Analytical investigation of nanofluids dispersion stability
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ABSTRACT

This paper intends to theoretically study the dispersion stability of nanofluids considering Brownian motion, thermophoresis, drag force and DLVO (Derjaguin, Landau, Verwey and Overbeek) surface forces. The kinetic energy of particles is resulted from the balance of the Brownian force, thermophoretic force and drag force while the potential energy between the nanoparticles is determined using DLVO theory. It is considered the particles agglomerate if the particle kinetic energy could overcome the DLVO barrier potential energy exists around the target particle. The values of these forces depend on different parameters such as fluid temperature, temperature gradient, nanoparticle diameter and base fluid and particles physical properties. Therefore, the effects of these parameters including temperature of nanofluid, thermal gradient and nanoparticles mean diameter on the stability of different nanofluids have been studied.

Keywords: nanofluid, stability, stability diagram

1 INTRODUCTION

An overview on growth of energy consumption in different industrial installations indicates that intensification of heat transfer processes and preventing the energy lost is of a great concern. Various methods introduced to enhance heat transfer including using that However, there are many problems that must be overcome prior to any application Among them is Nanoparticles’ aggregation and sedimentation or physicochemical stability of nanofluids. In the literatures, various methods proposed for stabilization of nanofluid such as applying ultrasonic waves for breaking nanoparticle aggregates, coating nanoparticles with polymeric surfactants to prevent aggregation, external force field employment on nanofluid and changing of electrostatic properties of nanoparticles’ surfaces by variation of PH. Although, some of these methods are effective on stabilization of nanofluids to some extent but none of them can solve nanofluid stability problem perfectly. It is well known that the interparticle forces in nanofluid play an important role on the nanofluid stability.

In 1917 Smoluchowski [1] made the first attempt to estimate the effect of direct motion of particles on coagulation. In 1964, Fuchs [2] introduced a critical diameter for particles, above which aggregation dominates (about 1 micrometer). In 2006, Xinfang et al. [3] studied the influence of CATB on Stability of copper nano-suspensions at different PH numbers. They introduced an optimum PH number in which maximum stability achieved. In 2007, Dongsheng et al. [4] studied stability of alumina-water nanofluid at different PH numbers and various concentrations of SDBS. They presented optimum values for PH number and SDBS concentration in which the stability of the nanofluid would be maximized. Xinfang et al. [5] also studied stability of copper water based nanofluid and with the presence of CATB, TX-10 and SDBS surfactants. They determined the optimum values of PH number and concentration of surfactants in order to achieve maximum nanofluid stability. In 2008, Hwang et al. [6] used various methods for stabilization of different nanofluids. They studied different physical treatment techniques based on two-step production method, including stirrer, ultrasonic bath, ultrasonic disruptor, and high-pressure homogenizer, to verify the versatility of methods for preparing stable nanofluids. They concluded that high-pressure homogenizer method is the most effective method to break down the agglomerated nanoparticles suspended in the base fluids in which nanoparticles with 45 nm diameter achieved. Finally they could produce Ag nanoparticles with the diameter of about 3 nm by modified magnetron sputtering method that is also an effective one-step method to prepare stable nanofluids. In 2009, Huang et al. [7] studied the stability of two different, alumina and copper, water based nanofluids at different PH numbers. By studying of the influence of PH on zeta potential layer, they introduced an optimum PH number in which zeta potential layer has its maximum thickness on particle’s surface. Whereupon maximum stability for nanofluid is achieved. These works have tried to prepare the stable nanofluids but none of them investigated the conditions for which the nanofluids remain stable. In 2010, Weiting et al. [8] modeled the process of aggregation and sedimentation of nanoparticles in nanofluids based on an analytic solution of nanoparticle’s motion in base fluid and calculation of nanoparticle’s speed and location. They estimated variations of nanoparticle concentration with time but they did not do any discussion on the nanoparticles’ aggragation in nanofluids.

As mentioned, researches have been focused on stabilization of nanofluid in a certain condition (at initial time) and attempts on nanofluid stabilization was limited to amplifying zeta potential layer around nanoparticles. Furthermore, in some cases experimental works have been
carried out on breaking aggregates down to smaller ones. At the author knowledge there is not any attempt to show and to present the conditions for which the nanofluid to be stable and the nanoparticle aggregation does not occur with time. Thus So, it is very important to have a new and deep look on the nanofluid dispersion stability. The objective of this study is to propose stability diagram for nanofluid at different thermophysical conditions. This is done based on an analytical study of forces, to represent conditions that nanofluid would be stable forever. Hence, the "energy zones contact" theory for different cases (2, 3 and 7 particle methods) are implemented to study the dispersion stability of nanofluid at different thermophysical conditions. Then the stability diagram for various nanofluids at different conditions are drawn based on the nanofluid characteristics including nanoparticle diameter, types of nanoparticles, types of base fluids, temperature, temperature gradient.

2 FORCES ON THE NANOPARTICLE
There are different forces acting on nanoparticles suspended in a base fluid. However, each of these forces has a particular range of effectiveness and some limitations to act. In addition, the forces between nanoparticles can be attractive or repulsive. They may also be short-range or long-range forces [9]. Some of the forces have more important role on particles aggregation at nano-scale. These forces are drag, thermophoresis, Brownian, van der waals and electrical double layer force. Van der waals and electrical double layer forces are interparticle forces that combination of them has been introduced as DLVO theory [10]. Other forces mentioned above are hydrodynamic forces acting on each particle individually.

These forces mathematically could be defined as follows:

2.1 Drag force

\[ F_D = \frac{18\mu}{p_p d_p^2} \times \frac{C_D \text{Re}}{24} \times (V_1 - V_p) \times m_p \]  

(1)

Here \( V_p \) is the particle velocity, \( V_1 \) the fluid velocity, \( m_p \) nanoparticle mass, \( c_D \) drag coefficient, \( p_p \) density of nanoparticle, \( \mu \) dynamic viscosity of base fluid, and \( d_p \) the particle diameter. \( \text{Re} \) is the relative Reynolds number, given by

\[ \text{Re} = \frac{\rho}{\mu} \frac{d_p |V_p - V_1|}{d_p} \]  

(2)

There are various models of the drag coefficient \( C_D \) for nanoparticles. Stoke’s law seems to be appropriate [12]:

\[ F_D = \frac{18\mu}{c_p d_p^2 c_c} \times (v_1 - v_p) \times m_p \]  

(3)

Where \( c_c \) is Cunningham correction factor for stoke’s drag force, given by:

\[ c_c = 1 + \frac{2\lambda}{d_p} (1.257 + 0.4 e^{-\frac{1.1 d_p}{2 \lambda}}) \]  

(4)

\( \lambda \) is the molecular mean free path.

2.2 Brownian force

Recommended correlation for Brownian force, given by [13]:

\[ F_B = m_p \times \zeta \frac{\pi s_0}{\Delta t}, s_0 = \frac{216 \nu k_B T}{\pi^2 \rho d_p^5 (\frac{dp}{\rho})^2 c_c} \]  

(5)

Where \( \zeta \) is a Gaussian random number between one and zero. For simplicity we considered \( \zeta=0.5 \). The Brownian force arises as a result of the collisions of molecules with the particles and acts for the time corresponding to the time of contact during a collision (\( \sim \) picoseconds). So, for this time interval, drag force is considered constant and stoke’s correlation would be acceptable [13].

2.3 Thermophoresis force

Nanoparticles suspended in a base fluid with a temperature gradient, experience a force in the direction opposite to that of the gradient. This phenomenon is known as the thermophoresis. Historically, there have been three theoretical approaches in thermophoresis study that correspond to the Knudsen number range including free molecule regime, near continuum regime and transient regime. However, the corresponding equations are derived for the suspension of solid particles in ideal gases. A modification may be necessary to use them for solid–liquid suspensions (nanofluids) [14]. As it is known water molecules linked with each other by hydrogen bonds which has three 3 angstroms length in maximum and average length of about 1.9 angstrom. So, free molecule length for water molecules is of order \( 10^{-11}(m) \). On the other hand, characteristic length of water molecule (diameter of water molecule) is about 2 angstroms thus the Knudsen number is:

\[ k_n = \frac{\lambda}{a} \rightarrow k_n = \frac{10^{-11}}{2 \times 10^{-10}} \approx 0.05 \]  

(6)

Where \( a \) is characteristic length of water molecule (diameter of it) and \( \lambda \) is the molecular mean free path. Since the Knudsen number is very small (\( k_n < 1 \)) and there is liquid instead of gas, a correlations corresponding to the near continuum regime for liquid nanofluid could be used. This is, in non-dimensional form, [14]:

\[ F_T = \frac{24}{5} \times \frac{c_t k_n (k_{21} + c_t k_n)}{(1 + 3 c_m k_n) (1 + 2 k_{21} + 2c_t k_n)} \]  

(7)

Where \( k_{21} \), given by:
$$k_{21} = \frac{k_f}{k_p}$$  \hspace{1cm} (8)

However, dimensional form of this correlation is [11]:

$$F_r = \frac{6 \pi \mu^2 d_p c_s (k_r + c_t k_n)}{\rho (1 + 3 c_m k_n) (1 + 2 k_r + 2 c_t k_n)} \times \frac{1}{T} \times \frac{\partial T}{\partial x}$$  \hspace{1cm} (9)

Where \( k_r = \frac{k_f}{k_p} \), \( c_s = 1.17 \), \( c_m = 1.14 \) and \( c_t = 2.18 \)

3 METHOD OF ANALYSIS

First, for simplicity, two nanoparticles suspended in a base fluid is considered in one-dimensional form. Then it will be extend in three-dimensional form.

Static nanofluid with uniform distribution of particles at initial time is assumed. As shown in figure 1, two nanoparticles with initial distance of \( L \), which depends on the nanoparticle volume fraction, is considered.

![Figure 1. Schematic of two nanoparticles in a base fluid at initial time](image)

Thus, interparticle distance \( L \) can be calculated as follow:

$$L = \frac{3 \pi \times d_p^3}{6 \times \phi} - d_p$$  \hspace{1cm} (10)

Now assume that particle 1 is fixed and particle 2 moves toward it. Initial speed of particle is represented as \( u_0 \) and \( x(t) \) is the particle location at any time (see figure 2).

![Figure 2. two particles method](image)

So interparticle distance at any time is \((L-x(t))\). The initial velocity, \( u_0 \), is considered to arise from the Brownian motion so it is determined by the following equation [15]:

$$u_0 = \frac{3 k_B T}{m_p}$$  \hspace{1cm} (11)

An energy balance approach is considered for the analysis. On this method kinetic energy of moving particle and potential energy between the particles (attractive and repulsive) are calculated. Then an energy balance is carried out to see if the kinetic energy of the moving particle could overcome the repulsive potential energy between these two particles. If it happens the agglomeration would take place. Otherwise the initial dispersion stability would remain with time.

To calculate the energy of particles, all forces that are exerted on particle 2 except DLVO forces are considered. Balance of these forces could determine the velocity of particle 2 at each location and consequently its kinetic energy at that location.

On the other hand, the interparticle potential energy via DLVO forces is calculated. Then it is investigated whether kinetic energy of particle can overcome the DLVO potential energy barrier between two particles or not. This analysis is named as “two particle method”.

4 MATHEMATICAL FORMULATION

Using the Newton second law for a particle motion and considering the mentioned forces the velocity and displacement of the particle could be determined by the following equations respectively:

$$V_p(t) = (u_0 - \frac{A_1 + B}{C}) e^{-ct} + \frac{A_1 + B}{C}$$  \hspace{1cm} (12)

$$x(t) = (u_0 - \frac{A_1 + B}{C}) \times \frac{-e^{-ct}}{C} + \frac{A_1 + B}{C} \times t + (\frac{u_0}{C} - \frac{A_1 + B}{C^2})$$  \hspace{1cm} (13)

Where

$$A_1 = \frac{1}{m_p} \times \frac{6 \pi \mu^2 d_p c_s (k_r + c_t k_n)}{\rho (1 + 3 c_m k_n) (1 + 2 k_r + 2 c_t k_n)} \times \frac{1}{T} \times \frac{\partial T}{\partial x}$$  \hspace{1cm} (14)

$$B = \frac{\sqrt{\pi S_0}}{\Delta t}$$  \hspace{1cm} (15)

$$C = \frac{18 \mu l}{\varphi_p d_p^2 c_c}$$  \hspace{1cm} (16)

Then the kinetic energy of particle \( k \) and DLVO potential energy \( (E_{DLVO}) \) is calculated.

So, we discrete problem to very small time intervals and calculate the kinetic energy of particle \( K \) and DLVO potential energy \( (E_{DLVO}) \) in each time interval and do a comparison between them.
\[ K = \frac{1}{2} m_p V_p(t)^2 = \frac{1}{2} m_p (u_0 - \frac{A_t + B}{C}) e^{-ct} + \frac{A_t + B}{C} \]

\[ E_{DLVO} = \pi \varepsilon_0 \varepsilon_\infty \frac{d_p^2}{24(L - x(t))} e^{-k(L-x(t))} \]

Where \( K \) is inverse Debye length (\( K = 3.29 \times 10^{-12} \) (nm\(^{-1}\))), \( c \) is molar concentration of monovalent electrolyte and \( \varepsilon_0 \) is permittivity of free space (\( \varepsilon_0 = 8.85 \times 10^{-12} \) C\(^2\)/(J/m)) [16].

If the magnitude of DLVO potential energy be larger than the kinetic energy of particle in a specific, it could be said the nanofluid is stable in such condition. With changing the thermo-fluid conditions the stability could also change and then “stability diagram” would be obtained.

For instance, stability diagram for alumina-water nanofluid with volume fraction of 0.01, \( \text{PH}=7 \) and \( \frac{dT}{dx}=0 \) (K/m) presents in Figure 3.

![Figure 3](image)

Figure 3. Stability diagram for alumina-water nanofluid with \( \phi=0.01, \text{PH}=7 \) and \( \frac{dT}{dx}=0 \) (K/m) based on 2 particle method.

As shown in figure 3, for a given temperature gradient the area that is under the of curve is stable area and that is over the curve is unstable area. As seen, if the temperature of nanofluid working media increases the diameter of nanoparticles that are used for preparation the nanofluid must be decreased to be stable. It should be mentioned that unstable conditions means the aggregation may be occurred in lapse of time. Figure 4 shows the effects of different fluid temperature gradient on the stability of Al\(_2\)O\(_3\)/water nanofluid at different fluid temperature and the nanoparticle mean diameter.

![Figure 4](image)

Figure 4. Effect of temperature gradient on the stability of Al\(_2\)O\(_3\)/water nanofluid, \( \phi=0.01, \text{PH}=7 \) and \( \frac{dT}{dx}=0 \) (K/m).

**5 CONCLUSION**

The stability of nanoparticle dispersion in a base fluid is investigated analytically by considering different effects including Brownian motion, thermophoresis, drag force and DLVO (Derjaguin, Landau, Verwey and Overbeek) surface forces. Based on the energy analysis different stability diagram could be obtained to show the conditions for which a nanofluid would be table and agglomeration does not occur.

**REFERENCES**


