Topical Review

Thermal transport phenomena in nanoparticle suspensions

Annalisa Cardellini, Matteo Fasano, Masoud Bozorg Bigdeli, Eliodoro Chiavazzo and Pietro Asinari

1 Department of Energy, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
2 University of Alberta, Department of Mechanical Engineering, 9211-116 Street NW, Edmonton Alberta, Canada

E-mail: pietro.asinari@polito.it

Received 28 July 2015, revised 11 June 2016
Accepted for publication 29 June 2016
Published 4 October 2016

Abstract

Nanoparticle suspensions in liquids have received great attention, as they may offer an approach to enhance thermophysical properties of base fluids. A good variety of applications in engineering and biomedicine has been investigated with the aim of exploiting the above potential. However, the multiscale nature of nanosuspensions raises several issues in defining a comprehensive modelling framework, incorporating relevant molecular details and much larger scale phenomena, such as particle aggregation and their dynamics. The objectives of the present topical review is to report and discuss the main heat and mass transport phenomena ruling macroscopic behaviour of nanosuspensions, arising from molecular details. Relevant experimental results are included and properly put in the context of recent observations and theoretical studies, which solved long-standing debates about thermophysical properties enhancement. Major transport phenomena are discussed and in-depth analysis is carried out for highlighting the role of geometrical (nanoparticle shape, size, aggregation, concentration), chemical (pH, surfactants, functionalization) and physical parameters (temperature, density). We finally overview several computational techniques available at different scales with the aim of drawing the attention on the need for truly multiscale predictive models. This may help the development of next-generation nanoparticle suspensions and their rational use in thermal applications.

Keywords: nanoparticles suspensions, nanofluids, interface phenomena, particle aggregation, heat and mass transfer, multiscale modeling

(Some figures may appear in colour only in the online journal)

1. Introduction

Solid nanoparticles (i.e. particles with size less than 100 nm) have been adopted to alter the properties of bulk materials for thousands of years: a prototypical example is offered by the glittering effect of gold-ruby glass in ancient artifacts [1]. However, the controlled synthesis of nanoparticles was only achieved with the modern advancement in nanotechnology in the 1980s [2]. While first years of nanoparticle research focused on synthesis techniques, later studies shifted the attention to the applications, with particular focus on nanoparticle suspensions or nanosuspensions in liquids [2, 3]. In fact, suspending nanoparticles in a liquid may be an effective way of tuning the thermophysical, optical, electromagnetic and chemical properties of the base fluid [4].

One of the main features of colloidal nanosuspensions is the large thermal conductivity of solid nanoparticles, which can be 2 or 3 orders of magnitude greater than that of conventional
heat transfer fluids. The challenge is to exploit this property for enhancing the mean-field thermal conductivity of the suspension as a whole [3, 5–12]. Early experimental findings suggested that fluids containing a limited concentration of dispersed nanoparticles (nanofluids) can lead to considerable increase in thermal transfer properties (e.g. 30% thermal conductivity enhancement for TiO$_2$–water suspensions [13]) with respect to those of the base fluids. Moreover, nanofluids are generally more stable than suspensions of milli- or microparticles, mainly because of the significant Brownian motion of particles with nanometer size [14, 15]. Therefore, nanofluids have been extensively investigated as novel coolants for electronic [16, 17], nuclear or automotive components [18–23], with the purpose to decrease the dimensions of traditional heat exchangers. However, nanoparticles also cause a general increase in fluid viscosity, thus leading to larger pumping power and corrosion of mechanical components. As a result, those issues are still limiting a wide commercial exploitation of nanofluids [8, 24–27].

Nanofluids have been the subject of much hype for many years, with many claims of exceptional properties implying the existence of new physical processes that are still not understood. More recently, many controversial results have been clarified and well-understood physics restored to the place to which it belongs. It is now quite well understood that the actual heat diffusivity of nanofluids depends on three aspects: the properties of the solid particles and suspending fluid, the interfacial resistance, and most importantly the morphology of the aggregates that form in the suspension [28]. Firstly, nanoscale solid materials are characterized by large thermal conductivities, e.g. 35000 W m$^{-1}$K$^{-1}$ of carbon nanotubes [29]. Secondly, thermal boundary resistance or Kapitza resistance is observed at solid–liquid interfaces due to phonon scattering [30]. Thermal boundary resistance is a critical quantity in the heat transfer between structures approaching nanometer dimensions, due to the large density of interfaces [31]. Moreover, temperature, surface chemistry, shape, roughness and functionalization of nanoparticles are observed to affect Kapitza resistance at solid–liquid interface [32–37]. Thirdly, the agglomeration of nanoparticles favors the creation of percolation paths in the nanosuspension, therefore altering the overall thermal transmittance [38–40]. In general, it can be said that the benefit of nanofluids for heat transfer applications has been largely exaggerated [41], as the presence of aggregates also affects the viscosity. Hence, future researches should focus on optimizing the morphology of nanoparticle aggregates in order to achieve the best combination of viscosity and thermal conductivity [28], still preserving stability and good optical properties.

Other peculiar properties of nanosuspensions are contributing to shift the attention to alternative thermal engineering applications. For example, both surface wettability and curvature influence the boiling behavior of water in the proximity of nanoparticles [42, 43], and large increases in the critical heat flux (boiling heat transfer) have been noticed in nanosuspensions [44, 45]. Moreover, a temperature gradient can work as a driving force for mass diffusion in Brownian mixtures of two or more species (thermophoresis) [46–48]. New perspectives are also offered by nanofluids designed with more than one optimized feature. The nanofluids designed for enhancing more than one thermo-physical property, e.g. both thermal conductivity and optical absorption, are called hybrid nanofluids. For example, nanosuspensions have the potential to revolutionize the solar thermal sector because nanoparticles (i) can increase the thermal conductivity and hence the heat transfer efficiency and (ii) can be optically active and therefore used as direct absorbers [49, 50]. Therefore, volumetric solar receivers based on nanosuspensions have been studied for enhanced solar-to-thermal energy conversion [50–53]; whereas, several types of nanoparticles in aqueous solutions have been found to efficiently convert solar energy to steam, such as gold by plasmonic effect and graphene by large solar light absorbance [54–56].

In addition to the more traditional thermal engineering ones, other fields of application for nanosuspensions are currently gaining momentum [9, 49]. For example, nanoparticle suspensions find application as magnetic sealants [57], lubricants [58, 59], fluids for enhanced oil recovery [60], dielectric transformer oils [61], photocatalysts [62–64], catalysts [65], fuel additives [66], preparation of antireflective [67] and hydrophobic [68] surfaces. Colloidal dispersions of magnetic nanoparticles [69–71], also referred to as ferrofluids, exploit their response to applied magnetic fields in several applications, including actuators, lubrication, sensors, seals and assembly of structures by magnetic effects [72]. Furthermore, Janus particles with two or more distinct physical properties are recently being investigated in colloids with smart self-assembly capabilities [73]. Nanosuspensions exhibit great potential also in the biomedical sector, especially in nanocrystal surgery [74], antibacterial [75], drug delivery [76, 77], proteomics [78, 79], diagnostic [80, 81] and therapeutic [82–84] purposes. In particular, gold- and iron oxides-based nanosuspensions are showing promising potential for hyperthermic therapies, where a strong, localized hyperthermia treatment has been demonstrated to be effective against tumors [85].

Despite the encouraging commercialization of nanosuspensions in some specific applications [86], a widespread industrial adoption of nanoparticle suspensions is hindered by limitations such as increased pressure drops, lower specific heat, long term stability and limited synthesis repeatability [9, 15]. Hence, a more comprehensive understanding of the involved multiscale heat and mass transfer mechanisms is still needed for a rational design of nanosuspensions. In fact, design parameters such as viscosity and thermal conductivity are function of a large variety of geometrical (nanoparticle shape, size, aggregation, concentration), chemical (pH, surfactants, coating) and physical (temperature, density) characteristics of the nanosuspension [8]. This pronounced sensitivity is the main reason for some contradictory results between experimental evidences and theoretical considerations presented in the literature [44]. Molecular simulations can indeed support experiments to achieve a mechanistic comprehension of the transport properties of nanosuspensions, especially with complex phenomena such as particle aggregation; whereas the development of better synthesis techniques is progressively facilitating more accurate experimental investigations [9].
In this article, the main thermal transport phenomena occurring in nanoparticle suspensions are reviewed. Experimental evidences and current theoretical understanding are first presented. Then, computational tools for investigating transport properties of nanoparticle suspensions at multiple scales are reported. Finally, future directions and perspectives of nanosuspension research are outlined. The present review is intended to offer a wide overview of the main experimental, theoretical and computational tools and evidences to achieve multiscale predictive models for the heat transport properties of nanoparticle suspensions, which may unlock a more systematic transfer from lab-scale tests to industrial commercialization.

2. Experimental investigations

2.1. Synthesis and measurement techniques

Nanosuspensions are made out of solid nanoparticles suspended in a base fluid. Generally, surface active agents (surfactants) are also introduced, in order to achieve a better stability of the suspension [87]. Based on the thermophysical properties required for the intended application, a suitable particle core, coating and base fluid should be carefully engineered. Typically synthesized nanoparticle cores are metallic (Ag, Al, Au, Cu, Fe), ceramic (AlN, Al2O3, CuO, Fe2O4, SiC, SiN, SiO2, TiC, TiO2, ZnO, ZrO2) or carbon-based (graphene, fullerene, single- or multi-walled carbon nanotubes) [3, 88, 89]. Nanoparticles can be generated by various physical or chemical synthesis techniques, e.g. mechanical attrition, gas condensation or chemical precipitation [3, 4]. From both quality and economical reasons, gas phase techniques are the most appropriate for large-scale synthesis of nanoparticles [8]. In thermal applications, the base fluids in which nanoparticles are usually suspended are conventional heat transfer fluids (e.g. ethylene glycol, oil or water [27]), whereas other continuous media (e.g. acetone, decene, PBS, liquid gallium or mercury [90, 91]) can be adopted in different applications [4].

Nanosuspensions are typically produced by either two- or one-step techniques [3]. In two-step techniques (top-down approach), dried nanoparticles are first synthesized by physical or chemical process, then directly dispersed into the base fluid. The top-down approach has been extensively adopted in synthesizing nanosuspensions because of the widespread commercial availability of various nanopowders [92–94], therefore allowing large-scale and economical synthesis [12]. However, two-step techniques are generally unsuitable for suspensions of pure metal nanoparticles, because of possible surface oxidation during drying, storage, transportation and dispersion of nanoparticles [15]. These intermediate production steps may be also responsible for increased particle aggregation phenomena [12]. On the other hand, in one-step techniques (bottom-up approach) nanoparticles are simultaneously synthesized and dispersed into the base fluid [8, 95, 96]. Therefore, one-step methods prevent surface oxidation and limit nanoparticle aggregation, improving the suspension stability [27, 53]. Nevertheless, the bottom-up approach may leave residual reactants due to incomplete reactions in the nanoparticle suspension, thus altering the resulting properties [8]. Single-step methods are usually characterized by lower productivity and higher production costs [97, 98].

The stability of nanocolloids is given by the long time suspension of nanoparticles in the base fluid. This is usually achieved by avoiding the formation of large particle clusters and agglomerates, thanks to either simple physical (e.g. sonication, high-shear mixing [14, 24]) or chemical dispersion methods. In chemical dispersion methods, electrostatic interactions, steric effects or functional group attachment on the nanoparticle surface are adopted to limit the interparticle van der Waals forces leading to clustering phenomena [24]. While electrostatic surface charge of nanoparticles can be tuned by pH [7], steric repulsion is obtained by introducing surfactants in the suspension [87]. Surfactants are macromolecules with both lipophilic and hydrophilic groups, which lower the surface tension of nanosuspensions. Surfactants should be carefully chosen according to the properties of particles solution [7]. Surfactants commonly used in nanofluids are SDS, gum Arabic, chitosan, CTAB, Gemini and Triton X-100 [53, 99, 100]. However, surfactants may significantly alter the heat transfer, optical and visco-elastic properties of nanosuspensions, especially at high temperatures [7, 8, 49]. Beside surfactants, the modification of particle surface properties by chemical functionalization can be also adopted to avoid aggregation [53]. For example, the suspension of hydrophobic particles in water requires chemical functionalization of the particle surface with hydrophilic coating, and vice versa in case of hydrophilic particles suspended in oil [101]. Therefore, the optimal surface properties of nanoparticles can be achieved by modifying (i.e. coating) the nanoparticle core surface with functional layers or stabilizers, which are added during the synthesis.

Several techniques have been used for measuring the main thermal and fluid properties of nanosuspensions. Thermal conductivity, for example, is usually evaluated by either steady state methods or transient ones [11]. Steady state methods include cylindrical cell [102] and steady state parallel plate [103]; whereas transient methods include: hot-wire method [104], temperature oscillation [105], thermal constants analyser [106] and 3ω method [107]. Furthermore, thermal comparator techniques can be also employed [108]. Transient hot wire is the most adopted experimental method to assess the thermal conductivity of nanofluids [7, 15]. Specific heat capacity of nanosuspensions is typically measured by differential scanning calorimeter [109–111]; whereas viscosity by piston-type [112], capillary [113] or rotational [114] viscometers. Finally, density of nanosuspensions can be evaluated by pycnometers or oscillating U-tube technique [115, 116].

2.2. Experimental evidences

In average, studies with different nanoparticle/base fluid combinations and volume concentrations between 0.5–4% have found 15–40% increases in the effective thermal conductivity of nanosuspensions \(k_{\text{n}}\) respect to base fluid one \(k_{\text{bf}}\) [3]. However, while some studies reported thermal conductivity enhancements apparently beyond the classical Maxwell’s
limit [117, 118], other investigations found good agreement with classical models [41, 119]. Nowadays, an emerging consensus is being reached that these discrepancies arise from the different methods (and surfactants) adopted in nanofluid synthesis, which significantly alter the particle aggregation phenomena and thus compromise the hypothesis of well-dispersed nanoparticle suspensions underlying classical models [28, 49]. However, while the production and physical understanding of well-dispersed colloids have achieved a fair maturity, targeted nanoparticle configuration and aggregation in base fluids and the involved phenomena therein are still extensively investigated, in order to achieve a good compromise between thermal conductivity and viscosity enhancements [26, 28, 49]. Hundreds of research articles and several reviews have reported thermal conductivity of nanofluids with different characteristics [3, 7, 8, 10, 14, 15, 17, 24, 27, 120, 121]; here, experimental evidences are only summarized to identify the main geometrical, physical and chemical parameters affecting thermophysical properties of nanosuspensions.

Concerning geometrical characteristics, thermal conductivity of nanosuspensions increases with the volume concentration of nanoparticles, with either linear or nonlinear correlations [15, 122]. Moreover, the majority of studies agrees on larger thermal conductivities of nanosuspensions with decreasing nanoparticle diameter [123, 124], but opposite trends can be also found in the literature [17, 125]. This contrasting behavior is due to the competing effect of both larger thermal boundary resistance and solid–liquid heat transfer area with decreasing volume-to-surface particle ratios, at fixed volume concentration. Particle shape also affects $k_n$, being suspensions of nanoparticles with rod or plate shapes typically characterized by larger thermal conductivity enhancements respect to spherical ones [126–128]. This is generally due to the eased creation of percolation paths and to the higher thermal conductivity in the elongated direction [15, 17]. Particle aggregation is also clearly related to $k_n$. However, only a controlled (i.e. percolating) nanoparticle clustering can lead to increased thermal conductivity of nanosuspension [38, 129, 130], while severe aggregation may end up with particle sedimentation and thus nanofluid degradation [131, 132]. Regarding chemical features, nanoparticle material affects $k_{ns}$: materials with high thermal conductivity (e.g. carbon nanotubes, metals) display larger $k_{ns}/k_{bd}$ enhancements [17]. Similar trends should be expected with $k_{bd}$, namely the thermal conductivity of base fluid [24]. Surface functionalization, pH and addition of additives strongly modify $k_{ns}/k_{bd}$, because they control the solubility and suspension of nanoparticles and thus the resulting clustering events [106, 133–136]. In particular, surfactant concentrations above the critical micelle concentration (CMC) lead to nanofluid degradation and consequent $k_{ns}/k_{bd}$ drop [137]. Physical conditions also influence $k_{ns}$. In fact, temperature has an important role in the Brownian motion and aggregation of suspended nanoparticles [105, 138]. The general trend reported in the literature is a $k_{ns}/k_{bd}$ increase with temperature [17, 139].

Other thermal properties of nanosuspensions are altered respect to the base fluid’s ones. On the one hand, nanoparticles in the proximity of a heated wall contribute to disrupt the boundary layer and then to generally increase the convective thermal transport [140], especially in developing laminar flows [141]. On the other hand, radiative properties of nanosuspensions have only recently been starting to receive attention, particularly for solar applications [142, 143]. Nanoparticle suspensions display also enhanced (25%–250%) [49] Critical Heat Flux (CHF) in pool boiling conditions [144, 145], because the deposition of nanoparticles on boiling surfaces increases the amount of nucleation sites [146]. The specific heat capacity of nanoparticle suspensions ($c_{p,ns}$) is typically lower than the pure liquid one, since specific heat capacity of liquids is generally larger than that of solids [147, 148]. Moreover, $c_{p,ns}$ increases with temperature [147], while it decreases with particle size [149]. The addition of nanoparticles also affects the thermal expansion of base fluid [150, 151] and the latent heat of phase change materials [152, 153].

In the overall evaluation of nanofluid performances, non-thermal properties should be also considered. For example, viscosity is essential to determine the adequate pumping power, which contributes to define the efficiency of nanosuspensions in thermal applications. Viscosity significantly increases with nanoparticle concentration [128, 154], and it is also influenced by particle size and shape [128, 155], aggregation [24], pH [156, 157], surfactants [158, 159] and temperature [112, 160]. Moreover, a critical temperature beyond which the viscosity of the nanoparticle suspension dramatically changes has been also observed [112]. Further information regarding the viscosity of nanosuspension can be found in [98, 161–164]. Finally, the density of nanosuspensions is generally close to base fluid one [24].

2.3. Classical and semi-empirical models

The current physical interpretation of the effective thermal conductivity of nanosuspensions comes from continuum-inspired phenomenological formulations, such as effective medium theory (EMT), which usually consider only the material of suspended particles, base fluid and the particle volume fraction as variables [165]. In this classical formulation, heat transport is considered as diffusive in both solid and liquid phases, while nanoscale phenomena involved in nanosuspensions are typically neglected. Hence, several studies have been devoted to introduce nanoscale effects in the classical EMT model, in order to provide a better explanation of the thermal transport in nanosuspensions. These nanoscale mechanisms include liquid nanolayering [6, 166, 167], particle aggregation [6, 38, 39, 167, 168] and the thermal boundary resistance [169]. Here, we report a selection of the most widely adopted EMT models to predict thermal conductivity of nanosuspensions, whereas dedicated studies can be found in [7, 15, 24, 27, 170, 171].

The classical modelling of effective thermal conductivity of nanoparticle suspensions is based on the analysis of Maxwell for solid–liquid mixtures [172]. Despite the Maxwell–Garnett (MG) model was initially proposed for particles with micrometric size, it has shown good prediction capabilities at low volume concentrations and ambient conditions also with suspension of spherical nanoparticles:
where }$k_p$ is the thermal conductivity of particles and }$φ$ their volume fraction in the base fluid.

MG model is valid for nanosuspensions of spherical particles that are well-dispersed and do not interact each other. Furthermore, equation (1) considers as negligible the thermal boundary resistance at the solid–liquid interface. Hence, Nan and colleagues [173] generalized MG model to include the effects of both particle shape and thermal boundary resistance (Kapitza resistance, }$R_k$), namely

$$k_r = \frac{k_m}{k_{bf}} = \frac{k_p + 2k_{bf} + 2(k_p - k_{bf})\phi}{k_p + 2k_{bf} - (k_p - k_{bf})\phi},$$

being

$$L_{11} = \frac{p^2}{2(p^2 - 1)} - \frac{p}{2(p^2 - 1)^{3/2}} \cosh^{-1}p,$$

$$L_{33} = 1 - 2L_{11},$$

$$\beta_{ii} = \frac{k_{ii} - k_{bf}}{k_{bf} + L_{ii}(k_{ii} - k_{bf})},$$

$$k_{ii} = \frac{k_p}{1 + \gamma L_{ii}k_p/k_{bf}},$$

and

$$\gamma = \frac{(2 + 1/p)R_kk_{bf}}{\alpha_{11/2}}.$$

Equation (2) takes into account ellipsoidal nanoparticles (}$$p = a_{33/\alpha_{11}}$$), where the principal axes are either }$a_1 = a_2 < a_3$ (prolate) or }$a_1 = a_2 > a_3$ (oblate). Note that equation (2) reduces to equation (1) by considering both negligible Kapitza resistance and spherical particle shape. The Nan’s model has shown good accordance with a large set of thermal conductivities of nanocolloids characterized by a broad variety of geometrical and chemical characteristics [41]. However, such model is valid under the hypothesis of well-dispersed suspensions, while Prasher et al extended its validity to configurations with particles clustering [38]. Other authors have suggested additional modifications and extensions to include further characteristics of nanosuspensions, therefore refining the prediction capabilities of EMT models for particular subsets of nanosuspensions (see a detailed list in [10]). For example, Yu and Choi investigated the effect of liquid nanolayer (i.e. liquid molecules in the proximity of nanoparticle surface shaping ordered structures) on the effective thermal conductivity of nanosuspensions [166]; Xuan et al the Brownian motion of nanoparticles and the resulting aggregation phenomena [174]; Murshed et al the particle size, surface chemistry, Brownian motion and nanolayer [175].

On the other hand, semi-empirical models have been also widely adopted to fit experimental thermal conductivity of particular nanosuspensions (see a comprehensive overview in [15] and [27]). The most interesting example is reported by Corcione, who proposed an empirical model based on a large amount of experimental data in the literature (and thus with wide regions of validity) [176]. Other examples are provided by Chon et al, who suggest an experimental correlation based on Buckingham-Pi theorem for the thermal conductivity of }$\text{Al}_2\text{O}_3$ nanofluids [177]; Timofeeva et al, with an experimental relation between thermal conductivity, shape and surface effects of suspended nanoparticles [128] and Khanafir and Vafai, with a semi-empirical correlation for }$\text{Al}_2\text{O}_3$ and }$\text{Cu}$ nanofluids accounting for volume fraction and nanoparticle diameter [10].

The specific heat capacity of nanosuspensions, instead, has been generally predicted by two models. The first one was introduced by Pak and Cho [178] and then successfully adopted in several studies [105, 179]. Such model exhibits strong similarity to mixing theories for ideal gas mixtures:

$$c_{p,ns} = (1 - φ)c_{p,bf} + φc_{p,p},$$

being }$c_{p,bf}$ and }$c_{p,p}$ the base fluid and particle specific heat capacity, respectively. The second model has found better agreement with experimental results [180–182], and it is derived by classical and statistical mechanics while considering thermal equilibrium between base fluid and particles:

$$c_{p,ns} = \frac{(1 - φ)c_{p,bf} + φc_{p,p}}{\rho_{ns}},$$

where }$(c_{p,bf})$ and }$(c_{p,p})$ are the base fluid and nanoparticle volumetric heat capacity [147, 183]. In good agreement with experiments [178, 184], the nanosuspension density is generally estimated as [178, 184]:

$$\rho_{ns} = (1 - φ)\rho_{bf} + φ\rho_p,$$

where }$\rho_{bf}$ and }$\rho_p$ are the densities of base fluid and particles, respectively. However, equations (8) and (9) may sometimes exhibit non-negligible deviations from experimental results [147, 185, 186]; therefore, more accurate semi-empirical models can be also adopted for specific configurations [148]. Note that expressions similar to equations (8) and (9) are also employed for modelling the thermal expansion coefficient of nanosuspensions [187, 188].

Finally, several models of viscosity have been proposed for predicting the effective viscosity of nanosuspensions. First, the Einstein model [189] for suspensions of infinitely diluted (}$$φ \ll 0.02$$) rigid spheres in a viscous fluid is obtained by phenomenological hydrodynamic equations, namely

$$\mu_r = \frac{\mu_{ns}}{\mu_{bf}} = 1 + 2.5φ,$$

where }$\mu_{bf}$ and }$\mu_{ns}$ are the viscosity of base fluid and nanosuspension, respectively. Aiming to extend the validity of Einstein’s analysis towards larger particle concentrations, Brinkman [190] and then Lundgren generalized (}$$φ < 0.35$$) equation (11) by Taylor expansion as

$$\mu_r = \frac{1}{1 - 2.5φ} = 1 + 2.5φ + 6.25φ^2 + ...$$
Equation (12) is in good agreement with results from Batchelor studies on Brownian motion of suspensions of rigid spherical particles [192]. Theoretical models for the viscosity of nanosuspensions can also include the effect of particle aggregation [193–195]. Moreover, several semi-empirical models have been adopted to fit experimental viscosity of nanoparticle suspensions [10, 112, 140, 186, 193, 196–199]. Further theoretical and semi-empirical models for the viscosity of nanoparticle suspensions can be found in [10].

3. Mass transport phenomena in nanoparticle suspensions

Thermal transport phenomena in nanoparticle suspensions are definitely influenced by physical and chemical characteristics of the base fluid as well as by nanoparticle dynamics. On one hand, the peculiar properties of water molecules at the solid–liquid interface can drastically modify the heat exchange between solid and liquid phase, thus altering the overall properties of the suspension. On the other hand, particle aggregation and clustering are the main responsible of the thermal percolation path creation along the particle aggregates. In this section, we first review the water molecules dynamics in the proximity of nanoparticle surface. The physics underlying nanolayer formation is explained and the main properties of water at the interface are described. Second, we focus on the kinetic of particle aggregation, by reviewing the fundamental theories dealing with particle clustering.

3.1. Water nanolayer

Nonbonded interactions (i.e. Coulomb and Van der Waals potentials) at solid–liquid interface tend to strongly modify the hydrogen-bonding structure typically found in bulk water. Such interface effect induces a local densification of water molecules, which arrange in a more structured layer also known as nanolayer or hydration layer (figure 1). The properties of water in proximity of the solid surface are significantly different from those in the bulk region, and they have been extensively investigated, both experimentally and theoretically [101, 200–203]. However, although several authors refer to distinct characteristics for bound and bulk water, it is worth to notice that a progressive and gradual variation of water properties is expected by moving from solid interface towards the bulk region. Moreover, the degree of confinement, the chemical molecular structure of the solid surface and temperature should be considered for describing the length-scale of nanolayer.

Puliti et al [201] studied the nanolayer in gold-water mixtures by molecular dynamics (MD) simulations. Their results showed an increase of water density while approaching the nanoparticle surface, and they attributed this evidence to the peculiar ordered structure of water molecules at the metallic-liquid interface. Chiavazzo et al [202] and Fasano et al [206] performed MD simulations to evaluate the self-diffusion coefficient ($D$) of water molecules in different nanoconfined configurations. They systematically calculated the diffusion coefficients within nanopores, around nanoparticles and within nanopores filled by magnetic nanoparticles. In order to provide more general insights, they also evaluated the self-diffusion coefficient within carbon nanotubes (CNTs) and in the proximity of proteins. After studying the interactions of water molecules with the solid surface, they proposed a scaling law for the self-diffusion coefficient of water, which is found to be linearly decreasing with a dimensionless parameter proportional to the water confinement degree. This scaling law has been confirmed by quasi-elastic neutron scattering experiments [207, 208]. Regarding the direct observation of nanolayer, Gerardi et al [203] studied the liquid layering in alumina-water nanosuspension. In this study, they measured the self-diffusion coefficient of water by means of nuclear magnetic resonance (NMR), and they found that $D$ decreased by increasing the particle volume fraction. The latter evidence was attributed to the increased tortuosity of the water molecules diffusion path, which is due to both the nanoparticle obstacle and to the liquid layering around the particle surface. Based on their experimental results and model, Gerardi and colleagues estimated the length-scale of nanolayer as approximately equal to five layers of water molecules. In another work, Turanov and Tolmachev [209] used NMR technique to measure the self-diffusion coefficient of water in silica nanoparticle suspensions, and they confirmed the reduced mobility of water molecules in the proximity of solid–liquid interface.

Besides density and self-diffusivity, several works also focused on the water viscosity at solid–liquid interfaces, shedding light on the differences from the bulk region [200, 210–212]. Numerous studies have demonstrated that the viscosity of water in the proximity of solid surfaces may be orders of magnitude larger than those in the the bulk, suggesting strong similarities with the behaviour of supercooled liquids [200, 213–215]. On the other hand, Raviv et al have proved that the fluidity of bound hydration layer persists even below 1 nm thickness [216, 217]. These conflicting results remark that the viscosity of nanoconfined water is still poorly understood.
3.2. Particle aggregation kinetics

The mass transport phenomena in nanosuspensions mainly involve the nanoparticles dynamics and their aggregation. One of the most known theory for describing particle aggregation is based on the Smoluchowski equation [218, 219], where the agglomeration frequency \( k_{ij} \) for a couple of particles \( i \) and \( j \) is given by:

\[
k_{ij} = \frac{\beta_{ij}}{W_{ij}}.
\]

(13)

\( \beta_{ij} \) is the collision frequency function, derived by Brownian motion [220, 221], whereas \( W_{ij} \) is the stability ratio, namely:

\[
W_{ij} = 2 \int_{2}^{\infty} \frac{\exp\left(\frac{E_{ij}}{kT}\right)}{s^2} ds,
\]

(14)

where \( E_{tot,ij} \) is the total interaction energy between the particle pair and \( k_B \) the Boltzmann constant. The dimensionless separation distance, \( s \), between particles is given by \( s = 2R(r_i + r_j) \), where \( R \) is the center of mass distance between \( i \) (radius \( r_i \)) and \( j \) (radius \( r_j \)) particles. Thus, only ‘successful’ collisions can lead to coagulation events, while the rate of aggregation depends on \( E_{tot} \). Even if Smoluchowski theory is able to describe the particle aggregation dynamics for a limited class of cluster shapes, such model highlights the fundamental role of the interaction energy between the suspended particles in a bulk fluid.

In colloidal science, the milestone for understanding the interaction energy between suspended particles is the DLVO theory, so called because of the pioneering work by Derjaguin, Landau, Verwey and Overbeek [222–224]. According to such theory, the interparticle energy depends on the sum of attractive and repulsive interactions, which are both function of the particle distance:

\[
E_{tot} = E_{vw} + E_{elec}.
\]

(15)

The London–van der Waals contribution, \( E_{vw} \), between two particles of the same material was derived by Hamaker [225], and it is always attractive thus promoting the aggregation of suspended particles. Instead, the repulsive component of the DLVO theory, \( E_{elec} \), can be explained by recalling the electric double layer formation, i.e. the chemical phenomena occurring on particle surface in a polar host fluid. In such conditions, the nanoparticle develops a surface charge according to the particle material. For example, in case of metal oxides, the charge formation is due to the hydroxylation of their surfaces, which can then react with either \( \text{H}_2\text{O}^+ \) or \( \text{OH}^- \) in water [226]. The consequent protonation or deprotonation of the surface group results in the positive or negative charge on the particle surface [227]. Instead, in case of functionalized carbon-based particles dispersed in water, a negative surface charge is developed on the particle’s surface by the ionization of the surface groups (e.g. -COOH). Because of the surface charge, an electrostatic potential is created in the proximity of nanoparticle, and a concentrated layer of counter ions, known as Stern layer, is formed. Moreover, a diffuse layer of anions and cations is observable beyond the Stern layer (figure 2). The charged surface, the Stern layer and the diffuse layer constitute the three levels of the electric double layer (EDL) typically observed around a solvated nanoparticle [228]. It is worth noticing that the strength of the surface potential can be adjusted by experimentally tuning the pH value of the suspension [101, 229, 230]. Based on equation (15), when the electrostatic component is prevailing, particles repel each other, and the potential barrier prevents the particles to agglomerate in the primary minimum. On the other hand, if the van der Waals contribution dominates, particles can overcome the potential barrier and agglomerate in the primary minimum (figure 3) [226].

From the experimental point of view, the effect of interaction energies between particles can be measured by zeta-potential (\( \zeta \)). This potential depends on the chemical properties of both particle surface and solution composition (i.e. pH) [231]. The pH value corresponding to \( \zeta = 0 \) mV is known as the isoelectric point (IEP) and, when the magnitude of the zeta-potential is close to the IEP or smaller than a certain threshold (e.g. \( \zeta \approx 10 \) mV for \( \text{Al}_2\text{O}_3 \)-water suspensions [231]), the repulsive forces between particles are weak and particle agglomeration occurs. The measurement of zeta-potential offers a link between experiments and theoretical background. In particular, zeta-potential is often associated with the value of electrical surface potential found in the DLVO theory.

Although DLVO theory is considered as a consolidated theory for modelling colloidal interactions, several works have been carried out for including steric [8, 232–234] and hydration [235, 236] contributions in the base theory. In fact, such nanoscale effects are missing within the continuum framework of DLVO theory, even though they can strongly alter the interaction energy between suspended nanoparticles and thus influence aggregation kinetics [237].

4. Thermal transport phenomena in nanoparticle suspensions

In this section, the main thermal transport mechanisms occurring in nanoparticle suspensions are reviewed. A special emphasis is given to the effective conductivity of colloidal suspensions, and to the effect of mass transport phenomena on heat exchange. Hence, nanoscale thermal conduction, micro-convection and percolation effects are studied for a comprehensive understanding of the overall conduction in nanosuspensions. A brief analysis of the radiative heat transfer phenomena concludes the section.

4.1. Conductive heat transfer

Conduction phenomena in nanoparticle suspensions have been extensively investigated in the last decades [3, 5–12]. If thermal conduction within the single phases can be considered as straightforward, it results particularly complex when the overall mixed system is considered. Moreover, the size of the particles, their diffusion and aggregation phenomena make more difficult the understanding of thermal conduction in nanosuspensions. It is evident that a clear scenario of the energy transport mechanisms in colloidal systems would allow
to accurately define the overall thermal conductivity, hence to study the temperature trends in heat exchange applications.

4.1.1. Nanoscale heat transfer. Thermal conduction within the nanoparticles is a typical phenomena occurring in size-affected domains, where the classical governing laws, such as Fourier’s law, break down because of the small size [31, 238–240]. For this reason, nanoscale heat transfer in colloidal suspensions is usually better described by discrete particle-based descriptions rather than continuum approaches. In order to identify the nanoscale heat transfer regime, a comparison between the typical size of system and the characteristic length scales of energy carriers is required. Recalling the wave-particle duality of energy carriers, the characteristic length scales can be associated either to the mean free path, i.e. the average distance between successive collisions of the energy carriers, or to the average wavelength of phonons. For the former case, the mean free path $\Lambda$ can be estimated as:

$$\Lambda = \frac{kmv_F}{\pi^2nk_B T}$$  \hspace{1cm} (electrons in metals particles),  

(16)

$$\Lambda = \frac{3k}{\int_0^{\omega_{max}} C_\nu \omega d\omega}$$  \hspace{1cm} (phonons),  

(17)
where $C_v$ is the volumetric specific heat, $v_c$ is the velocity of the carriers, $m$ the energy carriers mass and $k$ the thermal conductivity. For the latter case, instead, the average wave length is given by:

$$\lambda = \frac{2\hbar v}{k^2 T},$$

(18)

where $\hbar$ is the Planck's constant. A third characteristic length scale considers the coherence length in optics, which takes into account the spread in energy of the wave packets:

$$l_c = \frac{c}{\Delta \nu},$$

(19)

where $c$ is the speed of light and $\Delta \nu$ is the bandwidth of radiation. Thus, the comparison between the typical size of colloids and the above mentioned lengths allows to tune the correct techniques for describing thermal conduction within nanoparticles.

4.1.2. Effect of thermal boundary resistance. A complete analysis of nanoscale heat transfer in nanosuspensions should also include thermal mechanisms at the solid–liquid interface and across the solvent nanolayer. For example, the interfacial thermal resistance, also known as Kapitza resistance ($R_k$), plays a fundamental role in the study of nanoscale heat transport phenomena at interfaces and within particle suspensions. From a theoretical point of view, two models are adopted to describing interfacial thermal resistance: the acoustic mismatch model (AMM), which accounts for long-wavelength phonons and the diffuse mismatch model (DMM), which assumes a complete diffuse scattering at the interface. However, both AMM and DMM models do not include details of the interfacial nanostructure: in both models, thermal boundary resistance is only determined by the materials of phases in contact, without considering the nature of the joint. For this reason, experimental, computational and semi-empirical nanoscale techniques are preferred for studying thermal transport at solid–liquid interfaces.

In general, Kapitza resistance is due to local phonon scattering at the interface of dissimilar materials, e.g. at the particle-fluid interface in nanosuspensions [33, 169, 241–243]. It is worth to underline that Kapitza resistance exists even at atomically perfect interfaces and, therefore, it is different from contact resistance, which is due to poor mechanical connections between two materials [169, 244]. Generally, Kapitza resistance is expressed as:

$$R_k = \frac{1}{G_k} = \frac{\Delta T}{q},$$

(20)

where $G_k$ is the thermal boundary conductance (transmittance), $\Delta T$ is the temperature difference between solid and liquid at the interface and $q$ is the heat flux per unit area. Such thermal resistance can be also expressed in terms of Kapitza length (or radius) ($l_k$), which represents the equivalent thickness of a bulk material having the same thermal resistance of the interface [245, 246]:

$$l_k = R_k k_{bf} = \frac{k_{bf}}{G_k},$$

(21)

where, $k_{bf}$ is the thermal conductivity of the base fluid or matrix.

For low concentration of well-dispersed spherical nanoparticles, Putnam et al introduced the effect of interfacial thermal resistance in the expression of nanosuspension thermal conductivity [247]:

$$k_f = 1 + 3\phi \frac{\Gamma - 1}{\Gamma + 2} = 1 + 3\phi \frac{\frac{c}{k} - 1}{\frac{c}{k} + 2},$$

(22)

where $\Gamma = G_k v_p / k_{bf}$. Therefore, it is possible to define a critical particle radius equal to the Kapitza length at which there is no heat conduction enhancement. Instead, for particles with radii higher than the Kapitza length, the thermal conductivity of the suspension increases.

Other studies demonstrated that the hydrophobicity or hydrophilicity of the solid surface has a substantial impact on the interfacial thermal resistance [245]. Ge et al experimentally measured the thermal boundary conductance for either hydrophilic or hydrophobic Al-water and Au-water interfaces [245]. Specifically, they evaluated the thermal transmittance of the functionalized Al and Au interfaces by considering four heat transport mechanisms:

(i) heat transport from metal surfaces to functional groups;
(ii) heat transport across the functional groups;
(iii) heat transport from terminal groups to surrounding confined water;
(iv) heat transport from confined water gap to bulk water.

Based on their measurements, thermal boundary conductance for hydrophobic surfaces was $60 \pm 6$ MW $m^{-2}$ $K^{-1}$ (Al) and $50 \pm 5$ MW $m^{-2}$ $K^{-1}$ (Au); while for hydrophilic surfaces $G_k = 180 \pm 30$ MW $m^{-2}$ $K^{-1}$ (Al) and $G_k = 100 \pm 20$ MW $m^{-2}$ $K^{-1}$ (Au), respectively. From these measures, Ge and co-workers observed that hydrophilic surfaces were characterized by a larger thermal boundary conductance. Thus, such surfaces are preferable for efficient heat conduction in nanosuspension. The large difference between $G_k$ of hydrophobic and hydrophilic interfaces was attributed to the critical role of water layering across the solid–liquid interfaces with different surface properties.

4.1.3. Effect of nanolayer. A number of studies attempted to explain the thermal conductive mechanisms within nanosuspensions by including the effect of solvent nanolayer. Specifically, by recalling the ordered structure of water molecules at the interface, some authors assumed a more conductive region in the proximity of solid surface than in the bulk fluid [166, 248, 249]. According to such consideration, the thermal boundary resistance at the solid–liquid interface should reduce while the overall thermal conduction properties increase, thus explaining experimental results. Although several models have been proposed to represent this phenomenon, rigorous measurements of thermal properties at the interface are still lacking.

Jiang et al [248] proposed a mathematical model for the thermal conductivity of alumina-ethylene glycol nanosuspension. By introducing the effect of a interfacial nano-shell with
higher thermal conductivity, they derived a nonlinear distribution of thermal conductivity in the proximity of nanoparticles. Moreover, they proved that the effect of liquid layering around nanometer-sized particles was more pronounced for smaller particles.

Yu and Choi [166], instead, suggested a model of nanoparticle suspension characterized by a three phase system, i.e. nanoparticle, nanolayer and bulk fluid. They supposed that the nanolayer could provide a percolation between solid nanoparticles and bulk liquid, thus enhancing the overall thermal conductivity. Hence, they modified the MG model in equation (1) by introducing the thermal conductivity of an equivalent particle \( k_{pe} \) with radius \( r_p + \delta \), where \( \delta \) is adopted to approximate the nanolayer thickness:

\[
\frac{k_r}{k_{pe} + 2k_{bf} - 2(k_{pe} - k_{bf})(1 + \vartheta)} = \frac{1}{k_{pe} + 2k_{bf} - 2(k_{pe} - k_{bf})(1 + \vartheta)} \phi \frac{1}{D_{bf}}.
\]  

where \( \vartheta = \delta/r_p \). In line with this idea, Xue and Xu [249] also suggested a model by considering the effect of interfacial shell on the thermal conductivity of nanosuspensions. In order to provide further insights on the effect of nanolayer formation in suspended nanoparticles, some researchers performed molecular dynamics analysis. For example, Li et al [250] studied the effect of nanolayer on the thermal conductivity of copper-liquid argon nanofluid through molecular dynamics simulations.

\[
D_p = \frac{k_B T}{3 \pi \mu_{ad} d_p^2}. 
\]  

where, \( d_p \) is the nanoparticle hydrodynamic diameter. However, Keblinski et al [6, 28] analyzed the Brownian motion effect on thermal conduction by comparing the time scale of heat diffusion

\[
\tau_H = \frac{\rho c_{bf} d_p^4}{6 k_{bf}},
\]  

with the time scale of particle motion in the fluid

\[
\tau_D = \frac{3 \pi \mu_{bf} d_p^3}{6 k_B T}.
\]  

From equations (25) and (26), they realized that, in case of water at room temperature and particles down to atomic size (e.g. 0.5 nm), Brownian diffusion is much slower than thermal diffusion, namely: \( \tau_D/\tau_H \approx 25 \). Consequently, the heat transferred by thermal diffusion results much faster than the heat transferred due to the nanoparticle diffusion. Other works confirmed the minor role of Brownian motion for explaining the anomalous thermal conductivity in nanosuspensions [255, 256]. For example, Evans et al [255] demonstrated, by means of molecular dynamics simulations, the negligible contribution of hydrodynamic effects on the thermal conduction in nanofluids.

Currently, scientists are paying less attention to micro-convection. On the other side, many works suggest the important effect of Brownian motion on the aggregation of nanoparticles: the probability of particle clustering increases by reducing the particle size while maintaining the same volume fraction. Aggregation in turn causes the decrease of Brownian motion, due to the formation of heavier clusters [224, 257].

4.1.5. Effect of particle aggregation. Aggregation of nanoparticles is a time-dependent phenomenon that strongly affects the overall thermophysical properties of nanosuspensions [32, 195, 231, 258, 259]. An example of particle aggregation is presented in figure 4.

The effect of aggregation on the effective thermal conductivity of nanoparticle suspensions is treated in several experimental and theoretical works [38, 40, 260–262]. Aggregates

\[
D_p = \frac{k_B T}{3 \pi \mu_{ad} d_p^2}. 
\]  

where, \( d_p \) is the nanoparticle hydrodynamic diameter. However, Keblinski et al [6, 28] analyzed the Brownian motion effect on thermal conduction by comparing the time scale of heat diffusion

\[
\tau_H = \frac{\rho c_{bf} d_p^4}{6 k_{bf}},
\]  

with the time scale of particle motion in the fluid

\[
\tau_D = \frac{3 \pi \mu_{bf} d_p^3}{6 k_B T}.
\]  

From equations (25) and (26), they realized that, in case of water at room temperature and particles down to atomic size (e.g. 0.5 nm), Brownian diffusion is much slower than thermal diffusion, namely: \( \tau_D/\tau_H \approx 25 \). Consequently, the heat transferred by thermal diffusion results much faster than the heat transferred due to the nanoparticle diffusion. Other works confirmed the minor role of Brownian motion for explaining the anomalous thermal conductivity in nanosuspensions [255, 256]. For example, Evans et al [255] demonstrated, by means of molecular dynamics simulations, the negligible contribution of hydrodynamic effects on the thermal conduction in nanofluids.

Currently, scientists are paying less attention to micro-convection. On the other side, many works suggest the important effect of Brownian motion on the aggregation of nanoparticles: the probability of particle clustering increases by reducing the particle size while maintaining the same volume fraction. Aggregation in turn causes the decrease of Brownian motion, due to the formation of heavier clusters [224, 257].

4.1.5. Effect of particle aggregation. Aggregation of nanoparticles is a time-dependent phenomenon that strongly affects the overall thermophysical properties of nanosuspensions [32, 195, 231, 258, 259]. An example of particle aggregation is presented in figure 4.

The effect of aggregation on the effective thermal conductivity of nanoparticle suspensions is treated in several experimental and theoretical works [38, 40, 260–262]. Aggregates

\[
D_p = \frac{k_B T}{3 \pi \mu_{ad} d_p^2}. 
\]  

where, \( d_p \) is the nanoparticle hydrodynamic diameter. However, Keblinski et al [6, 28] analyzed the Brownian motion effect on thermal conduction by comparing the time scale of heat diffusion

\[
\tau_H = \frac{\rho c_{bf} d_p^4}{6 k_{bf}},
\]  

with the time scale of particle motion in the fluid

\[
\tau_D = \frac{3 \pi \mu_{bf} d_p^3}{6 k_B T}.
\]  

From equations (25) and (26), they realized that, in case of water at room temperature and particles down to atomic size (e.g. 0.5 nm), Brownian diffusion is much slower than thermal diffusion, namely: \( \tau_D/\tau_H \approx 25 \). Consequently, the heat transferred by thermal diffusion results much faster than the heat transferred due to the nanoparticle diffusion. Other works confirmed the minor role of Brownian motion for explaining the anomalous thermal conductivity in nanosuspensions [255, 256]. For example, Evans et al [255] demonstrated, by means of molecular dynamics simulations, the negligible contribution of hydrodynamic effects on the thermal conduction in nanofluids.

Currently, scientists are paying less attention to micro-convection. On the other side, many works suggest the important effect of Brownian motion on the aggregation of nanoparticles: the probability of particle clustering increases by reducing the particle size while maintaining the same volume fraction. Aggregation in turn causes the decrease of Brownian motion, due to the formation of heavier clusters [224, 257].
provide highly conductive percolation paths enhancing the overall thermal conduction of colloidal suspensions, as shown in figure 5. Starting from the BG formulation and taking into account the theory of completely misoriented ellipsoidal particles [173], Prasher et al evaluated the thermal conductivity of particle aggregates \( (k_a) \) as [38]:

\[
\phi_{\text{int}} \left( \frac{k_p - k_a}{k_{\text{bf}} + 2k_a} \right) + \left( 1 - \phi_{\text{int}} \right) \left( \frac{k_{\text{bf}} - k_a}{k_{\text{bf}} + 2k_a} \right) = 0,
\]

where \( \phi_{\text{int}} \) is the volume fraction of particles in the aggregates. After calculating \( k_a \) from equation (27), they determined the overall thermal conductivity by MG model [38]:

\[
k_a = \frac{k_a + 2k_{\text{bf}} + 2(k_a - k_{\text{bf}})\phi_a}{k_a + 2k_{\text{bf}} - (k_a - k_{\text{bf}})\phi_a},
\]

where \( \phi_a = \phi_p/\phi_{\text{int}} \) and \( \phi_p \) are the volume fraction of the aggregates and the nanoparticles, respectively. For a fully-aggregate system (\( \phi_{\text{int}} = 1 \)), the volume concentration of nanoparticles is equal to the volume fraction of particles in aggregates (\( \phi_a = \phi_p \)). For a well-dispersed system (\( \phi_{\text{int}} = 1 \)), there is only one particle in each aggregate, thus the volume concentration of nanoparticles is equal to the volume fraction of aggregates (\( \phi_a = \phi_p \)). It has been observed that the maximum thermal conduction occurs between these two limits [38].

Philip et al [261] experimentally studied the thermal conductivity enhancements in aqueous suspensions of magnetite nanoparticles subject to a magnetic field. By increasing the magnetic field, these nanoparticles could align in the direction of the field and form a chain-like structure. In this way, they could accurately evaluate the relation between overall thermal conductivity, nanoparticle aggregation and chain length. They attributed the improvement of thermal conduction to the formation of chain-like structures promoting thermal percolation paths, as formerly proposed by Prasher et al [38].

Further confirmations of such influence derive from the study by Eapen et al [264], where the Hashin and Shtrikman mean-field bounds model was tested and validated for a large variety of nanosuspensions. Specifically, their results showed good agreement with the model by considering linear-chain like arrangement of nanoparticles rather than well-dispersed conditions. Dhar et al [265] also proposed a theoretical model to predict the role of percolation paths for the thermal conductivity enhancement in graphene based nanosuspensions.

Although several works investigated percolation phenomena in nanosuspensions, a clear connection with the effective thermal conductivity of nanosuspensions is still missing, due to the numerous physical and chemical parameters involved.

4.2. Radiative heat transfer

Among the various thermophysical benefits, the addition of nanoparticles in liquid also offers the potential of improving the radiative absorbing properties of the base fluid [142, 266, 267]. Hence, the use of nanoparticle suspensions for harvesting thermal energy is receiving remarkable attention in the energy field [50, 268–270]. One of the main benefits offered by such suspensions is that nanoparticles are smaller than the mean free path of the incident radiation, thus the scattering is negligible and the absorption spectrum is typically broadened [271], which leads to enhanced absorption efficiency.

The formal light scattering theory can be explained by recalling two theoretical frameworks: the Rayleigh and the Mie scattering theories [271]. Hereby, we present the former one, whereas the latter theory is extensively presented elsewhere [142]. Planck’s law describes the electromagnetic radiation spectrum emitted by a black body (e.g. sun) in thermal equilibrium as a function of wavelength and temperature:

\[
I_0(\lambda, T_{\text{sun}}) = \frac{2hc^2}{\lambda^4 (e^{hc/\lambda kT} - 1)},
\]

being \( T_{\text{sun}} \) the surface temperature of the sun, \( h \) the Plank’s constant, \( c_0 \) the light speed in vacuum and \( \lambda \) the radiation wavelength. Within any medium, an attenuation of the total radiation intensity is measured by the Beer–Lambert law:

\[
I(\lambda) = I_0(\lambda) \exp(-\mu(\text{tot}, \lambda)),
\]

where \( L \) is the fluid depth and \( \mu(\text{tot}, \lambda) = \mu(\text{particle}, \lambda) + \mu(\text{base fluid}, \lambda) \) is the extinction coefficient of the suspension. Specifically, the particle extinction coefficient \( (\mu(\text{particle}, \lambda)) \) includes both scattering and absorption contributions, namely:

\[
\mu(\text{particle}, \lambda) = \frac{3}{2} f_v (Q_{\text{sca}, \lambda} + Q_{\text{abs}, \lambda}),
\]

where \( f_v \) is the particle volume fraction, \( Q_{\text{sca}, \lambda} \) and \( Q_{\text{abs}, \lambda} \) are the scattering and absorption efficiency, respectively. Both \( Q_{\text{sca}, \lambda} \) and \( Q_{\text{abs}, \lambda} \) strongly depend on the particle size parameter \( \alpha = \frac{2\pi}{\lambda} \). In particular, \( Q_{\text{sca}, \lambda} \) is proportional to the fourth power of \( \alpha \). When the particle diameters are much smaller than the wavelength of the incident light and hence in case of nanoparticle, \( \alpha \) and consequently \( Q_{\text{sca}, \lambda} \) are \( \ll 1 \). Therefore, the suspended nanoparticles can be considered as transparent to the elastic collision, and the role of solar absorption is globally enhanced by the suspension.

The large variety of combinations in synthesizing nanosuspensions implies strong sensitivity of the effective optical properties on the physical and chemical characteristics of the...
5. Computational modelling approaches

Computational modelling techniques represent effective tools to observe, describe and understand the thermal physical mechanisms occurring in nanoparticle suspensions. In this section, we review the modelling techniques used for simulating nanoscale and macroscale heat transfer, with particular focus on the simulation of particle aggregation dynamics.

5.1. Nanoscale simulations

Several simulation tools are employed for dealing with nanoscale heat transfer, in particular by studying phonon properties [274–276]. First principle calculations, classical molecular dynamics, atomistic Green’s function and Monte Carlo simulations are some examples of such nanoscale techniques. In the context of particle suspensions, studies on nanoscale heat transport are generally focused on thermal phenomena occurring at the interfaces, e.g. thermal boundary resistance at solid–solid and solid–liquid interfaces [37, 277].

Lattice dynamics is largely carried out to study nanoscale heat transfer. In fact, reasonable predictions of thermal conductance and phonon properties can be done by combining lattice dynamics with first principle calculations [278–280]. However, systems with interfaces and defects are still too complex to be treated by first principle simulations. Thus, an alternative approach to study thermal transport at the nanoscale interface is represented by the atomistic Green’s function method, first developed by Mingo and Yang [281] for modelling electron transport. In such method, the heat current is modeled by the Green’s function, and the phonon propagation is calculated as a function of phonon frequency [282–284].

Recently, great attention has been also devoted to molecular dynamics approach. Non-equilibrium (NEMD) and equilibrium molecular dynamics (EMD) simulations are used to calculate thermal transport properties at particle-solvent interfaces [277, 285], as well as to show the role of particle aggregation in the overall thermal conduction [286, 287]. For example, Zhou et al [277] simulate the heat transfer process from a gold nanoparticle, heated by continuous laser pumping, to a pool of water. Specifically, they showed how particle wettability can influence Kapitza resistance: surface hydrophilicity enhances interfacial interactions, thus increasing the thermal conductance at particle-liquid interface. Such a finding is also confirmed by the MD simulations of Shenogina et al [288]. Another example is offered by Desai and coworkers [289], who studied by NEMD and EMD the thermal transport phenomena in a silicon cluster made of 15 nm diameter nanoparticles, focusing in particular on the effect of ballistic regime within the nanosized neck region.

Although the above methods can model the nanoscale heat transfer phenomena in nanosuspensions, they are intrinsically affected by the small simulation domain. Moreover, the multiscale nature of nanosuspensions requires the integration of several simulation techniques to fully modelling the effect of nanoscale phenomena on overall properties. In other words, nanosuspensions involve length scales much larger than molecular dimensions (i.e. nanoparticles and aggregates, typically in the range 10^{-8}–10^{-6} m), but small enough to be affected by thermal fluctuations and colloidal forces. Hence, nanoscale techniques are not enough to fully describe the properties of nanosuspensions, and multiscale simulation tools are fundamental to link the atomistic length-scale and time-scale with the macroscopic properties of real materials and devices.

5.2. Mesoscale simulations

Modelling the dynamics of nanoparticles plays a fundamental role in studying thermal phenomena in colloidal dispersions. We have already stressed that the creation of percolation networks along nanoparticle clusters represents a key mechanism for thermal conductivity enhancement in nanosuspensions. However, cluster structures are influenced by several chemical and physical factors, and the hypothesis of randomly oriented particles may easily break down. Consequently, understanding the dynamics of percolation path creation is essential to precisely control and describe the effective thermophysical properties.

Many simulation techniques are available to study the dynamics of suspended nanoparticles and their aggregation [290]. A first class of tools includes lattice-based models, where the solvent is treated as lattice (Lattice–Boltzmann techniques [291–294]) or continuum (Navier–Stokes based techniques [295–297]) and the particles are described by immersed boundary method in Brownian motion. The second class, instead, is represented by particle-based methods, where particles are treated explicitly and the solvent can be described either explicitly or included in the colloid-colloid interaction (implicit). On the one hand, multi-particle collision dynamics (MPCD) [298, 299], also known as stochastic rotation dynamics (SRD) [300, 301], and dissipative particle dynamics (DPD) [302–304] are some examples of particle based techniques with explicit description of the solvent. In particular, dissipative particle dynamics was developed to overtake the computational limit of MD. The DPD method includes both hydrodynamic and Brownian fluctuations effects on nanoparticles, while the fluid is represented by groups of dissipative particles interacting each other by exchanging momentum. On the other hand, in fast lubrication dynamics (FLD) [305] or Stokesian dynamics (SD) [306] method, the effect of hydrodynamics is implicitly included in the Brownian motion of the particles. An example of implicit solvent simulations is provided by Liu et al [307, 308], where particle agglomeration is studied by Monte Carlo simulations to include Smoluchowski equation and Brownian motion. Moreover, they investigated the role of hydration repulsion within the extended version of classical DLVO theory. Instead, a recent study combining deterministic and stochastic modelling of nanoparticle agglomeration is presented by Mortuza et al [309]. Here, we remark the importance of correctly modelling the interaction potential between nanoparticles because, as pointed out in
paragraph section 3.2, non-DLVO interactions (i.e. hydration and steric forces) should be also taken into for a realistic modelling of particle kinetics and aggregation.

These simulation techniques provide effective means for predicting suspended particle kinetics and eventually aggregates morphology. Such information is fundamental to evaluate the contribution of thermal percolation on the overall thermal conductivity of nanosuspensions [168, 310–312]. For example, by Monte Carlo simulations of aggregate fractal structures, Evans et al [168] provided a first validation of the cluster homogenization theory expressed in equation (28). Specifically, the aggregation phenomena were modeled by a diffusion-limited cluster–cluster aggregation (DLCCA) algorithm, and the global analysis included the effect of interfacial thermal resistance and cluster aspect ratio. Gharagozloo and colleagues [311, 312] also performed Monte Carlo simulations to model the dynamics of suspended nanoparticles and to calculate the average number of particles in the aggregates, their radius of gyration and hydraulic diameter. These parameters were then coupled to effective medium theory for the evaluation of the overall thermal conductivity. More precisely, the thermal conductivity of aggregates was calculated by differentiating the ‘percolation contributing backbone’ and the ‘non-percolation contributing dead-ends’: the former is calculated by composite theory for completely misoriented ellipsoidal particles [173]; the latter by the Bruggeman model. The authors demonstrated a good agreement between modelling results and experimental measures.

An interesting study on modelling the thermal conduction along nanostructured aggregates is presented by Sastry et al [313]. This work is based on the formation (percolation) of three-dimensional CNT chains and the calculation of the corresponding thermal resistance network. Results highlighted that the enhancement in thermal conductivity critically depends on the CNT geometry, volume fraction and suspension properties. Other investigations on the effect of percolation in CNT based nanosuspension were carried out by Lamas et al [314].

6. Conclusions and perspectives

This review is focused on the heat and mass transport phenomena occurring in nanoparticle suspensions. 

Suspending nanoparticles in traditional heat transfer fluids can be an effective way to enhance their thermophysical properties. Several studies investigated transport phenomena in nanoparticle suspensions, particularly focusing on thermal conductivity and viscosity. However, clear guidelines for a rational design of nanosuspensions are still missing, mainly because of the lack of understanding and control of aggregate morphology and dynamics on suspension stability and thermal properties. Hence, there is a need for bottom–up predictive models including all relevant molecular effects.

One of the main modelling issues is the pronounced sensitivity of the suspension properties and particle aggregation on the characteristics of their constituents, namely particle material, shape, size and volume fraction, as well as base fluid, pH and surfactant concentration. In this sense, the first step to predict the effective mean-field properties of nanosuspensions is provided by the effective interaction potential between nanoparticles. Typically, the standard DLVO theory only provides a qualitative understanding of such interaction potential. However, additional non-DLVO forces should be also considered for a more quantitative modelling of colloidal stability and nanoparticle aggregation. For example, the hydration forces arising in the nanoscale gaps between approaching nanoparticles should be properly modeled. Moreover, when surfactants are added to stabilize and disperse nanoparticles, steric repulsion forces should be also taken into account. Both hydration and steric forces are dependent on the atomistic details of the nanoparticle surface. In the field of computational modelling, an effective tool for evaluating the total interaction potential, including the non-DLVO forces, is represented by the potential of mean forces (PMF) obtained by atomistic calculations [87, 234, 237]. Such PMF can be used to upscale molecular details in coarse-grained simulations at time and length scales much larger than those of all-atom description, therefore allowing to accurately take into account the dynamics of aggregation in implicit solvent modelling (see equation (14)).

The development of multiscale models and a better understanding of the effects of particle aggregation are essential (and still missing) to predict the transport properties of nanosuspensions. This would pave the way to a more rational design of nanoparticle suspensions in a broad range of applications, from biomedicine to engineering.

Acknowledgments

Authors would like to acknowledge the NANO-BRIDGE—Heat and mass transport in NANO-structures by molecular dynamics, systematic model reduction, and non-equilibrium thermodynamics (PRIN 2012, grant number 2012LHP5JC) and the NANOSTEP—NANOfluid-based direct Solar absorption for Thermal Energy and water Purification (Fondazione CRT, Torino) projects.

References

[1] Wagner F E, Haslebeck S, Stieveno L, Calogero S, Pankhurst Q and Martinek K P 2000 Nature 407 691–2
[2] Heiligtag F J and Niederberger M 2013 Mater. Today 16 262–71
[3] Yu W, France D M, Routbort J L and Choi S U 2008 Heat Transfer Eng. 29 432–60
[4] Trisaksri V and Wongwises S 2007 Renew. Sustain. Energy Rev. 11 512–23
[5] Choi S U and Eastman J 1995 Enhancing thermal conductivity of fluids with nanoparticles Technical Report Argonne National Lab., IL, USA
[6] Keblinski P, Phillpot S, Choi S and Eastman J 2002 Int. J. Heat Mass Transfer 45 855–63
[7] Wang X Q and Mujumdar A S 2007 Int. J. Therm. Sci. 46 1–19
[8] Wen D, Lin G, Vafaee S and Zhang K 2009 Particuology 7 141–50
[9] Saidur R, Leong K and Mohammad H 2011 Renew. Sustain. Energy Rev. 15 1646–68
