A SIMPLE ALGORITHM TO SIMULATE NANOPARTICLES MOTION IN A NANOFLUID

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Nanofluids are suspensions of nano to micrometer sized particles in liquids. In a suspension the nanoparticles have a complex movement of both sedimentation and Brownian motion. A computer code to simulate the nanoparticles Brownian motion by individually handling each nanoparticle and an algorithm to assess the time step is described. A simple ansatz to calculate the time step for a specific nanoparticle diameter in an aqueous suspension is presented, as well.

Keywords: Nanoparticles, Brownian motion, suspension.

1. Introduction

The nanofluid notion was first mentioned by Choi in 1995 [1] as he noticed that a small amount of nanoparticles, added in a fluid, considerably enhanced the heat transfer properties [2].

The nanoparticles have a continuous, irregular motion in nanofluids, which is the effect of several forces such as gravity, Brownian, buoyant and friction between fluid and the particles. The irregular nanoparticle motion in the fluid is the cause of the heat transfer properties enhancement of the nanofluids [3-6].

Coated nanoparticles are already considered for commercial application in medicine. Some possible applications are: tumour destruction via heating (hyperthermia) [7], bio detection of pathogens [8], fluorescent biological labels [9], drug and gene delivery [10], detection of proteins [11], probing of DNA structure [12], tissue engineering [13], separation and purification of biological molecules and cells [14] and many others. Nanoparticle Brownian motion simulation might be useful in assessing the nanoparticle transport through different human body fluids.

In this work a program to simulate the nanoparticles Brownian motion and an algorithm to assess the time step for modeling nanoparticles diffusion is presented. A simple ansatz to calculate the time step for a specific nanoparticle diameter can be found in the third section.

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2. Sedimentation or Brownian motion?

First we should ask whether sedimentation is significant or not when doing a computer simulation of a nanofluid located in a small dimension volume, like a cuvette. The sedimentation motion of the nanoparticles carries on with a constant velocity, which is the consequence of the null resultant of three forces: gravity, buoyant and the viscous force in laminar flow regime (Stokes). Considering the nanoparticle with a spherical shape, the velocity is given by equation (1):

$$v_s = \frac{2r^2 g}{9\eta} \cdot (\rho - \rho_0) \tag{1}$$

where r is the radius of the sphere, ρ is the density of the nanoprticle, ρ_0 is the density of the carrier fluid, η is the dynamic viscosity coefficient of the fluid. The fluid was considered to be water and the variation of the water density and dynamic viscosity with temperature was calculated using a four degree polynomial. The polynomial coefficients were found by performing a fit on the experimental data in [15].

In order to find out which one of the two different type of motions, sedimentation or Brownian motion, has the biggest role in changing the concentration or in causing the fluctuations of the scattered light intensity, when the nanofluid is the target of a coherent light beam in a Photon Correlation Spectroscopy (PCS) experiment [16], [17] we notice that the mean square value of the velocity module, also called the thermal velocity, given by equation (2), is a measure of the Brownian motion intensity [17]:

$$v_t = \sqrt{\frac{3kT}{m}} \tag{2}$$

In (2) k is Boltzman's constant, T is the absolute temperature and m is the mass of the particle in thermal equilibrium with the environment. Figures 1 and 2 present the variation of the Brownian and of the sedimentation motion velocities at 293.15 K for particles having a diameter from 4 to 37 nm, hence a radius in the range 2 to 18.5 nm.

Examining Figures 1 and 2 we notice that the sedimentation motion velocity is roughly 10^9 times smaller than the thermal velocity. This proves that for nanoparticles the Brownian motion is the main cause of the major concentration changes or of the speckle fluctuations in [16], [17]. If we move to bigger particles, having diameters of the micron magnitude, the sedimentation motion velocity increases while the thermal velocity decreases to such an extend that they become comparable, which should be accounted in simulating the dynamics of such a suspension.

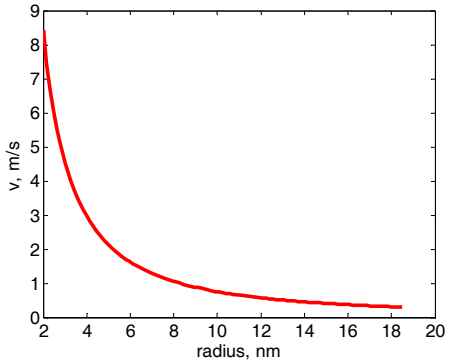

Fig. 1 – The thermal velocity versus particle radius in the range 0.2 – 18.5 nm at 293.15 K.

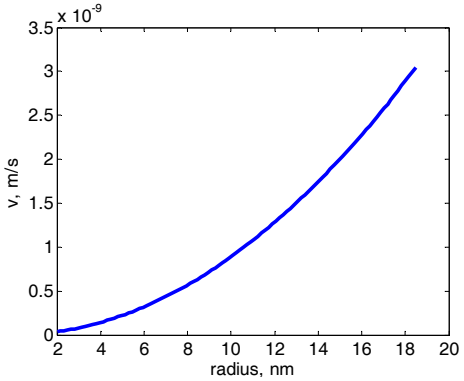

Fig. 2 – The sedimentation motion velocity versus particle radius in the range 0.2 – 18.5 nm at 293.15 K.

3. Brownian motion simulation

In the code we developed and used to simulate the Brownian motion each nanoparticle was handled invidually, considering a Maxwell-Boltzman distribution for the nanoparticles velocity.

A set of simple computer diffusion experiments was done using 5000 nanoparticles, in order to have a good statistics. Their positions were *(0,0,0)* in cartezian coordinates at time *t=0*. A certain value was selected for the Brownian motion time step modeling, and the system was allowed to evolve for a total preselected time *t.* At each time step the particles velocities were generated having a Maxwell – Boltzman velocity distribution, and the new positions were calculated for each particle adding to the old positions the velocity times the time step. When the preset time elapsed, the positions were saved, $\langle r^2 \rangle$ was computed for the statistical ensemble and finally D_{comp} was calculated for that particular value of the time step from (3).

$$\left\langle r^2(t) \right\rangle = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} r^2 \cdot P(\vec{r},t) \cdot r^2 \cdot \sin\theta \, d\theta \, d\varphi \, dr = 6Dt \tag{3}$$

Different time step values were used for each experiment, a curve was drawn with D_{comp} values versus the time step. The time step that produced a D_{comp} value equal to the one calculated using Einstein equation [18], [19] was chosen as the realistic value for Δt. A detailed explanation of the procedure, containing the equations used in assessing the proper value of the time step for a specific nanoparticle size and density are presented in detail in [18] and [19].

The results for 10.5 nm diameter nanoparticles in water at 293.15 K are presented below as an example. The diffusion coefficient calculated with (9) is

$4.2781 \cdot 10^{-11}$ m^2s^{-1} and the Brownian motion time step produces a D_{comp} that matches this value is $6.0803 \cdot 10^{-11}$ s. Figure 3 presents the variation of the computed diffusion coefficient with the Brownian motion time step. We notice that for the small time step range that was used for assessing the Brownian motion time step the variation appears to be linear. Other example of using the procedure in assessing the time step required for this Brownian motion simulation that treats each particle individually, for micron sized particles this time, is presented in detail in [19]. A further improvement and generalization, aiming to find a simple ansatz for a rapid assessment of the time step value for a certain particle diameter and solvent temperature is presented further on.

The Δt assessment procedure was repeated for nine temperatures: 5, 20, 37, 45, 55, 65, 75, 85 and 95 ^oC. At each temperature the diffusion computer experiment was carried on for nanoparticles with four diameters, which are: 5, 10, 15, and 20 nm and for each nanoparticle diameter the value that produced the realistic diffusion coefficient was selected using the procedure briefly described above and in detail in [18], [19].

This direct procedure described above that has to be carried on before a Brownian motion simulation for each combination of nanoparticle, solvent and temperature is time consuming though. A simplified yet precise procedure for assessing the time step value is presented further on.

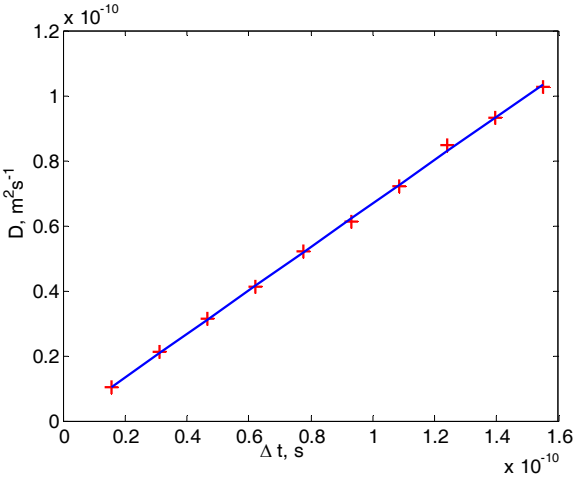

Fig. 3. The variation of the computed diffusion coefficient (crosses) with the Brownian motion time step for 10.5 nm diameter nanoparticles in water at 293.15 K.

A polynomial fit on the Δt – nanoparticle diameter data set for each temperature, in aqueous solution, was done. The variation of the time step with the nanoparticle diameter for each of the nine temperatures used in the computer experiment are presented in Fig. 4.

Examining Fig. 4 we notice that the time step increases fast with the nanoparticle diameter and increases with the temperature, as well. We also notice that the second degree polynomial fits very well the time step calculated with the procedure described above and the coefficients are presented in equation (4):

$$\Delta t = p_1 \cdot d^2 + p_2 \cdot d + p_3 \tag{4}$$

In (13) d is the nanoparticle diameter, expressed in nanometers and Δt is the time step, in seconds.

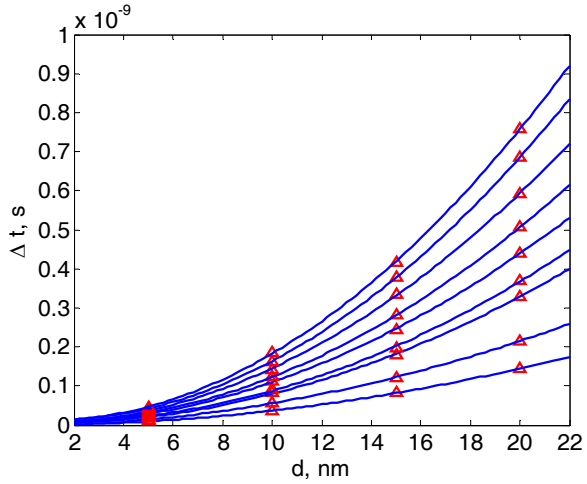

Fig. 4. The time step variation with the nanoparticle diameter: calculated data - triangles, solid lines – interpolated data, for nine temperatures. From the lower set to the upper set: 5°C, 20°C, 37°C, 45°C, 55°C, 65°C, 75°C, 85°C, 95°C.

Table 1 presents the values of the coefficients for the nine temperatures the computer experiment was run for. Examining Table 1 we notice that the p_1 coefficient presents a monotone increase with the temperature, p_2 a decreasing trend and p_3 an increasing trend.

The procedure described in this section, of running a computer experiment with different values of the time step and comparing the results with the actual diffusion coefficient leads to exact values for the time step to be used in a Brownian motion computer simulation for each diameter and temperature, typical for modeling nanoparticle diffusion, but is time consuming.

A much faster recipe consists of using a simple equation to calculate first the p_1, p_2 and p_3 coefficients for a certain temperature t. A simple approach would consist in "drawing" a line for each of the three coefficients variation with the temperature. The linear fit produced the variation of the coefficients with the temperature t (in °C) and is presented in equations (5) through (7):

Table 1

Table 1- the values of the polynomial coefficients for nine temperatures

t, ^oC	p_1, s/nm^2	p_2, s/nm	p_3, s
5	$3.538 \cdot 10^{-13}$	$1.856 \cdot 10^{-13}$	$-2.777 \cdot 10^{-13}$
20	$5.031 \cdot 10^{-13}$	$8.249 \cdot 10^{-13}$	$-2.600 \cdot 10^{-12}$
37	$8.766 \cdot 10^{-13}$	$-1.364 \cdot 10^{-12}$	$5.728 \cdot 10^{-12}$
45	$1.019 \cdot 10^{-12}$	$-2.585 \cdot 10^{-12}$	$1.141 \cdot 10^{-11}$
55	$1.100 \cdot 10^{-12}$	$-1.554 \cdot 10^{-13}$	$1.753 \cdot 10^{-12}$
65	$1.334 \cdot 10^{-12}$	$-1.701 \cdot 10^{-12}$	$6.533 \cdot 10^{-12}$
75	$1.533 \cdot 10^{-12}$	$-1.188 \cdot 10^{-12}$	$4.088 \cdot 10^{-12}$
85	$1.864 \cdot 10^{-12}$	$-3.733 \cdot 10^{-12}$	$1.461 \cdot 10^{-11}$
95	$2.016 \cdot 10^{-12}$	$-3.063 \cdot 10^{-12}$	$1.210 \cdot 10^{-11}$

$$p_1(t) = 1.888 \cdot 10^{-14} \cdot t + 1.667 \cdot 10^{-13} \quad (5)$$

$$p_2(t) = -3.947 \cdot 10^{-14} \cdot t + 6.943 \cdot 10^{-13} \quad (6)$$

$$p_3(t) = 1.450 \cdot 10^{-13} \cdot t - 1.840 \cdot 10^{-12} \quad (7)$$

Calculating the p_1, p_2 and p_3 coefficients with the equations (5), (6) and (7) and then the time step values for each nanoparticle diameter with equation (4) produces very close values as compared with the time step calculated with the coefficients in Table 1. In order to estimate the accuracy of the time step estimation with this simplified procedure, the latter was calculated using the three recipes. Fig. 5 presents the variation of the time step with the nanoparticle diameter, calculated with the coefficients from Table 1, with the interpolated coefficients (5) – (7) and the time step calculated from the diffusion computer experiment, at 37 ^oC. We notice that the differences are very small.

4. Results and conclusion

This algorithm in its precise version, of running a computer diffusion experiment with different values for the time step and comparing the computed diffusion coefficient [18], [19] for assessing the time step value was used in calculating the time step and in simulating the Brownian motion in a program that simulates the coherent light scattering dynamics on nanoparticles in suspension [18]. The far interference field calculated with the program was compared with an experimental far field recorded during a light scattering experiment and was found to be realistic [18]. The computed time series of the intensity recorded in a far field location was compared with the time series recorded during an experiment and was found to be very realistic, as well [19].

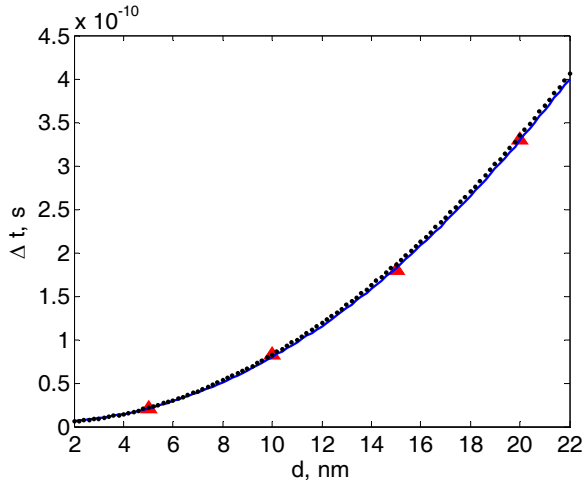

Fig. 5 - The variation of the time step at 37 ^{o}C calculated from the diffusion computer experiment (triangles), with the coefficients in Table 1 (solid line) and with the p_1, p_2 and p_3 coefficients calculated with equations (14), (15) and (16) (dot line) with the nanoparticle diameter.

This suggests that the Brownian motion simulation procedure presented here and the simple and fast ansatz presented in this work to calculate the time step can be successfully used to simulate in a realistic manner the nanoparticle motion of each individual nanoparticle in suspension, for a total number nanoparticles of the magnitude of 10^4, using a dual core processor on a PC and for a realistically bigger number of nanoparticles, of the magnitude of 10^9, using a High Power Computing platform with hundreds of cores, in a computer experiment lasting foe a few hours.

The simple algorithm described in this paper can be easily implemented in any programming language and can be used both in assessing the time step and than in modeling the nanoparticle diffusion in any aqueous solution, including biological fluids, provided that the dynamic viscosity coefficient is known, by individually handling each nanoparticle for the time span of the computer experiment.

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