Science of the very small has become big. It raises issues that are interesting and important to scientific understanding and seems to possess clues to the solution of knotty technological problems. The focus of the present news item concerns thermal properties of suspensions of nanoparticles in fluids, commonly referred to as nanofluids. Investigations of their thermal properties have thrown up many findings that are interesting and challenging to explain. The importance of thermal properties is in the context of heat removal from small spaces. It is a technological challenge arising from the need to cool high-speed microelectronic devices.

Conventional approaches and designs have reached their limit and cooling threats to be the limit to both further miniaturization and increased speeds. One of the conventional approaches is to circulate cooling fluids in microchannels incorporated in a device. Here, the limitation eventually arises from the ability of the fluid to conduct heat away from hot surfaces. Thermal conductivity reflects the ability of a medium to conduct heat. Typically, liquids are better conductors than gases and vapours. For example, while air has a conductivity of the order of 0.03 W/(m K), water has a conductivity of the order of 0.6 W/(m K). Many solids, however, are even better conductors than liquids. Thus, even common red brick has a conductivity of 60 W/(m K), while metals like silver and copper have a conductivity of 400 W/(m K). An exotic material like the carbon nanotube (CNT) has a conductivity of 3000 W/(m K). One obvious solution to the cooling problem is to boost the conductivity of a fluid by using a suspension of particles of a highly conducting solid in it. However, the size of the microchannels prevents the use of conventional ‘fine’ particles, which are typically micron-sized, since they can clog the channels. Nanoparticles are the obvious substitute candidates and can make the solution feasible. Thus, studying the thermal properties of nanofluids has grabbed the attention of scientists and engineers.

Three main experimental observations have been made during studies on thermal properties of nanofluids, and have been summarized by Eastman et al. The salient features are as follows.

First and this is the most enigmatic feature, it was found that thermal conductivity of a fluid was enhanced by large factors when nanoparticles were added up to only a small volume fraction. Thus, Lee et al. found that addition of 4% of Al2O3 particles increased thermal conductivity by a factor of 8%, while according to Eastman et al., particles of CuO at the same volume fraction enhance the conductivity by about 12%. This is interesting since conductivity of CuO is less than that of Al2O3. Metal particles have been found to be much more effective. Patel et al. found that even at as low a volume fraction of about 0.0001, thiol-protected gold particles increased thermal conductivity by 10%. Other researchers have found greater enhancement with metal particles than with the lesser conducting oxide particles, though quantitatively less than that reported by Patil et al. Thus, ferrofluids containing 0.5% of iron particles were found to increase conductivity by 18%.

Secondly, Das et al. found that thermal conductivity of nanofluids increased with increasing temperature. Clearly, this property is very advantageous in cooling applications.

Lastly, You et al. found that nanofluids exhibited three-fold increase in critical heat flux (CHF) over that of the liquid in which the particles were suspended. This parameter plays an important role in heat transfer where boiling is involved.

All these features indicate the potential of nanofluids in applications involving heat removal. Issues concerning stability of nanofluids, since they do aggregate with ageing, have to be addressed before they can be put to use. Ironically, nanofluids of oxide particles are more stable but less effective in enhancing thermal conductivity in comparison with nanofluids of metal particles and CNTs. Though we will confine ourselves here to a discussion of enhancement of thermal conductivity, it is worthwhile to mention that enhancement of CHF may prove to be of wider utility.

Maxwell developed a theory for predicting the effective conductivity of composite dielectric media. It was adopted by Hamilton and Crosser to predict the thermal conductivity of dilute suspension of spherical particles in a medium, which could be fluid or a solid, and they gave the following equation:

\[
\frac{k_{\text{eff}}}{k_m} = 1 + \frac{3\phi}{k_p + 2k_m - \phi} - \frac{k_p}{k_m} - \phi
\]

where \( k_p \) and \( k_m \) are the thermal conductivity of the particles and the medium respectively, and \( \phi \) is the volume fraction of the particles. It is interesting to note that particle size does not appear here and eq. (1) has been verified for large particles. In the limit of particle thermal conductivity being much larger than that of the medium, and low volume fractions, eq. (1) predicts that enhancement in thermal conductivity should be three times the volume fraction. Obviously, in this limit, the nature of the particles should also have no effect. Both these are not true in the case of nanofluids. Thus, as mentioned earlier, suspensions of CuO show lesser enhancement than those of metal particles, which are better conductors and show greater enhancement than suspensions of nanoparticles of Al2O3, which also are good conductors. Kumar et al. refer to earlier measurements of their own as well as others, where enhancement was found to decrease with increasing size of the nanoparticles. What could be the possible explanations for all this?

**Effect of material and size**

Maxwell’s theory assumes that temperature is continuous across the interface between the medium or that the interface offers no resistance to heat transfer. However, such resistance can arise due to various factors such as scattering of phonons and layers of fluid molecules adsorbed on the particle surface. As interfacial resistance can be material dependent, it is possible that this could be the reason for different materials showing different enhancements. The interfacial resistance is represented by a coefficient \( R_\tau \), and \( \gamma = R_\tau k_m R \), where \( R \) is the particle size, is an estimate of the ratio of interfacial resistance to resistance to
conduction in the medium. Nan et al.\textsuperscript{5} modified Maxwell’s theory to predict the effect of interfacial resistance on $k_{\text{eff}}$, and in the limit of $k_{\text{eff}}/k_{p} \ll 1$ and small volume fractions, they predict

$$\frac{k_{\text{eff}}}{k_{p}} = 1 + 3\phi \frac{1 - \gamma}{1 + 2\gamma}. \quad (2)$$

It should be noted that existence of interfacial resistance can in effect reduce the estimated maximum enhancement of thermal conductivity. In fact, if $\gamma > 1$, the effective thermal conductivity is less than that of the medium. Thus, the presence of interfacial resistance is unable to provide an understanding of data.

**Effect of Brownian movement**

Measurements on effective thermal conductivity of a polymer matrix embedded with alumina nanoparticles\textsuperscript{10} showed that they followed the mixture theory. Thus, enhancements were attributed to some kind of movement, and Brownian motion of nanoparticles was hypothesized to be the cause. It turns out that the heat carried by diffusion of the centre of mass is negligible. An alternative is the mixing caused by random Brownian movement. At present no theory exists to predict the effect of such convection, though there are some semi-empirical theories\textsuperscript{8,11,12} which seem partially successful. It may be mentioned that this effect is dependent on particle size, and the theories seem to predict the correct trend. However, molecular simulations\textsuperscript{13} seem to indicate that Brownian motion does not have any effect.

**Effect of adsorbed layers and cluster formation**

If the layers of molecules of fluid adsorbed on the solid have different properties, this could be a possible explanation. Another hypothesis depends upon formation of loose clusters of nanoparticles due to the attractive forces between them. The size of the structure is larger than the individual particles, and hence, the volume fraction of the clusters is larger than that of the collection of particles. The effective thermal conductivity based on the volume fraction of the clusters would be more than that predicted based on particle volume fraction. While this proposal has the correct trend, it implicitly assumes that conductivity of the trapped fluid molecules is higher than that of the fluid. Eastman et al.\textsuperscript{1} discuss this in detail. However, in both the hypotheses it is not clear that there exists a basis for the assumed properties.

It is apparent that no clear explanation of enhanced thermal conductivity has been offered so far. It is but natural under such circumstances that the experiments are repeated using a different technique. Conductivity of nanofluids has been measured mostly using hot-wire method, but a few measurements have been made using the standard parallel-plate method. Putnam et al.\textsuperscript{14} used a technique that is based on measurement of the extent of bending of a laser beam due to a gradient in refractive index caused by the temperature gradient, to measure thermal conductivity of nanofluids of thiol-protected gold particles. They report that the enhancements are in accordance with the theory of Maxwell! They have thrown the gauntlet at fellow experimentalists and theoreticians by stating that ‘investigations of the properties of nanofluids have reached the awkward situation of having a greater number of competing theoretical models than systematic experimental results’. Thus it is clear that nanofluids will offer a lot more excitement, and perhaps controversy in the times to come.


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