Kinetic Langevin Description of Nanoparticle Diffusion

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Abstract. The paper deals with the study of the transport processes in dispersed media. The diffusion of the nanoparticles in gases and liquids are considered. In all cases the Langevin approach is used when the evolution of a dispersed particle is described by the stochastic equation. A solution for the autocorrelation function of the nanoparticle velocity is constructed and additional random force acting on it in addition to the usual Langevin force is analyzed. The model of the diffusion of the nanoparticles ensemble is developed. In the last section the diffusion of the carbon nanotubes in liquids is discussed. It is considered the translational and rotational diffusion of the carbon nanotubes.

1. Introduction

Over the past few decades, interest in nanoparticles, that is, particles with characteristic sizes from 1 to 100 nm, has been continuously growing. First of all, this is due to various applications; they are used in the creation of new materials for various purposes, in various biomedical technologies end etc. [1]. Separately, it should be said about nanofluids, which are a two-phase medium consisting of a carrier fluid and nanoparticles, their field of application is extremely wide [2,3].

However, it is necessary to distinguish between ordinary spherical nanoparticles and carbon nanotubes. The last have two significantly different sizes (diameter and length) which greatly complicate the study of the transport properties.

The carbon nanotubes (CNTs) are a rather complex object; they may be single-wall, two-wall and multi-wall depending on technology of their creation [4]. The diameter of single-wall CNTs is 1–2 nm, while the length can reach hundreds of nanometers or more. The diameter of multi-wall CNTs can reach several tens of nanometers, and the distance between the layers is actually on the order of the characteristic size of the molecules.

CNTs possess exceptional mechanical, electrical, and thermal properties. They can be conductive, and on the other hand, have semiconductor properties. The thermal conductivity of CNTs exceeds 3000 W/m. Nanotubes have unique mechanical properties, combining both high strength and high elasticity. The uniqueness of the properties of CNTs make them very popular in a variety of applications: in electronics, when creating materials with unique properties, a new type of filters, supercapacitors, batteries, sensors of various types, etc. (see, for example, [5]). Many of these applications are already implemented or are being implemented. The experimental data of the last twenty years show that the transport processes of nanoparticles in gases and liquids are not described by the classical theories of Maxwell, Einstein, etc. [6,7]. The diffusion of nanoparticles in rarefied gases does not generally described by well-known Cunningham–Millikan–Davis correlation [8]. The last was predicted by a specially constructed kinetic theory of such gas nanosuspensions [9] and then confirmed experimental-
ly [10]. The diffusion of nanoparticles in dense gases and liquids was also unusual. Using the molecular dynamics method, it was shown that the relaxation of the nanoparticle velocity proceeds in two stages, each of which has an exponential character [11]. At the same time, there are still virtually no models that at least qualitatively describe the transport processes in nanofluids. This article attempts to develop such models using the Langevin approach. The diffusion of nanoparticles in condensed medium and in gases is analyzed. Conventional spherical nanoparticles and CNTs are considered. In the latter case, both translational and rotational diffusion are analyzed.

2. Autocorrelation function of a random force acting on nanoparticle

The motion of Brownian particle is successfully described by the Langevin equation

\[ \dot{v} = -\gamma v + f(t) \]

where \( v \) is the particle velocity, \( \gamma = (6\pi \eta R)/M \) is the coefficient to the systematic friction force (the Stokes force), acting on the particle with radius \( R \) and mass \( M \) in liquid with the viscosity coefficient \( \eta \). \( f(t) \) is a random Langevin force with the properties

\[ \langle f(t) \rangle = 0, \quad \langle f(t) \cdot f(t') \rangle = \gamma \delta(t-t'). \]

Here and everywhere below angle brackets mean averaging over the ensemble.

The velocity of a Brownian particle is obtained by integrating equation (1)

\[ v(t) = v_0 e^{-\gamma t} + \int_0^t e^{-\gamma(t-t')} f(t') dt', \]

here \( v_0 \) is the initial velocity of the particle. Using this formula it is easy to verify that \( \Gamma = (3kT\gamma)/M \), and the autocorrelation function of the velocity (VACF) of the particle has the following form

\[ \langle v(t) \cdot v(t+\tau) \rangle = \chi(\tau) = \frac{(3kT/M)e^{-\gamma \tau}}{1 + \frac{1}{3} \int_0^\infty \chi(0,t) dt}. \]

where \( k \) and \( T \) are the Boltzmann constant and temperature, respectively.

Thus, the VACF of a Brownian particle decays exponentially fast with a relaxation time determined by the Stokes force and equal to \( \gamma^{-1} \). Exponential attenuation of the VACF of a Brownian particle means that there is a single mechanism of velocity relaxation. On the other hand, according to the fluctuation-dissipation theorem [12], the diffusion coefficient of the particle is determined by the evolution of VACF

\[ D = \frac{1}{3} \int_0^\infty \chi(0,t) dt. \]

It is easy to verify that in this case the diffusion coefficient of the Brownian particle, derived by Einstein [13], is obtained. In Eq. (5), \( t_p \) is the time to reach the plate value [14].

In [11], using the molecular dynamics method, it was shown that VACF of a nanoparticle is the sum of two exponents

\[ \chi_n(0,t) = a_1 e^{-\tau_1 t} + a_2 e^{-\tau_2 t}, \]

where \( a_1, a_2, \tau_1, \tau_2 \) are some constants depending on the characteristics of nanoparticles.

The presence of two relaxation branches of VACF nanoparticles (6) means the existence of two different mechanisms of velocity relaxation. The first of them is associated with individual interactions of a nanoparticle with carrier fluid molecules and has a characteristic time \( \tau_1 \). The second is due to the collective effects of the interaction of the nanoparticles with microfluctuations of the macroscopic fields of the carrier fluid (density and velocity) that form around the nanoparticle. The corresponding time of this interaction is \( \tau_2 \).

It can be shown that the time \( \tau_2 \), even for the smallest nanoparticles, is at least an order of magnitude longer than the time \( \tau_1 \) [15]. There are two significantly separated in time of the relaxation process. This means that the autocorrelation function of random force (RFACF) of the nanoparticle...
\( \psi_n(t,t') \) cannot be \( \delta \)-correlated. One more member must be present. It is clear that this function is decaying, and the attenuation process of the RFACF is quite fast, otherwise the diffusion coefficient simply will not exist. On the other hand, due to the uniformity of time, the condition \( \psi_n(t,t')=\psi_n(t-t') \) must be met. It is most simple (and reasonable) to model this second branch of the RFACF as an exponential. Therefore the total RFACF has the form

\[
\psi_n(t,t') = \Gamma \delta(t-t') + ae^{-\beta(t-t')}.
\]

Using then the solution (3) the average square of the nanoparticle velocity maybe calculated

\[
\langle v^2(t) \rangle = \langle v_0^2(t) \rangle e^{-2\gamma t} + \frac{\Gamma}{2\gamma^2} \left( 1 - e^{-2\gamma t} \right) + \frac{a}{\gamma^2 \beta^2} \left[ 1 - e^{-(\beta-\gamma)t} \right] e^{-2\gamma t}.
\]

This expression has a finite limit as \( t \to \infty \) only if \( \beta < \gamma \), and this limit is equal to

\[
\langle v^2(t \to \infty) \rangle = \frac{\Gamma}{2\gamma^2} + \frac{a}{\gamma^2 \beta^2} = \frac{3kT}{M}
\]

where it is taken into account that \( \langle v^2(t) \rangle = 3kT/M \).

Similarly, the VACF of a nanoparticle can be calculated; taking into account (8), it has the form

\[
\langle v(0) \cdot v(t) \rangle = \frac{\Gamma}{2\gamma^2} e^{-\gamma t} + \frac{a}{\gamma^2 \beta^2} e^{-\beta t}
\]

or

\[
\gamma_n(0,t) = \frac{3kT}{M} \left[ b_1 e^{-\gamma t} + b_2 e^{-\beta t} \right]
\]

The constants \( b_i \) are naturally determined (compare (9) and (9a)). Comparison of (9a) with (6) shows that the VACF (6) of nanoparticles observed by the molecular dynamics method is obtained when the RFACF has the form (7). Using now fluctuation-dissipation theorem (5) the diffusion coefficient of nanoparticle is obtained as

\[
D = \frac{kT}{M} \left( \frac{b_1}{\gamma} + \frac{b_2}{\beta} \right)
\]

The presence of a second relaxation time means that in addition to the systematic Stokes force and an \( \delta \)-correlated random force, another force that changes rapidly over time acts on the nanoparticle. The Stokes force is due to macroscopic perturbations of the fluid velocity field generated by moving with constant velocity particle. This force is formed at macroscopically observed times. At the same time, during the formation of this force near the nanoparticle, local microfluctuations of the fluid velocity field and its density take place [16]. The fluctuations of the velocity field formed around the nanoparticle are random. Therefore, in addition to the Langevin force \( f(\bar{t}) \), another random force \( q(\bar{t}) \) also acts on the nanoparticle. It is worth noting that these are forces of substantially different time scales. The force \( f(\bar{t}) \) has a characteristic scale of the order of the interaction time of the carrier fluid molecules with the particle, \( \sigma/c \), and this time can be called the microscale (here \( c \) is the thermal velocity of molecule and \( \sigma \) is its characteristic size). Whereas the force \( q(\bar{t}) \) acts on nanoscales of the order of the time of interaction of the nanoparticle with microfluctuations of the velocity and density fields formed around it. This time of the order of \( h/c_n \), where \( c_n \) is the thermal velocity of nanoparticle and \( h \) is the characteristic size of the microfluctuation, which is of the order of the nanoparticle size. This force is also random and its average value is equal to zero: \( \langle q(\bar{t}) \rangle = 0 \). On the other hand, molecular dynamics simulations show that these fluctuations are correlated [16] and decay rather slowly. Therefore their relaxation can be described by an exponential law: \( \langle q(\bar{t}) \cdot q(\bar{t}') \rangle = ae^{-\beta(\bar{t}-\bar{t}')} \). In this case, the total RFACF of the force acting on the nanoparticle will be described by law (7). As a consequence, the corresponding the VACF then has the form (9a).
Despite the fact that VACF of a nanoparticle is described by expression (9) and the RFACF is described by Eq. (7), a nanoparticle moves in a medium according to the same law as the Brownian. Its average square displacement is described by the following formula

$$\langle R^2(t) \rangle = 6Dt$$

(11)

defined here the diffusion coefficient is determined by the relation (10).

However, it should be noted that the output to the asymptote (10) is non-monotonous. At times \( t < 1/\gamma \), a superposition of law (11) and superdiffusion takes place: \( \langle R^2(t) \rangle = 6Dt + 6D_1t^2 \). This can be easily verified using the connection \( \langle R^2(t) \rangle \) with VACF (see, for example, [17])

$$\langle R^2(t) \rangle = \int_0^t ds(t-s) \chi(0,s).$$

3. **Nonlinear Langevin equation for small nanoparticles**

Langevin equation (1), as is known, was derived phenomenological. Of course, there was a certain inconsistency in his formulation, since not only the nature of the random force, but also the systematic friction force acting on the particle is molecular. However this equation can also be deduced from the first principles. It is necessary to consider the classical system consisting of \((N-1)\) structureless molecules of mass \( m \) and a heavy Brownian particle of mass \( M \) [18]. The Liouville equation for corresponding \( N \)-particle distribution function contains the small parameter \( \zeta = \sqrt{m/M} \). Further, it can be shown that, in the main approximation with respect to this parameter, up to terms of order of \( \zeta^2 \), the equation (1) is obtained [18, 19]. In general case, the right side of the equation for a Brownian particle is a series in powers of \( \zeta \). For Brownian particles, the parameter \( \zeta \) usually varies from \( 10^{-4} \) to \( 10^{-6} \) and the nonlinear correction (i.e., the order term \( \zeta^4 \)) in the equation of motion of a Brownian particle is very small. At the same time, the situation for nanoparticles can become significantly different. For the smallest nanoparticles, this parameter is already quite noticeable. It can be shown that the equation for the velocity of such a particle will have the form [18, 20]

$$\dot{v} = -v - \xi v^3 + f(t)$$

(12)

where \( v \) and \( \xi \) are some friction forces, the first term on the right-hand side is of the order \( \xi^2 \), and the second of the order of \( \xi^4 \).

The presence of a small parameter in equation (12) allows us to search its solution in the form of the power series

$$v = v^{(0)} + \varepsilon v^{(1)} + \ldots$$

Here \( \varepsilon = \zeta^2 \) and in the final relations it must be set equal to unity. Further, it is easy to see that, in the zeroth approximation, the nanoparticle velocity has the form (3), and in the following, it satisfies the inhomogeneous equation

$$\dot{v}^{(1)} = -\xi v^{(1)} - \xi v^{(0)}.$$

Solving this equation in the first approximation in small parameter the following relation is obtained

$$v(t) = v_0 e^{-\varepsilon t} + \int_0^t e^{\varepsilon(t-t')} f(t') dt' - \xi \int_0^t e^{\varepsilon(t-t')} \left[ v_0 e^{-\varepsilon t} + \int_0^t e^{-\varepsilon(t-t'')} f(t'') dt'' \right]^3.$$

It is not difficult to build a corresponding VACF. However, the explicit calculation of all contributions appearing here requires knowledge of the properties of the considered random fields. It is not
difficult to calculate the correlations of the form \( \langle f(t)f(t')f(t'') \rangle \) assuming (see relations (2)) that the random forces are determined by a Gaussian process. However, the approximation (7) that leads to the observed VACF for nanoparticles is non-Markovian. How to set such correlations for such a stochastic process is completely unclear. Moreover, a universal recipe can be unlikely formulated. At the same time, it is more or less obvious that neither the corresponding VACF nor the diffusion coefficient resulting from its integration will depend on the nanoparticle velocity. In addition, the emerging additional contributions will not significantly change the macroscopically observed behavior of the nanoparticle.

On the other hand, equation (12) is a consequence of the non-Markov character of the generalized Langevin equation, which in general has the form \[ \dot{v}(t) = -\int_0^t \Delta(t-\tau) \cdot v(t-\tau) + f(t) \] (14)

where the kernel of the integral term is the correlator defined by the forces \( F \) acting on the particle. If during the characteristic time of the change of the correlation function \( N(s) = \langle FF(s) \rangle, \langle F(t) - S_0 F(S) \rangle \) is the system evolution operator) the particle momentum does not change, then from equation (14) the local Langevin type equation is followed

\[ \dot{v}(t) = -\int_0^t \Delta(t-\tau) \cdot N(t-\tau) \cdot v(t-\tau) + f(t) \] (14a)

a friction force in which in the general case is a function of time

\[ \dot{v}(t) = -\gamma(t) v(t) + f(t). \] (14b)

In [21], it was shown by the molecular dynamics method that the force exerted by the fluid on sufficiently small nanoparticles is generally not equal to the Stokes force. The main difference is precisely that this force is nonstationary. At the initial moment of the particle movement the magnitude of this force is several times greater than the Stokes force, and this maximum increases with increasing particle radius. Then this force relaxes and reaches a certain limit level, which is also determined by the size and mass of the nanoparticle. Starting from sizes around 10 nm and higher, this limit is determined by the Stokes force. For sufficiently small nanoparticles whose VACF is described by formula (6), the force \( v(t) \) in equation (14b) is determined by the following correlation

\[ v(t) = \frac{a_1 t_1 \exp(-t/t_1) + a_2 t_2 \exp(-t/t_2)}{a_1 t_1 \exp(-t/t_1) + a_2 t_2 \exp(-t/t_2)} \gamma \] (15)

It is clear that the Langevin equation (1) with the friction coefficient (15) is much more complicated. Despite the fact that it remains linear, it is not possible to construct its analytical solution. Asymptotically at times \( t \gg t_1 \) the coefficient (15) simplifies and takes the form

\[ \gamma(t) = \frac{a_2 \gamma}{a_2 + a_1 \exp(-t/t_1)} \] (15a)

Generally speaking, for the Langevin equation with a drag coefficient (15a), it is already possible to construct an integrating factor. It may be shown that this equation is the Bernoulli type one. The resulting solution will be quite cumbersome and unsuitable for a qualitative explanation of the diffusion process.

4. The generalized Langevin equation of the dispersed particles system

In the study of the Brownian particle diffusion the evolution of an isolated particle is usually considered. In practice, however, some ensemble of particles always takes place. If their volume concentration is small and the particles are distributed homogeneously in the carrier fluid, then studying diffusion one can talk about the diffusion coefficient of an isolated particle. It is clear that as the concentration of particles increases, their diffusion coefficient will change. So the question is, why? The diffusion of an ensemble of the Brownian particles can also be described using a Langevin-type equation.
In the monograph [18], this equation was derived from the first principles by methods of non-equilibrium statistical mechanics and has the form

$$\dot{v}_i(t) = -\gamma v_i(t) - \sum_{j \neq i}^N h_{ij}(t,R_{ij}) \cdot v_j(t) + f_i(t), \quad i = 1, 2, ..., N.$$ 

The tensor of friction coefficients \(h_{ij}(t,R_{ij})\) included here is generally a function of time and instantaneous mutual distance between particles \(R_{ij}\). It is not easy to calculate this friction tensor explicitly, in particular, we need to know the distribution of particles in the system. In addition, these friction coefficients are associated with two different types of interaction. Firstly, these are forces arising from the direct interactions of particles, and secondly, the forces of their interaction through the medium. This interaction of particles is called hydrodynamic. An example of calculating such an interaction for two particles can be found in [22]. It is not possible to solve this problem in the general case. Nevertheless, the problem of the movement of an ensemble of dispersed particles in a fluid is extremely important. It is especially interesting for nanofluids. The solution of this problem in the model formulation for nanofluids is proposed below.

Let us consider the evolution of \(N\) nanoparticles in liquid. Each of these particles from the liquid will be subjected to a systematic friction force with a coefficient of \(\gamma\) and a random force \([f_i(t) + q_i(t)]\). Now we need to take into account the force acting on each of the nanoparticles from the entire ensemble of particles. We will assume that there are enough particles to model them as a continuous medium. Then the pseudo-gas of the nanoparticles will also be characterized by some viscosity \(\mu_p\). In this case, when moving in this pseudo-gas, any of the particles of the ensemble under consideration will be affected by the Stokes force with a coefficient of \(6\pi\mu_p R\). As a result the Langevin equation of the particle has the obvious form

$$\dot{v}_i(t) = -(\gamma + \gamma_p) v_i(t) + f_i(t) + q_i(t), \quad i = 1, 2, ..., N$$

(16)

The friction coefficient \(\gamma_p = (6\pi\mu_p R)/M\) is universal, but it is still necessary to calculate the corresponding viscosity coefficient. Since the volume concentration of particles in practically used nanofluids is low, one can consider the pseudo-gas of nanoparticles to be rarefied, the dynamics of which is described by Boltzmann’s kinetic theories. Then the indicated viscosity coefficient is easy to write, in particular, simulating nanoparticles by solid spheres, we have [23]

$$\mu_p = \frac{5\sqrt{3}MT\pi}{64d^2}.$$ 

(17)

here \(d\) is the characteristic size of pseudo-gas particle.

If the considered particle has the same size, then \(d = 2R\) and \(\gamma_p \sim 1/R\). Otherwise (if particles of different sizes are present) \(\gamma_p \sim R/d^2\).

In its case the velocity of particle \(i\) is equal to

$$v_i(t) = v_{i0}e^{-(\gamma + \gamma_p)t} + \int_0^t e^{-(\gamma + \gamma_p)(t-t')} [q_i(t') + f(t')] dt'.$$

(18)

Now it is easy to calculate the corresponding diffusion coefficient of nanoparticles. The obtained coefficient will be naturally less than the coefficient of the isolated particle (10). This is due to the additional friction force \(\gamma_p\) acting on each nanoparticle. Now one can calculate the corresponding diffusion coefficient of these nanoparticles. The simplest way is to use the fluctuation-dissipation theorem, the formulation of which goes back to Einstein’s formula, which relates the diffusion coefficient with the force acting on a Brownian particle

$$D = kT/(M\gamma).$$

(19)
Then, the diffusion coefficient of a nanoparticle in the presence of an ensemble of such particles is equal to

$$D=\frac{kT}{(\gamma + \gamma_p)}.$$  \hspace{1cm} (19a)

In addition, if the diffusion coefficient of an ordinary Brownian particle is inversely proportional to its radius, this dependence becomes more complicated for a nanoparticle. The coefficient $\gamma_p$ increases with decreasing particle size. This term will dominate in formula (19) for sufficiently small particles. On the contrary, with increasing particle size, this force decreases, and for the Brownian particles and large nanoparticles it can be neglected. However, it should be understood that we are talking about low concentrations of particles. In this case pseudo-gas of the Brownian particles is very rarefied. Speaking of nanoparticles, it is necessary to understand that if they are sufficiently small, then even at low volume concentrations such pseudo-gas cannot be considered rarefied. In this case, the distances between the nanoparticles become comparable with their size. Therefore the formula (17) cannot be used for the viscosity coefficient for such pseudo-gas. However, this can be completely corrected using the dense gas of solid particles (so named Enskog’s gas) [23]. The configuration correlation function, which determines the corresponding corrections for density, should be simply entered into formula (17). However it is better to use not the correlation function introduced by Enskog himself, but the Carnahan–Starling function [24].

5. Modelling the diffusion of the carbon nanotubes

The approach for describing the diffusion of nanoparticles, based on the use of the Langevin equation (1), works well for ordinary spherical nanoparticles. The situation with CNTs is more complicated, since they are nonspherical. Moreover, in real CNTs, the aspect ratio can reach hundreds or even thousands. This, in particular, suggests that along with the usual translational diffusion, it is necessary to consider the rotational diffusion of nanotubes. In practice, the dynamic light scattering method is usually used to measure the diffusion coefficient of CNTs. In our experiments, we used the Malvern Zetasizer ZSP instrument, which can measure particles from 0.3 nm to 10.0 μm in size. The measured diffusion coefficient is then usually used to determine the effective size of the nanotubes, which is usually called hydrodynamic, $d_h$. For this aim, the Einstein's relation (19) is used, i.e., CNTs are modeled by some effective spheres. For nonspherical particles, relation (19) should be modified. One of the possible modifications for cylindrical tubes of length $L$ has the form [25]

$$D_t = \frac{kT}{6\eta L} \left( \ln \frac{L}{2R} + 0.32 \right).$$  \hspace{1cm} (20)

The application of this formula requires knowledge of the diameter of the nanotubes used. Typically, single-walled nanotubes have a characteristic diameter of 1.6 nm, and multi-walled nanotubes from several to tens of nanometers. The difficulty lies in the fact that usually in the nanofluid CNTs are collected in bundles, the average diameter of which can vary quite significantly. It is easy to verify that the hydrodynamic size of CNTs will differ from their average length by several times (5–8 times).

Another important circumstance in studying the diffusion of CNTs is the need to take into account rotational diffusion. Rotational diffusion of nanoparticles can also be described by the corresponding Langevin equation

$$\frac{d}{dt}(I\cdot\Omega) = -k\cdot\Omega + S,$$  \hspace{1cm} (21)

here $I$ is tensor of inertia moment of a particle, $\Omega$ is its angular velocity, $k$ is the friction coefficient tensor and $S$ is the principal moment of random forces acting on a particle relative to its centre of mass.

As in the case of translational Brownian motion, the principal moment of random forces can be modeled by white noise (compare with the formula (2))
However, one need to understand that random force in Eq. (1) and the principal moment of random forces in Eq. (21) are connected with each other. In equation (21), it is taken into account that in the general case the tensor of the inertia moments can change, but if this is not so, this equation is simplified. It has a particularly simple form for a spherical top, when the principal values of the tensor of the inertia moments with respect to the three axes of the Cartesian coordinate system coincide ($I_{xx}=I_{yy}=I_{zz}=I$)

\[ I\dot{\Omega} = -k_r\Omega + N, \]

where the friction coefficient is equal to

\[ k_r = \frac{\mu d_i^3}{l}. \]  

(23)

If we now use the fluctuation-dissipation theorem of the form (19), then the coefficient of rotational diffusion is equal to

\[ D_r = \frac{kT}{(\pi\mu d_i^3)}. \]  

(24)

This formula is also applicable to the description of the rotational diffusion of CNTs, since their hydrodynamic size is in the denominator. However, in this case, the value of the coefficient of the rotational diffusion will be significantly overestimated. In order to obtain a more correct estimate, it is necessary to go from equation (21) to the equation for CNTs, which can be modeled with long solid rods of diameter $d$ and length $L$. For such particles, the rotational movement around the axis of the tube cannot be considered. The components of the inertia tensor associated with rotational motion around the axis of the tube are very small compared to its other components and may not be taken into account. The angular velocity $\Omega$ in this case is the component of the angular velocity perpendicular to the axis of symmetry of the tube. In this case $I\dot{\Omega} = ML^2\Omega/12$ and equation (21) takes the following form

\[ \frac{ML^2}{12}\dot{\Omega} = -k_r\Omega + S, \]  

(21b)

where the following friction coefficient has been introduced

\[ k_r = \frac{\mu d_i L}{3ln(L/d)}. \]  

(25)

As a result, it can be established that the coefficients of translational and rotational diffusion are respectively equal to

\[ D = \frac{kTln(L/d)}{3\mu L}, \quad D_r = \frac{3kTln(L/d)}{\pi\mu L^3}. \]  

(26)

It is easy to establish that the coefficient of the rotational diffusion is much less than the coefficient of the translational diffusion for CNTs with large aspect ratio.

6. Conclusion

The diffusion of molecules or dispersed particles is related to their mobility in a molecular disordered medium. Strictly speaking, their movement is described by the Newton's system of differential equations and is completely deterministic. The paradox of the situation is that this completely deterministic interaction of a huge number of molecules (particles) is effectively modeled by a stochastic process. The Langevin approach is therefore extremely useful in modeling any collective interactions or processes that are a superposition of a huge number of completely determined acts of interaction of particles of the system under consideration.

As is known (see, for example, [18]), the evolution of a Brownian particle in the configuration space is described by the Wiener process and in the velocity space by the Ornstein–Uhlenbeck pro-
cess. It was shown above that the movement of a nanoparticle is determined, like the usual Brownian one, by Einstein's law. Therefore, the motion of a nanoparticle in the configuration space is also described by the Wiener process. However, just as for a Brownian particle, one can speak strictly about the Wiener process only asymptotically at sufficiently long times. At short times; motion of a nanoparticle is, of course, non-Markovian.

The evolution of nanoparticle in the velocity space everything is more complicated. In view of the above, this process is non-Markovian. So the movement of a nanoparticle in the velocity space is not described by the Ornstein-Uhlenbeck process. However, it is worth noting that the latter is characterized by an exponentially declining VACF. The VACF of nanoparticle is a superposition of two exponents. There are two different mechanisms of the velocity relaxation of nanoparticle with very different relaxation times. These mechanisms are related with significantly different RFACF.

And one more important motive. There are two significantly different formulations of fluctuation-dissipation theorem in the literature today. The first of them (19) goes back to the famous work of Einstein [13] and establishes a relation between the diffusion coefficient and the dissipative force acting on it. The generalized Langevin equation may be rewritten in the following form

\[ \ddot{v} = -\zeta(v)v + f(t), \]

where the friction coefficient depended on the particle velocity was introduced. Using the fluctuation-dissipation theorem (19) we see that diffusion coefficient of the nanoparticle is the function of its velocity

\[ D = kT/\langle Mv(v) \rangle. \]

In this case the diffusion coefficient of the nanoparticle should be depended on the particle velocity also. However molecular dynamics simulation has shown that the diffusion coefficient of nanoparticles does not depend on their velocity [16]. Thus the fluctuation-dissipation theorem (19) has not universal character. It is necessary to exercise some caution when applying formula (19). The formulas of this type, of course, is not universal and is not applicable for other transport coefficients (viscosity and thermal conductivity), since they are no longer determined solely by mobility or any other similar characteristic.

On the other hand, the second formulation of the of fluctuation-dissipation theorem (5) establishes a relation between the transport coefficients and the equilibrium correlations of the corresponding dynamic variables. The second is universal and is a consequence of nonequilibrium statistical mechanics. Moreover, it reveals the physical cause of the dissipation of Newtonian fluids. This dissipation is associated with the redistribution of mass, momentum, and energy in the system, due to the presence of precisely equilibrium molecular fluctuations. This is the law of nature. However this situation is realized only for so named weakly nonequilibrium systems in which the dissipative fluxes are proportional to the thermodynamic forces. In general case the dissipative fluxes may be depended on the shear rate. Such situation is realized for example in non-Newtonian fluid. The variation of the fluid viscosity with increasing of the shear rate in this case is determined by the change the fluid structure during the change of the shear rate.

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