Stability of Nanofluids

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Abstract Nanofluids are the dilute suspensions of nanomaterials with distinctive and enhanced features. Nanofluids can be used in a variety of industrial applications because of improved thermophysical properties. Stability of nanofluids is the only quandary factor which decreases the efficiency of such smart fluids in engineering applications. The information and studies on interaction of nanomaterials with the liquid have significant importance toward their usage in industrial applications. Agglomeration among particles is a common issue due to interactive forces, which effects the dispersion, rheology, and overall performance of nanosuspensions. Characterization of nanofluids plays an important role to evaluate the stability of nanofluids. The effect of agglomeration on the stability of nanofluids can be reduced by introducing different mechanical and chemical techniques to prolong dispersion of suspended particles in liquids. Complete understanding on the stability of nanofluids can lead to the preparation of different combinations of stable nanofluids with enhanced properties for variety of applications.

Keywords Agglomeration · Dispersion · Nanofluids · Nanoparticles · Stability

Nomenclature

a	Particle radius
a_1	Particle radius of sphere 1
a_2	Particle radius of sphere 2
A	Hamaker constant
A_1	Darcy's permeability constant
A_2	Modified permeability constant
d	Average diameter of particle, nm
d_0	Reference average particle diameter, 100 nm

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D_P Diameter of particle
g Gravitational constant
h Surface-to-surface separation distance
H Height of sediment due to consolidation
H_S Height of sediment/bed height
H_T Total height of sample
H_o Initial height of the sediment due to consolidation
H_∞ Equilibrium height of the sediment due to consolidation
K Thickness of electrical double layer
n Empirical constant
pH_f pH of base fluid
pH_{nf} pH of nanofluids
P_L Hydraulic excess pressure
T Absolute temperature, K
T_0 Reference temperature, 273 K
T_C Consolidation time factor
u Relative velocity of liquid to solids
U_C Average consolidation ratio
v Terminal settling velocity
v_R Potential energy per unit area between two spheres or plates
V_A Energy due to attractive forces
V_B Born interaction potential energy
V_R Electrical double-layer interaction potential energy
V_T Total interaction potential
x Distance
z_{1-8} Regression constants

Greek letters

σ_c Collision diameter
ρ_P Density of particles
ρ_f Density of fluid
μ Viscosity of liquid
ε Porosity
ω Volume of solids per unit cross-sectional area
φ Volumetric concentration of particles
ψ_o Particle surface potential

1 Introduction

Nanoscience and nanotechnology deal with the studies of atoms and molecules at nanoscale and controlling them for the development of efficient materials. The superlative explanation of nanotechnology in a single sentence by Pietsch (2005) states that '*Nanotechnologies deal with the border between the realm of individual atoms and molecules, where quantum mechanics rule, and the macroworld, where bulk properties of materials emerge from the collective behavior of a large number of atoms and molecules.'* In general, nanomaterials with size less than 100 nm are considered to be in the region of nanotechnology. However, micron-sized particles are considered to be bulk materials. A comparison of different materials and substances with respect to size is shown in Fig. 1.

Nanofluid is a subclass of nanotechnology which involves two-phase system, i.e., solids (nanomaterials) in liquids (base fluid). The nanomaterials are termed as engineered materials with nanoscale size. Nanomaterials can be in the form of particles, rods, tubes, sheets, and fibers. Some of the nanomaterials are shown in Fig. 2. Base fluid is termed as the solvent or liquid in which the nanomaterials are suspended to form a nanofluid.

The addition of engineered nanoparticles in liquids alters the overall thermophysical properties of liquids such as thermal diffusivity, thermal conductivity, density, viscosity, and specific heat capacity. Nanomaterials are usually dispersed in dilute concentrations (up to 9 %) in liquids to produce nanofluids. Higher concentrations of nanoparticles in liquid can lead to sedimentation due to poor stability. The notion of using tiny particles (up to micron level) in liquids to improve liquid properties was first experimentally studied by Maxwell in 1873 (Maxwell 1873). The concept was then followed by Ahuja in the 1970s (Ahuja 1975a, b) and later on by Choi and Eastman in the 1990s (Choi et al. 1992; Choi 1995; Eastman et al. 1999, 2001). The former studies include dispersion of 50–100 μm polystyrene spheres in glycerin to increase effective thermal conductivity for biomedical applications. The latter studies include experimental investigations on metallic and

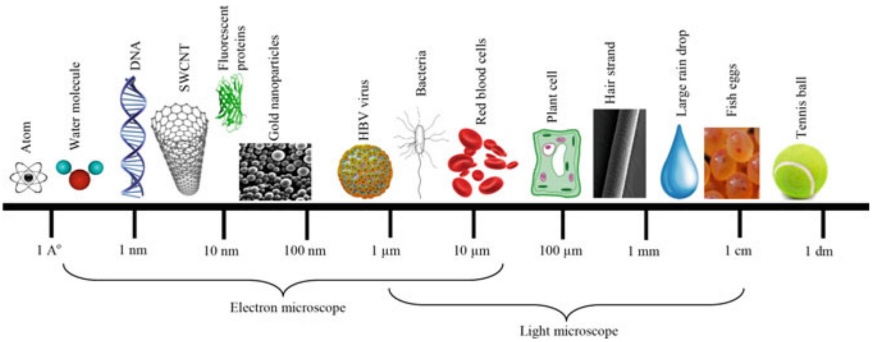

Fig. 1 Comparison of different materials with respect to size

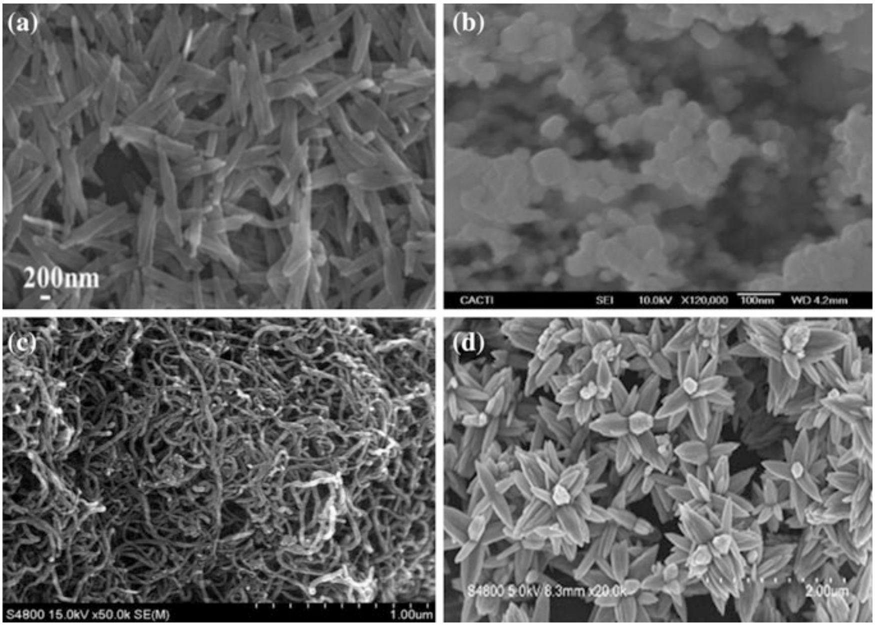

Fig. 2 SEM image of **a** CuO nanorods (Farbod et al. 2015) *adapted with permission*, **b** CuO nanopowder (Pastoriza-Gallego et al. 2011) *adapted with permission*, **c** multi-wall carbon nanotubes (MWCNTs) (Teng et al. 2015) *adapted with permission* and **d** ZnO nanoflower (Fang et al. 2009) *adapted with permission*

metallic oxide nanoparticles as heat carriers in ethylene glycol–water mixtures. A significant enhancement in effective thermal properties was found by the applications of such nano-sized particles. After successful experimental exploitation of these improved results, many researchers started investigations on the advancement and development in the field of nanofluids. Many articles have been published in the last decade demonstrating the significant potential of such smart fluids in wide range of industrial applications.

Stability of nanofluids is very important toward industrial applications. Many researchers have termed stability as the 'validity of nanofluids.' Dispersion behavior of different nanomaterials in solvent is different and depends on many factors. A complete understanding of interaction between particle–particle and particle–liquid is required to prepare a stable fluid. Over the years, the advancement in the equipment for characterization of nanofluids has helped researchers to synthesis nanomaterials in broad range of sizes and shapes. However, there are still some gaps toward the detailed information on the stability of nanofluids.

Recent progress and advancement in the field of nanofluids are discussed. A complete understanding on the dispersion behavior of colloids, interaction among particles, evaluation techniques to measure stability, and methods to prolong stability of nanomaterials in liquids is explained in detail.

1.1 Industrial Applications

Colloidal dispersions of nanoparticles have wide range of chemical industrial applications. Nanofluids have gained the attention of researchers due to attractive features. One of the main incentives of nanofluids is that it can be replaced with any conventional fluid depending on the application. One of the main applications of nanofluids is heat transfer intensification. There are numerous studies on the improved thermal properties of nanofluids. Nanoparticles with high thermal conductivities, when dispersed in liquid, increase the overall thermal performance of nanofluid (Ilyas et al. 2014c). Researchers have prepared highly effective thermal fluids by dispersing metallic (Au, Ag, Cu, Fe, Al, etc.), metallic oxides (Fe_3O_4, TiO_2, Al_2O_3, ZnO, CuO, MgO, etc.), and non-metallic (BN, SiC, synthetic diamond, etc.) nanoparticles in different base fluids and have found significant improvement in effective thermal conductivity and overall convective heat transfer coefficient.

The application of nanofluids in heat transfer processes has been reviewed and investigated in many studies. Experimental and theoretical studies by Xuan and Li (2000), Yu and Xie (2012), Wang and Majumdar (2007), Nguyen et al. (2008), and many others have opened a new horizon to prepare different combinations of nanofluids for heat transfer enhancement.

Nanofluids can provide much higher convective heat transfer rates than the conventional fluids and hence possess a great potential in automotive industry. The size of the radiator or engine cooling jackets can be reduced by the application of smart fluids in heavy duty engines (Pendyala et al. 2015). The overall efficiency of the automotive vehicles can be improved considerably by dispersing nanoparticles in engine oil and radiator coolant.

In a recent study by Sonage and Mohanan (2015), zinc and zinc oxide-based nanofluids in water were prepared at low concentrations (0.15–0.5 vol%) to study the enhancement in heat transfer coefficient at turbulent conditions (Re: 4000–20,000). It was found that the higher concentrations of nanofluids, i.e., 0.5 vol%, provide better heat transfer performance than lower concentrations. Surface area of the car radiator, fluid inventory, and pumping power can be reduced by 24, 40, and 16 %, respectively, by the usage of 0.5 vol% Zn/water nanofluids. Similar results were reported by Srinivas et al. (2015). They prepared Cu-, CNT-, Ag-, and Al_2O_3-based nanofluids in carboxylates of sebacic acid and water for automotive applications. There are some studies available on the nanoparticles dispersion in car fuel. In a recent investigation (Smirnov et al. 2015), Al (20 nm)/n-decane-based nanofluids were prepared and it was found that fuel with 2.5 % aluminum nanoparticles gives much higher temperature upon burning than the combustion of pure n-decane. The overall performance and fuel economy of automotives can be improved by the substituting nanofluids in car radiator, engine oil, brake oil, or fuel itself. The size of the heat transfer equipment can be reduced with the implementation of nanofluids. These fluids can be used as the future-generation cooling/heating media in aerospace industries which require lighter weight and decreased size of heat transfer equipment.

Investigations into nanofluids have proved that these fluids possess high boiling point than the base fluid alone. This can broaden the operating temperature range of coolant and dissipate more heat from the system. The efficiency of solar collectors can be improved by the implementation of nanofluids, as it depends on the absorption rate of operational fluid in solar collectors (Otanicar et al. 2010).

The advancement in electronic devices requires high level of heat dissipation systems in confined space due to compact design of systems. Nanofluid is an excellent choice of researchers to optimize thermal management as it can provide much better cooling than ordinary coolants in electronic devices with low surface areas to provide smooth operation. Duangthongsuk and Wongwises (2015) investigated the heat transfer behavior of SiO_2/water nanofluids at different concentrations (0.2–0.6 vol%) and found a significant enhancement (4–14 %) in thermal performance in heat sinks. In another study (Sohel et al. 2015), Al_2O_3/water-based nanofluids were used to dissipate heat from a mini-channel heat sink. It was reported that the thermal entropy generation rate reduced around 11.50 % as compared to water.

Nanofluids can be applied in building heating systems especially in the regions with cold environment. Ethylene glycol (EG) or propylene glycol (PG) mixtures with water (60:40) are usually used as heat transfer media. There are many studies available in literature on EG/water- or PG/water-based nanofluids. Experimental investigations by Eastman et al. (2001), Witherana et al. (2013), and Pastoriza-Gallego et al. (2014) have proven the applicability of such fluids in many engineering applications.

Applications of smart fluids in brake oil system are gaining attention of researchers. Brake systems require more improvement as drag force of the vehicle is reduced because of the improvement in aerodynamics of the vehicle. The efficiency of the brake systems depends on the mechanism of heat dissipation. Kao et al. (2007a, b) prepared CuO- and Al_2O_3-based nanofluids in brake oil using arc-submerged and plasma charging arc nanoparticle synthesis system, respectively. The increase in boiling point and thermal conductivity suggests that nanofluids can revolutionize lubrication and heat transmission industry.

Nanofluids play an important role in the field of drug delivery. Polymeric nanoparticle suspension is one of the important examples for efficient drug deliveries. A typical example of drug delivery is the control release of doxorubicin, for cancer treatment, entrapped in polyalkylcyanoacrylate polymeric systems. The particles contain an active component entrapped in polymeric core. Generally, a layer of surfactant surrounds the core to stabilize the system. Drug delivery systems can be improved by using nanofluids in pharmaceuticals and food industry (especially in delivery of bioactive components). The application of nanofluid technology can provide many advantages such as enhanced activity, control release, drug protection, and reduced side effects (Astete 2015).

Nanopaint is one of the recent advancements of nanotechnology in paints and pigment industry. There are many studies available on the insulating properties of nanopaints for interior and exteriors walls to act as a barrier for heat transmission. MgO-based nanofluids are also used as an additive to enhance bactericidal efficacy for interior wall paints (Huang et al. 2005).

Utilization of nanofluids in fuel cell industry is significant accomplishment in the field of nanotechnology. Nanofluid-based microbial fuel cells (MFCs) can be used to high energies from bacteria by improving MFCs efficiency (Sharma et al. 2008). In an investigation, zinc oxide nanofluids were used as anti-bacterial agent against *E. coli* bacteria, presumably due to interaction (electrostatic forces) between ZnO particles and bacteria cells (Zhang et al. 2008).

Researchers have used nanofluids with high thermal potential in three types of nuclear cooling applications, i.e., main reactor coolant, emergency core cooling systems, and in-vessel retention coolant. Recently, Nematolahi et al. (2015) investigated Cu-, CuO-, Al_2O_3-, Gd_2O_3-, HfO_2-, TiO_2-, and CdO-based nanofluids at different concentrations from 0.001 to 10 vol% as an efficient cooling media to control the temperature of hot core.

2 Agglomeration in Nanofluids

Stability of nanofluids is the main challenge toward their usage in applications and there are some important issues to be faced in two-phase system. The interactions among particles become dominant due to smaller size of particles and high surface area. Each particle in nanofluid system experiences different kinds of interactions. These interactions can be generated between particle–particle system and particle–liquid system (Ilyas et al. 2014a). These interactions are due to attractive and repulsive forces which generate or act on the particle surface. In general, attractive molecular forces are more dominant than other kind of interactions, which causes the particles to come closer. A lump of particles is formed because of attractive forces, which is termed as agglomeration. In general, the transformation of particulate material into larger entities due to interactions is known as aggregation effect. The agglomeration in nanofluids reduces the stability and uniformity of the nanosuspensions. Different scenarios of stable and unstable nanofluids are shown in Fig. 3.

Aggregation among particles is attributed to the following principles (Elimelech et al. 2013):

- Suspended particles in a fluid media must be in motion in such a way that particles remain in contact with each other. These collision phenomena can take place because of fluid motion, Brownian diffusion, or sedimentation.
- Interactions among particles must be in such a way that colloidal particles should remain intact. Particles that dominant repulsive interactions are known to be stable as they do not form aggregates.

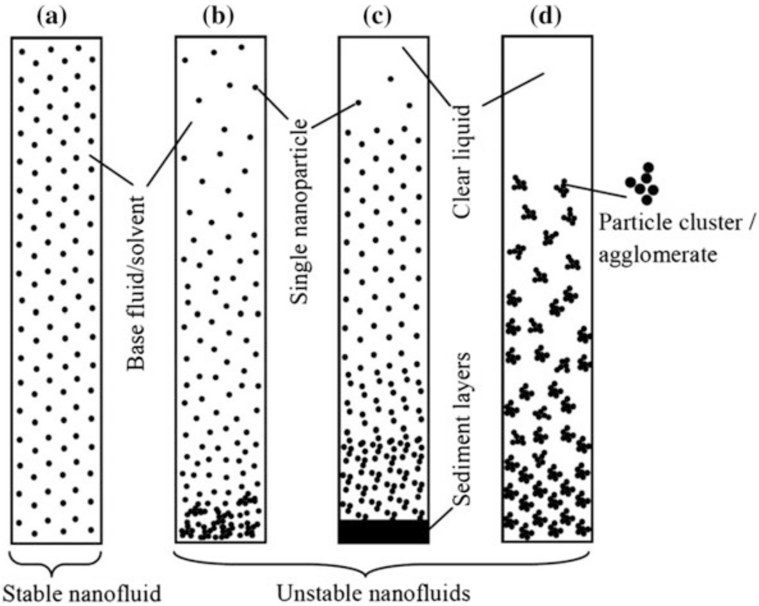

Fig. 3 Different scenarios of stable and unstable nanofluids

The types of interactions among particles during agglomeration process are explained by Pietsch (2005). There are three types of interactions between two moving particles in any suspension, i.e., molecular forces, electrical forces, and magnetic forces (Fig. 4). Molecular forces consist of van der Waals forces, valence forces (Free chemical bonds), and non-valance forces (hydrogen bonding). Interactions due to electrical forces can be due to electrical double layer, electrostatic or excess charge present on the particle surface.

Dispersion of particles in a suspension is also named as colloidal dispersions. Colloid can be liquid–liquid mixture or solid–liquid mixture. In the case of nanofluids, a colloid is termed as two-component system with particles of range from 1 nm to 1 μm, and the motion of the particles is highly affected by thermal forces. Examples of colloidal suspensions are found in multitude of industrial, biological, and natural processes. The information and understating of interactions and rheological flow behavior and the factors affecting rheology of such suspensions have significant importance toward preparation of desired product. By manipulating interactions among particles, nanosuspensions can become ultra-efficient for advanced applications such as heat transfer processes, pharmaceuticals, food, polymers, paints, and pigments.

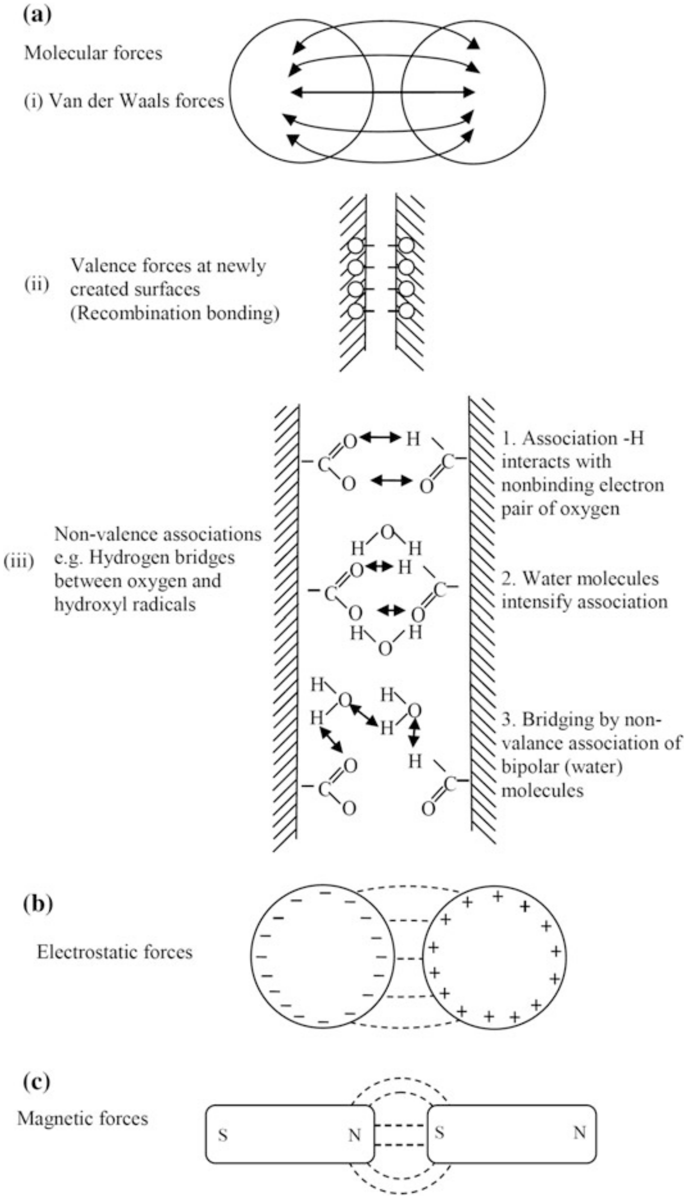

Fig. 4 Different types of interaction forces among particles and solid surfaces (Pietsch 2005) *adapted with permission*

2.1 DLVO Theory

Stability of nanofluids strongly depends on the interaction between particles and suspension. DLVO theory was proposed by B. Derjaguin, L. Landau, E. Verwey, and J. Overbeek in 1940s (Verwey and Overbeek 1948). This theory is a quantitative explanation of such forces which affects the stability of colloids in suspension. The theory is quintessential for explanation about the interactions and separations of colloids caused by the balancing of two adverse forces, i.e., electrostatic repulsion forces and van der Waals attraction forces. The total interactions between two particles are associated with both electrostatic double-layer forces and van der Waals forces. The double-layer repulsive forces are stronger at larger separations of particle surfaces while the attractive forces are dominant when the distance between the two particle surfaces is less. The total interaction energy is the sum of all repulsive, and attractive forces are given as (Eq. 1)

$$V_T(h) = V_A(h) + V_R(h) \tag{1}$$

where $V_T(h)$, $V_A(h)$, and $V_R(h)$ are the total interaction potential, van der Waals attractive energy, and electrostatic repulsive energy as a function of h, which represents minimum separation distance between two surfaces. The theory proves that the electrostatic double-layer forces prevent the particles to approach one another due to an energy barrier between them. In such scenario, a stable dispersion can be obtained which can resist agglomeration due to the repelling forces among particles. Formation of aggregates will be highly likely if the repulsion is not enough. If the particle surfaces collide with adequate energy, the van der Waals forces can attract the particles toward each other to overcome the barrier to form agglomerate.

The van der Waals attractive interaction and electrostatic repulsion are given in Eqs. (2) and (3), respectively (Zhu et al. 2009).

$$V_R(h) = 2\pi\varepsilon\psi_o^2 \ln\left[1 + e^{-kh}\right] \tag{2}$$

$$V_A(h) = -\frac{A}{6}\left[\left(\frac{2a^2}{h^2+4ah}\right) + \left(\frac{2a^2}{h^2+4ah+4a^2}\right) + \ln\left(\frac{h^2+4ah}{h^2+4ah+4a^2}\right)\right] \tag{3}$$

where ε, ψ_o, and k represent permittivity of the medium, particle surface potential, and thickness of electrical double layer surrounding the particle, respectively. The double-layer interaction energy between spherical particles can also be given by integral equation (Eq. 4) by Derjaguin (1934)

$$V_R = \frac{2\pi a_1 a_2}{a_1 + a_2}\int_h^\infty v_R \mathrm{d}x \tag{4}$$

2.2 Non-DLVO Forces

The importance of two principal interactive forces has been well demonstrated by classical DLVO theory. However, there are more forces which should be taken into account because combinations of two principal forces alone are not in agreement with experimental results by many researchers (Elimelech et al. 2013). The major non-DLVO forces are Born repulsion, hydration forces, and hydrophobic interactions.

The Born repulsion forces are originated when the electron shells are interpenetrated with each other because of strong repulsive forces between atoms. The Ruckenstein and Prieve (1976) equation (Eq. 5) explains the phenomenon of Born repulsion in sphere plate

$$V_B = \frac{A\sigma_c^6}{7560}\left[\frac{8a+h}{(2a+7)^7} + \frac{6a-h}{h^7}\right] \tag{5}$$

where σ_c represents collision diameter of the order 0.5 nm.

The hydration force is a repulsive interaction which takes place due to adsorption of water molecules at each interface. There is a possibility of hydration of particles with ions present in solution because most of the nanoparticles carry a surface charge or ionic groups (Elimelech et al. 2013). The effect of hydration forces on the overall interaction becomes stronger below 5 nm. The particle surface is termed as hydrophobic when there is no hydrogen bond or ionic group attached and there is no room for water molecules. The attractive interactions take place because of the strong interaction between water molecules and weak interaction between water and organic groups. The effect of these forces can be significant below 8 nm.

2.3 Effect of Stability on Thermal Properties

Thermal properties of nanofluids such as thermal conductivity, specific heat capacity, density, and viscosity depend on the stability of nanofluids. Most of the suspended particles in unstable nanofluids are in the form of large agglomerates. The average agglomerate diameter of the particles can reach up to micron sizes from few nanometers of primary size of nanoparticles. The size of particles is a main factor for the estimation of thermophysical parameters of nanofluids. There are questions raised by many researchers on the validity of reported thermophysical data of nanofluids. To ensure the accuracy of data, characterization analysis on each stage of preparation must be done to ensure proper stability of nanofluids.

3 Nanofluids Preparation Methods

Nanofluid stability is highly dependent on the method of preparation. In order to fully understand the phenomenon of stable nanofluid preparation, the information on the production and properties of primary nanomaterials and base fluids is very important. Nanomaterials production involves two different approaches, i.e., top-down methodology and bottom-up methodology. In the former method, a bulk material is modified into desired shape and size with the help of different machining techniques in such a way that the original integrity of the material remains constant. Milling and grinding of bulk materials is one of the important synthesis techniques of top-down method. The bulk material with micro-sized crystals is broken down into nano-sized crystal structures. This method is mostly used to produce metallic or metallic oxide nanomaterials. During this process, crystallites react with each other in the presence of kinetic energy to get desired shape and size of the product. Another example of the top-down methodology is the production of integrated circuits which includes crystal growth, lithography, etching, and ion implementation. The latter technique of producing nanomaterials involves the assembly of complex nanomaterials from simple atoms or molecules. This technique is not as extensively used in industrial scale as compared to top-down approach but extensive research is being carried out as an alternative method to lithographic approach. Examples of bottom-up methodology include laser ablation and sol–gel technology.

Nanofluids can be produced by two methods: single-step method and two-step method. In the single-step method, nanomaterials are prepared and dispersed in the liquid simultaneously. In two-step method, nanoparticles are produced separately and then dispersed in the base fluid using different mixing techniques to form a nanosuspension.

3.1 Single Step

In this method, nanoparticles are produced and dispersed in the primary liquid simultaneously. Generally, a chemical reaction is involved to carry out nanofluids preparation. The different techniques include microwave irradiation technique, vapor deposition (VP) methods, thermal decomposition, grafting, submerged arc nanoparticle synthesis system (SANSS), and phase transfer techniques. Some of the nanofluids can only be prepared by single-step method which depends on the properties of particles, properties of base fluid, interactions, and product application requirement. The advantage of this nanofluid preparation approach over two-step method is that a highly stable nanoparticle dispersion can be obtained. Agglomeration effect in these types of nanofluids is not significant. A better stability is obtained with longer dispersion periods of nanoparticles in liquids.

Despite of better stability, there are many disadvantages of single-step approach. The applications of such nanofluids, prepared from single-step method, are limited to process with low vapor pressure. The other predicament in this method is the challenging issue of controlling the size and structures of nanoparticles. The reactants are not completely converted into products and the possibility of presence of different impurities is very high. One more quandary factor in this process is the high cost of preparation as compared to two-step approach (Yu and Xie 2012).

Studies are available on the preparation of nanofluids with highly stable dispersion characteristics using single-step approach. In an investigation (Zhu et al. 2007), copper nanofluids were synthesized using transformation method aided with microwave irradiation of copper hydroxide. To achieve good stability, ammonium citrate was used to stop aggregation process of nanoparticles. Yu et al. (2010) prepared Fe_3O_4/kerosene oil-based nanofluids using phase transfer method. Feng et al. (2006) synthesized Au-, Ag-, and Pt-based nanofluids using phase transfer method in oil–water systems. In investigations by Singh and Raykar (2008) and Kumar et al. (2003), silver-based nanofluids were prepared in ethanol and hexane using microwave-assisted synthesis and phase transfer method, respectively. In another study, zinc-based nanofluids were prepared in aqueous media using vapor condensation process. First, the bulk zinc material was heated up to 907 °C (boiling point) and then vapors were condensed into water. The estimated size of the zinc nanoparticles was reported to be 41 nm with high dispersion behavior in water (Sonage and Mohanan 2015).

3.2 Two Step

Two-step method is the most widely used preparation technique for nanofluids. In this method, dry nanopowder is obtained from physical or chemical synthesis and then dispersed in the liquid media to prepare nanofluids. A growing number of industrial-scale nanoparticles with high purity and variety of controlled sizes are commercially available. Generally, a shear mixing is required to disperse nanoparticles in base fluid. Nanofluids dispersed using two-step method show higher agglomeration rates than nanofluids prepared from single-step method.

Nanofluids can be prepared in different concentrations while in single-step method the nanofluid concentration is not uniform. In single-step method, the concentration of nanoparticles in host fluid is mostly altered by dilution or evaporation. Characterization analysis is carried out before and after preparation process to evaluate the stability of nanosuspensions. There are many ways to enhance the stability of nanofluids, mentioned in next sections. A generalized methodology to prepare stable nanofluids using two-step approach is shown in Fig. 5.

During storage, transportation, and handling of dry nanoparticles, the primary size of nanoparticles can change up to micron level due to dominant particle–particle attractive interactions. There are several investigations on the preparation of different nanofluids using two-step method. Preparing nanofluids using two-step method is the most economical method. Nanofluids can be prepared in bulk quantity using this approach. Some of the studies are tabulated in Table 1.

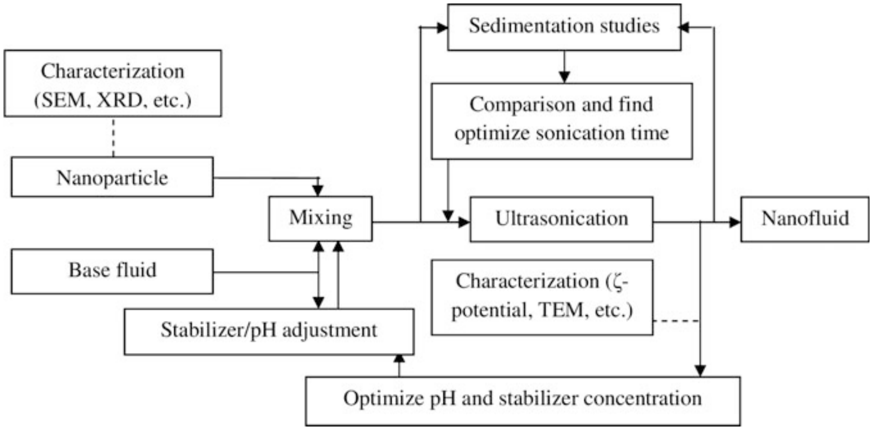

Fig. 5 Methodology for preparing stable nanofluids using two-step method (Ilyas et al. 2014a) *adapted with permission*

Table 1 Investigations using two-step method

Investigator	Nanofluids system	Remarks
Nayak et al. (2009)	Alumina/water	Nanofluids were prepared after ultrasonication (ultrasonic bath) for 4 h. Settling velocities and thermal hydraulic characteristics of nanofluids at different concentrations were estimated
Mahbubul et al. (2014)	Alumina/water	Increase in ultrasonication time decrease average agglomerate size
Sunder et al. (2012)	Fe_3O_4/water	Heat transfer coefficient increases from 21 to 31 % by the addition of 0.6 vol% nanoparticles at different Reynolds number
Farbod et al. (2015)	CuO/engine oil	8.3 % increase in effective thermal conductivity with 6 wt% of nanorods dispersions
Sekhar et al. (2013)	Al_2O_3/water	8–12 % increase in heat transfer coefficient using nanofluids in plain tube as compared to water
Alberola et al. (2014)	Halloysite/water	8 % increase in thermal conductivity with 5 vol% of Hal nanotubes in water at 80 °C as compared to water
Suresh et al. (2012)	Al_2O_3–Cu (hybrid) /water	10.94 % increase in average Nusselt number using hybrid nanofluid system as compared to pure water
Zhang et al. (2013)	Al_2O_3/R141b	Heat transfer effectiveness increases by 110 % by using 0.01 vol% alumina/R141b as compared to R141b as a working fluid

4 Stability Evaluation Methods

Stability of nanofluids can be determined by performing characterization analysis. The recent development in the field of material science especially nanotechnology could not be possible without the innovation and development of characterization equipment.

4.1 *Electron Microscopy*

The essential characterization technique involved to evaluate stability of nanofluids is the use of electron microscopy. Electron microscopy focuses on the illumination of electrons to generate an image of the material. This technique is useful to display the nanoscale materials with much detail because of high magnification. Electron microscope can determine the particles with lower wavelengths than ordinary. Optical microscopes are the most commonly used technique to examine the quality of dispersion. However, it is not possible to examine nano-sized particles. The function of electron microscopy is similar with the optical microscopy; however, the former analysis uses a focus beam of electrons while the latter analysis uses electromagnetic radiation to generate the image of the material. Generally, particles with average diameter less than 0.5 μm are not visible in optical microscopes. Electron microscopy generates the image of the material through electromagnetic and electrostatic lenses. The advancement in electron microscopy makes it very useful to get the material properties such as morphology, crystalline structure, composition, and topography of the specimen. Information on morphology of the nanomaterials helps to determine the shape, size, strength, and ductility of the particles. The recent progress in this field helps the researchers to identify the arrangement of atoms and molecules in the crystalline structure as well as the composition of compounds and elements present in the specimen using energy dispersive X-ray (EDX) analysis. Two of the major types of electron microscopic analysis used in nanotechnology are scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

4.1.1 SEM

The scanning electron microscope (SEM) is a proficient type of electron microscopy which can produce high-resolution images of the nanomaterial surface to characterize surface structure of the nanomaterial by three-dimensional appearance. The structure, texture, and the agglomerate size can be determined using SEM analysis.

4.1.2 TEM

Transmission electron microscopy (TEM) is another type of electron microscopy which comprises an electron gun. This gun emits electron beam of high energy to transmit through the nanomaterial sample and creates an image of the inner structure of the material. Two major modes of TEM are dark-field imaging and bright-field imaging. The development of high-resolution transmission electron microscopy (HRTEM) can indicate the crystallographic structure of specimen even at atomic level. Currently, the accessible highest resolution of TEM is equivalent to 0.5 A^o. Some of the examples of TEM analysis of different nanofluids are shown in Fig. 6.

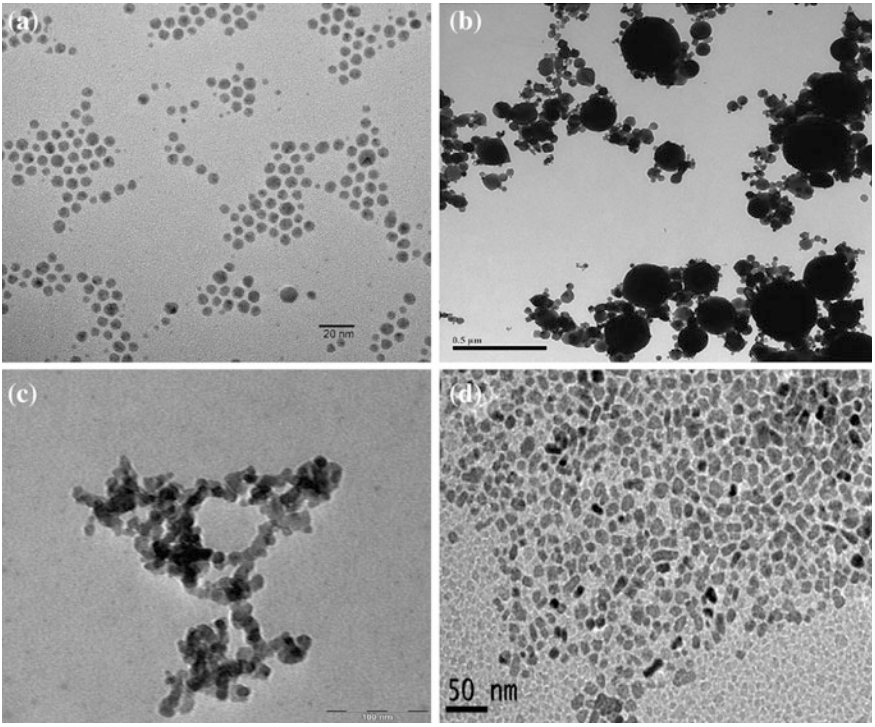

Fig. 6 TEM image of **a** silver nanoparticles in basic media (Li et al. 2010) *adapted with permission*, **b** TiO_2/water nanofluid (Allouni et al. 2009) *adapted with permission*, **c** Al_2O_3/water nanofluid (Said et al. 2013) *adapted with permission* and **d** CuO/water nanofluid (Pastoriza-Gallego et al. 2011) *adapted with permission*

4.2 Sedimentation Techniques

Sedimentation of nanoparticles in nanosuspensions is a natural phenomenon due to gravity which is aided by aggregation among particles. Sedimentation analysis is a simple technique to evaluate the stability of nanofluids. Due to the smaller size of dispersed nanoparticles in liquid, the particle motion behaves as fluid motion. Theoretically, gravity forces on particles with diameter less than 1 μm are not effective. However, agglomeration among particles increase the average diameter of the particle cluster and particle tends to settle down much faster due to dominant gravity forces acting on the agglomerate. There are three types of sedimentation in nanosuspensions, i.e., dispersed-type settling, flocculated-type settling, and mixed-type settling (Ilyas et al. 2013).

Dispersed-type settling behavior can be seen in nanosuspensions with low particle loading where the sediment height increases from bottom to top. The nanoparticle concentration more than critical concentration (equivalent to 1 %) exhibits flocculated-type settling behavior. In this case, the sediment height decreases from top to bottom and the solution becomes clearer from the top. In mixed-type settling, multilayer separations of the particles can be seen. This appearance of multilayers is due to the different agglomerate sizes which settle down at different terminal velocities and hence creating multi-phase separations. Dispersed-type sedimentation process of particles follows Stokes law and is highly dependent on the square of particle/agglomerate size, given as (Eq. 6)

$$v = \frac{gD_P^2(\rho_P - \rho_f)}{18\,\mu} \tag{6}$$

The sediment heights can be recorded over time using visualization technique. Generally, a high-speed camera is used to determine settling velocities of nanosuspensions. Sediment ratios (SR) can be obtained in terms of sediment height (H_S) and total height of the sample (H_T) using Eq. 7

$$\mathrm{SR} = \frac{H_S}{H_T} \tag{7}$$

The settling of particles exhibiting flocculated-type sedimentation is due to consolidation process. In this process, the liquid move upwards through different pores of solid particle clusters. These particle clusters form a bed of different sediment layers and settle down with the passage of time. The sediment bed further consolidates under its own weight, when the upper layers of the sediment exert pressure on the lower sediment layers. The consolidation effect was extensively explained by Shirato et al. (1970). A correlation of relative liquid velocity was proposed using Darcy's law in terms of porosity, differential volume, and hydraulic excess pressure, given in Eq. 8. To determine the average consolidation ratio (U_C), the simple analytical solution was derived by Iritani et al. (2009), given as (Eq. 9)

$$u = -\left(A_1 \frac{(1-\varepsilon)}{\mu}\right) \frac{\partial P_L}{\partial \omega} = -A_2 \frac{\partial P_L}{\partial \omega} \tag{8}$$

$$\begin{aligned} U_C &= \frac{H_o - H}{H_o - H_\infty} \\ &= 1 - \frac{32}{\pi^3} \sum_{n-1}^{\infty} \frac{(-1)^{n-1}}{(2n-1)^3} e^{\left(-\frac{\pi^2 (2n-1)^2}{4} T_C\right)} \end{aligned} \tag{9}$$

4.3 Spectral Analysis

Spectral analysis is one of the important techniques to analyze stability of nanofluids. This type of analysis is carried out on the basis of degree of absorption to examine different properties of nanofluids. Ultraviolet (UV)-visible (Vis) spectroscopy is the most widely used method for spectral analysis of nanofluids. It operates on the principal of absorption spectroscopy in UV visible spectral region. This analysis is only limited to UV-active nanomaterials. Quantitative results are obtained through UV–Vis spectroscopy analysis on the basis of concentration of nanofluids.

LotfizadehDehKordi et al. (2013) investigated the stability of TiO_2/water nanofluids using UV–Vis spectrophotometer at different concentrations and sonication time and power. The optimum conditions were found using Box–Behnken method to achieve high stability after 1 week and 1 month of study on the basis of quantitative analysis of absorption values.

4.4 Zeta Potential

Zeta potential is the measure of interfacial potential between the attached thin layer on the surface of the particle and the dispersion medium. This quantitative analysis determines the repulsive interactions between the particle and the dispersant. Zeta potential is denoted by ζ with the units of mV. Higher zeta potential values indicate high stability of nanosuspensions. Colloidal suspension with ζ-potential 0 to ± 5 mV exhibits poor stability with high agglomeration rates. Nanosuspensions with ζ-potential values more than ± 30 mV are considered to be stable for longer time. Zeta potential values can be altered by changing the pH of the suspension, surface coatings, and functionalization of nanomaterials or by adding surfactants.

Allouni et al. (2009) studied the aggregation affects of titanium dioxide particles in cell culture medium using zeta potential analysis. The effect on ionic strength and electrokinetic properties of titania nanofluids by the addition of human serum albumin (HSA) and fetal bovine serum (FBS) was investigated.

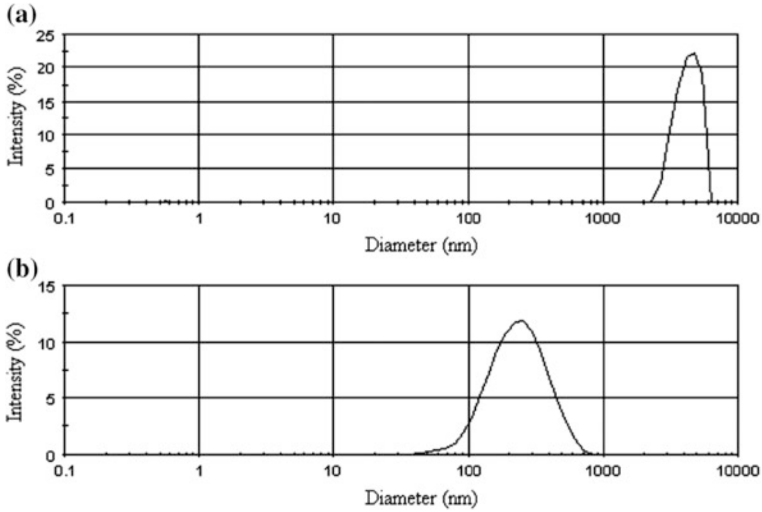

Fig. 7 Particle size distributions of alumina/water nanofluids (0.05 wt%) **a** without and **b** with surfactant (SDBS) (Zhu et al. 2009) *adapted with permission*

4.5 Dynamic Light Scattering

Dynamic light scattering (DLS) technique is used to quantify particle size in nanosuspensions. This analysis identifies the average agglomerate size in liquid. The average particle size is analyzed when the specimen is illuminated using a laser beam and then the fluctuations of scattered light is detected by photon detector. Particle size distribution curves are obtained on the basis of intensity or volume. This method can obtain particle size distribution curves for particles of size as low as 1 nm. Li et al. (2012) investigated the dispersion behaviors of natural- and surface-modified Fe_3O_4/oil nanofluids using particle size distribution curves. In another study, Zhu et al. (2009) studied the effect of surfactant (Sodium dodecyl benzene sulfonate, SDBS) on the stability of alumina nanofluids using particle size distribution curves, as shown in Fig. 7.

5 Ways to Improve Stability

With the help of modern advancement in characterization techniques, it is possible to alter the interactions in nanosuspensions. A uniform and highly stable nanofluid can be obtained by the application of certain mechanical and chemical methods.

5.1 Mechanical Mixing Techniques

Nanofluid preparation includes different mechanical mixing techniques to attain high stability. Mechanical mixing has significant importance toward de-agglomeration of nanoparticles without changing the original particle size. Major examples of this technique include ultrasonication, high-pressure homogenizer, and wet milling. These types of methods are more suitable for nanofluids with low particle concentrations.

5.1.1 Ultrasonication

Ultrasonic agitation is a type of mechanical mixing technique in which the ultrasonic waves are passed through the nanosuspension causing distortion among different layers of sediment. This distortion breaks big agglomerates into smaller agglomerates and a uniform nanosuspension is achieved. Stability of nanofluids is influenced by sonication frequency and sonication time. Both parameters are directly proportional to the better stability of nanosuspension. However, few studies illustrate that excess sonication has negative impact on the stability of nanofluids. Studies by Kole and Dey (2012) indicated that average agglomerate size increases after excess sonication (i.e., 60 h) of ZnO/ethylene glycol nanofluids. Lee et al. (2008) reported the decline in stability of alumina/water nanofluids after 5 h of sonication. In another study (Kwak and Kim 2005), average particle size of CuO/ethylene glycol nanofluids was observed to be increasing after continuous sonication of 9 h.

Different types of commercial ultra-sonication agitators are commercially available such as bath-type sonicators and probe-type sonicators. Probe-type sonicators are found to be effective than all other types of sonicators. The probe-type sonicator or ultrasonic rupture operates in such a way that all waves generated from the probe pass through the suspension. This causes deterioration of sediment folds and a uniform suspension is obtained. Some of the energy from ultrasonic waves is absorbed by the nanosuspension which increases the kinetic energy of molecules. The transport of ultrasonic waves increases the temperature of the specimen. A cooling jacket with continuous flow of cooling media is required to dissipate the excess heat from the sample as agglomeration effects are aided by the increase in temperature. Bath-type sonicators are less effective than probe-type sonicators. In this case, the nanosuspension is immersed in a water bath and the sonication waves pass through the water toward the specimen. Most of the sonication waves do not pass through the sample due to the resistance of glass wall of the sample container. This resistance decreases the effectiveness of this process. Generally, bath-type sonicators take more time and power to de-agglomerate nanosuspension as compared to probe-type sonication.

Rehman et al. (2012) studied sedimentation rates of alumina/water suspensions at different concentrations (1–5 wt%) and ultrasonication times. It was found that

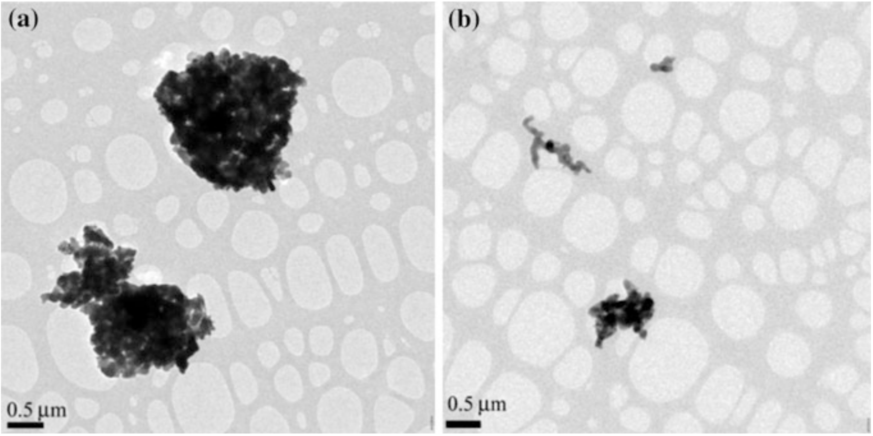

Fig. 8 TEM images of alumina/water nanofluids (1 vol%) after **a** 1 h and **b** 5 h of ultrasonication (Barrett et al. 2013) *adapted with permission*

nanosuspensions with high particle loading showed high agglomerate sizes. In another study (Ilyas et al. 2014b), the settling rates of zinc oxide nanoparticles in ethanol–water mixtures were reduced by the application of ultrasonic bath. Ultrasonication of nanofluids was found to be an effective method to reduce average particle size. The size of agglomerate was decreased by the increase in ultrasonication time. Similar results were found in the studies by Barrett et al. (2013). A stable nanosuspension of alumina/water (1 vol%) was obtained after 5 h of ultrasonication. The TEM images of alumina/water nanofluids are shown in Fig. 8. The effect of ultrasonication on the settling behavior of ZnO nanoparticles in the ethanol–water mixtures is illustrated in Fig. 9 (Ilyas et al. 2014b).

5.1.2 High-Pressure Homogenizer

The most effective de-agglomeration method is the high-pressure homogenization, which is purely a mechanical process. The nanofluids are stabilized by passing through with force in a narrow gap at high-pressure conditions. The subjected shear stress on the nanofluid ruptures big agglomerates into smaller agglomerates. The process is repeated many times until a stable and well-dispersed nanofluid is obtained. Ultra-high-pressure homogenizers operate at very high-pressure and micro-sized agglomerates are converted into primary nano-size.

Hwang et al. (2008) used high-pressure homogenizer to stabilize carbon black (CB) nanoparticles in water and silver nanoparticles in silicon oil. Different mixing techniques were used and comparative studies showed that high-pressure homogenizer is the most effective method to attain uniform nanosuspension. The comparative studies of different mixing techniques by Hwang et al. (2008) are shown in Fig. 10. The quality of CB/water dispersion (0.5 wt%) with normal mixing

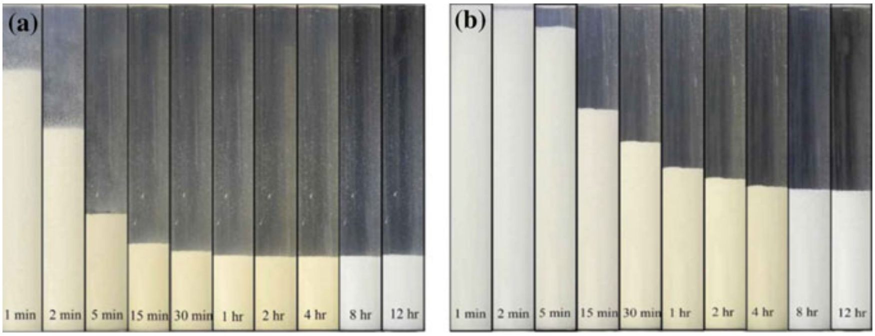

Fig. 9 Settling rates of nanoparticles in base fluid with and without sonication (Ilyas et al. 2014b) *adapted with permission*

(stirring), ultrasonication (bath type and probe type), and high-pressure homogenization is described.

In a recent investigation by Fontes et al. (2015), high-pressure homogenizer was used to disperse multi-wall carbon nanotubes (MWCNTs) and synthetic diamond in mineral oil. The nanosuspensions with different particle loadings exhibit better stability over 24 h. This technique can be applied in many industries to produce nano-emulsions, especially in foods, pharmaceuticals, cosmetics, and paint and pigment industries. The heat of compression causes a sudden increase in temperature of nanofluid. In general, 17–21 °C of rise in temperature takes place per 100 MPa of homogenization. This predicament in this process can affect the production and quality of sensitive food components. The temperature-controlling mechanism or heat dissipation systems are required to achieve better quality of nanosuspension.

5.1.3 Wet Milling

Milling process is used in size reduction of materials. Dispersion characteristics of nanoparticles in liquid can be improved by the use of wet milling process. Wet ball/bead milling of nanofluids can enhance the stability of nanoparticles as the agglomerates are broken into smaller ones. The stability of nanofluids using this method is highly dependent on the sizes of different grinding media, operational time, and rotational speed of the mill. In an investigation by Munkhbayar et al. (2013), influence of milling on the stability of carbon nanotubes in aqueous solutions was investigated. It was reported that milling has significant impact on the dispersion characteristics of nanosuspensions. This process is highly effective when combined with chemical technique (surface modification). The surface area of the nanomaterial increases with the operational time and helps the chemical agent to retain and make bonds on the surface of nanomaterial. Joni et al. (2009) prepared TiO_2/diglyme nanosuspensions using bead milling process. Silane coupling agents

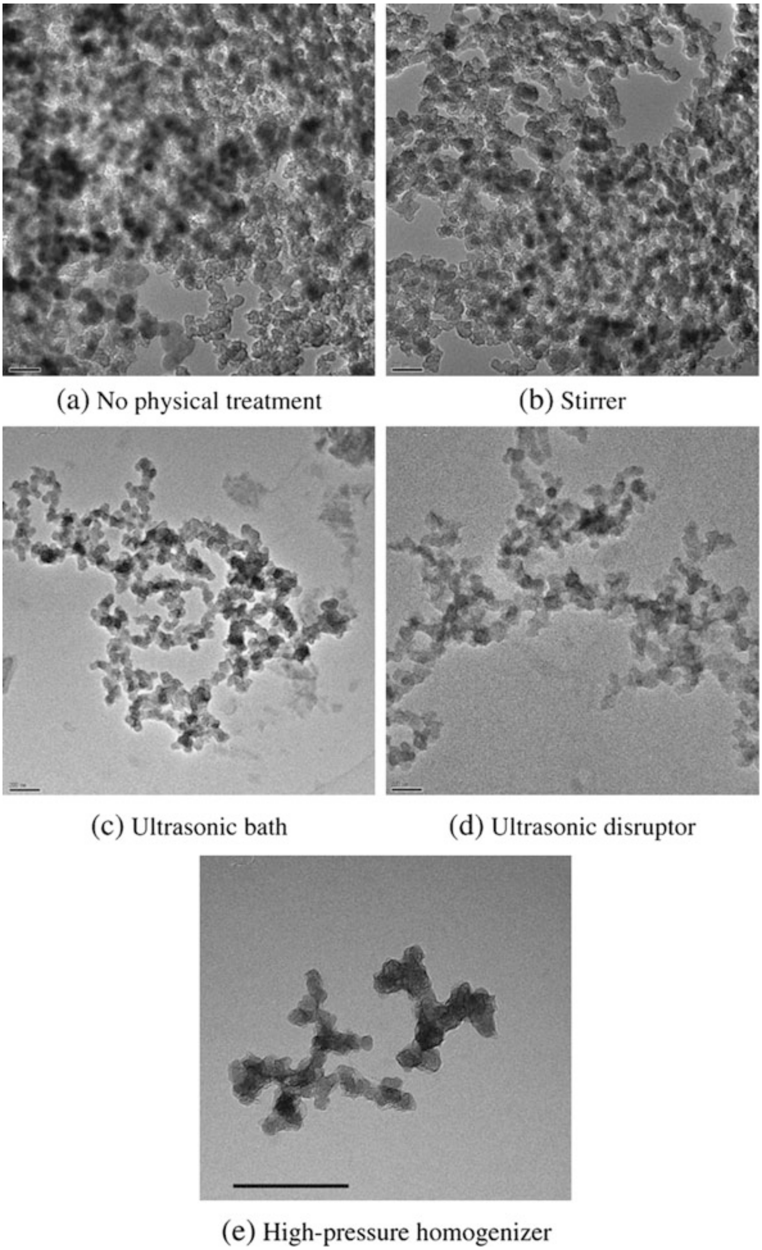

Fig. 10 TEM images of carbon black nanoparticles in water using different mechanical mixing techniques (Scale bar: 200 nm) (Hwang et al. 2008) *adapted with permission*

were introduced to modify the surface of titania during milling process to enhance dispersion stability. A uniform nanosuspension was obtained with 80 mV of zeta potential and particle size was reported to be very close to primary particle size, i.e., 15 nm. In a recent investigation by Farbod et al. (2015), a better stability of copper oxide was found in engine oil by the application of milling process for 3 h at 300 rpm.

Nanomaterials in low quantity can be lost during operation and cleaning of milling process. Furthermore, this method is not effective as compared to other methods because of the possibility of change in the primary shape and size of the nanomaterials. The particle size distribution of the original nanomaterial particularly nanotubes, 2D nanofillers, nanowires, and other structural nanomaterials can be altered during wet milling of nanofluids.

5.2 Chemical Techniques

Chemical techniques have peculiar advantages over mechanical mixing techniques. Mechanical mixing techniques can separate nanoparticles from particles cluster but they are likely to agglomerate again over time during operation. The stability of nanofluids can be prolonged by the use of chemical techniques such as addition of surfactants, pH adjustment, and surface modification of nanoparticles. Investigations till date report that the combination of mechanical and chemical techniques is the most effective way of preparing stable nanofluids for their application at industrial level. There are two types of stability mechanisms, i.e., steric repulsion and electrostatic repulsion. Steric stabilization mechanism involves the use of polymeric compounds which are adsorbed on the particle surface and provides extra repulsive forces on the surface of particles. These surface modifications weaken the attractive forces between particles, and a better stability is achieved. Electrostatic stabilization is a kinetic stability method that involves surface charges which are developed on the surface of nanoparticles creating a barrier between particles. Existences of these charges on the particle surface are due to the depletion or accumulation of electrons on the surface of the particle. Steric stabilization is insensitive to the electrolytes or pH. A large quantity of surfactant is required to functionalize or coat the particle surface as compared to electrostatic stabilization. Electrostatic stabilization is highly sensitive to pH or presence of electrolyte in the nanosuspension. Both colloidal stabilization mechanisms are well demonstrated by Yu and Xie (2012), as shown in Fig. 11.

5.2.1 Surfactant Addition

Surfactants are used to alter the surface properties of nanoparticles in nanofluids. Surfactants are also termed as dispersants or stabilizers. Addition of surfactants in nanofluids, exclusively in two-step preparation method, is the most simple and

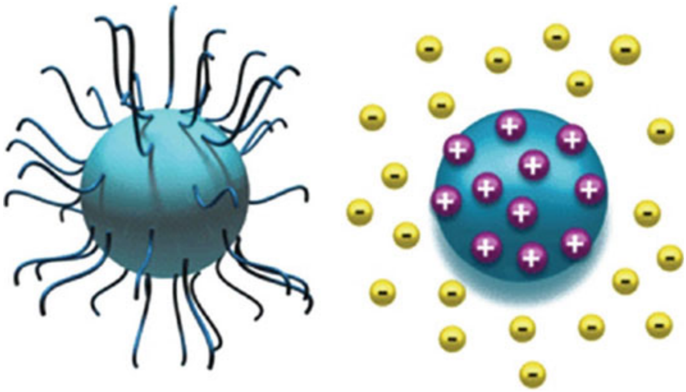

Fig. 11 Difference between steric and electrostatic stabilization (Yu and Xie 2012) *adapted by permission*

economical method of preparing stable nanofluids. The surface tension of the liquid is abated and the particle engagement is escalated in the host fluid by the introduction of surfactants. A rise in zeta potential is obtained due to increase in repulsive force generating from the particle surface. The hydrophobic surfaces of the nanomaterials in aqueous-based nanosuspensions are modified into hydrophilic surface. Similarly, the hydrophilic surfaces of the nanomaterials are modified into hydrophobic for non-aqueous nanofluids. Most of the surfactants consist of long-chain hydrocarbons with hydrophobic component in one corner and hydrophilic component on the other. The presence of these two components provides a strong linkage on the interface between particle and liquid. Sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), cetrimonium bromide (CTAB), and gum Arabic are the most widely used surfactants used to disperse nanoparticles in many commercial fluids.

Selection of suitable surfactant has significant importance toward dispersion characteristics of nanofluids. Yu and Xie (2012) stated that there are four types of surfactants, i.e., cationic, anionic, nonionic, and amphoteric surfactants.

- Cationic: long-chain quaternary ammonium compounds and long-chain amines
- Anionic: sulfonates, sulfosuccinates, long-chain fatty acids, phosphates, and alkyl sulfates
- Nonionic: alcohols, polyethylene oxide, and other polar groups
- Amphoteric: betaines and lecithins

The concentration of surfactant can influence the surface properties. Inadequate concentrations of surfactants in the suspension can dissuade repulsive forces and persuade attractive forces due to improper surface coating. High concentrations of surfactants can alter thermophysical properties of the nanofluid system. The risk of failure of surfactants in high-temperature applications is very likely. Another quandary factor in the use of surfactant is the production of foam during operation of nanofluids with surfactants.

Kole and Dey (2010) stabilized alumina/EG:water-based nanofluids by using oleic acid as surfactant. Nanosuspensions with surfactants exhibit no sediment even after 80 days of preparation while nanofluids without surfactants exhibited sediments after two hours of preparation. Iyahraja and Rajadurai (2015) used polyvinylpyrrolidone (PVP) and SDS to stabilize silver nanoparticles in water. SDS-based nanofluids exhibit better stability than PVP-based nanofluids. However, PVP-based nanofluids demonstrated higher thermal conductivity values than SDS-based nanofluids.

5.2.2 Surface Modification

Surface modification of nanoparticles is a surfactant-free method and a long-term solution of attaining high dispersion characteristics of nanofluids. This method includes grafting, chemisorptions, plasma treatment, and many other techniques. The surface of the nanoparticle can be linked or modified with hydrophobic or hydrophilic component, depending on the application, to perform better stability in the nanosuspensions. The advantages of this method of stabilizing nanomaterials over other methods are that the modified particles tend to remain suspended for longer time. The effect on thermophysical properties of the nanofluids is negligible; however, effective thermal conductivity and specific heat capacity can be elevated depending on the properties of functionalizing agents. The toxicity and the polarity of some nanoparticles can be altered using this surface modification process.

Yu-zhen et al. (2010) dispersed three types of TiO_2 nanoparticles in transformer oil. Nanoparticles without surface modification, surface modification with stearic acid, and surface modification by silicon oil were used to study the effect of different types of particles on the breakdown strength of transformer oil. It was found that alternating current (AC) and impulse breakdown strength of transformer oil can be improved by dispersing TiO_2 nanoparticles modified with stearic acid as it exhibits less agglomeration. In another study by Li et al. (2010), silver-based nanofluids were prepared in oil. Silver nanoparticles of 5 nm average sizes were prepared by reducing Ag^+ with ascorbic acid. Oleic acid and n-butylamine were used to coat particle surface and stabilizer, respectively. Nanofluids were observed to be highly stable using this process. Surface-modified Fe_3O_4-based uniform nanofluid was prepared in vegetable insulation oil to study the dielectric properties of nanofluids (Li et al. 2012). Oleic acid was coated on the particle surface in ethanol solution before dispersing it into the vegetable oil. A uniform nanosuspension was achieved and nanoparticles remain suspended for 30 days after preparation.

5.2.3 pH Adjustment

pH of the nanofluids is strongly related to the rheological behavior of the suspensions. The adhesive forces present in the nanosuspensions depend on pH of the system. Degree of ionization has significant effect on the electrostatic interactions among charged particles. Changing the degree of ionization in the nanofluid system can improve the stability of suspended nanoparticles.

In a recent study by Konakanchi et al. (2014), Al_2O_3/PG:Water-, SiO_2/PG: Water- and ZnO/PG:Water-based nanofluids were prepared to study the relation of pH with temperature (T), concentration (φ), and size of nanoparticles (d). It was found that the pH values of nanofluids were directly proportional to the temperature and particle diameter. It was reported that the addition of SiO_2 nanoparticles (30 nm) in EG/water turned initially acidic nature of the host fluid to alkaline nature. Similarly, alumina and zinc oxide nanofluids exhibit less acidic behavior. A generalized correlation (Eq. 10) for pH was given as:

$$\frac{\mathrm{pH}_{nf}}{\mathrm{pH}_f} = \left(z_1\varphi^2 + z_2\varphi + z_3\right)\left\{z_4\left(\frac{T}{T_0}\right)^2 + z_5\left(\frac{T}{T_0}\right) + z_6\right\}\left\{z_7\left(\frac{d}{d_0}\right)^2 + z_8\right\} \quad (10)$$

Ho et al. (2010) prepared alumina–water nanofluids with average particle size of 33 nm to study the natural convection of nanofluids in squared enclosures. The pH of nanofluids was adjusted to 3 for different concentrations and stable nanofluids were obtained for at least two weeks.

6 Conclusions

Stability of nanofluids is the important characteristic toward their usage in industrial applications. The knowledge of interactions (DLVO and non-DLVO forces) among nanoparticles and particle–liquid has significant role to prepare stable nanofluids. Different techniques can be used during preparation of nanofluids to obtain uniform stable nanosuspension. Aggregation among particles is a natural phenomenon; however, the agglomeration process can be delayed by mechanical and chemical techniques. Mechanical mixing technique is more suitable for low particle concentrations. Appropriate surfactant concentration should be used to prolong the dispersion of nanoparticles in liquid. The application and advancement of characterization equipment is necessary to evaluate the stability of nanofluids. Different combinations of highly stable nanofluids can be prepared with enhanced properties such as improved reactivity, intensified thermal properties, and light weight for different applications.

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