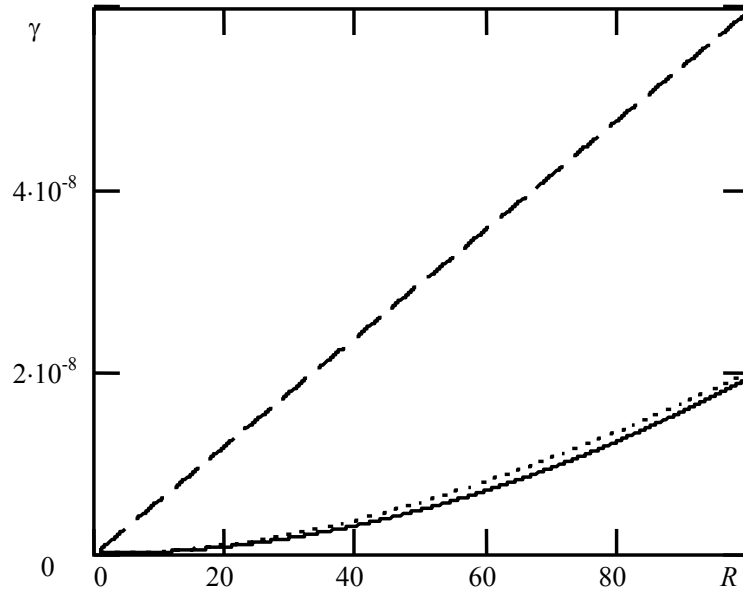
where  $Kn_R = l / R$  is the Knudsen number constructed with respect to the particle radius  $R$  and  $l$  is the mean free path of the carrier gas molecule. For typical nanoparticles, the Knudsen number  $Kn_R$  is of the order of one or higher. To calculate the force acting on a nanoparticle, it is necessary to solve the Boltzmann equation. However, information on the drag coefficient can be obtained from the value of the nanoparticle diffusion coefficient. Let us assume that an Einstein-type formula is correct for nanoparticles, i.e.,

$$\gamma = kT / D, \quad (7)$$

where  $\gamma$  is the drag coefficient,  $m$  and  $M$  are the masses of the carrier gas molecule and nanoparticles, respectively,  $D$  is the diffusion coefficient of the nanoparticle, and  $T$  is the carrier-gas temperature. The kinetic theory of nanoparticle diffusion gives the following value for the diffusivity [2, 9]:

$$D = 8 \sqrt{2 \pi m_{ij} kT} n R^2 \Omega_{ij}^{(1,1)*} (T^*, \sigma_{ij} R) / 3, \quad (8)$$

Here  $n$  is the number density of the carrier gas,  $m_{ij} = mM/(m+M)$ ,  $T^* = T/\varepsilon_{ij}$  is the reduced temperature,  $\Omega_{ij}^{(l,m)*}$  are the so-called reduced  $\Omega$ -integrals dependent on the nanoparticle-molecule potential [1, 2],  $\sigma_{ij}$  and  $\varepsilon_{ij}$  are the Lennard-Jones constants of the interaction potential of the carrier gas molecules with an atom of the nanoparticle.



**FIGURE 4.** Drag coefficient vs. nanoparticle radius  $R$  for Zn nanoparticles.

The dependence of the drag coefficient (g/sec) on radius (nm) for zinc nanoparticles in neon at  $T=300$  K is presented in Fig. 4. Here the dashed curve corresponds to the Stokes drag coefficient  $\gamma_s(1)$ , the dotted curve to the CMD one (6), and the solid curve was obtained using the kinetic theory with the potential of [1, 2]. In this case,  $m/M \sim 10^{-2}$ . The experimental CMD correlation (6) agrees well with the data of the kinetic theory and gives values much smaller than the Stokes drag coefficient (1). This is not surprising, however, because the Knudsen number constructed with respect to the particle radius is usually large even for particle sizes of about 100 nm. In this range, the continuum approach is no longer applicable. Obviously, formula (7) is meaningful only outside the nanoparticle velocity relaxation range; therefore, the drag coefficients given in Fig. 4 are stationary. The results of numerical calculations based on the kinetic theory are shown to be in good agreement with the CMD correlation (6) over a wide range of nanoparticle sizes.

## CONCLUSIONS

The drag force of nanoparticles is not adequately described by the Stokes formula. Therefore, the CMD correlation cannot be used to calculate the drag force and size of nanoparticles. The drag coefficient of nanoparticles depends greatly on the temperature of the medium. The CMD experimental correlation has a narrow temperature range of application. It is consistent with our calculation data with an accuracy of 15% only in the temperature range from 100 to 300 K. At higher temperatures, it leads to strongly underestimated drag coefficients and thus cannot be applied.

The main result of the molecular dynamics calculation is the proof of the inadequacy of the Stokes law for condensed nanodispersed system. At the beginning of the nanoparticle relaxation process, the drag force is found to exceed the Stokes value by a factor of 2 to 3. After that, the ratio of the drag force to the Stokes one decreases monotonically. Long-time values of the drag force differ from the Stokes results for small nanoparticles. The calculation results agree with theoretical predictions at the long-time limit only for large and massive nanoparticles.

The friction force on each element of the nanoparticle surface was also calculated by the MD method. This force in the frontal area of the nanoparticle surface always exceeds the Stokes value, sometimes, by a factor of 5. The drag

force is always smaller than the Stokes force in other regions of the particle surface. This behaviour of the calculated force is due to microfluctuations of the carrier fluid.

## ACKNOWLEDGMENTS

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