Kinetic simulation of the viscosity of rarefied gas nanosuspensions with composite particles

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Abstract. The viscosity of rarefied gas suspensions with composite nanoparticles was studied using the previously developed kinetic theory. The interaction of carrier gas molecules is described by the Lennard-Jones potential, the interaction of the gas molecules with a nanoparticle does by Rudyak–Krasnolutskii (RK) potential, and the interaction of the nanoparticles with each other does by the Rudyak–Krasnolutskii–Ivanov potential (RKI). Nitrogen-based gas suspensions with carbon (graphite) nanoparticles in a 1 nm thick uranium shell and with solid carbon and uranium nanoparticles at a temperature of 300 K and atmospheric pressure are considered. The diameter of the nanoparticles varied from 2 to 100 nm. It is shown that the viscosity of gas suspension with composite nanoparticles with a core of less dense material than the material of the shell is always lower than the viscosity of the gas suspension with solid nanoparticles of the same material as the shell composite. The decrease in the viscosity of the above-mentioned gas suspension with composite nanoparticles can be explained on the basis of the kinetic theory by the smaller mass of such nanoparticles compared to solid ones.

1. Introduction
Nanofluids are a two-phase system consisting of a base fluid and nanoparticles. Even today, it can be stated that nanofluids are an extremely promising material. They are successfully used or are planned to be used in chemical installations and reactors, including catalytic ones, for cooling various devices, for creating new systems for transporting and producing thermal energy, in bio-, MEMS- and nanotechnologies for various purposes, for creating new medicines and cosmetics, for delivering medicines, for creating systems for recognizing various types of pollutants, cleaning air and water, new lubricants, lacquers and paints, construction materials, etc. [1].

Gas nanosuspensions are nanofluids in which the carrier component is a gas. Previously, we developed the kinetic theory of rarefied ultrafine gas suspensions. In particular, we studied the viscosity of rarefied gas nanosuspensions. It was shown that the viscosity of gas nanosuspensions, in contrast to the viscosity of coarse particle suspensions, can be not only greater, but also less than the viscosity of the carrier gas. The increase or decrease in the viscosity of a gas nanosuspension compared to a pure gas depends mainly on the size of the nanoparticles and the ratio of the densities of the nanoparticle material and the carrier gas molecules [2–3]. In gas suspensions with hollow nanoparticles, a similar effect is also observed. In addition, with a certain choice of nanoparticle material in a certain size range, the addition of hollow and solid nanoparticles can cause the opposite effect: the addition of hollow nanoparticles reduces the viscosity of the gas suspension compared to the viscosity of a pure carrier gas, but the addition of solid nanoparticles of the same diameter
increases the viscosity [4]. With a decrease in the radius of nanoparticles and an increase in temperature, the effect of changing (increasing or decreasing) the viscosity coefficient of the gas nanosuspension in all cases increases significantly.

The diffusion of nanoparticles in a rarefied gas was also studied using the kinetic theory developed. It was shown that any method for determining the diameter of nanoparticles by mobility using the Cunningham-Milliken-Davies (CMD) correlation [5–8] and, in particular, differential electrostatic analyzers and diffusion batteries, contains a systematic error in determining the size of ultradisperse (less than 10 nm in diameter) particles, since the obtained mobility value is associated with an incorrect value of the particle diameter [9]. The CMD correlation and the Epstein formula [10] work well for fairly large particles, but are not applicable for nanoparticles. The diffusion coefficient and mobility of nanoparticles generally depend not only on the diameter of the particles, but also on the type of carrier gas and the material of the dispersed particles [11–13]. The kinetic theory developed by us takes this into account through the parameters of the interaction potential of carrier gas molecules with a dispersed particle. In addition, the thermal diffusion of nanoparticles in a rarefied gas was studied [14].

However, nanofluids that have been studied so far usually contain homogeneous particles. However, in many biomedical applications, in the production of various cosmetic products, environmental protection products, etc., inhomogeneous particles are often used [1]. This, above all, is a variety of composite particles [1, 15–16]. The transport properties of gas suspensions with such particles are practically not studied. It is not easy to do this experimentally, for obvious reasons. Therefore, in this paper the peculiarities of transport processes in gas nanosuspension with composite particles are studied theoretically using the kinetic theory.

The aim of this work is to study the viscosity of rarefied gas nanosuspensions with such particles.

2. The simulation technique

The kinetic theory, developed earlier [2–3], is used to simulate transport processes in rarefied gas suspensions with composite nanoparticles. The interaction of carrier gas molecules is described by the Lennard-Jones potential [17,18]

$$\Phi_{LJ}^{mk}(r) = 4\varepsilon_{mk}\left[(\sigma_{mk}/r)^{12} - (\sigma_{mk}/r)^6\right],$$

where $r = |\mathbf{r}_m - \mathbf{r}_k|$ is distance between centers of the molecules (atoms) $m$ and $k$, $\sigma_{mk}$ is effective diameter of the atoms, $\varepsilon_{mk}$ is the depth of the potential well.

The interaction of carrier gas molecules with a nanoparticle is described by the RK potential [12,19]

$$\Phi(r,R,\Delta) = \Phi_{mp}(r,R) + \Phi_{ms}(r,R,\Delta),$$

where

$$\Phi_{mp}(r,R) = \Phi_{mp}^0(r,R) - \Phi_{mp}^3(r,R),$$

$$\Phi_{mp}^0(r,R) = C_{mp} \left\{ \frac{1}{(r+R)^n} - \frac{n}{(n-1)r} \frac{1}{(r+R)^{n-1}} \right\},$$

$$\Phi_{mp}^3(r,R) = C_{mp} \left\{ \frac{1}{(r+R)^n} - \frac{n}{(n-1)r} \frac{1}{(r+R)^{n-1}} \right\},$$

$$\Phi_{ms}(r,R,\Delta) = \Phi_{ms}^0(r,R,\Delta) - \Phi_{ms}^3(r,R,\Delta),$$

$$\Phi_{ms}^0(r,R,\Delta) = C_{ms} \left[ \frac{1}{(r-R-\Delta)^n} - \frac{1}{(r+R+\Delta)^n} \right],$$

$$\Phi_{ms}^3(r,R,\Delta) = C_{ms} \left[ \frac{1}{(r-R-\Delta)^n} - \frac{n}{(n-1)r} \frac{1}{(r-R-\Delta)^{n-1}} \right].$$
A solid composite two layer particle is considered. It is considered spherical and consists of a spherical core of radius \( R \) and a spherical shell of finite thickness \( \Delta \). Thus, the total radius of a nanoparticle with a shell is equal to \((R+\Delta)\). \( V_p, V_s \) are the effective volumes per molecule of the core and shell of the nanoparticle, respectively, and \( V_p^{-1} = \frac{n N_A}{\mu_p}, \quad V_s^{-1} = \frac{n N_A}{\mu_s}, \quad \rho_p, \rho_s \) are the densities of the core and shell material of the particle respectively, \( N_A \) is the Avogadro number, \( \mu_p, \mu_s \) are molar masses of the atoms (molecules) that make up the core and shell of the composite particle, respectively. The \( p \) index refers to the core atoms, and the \( s \) does to atoms of the shell of the nanoparticle. Parameters \( \sigma_{mk} \) and \( \varepsilon_{mk} \) were determined using the simplest combination rules \( \sigma_{mk} = \sqrt{\sigma_m \sigma_k} \) and \( \varepsilon_{mk} = \sqrt{\varepsilon_m \varepsilon_k} \).

\[
\Phi = \left[ \frac{1}{(r+R)^{\alpha}} + \frac{1}{(r+R)^{\beta}} \right] \sum_{n=1}^{\infty} \frac{1}{(n+1)^{\alpha}} \left[ \frac{1}{(r+R)^{(n+1)}(r+R)^{(n+1)}} \right]^{n},
\]

\[
C_{np} = \frac{8\pi n \sigma_{np} (n+3)^{n+3}}{n(n+1) V_p}, \quad C_{ns} = \frac{8\pi n \sigma_{ns} (n+3)^{n+3}}{n(n+1) V_s}.
\]

Figure 1. Nanoparticle–molecule interaction potentials.

The potential (2) depends on the thickness of the spherical shell \( \Delta \) surrounding the solid core. However, all these potentials are short ranged. Therefore, it is clear that if \( \Delta \) is greater than a certain value, the carrier medium (liquid or gas) molecule actually interacts only with the atoms of the spherical shell and does not feel the core atoms. The actual calculation of potential confirms this view. As an example, figure 1 shows the interaction potential of a 10 nm diameter uranium nanoparticle with a nitrogen molecule (dashed line). It also shows the interaction potential of a carbon (graphite) nanoparticle of the same diameter with a nitrogen molecule (dash-dotted line). Finally, the dotted line shows the potential of interaction of a nitrogen molecule and a composite nanoparticle made of carbon with a uranium shell. The thickness of the shell is 1 nm (i.e. the carbon spherical core has a diameter of 8 nm). Potentials \( \Phi \) (2) are measured in Kelvin, and the distance \( r \) from the center of the nanoparticle to the molecule of medium does in Angstroms. The first and last curves are almost identical. The interaction of nanoparticles with each other is described by the RKI potential [19,20].

To calculate the transport coefficients in the first approximation of the Chapman–Enskog method [21], we use the original KinSib package, which was previously successfully used for simulation of transport processes in rarefied gas nanosuspensions [2–4,11–14]. The formulas for the effective viscosity coefficient is given in [3] and in the classical literature on the kinetic theory [22].
The Lennard-Jones potential parameters for nitrogen molecules $\sigma = 3.798 \, \text{Å}$, $\varepsilon/k = 71.4 \, \text{K}$ [23], for uranium $\sigma = 3.343 \, \text{Å}$, $\varepsilon/k = 2703 \, \text{K}$, obtained on the basis of the principle of corresponding states [22], for carbon $\sigma = 3.415 \, \text{Å}$, $\varepsilon/k = 27.70 \, \text{K}$ [24] are used.

In all cases, the temperature of gas nanosuspensions was equal to $T = 300 \, \text{K}$, and the pressure was $p = 101325 \, \text{Pa}$. The diameter of the nanoparticles varied from 2 to 100 nm, and the composite nanoparticles had a wall thickness of 1 nm.

![Figure 2](image)

**Figure 2.** Dependence of the effective viscosity coefficient (mP) of gas suspensions on the volume concentration (%) of nanoparticles with a diameter of 5 nm.

### 3. Simulation results

The effective viscosity of rarefied nitrogen-based gas suspensions with composite carbon (graphite) nanoparticles with a 1 nm thick uranium shell, as well as gas suspensions with homogeneous uranium and carbon nanoparticles, were simulated. In particular, figure 2 shows the dependence of the effective viscosity coefficient of gas suspensions on the volume concentration of nanoparticles with a diameter of 5 nm. The dashed line corresponds to pure nitrogen, the solid line corresponds to gas suspension with solid nanoparticles of uranium, the dash-dotted line corresponds to gas suspension with solid nanoparticles of carbon, the dotted line corresponds to gas suspension with composite nanoparticles of carbon (graphite) with a uranium shell. At this value of the nanoparticle diameter, there is an approximately linear change in the viscosity of gas suspensions depending on the concentration of nanoparticles. Particles with a higher density of the material (uranium) increase the effective viscosity, while those with a lower density (graphite) reduce it. The value of the viscosity coefficient of gas suspensions with composite nanoparticles occupies an intermediate position.
Figure 3. Dependence of the effective viscosity coefficient (mP) of gas nanosuspensions on the diameter (nm) of nanoparticles at $\phi = 10^{-3}$.

Figure 3 shows the dependence of the effective viscosity coefficient of gas nanosuspensions on the total diameter of nanoparticles at a fixed volume concentration of nanoparticles $\phi = 10^{-3}$. The same line types represent the same gas nanosuspensions as in figure 2. Nanoparticles of small diameter have the greatest influence on the value of the viscosity coefficient of gas suspensions. As the nanoparticle diameter increases, this effect gradually decreases with a fixed volume concentration of nanoparticles. In particular, uranium nanoparticles of small diameter significantly increase the viscosity of gas nanosuspension compared to pure nitrogen. By increasing the diameter of more than 12 nm, uranium nanoparticles reduce the viscosity of the gas suspension. Carbon nanoparticles lower the viscosity of the gas suspension at any diameter of the nanoparticles, but much stronger at small diameters.

As already noted above, the value of the viscosity coefficient of gas suspensions with composite nanoparticles made of carbon with a 1 nm thick uranium shell occupies an intermediate position. Such small diameter composite nanoparticles almost do not differ from solid uranium nanoparticles in mass and have approximately the same effect on the viscosity of the gas suspension. However, when the diameter increases more than 6 nm, such nanoparticles begin to reduce the viscosity of the gas suspension.

4. Conclusion
The increase or decrease in the effective viscosity coefficient of a rarefied gas nanosuspension compared to a pure gas depends mainly on the particle size and ratio $\frac{m_2 \sigma_2^3}{(m_1 d_1)}$, where $m_1$ and $\sigma_1$ are mass and diameter of the carrier gas molecule, and $m_2$ and $d_2$ are mass and diameter of the nanoparticle.

The decrease in the viscosity of gas suspensions with composite nanoparticles made of carbon with a uranium shell is explained by the lower mass of such nanoparticles compared to homogeneous ones made of uranium. At the same time, as indicated above, the parameters of the interaction potential of such a composite nanoparticle with a carrier gas molecule practically do not differ from the corresponding parameters for solid uranium nanoparticles. Conversely, such composite nanoparticles have a larger mass than solid graphite nanoparticles. Therefore, the viscosity of gas suspensions with such nanoparticles is higher than with solid graphite ones. As the diameter of composite nanoparticles increases with a fixed thickness of the uranium shell, the relative difference in the mass of such nanoparticles and solid ones made of graphite gradually decreases. This leads to the fact that the viscosity coefficients of gas suspensions with such nanoparticles converge.

In contrast to rarefied gas nanosuspensions, the viscosity of any coarse dispersed gas suspension is always greater than the viscosity of the carrier gas [25,26].

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