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## **Simulation of Nanoparticle Thermal Diffusion in Dense Gases and Fluids by the Molecular Dynamics Method**

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**Abstract**—This paper is devoted to the study of the thermal diffusion of nanoparticles in dense gases and fluids by the method of molecular dynamics with Rudyak–Krasnolutski nanoparticle–molecule and Rudyak–Krasnolutski–Ivanov nanoparticle–nanoparticle potentials. The thermal diffusion and binary diffusion coefficients were calculated with the help of the fluctuation-dissipation theorem. Nanofluids simulated consisted of argon as a carrier medium and aluminum nanoparticles. Dependences of the nanoparticle thermal diffusion and Soret coefficients on the particle diameter and volume concentration were derived. The thermal diffusion coefficient showed a significant dependence on the particle size for small nanoparticles (1–4 nm diameter).

**Keywords:** thermal diffusion coefficient, Soret coefficient, nanoparticles, nanofluids, diffusion, aerosol

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### INTRODUCTION

Nanoparticles are intermediate in size between ordinary molecules and macroparticles, including Brownian. A fullerene is the smallest nanoparticle. Viruses, which are tens of nanometers in size, are in-between. The specific small sizes of nanoparticles determine a number of their unusual properties. The properties of nanoparticle transfer in gases and fluids are also unusual. As a rule, they cannot be described by classical theories. Thus, dispersed gases and fluids with nanoparticles have atypical viscosity and thermal conductivity [1–3], and diffusion of nanoparticles in fluids and gases is not described by the Einstein and the Cunningham–Millikan–Davies theories, respectively [4, 5]. In [6], nanoparticle thermal diffusion in rarefied gases was studied by the molecular thermodynamics (MD) method; its specific properties were shown, i.e., the absence of temperature inversion of the thermal diffusion factor; values of the thermal diffusion factor several orders of magnitude higher as compared to gas mixtures, etc.

The experimental study of nanoparticle thermal diffusion in dense gases and fluids has just begun. Such experiments are technically difficult; adequate data on the dependence of nanoparticle thermal diffusion coefficient on the particle size, material, and concentration can hardly be obtained from these experiments. It is stated in [7] that the thermal diffusion coefficient normalized to the mass fraction of colloid particles is independent of their sizes, if the particle size is much higher than the range parameter in the

interaction between the molecules of the particles and carrier medium molecules, equal to several molecular diameters. This condition is violated for small nanoparticles. It was shown earlier that the thermal diffusion coefficient depends on the particle size in nanoaerosols [6]. The aim of this work is to derive the dependence of the thermal diffusion coefficient of nanoparticles on their size by the MD method.

### SIMULATION TECHNIQUE

The common MD method was used for the simulation, along with the original SibMD software package, which was earlier used for the solution of different problems of the nanofluid transfer theory [8–10]. The simulation was carried out in a cubic cell with periodic boundary conditions. The interaction between carrier medium molecules was defined by the Lennard-Jones potential

$$\Phi_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where  $\sigma$  is the effective diameter of medium molecules,  $\epsilon$  is the potential well depth, and  $r = |\mathbf{r}_i - \mathbf{r}_j|$  is the distance between the centers of the  $i$  and  $j$  molecules.

The interaction between carrier medium molecules and a nanoparticle was described by the Rudyak–Krasnolutski potential [11] (see also [3, 4]):

$$\Psi(r) = \Psi_9(r) - \Psi_3(r),$$

$$\Psi_i = C_i \left\{ \left[ \frac{1}{(r-R)^i} - \frac{1}{(r+R)^i} \right] - \frac{a_i}{r} \left[ \frac{1}{(r-R)^{i-1}} - \frac{1}{(r+R)^{i-1}} \right] \right\}, \quad (2)$$

where  $i = 9, 3$ ;  $a_9 = 9/8$ ;  $a_3 = 3/2$ ;  $C_9 = (4\pi\epsilon_{12}\sigma_{12}^{12})/45V_p$ ;  $C_3 = (2\pi\epsilon_{12}\sigma_{12}^6)/3V_p$ ;  $V_p^{-1} = \rho_p/m_p$ . Here  $\rho_p$  is the nanoparticle material density;  $m_p$  is the mass of molecule (atom) matter composing the nanoparticle;  $R$  is the nanoparticle radius;  $\sigma_{ij}$  and  $\epsilon_{ij}$  are the parameters of potential (1) of interaction between the carrier fluid molecules and nanoparticle molecules.

The nanoparticles interaction potential used was specially constructed [12]; it has the following form for monodisperse nanoparticles:

$$U(r, R) = U_7(r, R) - U_1(r, R), \quad (3)$$

where

$$U_7(r, R) = \frac{\pi^2 \tilde{\epsilon} \tilde{\sigma}^{12}}{315 V_p^2} \left\{ \frac{R^2}{r} \left[ \frac{1}{(r-2R)^7} + \frac{2}{r^7} + \frac{1}{(r+2R)^7} \right] - \frac{R}{3r} \left[ \frac{1}{(r-2R)^6} - \frac{1}{(r+2R)^6} \right] - \frac{1}{30r} \left[ \frac{1}{(r-2R)^5} - \frac{2}{r^5} + \frac{1}{(r+2R)^5} \right] \right\},$$

$$U_1(r, R) = \frac{2\pi^2 \tilde{\epsilon} \tilde{\sigma}^6}{3 V_p^2} \times \left[ \ln \left( \frac{r^2 - 4R^2}{r^2} \right) + 2R^2 \left( \frac{1}{r^2 - 4R^2} + \frac{1}{r^2} \right) \right].$$

Here  $\tilde{\epsilon}$  and  $\tilde{\sigma}$  are the parameters of Lennard-Jones potential (1) of the nanoparticle molecule (atom) interaction.

Potentials (2) and (3) were derived under the assumption that interactions between carrier medium molecules and nanoparticle atoms and between nanoparticle atoms are described by potential (1) with the parameters  $\sigma_{12}$ ,  $\epsilon_{12}$  and  $\tilde{\sigma}$ ,  $\tilde{\epsilon}$ , respectively. The parameters of the argon molecule interaction potential were the following:  $\sigma = 3.405 \text{ \AA}$ ,  $\epsilon/k_B = 119.8 \text{ K}$  ( $k_B$  is the Boltzmann constant) [13]. The following parameters of potential (1) for aluminum were used for the calculation of the parameters of potentials (2) and (3):  $\sigma = 2.551 \text{ \AA}$ ,  $\epsilon/k_B = 857.6 \text{ K}$ . The last parameters were calculated on the basis of data on the Young's modulus and the structure of the crystal lattice (face-centered cubic) by the method similar to that described in [14]. The parameters  $\sigma_{12}$  and  $\epsilon_{12}$  were calculated from the simplest combination relations  $\sigma_{12} = \sqrt{\sigma\tilde{\sigma}}$  and  $\epsilon_{12} = \sqrt{\epsilon\tilde{\epsilon}}$ . The initial conditions, simulation cell size,

and the potential truncation radius were specified similar to the procedures described in [10].

The nanoparticle thermal diffusion and diffusion coefficients were calculated by the Green–Kubo relations [15]:

$$D_T = \frac{m_2 T}{\rho} \left[ -L_{22} m_2 \frac{\partial}{\partial T} \left( \frac{\mu}{T} \right)_{C_2, p} + \frac{L_2}{T^2} \right], \quad (4)$$

$$D = \frac{L_{22} m_2^2}{\rho T} \left( \frac{\partial \mu}{\partial C_2} \right)_{p, T},$$

where

$$L_{22} = \frac{V}{3} \int_0^\tau \langle \mathbf{J}_{d2}(0) \cdot \mathbf{J}_{d2}(t) \rangle dt;$$

$$L_2 = \frac{V}{6} \int_0^\tau \langle \mathbf{J}_Q(0) \cdot \mathbf{J}_{d2}(t) \rangle dt + \frac{V}{6} \int_0^\tau \langle \mathbf{J}_{d2}(0) \cdot \mathbf{J}_Q(t) \rangle dt; \quad (5)$$

$$\mathbf{J}_{d2}(t) = \frac{1}{V} \sum_{\alpha=2, i=1}^{N_2} \mathbf{v}_{2,i}(t)$$

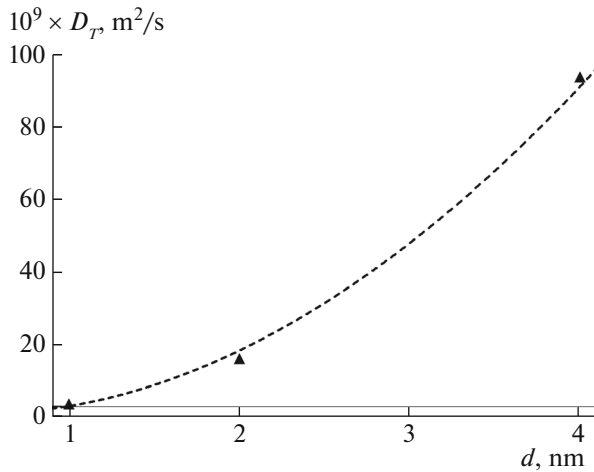
is the diffusion flux of the second component (nanoparticles);  $N$  is the number of nanoparticles in the simulation cell;  $\mathbf{v}$  is the velocity of the  $i$ th nanoparticle;  $\mathbf{J}_Q(t)$  is the heat flux ( $t$  is the time);  $\mu = \frac{\mu_1}{m_1} - \frac{\mu_2}{m_2}$

is the chemical potential [16];  $C_2 = \frac{m_2 n_2}{\rho}$  is the mass fraction of the second component (nanoparticles), and  $n$  is the number concentration of nanoparticles. The index  $\alpha = 1$  relates to molecules, and 2, to nanoparticles;  $m_i$  is the mass of a particle (molecule or nanoparticle);  $V$  is the volume of the system;  $\rho$  is the nanofluid density;  $T$  is the medium temperature;  $\tau$  is the plateau value attainment time [17]. Angle brackets in Eq. (5) mean averaging over the ensemble.

## SIMULATION RESULTS

To derive the dependence of the nanoparticle thermal diffusion coefficient on the particle diameter, the calculations were carried out for aluminum nanoparticles 1–4 nm in diameter in argon at a temperature of 300 K and constant nanoparticle mass fraction  $C_2 = 0.09$ . The simulation cell size was selected so that the nanofluid pressure was the pure argon pressure at the density  $n\sigma^3 = 0.707$ . In addition, adequate data acquisition requires averaging over phase trajectories of the system simulated [18, 19]. In those calculations, the ensemble of systems, the averaging was carried out over, included several thousand independent trajectories.

The dependence of the thermal diffusion coefficient  $D_T$  of nanoparticles on their diameter  $d$  is shown in Fig. 1. The triangles correspond to MD simulation data and the following calculation by Eq. (4). As seen



**Fig. 1.** Thermal diffusion coefficient of nanoparticles versus their diameter.

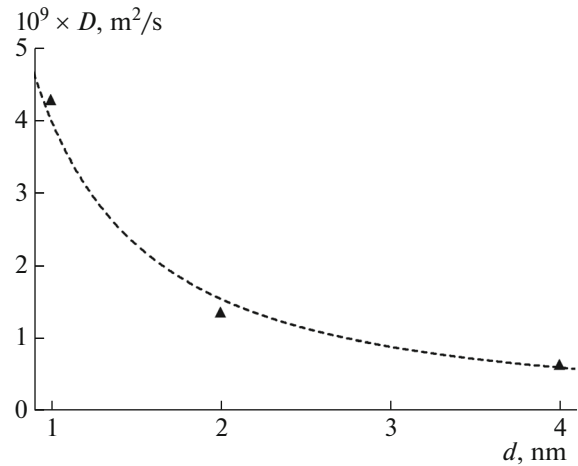
from Eq. (4), the thermal diffusion coefficient consists of two components. The simulation performed has proved their different dependences on the particle diameter. They can be sufficiently accurately approximated to power functions of the nanoparticle diameter  $d$ :

$$D_T = a_1 d^{k_1} - a_2 d^{k_2}. \quad (6)$$

In this case,  $a_1 = 1.342 \times 10^{-8} \text{ m}^2/\text{s}$ ;  $k_1 = 1.794$ ;  $a_2 = 1.334 \times 10^{-8} \text{ m}^2/\text{s}$ ;  $k_2 = 1.201$ . The thermal diffusion coefficient is measured in  $\text{m}^2/\text{s}$ , and the nanoparticle diameter, in nanometers. Approximation (6) is shown in Fig. 1 by the dashed curve.

The positive sign of coefficient (4) means that nanoparticles move to cold regions in the direction opposite to the temperature gradient due to the thermal diffusion. The first component in the brackets in Eq. (4) is positive, since the ratio  $(\mu/T)_{C_2,p}$  decreases with an increase in the temperature at constant pressure and mass fraction of nanoparticles. The second component is negative, since the direction of diffusion nanoparticle flux fluctuations is negatively correlated with the direction of heat flux fluctuations.

Typical values of the nanoparticle thermal diffusion coefficient normalized to their mass fraction for systems with large ( $d = 106\text{--}506 \text{ nm}$ ) nanoparticles [7], where the thermal diffusion coefficient is independent of the nanoparticle size, are  $D_T/C_2(1 - C_2) = (43\text{--}128) \times 10^{-9} \text{ m}^2/\text{s}$ . Thus, the values of the thermal diffusion coefficient calculated in this work (see Fig. 1) correspond well to the experimental data published. At the same time, the simulation has shown that both components of thermal diffusion coefficient (4) show significant growth with the particle diameter for small nanoparticles (1–4 nm in diameter).



**Fig. 2.** Coefficient of interdiffusion in a nanofluid versus the nanoparticle diameter.

It is also clear from physical grounds that the diffusion coefficient of nanoparticles should decrease with an increase in their size. Indeed, the MD data show a decrease in the diffusion coefficient  $D$  with an increase in the particle diameter. This dependence is shown in Fig. 2. The triangles correspond to MD simulation data and the following calculation by Eq. (4). This dependence can be approximated to a power function of the nanoparticle diameter

$$D = a d^{-k} \quad (7)$$

with  $a = 4.02 \times 10^{-9} \text{ m}^2/\text{s}$  and  $k = 1.384$ . Approximation (7) is shown by the dashed curve in Fig. 2. The dependence derived differs from the dependence that corresponds to the classical Einstein formula, according to which the diffusion coefficient of a particle is inversely proportional to its diameter. This difference is also observed for solitary nanoparticles [8].

The dependence of the Soret coefficient

$$S_T = D_T/D \quad (8)$$

is shown in Fig. 3. The triangles correspond to the MD simulation data and the following calculation by Eq. (8); the dashed curve shows the approximation by Eqs. (6)–(8).

## CONCLUSIONS

The simulation performed has shown that the thermal diffusion of small nanoparticles in dense gases and fluids strongly depends on their sizes. At the same time, when describing the thermal diffusion of large particles ( $d = 106\text{--}506 \text{ nm}$ ), the absence of this dependence is usually mentioned. Besides, it is shown [7] that experimentally measured characteristic values of the thermal diffusion coefficient  $D_T/C_2(1 - C_2) = (43\text{--}128) \times 10^{-9} \text{ m}^2/\text{s}$  change by three times, which might well be evidence of such a dependence. The

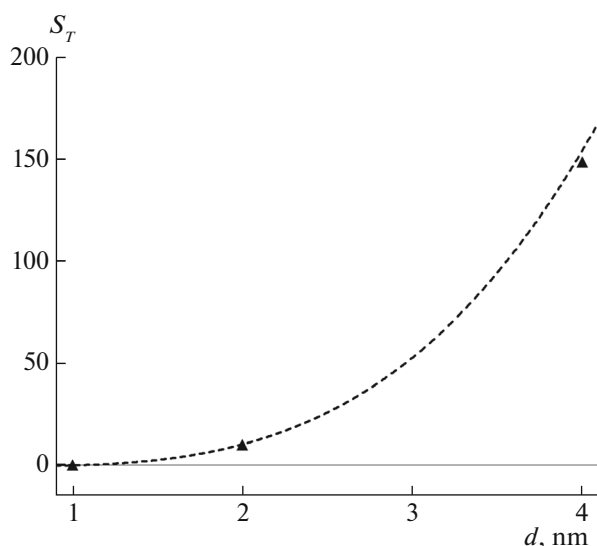


Fig. 3. Soret coefficient in a nanofluid versus the nanoparticle diameter.

thermal diffusion coefficient of Brownian particles decreases in inverse proportion to their diameters and, in addition, depends on the carrier fluid viscosity [20, 21].

It is also important to note that two absolutely different effects are observed during the study of the motion of macroparticles in the temperature field, i.e., thermal diffusion and thermophoresis (particle motion due to the temperature gradient along its surface). It is difficult to distinguish these two effects for large particles. Therefore, one should be extremely careful when interpreting experimental data on the thermal diffusion. In contrast, when studying the motion of nanoparticles in the temperature field, only the thermal diffusion takes place. It is almost impossible to produce noticeable temperature gradients, which could result in thermophoresis, at sizes of the particle diameter due to the small sizes of nanoparticles.

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