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Executive Summary

Nanofluids have been found to have great potential for improving heat-transfer efficiency due to their enhanced thermophysical properties. It is therefore not a surprise that the use of nanofluids in solar collectors has become a popular research area. Still, there are important challenges with the use of nanofluids, especially at temperatures above 100 °C. Stability is the main challenge, but it is also vital to understand how high temperatures affect the properties of the nanofluid. In this literature review, we present recent advances and research on nanofluids at high temperatures. We consider the progress in understanding stability mechanisms and methods, as well as thermophysical properties. We also consider the application of nanofluids to solar collectors, and parabolic-trough collectors in particular. In our summary, we present the main research gaps and suggest topics for further research.

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1. Introduction

The term "Nanofluids" was coined by Choi and Eastman [1] more than 26 years ago. Originally, the term described nanometer-sized copper particles dispersed in water to improve its thermal conductivity. Nanofluids now refer to a solid suspension into a liquid medium, also called a colloid. These materials 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 Figure 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 30 070.



Figure 1 The popularity of nanofluids for use in solar fields measured in the number of published papers. The numbers are collected from <u>Google Scholar</u> for the search phrase NANOFLUID SOLAR HEAT. The total number of papers found in the given period is 30070. The bar for 2021 is green to indicate that this is the current year. (The data was collected on 2021-03-11).

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. The working temperature is much higher than for FPCs and ETCs, often between 120 and 550 °C. In all collector types, the solar heat is absorbed and transferred to a 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 HTF for a solar collector is selected to optimise the output efficiency. For low and medium temperatures, i.e. below 100-200 °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 often used in high-temperature applications because of their high vapour pressure.

The operating temperatures in solar fields range from ambient, possibly sub-zero temperatures during night-time 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.

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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.

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, 4–10]. 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] 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.

As mentioned, the use of nanofluids for solar collectors has become a popular topic. Mahian et al. [11] 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. [12] 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. [13].

Nanofluids have also been proposed in novel PTC concepts where solar heat is absorbed directly into the nanofluid itself [14, 14–19]. This is made possible thanks to nanoparticles 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 hightemperature heat transfer. The main context of our interest is the use of nanofluids in concentrated solar-heat collectors and in PTCs, preferably at operating temperatures in the range 100–300 °C. In the following, we consider any temperature above 100 °C to be "high temperature", because from the nanofluid perspective, these are high temperatures. Our main interests are the improvement of heat-transfer properties and the nanofluid stability at high temperatures. The study is outlined as follows:

- In Chapter 2, we give an overview of nanofluids and their properties at a general level. Although this is already well covered in previous literature, it is useful to provide as a context for the remaining parts.
- In Chapter 3, we consider high-temperature aspects of nanofluids. In particular, we look into stability mechanisms and the thermophysical properties.
- In Chapter 4, we consider the use of nanofluids for enhancing the thermal efficiency of parabolic-trough collectors.
- Concluding remarks and suggestions for further research are provided in Chapter 5.

2. Nanofluids and their properties

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. In addition, due to the small size of the nanoparticles, Brownian motion acts against gravitational settling forces and gives inherent stability that is not found in colloids with larger particles.

Today, a nanofluid can be more accurately defined as an engineered colloidal suspension of nanoparticles in a base fluid. The nanoparticles are non-organics, like metals, oxides, carbides, or carbon materials. The particle size is usually in the range 10–100 nm. Common base fluids are water, ethylene glycol, and mineral oils.

Nanofluids can be engineered for different purposes, and there is a wide range of applications [2]. In the following, we are mostly concerned with properties that relate to heat transfer. 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, see more details in Ref. [20]. Similarly, Table 2 lists some common base fluids used as HTFs and their properties at room temperature. Figure 2 shows a simple mapping of various nanoparticle types to base fluids.

Table 1 Material properties of metallic and non-metallic solids at room temperature. The densities were all collected from Ref. [21]. The properties are bulk material properties, except for MWCNT and Graphene which were measured as nano powder/-material. We were not able to find a measurement of the specific heat of graphene.

Nanoparticle	ho (kg/m ³)	<i>k</i> (Wm/K)	$c_p (J/kg/K)$
Au	19320	320 [22]	128 [22]
Ag	10500	430 [22]	235 [22]
Cu	8933	400 [22]	380 [22]
Al	2800	235 [22]	900 [22]
MgO	3580	42 [23]	918 [24]
CuO	6000	30 [23]	528 [24]
Fe ₂ O ₃	5180	7 [25]	670 [13]
TiO ₂	4230	8.4 [26]	710 [26]
Al ₂ O ₃	3960	36 [26]	765 [26]
SiO ₂	2200	1.4 [26]	745 [26]
SiC	3100	490 [26]	675 [26]
Graphene	2267	3000 [23]	
MWCNT	1700–2100	2000 [23]	1200 [27]

Table 2 Properties of base fluid at room temperature.

Fluid	ho (kg/m ³)	<i>k</i> (Wm/K)	c_p (J/kg/K)	μ (mPas)
Water (10 bar) [24]	998	0.598	4180	1.00
Therminol VP-1 [28]	1064	0.136	1546	4.290
Syltherm800 [29]	934	0.135	1608	10.0



Figure 2 Mapping of various base fluids and nanoparticles.

The improvement of heat-transfer properties in nanofluids have traditionally been attributed to the increased thermal conductivity of the nanoparticles. As is apparent from Table 1 and Table 2, common nanoparticle materials have up to 1000 times greater thermal conductivity than common fluids. The enhancement of the thermal conductivity of nanofluids is also well established [2, 4–6]. However, it has become clear that the effects of the nanoparticles are more complex, and the complete mechanisms are still not fully understood. There is a large number of 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 and 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 colloidal nanofluids and solid-state nanomaterials.

In the following, we summarize the current state-of-the-art understanding of the main properties and aspects of nanofluids. The goal is to provide a background to the reader, as these topics are already well covered by other reviews. We first look at nanofluid preparation and stability. We then consider the most important thermophysical properties. Some properties are beneficial, such as the increased thermal conductivity. But the added nanoparticles also lead to undesired effects like increased viscosity. To select appropriate nanofluid compositions for a particular application, one must understand how these properties interact.

2.1. Preparation

As previously stated, nanofluids are produced by dispersing nanoparticles into a base fluid. However, in the synthesis of nanoparticles, agglomeration is a major challenge. There are several processes in use to prepare nanofluids. It is common to divide the processes into two main approaches: *One-step* and *two-step* methods [30–32]. A simple overview of these approaches is given in the following. This is also closely related to the topic of stability which is further discussed in Chapter 2.2.

In the one-step method, the nanoparticles and the resulting nanofluid are created simultaneously. This leads to less agglomeration and better stability, but it is difficult to scale up. The stability of nanofluids prepared using this technique is mostly superior compared to two-step method [31]. There are also other advantages, as listed in Table 3.

The two-step method is the most common method and can be used with commercial nanopowders. In this method, nanoparticles are produced first and then dispersed into a base fluid. The dispersion of the nanoparticles in the base fluid is the key step in this method. This can be achieved either by mechanical methods (ultrasonication, stirring, etc.) or chemical methods (electrostatic, steric, or electrosteric) [30, 31, 33]. A review on the preparation of different metals and non-metals nanofluid is given by Devendiran and Amirtham [33].

Table 3 Comparison between one-step and two-step method for nanofluid preparation. The table is based on the list of advantages and disadvantages given by [31].

Method	Advantages	Disadvantages	
One step	• Synthesis and its dispersion are done simultaneously.	• Nanofluids can only be prepared batch wise manner and in low quantity	
	• Drying of nanoparticles are avoided.	• It is expensive, in general.	
	• Stable nanofluids can be prepared without stabilizers.	• The unreacted molecules in the solution can cause problems during usage.	
	• Nanofluid is more sable in nature compared to two-step method.		
Two steps	• It is ideal for large scale and cost- effective production.	• Drying of particles is required, agglomeration can occur during the process.	
		• Nanoparticles can be agglomerated during synthesis.	

2.2. Stability

To discuss nanofluid stability, it is important to understand the governing mechanisms. As stated, nanofluids are characterised 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. For suspensions, the settling velocity v of a spherical particle is often obtained by Stokes' law [34],

$$v = \frac{2R^2}{9\mu} \left(\rho_{\text{particle}} - \rho_{\text{fluid}} \right) g \tag{1}$$

Where *R* is the particle radius, μ is the fluid viscosity, and ρ denotes the density. For very small radii, which is the case for nanoparticles, the settling velocity *v* can be smaller than the velocity of Brownian motion. In other words, if Brownian velocity is greater than the maximum settling velocity, then dispersion stability prevails [35]. 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 sedimentation effect and the particles will stay suspended in the base fluid.

Although nanofluids are initially stable for a given duration with respect to gravity due to the small size of the particles, stability is still one of the most important challenges for nanofluids [2, 30]. Because of their high specific surface and subsequent high surface energy, nanoparticles brought close enough can be subjected to short range Van der Waals attraction and consequently agglomerate. This effect increases if the frequency of particle collisions increases. If there is flocculation in the liquid, the effective particle size increases and the particles start to sediment when subjected to gravitational forces.

The DVLO theory, named after Derjaguin, Landau, Verwey, and Overbeek, describes how colloid stability is characterised by the sum of the Van der Waals attractive force V_A and electrostatic repulsion force V_R between particles [36]. This interaction of forces is sketched in Figure 3. If V_A dominates over V_R , then the nanoparticles tend to favour agglomeration into agglomerates/clusters [30], either in the form of *soft* clusters or *hard* clusters. Hard clusters are associated with sintering¹ 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 contacts through fragmentation of inter-particle contacts [2, 30, 31]. When particles have

¹ Sintering implies that particles create at least punctual bridges to create a rigid cluster. Advanced sintering leads to densification of nanoparticles.

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.



Figure 3 Colloid stability is defined by long-range electrostatic repulsion and short-range Van der Waals attraction forces.

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.
- *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 some agglomeration is in fact important for the enhanced thermal conductivity of nanofluids, and that a completely well-dispersed nanofluid will show less enhancement [30].

The topic of nanofluid stability has received considerable attention in the literature. In the following, we provide an overview of recent development. For more thorough reviews of nanofluid stability, see Refs. [30–32, 37, 38].

2.2.1. 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 Chapter 2.1. The second challenge is to keep the nanofluid stable for a sufficient amount of time during usage. Meeting this challenge commonly involves using one or more of the followingstabilisation mechanisms [39]. These mechanisms are also illustrated in Figure 4.

Electrostatic stabilization: A surface charge on the particle surface may create a cloud of ionic charges surrounding the particle that is 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 [31]. According to Yu et al. [40], the repulsion potential increases with higher dielectric constant of the dispersion fluid. The dielectric constant of conventional fluids such

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as water, ethylene glycol, and hexane is 78.5, 24.6, 1.89, respectively, at 20 °C. Addition of an electrolyte in 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). In practice, the repulsion potential can be achieved in two ways: i) by pH adjustment and ii) surface functionalisation [31].

• Steric stabilization: Steric stabilization can be attained by using non-ionic surfactant 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 [31].

• Electrosteric Stabilization: Electrosteric stabilization is a combination of the electrostatic and steric stabilization [31, 41]. 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.

Stabilisation mechanisms



Figure 4 An overview of stabilization mechanisms. (Source: Chakraborty and Panigrahi [31])

2.2.2. Stability improvement methods

Practical stabilisation methods that utilise one or more of the mechanisms presented in the previous section include: surfactant addition and pH control. These are chemical methods that can typically only be applied during preparation of nanofluids. In contrast to the chemical methods, physical methods can be applied during the whole life cycle of nanofluids, i.e. from synthesis to utilisation. In the following, we provide an overview of the most common stabilisation methods.

- **Physical methods**: There are various ways of breaking up soft agglomerates. These methods are external interventions that should be applied periodically, as opposed to the others which are in effect all the time. 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: [31, 32, 42].
- **Modification of pH value**: Given that the particles have a surface charge, the pH of the fluid may be modified to increase the electric repulsion effect. The pH value affects the electrical charge density around the nanoparticle surface which in turn influences the stability of the nanofluid [31]. 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 [31, 32, 43, 44]. However, high or low pH values could lead to corrosion of the pipe system, especially at high temperatures [31, 42]. Ali et al. [32] presents a table that summarizes some of the available studies where stability has been attained by adjusting the pH.

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• Adding surfactants: Surfactants are usually 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. When using surfactants for stabilisation, it is important to choose the right kind and the right amount [30, 45]. Some surfactants are cationic, others anionic, nonionic, or even amphoteric. By increasing their quantity, the suspension can improve or decline. An important criterion for choosing the right surfactants 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.

For steric stabilization, non-ionic block polymers and surfactants are used. Some examples are polyethylene oxide (PEO), polyethylene glycol (PEG), polymethacrilic acid (PMAA), polyvinylpyrrolidone (PVP), oleic acid, gum arabic (GA), and sodium octanoate (SOCT) [31, 41]. Similarly, 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) [41, 46].

The required amount and type of surfactant depend on the base fluid and particle type. Jiang et al. [45] 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. Zhuang et al. [47] give an example for ferrofluids, where MnZn ferrite nanoparticles (MZFNPs) are stabilised with about 1 g oleic acid for each 3 g dried MZFNPs. The main disadvantage of using surfactants is that it may lead to foaming that reduces the performance of the fluid. Another disadvantage is that the viscosity of the nanofluid can increase.

2.3. Enhancement of the thermal properties

The enhancement of the heat-transfer properties of nanofluids compared to the corresponding base fluid is mainly attributed to an increase of the mixture thermal conductivity. However, 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. See Ref. [4] for a recent thorough review; the following is a short overview of the main mechanisms.

2.3.1. Density and heat capacity

Given a noninteracting mixture of particles in a continuum, the classical definitions of density and specific heat capacity lead to straightforward expressions for the mixture equivalents [4, 48]. That is, the mixture density ρ_{nf} (kg/m³) is a volume-fraction average of the component densities,

$$\rho_{\rm nf} = \alpha_{\rm p} \rho_{\rm p} + \alpha_{\rm bf} \rho_{\rm bf} \tag{2}$$

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 [49].

$$c_{\rm nf} = \phi_{\rm p} c_{\rm p} + \phi_{\rm bf} c_{\rm bf} \tag{3}$$

where $\phi_i \alpha_i \rho_i / \rho_{nf}$ is the mass-fraction of component *i*. The densities and specific heat capacities of the components may them<u>s</u>elves be given by more complicated models.

These models may, however, become less accurate for small particle sizes. For instance, Sharifpur et al. [50] present experimental results that show that Eq. (2) 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 particlesurface. They propose a new model that accounts for this nanolayer:

$$\rho_{\rm nf,new} = \frac{\rho_{\rm nf}}{\alpha_{\rm bf} + \alpha_{\rm p} (1 + d_{\rm nl}/r_p)^3} \tag{4}$$

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where r_p denotes the average particle diameter and d_{nl} denotes the nanolayer thickness. 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. [51–53]. There is still a debate concerning the exact mechanisms that lead to the specific-heat enhancement in nanofluids. Hentschke [54] argue 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 utilises molecular dynamics simulations, Carrillo-Berdugo et al. [55] attribute some of the specific-heat enhancement of nanofluids to strong chemisorption interaction of the fluid molecules at the nanoparticle surfaces.

2.3.2. 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, 4–8, 56–58]. Of these reviews, the one by Sobti and Wanchoo [56] 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 Figure 5. Sajid and Ali [58] 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.



Figure 5 Schematic diagram for the dependence of thermal conductivity of nanofluids on volume concentrations. (Source: Qiu et al. [4])

There is still an ongoing discussion on which mechanisms lie behind the thermal conductivity enhancement compared 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, 30] and by modelling [59]. An emerging consensus is that agglomeration, the creation of nanoparticle clusters and chains, is one of the main factors. Other possible effects are interfacial layering of liquid [60], thermophoresis2, ballistic transport of energy carriers, pH values [61], and near-field radiation. Most of these effects are discussed in more detail by Sobti and Wanchoo [56]. Qiu et al. [4] also lists seven factors that are found by experimental studies to be strong factors for the obtained conductivity values:

- nanoparticle concentration,
- temperature,
- nanoparticle size,

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² Thermophoresis is diffusion of particles due to temperature gradients. It is also often called thermodiffusion, the Soret effect, or the Ludwig-Soret effect.

- nanoparticle shape,
- nanoparticle agglomeration,
- pH,
- sonication time.

Accurate models or correlations for predicting nanofluid thermal conductivity is still a hot research topic. The classical approach is the famous Maxwell's model [62],

$$k_{\rm nf} = k_{\rm bf} \frac{\left(\frac{k_{\rm p}}{k_{\rm bf}} + 2\right) + 2\alpha_p \left(\frac{k_{\rm p}}{k_{\rm bf}} - 1\right)}{\left(\frac{k_{\rm p}}{k_{\rm bf}} + 2\right) - \alpha_p \left(\frac{k_{\rm p}}{k_{\rm bf}} - 1\right)}$$
(5)

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 [56] and Qiu et al. [4] for lists of recent and improved models.

2.3.3. 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. The rheological behaviour of nanofluids has been subject to some debate [63]. 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, 30, 63]. The review by Sundar et al. [63] 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 Ref. [63]. 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. [5] presents some 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) [64] as well as molecular dynamics simulations [65].

Derived viscosity models typically follow in the tracks of Einstein [66]. He assumed a linearly viscous fluid containing a dilute suspension of spherical particles and obtained:

$$\frac{\mu_{\rm nf}}{\mu_{\rm bf}} = 1 + 2.5\alpha_{\rm p} \tag{6}$$

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 [63]. However, new models often describe the viscosity of nanofluids only in a narrow range of volume fractions [30]. Duangthongsuk and Wongwises [67] give a simple comparison of some of the different viscosity models. The comparison shows that most of the standard models underpredict the measured viscosity.

3. High-temperature nanofluids

In the previous section, we discussed nanofluids and their properties at a general level. In this section, we consider nanofluids at high temperatures. We are specifically interested in temperatures up to about 300 °C. As the temperature is increased, the fluid properties tend to change dramatically. For nanofluids, the stability is known to be a particular challenge as the temperatures increase. However, even as this challenge is met, it is important to understand how the properties of a nanofluid behave as the temperature is increased.

To this end, we find it useful to first consider various base fluids relevant for high-temperature nanofluids. We then review recent progress on high-temperature stability. In the last part of this section, we consider the heat-transfer enhancement of high-temperature nanofluids.

3.1. Base fluids

Water-based nanofluids have demonstrated excellent dispersion stability for nanoparticles [40]. Water is also a good HTF, as it has high heat capacity and low viscosity, see Table 5. 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. For example, water pressurized at 10 bar can be used as a HTF for applications up to 180 °C [68]. Also, glycol is often added to add anti-freezing properties to the water.

Oil-based nanofluids have a much broader range of application temperatures. The main advantage of oils as a base fluid is the high stability against thermal degradation. But fluid viscosity is an important parameter for oil-based fluids, as it impacts 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 the viscosity of water, see Table 5. Among the most reported oil-based fluids are:

Therminol [28] is a synthetic-oil based fluid with high thermal capacity and typically excellent stability at high temperatures. However, synthetic oils are toxic and the use of them may require a fire protection system [68].

Syltherm [29] is a silicon oil that 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. Syltherm also exhibits low potential for fouling and is noncorrosive. HELISOL is also a silicon oil with similar thermal properties than Syltherm, although Syltherm is less viscous than HELISOL [69]. HELISOL has a higher flash point (220 °C) than Syltherm, which makes it more suitable for operating temperature up to 200–220 °C. The flash point temperature needs to be higher than the operating temperature to avoid flammability risks.

Molten salts and ionic liquids can also be used as base fluids for nanofluids [70]. In fact, molten salts are very stable at high temperatures with no thermal degradation [71]. They also have a high heat capacity. Molten salts are therefore often used for applications at very high temperatures, as the operational range is from 100 to 700 °C [68]. Nanofluids based on molten salts are discussed in detail by Zhang et al. [72], 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. [73]. The high colloidal stability is explained due to strength of chemical bonding at the nanoparticle-base fluid interface.

An important restriction of molten salts is that they tend to crystallize below 100 °C. According to Krishna et al. [74], the melting temperature of HTFs is directly related to the operational cost of solar collectors because the temperature of the collector must be maintained above the freezing/melting point of the HTF. Thus, the main challenge with molten salts is the operational aspects since the solar collectors need to be protected against freezing, Tagle-Salazar et al. [68]. Since the governing topic of the present work concerns solar collectors like the PTC, molten salts will not be further considered in this work.

Gaseous HTFs like air, CO_2 , and He have been also reported in the literature [74]. Supercritical CO2 has favourable gas-liquid properties and is an abundant resource, which has motivated some recent work where it has been considered as a HTF at high-temperature applications. However, it has operational challenges: usage requires pressurized systems, and there is a risk of leakage. A feasibility study about its use is presented in Muñoz-Anton et al. [75]. All these gaseous HFT are used for very high-temperature applications.

Thus, oil-based fluids, including synthetic oil and silicon oil, seem the most promising or suitable for applications in the temperature range from room temperature to 300 °C. Pressurized water may also be a realistic alternative,

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although it puts an additional restriction that the system must be pressurized. Table 4 indicates the main operational temperature range of some possible base fluids and Table 5 shows the properties of some base fluids at different low and high temperatures.

Table 4 Operational temperature ranges (indicative) for various base fluids [68].

Base fluid	Operating temperature range (°C)		
	Low	High	
Water/glycol, 10 bar	-50	180	
Synthetic oil	-90	400	
Mineral oil	-10	300	
Silicon oil	-40	400	
Ionic liquid	-70	400	
Molten salt	100	700	

Table 5 Properties of three common HTFs at different temperatures.

Fluid	<i>T</i> (°C)	ho (kg/m ³)	μ (mPas)	<i>k</i> (Wm/K)	c_p (kJ/kg/K)
Water (10 bar) [24]	20	998	1.00	0.598	4.18
	160	917	0.17	0.608	4.33
Therminol VP-1 [28]	20	1064	4.290	0.136	1.546
	200	913	0.395	0.114	2.048
	300	817	0.221	0.096	2.314
Syltherm800 [29]	20	934	10.0	0.135	1.608
	200	773	1.05	0.107	1.916
	300	671	0.47	0.082	2.086

3.2. Stability

As has already been made clear, the long-term stability is a major concern for nanofluids at high temperatures. It has been reported to be a particular challenge [2]. According to Chakraborty and Panigrahi [31], Brownian motion of the nanoparticles is higher at high temperatures, as the diffusion coefficient is directly proportional to the fluid temperature. This increases the probability of nanoparticle collision and its effectiveness, and, as a consequence leads to more flocculation [40]. Furthermore, if we consider surfactant-coated nanoparticles, higher Brownian motion could damage their bonds. In this section, progress on methods to keep the nanofluid's stability at high temperature will be discussed and several examples will be listed.

3.2.1. Adding Surfactants

Surfactants have been used widely to maintain the stability at room temperature, see Sec 2.2. However, at high temperatures, many researchers have expressed their concerns of using surfactants. For example, Ghadimi et al. [30] report that an important disadvantage of surfactants is that the bonding between surfactants and nanoparticles can be damaged above 60 °C. The claim is based on results given in five cited papers [10, 76–79]. Assael et al. [78] show results from an experiment that indicate that a nanofluid becomes unstable at 60 °C. This is, however, based on an experiment where a dispersion is being sonicated. They say 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. [10] state that the temperature effect is

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a significant issue, and that stabilising with surfactants may fail at elevated temperatures. They say 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 [80, 81]. Wang and Mujumdar [77] have only one related remark, which is that the addition of surfactants may affect the heat transfer performance of nanofluids, especially at high temperatures. Murshed et al. [79] presented an experimental work: they measured the thermal conductivity of Al₂O₃-CTAB-water as a function of temperature up to 60 °C. They observed that thermal conductivity increased with temperature. At 60 °C, the thermal conductivity still showed the same trend, and we were not able to find that this paper supports the claim that the surfactants degraded.

In more recent work, Hordy et al. [82] state that most surfactants decompose upon modest heating and can lose effectiveness at temperature as low as 70 °C. This claim is also made by Wen and Ding [81]. Simultaneously, Amiri et al. [83] states 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 fluid. The deterioration of the nanofluids stability can be explained by three parameters:

- First, surfactants decompose at high temperatures. That is, when heating, the surfactant first dehydrates and then decarboxylates (RCOOH = CO₂ + R-H) leading to deterioration of the surfactant properties. For the surfactants GA, AF₃C, CTAB, SDS, the decomposition temperature is 90–95 °C [84], 210 °C [85], 235 °C [86], and 380 °C [84], respectively.
- Second, the interaction between nanoparticles and surfactant changes as a function of the temperature. According to Toerne et al. [87], the critical micelle concentration for non-ionic 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 [42] and they can increase the viscosity and reduce in some cases the thermal conductivity of the nanofluid.
- An increase of temperature will lead to higher Brownian motion, which may damage the bond between the nanoparticles and surfactants.

However, there does not seem to be evidence that these restrictions are valid for all nanofluids and/or surfactants. For example, Li et al. [88] studied the stability of surface-capped silver particles in the mixture of water, alkylamine, and oleic acid. The oleic-acid surfactant was 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 non-polar 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 Figure 6. After that time, the silver nanoparticles agglomerated and quickly deposited in the fluid.





Figure 6 Stability time of the silver nanofluids at different temperatures (Source: Li et al. [88])

Polydimethylsiloxane (PDMS) is another surfactant that was used by Chen et al. [89] to prepare a stable nanofluid with Fe₃O₄ nanoparticles dispersed in silicone oil. The PDMS was grafted on the surface of the nanoparticles. The grafted PDMS have a phosphate head group that could strongly bind onto the nanoparticle surface. Besides, the chemical composition of the PDMS is similar to the silicone oil, ensuring excellent miscibility and good stability between the base fluid and nanoparticles [40]. After such surface modification, the Van der Waals attraction is screened, thereby achieving a stable dispersion. Chen et al. [89] demonstrated PDMS capped-Fe₃O₄ nanoparticles could be steadily dispersed within silicone oil up to 150 °C for a concentration of 0.75 mg/mL. Aggregation has been observed when the nanoparticle concentration is increased, see Figure 7.



Figure 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. [89])

Guo et al. [90] used oleic acid/PEG/agar/oleic acid as a surfactant. They prepared a stable nano-ferrofluids coated with the tetralayer surfactants and dispersed in water. Thermogravimetric analysis (TGA) measurement shows that the nanoparticles coated with the surfactants does not degrade for temperatures up to around 200 °C. However, the long chain of the surfactant would increase the viscosity for the nanofluids. TGA measurement also shows that only PEG-4000 is stable up to 300 °C. Other researchers have used PEG as a surfactant, showing long-term stability at room temperature [91, 92].

Similarly, Asri et al. [93] show results on nanoferrofluids that were synthetized with PEG. PEG was used as a coating agent to reduce agglomeration. The maximum working temperature was 110 °C, but they did not state

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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 [94].

3.2.2. Surface modification

As discussed earlier, several researchers have suggested that surfactants lose their effectiveness at temperatures around 70 °C [42, 83, 95]. To overcome such problems, some researchers have reported that chemically bonded functional groups (covalent functionalisation being a strong chemical bonding) on the surface of the nanoparticles show greater promise in preventing agglomeration at high temperatures than employing surfactants, which imply weaker chemical bonding [31, 83, 96]. 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 [31]. 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. Christian and Bromfield [96] state that polymers functionalized to the nanoparticles can increase the degradation temperature of the polymer due to the strong binding to the nanoparticles. Thus, improving the stability performance of the functional groups at high temperature.

Amiri et al. [83] stated that nanofluids with covalent functionalized CNT show good stability at high temperature contrary to non-covalent groups (e.g. GA and SDS) where aggregation was observed. They further claim that chemically attached functional groups have higher decomposition temperature. These findings are also supported by Hordy et al. [82, 97, 98].

Thus, it seems that several researchers have reached a *consensus* that covalent functionalization can be considered a better method compared to surfactants to achieve higher dispersity at high temperatures. To prepare covalent functionalized nanofluids, one may use different methods including wet chemistry [99], chemical vapour deposition [100], plasma enhanced CVD [101] or a plasma process [82, 95]. Tavares and Coulombe [95] used a dual plasma process for a one-step synthesis of copper-ethylene glycol (EG) nanofluid. 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 Figure 8. Similar preparation methods have been used by Hordy et al. [82]. In the experiments of Tavares and Coulombe [95], 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 (boiling temperature of EG).



Figure 8 Sketch of the dual plasma setup used by Tavares and Coulombe [95]

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Hordy et al. [82] studied the stability at high temperature of multiwalled CNTs (MWCNTs) with different base fluids such as ethylene glycol, propylene glycol and Therminol VP-1. The nanofluids were produced using plasma functionalized MWCNTs. 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 [97] 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 into the surface (particularly carboxyl groups). These carboxylic functionalities produce a charged surface that limits agglomeration, i.e. electrostatic stabilization. Due to their functionalisation, the particle surface of the MWCNT is more compatible with polar fluids (glycol-based and water), and not with non-polar based fluids like Therminol VP-1.

Hordy et al. continued their studies with functionalized MWCNT to determine the stability at higher temperature [97, 98]. For that purpose, functionalized MWCNT were heated up to 600 °C in both argon and air. 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 in the 200–600 °C range), 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. Figure 9 shows that the stability of the sample heated to 200 °C rand 300 °C remained stable after the thermal treatment, while the sample heated to 400 °C and 600 °C resulted in agglomeration. Hordy et al. [98] concluded that, although some of the functional groups may be lost at high temperatures, nanofluid stability can still be maintained.

From the previous studies done by Hordy [82, 97, 98] indicate that glycol-based nanofluids with functionalized MWCNT are stable at high temperature. It must be noted that the stability test done in [82] at 170 °C was for a short time (hours). Therefore, more rigorous studies of the long-term stability need to be performed.



Figure 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. [98])

3.1. Enhancement of the thermal properties

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 [70], there are a few studies and measurements of thermophysical properties of nanofluids at temperatures above 100 °C. In this section, we present the main findings from the literature in the high-temperature regions.

3.1.1. Density and heat capacity

In the previous section, we presented the well-known and relatively basic relations that are often used for the density and heat capacity: Eqs. (2) and (3). Although there is evidence of specific nanoparticle effects such as the nanolayer [50], the basic relations may still be relevant even at high temperatures. The temperature dependence of the densities of the base fluid and nanoparticles or nanoparticle material is usually well-known.

We were not able to find any specific studies of density and heat capacity of nanofluids at high temperatures. However, in a recent study by Safaei et al. [102], they report that adding 0.1 wt% of SiO₂ and Al₂O₃ 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.

3.1.2. Thermal conductivity

As the thermal conductivity is one of the key properties of nanofluids, it has been the topic of many studies also at high temperatures. One common example of how the temperature affects the thermal conductivity is provided by Li and Peterson [103], who shows that the thermal conductivity increases with temperature.

Temperature effects on the thermal conductivity were 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 [79, 104]. This is also supported in literature not covered by Qiu et al., e.g. [105–108]. 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 [57], some studies indicate that the temperature dependence of the thermal conductivity of nanofluids followed closely that of the base fluid [109–111]. Also, it should be mentioned that there are also some results that provide evidence to the contrary [112–114].

There are 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. [115] 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.

3.1.3. Viscosity

Viscosity tends to be a highly temperature dependent fluid property. For instance, oils are known to display a highly non-linear temperature dependence. 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. Qiu et al. [4] again provides a good overall recent overview.

At high temperatures, the models by Masoumi et al. [116] or Hosseini et al. [117] may be interesting, as both include temperature effects. However, both of these models are correlations that depend on availability of experimental data, and both models only validated at temperatures below 100 °C.

As stated before, Safaei et al. [102] report that a small amount of nanoparticles did not lead to a significant change to the viscosity of 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.

4. Nanofluids in solar collectors/industry

As discussed in the introduction, nanofluids show great potential for many different applications. They can be used as a 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, 118]. 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. [11], Olia et al. [12], Bellos et al. [13], Javadi et al. [17], Okonkwo et al. [119], Elsheikh et al. [120]. In the following, we mainly consider the parabolic trough collector (PTC). The review by Manikandan et al. [121] considers the enhancement of the optical and thermal efficiencies of the PTC at a more general level, including the use of nanofluids. According to [13], one of the most critical issues of PTC technologies is to increase thermal efficiency, especially at high temperature, to be energetically and financially viable.

Different technologies have been developed to increase the solar PTC efficiency. For instance, see Figure 10 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 [122]. 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 and 300 °C. Thereafter we will consider some of the main barriers to implement nanofluids in the industry in a more general manner.



Figure 10 Overall efficiency of solar collectors with different technologies including the use of nanofluids. (Source: Kasaeian et al. [122])

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 is the ratio of the *useful* energy absorbed to the total *available* energy [11, 13].

4.1. Progress in thermal efficiency of PTC

For temperatures below 100 °C, there are several studies with water-based nanofluids where long-term stability and overall efficiency enhancement up to 24 % have been achieved, see Ref. [5] for a good overview. The nanofluid tested experimentally was Al_2O_3 dispersed in water [123].

For operating temperatures above 100 °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

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single experimental study of oil-based nanofluids in PTCs. This was by Kasaeian et al. [122], 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%. They calculated the thermal efficiency using ASHRAE Standard parameters [124]. 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 [13, 119, 125–138]. 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 [13]. 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. [119] used CFD models to investigate the heat transfer enhancement of PTCs numerically. They studied six different working fluids: pressurized water, supercritical CO2 (sc-CO2), Therminol VP-1 and oilbased nanofluids using 3 vol% of CuO, Fe3O4, Al2O3 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 Al2O3 showed the highest enhancement of thermal efficiency of 0.22 % while CuO-Therminol VP-1 and Fe3O4-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 CO2 shows the lowest, see the Figure 11. However, the use of an unpressurized system can reduce costs, therefore oil-based fluids are most attractive at high temperature.



Figure 11 Thermal efficiency comparison for six different working fluids. Pressurized water, Therminol VP-1, CO_2 , and three oil-based nanofluids with 3 vol% CuO, Fe_3O_4 , Al_2O_3 dispersed in therminol VP-1 (Source: Okonkwo et al. [119])

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 [13, 125–129]. The parameters they investigate are usually the energy and exergy performance and pressure losses. Bellos and Tzivanidis [129] investigate the use of various nanoparticles (Cu, CuO, Fe₃O₄, TiO₂, Al₂O₃, SiO₂) dispersed in Syltherm 800. The thermal efficiency

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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, Fe3O4, TiO2, Al2O3, SiO2 respectively, see Figure 12. Bellos and Tzivanidis [129] 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 [126] investigated the thermal efficiency enhancement of a 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 0.8 %, see Figure 12. In addition, they conclude that the use of nanofluids enhance the thermal performance of the linear Fresnel collector, especially at high temperatures, due to a decrease in pumping power.



Figure 12 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 [129]; Bellos and Tzivanidis [126])

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, Al₂O₃, and single-wall CNTs (CWCNTs) dispersed in Therminol VP-1, and Al₂O₃, CuO dispersed in Syltherm 800 [130–133]. They investigate both the thermodynamic performance and the thermal performance of the solar collector with the nanofluids. In Refs. [131, 133], they studied the use of Al₂O₃-Syltherm 800 and Al₂O₃, 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. [130] 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. [130], 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, and that the specific heat capacity needs to be considered as an important property. 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 Table 1 and Table 6.

Base fluid	Nanoparticle	Concentration	Type of study	Inlet Temp. (°C)	Imp. HTC (%)	Imp. therm. eff. (%)	Ref.
Syltherm-800	CeO ₂ Al ₂ O ₃	2 vol% 2 vol%	Model	302	167.8	1.09	[138]
Syltherm-800	Cu	4 vol%	Model	327	24	0.54	[129]
Syltherm-800	CuO	4 vol%	Model	327	19	0.46	[129]
Syltherm-800	Fe ₂ O ₃	4 vol%	Model	327	17	0.41	[129]
Syltherm-800	TiO ₂	4 vol%	Model	327	14	0.35	[129]
Syltherm-800	Al ₂ O ₃	4 vol%	Model	327	14	0.35	[129]
Syltherm-800	Si ₂ O ₃	4 vol%	Model	327	7	0.19	[129]
Syltherm-800	CuO	6 vol%	CFD	227	31.7	0.3	[127]
Syltherm-800	Al ₂ O ₃	4 vol%	CFD	250		10	[134]
Syltherm-800	Ag	6 vol%	CFD	127–377		13.9	[133]
Syltherm-800	Cu	6 vol%	CFD	127–377		12.5	[133]
Syltherm-800	Al ₂ O ₃	6 vol%	CFD	127–377		7.2	[133]
Therminol VP-1	Al ₂ O ₃	8 vol%	CFD	77–327		7.8	[131]
Therminol VP-1	SWCNTs	2.5 vol%	CFD	127–377	234	4.4	[130]
Therminol VP-1	Al ₂ O ₃	3 vol%	Model	127		0.22	[139]
Therminol VP-1	Fe ₂ O ₃	3 vol%	Model	127		0.18	[119]
Therminol VP-1	CuO	3 vol%	Model	127		0.15	[119]
Therminol VP-1	Al ₂ O ₃	3 vol%	CFD	327		15	[140]
Thermal oil	Al ₂ O ₃		CFD	200	7.02	5.06	[125]
Thermal oil	Al ₂ O ₃		CFD	300	10.27	7.77	[125]
Mineral oil	MWCNT	0.2 wt%	Experimental			4–5	[122]
Mineral oil	MWCNT	0.3 wt%	Experimental			6–7	[122]
Synthetic oil	Al ₂ O ₃		CFD	227		6	[135]
Synthetic oil	Al ₂ O ₃		CFD	127		9	[135]

Table 6 Comparison of various nanofluid experiment/simulation results.

Kaloudis et al. [134] used CFD to study a PTC system with Syltherm 800/Al₂O₃ nanofluid with nanoparticle concentration from 0–4 vol%. Their models were validated and the 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. [135] used numerical simulations to study the effect of nanoparticle concentration in a nanofluid composed of Al₂O₃ particles in synthetic oil at operational temperatures in the range 27–227 °C. Their results showed that the heat-transfer coefficient (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. [136] with an Al₂O₃/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. [137], 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 (Al₂O₃, CuO, and TiO₂), 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% Al₂O₃ in Therminol VP-1.

Hybrid nanofluids have been also studied; that is, nanofluids that combine two different nanoparticle types. Al-Oran et al. [138] 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 Figure 13.



Figure 13 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 %. (Source: Al-Oran et al. [138])

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. [119] 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 [122]. The numerical studies give different values. According to Bellos et al. [13], the differences may be due to the different methodologies used by the various researchers. In Table 6, 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.

4.2. Barriers to implement nanofluids in the industry

To our knowledge, nanofluids have not been used in any large-scale industrial application. According to Ref. [141], the barriers to implement them in the industry are the following:

- Develop nanofluids with the desired enhanced thermal and mechanical properties,
- Ensure that nanofluids consist of uniformly suspended particles,

- The thermal properties of the nanofluid depend on several parameters, including the size and shape of nanoparticles, agglomeration, dispersing agent, temperature, etc. [118]. This flexibility makes it difficult to standardize the nanofluid's thermal properties by the manufacture company [142],
- Demonstrate that nanofluids do not affect the viscosity and clog the system,
- Scale-up nanofluids production and ensure the economic viability of nanofluids production at commercial scale. Because the nanoparticles are not cheap, for example, the current cost for 25 g of copper oxide nanopowder is 116 EUR [143].

These barriers have been cited by a pilot project hosted by the Argonne Laboratory [141] where they have tried to demonstrate large-scale nanofluids production. 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 [118] and [144]. The world of nanofluid is progressing, and there are several patents on the preparation of stable nanofluid, e.g. [145], commercial nanofluids [146], and small PC-cooling equipment using nanofluids [147]. The global market for nanofluids for heat transfer applications according to CEA is 2 billion dollars per year [148]. Besides, projects like Nanouptake [149] and FRIENDSHIP [144] will help to overcome the commercial application barriers. A recent handbook by the Nanouptake [150] project cites the several industrial applications of nanofluids in the energy sector. The handbook summarizes different applications in small scale or testing compact system.

5. Conclusions and recommendations

We have presented a literature study on the use of nanofluids for high-temperature heat-transfer applications, and in particular 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 a review on 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. It is therefore 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:

- Stability is the most critical aspect of nanofluids, especially at high temperatures. Many researchers have used surfactants for stabilizing the dispersion of the nanoparticles into the base fluids. However, at high temperatures, the use of surfactants is not recommended due to several factors. First, surfactants can degrade/decompose at a temperature of around 90 °C. Second, the interaction between surfactants and nanoparticles changes 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 by pH modification. 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 stabilisation method for high temperatures. This method involves modifying the surface of the nanoparticles by covalent functionalization with molecules like hydroxyl, carboxyl grafted on the surface of the nanoparticle. Nanofluids created with this technique has been tested by several researchers, but they are mainly using some type of carbon nanotubes. Further studies are needed using other nanoparticles like Al2O3 or Cu, which are cheaper to produce. Further studies on the long-term stability for functionalized-nanofluids should be performed.

On thermophysical properties of nanofluids at high temperature:

- There has been a lot of work on understanding and characterising 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. Al2O3 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 of the 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 work is necessary on characterising 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 waterbased 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 Al2O3. From the numerical studies, we can observe that Al2O3 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. [119] 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 increases 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.

6. Degree of Progress

The degree of progress for this deliverable is 100%.

7. Dissemination Level

This Deliverable is Public and will be therefore available for downloading on the project's website and on demand.

8. Nomenclature

Abbreviations

AF ₃ C	Sodium alkyl polyethylene oxide carboxylate		
CO ₂	carbon dioxide		
CVD	Chemical Vapour Deposition		
CNT	Carbon nanotube		
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		
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-CO ₂	Supercritical CO ₂		
SDBS	Sodium dodecyl benzenesulphonate		
SDS	Sodium dodecyl sulphate		
SOCT	Sodium octanoate		
SWCNT	Single wall carbon nanotube		
TGA	Thermogravimetric analysis		
Symbols			
Α	Volume fraction		
μ	Dynamic viscosity		
ϕ	Mass fraction		
ρ	Density		
С	Specific heat capacity		
	WP2, D2.4		

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- gAcceleration of gravitykThermal conductivity
- R Particle radius
- Tarticic facility
- *v* Particle velocity
- *V*_A Attractive Van der Waals forces
- V_R Repulsive electrostatic forces

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