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Enhanced DC conductivity of low volume-fraction nano-particulate suspensions in silicone and perfluorinated oils

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Abstract
The contrasting DC conductivities of several different types of nanoparticles (nickel, barium titanate and magnetite) suspended in both silicone and perfluorinated oils have been measured and compared. Enhanced DC conductivity through interaction between the particles and the fluid has been demonstrated even at quite moderate fields and different types of nanoparticles have been shown to exhibit different behavioural trends. Whilst the DC enhancement is partly related to the concentration (or spatial arrangement) of the particles as expected, there is clear evidence that energy-activated (electric-field activated) processes also play a major role. It can be said that effective medium theories based solely on the electrical properties and volume fractions of the component materials have limited applicability when assessing the DC conductivity of these nanoparticle-fluid combinations at low volume fractions.

Classification Numbers
72.80Le, 72.80Ph, 72.80Tm, 72.80Sk, 77.22.-d, 77.65.-j, 77.84Py, 81.05Lg, 81.05Qk, 81.20Ev, 81.40Rs, 83.80Gv, 83.80Hj, 83.80Rs

1. Introduction

Nano-particulate suspensions or ‘nanofluids’ illustrate a classical conundrum whereby the continuum properties are often readily measurable (in terms of the across and through variables) and hence macroscopic behaviour can be modelled adequately for engineering purposes, but afterwards there remains a doubt that part of the story remains untold and a real technological breakthrough is only one step away. Researchers have sometimes found that very small volume fractions of nanoparticles suspended in a carrier fluid can produce quite remarkable increases in macroscopic properties, such as thermal conductivity. This cannot be easily dismissed. If these improvements could be stabilised at the higher end of expectations then the technological benefits could indeed be huge. However, when the experiments are repeated under ostensibly the same conditions, the results can sometimes be less encouraging than previously observed. One explanation could be that nanofluids are inherently unstable. Generally speaking, nanoparticles tend to cluster and agglomerate if they are not prevented from doing so. This leads to uncertainties in the effective particle size, particle shape, particle numbers and inter-particle spacing. For thermo-fluids, it is easy to conceive that synergies existing between the particles and the carrier fluid can be overshadowed when particle agglomeration occurs; causing the system to change its characteristics and, in effect, reverting to one with fewer, larger

particles. In this scenario the macroscopic fluid properties can be described broadly by effective-medium theories [1-5]. However this does not mean that synergistic effects between the particles and fluid do not exist, rather that they may be length-scale sensitive and they can become obscured by randomisation. For the case of fluids that exhibit the giant electro-rheological effect, mathematical models based only on the volume fractions and the physical properties of the individual phases, do not adequately describe the overall behaviour [6-9]. Here the free energy of the system has an electrical component, due to the applied electric field, that dominates over the randomising effects of thermal motion and there is a true synergistic effect. However, the physical explanation for this is not complete and the influence of the imaginary component of the dielectric permittivity is at present unclear. In the following study we demonstrate that the DC electrical conductivity of low volume-fraction nano-particulate suspensions in silicone and perfluorinated oils is enhanced even at very moderate electric field strengths and this effect is related intrinsically to the fluid-particle combinations. The experiments are designed to reveal trends by comparison and the findings do not rely on knowledge of the nanoparticles electrical properties.

2. Experimental Procedure

The DC electrical conductivities of six different nanofluid systems, (representing combinations of three different nano-particle types and two different carrier fluids), were measured experimentally. The nanoparticles were an electrical conductor (nickel - Ni), an electro-active ceramic (barium titanate - BT) and iron oxide (magnetite – which is one part wüstite FeO and one part haematite Fe_2O_3 - FO). All of these were synthesised in our laboratory, BT by hydrothermal synthesis, Ni and FO by wet chemical synthesis [10]. In all cases a narrow particle size distribution was achieved. The base fluids were silicone oil (Dow Corning 200/50cS) and a perfluorinated oil (3M™ Fluorinert FC70) which have almost the same electrical conductivity and similar relative permittivity, but which differ both in viscosity and specific gravity. Physical quantities for the fluids are listed in Table 1. Figures given in Table 1 for the nanoparticles are based on the mean particle size, which is the only measured quantity (derived from SEM image analysis). Hence the inter-particle spacing of particles is a notional figure. It assumes a perfect dispersion in the fluid and it is provided only as an aid to visualisation of the scale of inter-particle spacing at different volume fractions. Note that the chosen range is from around 9 to 3.5 particle diameters. Theory suggests that the inter-particle distances in these suspensions may be too large for multi-polar interactions to dominate the electrical behaviour [11]. However, in a practical context it is assumed that this may be a factor.

Particles were dispersed in an ultrasonic bath for 30 minutes. The concentration sets were 2g/l, 4g/l, 10g/l, 20g/l and 30g/l. The systematic weighing error in all cases was <0.001%. Volume fractions are calculated for each suspension using the bulk densities of the materials. DC current measurements were carried out using a Keithley 6517 electrometer for different applied voltages between 20V and 100V. The fluidic conductivity cell consisted of a 1mm gap between concentric copper electrodes and the effective electrode area was 21.88cm^2. The systematic error due to the measurement system was 0.05% at 20V and 0.01% at 100V. The current versus time profile showed a transient peak, due to capacitance, between 1-2 seconds after application of the voltage. Readings were therefore taken after 20 seconds representing the steady-state values. Measurements were carried out at 295K and the cell was dried scrupulously in nitrogen between measurements to exclude moisture.

All of the experiments were subsequently duplicated in order to confirm that the measurements represented a true record of systematic behaviour.

Table 1 – Physical quantities of the nanoparticles (nickel - Ni, barium titanate - BT and magnetite - FO) and two base fluids

	Mean particle diameter (nm)	Bulk density (kg/m^3)	Particle number density (m^{-3})	Inter-particle spacing (notional) – (nm) @ Vol. fraction (%)				
				0.05	0.1	0.2	0.4	0.6
Ni	90	8800	2.62E21	824	635	486	367	309
BT	130	5850	8.69E20	1190	918	702	530	447
FO	10	5240	1.91E24	92	71	54	41	34

Manufacturers Data	Viscosity (mPas)	Relative permittivity	Specific gravity	Conductivity @ 1kV/m (Sm^{-1})
200/50cS silicone oil	50	2.60	0.973	10E-12
3M™ Fluorinert FC70	14	1.98	1.940	10E-12

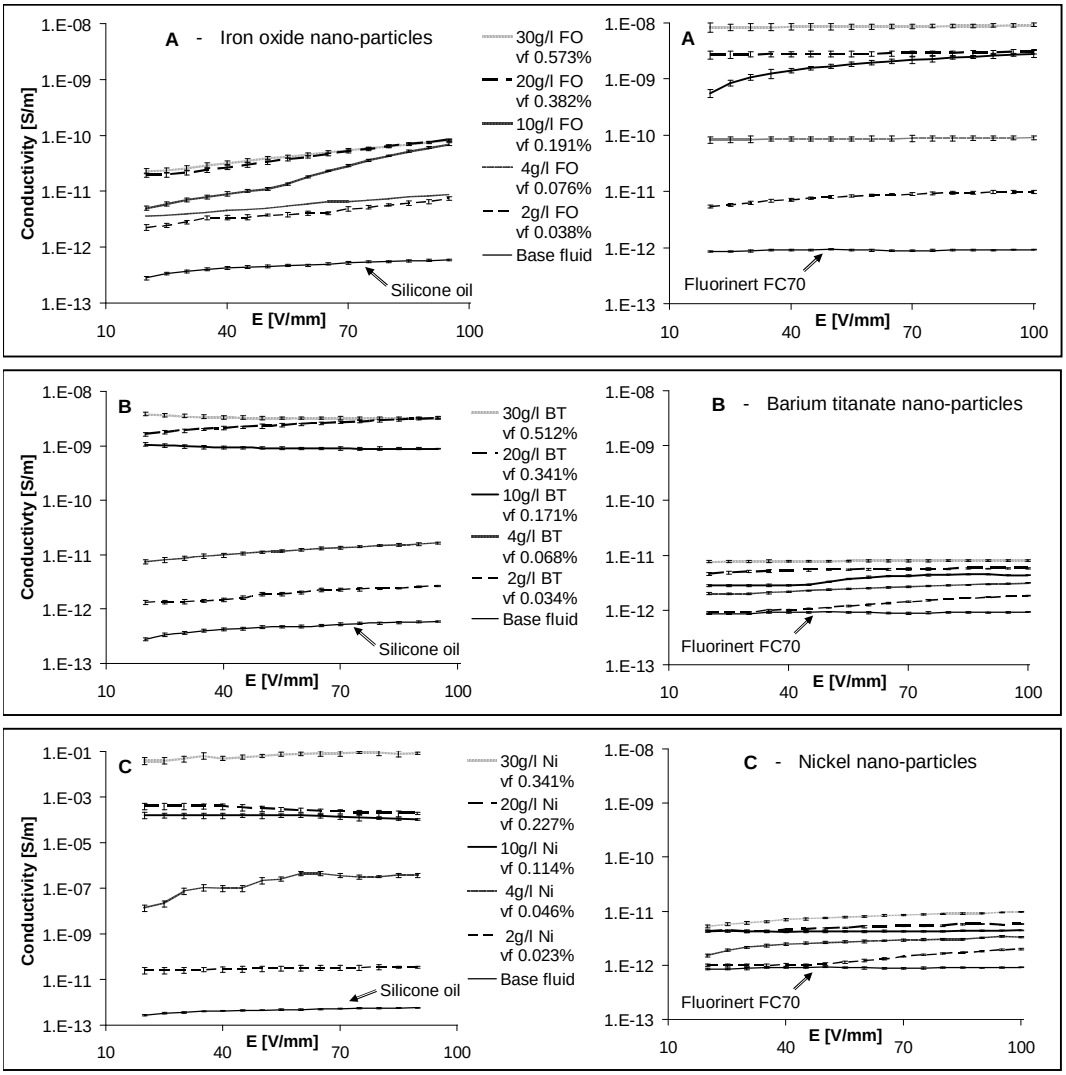


Figure 1: DC conductivities of three types of nanoparticles in two different insulating fluids: silicone oil (left side) and 3M™ Fluorinert FC70 (right side). Row A – 10nm diameter iron oxide nanoparticles (FO) ; Row B – 130nm diameter barium titanate nanoparticles (BT) ; Row C - 90nm diameter nickel nanoparticles (Ni).

3. Results and Discussion

Figure 1 shows DC conductivities for the six different nanoparticle-fluid combinations measured for different particle loadings and under moderate electric field conditions. When considering the results it is useful to take the following correlations into account: i) The barium titanate particles and the iron oxide particles have quite similar bulk densities, but their sizes are very different and their effective electrical conductivities at the nano-scale are uncertain; ii) The nickel particles and the barium titanate particles have very similar masses (BT larger particles, Ni higher density), but the materials have very different electrical properties (high dielectric permittivities, but contrasting electrical conductivities); iii) The iron oxide and the nickel particles both have some magnetic character, but they are very different in size and mass; iv) The two fluids have almost the same (very low) electrical conductivity; v) The viscosity of the silicone oil is higher than that of the FC70 and its specific gravity is around half; vi) The dielectric permittivity of the silicone oil is a little higher than that of the Fluorinert FC70; for particles of the same type, the effect this has on the real part of the complex Clausius-Mossotti value is therefore estimated in

the ratio of ~ 11:10 [1,12]. By consideration of the applied electric field threshold for particle agglomeration [13] and using the 'non-equilibrium phase diagram of structures' approach adopted by Melrose [14], it can be said that, in all cases, the inter-particle forces due to polarisation are estimated by calculation to be much too small for any polarisation-induced aggregation of particles to occur.

In Figure 1 (top row) it can be seen that the silicone oil base fluid has some field-dependent character over the observed range, shown as an increase in measured conductivity as the applied voltage is increased; but this is not the only effect observed. The conductivity of iron-oxide particles in FC70 is higher than it is in the silicone oil. There is evidence of field-induced behaviour in silicone oil at all concentrations and particularly at 10g/l. At 10g/l in FC70 an increase is also observed and this occurs at a lower applied field; repeated experiments have confirmed that this is a consistent occurrence. More detailed analysis shows that the observed increases follow the relationship: $\ln J \propto \sqrt{E}$ (where J is the current density and E the applied electric field) characteristic of energy-activated, Poole-Frenkel type behaviour [15,16].

The barium titanate suspensions, in contrast, exhibit an opposite tendency; they have higher conductivities in silicone oil than in FC70. In FC70 both nickel and barium titanate show very modest increases with increasing particle concentration. Note that 20g/l BT and 30g/l Ni have similar volume fractions of particles. Some small increases are observable at low concentrations for both materials, however the overall flat response would suggest that there is no significant Hall-effect contribution, although this may have been expected.

The DC conductivity of the nickel nanoparticles in silicone oil shows an exceptionally high increase even at very low volume fractions (~0.05%). Note that the peak conductivity measured here is more than six orders of magnitude greater than for the iron oxide and barium titanate suspensions. When this nanoparticle-fluid combination was repeated the trends remained the same, however, the measured values are not consistent. Under the same experimental conditions the DC conductivity value at 30g/l nickel in silicone oil has also been measured at 1E-4 S/m (20g/l, 8E-6 S/m, 10g/l, 8E-8 S/m). This range of variability is not present in any of the other particle fluid combinations; the nickel-FC70 combination provides consistent repeatable values at all concentrations. Given the experimental conditions it is concluded that the observed instability is a consequence of a difference in the spatial distribution of the particles. It is known that particle chains are able to grow from asperities [17-19] with concomitant changes to the local electric field distribution. Electrohydrodynamic forces also pertain [20-22].

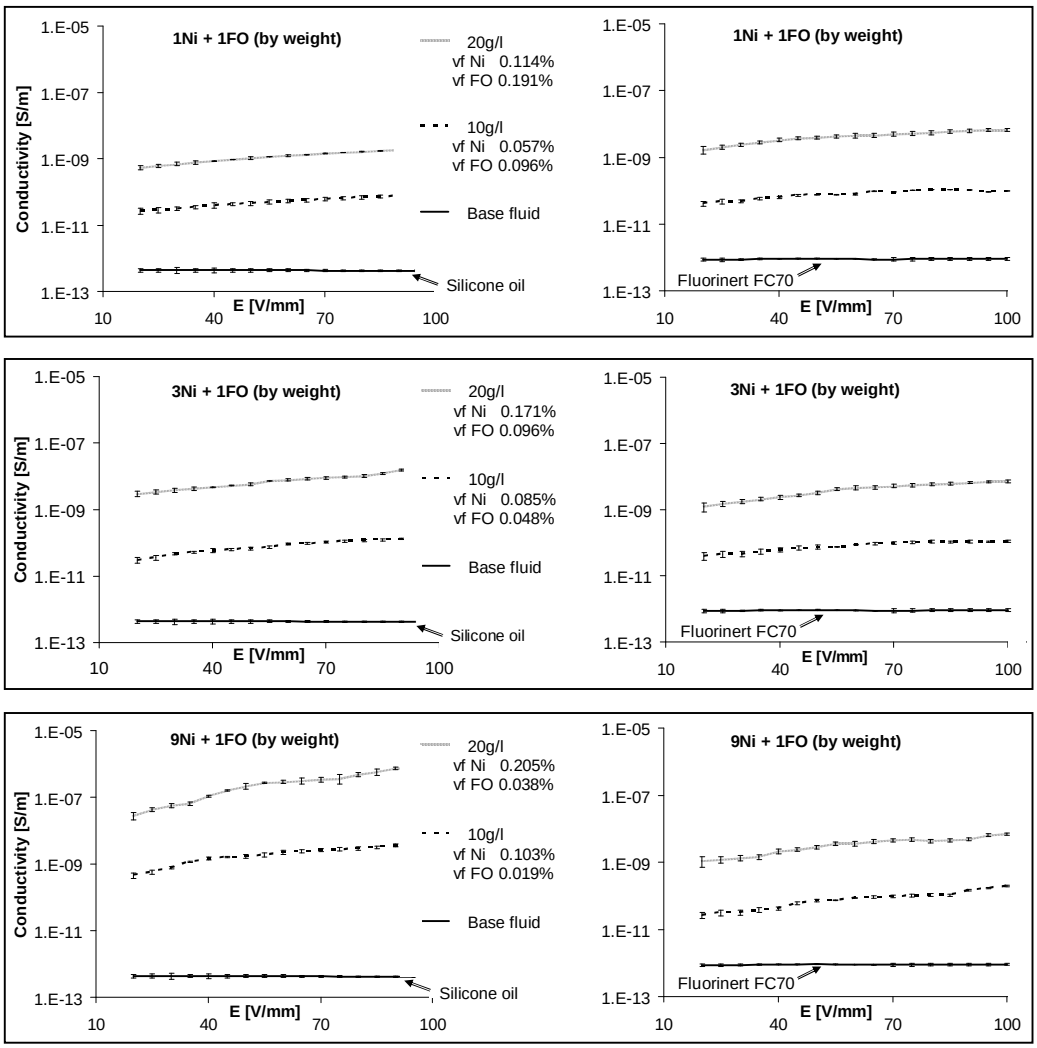


Figure 2: DC conductivities of suspensions containing both nickel (90nm diameter) and iron oxide (10nm diameter) nanoparticles - silicone oil (left side) and 3M™ Fluorinert FC70 (right side). The particle combinations are nickel:iron oxide - top row in the ratio 1:1 by weight, middle row 3:1 by weight, bottom row 9:1 by weight.

In Figure 2 the DC conductivities of suspensions containing both nickel nanoparticles and iron oxide nanoparticles are shown over a range of volume fractions. The main features to note are that in silicone oil the measurements correspond to what might be expected from particle mixtures given the earlier results, with the nickel particles assuming a dominant role. In FC70 however the findings are more surprising, in that the DC conductivity of the suspension varies very little when the proportions of nickel and iron oxide are varied over quite a wide range. For all combinations some field-activated character has been introduced that was absent in the single particle-type suspensions. Conductivities are higher than could be expected from either particle-type acting alone and overall behaviour is, therefore, dependent on the particle–fluid interaction. Note that both types of particle have some magnetic character which may promote a Hall-effect contribution.

4. Conclusion

Effective medium theories based solely on the electrical properties and volume fractions of the component materials have limited applicability when assessing the DC conductivity of the above nanoparticle-fluid combinations at low volume fractions.

Enhanced DC conductivity through interaction between the particles and the fluid has been demonstrated even at quite moderate fields and different types of nanoparticles have been shown to exhibit different behavioural trends. Whilst the DC enhancement is partly related to the spatial arrangement of the particles as expected, there is clear evidence that energy-activated (electric-field activated) processes also play a major role. The DC conductivity of a perfluorinated oil, 3M™ Fluorinert FC70, is increased in the presence of 10nm diameter iron-oxide nanoparticles. Combinations of different species of nanoparticles appear to influence percolation, sometimes enhancing and sometimes moderating the observed systems behaviour. Synergies clearly do exist between nanoparticles and carrier fluids that can have a major influence on their systems properties, hence they may be exploitable in the future development of engineering nanofluids.

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