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A Review on Stability and Preparation of Nanofluids

Adarsh Mankar, Gaurav Wale, Dhiraj Malthane, Samir Pathan, Manisha Wakade
Pankaj Laddhad Institute of Technology and Management Studies, Yelgaon, Buldhana, Maharashtra, India
adarsgmankar2002@gmail.com, gauravwale123@gmail.com, dhirajkumarmalthane@gmail.com,
samirpathan1456@gmail.com, manisha7wakade@gmail.com

Abstract*: The past decade has seen the rapid development of nanofluid science in different aspects, where the researchers focused mainly on the enhancement of heat transfer. However nanofluids preparation also deserves the same attention since the final properties of nanofluids are dependent on the stability of the dispersion. In this paper, we summarize the nanofluid preparation methods reported by different investigators in an attempt to find a suitable method for preparing stable nanofluids. In this context, nanofluids are classified according to material type as metallic and nonmetallic nanoparticles since different nanoparticles need their own stability method. Various types of nanoparticles with different base fluids are investigated. Also, the available data for the zeta potential as a function of pH is discussed.*

Keywords: Nanoparticles, Stability, Nanofluid preparation

I. INTRODUCTION

Over the last several decades, researchers have attempted to overcome the limited heat transfer capabilities of traditional heat transfer fluids such as water, engine oil, and ethylene glycol (EG), by developing a new class of fluids which offer better cooling or heating performance for a variety of thermal systems. Applying nanotechnology to thermal engineering, the novel concept of "nanofluid" which was coined by Choi in 1995 [1] has been proposed to meet these cooling challenges. Nanofluids, which are solideliquid composite materials consisting of nanometer sized solid particles suspended in different base fluids, provide a promising technical selection for enhancing heat transfer because of its many advantages besides anomalously high thermal conductivity. Nanofluids represent improved stability compared with conventional fluids added with micrometer- or millimeter-sized solid particles because of size effect and Brownian motion of the nanoparticles in liquids. With such ultrafine nanoparticles, nanofluids can flow smoothly in a microchannel without clogging and the size of the heat transfer system can be reduced for the use of nanofluids with high heat transfer efficiency. Preparation of stable nanofluids is the key issue of nanofluid research. The stability of nanofluids refers to several aspects: 1) Nanofluids are multi-phase dispersion system with high surface energies and are, therefore, thermodynamic unstable. 2) Nanoparticles dispersed in the nanofluids have strong Brownian motions. The mobility of the nanoparticles can offset their sedimentation caused by the gravity field. 3) Dispersion of nanoparticles in the fluids may deteriorate with time due to the aggregation of nanoparticles, which is caused by van der Waals forces. 4) No chemical reactions either between the suspended nanoparticles or between the base fluid and nanoparticles are desired at working conditions of the nanofluid. Therefore, there are two phenomena that are critical to the stability of nanofluid, aggregation and sedimentation. It was found that only a few review papers have discussed on the preparation methods for nanofluids [2- 4]. In the present paper, we attempt to review the preparation methods of nanofluids presented in previously published data with much more details. The purpose of this paper is to understand the lack stability of nanofluids, which is a key issue that influenced the nanofluid properties for application, and to propose suggestions that could lead to prepare stable nanofluid over a long time, with negligible agglomeration and without chemical change of the fluid properties. The review discussed different types of nanoparticles; nonmetals (Al2O3, ZnO, CuO, TiO2, Fe3O4, CNTs, SiO2 and AlN) and metals (Al, Ag and Cu). Also, we present the available data for the zeta potential as a function of pH values.

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II. PREPARATION OF NANOFLUIDS

Nanoparticles, the additives of nanofluids, play an important role in changing the thermal transport properties of nanofluids. At present, various types of nanoparticles, such as metallic nanoparticles and ceramic nanoparticles, have been used in the nanofluids preparation. In the following part, we will present the nanofluid preparation methods for eleven different nanoparticles reported in the literature.

2.1. Preparation of non-metallic nanofluids

2.1.1. Aluminum nitride -nanofluids

Aluminum nitride (AlN) is a nontoxic newer material in the technical ceramics family. While its discovery occurred over 100 years ago, it has been developed into a commercially viable product with controlled and reproducible properties within the last 20 years. AlN is one of the typical ceramics that have special properties such as high thermal conductivity (8-10 times that of Al2O3), low dielectric coefficient (about 8.15), high electrical resistance, corrosion & erosion resistance and low density. Because of these advantageous properties, it is used in various engineering applications and has attracted the intense interest of researchers. However, till date very few results concerning AlN nanofluids have been reported in the literature. In this context, Hu et al. [5] were the first to disperse AlN nanoparticle, produced by plasma arc in the gas phase into ethanol with castor oil as a dispersant to improve suspension stability. The suspension was then stirred with a highspeed magnetic stirrer. The resulting suspension was placed in an ultrasonic homogenizer for 10 min. It was observed that the prepared sample can remain stable for more than 2 weeks without settling. Choi et al. [6] mixed the agglomerated Al2O3 and AlN nanoparticles with n-hexane and a proper amount of oleic acid. The mixture was subjected to bead-milling with ZrO2 beads in a vertical super-fine grinding mill. The powders were hydrophobic modified by esterification reaction simultaneously with bead milling by circulating the suspensions between bead mill and ultrasonic reaction bath. A surface modified solution was then filtered using ultra filtration (UF) membrane to remove excess oleic acid which did not form stable chemical bonds with the particle surface. The filtered solution was mixed with transformer oil, and then finally dried off the n-hexane using a rotary vacuum evaporator. They observed that for a period of one month, filtered and non-filtered Al2O3 nanofluids are well dispersed at the beginning, while sedimentation was very clear for non-filtered nanofluid after one month. The settling phenomenon for non-filtered suspension was interpreted as the formation of double chain of oleic acid (OA) on the particle surface, making it hydrophilic again. Yu et al. [7] prepared AlNeethylene glycol and AlNepropylene glycol nanofluids by stirring and continuous sonication for 3 h, to ensure uniform dispersion of nanoparticles in the base fluid. As shown in Fig. 1, they found that the average particle sizes for AlNeEG and AlNePG nanofluids are 165 and 169 nm, respectively. Wozniak et al. [8] suspended AlN nanopowder in poly propylene glycol PPG 425 and PPG 2000, and then the suspensions were homogenized by using a magnetic stirrer for 3 h. More concentrated AlN dispersions were prepared using a laboratory dissolver, which had a mechanically modulated dispersive disk. The powder was slowly and incrementally added to PPGs. Each addition was followed by homogenization step. When all the powder was added, the dispersions were stirred for 40 min at 3000 rpm. It was reported that the suspensions were of high flow-ability and noticeable homogeneity. AlNePPG 425/2000 were of much higher sedimentation in PPG of lower average molecular mass, i.e. 425. In addition, the particles settled quite rapidly in PPG 425; after 30 h the sedimentation rate was >90% and afterward it remained at the same level. However, AlNePPG 2000 suspension demonstrated its sedimentation behavior only slightly, which was confirmed by its low sedimentation rate (max. w10% in 72 h), as shown in Fig. 2. The zeta potential measurements in PPG media showed that zeta potential is negative for both liquids; it averaged (30) mV for AlNePPG 425 dispersion and below (10) mV in case of AlNePPG 2000 system. Although different surfactants and physical treatments were used for the preparation of AlNenanofluids, only more than two weeks stable time of nanofluids was reported [5]. Thus, other preparation methods are highly desired to prepare stable AlNe nanofluids.

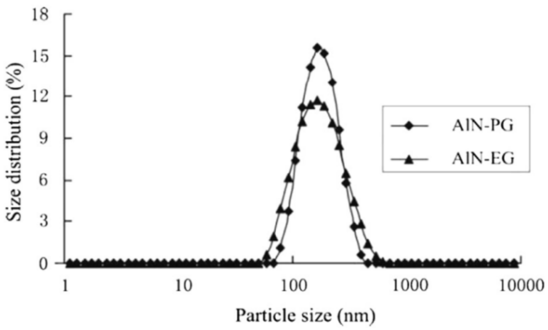

Fig. 1. Particle size distributions of AlN filtered nanofluid [7].

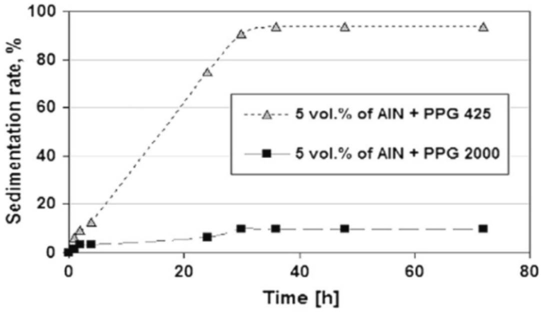

Fig. 2. Sedimentation rate of AlNePPG 425/2000 diluted systems [8].

2.1.2. Zinc oxide-nanofluids

Zinc oxide is emerging as a material of interest for a variety of electronic applications such as semiconductor for making inexpensive transistors and thin film batteries. It can be used in a large number of areas, and unlike many of the materials with which competes, is inexpensive, relatively abundant, chemically stable, easy to prepare, antibacterial and nontoxic. One of the first investigations dealt with this type of nanofluids was presented by Yu et al. [9]. They prepared ZnO nanofluids by dispersing ZnO nanoparticles in ethylene glycol. The mixture was stirred and sonicated (40 kHz and 150 W) continuously for 3 h to ensure uniform dispersion of nanoparticles in the base fluid. Based on the influence of ultrasonification on the particle size, it was reported that the average size decreases rapidly in the first 3 h, after 3 h the average size was about 210 nm (w10e20 times the primary size). It was concluded that ultrasonification was not effective in avoiding particle aggregation and producing uniformly distributed and well-controlled size of ZnO nanoparticles. Moosavi et al. [10] first synthesized the ZnO nanoparticles, which were then mixed with ethylene glycol and glycerol as base fluids with the aid of magnetic stirrer. Ammonium citrate was added as dispersant to enhance the stability of the suspension. The weight ratio of dispersant to nanoparticle was 1:1. As a result, the samples were stable for several months and no sedimentation and agglomeration of the particles in the samples was observed. Raykar and Singh [11] synthesized water soluble ZnO nanoparticles. The solutions were sonicated for 1 h and a proper amount of acetylacetone (acac) was added as a dispersant to the solutions, which were sonicated again for 10 min. They showed that the nanofluids were stable over 9 months to 1 year, and the size of ZnO nanoparticles was reduced from 150 nm to 80 nm due to the reaction with acac, and. Kole and Dey [12] dispersed fairly agglomerated ZnO nanoparticles in ethylene glycol by intense ultrasonication (200 W). The cluster size of ZnO nanoparticles in suspension was plotted against sonication time to ascertain the optimum time of sonication. As shown in Fig. 3, it was observed that ZnO clusters size rapidly decreases from w459 nm to w91 nm between 4 and 60 h. However, beyond 60 h of sonication, cluster size increased and for 100 h of sonication ZnO clusters increased to w220 nm. Therefore, an optimum duration for sonication was chosen to be 60 h. As a result, the suspension was stable for 30 days without any trace of visible sedimentation. Chung et al. [13] dispersed two types of zinc oxide powders, produced by solegel and physical vapor synthesis in deionized water containing ammonium polymethacrylate as a dispersant. The mixture was stirred at 25 C for 30 min, and sonicated using several ultrasonic agitation systems, including a single piezoactuated bath, a solenoid-actuated bath and a static bath with immersed horn. They found that dispersion by ultrasonic horn was more effective in terms of the size reduction rate, the minimum achievable size, and sedimentation rates. Suganthi and Rajan [14] synthesized zinc oxide nanoparticles by chemical precipitation method using zinc nitrate hexahydrate as precursor. The ZnOe water nanofluid was prepared with the aid of ultrasonication for 3 h and stabilization using sodium hexametaphosphate (SHMP) as a dispersant. A predetermined quantity of ZnO was added to the surfactant solution under high shear homogenization and homogenized for 20 min at 7000 rpm, followed by ultrasonication for 180 min (750 W and 20 kHz). Surfactant: nanoparticle ratio was fixed at 1:5. The obtained higher values of absolute value of zeta potential ensured higher colloidal stability of dispersions, which was confirmed also through visual observation as well. ZafaraniMoattar and Majdan-Cegincara [15] dried ZnO nanoparticles in an electrical oven at about 110 C for 24 h prior to use for removing adsorbed water moisture on the surface. The nanoparticles were dispersed in poly ethylene glycol and its aqueous solutions using sonication. It was found that the average particle size measured for the nanofluids investigated was much larger than the size of primary particles. It was also found that ZnOePEG nanofluid was stable at least for 140 min. Saleh et al. [16] synthesized ZnO powders using chemical precipitation method. The nanoparticles were dispersed in ethylene glycol using a magnetic stirrer and ultrasonic processor under continuous pulse for 2 h. Lee et al. [17] prepared EG-based ZnO nanofluids using a one step method known as pulsed-wire evaporation (PWE). The synthesized nanoparticles came into direct contact with EG inside the chamber wall and the ZnO nanoparticles were obtained without any surface contamination.

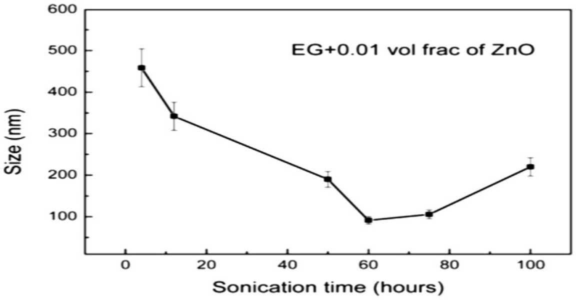

Fig. 3. The ZnO cluster size in suspension as a function of sonication time [12].

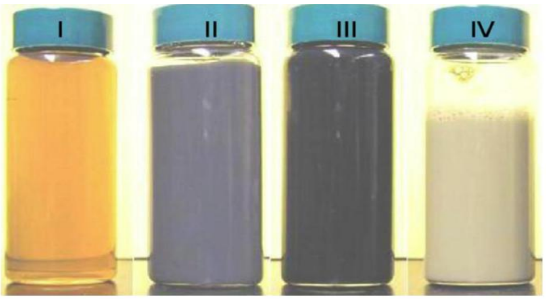

Fig.4. Typical samples of Ag-deionized nanofluids generated by multi beam ablation in liquid technique [119].

2.2. Preparation of metallic nanofluids

2.2.1. Gold & silver-nanofluids

Metal nanoparticles such as gold (Au) and silver (Ag) have recognized importance in chemistry, physics, and biology because of their unique optical, electrical, and photothermal properties. Such nanoparticles have potential applications in analytical chemistry and have been used as probes in mass spectroscopy, as well as in the colorimetric detection for proteins and DNA molecules. Furthermore, Au nanoparticles have photothermal properties that can be exploited for localized heating resulting in drug release. Thus, increasing their potential for therapeutic applications. The ease of synthesizing Au and Ag nanoparticles and their affinity for binding many biological molecules, makes them attractive candidates for study Patel et al. [118] used gold and silver for the first time to prepare nanofluids. The gold and silver nanoparticles were prepared by the citrate reduction route. Also, the gold nanoparticles with thiolate covering were prepared using two-phase (wateretoluene) reduction of AuC14- by sodium borohydride in the presence of an alkanethiol. The samples were stable over a period of several months and no degradation was observed during storage or in the course of the experiment. Phuoc et al. [119] prepared different samples of Agedeionized water using multi-pulse laser ablation in liquid approach. The first sample (sample I, brownish yellow) was prepared by ablating the silver target in deionized water for 30 min. The second sample was prepared by ablating the silver target in the previously produced sample that was aged for 2 weeks. The ablation durations for the last three samples were 3 h. All the samples were more than 7 months old and they were stable without using any dispersants or surfactants, as shown in Fig. 11. Parametthanuwat et al. [120] prepared silver nanofluids using an ultrasonic bath at 43 kHz for 3 h. It was found that the stability was up to 48 h. Hajian et al. [121] produced Silver in DIewater nanofluid by a chemical method which consists of reduction of Ag ions. The nanofluids were put in an ultrasonic bath for about 15 min before injection into the heat pipe. Tamjid and Guenther [122] used a colloid of silver nanoparticles produced by the Sputtering on Running Liquid technique (VERL) at volumetric solids concentration of 4.37%. The colloid was stirred and agitated thoroughly for 5 min by an ultrasonic agitator in continuous mode to ensure uniform dispersion of the nanoparticles in diethylene glycol. Asirvatham et al. [123] mixed silver nanoparticles with deionized water under ultrasonic vibration with power density of 750 W at frequency of 20 kHz for 12 h. The measured pH values were 7.4, 7.1 and 6.8 for volume concentrations of 0.3%, 0.6% and 0.9%, respectively. They reported that the nanofluids were essentially uniform, but not without some agglomeration of the particles. Sharma et al. [124] synthesized silver nanofluids using silver nitrate (precursor), ethylene glycol (reducing agent), and poly (acrylamide-co-acrylicacid) (dispersion stabilizer). They found that the size of nanoparticles and dispersion stability are controlled by the concentration of PAAeco-AA and the reaction conditions. Hari et al. [125] produced spherical and rod silver nanoparticles. The silver nanorods were prepared by seed mediated chemical synthesis and stabilized with CTAB surfactant micelle, while the spherical nanoparticles were stabilized with trisodium citrate. It was found that the nanofluids were stable for a maximum period of one week. Paul et al. [126,127] synthesized nano-gold and silver dispersed water based nanofluids by wet chemical bottom up approach. It was revealed that uniform distribution, chemical nature (metallic) or purity of the gold nanoparticles and color of the nanofluid remained unchanged without sedimentation or agglomeration even after 48 h. Kim et al. [128] dispersed Au-powders in water by 6-h ultrasonic-wave irradiation. Also, they produced gold nanoparticles suspended in water by pulsed laser ablation in liquids. They reported that in spite of 6 h ultrasonic-wave irradiation, almost all of the Au-powder was precipitated in water. The AueNPs were still suspended in water after 1 month without any surfactants. Lo et al. [129] prepared silver nanofluid by the submerged arc nanoparticles synthesis system (SANSS). They observed that the nanoparticles were well dispersed in deionized after using ultrasonic vibration for 15 min. Kang et al. [130] added silver nanoparticles produced by a catalytic chemical vapor deposition method, using an ultrasonic homogenizer.

2.2.2. Copper-nanofluids

Intrinsically high resistance to corrosion makes copper as an ideal metal for heat exchangers of all kinds, including solar water heating systems. Nano copper can be used in the manufacture of printing inks allowing conductive patterns that have to pass through a thin film, creating a path of electrical conductivity for use in scientific experiments, and also to create printable circuits for electronic applications. Also in water, nano copper has been used at least since 1931, as a fungicide in the cultivation of vines and fruit trees, and as an algaecide in swimming pool water treatment. Xuan and Li [131] prepared transformer oileCu suspensions and watereCu suspensions. The first suspension was stabilized using 22 wt.% of oleic acid as dispersant (Several percentages of oleic acid was tested). Then, the suspension was vibrated for 10 h in an ultrasonic vibrator. It was found that the stabilization of the suspension can last about one week in the stationary state without sedimentation. The second suspension was stabilized using 9 wt.% laurate salt (Several percentages of laurate salt was tested), and then vibrated in an ultrasonic vibrator. It was observed that the suspension can be stable more than 30 h with some clusters. Yang et al. [132] used an aqueous solution of cetyltrimethyl ammonium chloride (CTAC)/sodium salicylate (NaSl) to prepare copper nanofluids. NaSl was added to the solution with the same weight concentration of that of CTAC, and distilled water was used as solvent. The CTAC/NaSl solution was stirred about 8 h. Then the nanoparticles were added into the base fluid by introducing an intensive sonication of ultrasonic disruptor. Furthermore, an optimum time of sonication was determined by measuring the thermal conductivity of 0.6 vol.% Cu nanoparticles suspended in 50 ppm CTAC/NaSl aqueous solution for different ultrasonic time. It was observed that when the ultrasonic time is over 3 h, the thermal conductivity of Cu nanofluids tends to be a constant value, meaning that 3-h ultrasonic time is enough to disperse the Cu nanofluid. Also, it was reported that the prepared nanofluids by introducing 3-h intensive sonication show a stable property. Peng et al. [133] dispersed copper nanoparticles, produced by hydrogen direct current arc plasma evaporation method in a refrigerant R113. They used three types of surfactants which are miscible with R113; Sodium Dodecyl Sulfate (SDS), Cetyltrimethyl Ammonium Bromide (CTAB) and Sorbitan Monooleate (Span-80). The mixture of CuR113 with surfactants was vibrated for 1 h. It was found that the mixture can be kept stable for 24 h, and the duration of the experiment for each sample of Cu-R113 nanofluid with surfactant was less than 4 h which is shorter than 24 h. Kole and Dey [134] prepared surfactant free copperewater nanofluids by addition of an appropriate amount of Cu nanoparticles in distilled water. The dispersion was done by intense ultrasonication for 10 h at 200 W and subsequent homogenization for another 10 h using a magnetic stirrer. The suspension stability of Cu nanoparticles in the prepared nanofluids was tested for more than15 days without any visible trace of sedimentation, but with the presence of clusters with an average diameter between around 122 and 164 nm. Li et al. [135,136] mixed copper nanoparticles and water with (SDBS or CTAB) surfactant. The pH was controlled using HCl and NaOH. It was shown that the average particle sizes obtained in the absence of SDBS surfactant was 6770 nm and in the presence of SDBS surfactant was 207 nm, indicating better stability of CueH2O suspension when using SDBS surfactant. In addition, pH ¼ 8.5-9.5 can be selected as an operating pH for the suspensions with SDBS surfactant. It was observed that the stabilization of the suspension with CTAB dispersant can last about 1 week in the stationary state without sedimentation, while the suspension without dispersant exhibits weaker dispersion and quickly occurs aggregation. Kathiravan et al. [137] prepared copper nanoparticles by the sputtering method. Then the nanoparticles were dispersed in water and water with 9.0% SDS anionic surfactant using an ultrasonic bath for about 10 h. It was found that the nanoparticles were dispersed in water evenly even after 10 h of ultrasonic vibration with some agglomerates. Robertis et al. [138] prepared copper nanofluids using a one-step technique. They used ethylene glycol as base fluid, copper (II) nitrate hydrate as copper source; sodium hypophosphite monohydrate as reducing agent and polyvinyl pyrrolidone (PVP) as stabilizer. The nanofluids were synthesized using a microwave oven without further dispersion. The particles settlement was about 28.5% in 50 days. They claimed that smallest particles tend to remain suspended for longer periods. However, larger particles can drag down these small particles and therefore reduce the stability period of the suspension. Riehl and Santos [139] stated that an agitation of copper nanofluids using an ultrasonic bath for 1.5 h was enough to achieve a homogeneous solution, as no sedimentation was observed after 4 h of observation. Senthilkumar et al. [140] used an ultrasonic homogenizer for 6 h. Li et al. [141] vibrated the suspension for 4 h in an ultrasonic vibrator, and they found that the sample suspensions were kept stable in the stationary state with little apparent sediment during the whole experiment process. Lu et al. [142] dispersed copper nanoparticles using an ultrasonic box with a working frequency of 25-40 kHz for 10 h. All the mentioned copper preparation methods showed that copper nanofluids cannot be stable more than one month. The preparation of nanofluids containing different concentrations,

III. CONCLUSION

The present paper presents an inclusive review on the nanofluids preparation methods. Although many preparation methods were proposed, it is still a challenge to make a nanofluid homogeneous and long-term stable with negligible agglomeration, and without affecting the thermophysical properties. Three methods have been used to prepare nanofluids: 1) Sonication: it was shown that sonication time has an effect on the zeta potential and nanoparticles sizes. Therefore, an optimum time of sonication should be taken into account. In addition, some nanofluids were sonicated just to be kept stable for the duration of the experiment, which limits the commercialization of nanofluids. 2) pH control: the value of zeta potential is generally obtained by adjusting the pH value according to just one small volume fraction value even though the particle volume fraction affects the zeta potential, i.e., pH value. 3) Surfactants: a critical miscell concentration should be respected to avoid speedly sedimentation of nanoparticles. Some researchers prepared their nanofluids without using surfactants or adjusting pH since they aim at changing the thermophysical properties of nanofluid. For such case, only TiO2 in EGe TNT that showed a maximum stability of over the period of two months. Therefore, it is unavoidable to prevent particle sedimentation without using dispersants or pH control. However, an optimum amount of surfactant and pH value can be found to keep the physical properties constant. The most attractive property of nanofluids is the enhancement of the thermal conductivity. Therefore, further research investigations are needed to comprehensively understand the stability of nanofluids before evolving new energy efficient heat transfer fluids specific to applications.

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