Review

Fouling Behavior and Dispersion Stability of Nanoparticle-Based Refrigeration Fluid

Eleonora Ponticorvo 1,2,†, Mariagrazia Iuliano 2,3,*†, Claudia Cirillo 1,2,†, Angelo Maiorino 3, Ciro Aprea 3 and Maria Sarno 1,2

1 Department of Physics “E.R. Caianiello”, University of Salerno, 84084 Fisciano, Italy; eponticorvo@unisa.it (E.P.); clcirillo@unisa.it (C.C.); msarno@unisa.it (M.S.)
2 Nano_Mates (Research Centre for Nanomaterials and Nanotechnology at the University of Salerno), University of Salerno, 84084 Fisciano, Italy
3 Department of Industrial Engineering, University of Salerno, 84084 Fisciano, Italy; amaiorin@unisa.it (A.M.); aprea@unisa.it (C.A.)
* Correspondence: maiuliano@unisa.it; Tel.: +39-089-964335
† These authors contributed equally to this work.

Abstract: Nanofluids as heat transfer fluids have been acquiring popularity ever since their beginning. Therefore, the refrigeration research could not keep itself away from the ever-rising horizon of nanofluid applications. On the other hand, nanofluid stability remains the critical bottleneck for use. A significant reduction in nanofluids’ performance can derivate from instability phenomena. Looking to industrial applications, nanofluid long-term stability and reusability are crucial requisites. Nanoparticles’ deposits induce microchannel circuit obstruction, limiting the proper functioning of the device and negating the beneficial characteristics of the nanofluid. The aggregation and sedimentation of the particles may also determine the increased viscosity and pumping cost, and reduced thermal properties. So, there is a need to address the features of nanofluid starting from realization, evaluation, stabilization methods, and operational aspects. In this review, investigations of nanorefrigerants are summarized. In particular, a description of the preparation procedures of nanofluids was reported, followed by a deep elucidation of the mechanism of nanofluid destabilization and sedimentation, and finally, the literature results in this field were reviewed.

Keywords: nanoparticles; nanofluids; nanorefrigerants; stability

1. Introduction

The history of nanofluids was born with the paper of Choi and Eastman in 1995 [1]. They showed, for the first time, an innovative idea of heat transfer fluids by realizing a colloidal suspension of nanoparticles (NPs) in common fluids, which were named “nanofluids”. The nanofluids show new thermal and physical properties thanks to the presence of NPs. In particular, materials such as pure metals, metallic oxides, and carbon-based materials, capable of enhancing the thermal conduction and convection coefficients [2–5] without modifying the base fluid Newtonian behavior, have been explored [6].

To better understand the behavior of these fluids and their characteristics, experimental and numerical studies were carried out [7]. Different properties have been explored [8], such as the convective heat transfer coefficient, thermal conductivity, evaporation phenomena, viscosity, particles size distribution, and NPs’ concentration. Nanofluids, such as ethylene glycol-based, water-based, etc., [9] possess the following advantages [10]:

• Elevated specific surface area and hence higher heat transfer surface between fluid and particles.
• Better stability of the dispersion, in which the Brownian motion of the particles prevails, compared to a normal solid/liquid suspension.
• Decreased pumping power compared to obtaining a quite similar heat transfer.
- Decreased particle obstruction, for heat transfer intensification, in comparison to conventional solid–liquid suspensions (such as fluids containing micro-sized metallic particles or as well as conventional solid/fluid mixtures).
- Facilitated system miniaturization.
- Variety of properties by changing NPs concentration.

Although nanofluids’ features [2,11], such as thermal conductivity, particles’ Brownian motion and migration, thermal and physical properties’ variability with temperature change, increased viscosity with a higher particle concentration, low specific heat to the base fluid, costs and production processes, pressure drop, and pumping power, have been explored, they must be considered simultaneously for a real implementation of nanofluids. On the other hand, the deposition of nanoparticles inside the heat transfer media is an additional crucial challenge. The accumulation of unwanted materials on heat transfer surfaces, due to nanoparticle sedimentation, is defined as fouling [12].

Fouling appears in various classes [12]. Scheme 1 depicts the different classes of fouling [13,14]. Fouling is a constant phenomenon, which starts from an “initiation” stage and then moves on towards other stages [15,16]. Conditioning of heat transfer surfaces occurs during the initiation, or incubation, stage. The second stage is the “transport period”. During this stage, suspended particles are transported near heat transfer surfaces through the phenomena of diffusion, sedimentation, osmophoresis, and thermophoresis. The attachment of transported particles over the heat transfer surface happens during the third stage of fouling, named the deposition period. The detachment of particles from the heat transfer surface regards the last stage of fouling, named the removal period. Several factors, such as temperature and mass flow rate of the working fluid, influence the removal stage of fouling [17].

![Scheme 1](image_url)  
**Scheme 1.** Scheme demonstrating the classification of fouling.

Nanofluid fouling falls into the category of particulate fouling [18]. Due to the interaction of NPs with the base fluid and walls of the heat transfer surfaces, together with temperature differences within the base fluid, particles can lose their stability and stick to the heat transfer surfaces [18]. This is due to particulate fouling, where time is the crucial aspect. The other two main parameters are the mass fraction of NPs and the nanosuspensions’ flow rate [19]. In general, other parameters [12] determining fouling concern the characteristics of the feeds, such as their chemical composition, viscosity, diffusivity, pour and cloud points, density, longevity factors, and interfacial properties. In particular, the feed behavior is due to the chemical composition, homogeneity, their compatibility with one another, and with the heat transfer surfaces. In addition, the nanofluids’ storage conditions and their exposure to oxygen influence the rate and nature of fouling. Moreover, equipment design and operating conditions, such as the heat transfer surfaces’ geometry, temperature, nature of used alloys, and surface properties are the other elements. Fouling on the heat transfer surface was also caused by a very high amount of nanoparticles in a nanofluid. Sedimentation problems in base fluids, with an excessive concentration of suspended solid
nanoparticles, tend to induce particulate fouling over heat transfer surfaces which leads to a significant reduction in thermal performance. Another main critical outcome of long-term particulate fouling is clogging due to the agglomeration and clustering of nanoparticles. On the other hand, the pressure drop and friction factor, if the volume fraction and size of nanoparticles exceed optimal values, tend to rise [20–23], leading to an enhancement of pumping power demand [24].

Fouling is one of the major problems in this field, and its prevention or mitigation is still a challenge. Fouling on process equipment surfaces has a substantial and undesirable influence on the unit’s operational efficiency, with negative economical impacts [25,26], i.e., efficiency reduction inducing manufacture losses and the damage of manufacturing during shutdowns due to fouling, and maintenance costs associated to the surfaces’ cleaning and replacement of the equipment [27]. Fouling determines a cross-sectional reduction of the flow channels [28]. Heat transfer reduction is the typical negative effect of fouling [29,30] due to the low thermal conductivity of the fouling layer, and increases in the pressure drop, blocked pipes, pollution, and corrosion. Moreover, increased tribological resistance is a consequence of fouling. To control a heat transfer system, a plot of the outlet temperature versus time can be used. Fouling has a significant environmental impact, leading to the release of several million tons of carbon dioxide [31], as well as the use of harmful cleaning chemicals.

Along with the concept of nanofluids, its disadvantages should be considered and actions should be taken accordingly to eliminate problems that could reduce its performance caused by the deterioration of heat transfer surfaces and an increased pressure drop.

The pressure drop, thermal performance, and fouling factor of water-based multi-walled carbon nanotube nanofluids at 0.5–1.5 vol% concentrations, in the Reynolds number range from 700 to 25,000, were studied by Sarafraz and Hormozi [32]. A nonlinear fouling behavior and a heat transfer coefficient reduction were observed. An enhanced fouling rate, by increasing the nanofluid mass concentration, was observed in TiO$_2$-water nanofluids, under different operating conditions such as mass loadings, heat flux, and the inclination of thermosyphon [33]. The thermal performance of CuO/water nanofluid in the heat exchanger was investigated by Sarafratz et al. [34]. Experimental evidence highlights that NP fouling can be controlled by applying low-frequency vibrations determining the thermal resistance’s decrease. Moreover, fouling determines the increased roughness and pressure drop. The fouling behavior of CuO NPs on the heat exchanger surface was experimentally investigated at different operating parameters, and a correlation based on the isothermal-diffusive particulate flow was proposed by Nikkhah et al. [35]. In particular, the higher the amount and flux of nanofluids, the more fouling occurs. Furthermore, with increasing the wall temperature, a reduction in fouling resistance was found. The most challenging issue, to date considered as limiting the concrete usage and additional development of nanofluids, was the dispersion stability [2].

In particular, the repeated heating/cooling cycles or high temperature in thermal nanofluids tend to induce the NPs’ impact probability and aggregation tendency. Therefore, in thermal nanofluids, it is more difficult to reach a stable dispersion. To cross this critical problem, several approaches have been explored to improve the dispersion stability of thermal nanofluids, such as ultrasonic treatment, mechanical stirring, utilizing chemical surface modifications with surfactants, or introducing surface charges. To avoid the settling and sedimentation of particles, an appropriate choice of the preparation approaches for the nanofluid must be considered. To consider a nanofluid stable, the agglomeration predisposition must be avoided [36]. Liquids with suspended particles are subjected to instability and form deposits because they are exposed to different actions, such as gravitational force, Van der Waals attractive interactions, electrostatic repulsive interactions, and buoyancy forces. The gravitational and Van der Waals forces have adverse effects on colloidal stability. According to the DLVO theory, particles tend to agglomerate, inducing sedimentation when Van der Waals attraction prevails over electrostatic repulsive forces [10]. Furthermore, the operational parameters (i.e., concentration, shearing, temperature, magnetic field, and
salinity) can also unfavorably affect stability. So, there is a need to address the aspect feature of nanofluids from the preparation phase and during stabilization evaluation, and the choice of operating conditions.

A special type of nanofluid containing refrigerants (R134a, R123, R141b, etc.) as the base fluid is called a “nanorefrigerant” [37]. Nanorefrigerants show improvement in thermal conductivity [38] and heat transfer performance [39]. A lot of studies have been performed in this field [40,41] because the addition of nanoparticles to refrigerants can largely influence the energy efficiency of air conditioning systems and refrigerators. A nanorefrigerant study is typically ordered into two groups. The first regards the base fluids, which are in liquid at atmospheric conditions and a temperature uploaded directly by suspending nanoparticles. In the second group, nanoparticles are suspended in lubricants (nanolubricant), which are employed for refrigerant compressors, to carry traces of nanoparticles during system working time. It should be noted that the significance of nanoparticles’ suspension in lubricants triggered strong interest among researchers. In particular, they remarked a better system performance in the presence of nanoparticles in lubricants. Several works have been carried out using a refrigerant–nanolubricant match [11,42,43].

In this work, we pay attention to the dispersion stability of thermal nanofluids, preceded by a review of fabrication [44–46], thermo-physical properties [47–52], or applications [53–57] of thermal nanofluids. In the following, after a systematic description of the particulate fouling, nanofluid preparation procedures and stability evaluation approaches were reported. Finally, the mechanism of nanofluid destabilization and sedimentation was elucidated, nanofluid stabilization methods were explored, and the literature results in this field were reviewed. Particular attention was devoted to the impact of various types of nanofluids on the fouling of engineering thermal devices and the investigation of avoiding a particulate fouling formation.

2. Particulate Fouling: Towards a Description

Fouling can be addressed as a result of the coupling and interplaying of four simple phenomena (see Figure 1) [27]:

- **Deposition:** operated by the contacts between the fluid and particles and then also by the contacts between the wall surfaces and particles.
- **Re-entrainment:** Happens after the deposition. Indeed, the settled NPs can be re-suspended. This phenomenon is determined by contact forces and hydrodynamic forces: whether the particles stay on the surfaces or are re-suspended depending on the equilibrium between these forces.
- **Agglomeration:** It intervenes only when the NPs’ concentration is high enough to permit surface–surface interactions to occur repeatedly. Similar to the deposition phenomenon, the frequency of particle–particle collisions is governed by the hydrodynamic transport of the particles, while the resulting adhesion between two particles can be limited by the interactions between the short-range particles. Furthermore, when adhesion forces are lower than hydrodynamic forces, the break-up of aggregates can happen.
- **Clogging:** Occurs when several NP layers collect on the surface leading to a multilayer formation. After the growth of several layers of particles, the deposit disturbs the hydrodynamic flow, and, when the deposit reaches a size similar to the section of the pipe, the blockage occurs.

In each of the elementary phenomena, three main physical interactions are involved: particle–fluid, particle–particle, and particle–surface interactions, and their relative importance depends on the situation considered. Moreover, the hydrodynamic particles’ transportation and the attachment mechanism are the major fundamental phenomena involved. This two-step process is the main one used in the structure of fouling [58–61] since the transport and attachment happen at two different times and spaces.
In particular, in the case of particulate fouling, the processes involved are [62]: particles’ movement (inertia, diffusion, thermophoresis), linkage (Van der Waals forces, surface charges), and erosion. Since the particle deposits are not very robust, at a consistent fluid shear, abstraction occurs. Particulate fouling is due to [63]:

- Flow velocity. Indeed, the fouling resistance decreases continuously with the increasing velocity, except for a very low velocity.
- Heat flux. With an increasing heat flux, the resistance to fouling phenomena reaches a maximum, which drops in amplitude and moves towards higher heat fluxes depending on whether the wall shear stress is increased.
- Suspension pH. The fouling resistance is pH-dependent, showing a maximum at a specific pH value. Attachment and agglomeration are due to electrical double layer forces and Van der Waals forces. Repulsion due to the first-mentioned force is due to the charges building up on the surface of hydroxides and metal oxides in solutions. These charges are closely related to the solution pH and its ionic content.
- Surface temperature. This effect is lower than in the case of the other fouling mechanisms. In general, the fouling resistance increases with the temperature more rapidly at higher temperatures and slowly at low temperatures.
- Surface roughness. Non-wetting surfaces delay fouling and a better surface finish leads to the delay of fouling and easiness of cleaning. On the other hand, rough surfaces boost particulate deposition. During fouling, the roughness will be influenced by the deposit itself.
- Particle concentration. Fouling resistance increases with particle increases reaching a constant value.
- Particle size. The fouling resistance is also dependent on the particles’ size.

3. Preparation Procedures

Nanofluids are generally synthesized using two different approaches [45, 64, 65], i.e., (a) one-step method, or (b) two-step method. The one-step synthesis method consists of the preparation of nanomaterials directly in the base fluids, particle drying, and a final dispersion of NPs [44]. The one-step synthesis method allows for the contemporaneous synthesis and compatibilization of the NPs in the base fluid. The stability for these nanofluids is intrinsically more efficient than for the two-step method. This is mainly due to there being no need for the drying step which, potentially, can determine the NPs’ agglomeration. However, this process is possible only for fluids with a low vapor pressure and often can require high production costs [66]. Other disadvantages to be overcome are the intrinsic batch approach and the difficulties for the NPs’ size control. An example is the one-step synthesis of cuprous oxide-based nanofluid, in which polyvinyl-pyrrolidone (PVP) was used for stabilization [67]. Vapor Deposition, developed by Choi in 2001 [68], is a typically
employed single-step approach. It consists of the formation of a thin film of base fluid on the walls of the reactor under centrifugal forces. The NPs’ precursor materials heated on a resistive crucible evaporate and condense into nanoparticles in the cold base-liquid fluid. The high cost is the main disadvantage of the one-step method, although cheaper technologies are being developed. Additionally, the one-step synthesis can only be in batch processes and for small quantities of materials. Therefore, this approach is not yet appropriate for industrial production. Moreover, the nanofluid obtained following this approach may have residues of non-converted reagents, negatively affecting the nanofluids’ performance. In the case of the two-step methods (Figure 2), NPs are prepared alone by both chemical and physical processes. NPs are then dispersed into a base fluid using stirring and homogenization. Magnetic stirring is the usual method adopted to disperse NPs from eventual clusters. In this case, the stirring rate has to be controlled to avoid a bubble formation causing a chemical modification of the treated materials. Among the other possible ultrasonication processes [69], which can use ultrasonication baths or probes, are commonly and widely accepted physical methods to disperse NPs in base fluids. Probe ultrasonication is potentially more promising than an ultrasonication bath, allowing, at different power and frequency levels and for different time intervals, good results. The main drawback of the two-step method is the possible aggregation of the nanoparticles caused by the considerable Van der Waals attractive forces. Typically, surfactants are used to help stability. This is the commercial approach for nanofluid preparation. Most researchers prefer this method because it is comparatively easier and more economical.

![Figure 2. Two-step method.](image)

4. Stability Evaluation

The theory from Derjaguin, Landau, Vewey, and Overbeek (DLVO) can be used to explain colloidal stability. The theory is based on the following considerations: (i) a diluted particle dispersion; (ii) the forces acting on the NPs are electrostatic forces and Van der Waal attractive forces; (iii) the gravity and buoyancy forces can be neglected; (iv) homogeneity of the suspension; and (v) in the colloidal system the distribution of ions depends on three factors which are Brownian motion, electrostatic force, and entropy-induced dispersion. However, a new extension to the DLVO theory better describes the constancy of nanofluids. The total potential energy \( V_T \) determining colloidal stability, according to the extended DLVO theory, can be expressed as:

\[
V_T = V_A + V_R + V_S
\]
where $V_A$, $V_R$, and $V_s$ are the contribution from the Van der Waal attractive potential, and electrostatic repulsive and steric potentials, respectively [70]. The total potential energy depending on $V_A$ and $V_T$ is directly correlated with the distance between the NPs, which is affected by Brownian motion changing the separation distance and interaction potential. In the case in which $V_A$ prevails over $V_R$, NPs tend to form large clusters with suspension destabilization. Stability was ensured by a high repulsive interaction potential. Indeed, if the high interaction potential is attractive, the stability will be poor (Figure 3a) and the particles settle faster. In other words, if an attractive potential prevails over repulsive forces, the collision will occur, resulting in a non-stable suspension. On the other hand, if repulsion prevails, the suspensions will be stable. Stable nanofluids need repulsive forces dominating the solution.

On the other hand, depending on the temperature, two different particles can overcome the energy barrier and aggregates, forming clusters. These clusters are irreversible in nature. For low zeta potential values, a high Van der Waal potential can dominate over the repulsive potential creating the secondary minimum (Figure 3a), creating bonded clusters. These clusters can be forced to separate under vigorous agitation and ultrasonication to form a stable nanofluid suspension. More in general, to ensure long-term stability, high repulsive potential is needed. Figure 3b shows the dependence of the high potential barrier affecting the nanofluid stability.

Several techniques can be used for the evaluation of the nanofluid stability, i.e., sedimentation under centrifugation; spectral absorbance; zeta potential evaluation; a transmittance measurement; transmission electron microscopy; the 3$i$ω method; and dynamic light scattering. For stability evaluation, the most common technique is sedimentation (Figure 4). It consists of the formation of sediment due to gravity in a liquid column. The sedimentation method, which is a time-consuming process, highlights the quality of dispersions: a good dispersion takes a long time to observe obvious sedimentation. The centrifugation technique requires a relatively lower time to evaluate the nanofluid stability, following the same principles of sedimentation. In this case, the centrifugal force accelerates the sedimentation process. In this case, centrifugation is applied to accelerate the evaluation of long-term stability. Both spontaneous and centrifugal sedimentation techniques only provide a qualitative analysis of the stability of the nanofluids.

Zeta potential, which is the electric potential difference between the dispersing medium and the stationary layer of fluid, can be used to check and predict dispersion stability [68,71]. Low zeta potential values mean instability, and vice-versa. Quantitative measurements of the nanofluid stability can be obtained by spectral absorbance and transmittance measurements [72]. Stability is evaluated by analyzing the absorption peak under UV–VIS spectroscopy during the time [73]. If absorbance decreases with time, instability occurs. It is an easy and reliable method if the dispersed nanomaterials have absorption bands in the range 190–1100 nm [74]. Stability measurements are difficult for nanofluids with dark-colored nanoparticles at high concentrations. Figure 5 shows a scheme of the apparatus for these measurements.

The 3$i$ω method of stability analysis exploits the nanofluids’ changes in thermal conductivity, which originates from particle agglomeration and settling [75]. Transmission Electron Microscopy (TEM) can be also used [68,76,77], allowing to measure particle size and distribution [68,78]. Additionally, high-resolution TEM allows the evaluation of particle arrangements and surface layers.

The dynamic light scattering (DLS) technique can be used to evaluate particle size distribution [79]. Figure 6 shows a DLS apparatus. The scattered light fluctuation under laser illumination is used to evaluate particle sizes [80].

Below is reported a literature overview, with particular attention to the nanoparticles used and the aspects related to the stabilization of the NPs affecting performance.
Figure 3. Schematic diagram of the potential energy as a function of the NPs’ distances in two cases: (a) low potential barrier, and (b) high potential barrier.

Figure 4. Scheme of sedimentation measurement.
5. Nanofluid Stabilization Methods

The stabilization methods can be classified into two main approaches: chemical and mechanical. The NPs hydrophilic or hydrophobic character can guide the choice of base fluids, which can be subdivided into non-polar or polar. NPs with a surface of a hydrophilic nature, e.g., graphene oxide and metal oxides (Al₂O₃, TiO₂, CuO), can be easily dispersed in water and other polar solvents. More in general, to favor hydrophobic nanoparticle dispersions, non-polar fluids such as oils have to be preferred. Typically, in this case, the addition of a stabilizer is not obligatory. On the other hand, in order to stabilize hydrophilic NPs in a non-polar solvent or vice versa, several additional functionalizations and chemical approaches can be employed. To reduce the size of the aggregate improving stability, different mechanical approaches can be explored, i.e., vibration and ball milling, ultrasonic methods, etc.

For chemical stabilization, three different approaches can be used (Figure 7): (a) electrostatic stabilization; (b) steric stabilization; and (c) electrosteric (a mixed electric and steric) stabilization.

In case (a), nanofluid stabilization can be obtained by using covalent functionalities on the surfaces, ionic surfactants, and pH change. Steric stabilization can be attained by the addition of polymer and non-ionic surfactants. Electrosteric stabilization can be obtained by a combination of electrostatic and steric approaches.
Figure 7. Schematic representation of electrostatic (a), steric (b), and electrosteric (c) stabilization scheme.
6. Nanoparticles in Nanofluids

Among the factors that govern fouling, the long-term stability of the nanoparticles’ dispersion to avoid particle accumulation and deposits is still a critical factor and a key challenge to be better explored before applications. The nanofluids’ stability means that the suspended nanoparticles do not form large aggregates inducing sedimentation in base fluids (water, oil, alcohol, etc.). The physical and thermal properties [81] are dependent on their stability. In particular, nanoparticle deposits induce microchannel circuit obstructions, limiting the proper functioning of the device and negating the beneficial characteristics of the nanofluid. The aggregation and sedimentation of the particles may also determine the increased viscosity and pumping cost, and reduced thermal properties. The predisposition of nanoparticles to form clusters in the suspended state induces instability for the nanofluids. On the other hand, particles in the nano-size show a much greater propensity to aggregation due to their bigger surface activity. Nevertheless, there are many advantages to using nanoparticles as reactants in refrigeration systems, some of them being related to the improvement in the heat transfer coefficient and thermal conductivity, reducing the system’s energy consumption. The substitution of conventional refrigerants with nanorefrigerants (Table 1), such as hydrofluorocarbons (HFCs), chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrocarbons (HCs), determines a reduction of the climate impact [41]. The performance of nanoparticles in air conditioning and refrigeration systems is a consequence of different factors such as shape, chemical nature, size, and concentration. In particular, in a refrigeration system, the increase in the coefficient of performance (COP) may depend not only on an increased amount of heat absorbed, but also on a decrease in compressor work [82,83]. In this sense, suitable lubrication for the compressor of the vapor-compression refrigeration (VCR) system can also improve the efficiency of operations. The thermal and physical properties of the lubricant oil can increase as well with the addition of nanoparticles [84]. Although the choice of nanoparticle materials for refrigerants and lubricants is restricted, there are numerous mixtures of nanoparticles in base fluids (oils and refrigerants), and different sizes and concentrations have been explored (Table 2). Typically, the used nano-additives are pure metals (i.e., copper, gold, nickel, aluminum, and so on), as well as metal oxides (i.e., Al$_2$O$_3$, TiO$_2$, CuO, ZnO, and SiO$_2$) and carbon-based materials. Other common base fluids, apart from that cited in Table 1, include water propylene compounds, ethylene glycol, and so on. [85].

In particular, nanofluids and/or nanorefrigerants, are a mixture of nanoparticles dispersed in a base fluid. Nanoparticles are prepared and dispersed by using single-step or two-step methods, consisting of the preparation of the nanoparticles and then dispersion [86]. Research has been carried out to explore the thermal conductivity of the nanofluids. Scientists concluded that the thermal conductivity of nanorefrigerants rises depending on the NPs’ nature and concentration [87]. The durable dispersion stability of nanoparticles acts on the thermal conductivity. Indeed, an improved dispersion performance determines the enhanced thermal conductivity of nanorefrigerants.

The diamond NPs have a higher thermal conductivity [88], so diamond nanoparticles/oil suspensions have a significant possibility to enhance the boiling heat transfer of the refrigerant and improve the performance of refrigeration systems more than metal or metal oxide NPs/oil suspensions. To increase the performance of a refrigeration system by adding diamond nanoparticles, the characteristics of the nucleate pool boiling heat transfer after the addition of diamond NPs have to be explored. Peng et al. [89] explored the nucleate pool boiling heat transfer performance of nanodiamonds added in R113/polyol-ester oil (POE), in the presence of VG68 ester oil, observing an improvement of the boiling heat transfer coefficient. In ref. [90], a new model based on the Rohsenow correlation was proposed to predict, in the presence of nanoparticles, the pool boiling heat transfer coefficient for refrigerant/oil blends. The approach allowed us to predict the boiling heat transfer coefficient values with high accuracy. Kedzierski [91] analyzed, in a horizontal pipe, the effect of the addition of diamond NPs on the boiling behavior of R134a/polyol-ester blend. A nanolubricant containing the nanoparticles (2.6%) in volume in a commercial polyolester
lubricant (RL68H) was blended in R134a. At a low addition, 0.5% mass fraction, the NPs determined an increase in the heat transfer in comparison with pure R134a/polyolester of 99.5%.

Table 1. List of main refrigerants used.

| Type            | Refrigerant |
|-----------------|-------------|
| HFC             | R23         |
|                 | R32         |
|                 | R125        |
|                 | R134a       |
|                 | R143a       |
|                 | R152a       |
| HFC blend       | R410a       |
|                 | R407c       |
|                 | R425a       |
| CFC             | R11         |
|                 | R12         |
|                 | R13         |
|                 | R113        |
|                 | R114        |
|                 | R115        |
|                 | R500        |
| HCFC            | R22         |
|                 | R123        |
|                 | R124        |
|                 | R141b       |
|                 | R142b       |
| HC              | R600        |
|                 | R600a       |
|                 | R290        |

Jiang et al. [38] analyzed the thermal conductivity of carbon nanotubes-based nanorefrigerants. In the paper, a numerical model was proposed to forecast the thermal behavior of the mixture. A Transient Plane Source (TPS) technique was employed for measurements. Different carbon nanotubes, based on the aspect ratio, were tested, observing that a sudden increase in thermal conductivity was obtained by increasing the aspect ratio.

However, in the case of CNTs, since they easily agglomerated to each other, degrading the nanofluids’ thermal characteristics [92], the stability of the fluid became a key challenge. To solve this problem, CNT can be functionalized [93], e.g., hydrophilic groups (–OH) and (–COOH) at the ends and the sidewalls of CNTs allowing direct stabilization in water [94]. In particular, Talaei et al. [95], for the use in a two-phase closed thermo-siphon, modified the CNT’s surface with COOH groups, measuring the thermal conductivity of the water-based nanofluids by a KD2 prob. The lower surface functionalization with COOH multi-walled carbon nanotubes (MWCNTs) exhibited improved homogeneity and higher thermal conductivity [95]. Sardarabadi et al. [96] experimentally examined the effects of functionalized MWCNTs/water nanofluids. Zeta potential was used to evaluate the stability of the nanoparticle dispersions in the base fluids. The surface of the MWCNTs modified with sodium and potassium persulfate exhibited a mean zeta potential value for K-CNTs and Na-CNTs based fluids (0.4 wt%) of $-36.39$ and $-46.33$ mV, respectively. On the other hand, Ozturk et al. [97] formulated graphene nanosheets (GNS) and MWCNT-based nanorefrigerants. At low NP concentrations, from 0.25 to 1 vol%, in hydrofluoroether (HFE) refrigerant and fluorocarbon stabilizer Krytox 157 FSL (DuPont), the unique potential of improving thermal conductivity yet exhibited by carbon nanotubes was shown [98–100]. Park et al. [101] measured the nucleate boiling heat transfer coefficients of R123 and R134a, the most usually employed refrigerants for chilling in buildings, in a 152.0 mm pipe with
a diameter of 19.0 mm in the presence of 1.0 vol.% CNTs. For these two refrigerants, the addition of CNTs resulted in heat transfer enhancement. At the small heat flux, the increase was 36.6%. Bubble generation, occurring as the heat flux increases, determines a decrease in the improvements. They found that CNTs did not cause fouling, as typically occurs with the other NPs. NPs show affinity to the metal surface but CNTs did not show this kind of behavior; however, this result must be confirmed in long-term experiments.

Mohan et al. [102] analyzed the behavior of gold, CNTs, and HAuCl₄ NPs dispersed in Polyalkylene Glycol lubricant, in a Vapor Compression Refrigeration System (VCRS). The results of their activities were very significant for the nanorefrigerants’ research. The increase in the volume fraction of nanolubricant determined a compression work reduction, enhancing COP up to 31.7%, with the addition of gold NPs (0.1%) and CNTs (0.005%) in Polyalkylene Glycol lubricant, with a reduction of 8% of the energy loss.

Metal oxide nanoparticles are chemically more stable than their metallic counterparts [103].

Copper, a good thermal and electrical conductor, is a d-block element. Copper can form two stable oxides. In particular, cupric oxide (CuO) is a semiconductor showing interesting thermal properties when mixed in the nanosize with a base fluid [104]. CuO nanoparticles in base refrigerants allow improvements in the heat transfer characteristics and cooling capacity [105]. The NPs’ concentration is an important factor that affects the boiling heat transfer coefficient [106]. Sun and Yang [107] performed tests to analyze the heat transfer during boiling and flow for Cu–R141b, Al–R141b, Al₂O₃–R141b, and CuO–R141b nanorefrigerants (weight fractions 0.1 wt.%, 0.2 wt.% and 0.3 wt.%), and in a horizontal pipe. To enhance heat transfer [108], Span−80 was used as the dispersant. The nanorefrigerants’ stability was monitored through the transmittance. They found that the transmittance decreased and the stability increased with an increased mass fraction. The transmittance was significantly higher in the absence of a dispersant. Thus, in the absence of a dispersant, the stability was poor. They concluded that the increase in the nanoparticle mass fraction allows for improving the heat transfer performance and the heat transfer coefficient. They also pointed out that the high thermal conductivity of Cu determines the highest enhancement in the heat transfer coefficient of the copper-based nanorefrigerants.

Samira et al. [109] analyzed CuO/EG-water nanofluid in radiators of cars and concluded that the nanoparticles’ addition determines an increased heat transfer rate and, at the same time, the pressure drop increases. This trend is highlighted more and more by increasing the Reynolds number and/or the nanoparticles’ volume fraction, which increases the viscosity. They studied the effect of the radiator inlet fluid temperature increases to reduce the viscosity, pressure drop, and friction factors. When the inlet temperature increased by 19 °C, the pressure drop was reduced by about 13.17%. The results indicated that nanofluids based on water/EG and CuO nanoparticles can increase the heat transfer rate [110], providing a promising route for the development of performing cars radiators. Moreover, the decrease in the weight of the cooling system determines fuel burning and provides an increased lifetime for different automotive components. HFCs, such as R425, R407C, R410a, R32, and R134a, exhibit low solubility in naphthene-based mineral oils (MOs), which are widely used in residential air conditioners (RAC). These significant solutions for HCFC22 typically exhibit good solubility in POE lubricants (usually employed as the lubricant for RAC compressors with an HFC refrigerant). Henderson et al. [111] investigated the possibility to mix silica and CuO NPs into R134a and R134a/polyester (POE). Silica nanoparticles were coated with hexamethyldisilazane (HMD) to favor the dispersion. Copper oxide NPs, with an average diameter of 30 nm, were then mixed with a commercial POE (RL68H-nominal kinematic viscosity 72.3 µm²/s at 40 °C). SiO₂ NPs in R134a determine a heat transfer coefficient decrease (up to 55%) in comparison to pure R134a. This is due to the difficulties in avoiding agglomeration. However, a significantly increased heat transfer coefficient was obtained by adding the NPs to a mixture of R134a and polyester. Moreover, the characterization showed no significant change in the pressure drop for the R134a/POE/CuO nanofluid. However, there are four main challenges in
using refrigeration systems using POE: (i) POE is hydrolytic and hygroscopic [112], so it is necessary to reduce the water and contaminations’ presence; (ii) compared with mineral oil/HCFC mixtures, POE/HFC shows poorer lubrication activity; (iii) POE is not suitable to replace refrigerants; (iv) some components of the refrigeration systems must be substituted determining additional manufacturing costs. More in general, what is needed is the improvement of HFC solubility in mineral oils. Blends of hydrocarbons can be used for this purpose [113], but the disadvantage is the flammability of hydrocarbons. Nanoparticles, enjoying some intrinsic properties, can activate the chemical polarity of mineral oil lubricants, improving the compatibility with HFC refrigerants.

Wang et al. [114] used an R410a/MNRO/NiFe$_2$O$_4$ nanorefrigerant in a residential air conditioner. They prepared a mineral-based nanorefrigeration oil (MNRO), obtained by adding modified NPs of NiFe$_2$O$_4$ in a naphthene-based mineral oil B32 lubricant. The blend was tested in RAC using HFC refrigerants. To obtain the MNRO, the NPs were modified in the presence of sodium lauryl benzenesulfate (DBS) and ethylene glycol by mixing in a mortar, and then functionalized in the presence of Span—80 in the range 8 to 5 of weight. The modified nano-NiFe$_2$O$_4$ particles were mixed with tricresyl phosphate (TCP) and the B32 lubricant. The new MNRO was tested spectrophotometrically to analyze the dispersion stability. The MNRO stability was evaluated enough for use in RAC.

Spherical and cubic shape ZnO/R134a nanorefrigerants were obtained by a two-step approach [115]. To disperse ZnO NPs in the R134a refrigerant, a 10% volume fraction of NPs were sonicated for 2 h. The experimental results show that fixed NP concentrations determine a nanorefrigerant-specific heat decrease, which is due to the lower specific heat of the ZnO NPs. Moreover, due to the high thermal conductivity of ZnO NPs, a significant increase in the thermal conductivity for both additions of cubic shaped and spherical ZnO NPs was observed (25.26% and 42.5%, respectively).

TiO$_2$ NPs have been widely used mainly because TiO$_2$ can be considered as a biocompatible material. TiO$_2$ is obtained at the industrial level and can be applied in different situations including heat transfer property improvements. Mahbubul et al. [116] investigated the R123/TiO$_2$ nanorefrigerant viscosity under NP increases from 0.5% to 2% in a horizontal pip. Temperature influence was also considered. It was found that the volume fraction can increase viscosity, which can be lowered by temperature increases. Bi et al. explored [11] the performance in refrigeration of TiO$_2$ NPs by using freeze capacity and energy consumption tests. The studies suggest that R134a and mineral oil added with TiO$_2$ NPs, safely and normally can work in refrigerators. The refrigerator performance was increased more than with pure R134a and POE, showing a 26.1% reduction in energy consumption in the presence of 0.1 wt.% TiO$_2$ NPs in comparison with a pure R134a/POE system. Stability for 60 h was detected under light transmission.

In the paper of Zhelezny et al. [117], an investigation of the parameters such as the viscosity, capillary constant, density, solubility, and surface tension of the R600a oil-based mineral compressor was reported. The NPs used were TiO$_2$ and Al$_2$O$_3$. The refrigerant nano-oil solutions (RONS) were obtained in a two-step approach. Oleic acid was employed as a surfactant (20 wt.% of the NPs weight). The stability under time increase was studied by measuring the mean NPs’ radius by a dynamic light scattering technique. The evolution of static and shaken samples was followed for days. The second sample was analyzed to simulate the mechanical stirring in the real conditions of a refrigeration system. The NPs’ sizes stayed constant in both cases, indicating the possibility of using these nanofluids in refrigeration compressor systems. In the paper of Fedele et al. [118], the results are very similar. In their experiments, the size of the TiO$_2$ NPs was evaluated in a water solution each day after nanofluid sonication.

Jwo et al. [119] explored Al$_2$O$_3$-based nanofluids produced from the direct synthesis method; an ultrasonicator was applied for the NPs’ dispersion at several fractions (1.0, 1.5, 2.0 wt.%). The lubricant of R134a was used as the base solvent. The main target of the studies was to analyze thermal conductivity dependence in the temperature range 20–40 °C. Mahbubul et al. [120] studied the physical characteristic of nano-added refrigerants under
temperature increases with particular attention to the air-conditioners. A mixture of R134a with the addition of 5% Al₂O₃ and other metallic oxide was studied as a nanorefrigerant in the range 283 K to 308 K of temperature. The studies highlight that the nanorefrigerant exhibits increased viscosity (+13.68%), density (+11%), and thermal conductivity (+28.58%) more than fluids alone. A wide number of applications and methods of preparation were proposed [121]. The nanofluids stability potential was also explored [121] which was found affected by the NPs’ amount.

**Table 2.** Overview of various studies of nano-refrigerants.

| NPs         | Size                  | Loading           | Base Fluid | Lubricant/Surfactant                  | [Ref.] |
|-------------|-----------------------|-------------------|------------|--------------------------------------|--------|
| Diamond     | 10 nm                 | 0 ÷ 5 wt.%        | R113       | VG68                                 | [89]   |
| Diamond     | 10 nm                 | 2.6 vol.%         | R134a      | RL68H                                | [91]   |
| CNT         | 100 nm, 667.7 nm, 18.8 nm, 125 nm | 0.2 ÷ 1 vol.% | R113       | -                                    | [38]   |
| CNT         | 20 ÷ 50 nm            | 0.1% Au + 0.005% CNT; 0.2% Au + 0.005% CNT (vol.%) | R134a      | -                                    | [102]  |
| CNT         | 15 ÷ 80 nm            | 0 ÷ 0.1 vol.%     | R113       | -                                    | [122]  |
| MWCNTs      | 8 ÷ 15 nm (length: 10–50 µm); 10 ÷ 30 nm (length: 0.5–40 µm) | 0.25 ÷ 1 vol.% | HFE-7500 | Fluorocarbon stabilizer: Krytox 157 FSL | [97]   |
| MWCNTs      | 20 nm                 | 1 vol.%           | R124, R134a | -                                    | [101]  |
| GNS         | 10 (length: 2–15 µm)  | 0.25 ÷ 1 vol.%    | HFE-7500 | Fluorocarbon stabilizer: Krytox 157 FSL | [97]   |
| Au          | 10 nm                 | 0.1 ÷ 0.2 vol.%   | R134a polyalkylene glycol | - | [102]   |
| Cu          | 40 nm                 | 0.1 ÷ 0.3 wt.%    | R141b Span 80 | - | [107]   |
| Al          | 40 nm                 | 0.1 ÷ 0.3 wt.%    | R141b Span 80 | - | [107]   |
| CuO         | 40 nm                 | 0 ÷ 1 wt.%        | R600a POE | - | [123]   |
| CuO         | 30 nm                 | 0.02 ÷ 0.08% vol.% | R134a POE | - | [111]   |
| CuO         | 60 nm                 | 0.05 ÷ 0.8 vol.%  | H₂O/ethylene glycol (40/60) | - | [110]   |
| CuO         | 60 nm                 | 0.05 ÷ 0.8 vol.%  | H₂O/ethylene glycol (40/60) | - | [109]   |
| SiO₂@HMD    |                      | 0.05% ÷ 0.5% vol.% | R134a | - | [123]   |
| NiFe₂O₄     | 35 nm                 | R134a R407c R410a R425a | Naphthenic-based mineral oil B32 lubricant/Span-80 | - | [114]   |
| ZnO         | 29.1 nm               | 10 vol.%          | R134a      | -                                    | [115]  |
| TiO₂        | 40 nm                 | 1.7 ÷ 8.3 wt./vol.% | R141b Lubricating oil | - | [124]   |
| TiO₂        | <25 nm                | R600a Mineral oil/oleic acid | - | - | [117]   |
| TiO₂        | 21 nm                 | 0.5 ÷ 2 vol.%     | R123       | -                                    | [116]  |
| NPs  | Size  | Loading   | Base Fluid       | Lubricant/ Surfactant                        | [Ref.] |
|------|-------|-----------|------------------|---------------------------------------------|--------|
| TiO₂ | <25 nm| 0.25 ÷ 1 vol.% | HFE-7500         | Fluorocarbon stabilizer: Krytox 157 FSL   | [97]   |
| TiO₂ | 50 nm | 0.06 ÷ 0.1 wt.% | R134a            | SUNISO 3GS                                  | [11]   |
| TiO₂ | 21 nm | 0.01 ÷ 0.05 vol.% | R141b           | -                                            | [125]  |
| Al₂O₃| 40 nm | 0.1 ÷ 0.3 wt.% | R141b            | Span 80                                     | [107]  |
| Al₂O₃| 13 nm | 0.05 ÷ 0.15 vol.% | R141b           | -                                            | [126]  |
| Al₂O₃| 30 nm | 5 vol.%      | R134a            | -                                            | [120]  |
| Al₂O₃| <50 nm| 2 ÷ 6 vol.%  | R600a            | Mineral oil/oleic acid                      | [117]  |
| Al₂O₃| ~10 nm| 1 ÷ 2 wt.%   | Water/ethylene glycol (50/50) | -                                           | [127]  |

ar aspect ratios.

7. Conclusions

Effective heat transfer enhancement is fundamental for effective use of the study results in agreement with industrial requirements. On the other hand, the overall thermal performance of refrigeration systems can be enhanced with the use of nanorefrigerants. Indeed, the NPs in refrigerants can act on the thermal conductivity and heat transfer coefficient. This results in the reduction of the energy and the power consumed.

However, the mechanism governing the heat transfer increase in nanofluids is still unclear. Among the different factors, for example, the increase of the nanoparticles’ concentration in base volumes determines a thermal conductivity increase, but results in increased viscosity, too. On the other hand, the nanofluids’ viscosity can be decreased with increasing temperature. Other factors, i.e., temperature, dispersion, and particle size, are also crucial in determining the nanofluid’s thermal conductivity. A key aspect is related to the NPs’ concentration: an increased amount determines an improved heat transfer performance, but after specific concentrations, stability problems occur. Indeed, in some previously published studies, the heat transfer increased up to a certain concentration of NPs in volume and then started to decrease. However, for the nanofluid’s stability, challenges such as fouling after sedimentation, erosion, and production cost are still the main issues in the commercialization of nanofluids. The challenge is developing nanoparticles for refrigerants with appropriate dispersion in the fluid to avert quick settling. For NPs obtained in the form of powders, clustering can occur that often favors settling. To facilitate dispersion, homogenization, stability, and to mitigate abrasion and clogging phenomena, a small particle size is preferable [128]. An increased surface area determines a reduction in the corrosion reduction and stabilization of the nanofluid. An intermitted controlled ultrasonicator was usually used for dispersion, controlling the NPs’ overheating.

The review also summarizes the previous literature on nanolubricants. It was found that nanoparticles blended in mineral oil perform better than POE oil.

The review highlights that the use of nanofluids is attractive, but its application is still hindered by many factors such as being needed for long-term stability, production costs, pumping power requirements, and the control of the high-pressure drop. In general, more research is needed for the use of nanofluids in refrigeration.

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