

Modeling Transport Mechanism in Nanofluids

Jacob Eapen
Department of Nuclear Engineering, MIT

Abstract

Nanofluid connotes a colloidal suspension with dispersed nano-sized particles. Experiments in the past decade reveal that nanofluids have a significantly higher thermal conductivity in comparison to that of the base fluid. Recently, a number of phenomenological models have been proposed to explain the anomalous heat transfer enhancement seen in nanofluids. In this paper, we make a systematic survey of experimental and modeling endeavors with nanofluids. We find that most of the models are phenomenological in nature and addresses only a part of the problem. In some models, inconsistencies are very conspicuous. We also note that the effectiveness of nanofluids depends not just on the thermal conductivity but also on other properties such as viscosity and specific heat. The concomitant changes in other transport properties such viscosity and diffusion are largely overlooked by the scientific community to date. To explain the property changes in a coherent way, we propose molecular dynamics simulations. We show that all the transport coefficients can be evaluated using the linear response theory. Finally, we discuss the enhanced phonon transport mechanism in low-dimensional quantum systems such as nano-tubes and quantum dots. We believe that such nano-structures are optimal for enhancing the heat transfer in nano-fluids.

1.0 Introduction:

Fine dispersion of solid particles in a liquid is generally known as a colloidal suspension. A colloid can be a solid, liquid or gaseous substance that is insoluble yet remains in suspension, and dispersed in another fluid medium. In contrast, dissolved solids are ionic and not colloidal. Colloids are ubiquitous. They are found in nature such as in living cells and are also common in many chemical agents. Typically, the solvent or more precisely, the base medium is water and the particles are macro molecules or large agglomeration of molecules.

Traditionally and not surprisingly, colloids are investigated for chemical and rheological properties. Colloids display very interesting shear behavior. Depending on the

shear rate, shear thinning and thickening can be observed. Thinning refers to a decrease in effective viscosity while thickening leads to the opposite effect.

The study of heat transport in solid dispersions is relatively recent. Ahuja [1] showed that sub-micron polystyrene suspensions in aqueous glycerine increased the heat transfer by a factor of two under laminar flow conditions. At the same time, negligible differences were seen for the pressure drop even with a high particle volume fraction of 9%. Even with such impressive data, dispersions were not considered very useful as a heat transfer enhancement technique. A major drawback stems from the size of the particles which are typically in the micron range. They pose significant corrosion and erosion hazards in engineering systems.

With the advent of nanotechnology in the early nineties, it became possible to manufacture nano-sized particles. These particles, due to their extreme sizes, can form very stable colloidal systems which are currently known as *nanofluids*. Unlike the suspensions with micron sized particles, nano-dispersions can form stable systems with very little settling in static conditions. This raises the exciting possibility of employing nanofluids for enhancing the heat transfer in systems where a fluid is used a medium to transfer energy.

The first heat transfer enhancement with nano-sized particles was reported by Masuda *et al* in Japan [2]. They demonstrated that the thermal conductivity of ultra fine suspensions of alumina, silica and other oxides in water increased by a substantial amount (maximum of 30%) for a particle volume fraction of 4.3%. At the same time, the friction factor almost quadrupled.

In the United States, Choi [3] at the Argonne national lab proposed to construct a new class of engineered fluids with superior heat transfer capabilities in 1995. Since then, a series of experiments have been performed with nanofluids. Incidentally, the term *nanofluid* was first coined by Choi for denoting this new class of engineered fluids. In some respects, the terminology is relevant because of the use of nano-sized materials even though it not appropriate. One diversion with the new terminology is that the colloidal aspects of the fluid have not got the right amount of attention or the required importance.

X. Wang *et al* [4] reported enhanced thermal conductivities for alumina and cupric oxide (CuO) with a variety of base fluids including water and ethylene glycol. They observed that the thermal conductivity enhancement increases as the particle size decreases. The enhancement was seen to roughly proportional to the volume fraction of the particles. With alumina particles, they observed a maximum of 12% increase in the

conductivity with a volume fraction of 3%. The viscosity on the other hand showed an increase of 20-30% for the same volume fraction. Another interesting trend is that viscosity ratio had a quadratic dependence on the volume fraction of the particles while thermal conductivity showed a linear variation. In a similar study, Pak *et al* [5] reported a three fold increase in the viscosity for alumina at the same volume fraction. By assessing the trends, it is clear that the nano-fluid dispersions need to be optimized (with respect to size, volume fraction, materials among many other possible variables such as shape and temperature) for its performance before they can be projected as a viable alternative for heat transfer enhancement.

Eastman *et al* [6] in 2001 showed that 10 nm copper particles in ethylene glycol could enhance the conductivity by 40% with very small particle loading fraction (less than 0.3%). With cupric oxide (35 nm), the enhancement was 20% for a volume fraction of 4%. These results clearly show the effect of particle size on the conductivity enhancement. However, we note that there are additional quantum size effects on such scales. Such effects are not addressed so far in the community. For example, Patel *et al* [7] shows that even with the same surface to volume ratio, we can get different conductivities when the materials are different. This indicates the quantum nature of transport phenomenon is not insignificant.

Das *et al* [8] measured the conductivities of alumina and cupric oxide (in water) for different temperatures ranging from 20 °C to 50 °C and for different loading conditions. They observed a linear increase in the conductivity ratio with temperature. However, for the same loading fraction, the rate of increase was higher for cupric oxide than alumina. Similar trends were seen with gold particles (4nm) in toluene [7]. At higher particle volume fraction, the conductivity enhancement varied more like \sqrt{T} where T is the temperature.

Incidentally, an astonishing 11% increase was reported for almost vanishing concentration of 0.008% for gold nanoparticles with a thiolate covering. These discussions highlight the complexity of the transport mechanism involved in nano-dispersions.

Two sets of experimental data are available for dispersions containing nanotubes. Note that carbon is hydro-phobic and cannot be dispersed in water without an additional surfactant. Choi *et al* [9] has reported significant enhancements for multiwalled carbon nanotubes (MWNT) in oil suspension. The MWNTs had a mean diameter of 25 nm and a length of 50 μm . The results show that, unlike with nanopowders, the thermal conductivity with nano-tubes portrays a quadratic variation with volume fraction. At 1% volume fraction, carbon nanotubes show a remarkable 250% increase in thermal conductivity. This is much more than what is seen with oxide nano-particles [8]. Data for pure metallic nanofluids for this loading condition is not available. Given the trend, it is conceivable that they may be comparable or exceed the enhancement observed in nanotubes. Xie *et al* [10] reports much more modest increase (20%) with MWNT made of carbon in synthetic poly oil. The quadratic signature however, is evident even for these low enhancements.

Even though a large number of experiments have been conducted for measuring thermal conductivity, only a handful were performed for other evaluating transport coefficients such as viscosity. We believe that viscosity is as critical as thermal conductivity in engineering systems that employ fluid flow. Pumping power is proportional to the pressure drop which in turn is related to the viscosity. In laminar flow, the pressure drop is directly proportional to the viscosity. In turbulent flow, the relationship is more complex which depends on the geometry and flow regime of the flow. It is therefore, evident that the effects of viscosity and

thermal conductivity should be considered together and not separate.

2.0 Modeling of Nanofluids:

The early attempts to explain the anomalous behavior seen in nanofluids were made with the classical theory of Maxwell [11] for composite materials. This theory is applicable to statistically homogenous, isotropic composite materials with randomly dispersed spherical particles having uniform particle size [4]. Maxwell's theory is applicable for dilute suspensions and it is also appropriate for predicting other properties such as electrical conductivity, dielectric constant and magnetic permeability. Later on, a second order extension was developed and modified by numerous workers. When tested against experimental data, Maxwell's formalism gave reasonable conformity for low particle concentrations and with particles which are in the micrometer region.

Hamilton and Crosser (H&C) subsequently modified Maxwell's theory for non-spherical particles [12]. Experimental confirmation was obtained a decade later for this model. This model became the backbone of most modeling work on nanofluids. The expressions for the ratio of effective conductivity to fluid conductivity from Maxwell's theory and H&C's modification are given below:

Maxwell:

$$\frac{k_e}{k_f} = 1 + \frac{3\phi(\alpha - 1)}{(\alpha + 2) - \phi(\alpha - 1)} \quad (1)$$

Hamilton and Crosser:

$$\frac{k_e}{k_f} = \frac{\alpha + (n - 1)[1 + \phi(\alpha - 1)]}{\alpha + (n - 1) - \phi(\alpha - 1)} \quad (2)$$

where α denotes the ratio of thermal conductivity of the particle to that of the

fluid, ϕ stands for the volume fraction or concentration of the dispersed particles and n is a shape factor to account for differences in the shape of the particles. For spherical particles n equals 3 and it is easy to verify that the H&C relationship for spherical particles becomes identical to Maxwell's relationship.

Early comparisons with nano-oxides showed that H&C theory predicted the right trend but the observed augmentation was far more than what was predicted by the theory. When the theory was tested with very fine metallic (Cu and Au) nano-particles, H&C theory under-predicted the effective thermal conductivity by almost an order of magnitude [6,7]. Further, the trend was clearly non-linear even at small volume fractions.

It is evident that the conductivity enhancement is not just a function of volume fraction and ratio of conductivities but also on the size of the nano particles. Hence it is not very surprising that H&C model which did not have any size dependency failed to make reasonable predictions.

Kebblinski *et al* [13] elucidated four possible mechanisms for the anomalous conductivity behavior seen in nanofluids. First, they discounted the theory of Maxwell and related modifications. This is largely based on the fact that these relationships do not have any explicit particle size dependency. They made a key observation that heat transport is strongly influenced by the Brownian motion of the particles. However, a simple order-of-magnitude calculation appeared to show that Brownian effects are small. This inference, may be unsubstantiated because latter papers do attribute the enhanced conductivity at higher temperatures to Brownian motion.

Liquid layering around the particles was offered as another mechanism by Kebblinski *et al*. The basic idea is that liquid molecules

can form a layer around the solid particles and thereby enhancing the local ordering. Since phonon transfer in crystalline solid is very effective, such local ordering in the liquid can lead to enhanced heat transport. Again, an order-of-magnitude analysis showed that particle clustering may not be the sole reason which can explain the enhanced conductivity.

The third mechanism was related to the nature of heat transport in nano-particles. The authors rightly point out that the generally accepted diffusive transport mechanism is not valid at nano-scales. Rather, the heat transport in the nano-particles is more ballistic. So for ballistic transport or even in fast diffusive phonon transport, the solid particles will be essentially at a constant temperature thereby, providing the same boundary condition for heat flow in the liquid regions. In addition, if the ballistic phonons initiated in one particle can persist in the liquid and get transmitted to another solid particle, the heat transport can significantly increase. The phonon mean free path in the liquid is typically small because local ordering is limited to few atomic diameters. Since, particles are constantly moving by Brownian motion, there is a possibility that somewhat coherent phonon transfer is possible even with low particle concentrations. Such coherent transport is reported for acoustic excitations in colloidal systems where diameter of the particles are comparable to the wavelength of sound.

We believe that the above mechanism may perhaps, embody the paradigm of heat transport in nanofluids. We will show later that molecular dynamics simulations with accurate inter-atomic potentials can predict very complex bulk and interface phonon transport. If needed, accurate potentials can be constructed from quantum mechanical simulations of materials such as density functional or Hartree-Fock methodologies. In addition, the same simulation technique along with statistical mechanics is appropriate for simulating other transport

coefficients such as viscosity, thermal conductivity and diffusion coefficient.

Lastly, Koblinski *et al* find that if the nano-particles form clusters, then we can expect a increase in the thermal conductivity. This kind of percolating structures prompted Wang *et al* to develop a model based on fractal dimensions [14]. This model showed some promise even though it may not be adequate as a general theoretical tool.

It must be mentioned that Bruggeman developed a mean-field approximation which resulted in a modified form of H&C relationship [15]. Kim *et al* [15] pointed out that the model developed by Xue *et al* [16] is very close to the Bruggeman model. The Xue model has reasonable success in predicting the quadratic trend seen for nanotubes. Again, this model does not have any temperature or explicit size dependence and cannot be treated as a general framework.

The first large-scale microscopic simulation was performed by Bhattacharya *et al* [17]. They assumed that the nano-particles are much bigger than the solvent or base fluid particles. Therefore, the solvent particles are omitted and their effects are represented by a combination of random and frictional forces. The solute particles are then allowed to move according to Newton's II law of motion. The forces on the solute particles are evaluated from an assumed form of a two-body empirical potential Φ which is given by:

$$\Phi = A \exp \left[-B \frac{|r| - d}{d} \right] \quad (3)$$

where d is the particle diameter and r is the separation. A and B are two coefficients which are medium specific. Since the coefficients are unknown, they were fitted to reproduce the experimental data. The simulation results showed the right trend for oxide particles. Results for metallic nano-particles and nanotubes are currently

unavailable. A drawback of this methodology is that we have to assume a potential for solute interactions. A better alternative is to employ actual inter-atomic potentials and perform true molecular dynamics simulations.

Two recent papers are claiming to have discovered the fundamental transport mechanisms in nanofluids. We think that they are both conceptually inconsistent. In the first one, Jang *et al* [18] rightly points out that Brownian motion is an important mechanism for heat transport. Then the heat fluxes for different particles are expressed in the form:

$$j = -\frac{1}{3} \phi \lambda \hat{C}_v \frac{dT}{dz} \equiv -k \frac{dT}{dz} \quad (4)$$

where λ is the mean free path of the molecules, \hat{C}_v is the heat capacity per unit volume, ϕ is the volume fraction of the particles, T is the temperature and k is the thermal conductivity. Note that the above form comes from a crude kinetic theory and it is not directly applicable to liquids without making significant corrections. The kinetic theory was originally developed for dilute gases and is not readily applicable for dense liquids.

The authors first assume that heat transport occurs through molecular collisions in dense liquids. This is not strictly true because liquids have a short range order which allows some phonon type conduction over a few atomic diameters. This process explains why liquids have much better thermal conductivity than dilute gases. To account for heat transfer between the particles and fluid, a micro convection model was postulated. This assumption is very arbitrary and its validity is questionable. Finally, macro-scale convection behavior was assumed at nano-scales by invoking macro-scale correlations for flow around a solid sphere. Again, this assumption needs to be validated.

The critical flow lies in the evaluation of Reynolds number which is defined as:

$$\text{Re} = \frac{Vd}{\nu} \quad (5)$$

where V is defined as the random motion velocity of the nano-particles and d the diameter of particle. The velocity is then evaluated as:

$$V = \frac{D_0}{\lambda_f} = \frac{k_B T}{3\pi\mu d\lambda_f} \quad (6)$$

where D_0 is Einstein diffusion coefficient and λ_f represents the mean free path of the fluid molecules. If we substitute Equation (6) in (5) we find that the Reynolds number becomes independent of particle size which is an absurd conclusion. This is of course, assuming that the mean path of the liquid is independent of the particle diameter even though for a dilute suspension, this is a reasonable assumption to make. The correlation for flow past a sphere, however, does assume that the Reynolds number is linearly dependent on the particle diameter. This way, the arguments presented in this paper are neither consistent nor convincing.

The other model proposed by Kumar *et al* [19] for estimating thermal conductivity in nano-fluids uses Fourier law of conduction and basic ideas from the kinetic theory. The model attempts to explain the anomalous heat transfer observed in nano-fluids for different temperatures and nano particle diameters. However, the arguments are mostly heuristic and somewhat disconnected. For example, the authors partition the model into ‘static’ and ‘kinetic’ components. Using the static part, the size dependency for the heat transfer enhancement was estimated and was shown to match the experimental data. Then an arbitrary ‘kinetic’ component was introduced which also had a size dependency. Taken together, the model predicts an inverse cubic dependency on the particle diameter ($1/d^3$) as opposed to a

simple inverse dependency ($1/d$) cited in the paper. What is interesting is that the experimental data shows both $1/d$ and $1/d^3$ dependency:

Another area where the model lacks consistency is in the formulation of velocity dependency on the heat transfer enhancement. In the Kumar model, an arbitrary velocity dependence was selectively introduced for the nano particles to account for the enhancement seen at higher temperatures. Consistency demands that we have to include similar effect for the fluid particles as well. The same Brownian motion effect attributed for the nano particles is just as well applicable for the fluid particles. The combined effect can be different from what is predicted by the Kumar model. Further, the effective heat transfer does not have a heat capacity term which accounts for the intrinsic energy of the microscopic carriers.

3.0 Transport Properties with Molecular Dynamics:

We now present a generalized technique where we can find the transport properties and even transport behavior of nanofluids. Transport coefficients, as the name implies, describe the material properties of fluid under non-equilibrium conditions. For example, thermal conductivity is a property associated with heat transport. Likewise, viscosity and diffusion coefficients are associated with momentum and mass transport respectively. These coefficients are typically taken as constants and are understood within the framework of continuum mechanics.

On the other hand, linear response theory in statistical mechanics provides a general framework to calculate all the transport coefficients using time correlation functions. Time correlation functions are spatio-temporal functions that describe the thermal fluctuations in a fluid [20]. What is remarkable is that these functions can also

describe the response of the fluid to a weak, external perturbation. The reason for this is that dynamic process that determines the thermal parameters also controls the fluid response. So linear response theory gives a framework where the transport coefficients can be evaluated in equilibrium conditions. While seemingly at odds with the continuum concepts, linear response theory is well accepted and is indispensable for evaluating the transport coefficients from molecular interactions.

The time correlation functions can be evaluated by molecular dynamics (MD) simulations [21,22]. The definition of time correlation does not assume anything on the physical state of the medium. A time correlation function can be calculated by averaging the appropriate dynamic variables over time and invoking the ergodic hypothesis of the equivalence of time averaging and ensemble averaging [20]. For computer simulations, especially in molecular dynamics, time correlations can be advantageously employed. The only true input for an MD simulation, other than initial conditions, is the inter-atomic potential. Hence, it is theoretically conceivable that all macroscopic transport coefficients can be determined once the inter-atomic potential is established.

In an MD simulation, we simulate the molecules directly without any recourse any simplifying assumptions. The molecules obey the classical laws of Newtonian mechanics. Closed form solutions do not exist for a general N -body problem (except $N=2$). In practice, it is possible to integrate the coupled equations of motions of each molecule in time using numerical techniques.

In classical MD, the molecules or atoms interact with each other through inter-atomic potentials. These potentials are known experimentally for well-known materials such as argon and carbon. For lesser known materials, it is possible to use density functional theory or related quantum

mechanical techniques to evaluate very accurate inter-atomic potentials. So in theory, it is possible to simulate complex nanofluids with many different solute materials and configurations without any simplifications or approximations. As an example, if we want to simulate nanofluids with single walled nanotubes, we can construct the nanotubes explicitly, surround them with water molecules, and conduct MD simulations. So it is not necessary to invoke additional unverifiable assumptions to explain the key aspects of transport in nanofluids.

Each transport coefficient can be derived directly from one of the continuum equations of fluid dynamics after taking the long wave-length (small k) limit of the Fourier transformed form of equation [20,23]. The eventual result of the derivation is a direct connection between a macroscopic transport coefficient and the time integral of a particular microscopic autocorrelation function measured in an equilibrium state [23].

The relationships between correlation functions and transport coefficients are known as Green-Kubo relationships. The Green-Kubo expression for the diffusion coefficient is given by [20]:

$$D = v_0^2 \int_0^{\infty} \psi(t) dt \quad (7)$$

where ψ is the normalized velocity autocorrelation and is given by:

$$\psi(t) = \frac{\langle v(t) \cdot v(0) \rangle}{[v(0)]^2} \quad (8)$$

where v stands for velocity. The angular bracket denotes ensemble averaging. In MD, ensemble average is substituted with time averaging by invoking ergodic hypothesis. The Green-Kubo relationship for shear viscosity is given as [23]:

$$\mu_{xy} = \frac{V}{3k_B T} \int_0^\infty \left\langle \sum_{x<y} \tau_{xy}(t) \tau_{xy}(0) \right\rangle dt \quad (9)$$

where τ_{xy} represents the shear stress tensor and is given by:

$$\tau_{xy} = \frac{1}{V} \left[\sum_j m_j v_{xj} v_{yj} + \frac{1}{2} \sum_{i \neq j} r_{xij} f_{yij} \right] \quad (10)$$

where f_{ij} is the force between two atoms and r_{ij} is the separation between them. For a two body potential, the shear stress tensor, just like in continuum Newtonian flow, is symmetric

The thermal conductivity can be computed in the following way:

$$k = \frac{V}{3k_B T^2} \int_0^\infty \left\langle \sum \mathbf{J}(t) \cdot \mathbf{J}(0) \right\rangle dt \quad (12)$$

where \mathbf{J} denotes the microscopic heat flux and is given by:

$$\mathbf{J} = \frac{1}{V} \left[\sum_j h \mathbf{v}_j + \frac{1}{2} \sum_{i \neq j} r_{ij} (\mathbf{f}_{ij} \mathbf{v}_j) \right] \quad (13)$$

Linear response theory is not just applicable to hydro-dynamic transport coefficients. It is also suited for evaluating electrical, magnetic and other properties where an appropriate flux can be defined. For example, the Green-Kubo relationship for electrical conductivity for an isotropic conductor is given by [24]:

$$\sigma(\omega) = \frac{V}{3k_B T} \int_0^\infty \left\langle j_x(t) j_x(0) + j_y(t) j_y(0) + j_z(t) j_z(0) \right\rangle e^{-i\omega t} dt \quad (14)$$

It can be easily noted that the combination of linear response theory and MD simulation can be used to evaluate the transport coefficients from molecular principles.

Next we present some results from equilibrium MD simulations on very simple systems. Lennard-Jones 12-6 potential is employed for simulating a dense liquid. The

transport coefficients are calculated with the Green-Kubo relationships. In MD, reduced or non-dimensional units are frequently used. These are constructed from the parameters of the potential used. For the present study, the reduced density is given by $\rho^* = \rho \sigma^3$ where σ denotes the length parameter in LJ potential which is 3.4 Å for Argon atoms. Similarly, the reduced temperature is given by $T^* = k_B T / \epsilon$ where ϵ stands for the energy parameter in L.J potential. $T^* = 1$ corresponds to a temperature of 120 K.

Figure 1 shows the radial distribution function (RDF) with a reduced density of 0.9 and reduced temperature of 1.0. Radial distribution is proportional to the probability of finding an atom on the volume element dr at a distance r from a given atom. In short, it describes the spherical averaged local organization around a given atom.

We can clearly note that the structure has a short range order. The highest peak corresponds to the nearest neighbor.

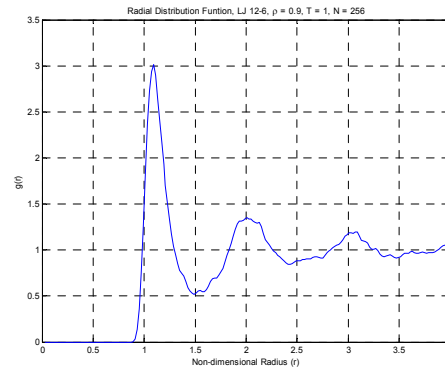


Fig. 1: RDF for a Dense Liquid

Figure 2 depicts the velocity auto-correlation function (VCF). As explained before, the area under this curve is a measure of the diffusion coefficient in the liquid.

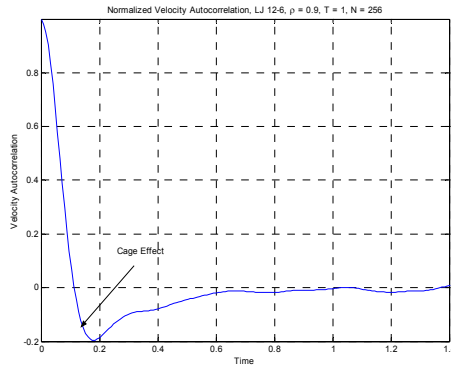


Fig. 2: VCF for a Dense Liquid

The negative VCF values are very typical of dense liquids. Physically, VCF gives the projection of the velocity of an atom at a subsequent time along the initial direction of motion [20]. Negative values mean that the atoms are back-scattered or the atoms get trapped in a cage for short duration of time. The diffusion constant for this state is evaluated to be 0.009 (reduced units).

The stress correlation function (SCF) is portrayed in Figure 3. The area under this curve gives the dynamic viscosity of the liquid. It is evaluated to be 2.65 (reduced units).

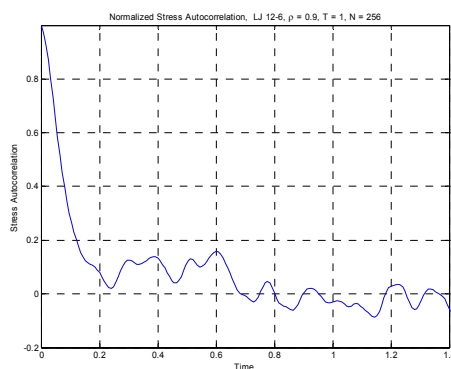


Fig. 3: SCF for a Dense Liquid

Similarly, the area under the heat flux correlation (HCF) curve will give the thermal conductivity. The heat flux correlation curve is depicted in Figure 4.

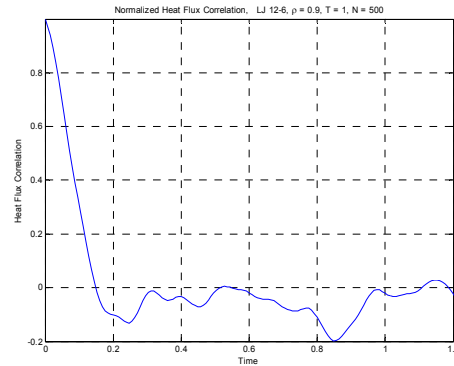


Fig. 4: HCF for a Dense Liquid

Note that due to the inherent noise in the simulations, it may be necessary to conduct simulations for different correlation lengths. An inordinately long correlation time may result in spurious values for the transport coefficients especially for viscosity and conductivity. To improve the statistics, a large number of independent sets may be required. For the present study these checks were not performed.

Now we will try to mimic the effect of solid particles in this fluid. At a few chosen locations, the interaction is increased to five times. This way, we are trying to simulate the effect of solid particles without explicitly creating them. It may be noted that this is a very crude model and is used to highlight the fact that transport coefficients do change when the interacting potentials are altered.

Figures 5 and 6 show the stress and heat flux correlation respectively. Note that the shape of the correlation functions are quite different from those in figures 3 and 4. This effectively demonstrates that changes in inter-atomic potentials even if is scattered across the simulation domain, can have a significant effect on the transport properties. In our study, the ‘solid particles’ occupy less than a tenth of the total simulation volume. Again, it is emphasized here that the actual interaction of solid particles will be quite different from that used in this model.

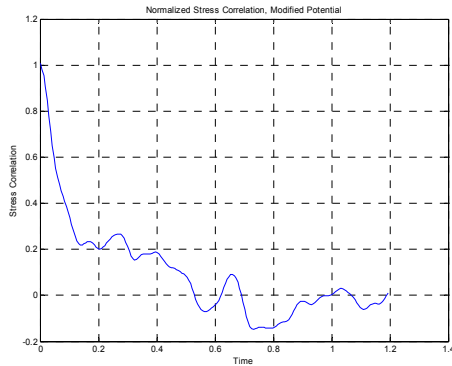


Fig. 5: SCF with Modified Potential

The comparisons show that viscosity increased by 30% while no significant changes were seen on thermal conductivity. This is somewhat surprising but more careful analysis is required to arrive at a definitive conclusion.

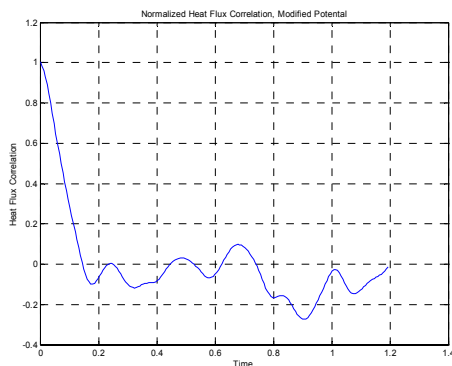


Fig. 6: HCF with Modified Potential

4.0 Enhanced Heat Transport with Low-Dimensional Nano-Structures:

In the past decade, significant progress has been made in devising nanostructures that have strikingly different thermal and other material properties from those observed in bulk materials which have considerable defects and dislocations. For example, Berber *et al* [25] calculated the thermal conductivity of a (10,10) carbon nanotube with MD. In isolation, the thermal conductivity at room temperature was

unusually high (6600 W/m-K) and was comparable to a hypothetical graphene monolayer diamond. The high value was attributed to the large phonon free paths in the nanotube. In comparison, substantially lower values were predicted for the basal plane of bulk graphite.

The thermal conductivity of multiwalled carbon nanotubes were measured by Kim *et al* [26] was found to be 3000 W/m-K. The phonon mean free path was found to be 500 nm. Hone *et al* [27] also showed that the thermal conductivity of a single nanotube may be comparable to that of diamond or in-plane graphite. In contrast, bulk graphite has a thermal conductivity of the order of 100 W/m-K which is many orders less than thermal conductivity of these quantum structures. Diamond has a very high thermal conductivity because of the lack of impurities and defect free structure.

In an exciting paper Noya *et al* [28] calculated the thermal conductivity of carbon nanotubes filled with C₆₀ fullerenes. They observed a phenomenal 40,000 W/m-K at 100 K. At room temperatures, they demonstrated that nanotubes with the fullerenes have a thermal conductivity which is twice as much as with nanotubes alone. They calculated 3500 W/m-K at 300 K for nanotubes with fullerenes and measured roughly 1500 W/m-K without the peapods. These results are consistent with the experimental data obtained by Vavro *et al* [29]. One possible reason for this behavior is that the peapods inside a nanotube introduces more phonons and therefore, more thermal conductivity. Another possible reason for enhancement stems from the stiffening of the nanotube by the forces between the fullerenes and the tube. It is also possible to have a reduced thermal conductivity if small clusters dominated over long ordered chains which can lead to stronger phonon scattering. So it is evident that we need an optimal nanostructure for maximizing the thermal transport

It is clear that low-dimensional structures such as nanotubes and fullerenes are very effective for enhancing the heat transport at the micro-scale. It is therefore, reasonable to expect that such structures can increase the thermal conductivity in nanofluids. This is consistent with the experimental data from nanofluids with carbon nanotubes. Low-dimensional systems are much better understood and offer a better framework for conceptualizing nanofluids.

Carbon nanotubes are hydrophobic and hence, unsuited for use in water. Nanotubes of other materials are not well-studied. We hope to continue in this direction and model nanofluids with low-dimensional nano-structures.

5.0 Summary:

Nanofluid connotes a colloidal suspension with dispersed nano-sized particles. In this paper, we have made a systematic survey of experimental and modeling endeavors with nanofluids. We find that most of the models are phenomenological in nature and address only a part of the problem. In some models, inconsistencies are very conspicuous. We also note that the effectiveness of nanofluids depends not just on the thermal conductivity but also on other properties such as viscosity and specific heat. The concomitant changes in other transport properties such as viscosity and diffusion are somewhat overlooked by the scientific community to date.

To explain the changes in property in a coherent way, we propose molecular dynamics simulations. We show that all the transport coefficients can be evaluated using the linear response theory. We also note that when the interactions are changed in few locations in the simulations, the correlations change significantly affecting the transport coefficients. Finally, we discuss the enhanced phonon transport mechanism in low-dimensional quantum systems such as nano-tubes and quantum dots. We believe

that such nano-structures are optimal for enhancing the heat transfer in nano-fluids.

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