

# Molecular dynamics simulation of nanoparticle diffusion in dense fluids

Valery Ya. Rudyak · Sergey L. Krasnolutskii · Denis A. Ivanov

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**Abstract** This article deals with a molecular dynamics simulation of the diffusion of nanoparticles in dense gases and liquids using the Rudyak–Krasnolutskii nanoparticle–molecule potential. Interaction of molecules of the carrier fluid is described by the Lennard-Jones potential. The behavior of the nanoparticle velocity autocorrelation function is studied. It is shown by molecular dynamics simulation that the diffusion coefficient of small nanoparticles depends greatly on the nanoparticle material. Relations are obtained between the diffusion coefficient of nanoparticles and the nanoparticle radius and the temperature of the medium. These relations differ from the corresponding Einstein relation for Brownian particles.

**Keywords** Velocity autocorrelation function · Nanoparticle · Diffusion coefficient · Temperature dependence · Nanofluid

## 1 Introduction

Understanding the transport properties of nanofluids is necessary for various applications being developed today. This issue is also important for basic research because it is already clear that transport processes of small nanoparticles differ from those of ordinary dispersed particles, in particular, Brownian particles. Nanoparticle diffusion plays a key role from this viewpoint. It has long been believed that it can be described as the diffusion of Brownian particles by the Einstein relation

$$D = kT/6\pi\mu R, \quad (1)$$

where  $T$  is the temperature of the carrier fluid,  $\mu$  is its viscosity coefficient (this coefficient is the temperature function, of course), and  $R$  is the nanoparticle radius. According to formula 1, the diffusion coefficient  $D$  depends only on the particle radius and the viscosity of the carrier fluid. However, with increasing interest in nanoparticles, experimental evidence has been obtained indicating that relation (1) does not describe nanoparticle diffusion (see, for example, Kato et al. 1993; Tuteja and Mackay 2007).

Equation 1 implies that velocity relaxation of a Brownian particle occurs under the action of the Stokes force, and, hence, its velocity autocorrelation function (VACF) has an exponential form with the relaxation time  $\tau = M/6\pi\mu R$ , where  $M$  is the mass of the particle. However, molecular dynamics simulations (Rudyak et al. 2000, 2001) have shown that the VACF of a nanoparticle in a dense fluid is a superposition of two exponential curves with significantly different relaxation times  $\tau_1$  and  $\tau_2$

$$\chi = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2), \quad (2)$$

where  $a_i$  are some constants. These results have been conformed by Ould-Kaddour and Levesque (2007). At the same time, in (Rudyak et al. 2000, 2001), interactions between molecules and between molecules and particle were described using the hard-sphere potential, which, though giving an adequate qualitative description of diffusion and the correct value of the corresponding coefficient, is a rather approximate model. For example, it does not allow one to predict the correct temperature dependence of transport coefficients. For this, it is necessary to use a more realistic potential.

Previous simulations of the transport properties of nanoparticles have used mainly three potentials: Lennard-Jones (L-J), Kihara, and Weeks–Chandler–Andersen potentials

V. Ya. Rudyak (✉) · S. L. Krasnolutskii · D. A. Ivanov  
Novosibirsk State University of Architecture and Civil  
Engineering, Leningradskaya, 113, Novosibirsk, Russia 630008  
e-mail: valery.rudyak@mail.ru

(see, e.g., McPhie et al. 2006; Nuevo and Morales 1998; Ould-Kaddour and Levesque 2007; Pozhar 2000; and the references therein). The main difficulty in modeling nanoparticle–molecule interaction with the above-mentioned potentials is the choice of their constants. These potentials were developed to describe intermolecular interactions, and known constants can be used only for this purpose. It is absolutely not clear what constants apply to the description of molecule–nanoparticle interactions. For this reason, the above potentials have been used only to study the qualitative characteristics of nanofluids.

At the same time, two of the authors of this article developed a special potential for interaction between nanoparticles and molecules of the carrier medium (Rudiyak and Krasnolutsii 1999), whose parameters are determined from the parameters of the L-J potential of interaction of molecules with the nanoparticle atoms (molecules). Later, it was employed as the basis for the development of the kinetic theory of rarefied gas nanosuspensions (Rudiyak and Krasnolutsii 2001, 2002, 2003), which has then been confirmed by experiments (Rudiyak et al. 2002). The purpose of this article is to study the diffusion of nanoparticles in dense gases and liquids based on the Rudiyak–Krasnolutsii (RK) potential.

## 2 Potential, method, and systems considered

In the study, the standard molecular dynamics method (see, e.g., Rapaport 2005) was used. The simulation was performed on a cubic mesh with periodic boundary conditions. Interaction between molecules of the carrier medium was defined by the 6-12 L-J potential

$$\Phi_{\text{LJ}}(r) = \begin{cases} 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6], & r \leq R_c \\ 0, & r > R_c \end{cases}, \quad (3)$$

where  $\sigma$  is the effective molecular diameter of the medium,  $\varepsilon$  is the depth of the potential well,  $R_c$  is the effective radius of activity of potential, and  $r = |\mathbf{r}_i - \mathbf{r}_j|$  is the distance between molecules  $i$  and  $j$ . Interaction of molecules of the carrier medium with nanoparticles was described by the RK potential (Rudiyak and Krasnolutsii 1999, 2001, 2002)

$$\Phi_{\text{RK}}(r) = \Phi_9(r) + \Phi_3(r)$$

$$\Phi_i = C_i \left\{ \left[ \frac{1}{(r-R)^i} - \frac{1}{(r+R)^i} \right] - \frac{a_i}{r} \left[ \frac{1}{(r-R)^{i-1}} - \frac{1}{(r+R)^{i-1}} \right] \right\}, \quad i = 9, 3, \quad (4)$$

where,  $a_9 = 9/8r$ ,  $a_3 = 3/2r$ ,  $V_p^{-1} = \rho_p/m_p$ ,  $C_9 = (4\pi\varepsilon_{12}\sigma_{12}^{12})/45V_p$ ,  $C_3 = (2\pi\varepsilon_{12}\sigma_{12}^6)/3V_p$ . Here  $\rho_p$  is the density of the dispersed particle material,  $m_p$  is the mass of the

molecule (atom) of the nanoparticle material,  $R$  is the nanoparticle radius, and  $\sigma_{ij}$ ,  $\varepsilon_{ij}$  are the parameters of the L-J potential of interaction of a medium molecule with a nanoparticle molecule.

Generally, it is also necessary to specify the potential of interaction between the nanoparticles. However, an adequate potential of their interaction has not yet been developed. In this study, low concentrations of nanoparticles were considered, so that their interaction could be neglected. Actually, we always modeled the diffusion of one particle in a mesh filled with molecules. The molecules of the medium were uniformly distributed in the simulation mesh according to the prescribed density. Initial velocities of the molecules were specified according to the Maxwell distribution at the given temperature. The initial velocity of the nanoparticle was set equal to zero. The calculation was started after a certain relaxation period when the entire system reached equilibrium. The evolution of the system was calculated by integrating the Newton equations using the Schofield scheme (Schofield 1973) or fourth order Runge–Kutta scheme. The number of molecules of the carrier medium in all calculations was equal to 8000. The length of the simulated volume was about  $22.3\sigma$ . The integration step was set to  $\Delta t = 4.6 \times 10^{-16}$  s. The minimum number of steps in the calculations was  $10^6$ .

Because the employed potentials are infinite-range potentials, they should be truncated during simulation. In the L-J potential (3), the radius  $R_c$  was set equal to  $2.5\sigma$  and the RK potential (4) was truncated at distances  $\tilde{R} = R + 4\sigma_{12}$ . At this distance, the value of the potential was not more than 1% of the potential well depth.

It should be noted that in simulations of the evolution of nanosuspensions, stricter restrictions are imposed on the size of the simulation mesh compared to homogeneous fluid. Since a nanoparticle should not interact with itself, it is necessary that the length of the side of the cubic mesh be much greater than the range of the potential  $L \gg \tilde{R}$ . In practice, to eliminate the corresponding correlations, the distance should be, at least, several times larger.

Argon was considered the carrier fluid. The potential (3) for argon had the following parameters:  $\sigma = 3.542 \text{ \AA}$ ,  $\varepsilon/k_B = 93.3 \text{ K}$  (Reid et al. 1987). Its density  $n\sigma^3$  varied from 0.7 to 0.28. Here  $n$  is the number density of the fluid. Diffusion of nanoparticles of lithium and aluminum in argon was studied. The nanoparticle diameter varied from 1 to 4 nm. The temperature of the carrier fluid varied from 248 to 420 K.

The parameters of the RK potential (4) were determined by means of elementary combination relations  $\sigma_{12} = \sqrt{\sigma_{11}\sigma_{22}}$ ,  $\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}}$ . So for Li–Ar potential  $\sigma_{12} = 3.74 \text{ \AA}$ ,  $\varepsilon_{12}/k_B = 215.99 \text{ K}$ ; and for Al–Ar potential  $\sigma_{12} = 3.32 \text{ \AA}$ ,  $\varepsilon_{12}/k_B = 343.93 \text{ K}$ .

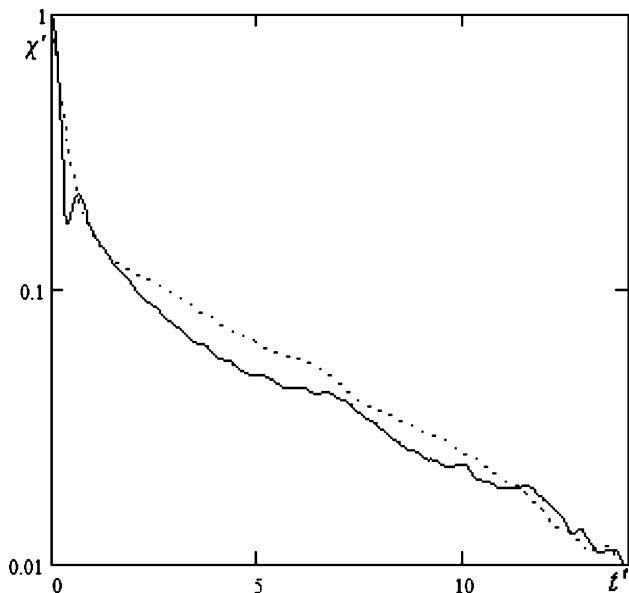
### 3 Nanoparticle VACF

During molecular-dynamic simulations, the dynamic variables of molecules and nanoparticle at sequential times are calculated. From these variables, using methods of non-equilibrium statistical mechanics it is possible to determine all thermodynamic characteristics of the system and calculate the transport coefficients. In particular, the self-diffusion coefficient  $D$  is determined from the Green–Kubo formula

$$D = \frac{1}{3} \int_0^T \chi(t) dt, \tag{5}$$

where  $\chi(t) = \langle \mathbf{V}(0) \cdot \mathbf{V}(t) \rangle$  is the VACF. Here  $\mathbf{V}$  is the nanoparticle velocity and the angular brackets denote averaging over the number of runs.  $T$  is the time when the VACF reaches the plateau value (see Rudyak et al. 2008).

Investigation of the nanoparticle velocity relaxation in the carrier fluid shows that it occurs in two stages (as for the hard-sphere system) and is described by relation (2). This is illustrated in Fig. 1, which shows as an example the time dependence of the normalized VACF  $\chi' = \chi / \langle V^2(0) \rangle$  for a lithium nanoparticle of 2 nm diameter in argon (solid curve). The time  $t'$  is in the units of  $\tau = \sigma/c$ , where  $c$  is the thermal velocity of the molecules of the medium. The density of argon is  $n\sigma^3 = 0.707$ . For comparison, the figure gives the VACF (dotted curve) for the hard-sphere system. Qualitatively, the behavior of the VACFs obtained for the



**Fig. 1** Time dependence of the normalized VACF for a Li nanoparticle in Ar (solid curve corresponds to the RK potential) and for the hard-sphere system (dashed curve)

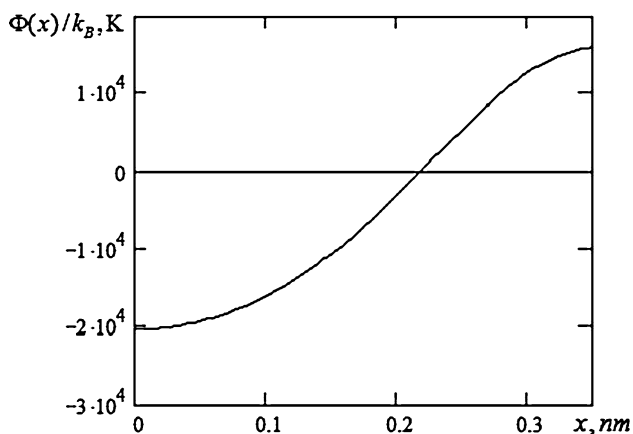
hard-sphere and RK potentials given in Fig. 1 is the same. There are two stages of relaxation. The relaxation times  $\tau_2$  (see formula 2) are practically similar for the two cases. At the same time, they have a systematic qualitative difference. The VACF for the RK potential (2) has a characteristic nonmonotonic region in the initial stage of relaxation.

This nonmonotonic region is absent for the pair interaction between a molecule and nanoparticle when the carrier medium is sufficiently rarefied. In dense carrier media, a nanoparticle is in a mean field of interaction forces between the nanoparticle and molecules of the medium. Thus, a certain collective effect takes place. Such a mean self-consistent field is typical of systems with long-range forces, for example, plasma, and it is practically absent in ordinary molecular fluids. The potential (4) is also a long-range one: its characteristic range is on the order of the nanoparticle size. Thus, in this case, there is also an analog of a self-consistent force. To show this, we simulate this potential below.

In equilibrium, a certain mean isotropic density distribution of carrier-fluid molecules is formed around a nanoparticle, which is described by the radial nanoparticle–molecule distribution function  $G(r)$ . The self-consistent field around the nanoparticle can be modeled as follows. We “freeze” the given (arbitrary) density distribution of carrier-fluid molecules by placing the coordinate origin at the center ( $r = 0$ ). Next, we place the nanoparticle at different points and calculate the total interaction potential with this distribution of carrier-fluid molecules for each position of the nanoparticle. Thus, we obtain a certain self-consistent potential field in which the nanoparticle moves. Summation over all molecules can be replaced by integration; then, the required potential energy for the nanoparticle at a point with spherical coordinates ( $r = x$ ,  $\theta = 0$ , and  $\varphi = 0$ ) is given by the expression,

$$\begin{aligned} \Phi(x) &= \iiint_V \Phi_{\text{RK}}(|(r, \theta, \phi) - (x, 0, 0)|) n_m G(r) dV \\ &= n_m \int_{R_p}^{R_c+x} G(r) 4\pi r^2 dr \int_0^\pi \Phi_{\text{RK}}\left(\sqrt{x^2 + r^2 - 2xr\cos\theta}\right) \\ &\quad \times \frac{\sin\theta d\theta}{2} \end{aligned}$$

where  $n_m$  is the mean density. The field  $\Phi(x)$  is spherically symmetric. As an example of the obtained potential, Fig. 2 shows the potential  $\Phi(x)$  which acts on a lithium nanoparticle of 1 nm diameter in argon; the coordinate  $x$  is in nanometers. This potential has very short acting radius. The nanoparticle oscillates near the equilibrium position. According to calculations, the characteristic period of



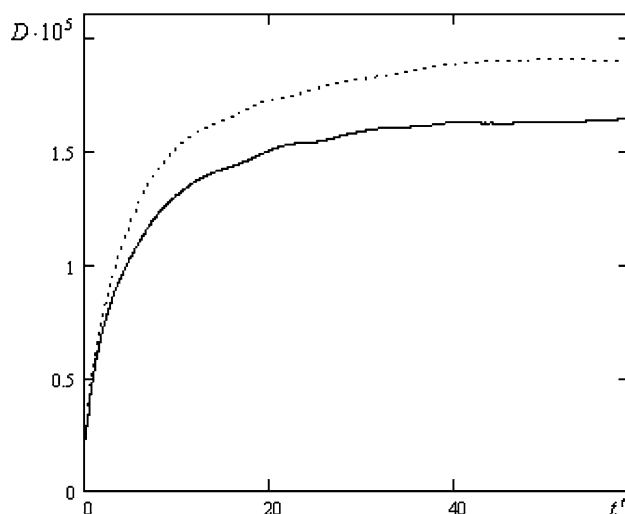
**Fig. 2** Potential of the self-consistent force acting on a Li nanoparticle of 1 nm diameter in Ar

oscillations of nanoparticle considered in the initial stage of relaxation is equal to  $0.4\tau$ , which agrees well with the period of small oscillations of a nanoparticle in the potential well constructed above. The last period is equal to  $0.42\tau$ .

#### 4 Diffusion coefficient of nanoparticles

The diffusion coefficient of a nanoparticle is given by formula 5. Actually, this is a function of time. The proper diffusion coefficient is obtained only upon reaching a certain plateau value (Rudyak et al. 2008). Typical behavior of the function (5) with time is presented in Fig. 3 for the diffusion coefficient of a lithium nanoparticle in argon whose VACF is presented in Fig. 1. Here the solid curve corresponds to the diffusion coefficient obtained using the RK potential (4), and the dotted curve to diffusion coefficient obtained using the hard-sphere potential. The diffusion coefficient is in the units of  $\text{cm}^2/\text{s}$ . The obtained values of the diffusion coefficients differ by 8% with a calculation accuracy of about 5%. The presence of the attractive branch of the RK potential and the much weaker repulsive part naturally reduce the mobility of the nanoparticle and, as a consequence, its diffusion coefficient is lower than that for the hard-sphere potential.

According to the Einstein formula 1, the diffusion coefficient of a particle is inversely proportional to its radius. In the case of small nanoparticles, this is not so. We simulated the diffusion coefficient of lithium and aluminum nanoparticles of 1–4 nm diameter in argon at a temperature of 322.5 K and argon density  $n\sigma^3 = 0.707$ . The obtained data are presented in Fig. 4. In all cases, formula 1 does not describe the observed values of the diffusion coefficient. In addition, the diffusion coefficients depend on the particle material. Generally, the dependence



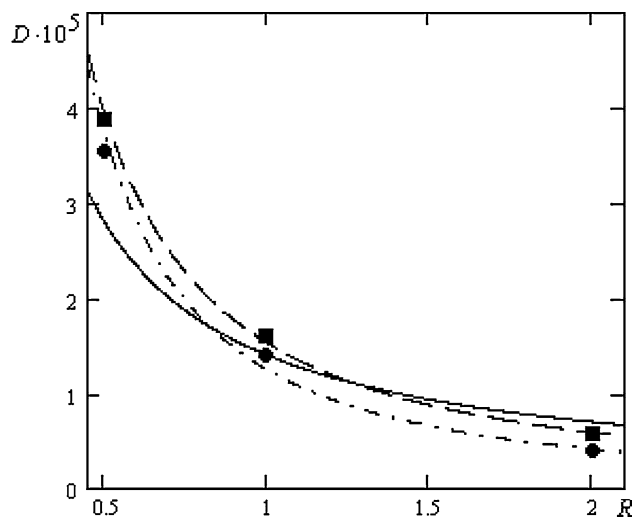
**Fig. 3** Time dependence of the diffusion coefficient of a Li nanoparticle in Ar. The *solid curve* corresponds to the diffusion coefficient obtained using the RK potential and the *dotted curve* to diffusion coefficient obtained using the hard-sphere potential

of the diffusion coefficient on nanoparticle radius is described by the exponential function

$$D = aR^{-k} \tag{6}$$

where  $k > 1$ . For lithium nanoparticles,  $k_{\text{Li}} = 1.37$ , and for aluminum nanoparticles,  $k_{\text{Al}} = 1.59$ .

In the Sect. 1, it was already noted that a correct temperature dependence of the diffusion coefficient can be obtained only using a realistic molecule–nanoparticle interaction potential. This dependence is also described by the exponential function



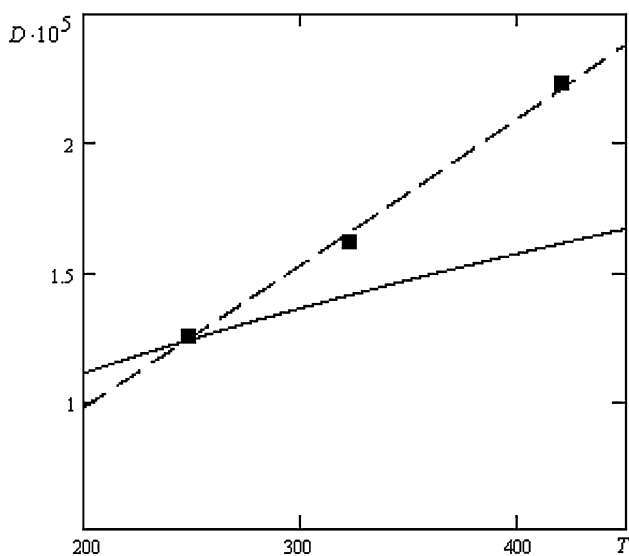
**Fig. 4** Diffusion coefficient ( $\text{cm}^2/\text{s}$ ) versus nanoparticle radius (nm). The *dashed curve* and *boxes* correspond to lithium nanoparticle, the *dot-dash curve* and *circles* to aluminum nanoparticles, and the *solid curve* to the Einstein formula

$$D = aT^n, \quad (7)$$

where the exponent  $n$  is not universal and depends on the nanoparticle material and size. As an example, Fig. 5 shows the temperature dependence of the diffusion coefficient for lithium nanoparticles of 2 nm diameter in argon ( $n\sigma^3 = 0.707$ ). Here the points correspond to our calculation and the dashed curve to its approximation by relation (7) with  $n = 1.1$ . The corresponding dependence determined from the Einstein formula (solid curve) gives much smaller growth, and this difference increases with temperature.

## 5 Conclusions

In this study, it was shown that the diffusion of nanoparticles in dense fluids differs significantly from the diffusion of Brownian particles. Molecular dynamics simulation using the RK potential (4) leads to qualitatively similar effects as when using the hard-sphere potential. At the same time, the use of the RK potential made it possible for the first time to obtain a number of new results. This is, first of all, the dependence of the diffusion coefficient on the nanoparticle material, which is not typical of macroscopic theories. On the other hand, similar results are also obtained in the kinetic theory of nanoparticle diffusion in rarefied gases (Rudyak et al. 2008b). The difference of the diffusion coefficients between different materials nanoparticles ranges from 9 to 32%. This discrepancy is decreased when the nanoparticle size increases.



**Fig. 5** Diffusion coefficient ( $\text{cm}^2/\text{s}$ ) of Li nanoparticle of 2 nm diameter in argon nanoparticles versus temperature of the medium (K). The boxes correspond to our calculation and the dashed line to its approximation by the formula 7 with  $n = 1.1$ , solid line to Einstein formula

The dependence of the diffusion coefficient on the carrier-fluid temperature is described by the formula 7. The similar dependence has been experimentally obtained for the diffusion coefficient of nanoparticles in gases at normal pressure (Rudyak et al. 2009). In cited article, it was shown that the temperature dependence of the diffusion coefficient was not described by the known Cunningham–Millikan–Davis correlation (analog of the formula 1 for gases).

The dependences of the diffusion coefficient of nanoparticles on their size and carrier-fluid temperature also differ significantly from the dependence obtained for Brownian particles (see formula 1). Of course, as the size of nanoparticles increases, their diffusion coefficient will approach the diffusion coefficient of Brownian particles. It follows from kinetic theory that the individual properties of nanoparticles have a significant effect on their diffusion up to nanoparticle sizes of about 20–30 nm. Apparently, for nanoparticles with sizes  $R > 50$  nm, this dependence can always be neglected in practice.

Now a few words about the limits of applicability of the RK potential (1) of nanoparticle–molecule interaction (Rudyak and Krasnolutskii 1999). This potential was obtained at the following assumptions:

- The interaction of molecules with the particle surface is described classically;
- The adiabatic approximation can be used;
- The interaction potential between molecules of the carrier gas with a molecule (atom) of the particle is assumed to be pairwise and additive;
- The influence of the surface structure was neglected;
- The possible internal degrees of freedom, including the possible thermal fluctuations of the particle surface, were not taken into account.

The above assumption actually imply that (i) the temperatures should not be too low (as for ordinary classical intermolecular potentials); (ii) the interaction energy should not be very high ( $\leq \text{keV}$ ); (iii) the criterion of the applicability of the classical approach is the smallness of the de Broglie wavelength, compared with the typical spatial scale of the problem. It is easy to see that at not too low temperatures, this condition is satisfied; (iv) accounting for lattice vibrations and surface structure can seriously affect quantitative calculation results. However, this is particularly important in considering adsorption, inelastic effects of the interaction, possible spraying, which are also not considered in this model. The contributions of these effects to transport processes, however, are usually not too great; and (v) the number of molecules (atoms) in nanoparticles should be much greater than 1. Therefore, particles with a characteristic size of 1 nm or larger may well be described by this potential.

Dependence of the diffusion coefficient nanoparticles on their material is very interesting property. The similar effect must be observed for other transport coefficients of the nanofluids. In particular, the viscosity of the nanofluids must be depended on not only the nanoparticles volume fraction but also on their material. The molecular dynamics simulation for hard spheres model confirms this point of view indirectly (see Rudyak et al. (2008a), but the simulation with the RK potential needs in future. This potential may be used in study of the all thermophysical properties of the nanofluids.

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