

PREPARATION METHODS FOR NANOFUIDS AND THERE STABILITY

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Abstract : Nanofluids, the fluid suspensions of nanomaterials, have shown many interesting properties, and the distinctive features that offer unprecedented potential for many applications in industry as well as research. This paper summarizes the recent progress on the study of nanofluids, such as the preparation methods, the evaluation methods for the stability of nanofluids, and the ways to enhance the stability for nanofluids, the stability mechanisms of nanofluids, and presents the broad range of current and future applications in various fields which includes energy and mechanical and biomedical fields. At last, the report identifies the opportunities for future research.

Nanofluids as a kind of new engineering material consisting of nanometer-sized additives and base fluids that have attracted great attention of researchers for its superior thermal properties and many potential applications. Many researches on nanofluids were investigated and especially some interesting phenomena, new experimental results and theoretical study on nanofluids, in which consistent and inconsistent even contrary conclusions were reported, have been presented in literature.

IndexTerms - Nanofluids, thermophysical, nanotubes, Preparation methods, Stability.

1. INTRODUCTION

Nanofluids are a new class of fluids developed by dispersing nano-sized materials (nanoparticles, nanofibers, nanotubes, nanowires, nanorods, nanosheet, or droplets) in base fluids. In other words, nanofluids are nanosized colloidal suspensions contains condensed nanomaterials. They are two-phase systems with one phase (liquid phase) in another (Solid phase). Nanofluids have been found to enhance thermal properties such as thermal conductivity, thermal diffusivity, viscosity, and convective heat transfer coefficients compared to the base fluids like oil or water. It has demonstrated great potential applications and approach in many fields.

For a two-phase system, there are some important points we have to face. One of the most important point is the stability of nanofluids, and it remains a tremendous task to gain desired stability of nanofluids. In this paper, we will see the new methods for preparing stable nanofluids and summarize the stability mechanisms.

In present years, nanofluids have attracted more and more attention of researches. The main attraction for nanofluids research lies in a wide range of applications. Although some review papers involving the advancement in nanofluids investigation were published in the past several years, most of the reviews are concerned of the experimental and theoretical research for the thermophysical properties and the convective heat transfer of nanofluids. The purpose of this paper will focuses on the new preparation methods and stability mechanisms, mainly the new application trends for nanofluids in addition to the heat transfer properties of nanofluids. We will try to find some challenging issues that need to be solved for future research based on the review on these aspects of nanofluids.

2. PREPARATION METHODS FOR NANOFUIDS

2.1. Two-Step Method

Two-step method is the mostly used method for preparing nanofluids. Nanoparticles, nanofibers, nanotubes, or other nanomaterials used in this method first produces dry powders by chemical or physical methods. Then, the nanosized powder will be dispersed into a base fluid with the help of intensive magnetic force agitation, ultrasonic agitation, high-shear mixing, homogenizing, and ball milling. Two-step method is the most economical method to produce nanofluids in large scale, because nanopowder synthesis techniques have already been scaled up to industrial production levels. Due to the high surface area and surface property, nanoparticles have the tendency to aggregate. The common technique to enhance the stability of nanoparticles in fluids is the use of surfactants. However, the functionality of the surfactants under high temperature is also a big deal, especially for high-temperature applications.

Due to the trouble in making stable nanofluids by two-step method, many progressive techniques are developed to produce nanofluids, including one-step method. In the following part, we will introduce one-step method in detail.

2.2. One-Step Method

To trim the agglomeration of nanoparticles, Eastman et al. introduced one-step physical vapor condensation method to prepare Cu/ethylene glycol nanofluids. The one-step method consists of synchronously preparing and dispersing the nanoparticles in the fluid. In this method, the processes of drying, storage, transportation, and dispersion of nanoparticles are eliminated, so the agglomeration of nanoparticles is minimized, and the stability of fluids is enhanced. The one-step processes can prepare uniformly dispersed nanoparticles and the particles can be suspended stably in the base fluid. The vacuum-SANSS (submerged arc nanoparticle synthesis system) is another efficient method to prepare nanofluids using different dielectric liquids. The different diagnosis are mainly influenced and determined by various thermal conductivity properties of the dielectric liquids. The nanoparticles prepared show needle-like, polygonal, square, and circular morphological shapes. The method avoids the unwanted particle aggregation.

One-step physical method cannot manufacture nanofluids in large quantity and the cost is also high so the one-step chemical method is modified rapidly. Zhu et al. presented a novel one-step chemical method for synthesizing copper nanofluids by reducing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ in ethylene glycol under microwave irradiation. Well-dispersed and stably suspended copper nanofluids are obtained. Mineral oil-based nanofluids that contain silver nanoparticles with a narrow-sized distribution have also been prepared by this method. The particles could be stabilized by Korantin, which coordinated to the silver particle surfaces via two oxygen atoms forming a dense layer around the particles. The silver nanoparticle suspensions were stable for about 1 month. Stable ethanol-based nanofluids containing silver nanoparticles could be prepared by microwave-assisted one-step method. In the method, polyvinylpyrrolidone (PVP) was employed as the stabilizer of colloidal silver and reducing agent for silver in solution. The phase transfer of the silver nanoparticles arises due to coupling of the silver nanoparticles with the ODA molecules present in organic phase via either coordination bond formation or weak covalent interaction. Phase transfer method has been developed for preparing homogeneous and stable graphene oxide colloids. Graphene oxide nanosheets (GONs) were successfully transferred from water to n-octane after modification by oleylamine, and the schematic illustration of the phase transfer process is shown in Figure 2.1.

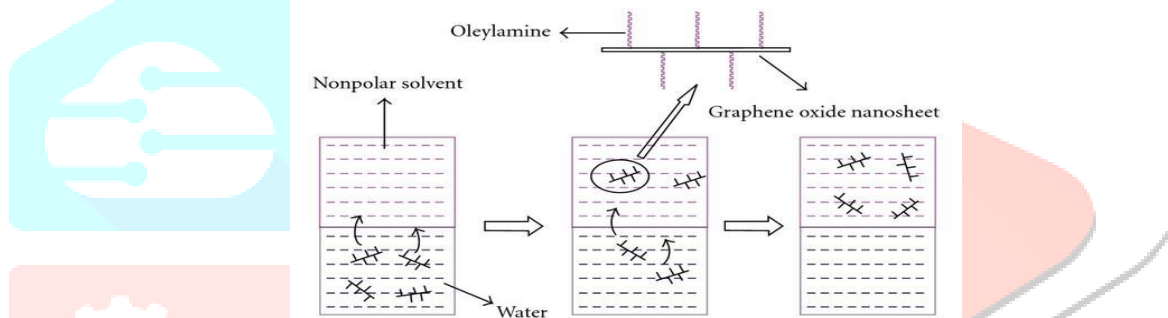


Figure 2.1: Schematic illustration of the phase transfer process.

However, there are some disadvantages for one-step method. The most important one is that the residual reactants are left in the nanofluids due to incomplete reaction or stabilization. It is difficult to elucidate the nanoparticle effect without eliminating this impurity effect.

3. THE STABILITY OF NANOFLUID

The agglomeration of nanoparticles results in not only the settlement and clogging of microchannels but also the decreasing of thermal conductivity of nanofluids. So, the research on stability is also a key matter that influences the properties of nanofluids for application and it is necessary to study and analyze influencing parameters to the dispersion stability of nanofluids. This section will contain-

- The stability evaluation methods
- The ways to enhance the stability
- The stability mechanisms of nanofluids.

3.1. The Stability Evaluation Methods for Nano-fluids

3.1.1. Sedimentation and Centrifugation Methods

Many methods have been developed to analyze the stability of nano-fluids. The simplest method is sedimentation method. The sediment weight or the sediment volume of nano-particles in a nanofluid under an external force field is an indication of the stability of the nanofluid. The nanofluids are considered to be stable when the particle size of bouncy particles keeps constant. Sedimentation photograph of nanofluids in test tubes taken by a camera is also a general method for observing the stability of nanofluids. Therefore, centrifugation method is developed to evaluate the stability of nanofluids. The centrifugation method to observe the stability of silver nanofluids prepared by the microwave synthesis in ethanol by reduction of AgNO_3 with PVP that act as a stabilizing agent. It has been found that the obtained nanofluids show its stability for more than 1 month in the stationary state and more than 10 h under centrifugation at 3,000 rpm without sedimentation. Excellent stability of the obtained nanofluid is due to the protective role of PVP, as it reduces its growth and agglomeration of nanoparticles by steric effect.

3.1.2. Zeta Potential Analysis

Zeta potential is electric potential in the interfacial double layer on the location of the slipping plane versus a point in the bulk fluid away from the interface and it shows the potential difference between the dispersion medium and the stationary layer of fluid attached to the scattered particle. The importance of zeta potential is that its value can be related to the stability of colloidal dispersions. So the colloids with high zeta potential (negative or positive) are electrically stabilized, while colloids with low zeta potentials tend to coagulate. In general, a value of 25 mV (positive or negative) can be taken as the subjective value that distinguishes low-charged surfaces from highly charged surfaces. The colloids with zeta potential from 40 to 60 mV are concerned to be good stable and those with more than 60 mV have excellent stability. The stability is due to a large negative zeta potential of Silver nanoparticles in water.

3.1.3. Spectral Absorbency Analysis

Spectral absorbency analysis is another way to evaluate the stability of nanofluids. In general there is a linear relationship between the absorbency intensity and the concentration of nanoparticles in fluid. The dispersion characteristics of alumina and copper suspensions using the conventional sedimentation method with the help of absorbency analysis by using a spectrophotometer after the suspensions deposited for 24 h. The sedimentation kinetics could be determined by examining the absorbency of particle in solution.

If the nanomaterials dispersed in fluids have characteristic absorption bands in the wavelength 190–1100 nm, it is an easy and good method to evaluate the stability of nanofluids using UV-vis spectral analysis. The variation of bouncy particle concentration of nanofluids with sediment time can be obtained by the measurement of absorption of nanofluids because there is a linear relation between the supernatant nanoparticle concentration and the absorbance of suspended particles. The outstanding advantage comparing to another methods the UV-vis spectral analysis can present the quantitative concentration of nanofluids.

3.2. The Ways to Enhance the Stability of Nanofluids

3.2.1. Surfactants Used in Nanofluids

Surfactants used in nanofluids are also called dispersants. Adding dispersants in the two-phase systems is an easy and more economic method to increase the stability of nanofluids. Dispersants can considerably affect the surface characteristics of a system in small quantity. Dispersants consists of a hydrophobic tail portion, usually a long-chain hydrocarbon, and a hydrophilic polar group. Dispersants are employed to increase the contact between two materials, sometimes known as wettability. In a two-phase system, a dispersant tends to located at the interface of the two phases, where it introduces a degree of continuity between the nanoparticles and base fluids. According to the composition of the head, surfactants are divided into four categories: nonionic surfactants without charge groups in its head (include polyethylene oxide, alcohols, and other polar groups), anionic surfactants with negatively charged head groups (anionic head groups include long-chain fatty acids, sulfosuccinates, alkyl sulfates, phosphates, and sulfonates), cationic surfactants with positively charged head groups (cationic surfactants may be protonated long-chain amines and long-chain quaternary ammonium compounds), and amphoteric surfactants with zwitterionic head groups (charge depends on pH.)

3.2.2. Surface Modification Techniques: Surfactant-Free Method

Use of functionalized nanoparticles is a good approach to achieve long-term stability of nanofluid. It represents the technique without surfactant. One of the unique characteristics of the nanofluids was that deposition layer is not formed on the heated surface after a pool boiling process. The prepared nanofluids, without any contamination to medium, good fluidity, low viscosity, high stability, and high thermal conductivity, have potential applications as coolants in advanced thermal systems. A wet mechanochemical reaction was applied to formulate surfactant-free nanofluids incorporate double- and single-walled CNTs. Results obtained from the infrared spectrum and zeta potential measurements demonstrate that the hydroxyl groups had been imported onto the treated CNT surfaces. The chemical modification to functionalize the surface of carbon nanotubes is a common method to increase the stability of carbon nanotubes in solvents.

3.2.3. Stability Mechanisms of Nanofluids

Particles in dispersion may stick together and form aggregates of increasing size which might settle out due to gravity. Stability means that the particles won't aggregate at a significant rate. The aggregation rate in general is determined by the frequency of collisions and the probability of cohesion. The stability of a particle in solution is determined by the sum of van der Waals attractive and electrical double layer repulsive forces that exist among particles as they approach each other due to the Brownian motion. If the attractive force is more than the repulsive force, the two particles will collide, and the suspension is unstable. If the particles have sufficient high repulsion then the suspensions will exist in stable state. For stable nanofluids the repulsive forces between particles must be dominant. According to types of repulsion, the fundamental mechanisms that affect colloidal stability are divided into two kinds, one is steric repulsion and another is electrostatic (charge) repulsion as shown in Figure 3.1. For steric stabilization polymers are always involved into the suspension system and they will adsorb onto the particles surface which will produces an additional steric repulsive force.

For electrostatic stabilization, surface charge will be developed through one or more of the following mechanisms:

- (1) Preferential adsorption of ions,
- (2) Dissociation of surface charged species,

- (3) Isomorphic substitution of ions,
- (4) Accumulation or depletion of electrons at the surface, and
- (5) Physical adsorption of charged species onto the surface.

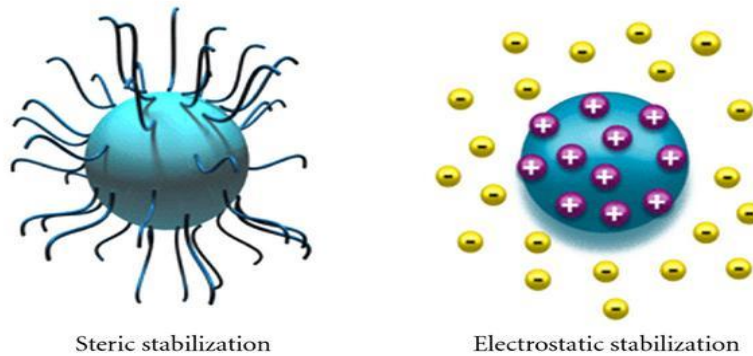


Figure 3.1: Types of colloidal stabilization.

3.3 ADVANTAGES, LIMITATIONS

3.3.1 Advantages Of Nanofluids

Large surface area and therefore more heat transfer surface between particles and fluids.

Brownian motion of particles gives high dispersion stability.

Pumping power is reduced as compared to pure liquid to achieve equivalent heat transfer intensification.

Particle clogging is reduced as compared to conventional slurries, thus promoting system miniaturization.

Adjustable properties including thermal conductivity and surface wet ability, by varying particle concentrations to suit different applications.

3.3.2 Limitations

Lower specific heat: From the literatures, it is observed that specific heat of nanofluids is lower than base fluid. It is observed that CuO/ethylene glycol nanofluids, SiO₂/ethylene glycol nanofluids and Al₂O₃/ethylene glycol nanofluids shows lower specific heat compared to base fluids. To remove more heat an ideal coolant should possess higher value of specific heat.

High cost of nanofluids: Higher production cost of nanofluids is among the reasons that may inhibit the application of nanofluids in industry. One step or two steps methods can be used to produce nanofluids. However the advanced and complex equipments are required for both the methods.

4. CONCLUSIONS AND FUTURE WORK

In the past decades many interesting properties of nanofluids have been reported. This research paper presents an overview of the recent advancements in the study of nanofluids, including the preparation methods, the evaluation methods for their stability, the ways to enhance their stability, the stability mechanisms, and their potential applications in heat transfer intensification, mass transfer enhancement, energy fields, mechanical fields, biomedical fields, and so forth.

Although nanofluids have displayed enormously exciting potential applications, some vital hinders also exist before commercialization of nanofluids. The following key issues should receive greater attention in the future.

Firstly, further experimental and theoretical research is required to find the major factors influencing the performance of nanofluids. Up to now, there is a lack of agreement between experimental results from different groups, so it is important to systematically identify these factors. The detailed and accurate structure characterizations of the suspensions may be the key to explain the discrepancy in the experimental data.

Secondly, increase in viscosity by the use of nanofluids is an important drawback due to the associated increase in pumping power. The applications for nanofluids with low viscosity and high conductivity are promising. Enhancing the compatibility between nanomaterials and the base fluids through modifying the interface properties of two phases may be one of the solution routes.

Thirdly, the shape of the additives in nanofluids is very important for the properties; therefore, the new nanofluid synthesis approaches with controllable microscope structure will be an interesting research work.

Fourthly, stability of the suspension is a crucial issue for both scientific research and practical applications. The stability of nanofluids, especially the long-term stability, the stability in the practical conditions, and the stability after thousands of thermal cycles should be paid more attention.

Fifthly, there is a lack of investigation of the thermal performance of nanofluids at high temperatures, which may widen the possible application areas of nanofluids, like in high-temperature solar energy absorption and high-temperature energy storage. At the same time, high temperature may accelerate the degradation of the surfactants used as dispersants in nanofluids and may produce more foams. These factors should be taken into account.

Finally, the properties of nanofluids strongly depend on the shape and property of the additive. The thermal conductivity enhancement was adjusted by ball milling and cutting the treated CNTs suspended in the nanofluids to relatively straight CNTs with

an appropriate length distribution. They proposed the concept of straightness ratio to explain the facts. Nanofluid research can be enriched and extended through exploring new nanomaterials.

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