Review

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Nanostructured phase-changeable heat transfer fluids

Abstract: Cooling is one of the most important technique challenges faced by a range of diverse industries and military needs. There is an urgent need for the innovative heat transfer fluids with improved thermal properties over the currently available. This review paper discusses the concept of using phase-changeable nanoparticles to increase the effective heat capacity and the heat transfer rate of the fluid. A large amount of heat can be absorbed or released when these nanoparticles undergo phase transition from solid to liquid or liquid to gas or vice versa and, thus, enhancing the heat transfer rate. Two types of phasechange fluids are introduced: one contains liquid nanodroplets that will evaporate at elevated temperatures or solidifies at reduced temperatures, called "nanoemulsion fluids"; the other is suspensions of solid-liquid metallic phase-change nanoparticles. The material synthesis and property characterizations of these phase-changeable fluids are two main aspects of this paper. The explosive vaporization of the dispersed nanodroplets would significantly improve the heat transfer in the nanoemulsion fluid. The solid-liquid metallic phase-change nanoparticles will increase the effective heat capacity and thermal conductivity of the base fluids simultaneously. This paper also identifies the several critical issues in the phasechangeable fluids to be solved in the future.

Keywords: nanoemulsion fluids; nanoparticles; phasechange material.

1 Introduction

Cooling is one of the most important technical challenges faced by a range of diverse industries: microelectronics,

optoelectronics, and especially power electronics [1–8]. This technology gap is the result of the higher currents, switching frequencies, and component densities of today's electronics and power electronics. The advances in the semiconductor materials and more precise fabrication techniques have the unfortunate side effect of generating higher amounts of waste heat within a smaller volume. Today, it is not unusual to see heat fluxes of 200 W/cm² in a power module, a figure that is expected to increase over 1000 W/cm² in the near future.

The thermal management of such high flux is becoming the bottleneck to the improvements in electronics and power electronics. The need for a higher capacity and more complex cooling systems is limiting the full potential of the advances in electronics and power electronics. The solution is the development of the significantly improved heat transfer systems and their kernel components. One important component of these heat transfer systems that has received little attention is the cooling fluid used inside. The inherently poor heat transfer properties of some of the coolants, lubricants, oils, and other heat transfer fluids used in today's thermal systems limit the capacity and compactness of the heat exchangers that use these fluids. Therefore, there is an urgent need for innovative heat transfer fluids with improved thermal properties over those currently available.

The strategy of adding the solid, highly conductive particles to improve the thermal conductivity of the fluids has been pursued since Maxwell's theoretical work was first published more than 100 years ago [9]. The early stage studies have been confined to the millimeter- or micrometer-sized solid particles dispersed in the fluids. In the past decade, the researchers have focused on the suspensions of the nanometer-sized solid particles, known as nanofluids [1–5, 10–50]. In general, the research of the nanofluids in heat transfer application fall in two directions: thermal conductivity and convective heat [1-4, 10-52]. The thermal conductivity in the various nanofluids has been extensively studied. The transient hot wire method, the steady-state parallel-plate technique, and the 3ω transfer technique are often employed to measure the thermal conductivity of the nanofluids. The significant

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enhancement in thermal conductivity has been reported in the various nanofluids by different groups [1–4]. Recently, an International Nanofluid Property Benchmark Exercise (INPBE) reported that the thermal conductivity of the nanofluids increase with the particle concentration and aspect ratio, but the effective medium theory can well explain the experimental data obtained in their study, and no anomalous enhancement of the thermal conductivity was observed in the studied nanofluids [4]. The boiling heat transfer in the nanofluids has also received considerable attention in the recent years. It has been observed that the pool boiling critical heat flux (CHF) can be increased significantly in the Al₂O₂ nanofluids [38]. This CHF enhancement can be attributed to the nanoparticle coating deposited on the heated surface, which will modify the nucleation site density and the wetting characteristics (such as bubble contact angle) [20, 29, 34, 53–57].

In this paper, it is intended to introduce some recent developments in another type of engineered heat transfer fluids, in which the nanoparticles made of phase-change materials (PCMs) are added to increase the effective heat capacity of the base fluids [33, 58-64]. These fluids can be categorized into two groups: liquid-vapor phase-change fluids and solid-liquid phase-change fluids. This paper starts with the introduction of the PCMs with the potential application in thermal fluids. It is followed by the discussion on the nanoemulsion fluids, in which the dispersed nanodroplets can be liquid-vapor PCM or liquid-solid PCM, depending on the PCM and the operating temperature [58-63]. Then, the suspensions of the low-melting metallic nanoparticles, such as Indium are discussed [33, 64]. Both the material synthesis and property characterization of these nanostructured phase-changeable fluids will be covered. In these fluids, the phase-changeable nanoparticles are typically smaller than 50 nm in size and remain stable in the fluids during the phase transition. This review article is not intended to serve as a complete description of all the phase-changeable fluids available for heat transfer applications. The selection of the coverage was influenced by the research focus of the authors and reflects their assessment of the field.

2 Use of PCMs to increase the fluid thermal properties

Most research on the thermal fluids, to date, has focused on how to increase the thermal conductivity. This paper will introduce the concept of using the PCM nanoparticles to increase the effective heat capacity as well as the effective thermal conductivity of the thermal fluids.

Both the heat capacity and thermal conductivity of the fluids strongly influence the heat transfer coefficient. For example, for a fully developed turbulent flow of a singlephase fluid, the convective heat transfer coefficient, *h*, can be described in terms of the thermal conductivity, k_{α} and specific heat, C_f , as $h \propto k_f^{0.6} C_f^{0.4}$ [65]. If the particles are made of PCMs, the effective specific heat of the PCM fluid will be increased by a factor of $1 + \frac{\alpha \cdot H_{PCM}}{\Delta T \cdot C_f}$, where α is the weight fraction of the PCM nanoparticles in the fluid, $H_{\rm PCM}$ is the latent heat of the PCM per unit mass, and ΔT is the temperature difference between the heat transfer surface and the bulk fluid. For example, a 5% mass fraction of the solid-liquid phase-changeable hexadecane (melting point, 291 K) may enhance the effective heat capacity of FC-72 by up to 100% at ΔT =10 K. Therefore, the use of the PCMs as the dispersed particles will be able to boost the thermal properties of the thermal fluids much more significantly than the non-PCM particles at the same volume fraction.

The current PCMs available for the thermal fluid application can be divided into two main categories: solidliquid transition and liquid-vapor transition. The thermophysical properties of the state-of-the-art PCMs with the potential use in the thermal fluids are listed in Table 1. The liquid-vapor PCMs, such as ethanol and water, have a much larger latent heat and, therefore, resulting in a higher heat transfer rate, but a condenser is needed for vapor condensation. The solid-liquid phase-change materials have small volume change during the phase transition, and therefore, the suspension of the solid-liquid phase-change particles can be used in the thermal management system designed for the single-phase fluids.

3 Phase-changeable nanoemulsion fluids

One fluid is dispersed into another immiscible fluid as the nanosized structures such as the droplets and tubes to create a "nanoemulsion fluid". Those nanostructures are reverse micelles swollen with the dispersed phase and stabilized by the surfactant molecules. The nanoemulsion fluids are part of a broad class of multiphase colloidal dispersions [58–63]. Some nanoemulsion fluids can be spontaneously generated by self-assembly without the need of external shear and are suited for the thermal management applications [59–62, 68–81]. The self-assembled nanoemulsion fluids are thermodynamically stable. Figure 1 shows a picture of the ethanolin-poly- α -olefin (PAO) nanoemulsion heat transfer fluids:

Category	Compound name	Phase-change temperature (°C)	Thermal conductivity (W/mK)	Latent heat (J/g)
Solid-liquid	Water	0	0.6 (liquid)	334
	Myristic acid+capric	24	0.15 (liquid)	147
	CaCl,∙6H,O	29	0.56 (liquid)	192
	Na,SO, 10H,O	32	0.54 (liquid)	251
	Paraffin C17	22	0.15 (liquid)	215
	Paraffin C18	28	0.15 (liquid)	245
	Paraffin C19	32	0.15 (liquid)	222
	Capric acid	32	0.15 (liquid)	152
	Zn(NO ₂),·6H ₂ O	36	0.47 (liquid)	147
Liquid-vapor	Indium	157	82 (solid)	29
	FC-72	56	0.06 (liquid)	88
	Ethanol	78	0.2 (liquid)	855
	Water	100	0.6 (liquid)	2260

Table 1 The PCMs with potential use in the thermal fluids [66, 67].



Figure 1 The pictures of the ethanol-in-PAO nanoemulsion fluids (Bottle A) and pure PAO (Bottle B). The liquids in both the bottles are transparent. The Tyndall effect (i.e., a light beam can be seen when viewed from the side) can be observed only in Bottle A when a laser beam is passed through Bottles A and B.

both PAO and PAO-based nanoemulsion fluids are transparent, but the nanoemulsion exhibits the Tyndall effect [58–63, 82, 83]. Note that the nanoemulsions are very different from the emulsions in terms of the microstructure and material properties. The emulsions are dispersions of micron-sized droplets and are stable only for a relatively short time [79, 84–91]. Table 2 is the comparison between the self-assembled nanoemulsion fluids and conventional emulsions. The self-assembled nanoemulsion fluids are a thermodynamically stable system and possess long-term stability.

3.1 Formation of self-assembled nanoemulsion fluids

The self-assembled nanoemulsion fluids are thermodynamically stable, and the formation of these fluids can be explained using the classical thermodynamic theory [70–75, 78–80, 92–94]. The nanoemulsion fluid consists of one oil phase, one water phase, and certain surfactants. The adding of the surfactant lowers the surface tension of the oil-water interface and the change in free energy of the system is given by Eq. (1),

$$DG_{\ell} = \gamma DA \cdot T \cdot DS \tag{1}$$

where DG_f is the free energy of the formation, γ is the surface tension of the oil-water interface, DA is the change in the

 Table 2
 Comparison of nanoemulsion fluids and emulsions.

Sample	Property	Nanoemulsion	Emulsion
1	Appearance	Transparent	Turbid
2	Interfacial tension	Ultra low (usually <<1 mN/m)	Low
3	Droplet size	<50 nm	>500 nm
4	Stability	Thermodynamically stable, long shelf-life	Thermodynamically unstable
5	Preparation	Self-assembly	Need of external shear
6	Viscosity	Newtonian	Non-Newtonian

interfacial area upon nanoemulsification, DS is the change in the entropy of the system, and T is the absolute temperature. The change in DA is very large due to the large number of nanosized droplets in the nanoemulsion fluids. However, the interfacial tension γ is very small (usually <<1 mN/m), and therefore, the increase in the surface energy, $\gamma \cdot DA$, could be smaller than the entropy arising from the mixing. The favorable entropic contributions also arise from the dynamic processes such as the surfactant diffusion in the interfacial layer and the monomer-micelle surfactant exchange. The entropy of mixing can be large enough to compensate for the positive interfacial free energy and to give the nanoemulsion system a free energy lower than that of the unmixed components. So the self-assembled nanoemulsion fluids can be formed via self-assembly and are, in fact, a thermodynamically stable system [79, 80, 95]. There are mainly two approaches to prepare the nanoemulsion fluids: the spontaneous emulsification method (or the so-called phase titration method) and the phaseinversion method [79, 80]. Figure 2 shows the typical phasebehavior diagram of a ternary system that contains two immiscible so-called oil and water phases and an amphiphilic surfactant component. The term "water" refers to a polar phase, while "oil" is used for an apolar organic phase. When a system has a composition that lies in the shaded areas, a nanoemulsion fluid, either oil-in-water or water-inoil, can be formed via self-assembly.

Phase inversion of the nanoemulsion fluids occurs upon the addition of the excesses of the dispersed phase or in response to temperature [79]. This method makes use of changing the spontaneous curvature of the surfactant layer. For non-ionic surfactants, this can be achieved by changing the temperature of the system, forcing a transition from an oil-in-water nanoemulsion at low temperatures to a water-in-oil nanoemulsion at higher temperatures (transitional phase inversion). During cooling, the



system crosses a point of zero spontaneous curvature and minimal surface tension, promoting the formation of finely dispersed oil droplets.

The phase-change nanoemulsion fluids can be divided into two groups, the liquid-vapor nanoemulsions and the liquid-solid nanoemulsions, depending on the phase transition behavior of the dispersed particles and the fluid operating temperature. These two types of nanoemulsion fluids are discussed in the following sections.

3.2 Liquid-vapor phase-change nanoemulsion fluids

Ethanol-in-PAO is a liquid-vapor phase-change nanoemulsion fluid in which the ethanol nanodroplets could evaporate explosively and, thus, enhance the heat transfer rate of the base fluid PAO [59]. The PAO has been widely used as dielectric heat transfer fluids and lubricants. It remains oily in a wide temperature range due to the flexible alkyl branching groups on the C-C backbone chain, but it has relatively poor thermal properties. The microstructure and thermophysical properties of the ethanol-in-PAO nanoemulsion fluids are discussed below.

3.2.1 Microstructure of ethanol-in-PAO nanoemulsion fluids

The microstructure of the nanoemulsion fluids is affected by many factors, including the surfactant type and concentration, the dispersed liquid type and concentration, the molar ratio of the dispersed liquid to the surfactant, the temperature, the pH value, and the salinity [79, 94– 100]. The characterization of the microstructure of the nanoemulsion fluids is a challenging task. Small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) are often used because they can be applied to the "concentrated" colloidal suspensions (e.g., >1 vol.%) [101–107]. Figure 3 shows the SANS data for the ethanolin-PAO nanoemulsion fluid. The wave vector is given by

$$\frac{q=4\pi\sin\left(\frac{\theta}{2}\right)}{\lambda}$$
 (2)

Figure 2 The schematic phase diagram of a water-oil-surfactant ternary system. The shaded areas are regions where self-assembled nanoemulsions are found.

where λ is the wavelength of the incident neutrons, and θ is the scattering angle. The analysis of the SANS data suggests that the inner cores of the swollen micelles, i.e., the ethanol droplets, are spherical and have a radius of about 0.8 nm for 9 vol.%.



Figure 3 The intensity *I* vs. the wave vector *q* measured in the ethanol-in-PAO nanoemulsion fluids.

3.2.2 Thermal conductivity and viscosity of ethanolin-PAO nanoemulsion fluids

The 3ω -wire method is used to measure the fluid thermal conductivity [39, 62, 63, 108]. This method is actually a combination of the transient hot-wire method and the 3ω method. In this method, a metal wire suspended in a liquid acts as both the heater and thermometer. A sinusoidal current at frequency ω is passed through the metal wire and generates a heat wave at frequency 2ω . The temperature rise at frequency 2ω in the metal wire can be deduced by the voltage component at frequency 3ω . The thermal conductivity of the liquid, *k*, is determined by the slope of the 2ω temperature rise of the metal wire with respect to the frequency ω .

Figure 4 shows the relative thermal conductivity in ethanol-in-PAO nanoemulsion fluids as a function of the ethanol loadings. The observed conductivity increase in the ethanol-in-PAO nanoemulsion fluids is rather moderate. The prediction by the Maxwell model is also plotted in Figure 4 for comparison. The relative thermal conductivity



Figure 4 The relative thermal conductivity increase with the ethanol loading in the ethanol-in-PAO nanoemulsion fluids. The estimate from the Maxwell's model is shown for comparison.

is defined as $k_{\rm eff}/k_o$, where k_o and $k_{\rm eff}$ are thermal conductivities of the base fluid and nanoemulsion fluids, respectively. The effective medium theory reduces to the Maxwell's equation for the suspensions of well-dispersed, non-interacting spherical particles,

$$\frac{k_{\rm eff}}{k_o} = \frac{k_p + 2k_o + 2\phi(k_p - k_o)}{k_p + 2k_o - \phi(k_p - k_o)}$$
(3)

where k_{o} is the thermal conductivity of the base fluid, k_{n} is the thermal conductivity of the particles, and ϕ is the particle volumetric fraction. This equation predicts that the thermal conductivity enhancement increases approximately linearly with the particle volumetric fraction for the dilute nanofluids or nanoemulsion fluids (e.g., $\phi < 10\%$), if $k_{p} > k_{a}$ and with no change in particle shape. It can be seen in this figure that the relative thermal conductivity of the ethanol-in-PAO nanoemulsion fluids appears to be linear with the loading of the ethanol nanodroplets over the loading range from 0 to 9 vol.%. However, the magnitude of the conductivity increase is rather moderate in the ethanol-in-PAO nanoemulsion fluids, e.g., 2.3% increase for 9 vol.% $(k_{PAO} = 0.143 \text{ W/mK and } k_{alcohol} = 0.171 \text{ W/mK} [109, 110])$. No strong effects of the Brownian motion on the thermal transport are found experimentally in those fluids, although the nanodroplets are extremely small, around 0.8 nm.

Viscosity is another macroscopically observable parameter that characterize a nanoemulsion fluid, and it may range anywhere between a low-viscous fluid and a gel state [59, 77, 81, 111, 112]. It is an important quantity for many practical applications of nanoemulsion fluids especially those used for hydraulic fluids. For instance, pumping such systems might be of interest in their application, and here, viscosity plays an important role. Figure 5 shows the relative dynamic viscosity, μ_{eff}/μ_0 , for the ethanol-in-PAO nanoemulsion fluids with varying alcohol loadings, which is measured using a commercial viscometer (Brookfield DV-I Prime).

An approximately linear relationship is observed between the viscosity increase and the loading of the alcohol nanodroplets in the range of 0–9 vol.%, a trend similar to the thermal conductivity plotted in Figure 4. However, the relative viscosity is found to be much larger than the relative conductivity if compared at the same ethanol loading. For example, the measured viscosity increase is 31% for 9 vol.% ethanol loading, compared to a 2.3% increase in thermal conductivity. The viscosity increase of the dilute colloids can be predicted using the Einstein equation [24],

$$\mu_{\rm eff}/\mu_0 = 1 + 2.5\phi$$
 (4)



Figure 5 The relative viscosities of the ethanol-in-PAO nanoemulsions measured at the different volumetric fractions of the ethanol nanodroplets. The measurements were conducted at room temperature using a Brookfield viscometer.

where μ_{eff} is the nanoemulsion viscosity, μ_0 is the base fluid PAO viscosity, and ϕ is the volumetric fraction of the encapsulated ethanol nanodroplets. This equation, however, underestimates slightly the viscosity increase in the ethanol-in-PAO nanoemulsion fluids, as can be seen in Figure 5. This discrepancy is probably because the droplet volume fraction, ϕ , used in the viscosity calculation does not take into account the surfactant layer outside the alcohol core, and the Einstein equation used here is derived from the dilute system.

3.2.3 Liquid-vapor phase transition in ethanol-in-PAO nanoemulsion fluids

The convective heat transfer experiment has been conducted to examine the influence of liquid-vapor transition of the dispersed droplets on heat transfer in ethanol-in-PAO nanoemulsion fluids [58, 60, 61]. Recently, the pool boiling CHF of these PAO-based nanoemulsion fluids have also been investigated. In these ethanol-in-PAO nanoemulsion fluids, the dispersed phase ethanol has a boiling point of 78°C at 1 atm, which is much lower than the boiling point of the base fluid PAO (277°C) [110].

The pool boiling experiment setup is shown in Figure 6. In this experiment, a platinum wire 25 μ m in diameter is horizontally hanged in the test vessel, which serves as both the heater and thermometer. It is heated electrically via a DC power supply (ePower SPS150-8-20V), and the voltage and current is recorded using multimeters (Agilent 34401A and 34410A). The test vessel is immersed in a water bath to maintain at a constant room temperature. Two K-type thermocouples are used to monitor the temperatures, one for the sample and the other for the water bath. The experimental system is controlled by a LabVIEW program. The wall heat flux is calculated from the measured voltage and current directly. The wire temperature is determined from the relation between the electrical resistance and temperature of the platinum wire.



Figure 6 The pool boiling experiment setup.

The pool boiling heat transfer curves are plotted in Figure 7 for the pure PAO and the PAO-based nanoemulsion fluids. When the wire temperature is <170°C, the heat transfer coefficient values of the pure PAO and the PAO-based nanoemulsion fluids appear to be the same. This indicates that these ethanol nanodroplets have little effect on the fluid heat transfer efficiency if there is no phase transition in these nanodroplets. This is also consistent with the measured thermal conductivity and viscosity shown in Figures 4 and 5. When the heater temperature is further increased, an abrupt increase in the convective heat transfer coefficient is observed in the PAO nanoemulsion fluids, compared to that of the pure PAO case. For example, the dissipated heat flux *q* is found to be 90 W/cm² and 400 W/cm² at T_{wire} =200°C for the pure PAO and the PAO nanoemulsion fluid, respectively. What is more interesting is that the CHF of the PAO nanoemulsion fluids is significantly larger than that of their pure components, ethanol and PAO.

The causes of the observed abrupt increase in the heat transfer coefficient can be first examined by evaluating the Morgan correlation that works for free convection over a long cylinder [113],

$$Nu_{D} = CRa_{D}^{n}$$
 (5)

where Ra is the Rayleigh number, and C and n are constants. The Rayleigh number is in the range 10^{-10} ~ 10^{-2} for the nanoemulsion experiment, so n=0.058. A direct impact of the nanodroplet vaporization would be the enhanced effective heat capacity due to the heat of



Figure 7 The surface heat flux as a function of the heater temperature for the pure PAO, pure ethanol, and PAO nanoemulsion fluids. These data were measured in a pool boiling setup with an untextured heater surface (Pt wire, 25.4 μ m in diameter), where the bulk liquid was at atmospheric pressure and room temperature (25°C, not at a saturated state). The CHF is determined within an accuracy of 5%.

vaporization. The effective heat capacity can be evaluated using the formula:

$$C_{\rm eff} = C_0 + \phi \cdot H_{\rm droplet} / \Delta T \tag{6}$$

where ϕ is the volume fraction of the phase-changeable nanodroplets, H_{droplet} is the heat of the vaporization of the nanodroplets per unit volume, and ΔT is the temperature difference between the heat transfer surface and the bulk fluid. In this experiment, if it is assumed that ΔT =10°C, the effective volumetric specific heat can be increased by up to 162% for the 4 vol.% nanoemulsion fluid when the ethanol nanodroplets undergo liquid-vapor phase transition. However, this would provide only 2.7% enhancement of the heat transfer coefficient according to the Morgan correlation.

The nanodroplet vaporization can enhance the heat transfer mainly through inducing the drastic fluid motion within the thermal boundary layer around the heat transfer surface. The ethanol-in-PAO interface constitutes a hypothetically ideal smooth surface, free of any solid motes or trapped gases, so the heterogeneous nucleation and ordinary boiling are suppressed. In this case, the ethanol nanodroplets can be heated to a temperature about 120°C above their normal atmospheric boiling point (78°C). Such a temperature is very close to the thermodynamic limit of superheat or the spinodal state of the ethanol and is only about 10% below its critical point. The spinodal states, defined by the states for which $\frac{\partial P}{\partial V}\Big|_{T,n} = 0$, represent the deepest possible penetration of a liquid in the domain of the metastable states [114-117]. When those ethanol nanodroplets vaporize after reaching their limit of superheat, the energy released could create a sound-shock wave, a so-called vapor explosion. This sound wave would lead to the strong fluid mixing within the thermal boundary layer, therefore, enhancing the fluid heat transfer. These fluids with enhanced heat transfer rate are expected to find the applications in the various energy conversion systems, heat exchange systems, air-conditioning, refrigeration and heat pump systems, and chemical thermal processes [113, 115, 118–122].

3.3 Liquid-solid phase-change nanoemulsion fluids

Water in the FC-72 nanoemulsion fluids are discussed as an example of the liquid-solid phase-change fluids, in which water could undergo liquid-solid transition and, thus, increase the heat transfer rate of the base fluid FC-72. FC-72 is one of a line of Fluorinert[™] Electronic Liquids



Figure 8 (A) The pictures of water in the FC-72 nanoemulsion fluids (Bottle A) and pure FC-72 (Bottle B). The liquids in both the bottles are transparent. The Tyndall effect can be observed only in Bottle A when a laser beam is passed through Bottles A and B. (B) The schematic diagram of a water nanodroplet dispersed in 3M's FC-72 thermal fluid. A micelle of amphiphiles surrounds the nanodroplet, with the polar head interacting with the water.

developed by $3M^{TM}$, which is used as the cooling fluids in liquid-cooled thermal management systems [123]. But it has poor thermal conductivity and heat capacity, compared to the other fluids such as water.

3.3.1 Microstructure of water in FC-72 nanoemulsion fluids

Water in the FC-72 nanoemulsion fluids are generated by emulsifying deionized water into the FC-72 with a small amount of perfluorinated amphiphiles. Figure 8 shows the picture of the prepared water in the FC-72 nanoemulsion fluids and the pure FC-72 liquid and schematic diagram of a water nanodroplet dispersed in the 3M's FC-72 thermal fluid.

The dynamic light scattering (DLS) technique is used to measure the size and the Brownian diffusivity of the nanodroplets in the prepared water in the FC-72 nanoemulsion fluid [124]. The autocorrelation function of the scattered light for the 12 vol.% water in the FC-72 nanoemulsion fluids is plotted in Figure 9. The curve shows a typical exponential decay of the correlation function vs. time [62, 63]. The Brownian diffusivity and effective hydrodynamic radius of the nanodroplets are found to be 3.5×10^7 cm²/s and 9.8 nm at $T=25^{\circ}$ C, respectively.

3.3.2 Thermal conductivity and viscosity of water in FC-72 nanoemulsion fluids

The thermal conductivity of the water in the FC-72 nanoemulsion is measured for the different water loadings, and the results are shown in Figure 10. The 3w-wire method is used to measure the fluid thermal conductivity. In water, in the FC-72 nanoemulsion fluids, the water phase has a thermal conductivity much higher than that of the base liquid FC-72. The water's thermal conductivity is 0.609 W/mK at 300 K, and the FC-72's thermal conductivity is much smaller, about 0.066 W/mK [123]. The addition of water is expected to improve the effective thermal conductivity of the FC-72.

It can be seen in Figure 10 that a very large increase in the thermal conductivity is achieved in the prepared water-in-FC-72 nanoemulsion fluids, with the thermal conductivity enhancements of up to 52% observed in the nanoemulsion fluid containing 12 vol.% (or 7.1 wt.%) of the water nanodroplets. The observed enhancement in the thermal conductivity is much larger than that predicted by the effective medium theory (EMT) with the assumption of the spherical droplets [125]. This suggests that the water droplets are column-like with a high aspect ratio of length to radius, which leads to a higher thermal conductivity enhancement in the nanoemulsion fluids than the spherical droplets.

The dynamic viscosity of water in the FC-72 nanoemulsions of the different nanodroplet concentrations is measured using a Brookfield viscometer at room temperature. The dynamic viscosity is found to be 0.65 cP in the pure FC-72 at room temperature, which agrees well with the literature values [123]. The results have been normalized to the viscosity of the pure FC-72 and are shown in Figure 11. The measured viscosity values are also compared to the calculated values according to the Einstein equation. This equation, however, underpredicts significantly the viscosity increase in the water in the FC-72 nanoemulsion fluids at relatively high water loadings, as can be seen in Figure 11. This is because the Einstein



Figure 9 The correlation function of the scattered light for the 12 vol.% water in the FC-72 nanoemulsion fluids. The measurements were taken by a Photocor-Complex DLS instrument.



Figure 10 The relative thermal conductivity of the FC-72 nanoemulsion fluids vs. the water volume concentration. The effective thermal conductivity estimated from the effective medium theory for the spherical particles is shown for comparison.



Figure 11 The relative viscosity of water in the FC-72 nanoemulsions vs. the volumetric fractions of the water nanodroplets. The measurements were conducted at room temperature on a Brookfield viscometer.

equation is derived based on the dilute systems (assuming a volume fraction <0.01). For the more highly concentrated systems, where the hydrodynamic interaction and aggregation of the nanoparticles become important, the Einstein equation must be augmented by the higherorder terms of the volume fraction as $\mu_{1}=1+2.5\phi+B\phi^{2}+...$ Although the coefficient for the first-order term, 2.5, can be strictly derived, it is not a simple task to theoretically determine the coefficients for the higher-order terms because of the difficulty in accounting for the effects of the increased concentrations. By fitting the experimental data in Figure 11, B is found to be about 117, indicating a strong nonlinear behavior, which is coincident with the nonlinear increase in the thermal conductivity. This nonlinear increase in the viscosity is common in the colloidal systems and has been interpreted by the aggregation of the nanodroplets, i.e., the formation of the column-like microstructure.

3.3.3 Liquid-solid phase-change in water in FC-72 nanoemulsion fluids

The heat capacity of the nanoemulsion fluid can be enhanced through two different mechanisms: one is due to the high specific heat of the dispersed phase; the other is due to the latent heat of the dispersed PCMs. The latter one, i.e., the use of the PCMs, is much more efficient for the heat capacity enhancement. In water in the FC-72 nanoemulsion fluids, the fluid's heat capacity can be increased by the high specific heat of water (i.e., C_{water} =4.2 J/g *C*, $C_{FC.72}$ =1.1 J/g *C*) or the latent heat of water (ΔH =334 J/g), depending on the operating temperature of the fluids [123].

When the water nanodroplets do not undergo a solidliquid phase change, the specific heat of the water in the FC-72 nanoemulsion fluids follows the simple mixture rule:

$$C_{\text{nanoemulsion}} = (1 - \Phi) c_{\text{oil}} + \Phi C_{\text{water}}$$
(7)

where Φ represents the concentration of the "water" phase. The specific heat of the pure FC-72 and water in the FC-72 nanoemulsion fluids are measured using a differential scanning calorimetry (DSC). The DSC is a thermoanalytical technique that has been widely used to measure the latent heat of the phase-change materials [126]. In this method, both the sample and reference are maintained at nearly the same temperature by adjusting the heat input to them. The difference in the amount of the heat supplied to the sample and the reference is recorded as a function of the temperature (or time). In

the curve of the heat flux vs. the temperature or vs. the time, a positive or negative peak corresponds to the exothermic or endothermic reactions in the sample, respectively. The enthalpies of the phase transitions can be calculated by integrating the peak corresponding to a given transition,

$$\Delta H = \mathbf{c} \cdot \mathbf{A} \tag{8}$$

where A is the area of the peak, and c is the calorimetric constant. In order to determine the sample heat capacity, three measurements are usually carried out: the sample, the baseline, and a standard. The baseline is subtracted from the sample record to obtain the absolute values of the heat flow to the sample. The heat capacity can be determined by the heat flow, the temperature rise, and the sample mass.

The specific heat of FC-72 and the water-in-FC-72 nanoemulsion fluids is measured using a TA-CC100 DSC. The measured and calculated heat capacities of the water in FC-72 nanoemulsion fluids are shown in Figure 12. It can be seen that over 15% increase in heat capacity can be achieved for a water volumetric fraction of 12%.

In contrast with the single-phase water droplets, the solid-liquid phase change of these droplets will significantly enhance the effective specific heat of the nanoemulsion fluids. The effective specific heat of the nanoemulsion fluid

will be increased by a factor of $1 + \frac{\alpha \cdot H_{\text{water}}}{\Delta T \cdot C_{\text{FC-72}}}$, where α is the

water volume fraction, H_{water} is the latent heat of fusion of the water per unit volume, and ΔT is the temperature difference between the heat transfer surface and the bulk fluid. The heat of fusion H_{water} of the pure water is 334 J/ml. The measured $\alpha \cdot H_{water}$ values of the water in the FC-72 nanoemulsions for the water loadings of 3 vol.%, 6 vol.%, 9 vol.%, and 12 vol.% are 10.52 J/ml, 15.44 J/ml, 25.48 J/ml, and 39.78 J/ml, respectively, as shown in Figure 13A and B. The effective heat capacity of FC-72 can be enhanced by more than 200% for a 12% volume fraction of water, according to these experimental data. However, a critical issue for this type of nanoemulsion fluids is the large subcooling, more than 20°C observed in the water in the FC-72 nanoemulsion fluids. More work needs to be conducted in the future to reduce the subcooling of the dispersed PCM nanodroplets.



Figure 12 (A) The DSC cyclic curves of the pure FC-72 and FC-72 nanoemulsion fluids. (B) The measured and calculated heat capacity of the water in the FC-72 nanoemulsion fluids. The dispersed water droplets remain in the liquid phase during the operation.



Figure 13 (A) The DSC cyclic curves of the water in the FC-72 nanoemulsion fluids with the different water loadings. (B) The measured and calculated heat capacity enhancement in the water in the FC-72 nanoemulsion fluids. The dispersed water droplets undergo the solid-liquid phase transition.

4 Solid-liquid phase-change metallic PCM fluids

The low-melting metals, such as indium and BiSn alloy, have a thermal conductivity much higher than the conversional dielectric thermal fluids; for example, the thermal conductivities of indium and PAO are 82 W/mk and 0.14 W/mk, respectively. The use of the low-melting metallic PCM nanoparticles provides a way to simultaneously improve the effective thermal conductivity and heat capacity of the base fluids [33, 64]. When the metallic PCM particles are small enough (e.g., below 50 nm in size) and stabilized with the surfactant molecules, the nanoparticle suspensions could remain stable during the freezing and melting of the PCM particles.

4.1 Nanoemulsification technique for synthesis of metallic PCM fluids

A one-step, nanoemulsification technique has been developed to prepare the suspensions of the metallic PCM nanoparticles in the PAO [64]. Briefly, this technique exploits the extremely high shear rates generated by the ultrasonic agitation and the relatively large viscosity of the continuous phase PAO, to rupture the molten metal down to a diameter below 100 nm. As an example, the preparation of indium (melting point: 156.6°C) and Field's metal (by weight: 32.5% Bi, 51% In, 16.5% Sn; melting point: 63.2°C), metallic PCM fluids is discussed below.

A large number of factors can affect the metallic particle size in the emulsification process. These include selecting an appropriate composition, controlling the reaction temperature, choosing the order of addition of the components, and applying the shear in an effective manner. However, the fundamental relationship governing how the dispersed phase can be ruptured in another immiscible liquid under a shear stress is given simply by Taylor's formula [127]:

$$d \approx \frac{2 \cdot \sigma}{\eta_c \cdot \hat{\gamma}},\tag{9}$$

where *d* is the droplet diameter, σ is the interfacial tension between the droplet and the continuous phase, η_c is the viscosity of the continuous phase, and $\hat{\gamma}$ is the shear rate. Based on Taylor's formula, it is possible to estimate the shear rate required to form the PCM nanoparticles.

The fabrication process of the metallic PCM fluids is illustrated in Figure 14. First, a pellet of low-melting metal (Field's metal or indium) was added to the PAO oil in the reaction vessel, and then, the mixture was heated 20°C above the metal melting temperature by using a silicone oil thermal bath. The significant excess of the surfactant would enable the new surface area of the ruptured droplets to be



Figure 14 The schematic illustrating the formation of the metallic PCM fluids. (A) The PAO and molten metals are in the reaction vessel. These two liquids are immiscible and phase separate. (B) The polymer surfactant is soluble in the PAO and preferentially adsorbs at the interface. (C) The mixture is stirred using a magnetic stirrer, and the bulk molten metal breaks into microscale droplets. (D) The microscale emulsion is exposed to high-intensity ultrasonication until the PCM fluid is formed.

rapidly coated during emulsification, therefore, limiting the shear-induced coalescence. The molten metal was dispersed in the PAO using a magnetic stirrer for 2 h to create the microscale droplets. This premixed microscale emulsion was then exposed to high-intensity ultrasound radiation (VCX 750, Sonics & Materials, Inc) for more than 2 h until the stable PCM fluids were formed. The emitted sound field was very strong in the vicinity of the horn tip, but attenuated rapidly with distance. This nanoemulsification method could become a general route to synthesize the well-dispersed nanoparticles of the low-melting materials, such as metals, salts, and polymers. The nanoparticle size may be effectively regulated by changing the synthesis temperature in order to vary the viscosity of the continuous phase.

The size distribution of the Field's metal and indium nanoparticles was examined using transmission electron microscopy (TEM, JEOL 2100F). The TEM bright field (BF) images of Field's and the indium nanoparticles are shown in Figure 15A and B, respectively. These nanoparticles are spherical because the liquid nanodroplets have a positive interfacial tension (i.e., surface energy) in the emulsion. In addition, these nanoparticles are highly dispersed. The polymer surfactants appear to provide sufficient steric stabilization despite the strong cohesion forces among the molten metal nanodroplets.

4.2 Thermal conductivity and viscosity of metallic PCM fluids

The thermal conductivity of the pure PAO and the 8 vol.% indium in the PAO PCM fluids are measured at 30°C, 45°C, 60°C, 75°C, and 90°C using the 3ω -wire technique. The thermal conductivity of the pure PAO and the indium in the PAO PCM fluid, as well as the relative thermal conductivity, are plotted against the temperature in Figure 16.

The results estimated from the Maxwell Model are also shown for comparison. The relative thermal conductivity is defined as $\frac{k_{nf}}{k_o}$, where k_o and k_{nf} are the thermal conductivities of the base fluids and the metallic PCM fluids, respectively. The thermal conductivity of the PAO at room temperature is experimentally found to be 0.143 W/mK, which compares well with the literature values [110].



Figure 15 The TEM images (bright field) and size distributions of (A) the Field's metal nanoparticles and (B) the indium nanoparticles, which were fabricated using the nanoemulsion method. The scale bars in both the TEM images represent 200 nm.



Figure 16 The thermal conductivity of the pure PAO and the indium in the PAO nanofluid (left x-axis) and the relative conductivity of the nanofluid (right x-axis) vs. temperature. The relative thermal conductivity estimated from the Maxwell model (solid line) is also shown for comparison. A temperature-independent interfacial resistivity $R_b = 3.22 \times \frac{10^{-8} m^2 k}{W}$ is used in this calculation.

It is evident in Figure 16 that the thermal conductivity enhancement increases slightly with the increasing temperature in the indium-in-PAO PCM fluids about 10.7% at 30°C and 12.9% at 90°C. This weak dependence on the temperature was measured with the 3ω -wire technique, which is very different from the very strong dependence observed in some other nanofluids obtained with the hot-wire technique. For example, the data of Hong et al. showed a factor of about 3 increase in the thermal conductivity enhancement for a temperature increase of 50° C [16]. As also seen in Figure 16, the solid indium nanoparticles increase the thermal conductivity of the pure PAO by about 12% for the volume fraction of 8%. The experimental data are well captured in the temperature range of 30° C to 90° C by the Maxwell model,

$$k_{nf} = \left(1 + 3\Phi \frac{\alpha - 1}{\alpha + 2}\right) k_o \tag{10}$$

when a constant interfacial resistivity $R_b = 3.22 \times \frac{10^{-8} m^2 k}{W}$ is used [39]. Here, ϕ is the volume fraction of the particles, $\alpha = \frac{r_p}{R_b k_o}$, r_p is the particle radius, and R_b is the thermal resistance per unit area of the particle/fluid interface. The interface resistance appears to play a significant role in the thermal transport in the metallic PCM fluid. The interface resistance plays a significant role in the thermal transport in the nanofluid, as predicted by the Maxwell model. For example, for a negligible interface resistance, $R_b=0$, the conductivity enhancement would increase to 24% in the PAO-based metallic PCM fluids containing 8 vol.% of the nanoparticles. These experimental data suggest that the thermal conductivity enhancement observed in the indium-PAO PCM fluids using the 3ω -wire technique can be explained using the Maxwell model, and no anomalous enhancement of the thermal conductivity is observed in this study. However, many other studies in nanofluids have shown a thermal conductivity increase beyond the Maxwell predictions [42].

The dynamic viscosity of the pure PAO and the indiumin-PAO PCM fluids is measured in the temperature range of 30°C–90°C using a commercial viscometer (Brookfield DV-I Prime). The results for the viscosity are shown in Figure 17. The prediction using the Einstein model is also plotted for comparison. The viscosity of the pure PAO was found to decrease with increasing temperature, in good agreement with the literature values. The Einstein equation, $\mu_{nf} = \mu_{o}(1+2.5\phi)$, is used here as well, where ϕ is the volume fraction of the dispersed phase, and μ_{a} and μ_{rf} are the viscosity of the base fluid and the PCM fluid, respectively, and it predicts a temperature-independent 20% increase in viscosity for the nanofluids with a volume fraction of 8%. For the indium-in-PAO PCM fluid, its viscosity exhibits a similar trend over the temperature range measured, but increases by about 30% in comparison to the pure PAO. This increase is significantly underestimated by the Einstein model, especially at the relatively low temperatures.

4.3 Phase-change behavior of metallic PCM fluids

Knowledge of the phase-change behavior of these lowmelting metallic nanoparticles is critical for their use as thermal fluids [10, 28, 27, 128]. The melting-freezing phase transition of the as-prepared Field's metal and indium nanoparticles is measured using a DSC (Model TA-Q100).



Figure 17 The dynamic viscosity of the pure PAO and the indiumin-PAO PCM fluids (left x-axis) and the relative viscosity of the nanofluid (right x-axis) vs. temperature. The relative viscosity estimated from the Einstein model (solid line) is also shown for comparison.

The DSC measurements were taken at an ordinary cyclic ramp mode, with a scan rate of 10°C/min. Figure 18 shows the cyclic DSC heating and cooling curves for the nanoemulsions containing Field's metal and the indium nanoparticles and similar data for each material in the bulk state.

A relatively large melting-freezing hysteresis, about 45°C for Field's metal nanoparticles and about 50°C for the indium nanoparticles can be seen in Figure 18. Based on the classical nucleation theory, the melting and freezing of these nanoparticles are dependent on the interface energies between the solid metal nanoparticles and the oil matrix, the liquid metal and oil matrix, and the solid and liquid metals [129]. The observed T_m slightly below the bulk value implies that $\gamma_{\rm SM} > \gamma_{\rm SL} + \gamma_{\rm LM}$ (or $\gamma_{\rm LM} > \gamma_{\rm SM} + \gamma_{\rm SL}$), where γ is the interfacial energy, and the subscripts S, L, and M represent the solid phase, the liquid phase, and the oil matrix. In this situation, the molten phase would not "presolidify" at the interfaces; instead, it would require



Figure 18 The DSC heating and cooling curves for the as-prepared (A) Field's metal and (B) the indium nanoparticles dispersed in the PAO oil. For comparison, the experimental data for the corresponding bulk metals are also plotted. The melting-freezing phase transition points correspond to the endothermal and exothermal peaks. The subscripts are as follows: b, bulk metal; n, nanoparticles; m, melting; f, freezing.

critical nuclei inside these nanoparticles, i.e., homogeneous nucleation. Therefore, these liquid nanoparticles supercool to tens of degrees below the bulk melting temperature, until the critical nuclei associated with solidification are formed. This characteristic may provide a mechanism to tailor the phase-transition behavior of the nanoparticles by varying their interfacial energy or size for the different applications.

The phase change within the metallic PCM fluid has its greatest impact on the effective specific heats of these fluids. The effective specific heat can be defined as $C_{\text{eff}} = C_{o} + \phi \cdot H_{\text{particle}} / \Delta T$, where ϕ is the volume fraction of the phase-changeable nanoparticles, H_{narticle} is the latent heat of the phase-changeable nanoparticles per unit volume, and ΔT is the temperature difference between the heat transfer surface and the bulk fluid or the difference between the nanoparticle melting and freezing temperature. If assuming ΔT =47°C, the effective volumetric specific heat can be increased by about 20% for the PCM fluids containing 8 vol.% indium nanoparticles. If ΔT could reduce to 10°C, which is feasible by introducing the external nucleating agents to suppress the meltingfreezing hysteresis, the effective volumetric specific heat of the metallic PCM fluids would be increased by up to 100%. The use of the phase-changeable nanoparticles is expected to provide a way to simultaneously increase the effective specific heat and thermal conductivity of the conventional heat transfer fluids.

5 Conclusion

The use of the PCM nanoparticles in the thermal fluids has emerged in recent years as a way to enhance the heat capacity and thermal conductivity of the base fluids simultaneously. Two types of the nanostructured phase-changeable heat transfer fluids are discussed in this paper, the solid-liquid PCM fluids (e.g., the indium in PAO nanofluids and water in the FC-72 nanoemulsion fluids) and the liquid-vapor fluids (e.g., ethanol in PAO nanoemulsion fluids). Many interesting properties have been reported in these nanostructured phase-changeable heat transfer fluids recently. The nanoemulsion heat transfer fluids can be formed by self-assembly and are thermodynamically stable. The explosive vaporization of the dispersed nanodroplets would significantly improve the heat transfer in the ethanol-in-PAO nanoemulsion fluids. In the water, in the FC-72 nanoemulsion fluids, a 12% volume fraction of water may enhance the effective heat capacity of the FC-72 by more than 200% when those droplets undergo the liquid-solid phase transition.

The use of the low-melting metallic nanoparticles, such as Field's metal and indium, will provide a means to increase the fluid conductivity and heat capacity simultaneously in the base fluids. The use of the nanostructured phase-changeable heat transfer fluids in a wide variety of applications appears promising. However, several critical

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issues remain to be solved in the future, for example, the large subcooling or superheating in the nanoparticles and the large viscosity increase.

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