A review of the use of nanofluids as heat-transfer fluids in parabolic-trough collectors

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ABSTRACT

Due to their enhanced thermophysical properties, nanofluids have great potential for improving heat-transfer efficiency. Nanofluids are employed in various thermal applications in the automotive industry, heat exchangers, solar power generation and more. Among the applications of this technology, its use to enhance the heat transfer of solar collectors appears promising. It is therefore not a surprise that the use of nanofluids in solar collectors has become a popular research area. Still, there are important obstacles with the use of nanofluids in solar collectors. Stability is the most evident, in addition to environmental aspects and the need to design suitable large-scale production processes for the application of nanofluids at the required scale for large solar collectors' fields. In this literature review, we study nanofluids in solar collectors, and parabolic-trough collectors in particular, at temperatures between 100 °C and 300 °C. We present recent advances and research on nanofluids and consider the progress in understanding stability mechanisms, characterization and preparation methods, as well as their thermophysical properties. We describe the main research gaps and suggest areas of further research.

1. Introduction

The term "nanofluid" was first coined by Choi and Eastman [1] more than 26 years ago. Originally, the term described nanometre-sized copper particles dispersed in water to improve its thermal conductivity. Today, a nanofluid can be more accurately defined as an engineered colloidal suspension of nanoparticles into a base fluid. The concentration range of nanoparticles is typically between 0.01 wt% and 5 wt% and the mean particle size is usually in the range 10–100 nm. The nanoparticles can be metals, metallic oxides, carbides, or carbon materials. Common base fluids are water and mineral oils.

Nanofluids present a large potential in several fields: in solar applications, to enhance the heat-transfer coefficient of solar water heaters or to improve the capacity of thermal energy storage systems; and in the area of refrigeration, to enhance the performance of refrigeration systems. Despite the significant potential of nanofluids [2], their use as a *heat-transfer fluid* (HTF) or *refrigerant* is still not very common. However, the use of nanofluids in solar-heat collectors has become a popular topic of research during the last decade. The novelty can be seen in Fig. 1, which shows the number of papers per year as discovered by Google Scholar for the search phrase `nanofluid solar heat`. The total number of papers found in the given period is 34 230.

There are several types of solar-heat collectors that operate at different expected temperature ranges. The main types include flat-plate collectors (FPC) (up to 100 °C), evacuated-tube collectors (ETC) (up to 200 °C), parabolic-trough collectors (PTC) (up to 500 °C), and linear Fresnel collectors (LFC) (up to 600 °C) [3]. One of the main differences between these is how the solar radiation is collected. In FPCs and ETCs, the heat is collected at the absorbing surfaces directly. In PTCs and LFCs, the solar radiation is reflected and focused onto receiver pipes. PTCs and LFCs are examples of concentrated-solar power (CSP) systems. CSPs are used both to produce electricity and to provide industrial process heating. In this work, we only consider the latter application.

In all collector types, solar heat is absorbed and transferred to an HTF that subsequently carries the heat out of the collector. For efficient heat transfer, the HTF is normally circulated at relatively high flow rates to ensure turbulence. The type of HTF is usually selected to optimize the output efficiency. For temperatures below 100 °C, water is often used, as it is cheap, has favourable transport properties and a high heat capacity. Above 100 °C, like for PTCs and LFCs, water must be pressurized, which increases the complexity and cost. Mineral oils are therefore used because of their high vapour pressure.

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Nomenclature

Abbreviations

AF_3C	Sodium alkyl polyethylene oxide carboxylate
CO_2	Carbon dioxide
CVD	Chemical vapour deposition
CNT	Carbon nanotube
CSP	Concentrated solar power
CTAB	Cetyltrimethylammonium bromide
DAC	Direct-absorption collector
DTAB	Dodecyl trimethylammonium bromide
EDL	Electrical double layer
EG	Ethylene glycol
ETC	Evacuated tube collector
FPC	Flat-plate collector
GA	Gum arabic
HTC	Heat-transfer coefficient
HTF	Heat-transfer fluid
LAL	laser ablation in liquid
LFC	Linear Fresnel collector
MWCNT	Multiwalled CNT
MZFNP	MnZn ferrite nanoparticle
PDMS	Polydimethylsiloxane
PEG	Polyethylene glycol
PEO	Polyethylene oxide
PMAA	Polymethacrilic acid
PTC	Parabolic trough collector
PVP	Polyvinylpyrrolidone
RF	Radio frequency
$sc\text{-}CO_2$	Supercritical CO_2
SDBS	Sodium dodecyl benzenesulphonate
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscopy
SOCT	Sodium octanoate
SWCNT	Single wall carbon nanotube
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis

Symbols

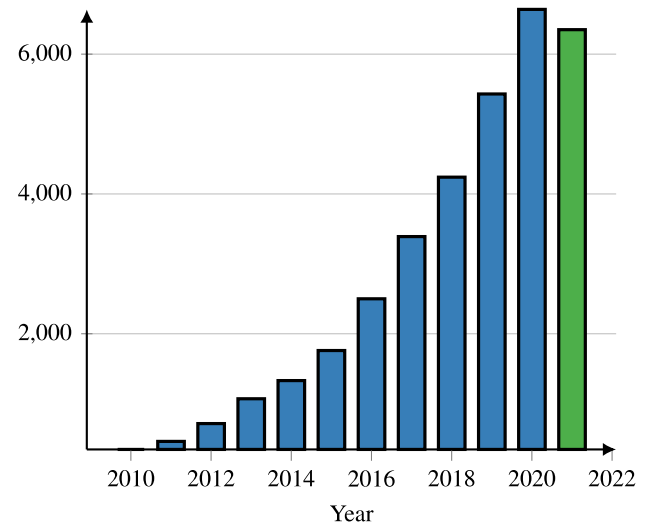|	
α	Volume fraction (vol%)
ΔT	Temperature difference (K)
μ	Dynamic viscosity (Pa s)
ϕ	Mass fraction (wt%)
Re	Reynolds number
ρ	Density (kg/m^3)
c	Specific heat capacity (J/(K kg))
h	Heat-transfer coefficient (W/(m^2 K))
k	Thermal conductivity (W/(m K))
L	Characteristic length (m)
q	Heat flux (W/m^2)
U	Flow velocity (m/s)
V_A	Attractive Van der Waals forces
V_R	Repulsive electrostatic forces

Fig. 1. The popularity of nanofluids for use in solar fields measured in the number of published papers. The numbers are collected from Google Scholar for the search phrase NANOFLUID SOLAR HEAT. The total number of papers found in the given period is 34 230. The bar for 2021 is green to indicate that this is the current year. (The data was collected on 2021-08-11).

The operating temperatures in solar fields often range from ambient, possibly subzero temperatures during nighttime and high temperatures at solar peak hours. The working fluids must therefore handle a wide range of temperatures. As an example, water is often combined with anti freeze additives like glycols to avoid freezing. Also, the viscosity of mineral oils is strongly dependent on temperature and can become very high at low temperatures. Mineral oils may also be subject to chemical degradation due to cyclic thermal stress.

In this work, we consider the use of nanofluids in high-temperature applications, specifically for use in PTCs. It should be noted that what counts as a *high temperature* depends on the context. For instance, the working temperatures in solar collectors can be above 600 °C, whereas nanofluids are mostly used at working temperatures below 100 °C. In this work, we therefore consider temperatures above 100 °C to be high temperatures, and we consider specifically temperatures between 100 °C and 300 °C.

Several nanofluids have been demonstrated to have superior heat-transfer properties compared to e.g. water and other HTFs [2,4]. However, a nanofluid for solar-heat collectors must both (i) provide a significant improvement to the heat-transfer properties as compared to a conventional refrigerant, (ii) remain stable over time at high temperatures and while undergoing large changes to the working temperatures, as well as (iii) have a reasonably low cost compared to the alternatives.

Thermophysical properties of nanofluids and heat-transfer applications have been the topic of a lot of earlier studies, many of which are covered in a range of previous literature reviews [2,4–11]. Okonkwo et al. [5] present a review of the progress made in 2019 concerning the use of nanofluids in heat-transfer devices. They cover a wide range of applications, but they also point out that more work is needed for temperature ranges above 100 °C. Qiu et al. [4] present a very thorough review of recent advances in thermophysical properties at the nanoscale. They consider both solid states and colloids/nanofluids. Mahian et al. [6,7] contribute a comprehensive review of recent advances in the modelling and simulation of nanofluid flows. They present a table with a summary of experimental studies which is very informative. The review by Taylor et al. [2] gives a very good introduction to nanofluids and their diverse applications. However, these earlier studies mainly consider low or medium temperature processes and applications.
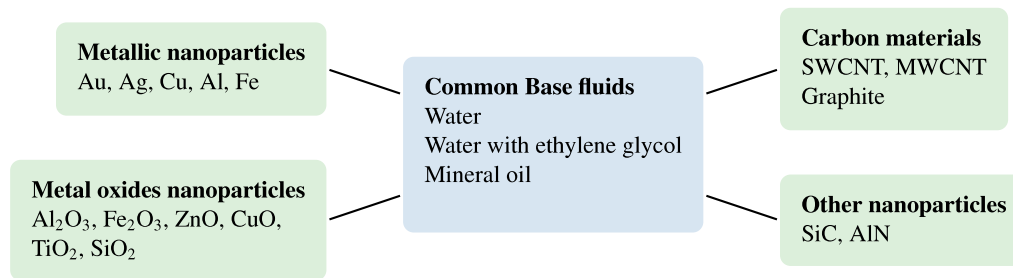
Fig. 2. Mapping of various base fluids and nanoparticles.

As mentioned, the use of nanofluids for solar collectors has become a popular topic. Mahian et al. [12] present an early review of the use of nanofluids in solar energy applications. It is interesting to note that, as of 2013, there were no experimental work on nanofluids as working fluids in PTCs. Olia et al. [13] provide a more recent review of the use of nanofluids as working fluid in PTCs. Another comprehensive review of nanofluids in solar concentrating technologies is presented by Bellos et al. [14]. Some research have also been conducted for nanofluids in LFCs. The most relevant are the following articles [15–17]. We also find some, like [18], who extrapolate information for LFCs by investigating the research done on PTCs.

Nanofluids have also been proposed in novel PTC concepts where solar heat is absorbed directly into the nanofluid itself [19–24]. This is made possible thanks to nanoparticles (mainly nanotubes) that are selected for their very high absorption properties within the sunlight wavelengths. Concepts that rely on this idea are called direct-absorption collectors (DAC). This type of concept is not within the scope of the present review.

In this study, we provide an overview of earlier and recent literature on the use of nanofluids for high-temperature heat transfer. The main context is the use of nanofluids in concentrated solar-heat collectors and in PTCs at operating temperatures in the range 100–300 °C. Our main interests are the improvement of heat-transfer properties and the nanofluid stability at high temperatures.

The literature review is outlined as follows. In Section 2, we give an overview of nanofluids and how they are prepared. Stability mechanisms are then discussed in detail in Section 3. We include a general introduction to the theory and overview of the common methods and mechanisms, before we discuss the high-temperature aspects. Next, in Section 4, we present an overview of the main properties of nanofluids for heat-transfer purposes: density, specific heat, thermal conductivity, and viscosity. Finally, in Section 5, we consider the use of nanofluids for enhancing the thermal efficiency of parabolic-trough collectors. Concluding remarks and suggestions for further research is provided in Section 6.

2. Nanofluid preparation

Nanofluids were first proposed and studied by Choi and Eastman [1] in 1995. The original idea was to suspend metallic nanoparticles instead of microparticles in conventional heat-transfer fluids to increase the thermal conductivity. According to Choi and Eastman [1], nanofluids were expected to exhibit superior properties when compared to microfluids, because of their high ratio of the surface area to volume of the particle.

Some common nanoparticle materials and their bulk properties at room temperature are listed in Table 1. Take into account that the properties of nanoparticles are not similar to bulk materials, but depend on their size and shape [25]. Similarly, Table 2 lists some common base fluids used as HTFs and their properties at room temperature and at higher temperatures. Fig. 2 shows a mapping of various nanoparticle types to base fluids.

In the following, we give a brief introduction to the common nanofluid base fluids relevant at high-temperatures. We then consider the most relevant nanofluid preparation techniques.

Table 1

Material properties of metallic and non-metallic solids at room temperature. The densities were all collected from [26]. The properties are bulk material properties, except for MWCNT and Graphene which were measured as nanopowder material. We were not able to find a measurement of the specific heat of graphene.

Material	ρ (kg/m^3)	k (W/(m K))		c_p (J/(kg K))	
Au	19 320	320	[27]	128	[27]
Ag	10 500	430	[27]	235	[27]
Cu	8933	400	[27]	380	[27]
Al	2800	235	[27]	900	[27]
MgO	3580	42	[28]	918	[29]
CuO	6000	30	[28]	528	[29]
Fe$_2$O$_3$	5180	7	[30]	670	[14]
TiO$_2$	4230	8.4	[31]	710	[31]
Al$_2$O$_3$	3960	36	[31]	765	[31]
SiO$_2$	2200	1.4	[31]	745	[31]
SiC	3100	490	[31]	675	[31]
Graphene	2267	3000	[28]		
MWCNT	1700–2100	2000	[28]	1200	[32]

Table 2

Properties of common HTFs at different temperatures.

Fluid	T (°C)	ρ (kg/m^3)	μ (mPa s)	k (W/(m K))	c_p (kJ/(kg K))
Water (10 bar) [29]	20	998	1.00	0.598	4.18
	160	917	0.17	0.608	4.33
EG/water (20 vol%) [33]	20	1030	1.65	0.512	3.90
	100	997	0.409	0.550	4.02
Therminol VP-1 [34]	20	1064	4.290	0.136	1.546
	200	913	0.395	0.114	2.048
	300	817	0.221	0.096	2.314
Syltherm 800 [35]	20	934	10.0	0.135	1.608
	200	773	1.05	0.107	1.916
	300	671	0.47	0.082	2.086

2.1. Base fluids

The most common nanofluid base fluids are water, possibly with some additives such as ethylene glycol (EG), and oils. Molten salts are also sometimes used as a base fluid at high temperatures. In the following, we discuss these common base fluids.

Water-based nanofluids have demonstrated excellent dispersion stability for nanoparticles [36]. Water is also a good HTF, as it has high heat capacity and low viscosity, see Table 2. However, water has a narrow operational range of temperatures between freezing and evaporation. For operational temperatures above 100 °C, water-based systems need to be pressurized to avoid evaporation. For example, water pressurized at 10 bar can be used as an HTF for applications up to about 180 °C [37]. Also, EG is often added to add anti-freezing properties to the water.

Oil-based nanofluids have a much broader range of application temperatures. An important advantage of oils as a base fluid is their high stability against thermal degradation. However, oils tend to have a significantly higher viscosity, which increases the pump power required

to circulate the fluid in a system. At room temperature, the viscosity of oil-based fluids is up to 10 times higher than that of water, see Table 2. Furthermore, oil-based fluids tend to be flammable and the use of them may require a fire protection system [37]. The following is a list of the most common oils for nanofluids:

- *Synthetic oil* is suitable for high temperature applications. They offer higher thermal efficiencies compared with others and relative low operational maintenance. However, it should be noted that synthetic oils are usually toxic.
- *Silicone oil* is odourless, non-toxic, noncorrosive, and has a low pour point and low viscosity. It is highly stable and long-lasting. Properly maintained, it can be aged continuously at 400 °C for more than 10 years before it needs replacement. It also exhibits a low potential for fouling. However, a drawback is that silicone oil is usually quite expensive.
  Two common commercial silicone oils are Syltherm 800 [35] and HELISOL [38]. These have similar properties, although Syltherm is less viscous and HELISOL has a higher flash-point temperature (220 °C). The higher flash-point temperature makes HELISOL more suitable for operating temperatures up to 200–220 °C, since the flash point should be higher than the operating temperature to avoid flammability risks.
- *Mineral oil* is stable against thermal degradation and oxidation, relatively inexpensive, noncorrosive and non-toxic. It tends to have a lower viscosity and density compared with other types of oil.

Molten salts and ionic liquids are also used as base fluids for nanofluids [39]. Molten salts are commercial fluids that are very stable at high temperatures with no thermal degradation [40] and are known to have a high heat capacity. They are therefore often used for applications at very high temperatures. The standard operational range is from 100 °C to 700 °C [37,41]. Nanofluids based on molten salts are discussed in detail by Zhang et al. [41], who report a class of colloidal systems in which nanoparticles form stable solutions in various molten inorganic salts. Stability of molten salt-based nanofluids is also tested and discussed by Navarrete et al. [42]. The high colloidal stability is explained by the strength of chemical bonding at the nanoparticle-base fluid interface. An important restriction of molten salts is that they typically crystallize at high temperatures, sometimes above 100 °C. According to Krishna et al. [43], the melting temperature of HTFs is directly related to the operational cost of solar collectors. This is because the temperature of the collector must be maintained above the freezing/melting point of the HTF. Thus, operational aspects are challenging with molten salts, since the solar collectors need to be protected against freezing [37]. For this reason, and since the present work mainly concerns solar collectors in the range of temperature from 100–300 °C, molten salts will not be further considered.

Gaseous HTFs like air [44], CO_2 [45], steam and Helium have been also reported in the literature, an overview is presented in Krishna et al. [43]. All these gaseous HFT are used for high-temperature applications, above 500 °C.

To conclude, we find that oil-based fluids seem most promising or suitable for applications in the temperature range from 100–300 °C. Pressurized water may also be a realistic alternative, although it puts an additional restriction that the system must be pressurized. Table 3 indicates the main operational temperature range of some possible base fluids and Table 2 shows the properties of some base fluids at different low and high temperatures.

2.2. Preparation

Nanofluids are produced by dispersing nanoparticles into a base fluid to form a stable suspension. Agglomeration is a major challenge in the synthesis of nanofluids. The preparation is therefore closely related

to the topic of stability, which is further discussed in the next section (Section 3).

It is common to divide preparation processes into two main approaches: *One-step* and *two-step* methods [48–50]. A simple overview of these approaches is given in the following.

One-step methods are methods where the nanoparticles and the resulting nanofluid are produced simultaneously. This usually leads to less agglomeration. The stability of nanofluids prepared using these techniques are therefore usually superior compared to two-step methods [49]. There are other advantages, as listed in Table 4. However, one-step methods are difficult to scale up.

The most common one-step techniques include *physical vapour condensation*, *laser ablation in liquid* (LAL), *microwave radiation*, and *ultrasonic-aided submerged arc*. Here, physical vapour condensation is based on direct condensation of metallic vapour into nanoparticles by contact with a flowing, low vapour-pressure liquid like in Eastman et al. [51]. LAL is a technique where nanoparticles are produced rapidly from simple precursor materials by focusing an intense laser beam into a liquid or onto a solid–liquid interface. The nanoparticles are thus released from the solid surface and dispersed into the liquid [52]. Microwave radiation involves a microwave irradiation of a precursor solution in presence of a reducing agent. The microwave irradiation provides energy for heating the solution and accelerates the nucleation process [53]. Finally, ultrasonic-aided submerged arc involves the use of a bulk metal material as an electrode submerged into a dielectric liquid integrated with an ultrasonic vibrator [54]. In this process, the metal is vaporized and condensed in the dielectric liquid by the submerged arc. Although the process looks more complex compared to the former three techniques, it has been found to be advantageous.

Two-step methods, on the other hand, are methods where nanoparticles are produced first and subsequently dispersed into a base fluid. These methods are more common and can be used with commercial nanopowders. The dispersion of the nanoparticles into the base fluid is the key step. The dispersion may be improved and maintained by chemical methods (electrostatic, steric, or electrosteric) [48,49,55]. For example, when mixing Cu nanoparticles and water, surfactants are added to achieve a stable solution. However, during the overall preparation, it is crucial to use mechanical methods to break contact between the particles and avoid agglomeration. The mechanical methods are external interventions that should be applied periodically, to make sure the suspension is properly dispersed. Some of the most relevant techniques include ultrasonication, ball milling, mechanical or magnetic stirring, and high pressure homogenizer. More details about these techniques can be found in the following reviews: [49,50,56]. A review on the preparation of different metal and non-metal nanofluids is given by Devendiran and Amirtham [55].

3. Nanofluid stability

Although nanofluids are initially stable after preparation, stability is still one of the most important challenges for nanofluids [2,48]. Due to the inherently high surface energy of nanoparticles, short-range attraction forces such as Van der Waals attraction forces may become dominant between particle pairs. This effect increases when the frequency of particle collisions increases and can result in agglomeration. If there is agglomeration/flocculation in the liquid, the effective particle size increases and the particles (or agglomerates) start to sediment when subjected to gravitational forces. Such agglomeration tendency has to be eliminated through *repulsive forces* between nanoparticles to bring the nanofluid to a stable state.

If the suspension becomes unstable and starts to agglomerate, several negative consequences may appear:

- *Sedimentation*: The new clusters are too large for the Brownian motion to counteract the gravitational pull, the particles will sediment at the bottom of the container.

Table 3

Operational temperature ranges (indicative) for various base fluids [33,37]. Some relevant commercial oils are indicated.

Base fluid	Operating temperature range (°C)		Commercial names
	low	*high*	
Water (10 bar)	0	180	
EG/water (20 vol%)	−10	100	
Synthetic oil	−90	400	Theminol-VP1 [34]
Mineral oil	−10	300	Therminol XP [46], Paratherm NF [47]
Silicon oil	−40	400	Syltherm [35], HELISOL [38]
Ionic liquid	−70	400	
Molten salt	100	700	

Table 4

Comparison between one-step and two-step methods for nanofluid preparation. The table is based on the list of advantages and disadvantages given by [49].

	One-step methods	Two-steps methods
Advantages	• Synthesis and dispersion are done simultaneously. • Drying of nanoparticles is avoided. • Allows stable nanofluids without stabilizers. • Resulting nanofluids tend to be more stable than with two-step methods.	• Ideal for large-scale and cost-effective production.
Disadvantages	• Nanofluids can only be prepared in batch-wise manner and low quantity. • High production cost. • The unreacted molecules in resulting solutions can cause problems during usage.	• Drying of particles is required. • Agglomeration may occur during preparation.

- *Abrasion*: In case of flow in a conduit/pipe, larger particles/clusters may increase the abrasion of the solid walls. This may damage equipment and increase the need for maintenance.
- *Loss of nanofluid enhanced effects*: As the clusters are larger than the original nanoparticles, the suspension is effectively no longer a nanofluid. This may result in reduced enhancement of the nanofluid compared to alternative HTFs.

Note that there is no complete consensus on the effects of agglomeration, and whether it is necessary or even beneficial to remove it completely. Some claim that a small amount of agglomeration is in fact important for the enhanced thermal conductivity of nanofluids, and that a completely well-dispersed nanofluid will show less enhancement [48]. However, we should be aware that small amount of agglomeration can quickly lead to more agglomeration/sedimentation.

The topic of nanofluid stability has received considerable attention in the literature. However, stability at high temperatures has not had much attention. For thorough reviews of nanofluid stability in the common temperature ranges, see Refs. [48–50,57,58]. In the following, we provide an overview of recent development and summarize the current state-of-the-art understanding of nanofluid stability at temperatures up to 300 °C. We first discuss the main theory that is believed to govern stability aspects. We then consider stabilization mechanisms and how to characterize the nanofluid stability. Finally, we consider stability improvement methods and destabilization factors.

3.1. The DVLO theory

Nanofluids are characterized by particles that are so small that Brownian motion, which is the seemingly random fluctuation of particles suspended in any medium, acts against gravitational settling forces. In other words, the settling velocity for small particles (i.e. nanoparticles) can be smaller than the velocity of Brownian motion. Then, if Brownian velocity is greater than the maximum settling velocity, dispersion stability prevails [59]. Nanofluids are considered *stable* as long as the particles stay small, i.e. the original nanoparticles stay separated from each other or *dispersed*. In this situation, the Brownian motion is sufficient to counteract the gravitational force and the particles will stay suspended in the base fluid.

As mentioned, nanoparticles may be dominated by short-range attraction forces. The interaction of the Van der Waals force and the repulsion force on colloids are explained in the DVLO theory, named after Derjaguin, Landau, Verwey, and Overbeek. The theory describes how colloid stability is characterized by the sum of the Van der Waals attractive force V_A and electrostatic repulsion force V_R between particles [60]. This interaction of forces is sketched in Fig. 3. If V_A dominates over V_R, then the nanoparticles tend to favour agglomeration into agglomerates/clusters [48], either in the form of *soft* clusters or *hard* clusters. Hard cluster have strong attraction and are not easily broken. Soft clusters, on the other hand, are loosely bounded. They may be broken by for instance ultrasound dispersion, which is the application of high-frequency sound waves to break particle contacts through fragmentation of inter-particle contacts [2,48,49]. When particles have sufficiently high repulsive force V_R, there is essentially no agglomeration. Thus, to ensure long-term stability, it is essential to have a high repulsive potential.

3.2. Stabilization mechanisms

The stability of a nanofluid depends on the extent of nanoparticle agglomeration. One of the main goals is to prevent the formation of particle clusters. At the very least, a nanofluid needs to be properly dispersed with little agglomeration during preparation, see Section 2.2. The second challenge is to keep the nanofluid stable for a sufficient amount of time during usage. Here we describe the main mechanisms relevant for maintaining the stability.

The stability of a nanofluid depends on several factors of the particles or base fluid properties themselves, as well as the couple they form:

- The dielectric constant of the base fluid, which is directly proportional to the repulsive potential — the higher the dielectric constant, the better the stability [49].
- The Zeta potential is the potential difference between the fluid layer adsorbed in the solid surface of the nanoparticle and the fluid far from the nanoparticle. In other words, the Zeta potential measures the mutual repulsion of the nanoparticle. It is therefore used as a tool to evaluate the stability [49]. However, Zeta potential is not a definite indicator of stability/instability in a nanofluid, unless the nanofluid is purely stabilized by electrostatic mechanism [61].
- The shape and size influence the attractive and repulsive forces between particles — smaller particles agglomerate more. The highest repulsive potentials are reported in case of brick shaped particles, whereas the lowest are observed in case of blade shaped particles [49].
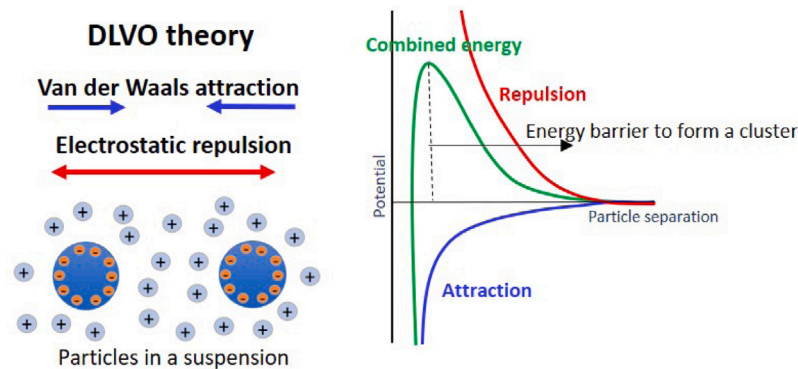
Fig. 3. Colloid stability is defined by long-range electrostatic repulsion and short range Van der Waals attraction forces.

• A higher concentration of particles increases the collision frequency and consequently the probability of flocculation by overcoming the energy barrier when bringing particles closer together [49].

Once the particle features have been settled by synthesis, the mechanisms influencing the stability of a suspension has to be assessed and adjusted according to the nature of the medium (polar, non-polar or ionic). Some suspensions do not need any additional additive to remain stable, however it is common to use one or two of the mechanisms described below to increase the dispersion of nanoparticles in the fluid [62]. These mechanisms are also illustrated in Fig. 4.

• **Electrostatic stabilization**: Electrostatic stabilization can be achieved by modifying or creating a surface charge on the nanoparticles. This surface charge creates an electric repulsion force between nanoparticles with the same positive or negative charges. In practice, the surface charge can be introduced by (i) pH adjustment or (ii) surface functionalization [49]. A surface charge on the particle surface may create a cloud of ionic charges surrounding the particle, called *electrical double layer* (EDL). The EDL is divided into two parts: The Stern layer, where ions are attached strongly to the surface, and the diffuse layer, where ions are loosely attached and is more interacting with the liquid medium. The highest electrical potential within EDL is observed on the particle surface. The potential drops gradually at the outer part of the nanoparticle. This electrical repulsion potential is known as a Zeta potential and is widely used to estimate the stability of the nanofluid [49].

According to Yu et al. [36], the repulsion potential increases with higher dielectric constant of the dispersion fluid. The dielectric constant of conventional fluids such as water, ethylene glycol, and hexane is 78.5, 24.6, 1.89, respectively, at $20\,°C$. Addition of an electrolyte into the fluid may screen the electrical repulsion of the nanoparticles, which can lead to reduced electrostatic stabilization. Therefore, electrostatic stabilization can only be effective within polar mediums like water (for low temperatures) or ethylene glycol (for high temperatures).

• **Steric stabilization**: Steric stabilization can be attained by using non-ionic surfactants and polymer addition. The polymeric molecules attached to a nanoparticle surface will occupy the surrounding space, hindering close contact with other particles by essentially "being in the way". The length of the polymeric chain and the adsorption ability are the crucial parameters for steric stabilization. A short polymeric chain and weak absorption will lead to poor steric stabilization. Strong binding (e.g. by chemisorption) between the nanoparticles and the polymeric chain is thus essential to achieve the steric stabilization [49].

• **Electrosteric Stabilization**: Electrosteric stabilization is a combination of the electrostatic and steric stabilization [49,63]. In this approach, ionic surfactants and polymers are used to get adsorbed into the charged nanoparticle surface. This creates both a protective barrier (steric mechanism) and an electrostatic barrier potential (electrostatic repulsion). The polymers used for the electrosteric stabilization are generally ionic polymers called polyelectrolytes.

3.3. Stability characterization

The study of nanofluid stability fundamentally depends on our ability to *characterize* or evaluate the stability itself. Common evaluation methods include natural sedimentation, Zeta potential measurement, three omega method, UV–VIS-spectrophotomer, optical spectrum analysis, centrifugation, electron microscopy (SEM and TEM) and dynamic light scattering. These methods are well described in [36,48]. In the following, we describe the methodology of some characterization techniques used to evaluate the stability of nanofluids. In particular, we highlight some relevant examples of characterization at high temperatures.

Hordy et al. [64] and Hordy [65] used several of the above-mentioned methods to evaluate the stability after heating to a certain temperature. For example, Hordy et al. [64] heated a batch of nanofluids samples in a loosely capped vial sitting on a temperature-controlled pot for 1 h at 85% of the boiling temperature of the base fluid. Since the vial were capped, this experiment resulted in no net loss of the base fluids. The fluid volume per sample was low, approximately 10 mL, thus limiting the thermal stratification. The samples after heating were then measured with UV–VIS spectrometer to evaluate their stability. Hordy et al. [64] also measured the stability of dry samples to estimate how the stability was affected by the loss of functional groups attached to carbon nanotubes (CNTs) at temperatures above $170\,°C$. They then prepared aqueous solutions at room temperature using the heated dry samples. The samples were then evaluated with UV–VIS spectrometer and natural sedimentation. Although their approach for characterizing the stability of the nanofluid is very practical, since there is no need for advanced instrumentation, the nanofluid characteristic and properties could be modified during the cooling or drying process.

Monitoring thermal stability of nanofluids at high temperature can be done using high temperature reactors connected to certain equipment. For example Kawamura [66] performed in-situ monitoring of samples up to $400\,°C$ using UV–VIS spectrometer. The samples were introduced into a high-temperature narrow-tubing reactor and allowed rapid heating and exposure with a short residence time. For UV–VIS measurement, they suggest to use fused-silica capillary as a material for the tubing reactor because of its large heat-transfer rate and high transparency in the UV–visible region. A sketch of their setup is depicted in
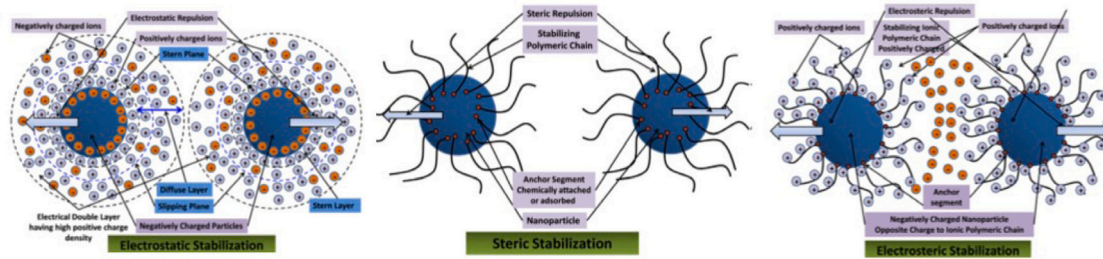
Stabilisation mechanisms

Fig. 4. An overview of stabilization mechanisms.
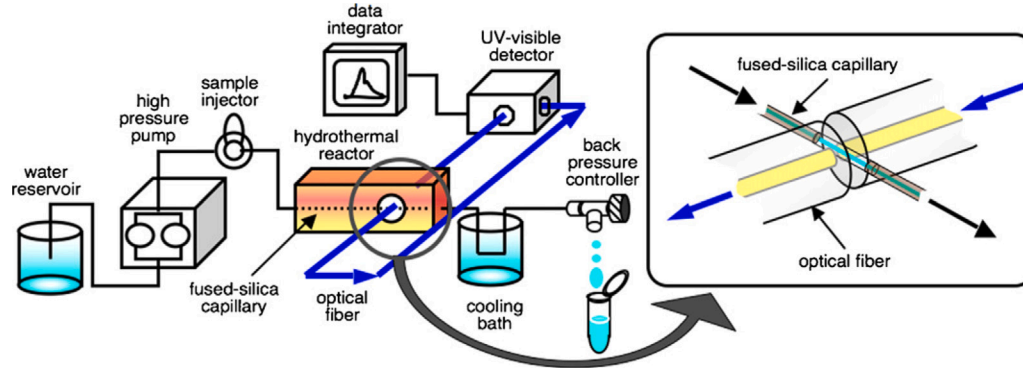*Source:* Chakraborty and Panigrahi [49].

Fig. 5. Capillary-flow hydrothermal UV–VIS spectrometer.
Source: Kawamura et al. [68].

Fig. 5. Similarly, Navarrete et al. [42] settled a nomad dynamic light scattering equipment to measure the stability of nanoparticles up to 300 °C in molten salts thanks to a dedicated cuvette. Further, Milanese et al. [67] measured the absorption characteristics of several gas-based nanofluids up to 500 °C in a dedicated setup.

3.4. Stability improvement methods

The previous sections introduce the most relevant concepts and mechanisms that are used to maintain nanofluids stability. Surfactant addition and pH control are among the most practical stabilization methods and have been used successfully at room temperature conditions. These are also chemical methods that can typically only be applied during preparation of nanofluids. In the following, we provide an overview of the most common stabilization methods. We discuss the methods in light of their relevance for high-temperature applications.

3.4.1. Modification of pH value

Since the particles have a surface charge, the pH value of the base fluid may be modified to increase electric repulsion. The pH value affects the electrical charge density around the nanoparticle surface which in turn influences the stability of the nanofluid [49]. For example, several studies have reported that aggregation has been observed when pH value is close to 7, whereas the stability is improved at higher or lower pH values [49,50,69,70]. However, high or low pH values could lead to corrosion of the pipe system, especially at high temperatures [49,56]. Ali et al. [50] present a table that summarizes some available studies where stability has been attained by adjusting the pH.

3.4.2. Adding surfactants

The use of surfactants is a common and well-known stabilization technique. Surfactants are compounds that contain both hydrophobic and hydrophylic groups. According to the hydrophilicity of the

medium, the heads and tails of the surfactant are permuted to create a continuity between the nanoparticles and base fluid. In the following, we give some more details on the use of various surfactants.

Some surfactants are cationic, others anionic, non-ionic, or even amphoteric. Non-ionic block polymers and surfactants such as polyethylene oxide (PEO), polyethylene glycol (PEG), polymethacrilic acid (PMAA), polyvinylpyrrolidone (PVP), oleic acid, gum arabic (GA), and sodium octanoate are used for steric stabilization [49,63]. Ionic surfactants can be used to achieve electrosteric stabilization. The most common ionic surfactants are cetyltrimethylammonium bromide (CTAB), dodecyl trimethylammonium bromide (DTAB), sodium dodecylsulphate (SDS), and sodium dodecylbenzenesulphonate (SDBS) [63,71].

When using surfactants for stabilization, it is important to choose the right kind and the right amount [48,72]. An important criterion for choosing the right surfactant is that one part should have affinity to the surface of the nanoparticle to get attached (chemically or physically) and the other part must be compatible with the base fluid. The amount is important, since too little leads to an unstable suspension, whereas too much may negatively influence the suspension properties, such as increasing the nanofluid viscosity. Furthermore, too much surfactant or the wrong type of surfactant may lead to foaming. Thus, the required amount and type of surfactant depend on the choice of the base fluid and particle type. Jiang et al. [72] state that the optimal composition of a stable dispersion of carbon nanotubes (CNTs) in water with SDS as surfactant is 0.5 wt% CNTs and 2.0 wt% SDS. Similarly, Zhuang et al. [73] give an example for ferrofluids, where MnZn ferrite nanoparticles (MZFNPs) are stabilized with about 1 g oleic acid for each 3 g of dried MZFNPs in hydrocarbon-based carriers. Other factors have been also investigated, such as the temperature and time of mixing [74].

Surfactants have been used widely to maintain the stability of nanofluids at room temperature. However, at high temperatures, many researchers have expressed concerns of using surfactants. For example, Assael et al. [75] report that an important disadvantage of CTAB is

that the bonding between surfactant and CNTs can be damaged above 60 °C. This is, however, based on an experiment where a dispersion is being sonicated. The sonication was accompanied by heating and the temperature reached 60 °C. They claim that the intense sonication and the mild heating could have affected the bonds of the surfactant with the nanotubes, which would lead to reduced stability. Wu et al. [76] state that at high temperatures, the surfactants are usually disabled, however, they do not support the claim with experiments or references. Wen et al. [11] state that the temperature effect is a significant issue, and that surfactant stabilization may fail at elevated temperatures. They claim that the issue occurs for some nano-dispersions from commercial suppliers, which they verified for a CNT nanofluid with SDBS as the surfactant at a temperature above 70 °C [77,78]. Wang and Mujumdar [79] also claims that the addition of surfactants may affect the heat-transfer performance of nanofluids, especially at high temperatures.

In more recent work, Hordy et al. [80] state that most surfactants decompose upon modest heating and can lose effectiveness at temperatures as low as 70 °C. This is similar to the claim made by Wen and Ding [78]. Simultaneously, Amiri et al. [81] state that surfactants may generate foam in the thermal equipment under heating and cooling cycles and subsequently cause diverse change in the fraction of surfactants that can be attached to the nanoparticle surface. This may also reduce the thermophysical properties of the fluid.

In summary, it seems there is evidence that certain nanofluids with certain surfactants deteriorate at high temperatures and reduce the performance of the fluid. The deterioration of the nanofluid stability can be explained by two parameters:

1. Surfactants decompose at high temperatures. That is, when heated, a variety of phenomena such as dissociation, oxidation, and other reactions can cause the surfactant structure to deteriorate. These changes in the structure of the surfactant lead to decomposition of the surfactant. For the surfactants GA, AF_3C, CTAB, SDS, the decomposition temperature is 90–95 °C [82], 210 °C [83], 235 °C [84], and 380 °C [82], respectively.
2. The interaction between nanoparticles and surfactant changes as a function of the temperature. According to Toerne et al. [85], the critical micelle concentration for nonionic surfactant depends on the temperature. This is because the compatibility of e.g. water and the surfactant depends on the extent of hydration of the hydrophilic portion of the surfactant, which is sensitive to the temperature. In addition, heating (above the clouding point) involves dehydration of the hydrophilic portion of the surfactant leading to formation of aggregates. This is known as clouding. As a consequence, surfactants may produce foam during cooling or heating cycles [56]. Surfactants can therefore increase the viscosity and in some cases reduce the thermal conductivity of the nanofluid.

However, there does not seem to be evidence that these restrictions are valid for all nanofluids and/or surfactants. For example, Li et al. [86] studied the stability of surface-capped silver particles in the mixture of water, alkylamine, and oleic acid. The oleic-acid surfactant were capped on the silver nanoparticles. They showed that, after preparation, the surface-capped silver nanoparticles had a hydrophobic nature which enabled it to be dispersed in a nonpolar solvent (oil-based fluid). Further, the stability was investigated on samples of 0.1 wt% silver nanoparticles prepared at 50 °C with *n*-heptane in the range of 120–160 °C. It is shown that the silver nanofluid had a stable time of 22 h at 120 °C and 2 h at 160 °C, see Fig. 6. After that time, the silver nanoparticles agglomerated and quickly deposited in the fluid.

Chen et al. [87] prepared a stable nanofluid with Fe_3O_4 nanoparticles dispersed in silicone oil. The used polydimethylsiloxane (PDMS) as surfactant, which was grafted on the surface of the nanoparticles. The grafted PDMS have a phosphate head group that could strongly bind onto the nanoparticle surface. The chemical composition of the PDMS
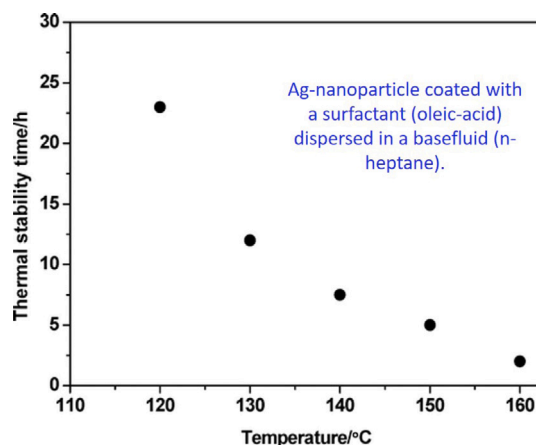

Fig. 6. Stability time of the silver nanofluids at different temperatures.
Source: Li et al. [86].

is similar to the silicone oil, which ensures excellent miscibility and good stability between the base fluid and nanoparticles [36]. After such surface modification, the Van der Waals attraction is screened, thereby achieving a stable dispersion. Chen et al. [87] demonstrated PDMS capped-Fe_3O_4 nanoparticles could be steadily dispersed within silicone oil up to 150 °C for a concentration of 0.75 mg/mL. However, aggregation was observed when the nanoparticle concentration is increased, see Fig. 7.

Guo et al. [88] used oleic acid/PEG/agar/oleic acid as a surfactant. They prepared a stable nano-ferrofluid coated with the tetralayer surfactants and dispersed in water. Thermogravimetric analysis (TGA) measurement shows that the nanoparticles coated with the surfactant does not degrade for temperatures up to around 200 °C. However, the long chain of the surfactant increased the viscosity for the nanofluids. TGA measurement also showed that only PEG-4000 was stable up to 300 °C. Others researchers have used PEG as a surfactant, showing long-term stability at room temperature [89,90].

Similarly, Asri et al. [91] also present results on nano-ferrofluids that were synthesized with PEG. PEG was used as a coating agent to reduce agglomeration. The maximum working temperature was 110 °C, but they did not state anything about PEG degradation or if it could be used at higher temperatures. PEG grafted on the surface of the nanoparticles provides steric stabilization that competes with the destabilizing effects of Van der Waals and magnetic attraction energies [92].

3.4.3. Surface modification

As discussed earlier, several researchers have suggested that surfactants lose their effectiveness at temperatures around 70 °C [56,81, 93]. To overcome such problems, some researchers have reported that chemically bonded functional groups on the surface of the nanoparticles show greater promise in preventing agglomeration at high temperatures [49,81,94]. Here, covalent functionalization represents one such strong chemical bonding, whereas surfactants imply weaker chemical bonding. A method to increase electric repulsion between the nanoparticles is to graft functional groups on the nanoparticle surfaces by acid, alkaline or plasma treatment, as proposed by Chakraborty and Panigrahi [49]. For example, functionalization with polar molecules (hydroxyl, carboxyl, sulphate, amine and phosphate, etc.) on the surface of the nanoparticle can lead to better dispersion into polar solvents [49]. Mesgari et al. [94] found that polar molecules such (carboxylic potassium, carbonyl and hydroxyl groups) attached to CNTs dispersed in a non-polar solvent (Therminol 55) form a stable solution.

To prepare covalent functionalized nanofluids, one may use different methods including wet chemistry [95], chemical vapour deposition [96], plasma enhanced CVD [97], acid or alkaline treatment [94],
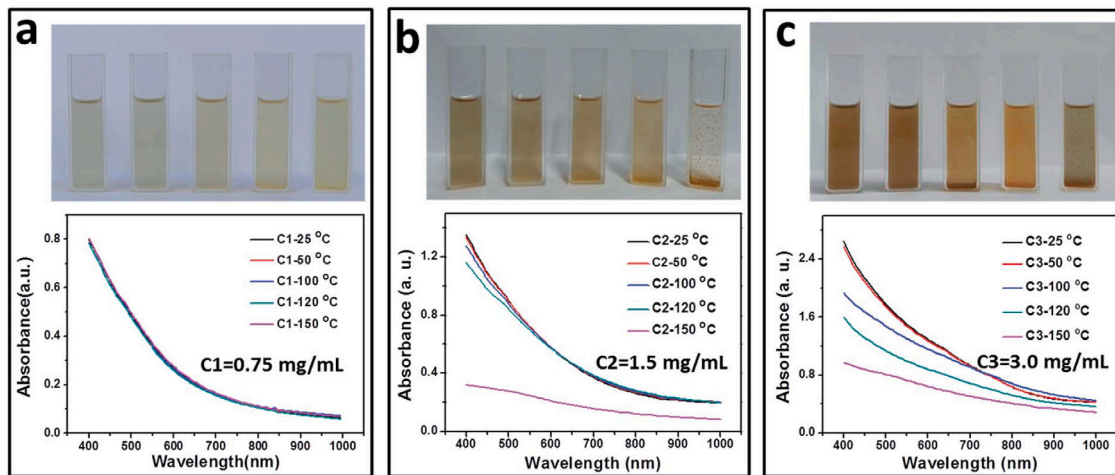
Fig. 7. Photographs and absorption spectra of silicon-oil bases PDMS-grafted Fe_3O_4 at different concentrations after ageing at different temperatures for 12 h.
Source: Chen et al. [87].

or a plasma process [80,93]. In the following paragraphs, we will present experimental work where covalent functionalization has been used to maintain nanofluid stability at high temperatures.

Mesgari et al. [94] studied several CNT-based nanofluids to identify the appropriate base fluid and stabilization method for stability up to 250 °C. Different nanofluids were tested varying (a) the type of CNT's, (b) the dispersion method, including surfactants (SBDS) and chemical functionalization, and (c) base fluids such as water, glycol and Therminol 55. Thermal tests were made up to 250 °C. They found that chemical functionalized multiwalled CNTs (MWCNTs) in a non-polar solvent (Therminol 55) showed better thermal stability compared to the others. In this case, the chemical functionalization was done by exposing the CNTs to potassium persulfate (KPS). The KPS solution introduces functional groups such as carboxylic potassium carboxylate (–COOK), carbonyl (–C=O) and hydroxyl (–C–OH) onto the surface of the CNTs.

Amiri et al. [81] stated that nanofluids with covalent functionalized CNT show good stability at high temperature contrary to GA and SDS surfactants, where aggregation was observed. They further claim that chemically attached functional groups have a higher decomposition temperature. This is also supported by several authors [64,65,80,93].

Tavares and Coulombe [93] studied stability of a copper-ethylene glycol nanofluid at high temperature. The synthesis was done using a dual plasma process. The process was a combination of low-pressure arc erosion and in-flight RF glow discharge plasma functionalization. The produced glow discharge served the purpose of depositing functional groups onto the surface of nanoparticles. As the nanoparticles pass through the RF discharge, they acquire a negative charge, making then able to adsorb hydroxyl groups on the surface of the nanoparticles from the ethylene cloud. The hydrophilic functionalized nanoparticles are then recovered in a falling film, see Fig. 8. In the experiments of Tavares and Coulombe [93], partial stability (little agglomeration) was observed in the suspension at 100 °C, but this agglomeration was demonstrated to be fully reversible using short-term ultrasound. Immediate agglomeration was observed in the suspension when the nanofluid was heated to temperatures above 197 °C, the boiling temperature of EG.

Hordy et al. [80] studied the stability of MWCNTs with different base fluids such as ethylene glycol, propylene glycol and Therminol VP-1 at high temperatures. The nanofluids were produced using plasma functionalized MWCNTs, similar to the method used by Tavares and Coulombe [93]. They report long-term stability up to 8 months at room temperature and high-temperature stability up to 170 °C, except with the Therminol VP-1. Hordy [65] claims that the stability is due to both the CNT growth process, which results in a porous 3D forest; and the

plasma treatment, which can penetrate the CNT forest to graft oxygen functional groups onto the surface (particularly carboxyl groups). These carboxylic functionalities produce a charged surface that limits agglomeration, i.e. electrostatic stabilization. Due to their functionalization, the particle surface of the MWCNT is more compatible with polar fluids (glycol-based and water), and not with nonpolar based fluids like Therminol VP-1.

Hordy et al. continued their studies on functionalized MWCNT to determine the stability at higher temperature [64,65]. In the more recent works, MWCNT were functionalized with a gas mixture in a plasma reactor, then heated up to 600 °C in different atmospheres. It was found that below 350 °C, 60% of the surface oxygen concentration decreased, indicating the functionalized groups were decomposed after the thermal treatment. As a test on how the loss of functional groups at temperatures higher than 170 °C would affect stability (specifically temperatures between 200–600 °C), aqueous suspensions were made at room temperature using the heated MWCNT samples. Aqueous nanofluids produced using the heated samples provided an indication of how the loss of oxygen functional groups affects the stability of the MWCNTs when in suspension. Fig. 9 shows that the stability of the sample heated to 200 °C and 300 °C remained stable after the thermal treatment, while the sample heated to 400 °C and 600 °C resulted in agglomeration. Hordy et al. [64] concluded that, although some functional groups may be lost at high temperatures, nanofluid stability can still be maintained.

The previous studies by Hordy [64,65,80] indicate that glycol-based nanofluids with functionalized MWCNT are stable at high temperatures. However, it must be noted that the stability test done in [80] at 170 °C was for a short time (hours). Therefore, more rigorous studies of the long term stability need to be performed.

As a conclusion, it seems that several researchers [49,65,81,93,94], have reached a *consensus* that covalent functionalization can be considered a better method compared to surfactants to achieve higher stability and dispersity at high temperatures.

3.5. Destabilization factors

At high temperatures, a nanofluid can be exposed to different destabilization factors that can lead to an unstable dispersion. In this section, we present a short discussion on the main destabilization factors at high-temperature applications. A more complete list is presented by Sharaf et al. [61].
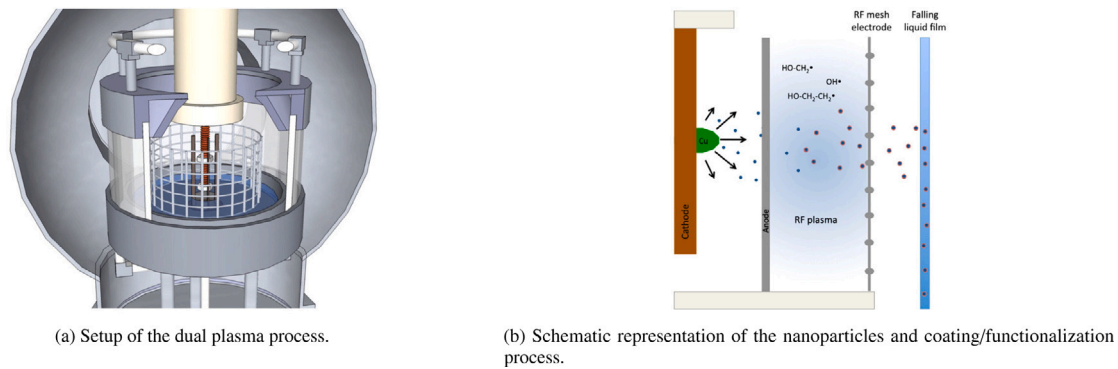
(a) Setup of the dual plasma process.

(b) Schematic representation of the nanoparticles and coating/functionalization process.

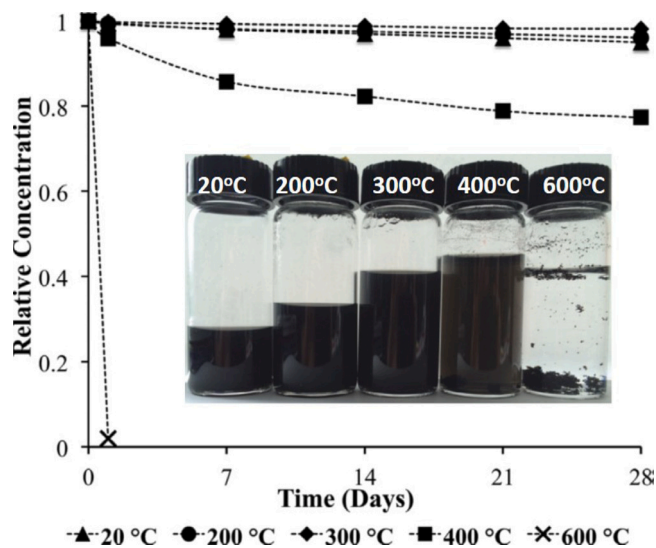**Fig. 8.** Sketch of the dual plasma setup used by Tavares and Coulombe [93].

Fig. 9. Relative concentration over time of the aqueous suspension with MWCNT heated to 200 °C, 300 °C, 400 °C and 600 °C. Inset: Photograph taken after four weeks. *Source:* Hordy et al. [64].

3.5.1. Working temperature and thermal cycling

According to Chakraborty and Panigrahi [49] and Sharaf et al. [61], Brownian motion of the nanoparticles is higher at high temperatures, as the diffusion coefficient is directly proportional to the fluid temperature. The increase of the Brownian motion is translated into an increase of frequency collision between the nanoparticles. The increase of the collision frequency favour flocculation and sedimentation of nanoparticles [36,61].

According to Sharaf et al. [61], temperature variations not only affect the collision frequency, but they have complex correlations with the collision efficiency (probability of particle attachment upon collision).

- For electrostatic-stabilized nanoparticles, temperature variation can modify the surface charge density on the nanoparticles and the Zeta potential, these changes can have effects on collision efficiency.
- For steric-stabilized nanoparticles, temperature variation can trigger a sharp transition from stability to instability due to reduction in affinity between the additive and base fluids and/or degradation of the additive. A more details discussion is given in Section 3.4 under "Adding surfactants".

During operations, the nanofluids will undergo heating during sun hours and cooling down to ambient temperature at nighttime hours. For high temperature applications, the difference between the daytime

and nighttime could be significant. As such, nanofluids are expected to withstand several *thermal cycles*. However, according to Sharaf et al. [61], thermal cycling can lead to oxidation of the metallic nanoparticles, break functional groups, changes the size and/or shape of nanoparticles, drop of the Zeta potential, and may consequently accelerate the particle clustering and sedimentation. It can also promote corrosion reactions between the nanoparticles and the tubes containers.

3.5.2. Storage time

Nanofluids need to remain stable during long periods of time. The long-term stability is a major concern for nanofluids at high temperatures [2].

3.5.3. Oxidation

Nanofluids are prone to chemical transformations such as oxidation [61]. Oxidation is more likely at high temperatures. Oxygen can be present due to air leak, or it can be generated due to chemical reactions between the nanofluid system (additive, nanoparticle, base fluid, container). The produced oxygen can oxidate the fluid or additive, and it can promote several alterations of the system and therefore instabilities.

It is becoming evident that the oxidation of the nanofluid components (e.g., base fluid, additive, nanoparticles) is a critical factor in the preparation method. This is independent of which mechanisms are used to obtain stable nanofluid, and it seems to be more critical at higher temperatures. Sharaf et al. [61] stated that chemical and physical deterioration of nanofluid operated at high temperature is due to presence of oxygen dissolved in the solution when exposed to the environment. This claim is also supported by several authors [94,98,99].

Singh and Khullar [98] presented a low cost and scalable method to prepare a stable nanofluid. They use engine oil as a source for the carbon soot particles and paraffin oil as a base fluid. In their study, they test the as-prepared sample at 240 °C. They observed oxidation of the engine oil and paraffin oil, which hinders the solubility of both components. However, when the tests were carried out using a sealed container to avoid the contact of nanofluid to the environment, no agglomeration was observed. Hence, they claimed that it is not thermal stresses but oxidation that causes nanofluid instabilities at elevated temperatures. Mesgari et al. [94] reached the same conclusion. They found that thermal degradation of the nanofluid was suppressed when the sample was first purged with nitrogen to remove the dissolved oxygen in the solution. Hjerrild et al. [99] prepared Ag-SiO₂ dispersed in glycerol, no additional additive or surface modification was used to obtain stable nanofluid. From their experiments, they conclude that the presence of water in the glycerol should be minimized as much as possible to prevent unnecessary oxidation of base fluid. The oxidation as a possible nanofluid destabilizing factor is a recent topic that need more study.

4. Nanofluid properties

The improvement of heat-transfer properties in nanofluids have traditionally been attributed to the larger thermal conductivity of the nanoparticles compared to the base fluid. As is apparent from Tables 1 and 2, common nanoparticle materials have up to 1000 times greater thermal conductivity than water. The enhancement of the thermal conductivity of nanofluids is also well established [2,4–6,100]. However, it has become clear that the effects of the nanoparticles are more complex, and the complete mechanisms are still not fully understood. For instance, adding nanoparticles also affects other important properties, such as density, heat capacity, and viscosity. The observed enhancement of heat-transfer properties is a combination of how these properties are affected by the addition of nanoparticles.

There are numerous related studies and several comprehensive reviews. The review by Mahian et al. [6] is thorough and covers most of the recent efforts on thermophysical models e.g. for thermal conductivity. Okonkwo et al. [5] presents a literature study of the advances made in 2019. They provide a useful overview of the most relevant models. An even more comprehensive review is provided by Qiu et al. [4]. They provide a very useful overview of the theory, experimental methods and comparisons between experiments and theory for the various thermophysical properties. They consider both solid state nanomaterials and colloidal nanofluids.

It is well known that, as the temperature of a fluid increases, its properties change and can be altered significantly. When we disregard molten salt-based nanofluids [39], there are only a few studies and measurements of thermophysical properties of nanofluids at temperatures above 100 °C. In this section, we present a general overview of nanofluid properties as well as the findings from the literature in the high-temperature regions.

4.1. Density and heat capacity

Given a non-interacting mixture of particles in a continuum, the classical definitions of density and specific heat capacity lead to straightforward expressions for the mixture equivalents [4,101]. That is, the mixture density ρ_{nf} (kg/m^3) is a volume-fraction average of the component densities,

$$\rho_{nf} = \alpha_p \rho_p + \alpha_{bf} \rho_{bf}, \tag{1}$$

where the subscripts nf, p, and bf indicate a nanofluid property, a property of the particles, and a property of the base fluid, respectively. α is the volume fraction and ρ is the density of the indicated component. Similarly, the specific heat capacity of the mixture c_{nf} (J/(K kg)) is a mass-fraction average of the component specific heat capacities [102],

$$c_{nf} = \phi_p c_p + \phi_{bf} c_{bf}, \tag{2}$$

where $\phi_i \equiv \alpha_i \rho_i / \rho_{nf}$ is the mass-fraction of component i. The densities and specific heat capacities of the components may themselves be given by more complicated models.

These models may, however, become less accurate for small particle sizes. For instance, Sharifpur et al. [103] present experimental results that show that Eq. (1) overpredicts the density. They theorize that the commonly used density model neglects the effect of the gap between the nanoparticles and the base fluid due to the nanolayer on the particle surface. They propose a new model that accounts for this nanolayer:

$$\rho_{nf,new} = \frac{\rho_{nf}}{\alpha_{bf} + \alpha_p \left(1 + d_{nl}/r_p\right)^3}, \tag{3}$$

where r_p denotes the average particle diameter and d_{nl} denotes the nanolayer thickness. Furthermore, they show that their model is in better agreement with the observed experimental results.

The effect of smaller particles is also present on the heat capacity. Some empirical regression models exist, see e.g. Refs. [104–106]. There

is still a debate concerning the exact mechanisms that lead to the specific-heat enhancement in nanofluids. Hentschke [107] argues that the common assumption of a nanolayer effect may not be the main cause of the enhancement. Instead, he proposes a different model that assumes longer range interactions between the nanoparticles in the surrounding liquid. In a recent study that utilizes molecular dynamics simulations, Carrillo-Berdugo et al. [108] attribute some of the specific-heat enhancement of nanofluids to strong chemisorption interaction of the fluid molecules at the nanoparticle surfaces.

In a recent study by Safaei et al. [109], they report that adding 0.1 wt% of SiO$_2$ and Al$_2$O$_3$ nanoparticles to Therminol 66 at temperatures in the range 280–320 °C does not lead to a significant change to the density and viscosity when compared to the base fluid. We were not able to find any further specific studies of density and heat capacity of nanofluids at high temperatures.

However, the temperature dependence of the densities of the base fluid and nanoparticles or nanoparticle material is usually well-known. Although there are evidence of specific nanoparticle effects such as the nanolayer [103], the basic relations in Eqs. (1) and (2) may still be relevant even at high temperatures.

4.2. Thermal conductivity

The enhancement of thermal conductivity of nanofluids compared to the base fluid is well established. It has been the subject of several literature studies [2,4–6,8,9,100,110–112]. Of these reviews, the one by Sobti and Wanchoo [110] was found to be the most extensive and critical when it came to the subject of thermal conductivity. The review by Qiu et al. [4] is more recent and also very extensive. They provide a very useful schematic diagram for the dependence of thermal conductivity of nanofluids on volume concentrations based on various studies, see Fig. 10. Sajid and Ali [112] present a review on the thermal conductivity of *hybrid* nanofluids, which is a nanofluid where two types of nanoparticles are combined in the same base fluid.

There is still an ongoing discussion on which mechanisms lie behind the thermal conductivity enhancement compared to conventional fluids. It has previously been argued that Brownian motion-induced micro-convection could have an important effect, but this mechanism has been shown to be insignificant both by experimental work [2,48] and by modelling [113]. An emerging consensus is that agglomeration, the creation of nanoparticle clusters and chains, is one of the main factors. A critical analysis in the clustering phenomena and thermal conductivity for Al$_2$O$_3$ nanofluid is presented by Fabrizio Iacobazzi et al. [114]. Other possible effects are interfacial layering of liquid [115], thermophoresis,[1] ballistic transport of energy carriers, pH values possible effect on phonon transport [116,117], and near-field radiation. Most of these effects are discussed in more detail by Sobti and Wanchoo [110]. Qiu et al. [4] also lists seven factors that are found by experimental studies to be strong factors for the obtained conductivity values:

1. nanoparticle concentration,
2. temperature,
3. nanoparticle size,
4. nanoparticle shape,
5. nanoparticle agglomeration,
6. pH,
7. sonication time.

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[1] Thermophoresis is diffusion of particles due to temperature gradients. It is also often called thermodiffusion, the Soret effect, or the Ludwig–Soret effect.
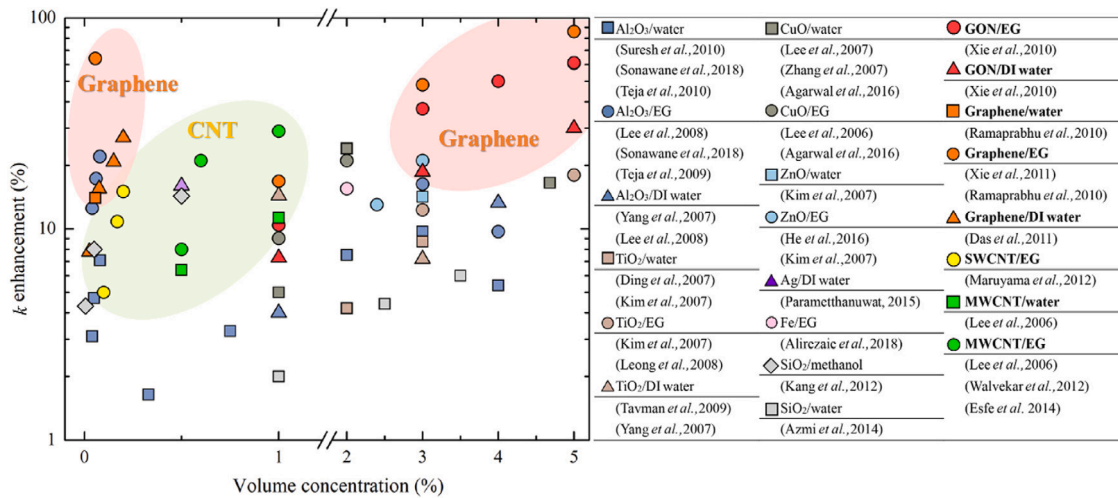
Fig. 10. Schematic diagram for the dependence of thermal conductivity of nanofluids on volume concentrations.
Source: Qiu et al. [4].

Accurate models or correlations for predicting nanofluid thermal conductivity is still a hot research topic. The classical approach is the famous Maxwell's model [118],

$$k_{\mathrm{nf}} = k_{\mathrm{bf}} \frac{\left(\frac{k_{\mathrm{p}}}{k_{\mathrm{bf}}} + 2\right) + 2\alpha_p \left(\frac{k_{\mathrm{p}}}{k_{\mathrm{bf}}} - 1\right)}{\left(\frac{k_{\mathrm{p}}}{k_{\mathrm{bf}}} + 2\right) - \alpha_p \left(\frac{k_{\mathrm{p}}}{k_{\mathrm{bf}}} - 1\right)}, \tag{4}$$

where k_{bf} and k_{p} are the thermal conductivities of the base fluid and particles, respectively. However, this model does not account for the previously mentioned enhancement effects such as temperature, particle size, agglomeration, and so on. There is still no single model that accounts for all effects and is shown to work well in all or most cases. We refer the reader to the previously mentioned reviews by Sobti and Wanchoo [110] and Qiu et al. [4] for lists of recent and improved models.

Temperature effects on the thermal conductivity were partly covered by the recent review by Qiu et al. [4]. They state that the thermal conductivity is usually enhanced with increased temperature, an effect that is mainly attributed to the increase of Brownian motion [119,120]. This is also supported in literature not covered by Qiu et al., e.g. [121–124]. The current consensus is claimed to be that the influence of temperature on k_{nf} is significant, and the higher the temperature, the greater the influence [4]. However, as discussed by Tawfik [111], some studies indicate that the temperature dependence of the thermal conductivity of nanofluids followed closely that of the base fluid [125–127]. Also, it should be mentioned that there are also some results that provide evidence to the contrary [128–130]. A common example of how the temperature affects the thermal conductivity is provided by Li and Peterson [131], who shows that the thermal conductivity increases with temperature.

There are very few studies of thermal conductivity of nanofluids at temperatures above 100 °C. In fact, we only found a single study where the conductivity was measured at these high temperatures: Jiang et al. [132] measured the thermal conductivity of Cu nanoparticles suspended in synthetic oil at temperatures in the range 30–210 °C. They find that the thermal conductivity is reduced with increasing temperature, and that the thermal conductivity enhancement increased less with increased nanoparticle concentration at temperatures above 150 °C. This is again contradictory with the above-mentioned consensus. It is clear that the thermal conductivity of a nanofluid has a complex dependency of many factors, where temperature is only one such factor.

4.3. Viscosity

The addition of particles to a liquid affects the mixture viscosity. This effect may be small for very small particle volume fractions. As the volume fraction increases, however, the mixture viscosity may increase substantially. Since viscosity is also a significant property due to its effect on friction and pumping power/pressure drop, it has been the focus of many studies. The rheological behaviour of nanofluids has been subject to some debate [133]. The recent review by Okonkwo et al. [5] claims that there is no clear pattern between the rheological behaviour and the particle concentration, and that the rheological behaviour appears to vary from material to material.

The viscosity of nanofluids has been the topic of many studies [4, 48,133]. The review by Sundar et al. [133] provides a good overview of models for nanofluid viscosity, both derived models and empirical correlations. Qiu et al. [4] also covers nanofluid viscosity models, but they do not feature more recent models than those presented in [133]. There exists no common empirical correlation or theoretical model for the estimation of viscosity for all nanofluids that include effects of both particle concentration, size and temperature. Okonkwo et al. [5] present more recent results, especially for hybrid nanofluids that combine two different nanoparticle types. Recent work on this topic includes both the use of artificial neural networks (ANN) [134] and molecular dynamics simulations [135].

Derived viscosity models typically follow in the tracks of Einstein [136]. He assumed a linearly viscous fluid containing a dilute suspension of spherical particles and obtained

$$\frac{\mu_{\mathrm{nf}}}{\mu_{\mathrm{bf}}} = 1 + 2.5\alpha_{\mathrm{p}}, \tag{5}$$

where μ_{nf} is the effective viscosity of the mixture, or in our case, the nanofluid, and μ_{bf} is the base fluid viscosity. This expression has been found to be at least partially applicable to relatively low particle volume fractions, but it underestimates the effective viscosity for higher volume fractions. Several studies have improved upon Einstein's model and taken into account for instance particle–particle interactions [133]. However, new models often describe the viscosity of nanofluids only in a narrow range of volume fractions [48]. Duangthongsuk and Wongwises [137] provide a comparison of some different viscosity models. The comparison shows that most of the standard models underpredict the measured viscosity.

Viscosity tends to be a highly temperature dependent fluid property. For instance, oils are known to display a highly non-linear temperature dependence. The temperature effects on nanofluid viscosity are discussed by Qiu et al. [4]. However, as before, there are not many studies
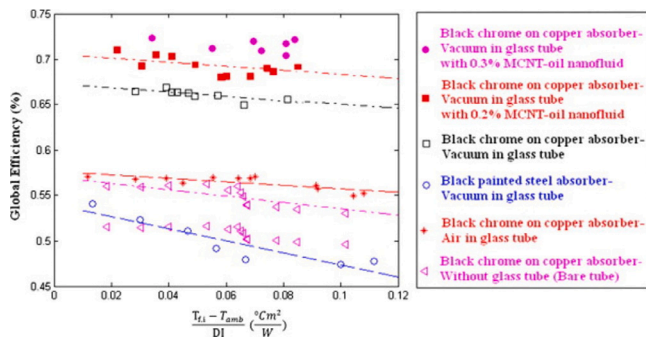
Fig. 11. Overall efficiency of solar collectors with different technologies including the use of nanofluids.
Source: Kasaeian et al. [144].

on the nanofluid viscosity at temperatures above 100 °C. As stated above, Safaei et al. [109] report that a small amount of nanoparticles did not lead to a significant change to the viscosity compared to the base fluid at temperatures up to 320 °C. This indicates that for a small amount of nanoparticles, the fluid viscosity may not change that much compared to the viscosity of the base fluid.

At high temperatures, the models suggested by Masoumi et al. [138] or Hosseini et al. [139] may be interesting, as both include temperature effects. However, these models are correlations that depend on availability of experimental data, and both models only validated at temperatures below 100 °C.

5. Nanofluids in solar collectors/industry

As discussed in the introduction, nanofluids show great potential for many applications. They can be used as an HTF for heating and cooling applications, including solar thermal collectors, chemical rubber processing, in electronic cooling, heat exchangers, automobile radiators, thermal storage, refrigeration, and more [2,5,140]. In this work, the main motivation is the use of nanofluids for solar collectors. Some useful overviews and reviews of nanofluids applied to solar collectors are presented by Mahian et al. [12], Olia et al. [13], Javadi et al. [21], Bellos et al. [14], Okonkwo et al. [141], Elsheikh et al. [142] and Manikandan et al. [143]. In the following, we mainly consider the parabolic-trough collector (PTC).

Different technologies have been developed to increase the solar PTC efficiency. For instance, see Fig. 11, which compares different absorber tubes and different HTFs. The use of nanofluids can increase the overall efficiency and the output temperature compared to base fluid equivalents due to its improved heat-transfer coefficient and thermal conductivity [144]. Despite the promising overall efficiency-enhancement potential observed by several researchers, there are still barriers to implement them in the industry. In the following, we will first look at the progress on the thermal efficiency enhancement for PTCs at high temperatures between 100 °C and 300 °C. Thereafter, we will consider barriers to implement nanofluids in the industry.

However, before we proceed, it is useful to first specify what is meant by thermal efficiency and thermal efficiency enhancement. First, with thermal efficiency enhancement, the common definition is the relative improvement of thermal efficiency as compared to the thermal efficiency of the base fluid. The thermal efficiency of a collector, often denoted η (%), is the ratio of the *useful* energy absorbed to the total *available* energy [12,14].

It is also useful to define the heat-transfer coefficient (HTC) and the Reynolds number, as these are common concepts for characterizing heat-transfer behaviour in pipe flows. The Reynolds number is usually defined as

$$\mathrm{Re} = \frac{\rho U L}{\mu}, \tag{6}$$

where U (m/s) is the flow velocity and L (m) is a characteristic length such as the pipe diameter. A high Reynolds number indicates a turbulent flow and is usually preferred in heat-transfer applications. The HTC relates the heat flux between a surface and the surrounding fluid to the temperature difference, that is

$$q = h\Delta T, \tag{7}$$

where q (W/m^2) is the heat flux, h (W/(m^2 K)) denotes the HTC, and ΔT (K) is the temperature difference between the surface and the surrounding fluid. Thus, a high value of the HTC implies efficient heat transfer between the surfaces and the fluid. One should note that the HTC and the thermal efficiency measure two distinct properties. The former refers to the *local* heat transfer between a surface and a fluid, whereas the latter refers to the heat transport through the entire collector.

5.1. Progress in thermal efficiency of PTC

For temperatures below 100 °C, there are several studies with water-based nanofluids where long-term stability and high efficiency enhancement have been achieved, see [5,14] for a good overview. One example is the work of Bretado de los Rios et al. [145], where Al$_2$O$_3$-water based nanofluid at 1 vol% was tested experimentally in a PTC. They found a high thermal-efficiency enhancement of up to 24%.

For operating temperatures between 100 °C and 300 °C, pressurized water or oil-based nanofluids are often used. Experimental studies of PTCs using nanofluids are difficult and can be costly compared to numerical studies. This is especially true at high temperatures. Therefore, it is not surprising to find that most of the current research has been performed using thermal models and computational fluid dynamics (CFD). In the literature, we only found a single experimental study of oil-based nanofluids in PTCs. This was by Kasaeian et al. [144], who investigated the enhancement of the thermal efficiency of a PTC collector with a MWCNT/mineral oil nanofluids. They manufactured a pilot PTC collector to investigate the performance of a PTC with different working fluids. They used two different nanoparticle concentrations: 0.2 wt% and 0.3 wt%. The ASHRAE Standard parameters [146] was used to calculate the thermal efficiency. Their results showed an enhancement in the thermal efficiency of 4–5% and 6–7%, respectively. The tests were conducted with inlet temperatures near the ambient temperature, but this was not specified properly. It seems the maximum temperature reached by the nanofluid in these tests was about 90 °C.

There are several numerical studies of nanofluids for PTCs [14–16, 141,147–158]. These rely on either *thermal models*, which are essentially an analysis of the energy balances in the absorber, or *CFD*, which is a more fundamental approach where the HTF flow is modelled in more detail [14]. Both approaches rely on correlations for the nanofluid properties, so the accuracy is intrinsically restricted by the accuracy of the underlying correlations.

Okonkwo et al. [141] used CFD models to investigate the heat transfer enhancement of PTCs numerically. They studied six different working fluids: pressurized water, supercritical CO$_2$ (sc-CO$_2$), Therminol VP-1 and oil-based nanofluids using 3 vol% of CuO, Fe$_3$O$_4$, Al$_2$O$_3$ dispersed in Therminol VP-1. The high pressure requirement for water is necessary for water to stay liquid at high temperatures. The thermal efficiency enhancement and other parameters have been analysed for the temperature range 27–377 °C. Their study showed that among all nanofluids investigated, Therminol VP-1 with Al$_2$O$_3$ showed the highest enhancement of thermal efficiency of 0.22% while CuO-Therminol VP-1 and Fe$_3$O$_4$-Therminol VP-1 obtained enhancement of 0.18% and 0.15%, respectively. Their study also showed that the use of nanoparticles enhanced the thermal conductivity and heat-transfer coefficient of the oil-based nanofluids while the specific heat capacity is reduced. In this study, pressurized water shows the best performance in terms of thermal properties and thermal efficiency, while CO$_2$ shows the lowest,
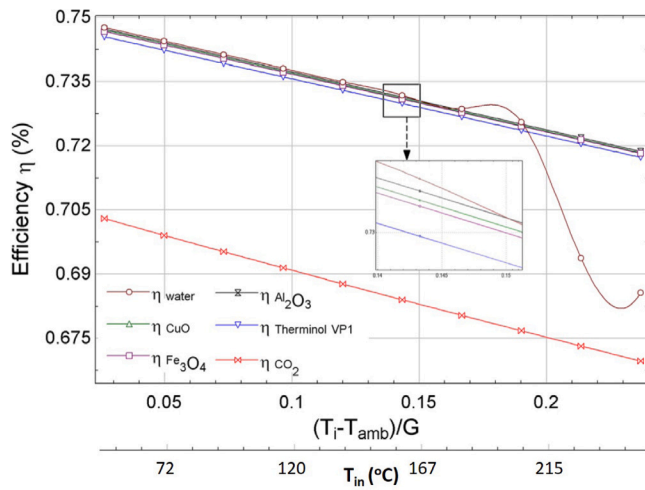
Fig. 12. Thermal efficiency comparison for six different working fluids. Pressurized water, Therminol VP-1, CO_2, and three oil-based nanofluids with 3 vol% of CuO, Fe_3O_4, Al_2O_3 dispersed in Therminol VP-1.
Source: Okonkwo et al. [141].

see Fig. 12. However, the use of an unpressurized system can reduce costs, therefore oil-based fluids are most attractive at high temperature.

Bellos et al. have carried out several numerical studies with various thermal models and correlations on the use of nanofluids for solar collectors at high temperatures [14–16,147–149]. The parameters they investigate are usually the energy and exergy performance and pressure losses. Bellos and Tzivanidis [149] investigate the use of various nanoparticles (Cu, CuO, Fe_3O_4, TiO_2, Al_2O_3, SiO_2) dispersed in Syltherm 800. The thermal efficiency enhancement has been analysed for the temperature range 27–377 °C and for a nanoparticle concentration of 6 vol%. According to the results, the most efficient nanofluids is Cu, followed by CuO, Fe_2O_3, TiO_2, Al_2O_3, SiO_2 respectively, see Fig. 13. Bellos and Tzivanidis [149] explain that the modelling results have been obtained using theoretical equations and correlations, because there is a lack of experimental studies of oil-based nanofluids in temperatures above 100 °C. Bellos and Tzivanidis [16] investigated the thermal efficiency enhancement of an LFR reflector based on Syltherm 800/CuO nanofluid with nanoparticle concentration of 6 vol%. With a flow rate of 200 L/min and inlet temperatures in the range 77–377 °C, the maximum thermal efficiency of the studied device was 0.78%, see Fig. 13. In addition, they conclude that the use of nanofluids enhance the thermal performance of the LFC, especially at high temperatures, due to a decrease in pumping power. Bellos et al. [15] has an additional paper studying Syltherm 800/CuO with nanoparticle concentration 2 vol%, 4 vol% and 6 vol% and with 200 L/min and inlet temperatures of 600 °C. In this study, the maximum thermal efficiency was with 6 vol%, however, it was found that the optimum nanoparticle concentration is about 4 vol% because higher nanoparticle concentration leads to higher pumping work. According to [17] these two papers are considered the most important works conducted on LFR solar collector using nanofluids.

Mwesigye et al. represents a different group that have also performed several numerical studies on nanofluids for PTCs. They used nanofluids with nanoparticles Ag, Cu, Al_2O_3, and single-wall CNTs (SWCNTs) dispersed in Therminol VP-1, and Al_2O_3, CuO dispersed in Syltherm 800 [150–153]. They investigate both the thermodynamic performance and the thermal performance of the solar collector with the nanofluids. In Refs. [151,153], they studied the use of Al_2O_3-Syltherm 800 and Al_2O_3, Cu, Ag-Therminol VP-1 for concentration up to 6 vol% in the temperature range 77–327 °C. Their studies indicate that Ag-Therminol VP-1 gives the highest thermal efficiency enhancement by up to 13.9%. They examined the PTC collector using an

entropy generation criterion, and they found the optimum Reynolds number regions at every inlet temperature. They conclude that there are Reynolds numbers beyond which the use of nanofluids makes no thermodynamic sense. Mwesigye et al. [150] also studied the thermal efficiency of SWCNTs/Therminol VP-1 for four different volume fractions 0.25 vol%, 0.5 vol%, 1 vol%, and 2.5 vol% and inlet temperatures in the range 127–377 °C. According to Mwesigye et al. [150], the heat-transfer coefficient of the nanofluid with SWCNTS can be enhanced by up to 234%. However, the mentioned improvement in the heat-transfer coefficient, attributed to the high thermal conductivity of SWCNTs, is not reflected in a thermal efficiency enhancement of around 4.4%. With this result, they demonstrate that higher thermal conductivity does not necessarily imply higher thermal efficiency. The specific heat capacity needs to be considered as an important property, together with the Reynolds number and the related HTC. Although MWCNT has a thermal conductivity of 10–100 times higher than Ag or CuO, the thermal efficiency enhancement is higher for nanoparticles Ag/CuO. See Tables 1 and 5.

Kaloudis et al. [154] used CFD to study a PTC system with Syltherm 800/Al_2O_3 nanofluid with nanoparticle concentration from 0–4 vol%. Their models were validated, and they claim good agreement with available test results. They reported up to 10% enhancement of the thermal efficiency with a concentration of 4%. Similarly, Sokhansefat et al. [155] used numerical simulations to study the effect of nanoparticle concentration in a nanofluid composed of Al_2O_3 particles in synthetic oil at operational temperatures in the range 27–227 °C. Their results showed that the HTC was increased as the nanoparticle concentration increased. For a given inlet Reynolds number, the nanoparticle HTC enhancement was found to decrease as the operational temperature of the absorber tube increased. The HTC enhancement was 9% at 127 °C and 6% at 227 °C. The PTC collector was also considered by Wang et al. [156] with an Al_2O_3/synthetic oil nanofluid. However, in this work they used a coupled optical–thermal-stress model to investigate the thermal and mechanical performance of the PTC collector. The results showed that use of nanofluids at high temperature reduces the temperature gradients in the absorber, which in turn reduces absorber deformation. The collector efficiency was improved by 1.2% with an inlet temperature of 377 °C.

Numerical energy and exergy analyses were also performed by Allouhi et al. [157], who studied the use of nanofluids in PTCs at high temperatures. They propose a mathematical model to examine the benefits of using nanofluids in real fluctuating PTC operating conditions. They studied several parameters, including nanoparticle types (Al_2O_3, CuO, and TiO_2), concentration, mass flow rate, and PTC inlet temperatures. Their main conclusions were that nanofluids enhanced the convective heat transfer and gave an increase of the thermal efficiency of up to 1.46% when middled throughout a day. This result was with 5 vol% Al_2O_3 in Therminol VP-1.

Hybrid nanofluids have been also studied; that is, nanofluids that combine two different nanoparticle types. Al-Oran et al. [158] compare the enhancement effect that occurred using mono and hybrid nanofluids. Mono nanoparticles Al_2O_3, CeO_2, CuO, and hybrid combinations with a total volume fraction of 4 vol% were dispersed in Syltherm 800. They observed that using Al_2O_3 and CeO_2 hybrid nanofluids were more efficient than using any other combination and any mono nanofluids. Thermal efficiency and heat-transfer coefficients of the different mono and hybrid nanofluid are shown in Fig. 14.

To summarize, we found that most studies of nanofluids used in the PTC relies on numerical simulations. The most commonly used nanoparticles are Cu and Al_2O_3, and the base fluid is typically an oil. Okonkwo et al. [141] also considered pressurized water and showed performance comparisons with different kinds of base fluids. There is a large variation of the results in the literature for the nanofluid enhancement of the PTC thermal efficiency. The experimental study shows that there is an important enhancement of 7% of the thermal efficiency using oil-based nanofluids [144]. The numerical studies give
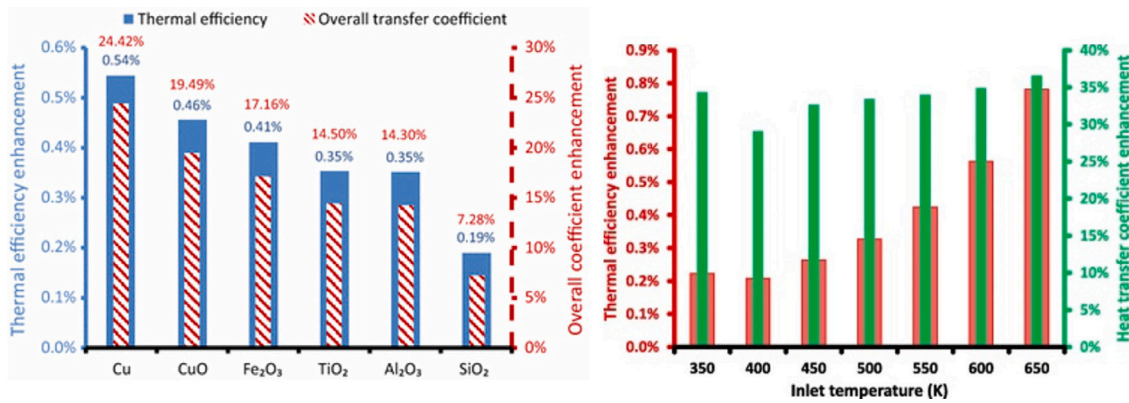
Fig. 13. Left: Thermal efficiency enhancement and overall heat transfer enhancement of different nanofluids. Right: Thermal efficiency and heat-transfer coefficient enhancement with the use of CuO/Syltherm-800 as a function of temperature.
Sources: Bellos and Tzivanidis [149] and Bellos and Tzivanidis [16].

Table 5
Comparison of various nanofluid experiment/simulation results.

Base fluid	Nanoparticle	Concentration	Type of study	Inlet Temp. (°C)	Imp. HTC (%) $(h - h_0)/h_0$	Imp. therm. eff. (%) $(\eta - \eta_0)/\eta_0$	Ref.
Syltherm-800	CeO_2 and Al_2O_3	2 vol% + 2 vol%	Model	302	167.8	1.09	[158]
Syltherm-800	Cu	4 vol%	Model	327	24	0.54	[149]
Syltherm-800	CuO	4 vol%	Model	327	19	0.46	[149]
Syltherm-800	Fe_2O_3	4 vol%	Model	327	17	0.41	[149]
Syltherm-800	TiO_2	4 vol%	Model	327	14	0.35	[149]
Syltherm-800	Al_2O_3	4 vol%	Model	327	14	0.35	[149]
Syltherm-800	Si_2O_3	4 vol%	Model	327	7	0.19	[149]
Syltherm-800	CuO	6 vol%	CFD	227	31.7	0.3	[148]
Syltherm-800	Al_2O_3	4 vol%	CFD	250		10	[154]
Syltherm-800	Ag	6 vol%	CFD	127–377		13.9	[153]
Syltherm-800	Cu	6 vol%	CFD	127–377		12.5	[153]
Syltherm-800	Al_2O_3	6 vol%	CFD	127–377		7.2	[153]
Therminol VP-1	Al_2O_3	8 vol%	CFD	77–327		7.8	[151]
Therminol VP-1	SWCNTs	2.5 vol%	CFD	127–377	234	4.4	[150]
Therminol VP-1	Al_2O_3	3 vol%	Model	127		0.22	[159]
Therminol VP-1	Fe_2O_3	3 vol%	Model	127		0.18	[141]
Therminol VP-1	CuO	3 vol%	Model	127		0.15	[141]
Therminol VP-1	Al_2O_3	3 vol%	CFD	327		15	[160]
Thermal oil	Al_2O_3		CFD	200	7.02	5.06	[147]
Thermal oil	Al_2O_3		CFD	300	10.27	7.77	[147]
Mineral oil	MWCNT	0.2 wt%	Experimental			4–5	[144]
Mineral oil	MWCNT	0.3 wt%	Experimental			6–7	[144]
Synthetic oil	Al_2O_3		CFD	227		6	[155]
Synthetic oil	Al_2O_3		CFD	127		9	[155]

different values. According to Bellos et al. [14], the differences may be due to the different methodologies used by the various researchers. In Table 5, we can observe that the thermal efficiency enhancement estimated by thermal models is around 1%, while results from CFD simulations tend to be higher. The differences indicate that there is significant development needed to achieve higher accuracy of the numerical simulations.

5.2. Barriers to implement nanofluids in the industry

To our knowledge, nanofluids have not been used in any large scale industrial application. There are several barriers that have impeded to implement them in the industry. Some of them has been cited by a project hosted by the Argonne Laboratory [161] where they have tried to demonstrate large-scale nanofluids production. The identified barriers related to the large-scale production of nanofluid and to the implementation of nanofluids in the solar collector are the following:

- Develop nanofluids with the desired enhanced thermal and physical properties [161].

- Preserve their stability in a long term perspective [161]. Ensure that nanofluids retain desired nanofluid properties against operating conditions (i.e. maintaining their thermal conductivity after undergoing heating and cooling cycles).
- The thermal properties of the nanofluid depend on several parameters, including the size and shape of nanoparticles, dispersing agent, and temperature [140]. This flexibility makes it difficult to standardize the nanofluid's thermal properties by the manufacture company to implement in solar plants [162].
- Demonstrate that the increased viscosity of nanofluids is insignificant and that the particles do not clog the system [161].
- Scale-up of nanofluid production and ensure the economic viability of nanofluid production at commercial scale [161]. A main concern is that the nanoparticles are not cheap, and neither the preparation. For example, the current cost of Al_2O_3 nanoparticles is 2840 EUR/kg [163]. The preparation cost depends on the operational procedure for stabilization. According to Wciślik [164], the cheapest and the least energy consuming systems are those that rely on surfactants. For temperatures above 100 °C, other methods, additives, and base fluids are needed to keep the nanofluid stable, as described previously. We have not found any
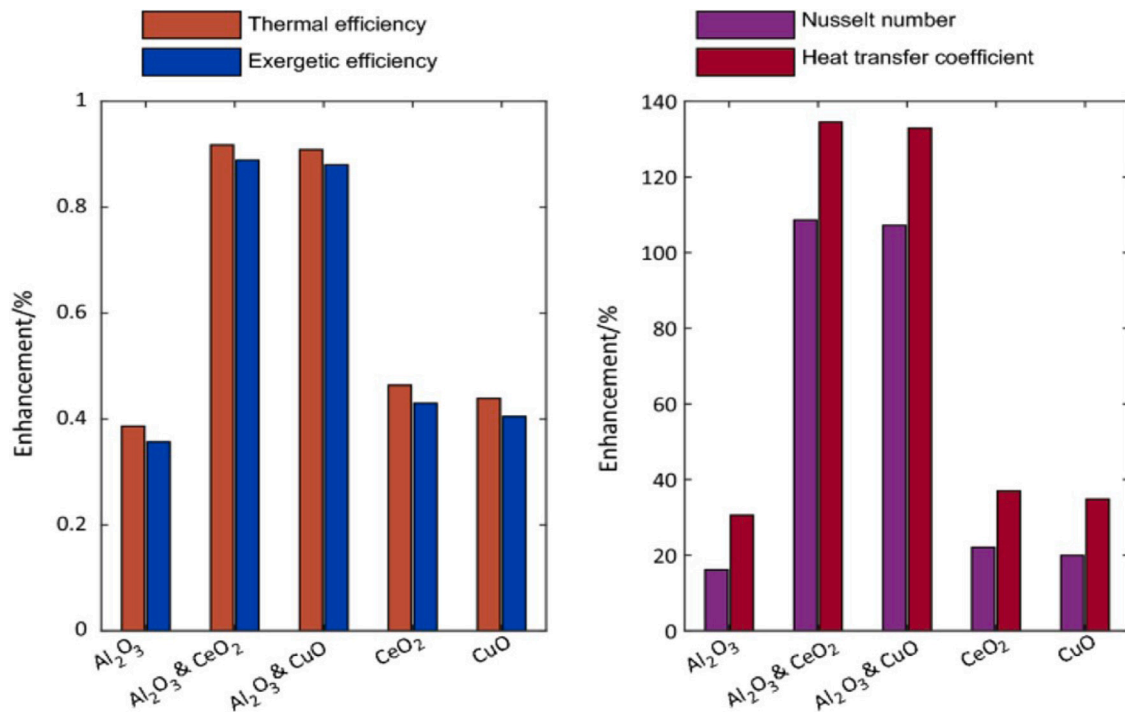
Fig. 14. Enhancement of thermal efficiency, exergetic efficiency, heat-transfer coefficient and Nusselt number for various mono and hybrid nanofluids at inlet temperature equal to 302 °C and total concentration 4%.
Sources: Al-Oran et al. [158].

estimate for these costs, and it is safe to assume that they are more costly.

However, pre-made nanofluids are commercially available. For example, pre-made nanofluids with Al_2O_3 dispersed in mineral oil at 20 wt%, commercialized by a research institute in the USA, costs 2570 EUR/L [165]. This nanofluid is compatible for temperatures above 100 °C.

A single PTC collector needs about 2.5 L of HTF [166]. The solar collectors are usually deployed in groups of 12 collectors, although commercial installations are often much larger and may consist of hundreds to thousands of collector groups. The amount of HTF required for a group of 12 collectors is about 30 L, according to ABSOLICON company. This does not include the volume needed in external piping and peripheries. The estimated cost of 30 L nanofluid with 0.1 wt% Al_2O_3 in mineral-oil is about 530 EUR. The corresponding cost of "HEAT TRANSFER FLUID 32", without nanoparticles, is approximately 170 EUR.

The above cost estimate may be inaccurate, e.g. because of the additional volume of nanofluid in the external pipes of PTC and the additional additives required to keep the nanofluids stable. We should also keep in mind that the price depends on several factors, such as type of nanoparticles (metal-based nanofluids are much more expensive than metal oxides), size of nanoparticles, and type of preparation.

- Lack of information on what happen to nanofluids in bends, valves, pumps, filters, calibrated orifices, flow metres, sensor, valves, etc.
- Demonstrate that nanofluids will not damage the thermo-hydraulic loop (including components and instrument). This may need pilot testing in real conditions.

Currently, most of the work is done by the research community under controlled conditions; however, the number of companies that see nanofluids' potential and are in active development work for specific industrial applications is increasing, see e.g. Refs. [140,167]. The world of nanofluid is progressing, and there are several patents on the preparation of stable nanofluid [168], commercial nanofluids [169], small

PC-cooling equipment using nanofluids [170], and commercial glycol-based nanofluids used for residential heating and data centers [171]. The global market for nanofluids for heat transfer applications according to CEA is 2 billions dollars per year [172]. Besides, projects like Nanouptake [173] and FRIENDSHIP [167] will help to overcome the commercial application barriers. A recent handbook by the Nanouptake project [174] cites the several industrial applications of nanofluids in the energy sector. The handbook summarizes different applications in small scale or testing compact system.

6. Conclusions and recommendations

We have presented a literature study on the use of nanofluids for high-temperature heat-transfer applications, particularly for use in solar collectors and parabolic trough collectors (PTCs). We first gave an overview of nanofluid literature for heat-transfer applications in general. The focus was on stability mechanisms, methods to ensure stability, and thermophysical properties. We then considered nanofluid challenges and properties at high temperatures, that is temperatures in the range 100–300 °C. The last section was devoted to reviewing the use of nanofluids in PTCs. These typically operate at high temperatures, generally above 100 °C. The following is a summary of the main conclusions and recommendations from the literature reviewed in this study.

First, there is a very decisive lack of experimental work on nanofluids at high temperatures, both in general and for use in solar collectors. Most of the available research on high-temperature applications are theoretical studies based on numerical simulations and predictions. Therefore, it is clear that more experimental research is needed on high-temperature use of nanofluids.

The main challenge at high temperatures is to prepare and ensure stable nanofluids. On this topic, we made the following conclusions:

On stability at high temperatures.

- Stability is the most critical aspect of nanofluids, especially at high temperature. Many researchers have used surfactants to stabilize the nanoparticles' dispersion into the base fluids. However,

at high temperatures, the use of surfactants is a key parameter due to several factors. First, surfactants can degrade/decompose at a temperature of around 70 °C. Second, the interaction between surfactants and nanoparticles change as a function of temperature, and the surfactants can produce foam during heating and cooling of the system. These mechanisms change the thermophysical properties of the nanofluids and reduce their performance.

- One alternative approach to achieve stability is pH modification for polar medium. Several studies have shown that aggregation is observed when the pH is close to 7, whereas the stability is improved at higher or lower values. However, high or low pH may lead to corrosion, especially at high temperatures. Therefore, this approach does not seem feasible for use in solar collectors.
- Surface modification of the nanoparticles seems to be a promising stabilization method for high temperatures. This method involves modifying the surface of the nanoparticles by covalent functionalization with molecules like hydroxyl and carboxyl grafted on the surface of the nanoparticle. Nanofluids created with this technique have been tested by several researchers, but they are mainly using some type of carbon nanotubes. Further studies are needed using other nanoparticles like Al_2O_3 or Cu, which are cheaper to produce, and studies on the long-term stability for functionalized nanofluids should also be performed.
- Oxidation of the nanofluid components is a critical factor for stability. It is pointed that the chemical and physical deterioration of nanofluids at high temperature is due to the presence of oxygen. More studies are needed to know what are the mechanism and methods to avoid oxidation.

On thermophysical properties of nanofluids at high temperature:

- There has been a lot of work on understanding and characterizing the properties of nanofluids. To some extent, the thermophysical properties are well understood, and they have been experimentally verified at temperatures up to 90 °C. There does not exist a single model or correlation for the thermal conductivity that fits all experiments. For some combinations of base fluids and nanoparticle types, e.g. Al_2O_3 in water or oil, there are correlations that are sufficiently good for predictions.
- We only found a single experimental study of thermal conductivity at high temperatures. The consensus from research at lower temperatures is that an increase in temperature will lead to increased conductivity. However, there exists evidence to the contrary at lower temperatures, but more importantly, the one experimental result we found at high temperatures also indicates the opposite. Thus, further experimental work is necessary on characterizing the thermal conductivity of nanofluids at higher temperatures.

The use of nanofluids for solar collectors is becoming a popular area of research. We looked into the literature on how nanofluids affected the thermal efficiency of PTCs, especially at operating temperature above 100 °C. Our main findings are:

- There are a lot of PTC studies with nanofluids in the literature. However, they mostly consider water-based nanofluids and temperatures below 100 °C.
- Most of the PTC studies are based on numerical simulations and predictions, and at high temperatures we did not find a single experimental study. The most common nanoparticles used are Cu and Al_2O_3. From the numerical studies, we can observe that Al_2O_3 dispersed in Therminol-VP1 showed the highest thermal efficiency enhancement of 15%. However, it should be noted that the numerical studies often give different results on the thermal efficiencies.
- Pressurized water has been compared with oil-based nanofluids by Okonkwo et al. [141] for applications at higher temperatures

by numerical simulations. In their study, pressurized water shows the best performance in terms of thermal properties and thermal efficiency, however pressurized system increase the maintenance energy and cost.

- Further experimental studies to investigate the thermal efficiency of oil-based nanofluids are required at temperatures above 100 °C. Stability studies, such as ageing studies and tests of robustness against thermal cycling, need to be included to judge the overall potential of the nanofluids.
- Experimental work should also address oxidation, corrosion, abrasion, and clogging effects of nanofluids on components and instruments at high temperatures.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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