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Discussion of proposed mechanisms of thermal conductivity enhancement in nanofluids

Chu Nie [1], W.H. Marlow, Y.A. Hassan *

Department of Nuclear Engineering, Texas A&M University, College Station, TX 77843-3133, United States

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Abstract

Based upon Green–Kubo linear response theory, we use the exact expression for the heat flux vector of the base fluid plus nanoparticle system to estimate the contribution of nanoparticle Brownian motion to thermal conductivity. We find that its contribution is too small to account for abnormally high reported values. The possibility of convection caused by Brownian particles is also found to be unlikely. We have estimated the mean free path and the transition speed of phonons in nanofluid through density functional theory. We found a layer structure can form around the nanoparticles and the structure does not further induce fluid–fluid phase transition in the bulk fluid. By analyzing the compressibility of the fluid, we have also investigated the sound speed in the nanofluid. For the models of an asymmetric hard sphere mixture representing the single spherical nanoparticles and a mixture of rods and hard spheres representing aggregates, both suspended in the fluid, we found that for the very low volume fraction cases, the compressibility changes little. This shows that the speed of phonon transition does not change due to the addition of nanoparticles of either type. Our results indicate that, besides the enhancement due to the high thermal conductivity of nanoparticles themselves, fluid molecules make no evident contribution to the enhancement of thermal conductivity attributable to the presence of the nanoparticles at volume fractions less than 5%.

1. Introduction

There are many mechanisms proposed to explain the abnormally high observed thermal conductivity found in nanofluids. Based upon experimental work [1], the enhancement of effective thermal conductivity shows concentration, size and temperature dependencies and the order of magnitude of enhancement falls outside the prediction of the conventional continuum theories, for example the Hamilton and Crosser model [2]. Numerous models have been proposed in order to explain this phenomenon and may be categorized into two types, the layer structure model [3–5] and the Brownian motion model [6–9]. The physical meaning is correct and clear for the layer structure model, but as pointed out by Kelblinski et al. [10], since the layer structure forms around the nanoparticle, it can be treated as part of the nanoparticle. No matter how large the thermal conductivity is in the layer structure, the whole contribution cannot exceed the upper limit predicted by the continuum model. Another weakness for the layer structure model is that it cannot account for the temperature-dependent effect observed in the experiments. Many groups pointed out that the Brownian motion may be one possible reason and have made enormous efforts to model it. The theoretical models are of two types, one is based on the translational Brownian motion of nanoparticles [6,7] and the other is based on the micro convection caused by the Brownian motion of nanoparticles [8,9]. Bhattacharya et al. [6] conducted molecular dynamic simulations to compute the heat flux correlation functions of nanoparticles. They assume there exist interactions between nanoparticles and the interaction parameters used in their simulation are fitted from the experimental enhancement of thermal conductivity. Kelblinski et al. [10] performed simulation of a single crystalline nanoparticle

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* Corresponding author. Tel.: +1 979 845 7090; fax: +1 979 845 6443.
E-mail addresses: niechu@hotmail.com (C. Nie), y-hassan@tamu.edu (Y.A. Hassan).

[1] Present address: School of Physics and Information Engineering, Jianghan University, Wuhan, 430056, P.R. China.

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suspended in fluid and found the Brownian motion has little effect on the total heat flux autocorrelation function. Shukla and Dhir [7] proposed a model based on the Brownian motion of particles at equilibrium, where they gave an analytical expression of excess thermal conductivity. Within their model, the kinetic heat flux of nanoparticles accounts for the enhancement of thermal conductivity. Besides the translational Brownian model, Jang and Choi [8] suggested that the Brownian motion of nanoparticles is a key mechanism governing the thermal behavior of nanofluid. Their model assumes the Brownian motion of nanoparticles in nanofluid produces convection-like effects on the nanoscale. Their model is able to predict the size-dependent, concentration-dependent and temperature-dependent thermal conductivity. However, Jang and Choi's modeling was criticized by Prasher et al. [12] for the unphysical assumptions such as the arbitrarily defined thickness of the boundary layer, the parallel path of heat transfer within the nanofluid and the unjustified heat transfer coefficient, etc. Prasher et al. [9] proposed that the Brownian motion of nanoparticle may introduce a localized convection which is the main reason of enhancement of thermal conductivity.

In the theoretical model based on the Green–Kubo linear response theory [6,7], the contribution to thermal conductivity by nanoparticles is added directly to that of the base fluid, which means the heat fluxes in fluid and in nanoparticle are parallel. Their assumptions of additivity are made without explanation. Molecular dynamics studies [6,10] indicate that the enthalpy of fluid molecules and atoms of nanoparticle can be neglected. In [10], the averaged enthalpy is used. Since the nanofluid consists of two different molecules with different phases, the two kinds of molecules are not well mixed, so it is not suitable to use the averaged enthalpy. Justification of these two assertions is very weak and needs to be discussed in detail. It is also very interesting to note that in a recent molecular dynamic simulation work conducted in [11], where the authors simulate a system consisting of monodispersed subnanometer clusters of Pt in liquid Xe and found that the enhancement of thermal conductivity may be ascribed to the strong Xe–Pt interaction.

It is recognized that the thermal conductivity in fluid and solid components of the nanofluid is related to the type of phonon excited, the phonon mean path, and the phonon transport speed, i.e., the speed of sound in the medium [13]. In [14,15], the propagation of sound waves in suspensions of hard sphere colloids is studied as a function of volume fraction with Brillouin light scattering. The authors found two kinds of modes of acoustic excitations. One sets up the deformation in both solid particles and liquid and the other is mainly localized near the interface between the solid particle and fluid, which is a surface. With the theory and experimental results, it is reasonable to conclude that if the fluid is responsible for the enhancement of thermal conductivity, then either the phonon mean free path, which relates to the structure of the fluid, or the speed of sound, which relates to the compressibility of the nanofluid, may change.

In the following section, we will give discussions on the possible reasons accounting for the enhancement of effective thermal conductivity in nanofluid from both sides of nanoparticles and the base fluid. First, we will show the unphysicalness of micro convection. Then, starting from Green–Kubo linear response theory, we define the heat flux vector of the nanofluid including the base fluid molecule and the atoms in nanoparticle. By doing the integral of the heat flux autocorrelation function, we give an analytical result for the enhancement of thermal conductivity due to the Brownian motion of nanoparticles; by doing rough estimation; we show that the translational Brownian motions of the nanoparticle make little contribution to the effective thermal conductivity of nanofluid. Later, the changes of the phonon mean free path and the speed of sound brought by the insertion of nanoparticles will be discussed.

2. Unphysicalness of micro convection model

The basis of the micro convection model is that the volume of fluid affected by the Brownian motion of nanoparticles is very large compared with that of a nanoparticle [16]. Hence, not only the nanoparticles move around due to the Brownian effect, but also significantly large bodies of fluid around nanoparticles interact with each other, which leads to a strong micro convection. Both [9,16] assumes Eq. (6) in [16] is correct,

$$\begin{aligned}\frac{u_x}{u_\mathrm{s}} = 1 &- \left[1 - 1.5\left(\frac{a}{r}\right) + 0.5\left(\frac{a}{r}\right)^3\right]\cos^2(\theta)\\ &- \left[1 - 0.75\left(\frac{a}{r}\right) + 0.25\left(\frac{a}{r}\right)^3\right]\sin^2(\theta)\end{aligned}$$

where the velocity field of the base fluid around a nanoparticle is given assuming steady flow condition and large amount of base fluid will be affected from the steady flow condition. However, the equation is assumed to be under the condition of steady flow in the Stokes regime, which is totally different from that of a nanoparticle in its Brownian motion. The existing literature describing the velocity field of the base fluid around a Brownian particle is limited, but a very recent simulation paper [17] demonstrates that the amplitude of velocity field around a Brownian particle decays much faster than that of a particle moving with a constant velocity. For example, they showed that the peak value of the velocity field correlated with the particle is 5% for the shell located $2.6R$ away from the center of the particle. The simulation result contradicts the steady state assumption. Therefore, the assumption of large value of the dynamic boundary layer induced by the Brownian motion of nanoparticles is questionable.

3. Translational Brownian model

In the constant energy (NVT) ensemble, thermal conductivity, λ for the pure fluid, can be computed from the integrated heat flux autocorrelation function [18]

$$\lambda = \frac{1}{3VkT^2}\int_0^\infty \langle \vec{S}(0)\cdot\vec{S}(t)\rangle\,\mathrm{d}t \tag{1}$$

where the heat flux, $\vec{S}$, is given by

$$\vec{S} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_i \vec{r}^{\,i}_{\mathrm{f}} e^i_{\mathrm{f}}\right) - \sum_i h_{\mathrm{f}}\vec{v}^{\,i}_{\mathrm{f}} \tag{2}$$

Here, i is the index for each molecule, $\vec{r}^{\,i}_{\mathrm{f}}$ denotes the position of a fluid molecule, e^i_{f} denotes the total energy of a fluid molecule including kinetic energy and interaction potential energy with all other fluid molecules and nanoparticles suspended in fluid. h_{f} denotes the entropy of fluid molecules, $\vec{v}^{\,i}_n$ denotes the velocity of a fluid molecule. For the nanofluid as a whole,

$$\vec{S} = \vec{S}_{\mathrm{f}} + \vec{S}_n \tag{3}$$

with

$$\begin{aligned}\vec{S}_{\mathrm{f}} = \sum_{i=1}^{N_{\mathrm{f}}}\Bigg[&\frac{1}{2}m_{\mathrm{f}}(\vec{v}^{\,i}_{\mathrm{f}}\cdot\vec{v}^{\,i}_{\mathrm{f}})\vec{v}^{\,i}_{\mathrm{f}} + \frac{1}{2}u_i\vec{v}^{\,i}_{\mathrm{f}} + \frac{1}{2}\sum_{\substack{i\neq j\\ j=1}}^{N_{\mathrm{f}}}\vec{r}^{\,\mathrm{f}}_{ij}(\vec{f}_{ij}\cdot\vec{v}^{\,i}_{\mathrm{f}})\\ &+\frac{1}{2}\sum_{g=1}^{N_n}\sum_{j=1}^{N_p}\vec{r}^{\,g}_{ij}(\vec{f}^{\,g}_{ij}\cdot\vec{v}^{\,i}_{\mathrm{f}})\Bigg] - \sum_{i=1}^{N_{\mathrm{f}}}h_{\mathrm{f}}\vec{v}^{\,i}_{\mathrm{f}}\end{aligned} \tag{4}$$

$$\begin{aligned}\vec{S}_n = \sum_{g=1}^{N_n}\sum_{i=1}^{N_p}&\frac{1}{2}m^i_p(\vec{v}^{\,g}_i+\vec{V}_g)\cdot(\vec{v}^{\,g}_i+\vec{V}_g)(\vec{v}^{\,g}_i+\vec{V}_g)\\ &+\frac{1}{2}u^{i,g}_p(\vec{v}^{\,g}_i+\vec{V}_g) + \frac{1}{2}\sum_{i\neq j}^{N_n}\vec{r}^{\,g,p}_{ij}(\vec{f}^{\,g,p}_{ij}\cdot(\vec{v}^{\,g}_i+\vec{V}_g))\\ &+\frac{1}{2}\sum_{j=1}^{N_{\mathrm{f}}}\vec{r}^{\,g}_{ij}(\vec{f}^{\,g}_{ij}\cdot(\vec{v}^{\,g}_i+\vec{V}_g)) - \sum_{g=1}^{N_n}\sum_{i=1}^{N_p}h^i_p(\vec{v}^{\,g}_i+\vec{V}_g)\end{aligned} \tag{5}$$

Here, N_{f} is the total number of fluid molecules, N_g is the total number of nanoparticles, N_p is the total number of atoms or molecules in one nanoparticle, m_{f} is mass of fluid molecule, m^i_p is mass of atoms or molecules of a nanoparticle, $\vec{v}^{\,i}_{\mathrm{f}}$ is velocity of fluid molecule i, $\vec{V}_g$ is mass center velocity of nanoparticle g, $\vec{v}^{\,g}_i$ is the velocity of ith atom or molecule of gth nanoparticle relative to its mass center, u_i is the total interaction potential energy of fluid molecule i, $u^{i,g}_p$ is the total interaction potential energy of ith atom or molecule of gth nanoparticle, $\vec{f}_{ij}$ is force between fluid molecules i and j, $\vec{f}^{\,g}_{ij}$ is force between a fluid molecule i and an atom or molecule j of a nanoparticle, $\vec{f}^{\,g,p}_{ij}$ is the force with atoms or molecules in gth nanoparticle, $\vec{r}^{\,\mathrm{f}}_{ij}$ is the relative position between fluid molecules, $\vec{r}^{\,g}_{ij}$ is the relative position between a fluid molecule i and an atom or molecule j of gth nanoparticle, $\vec{r}^{\,g,p}_{ij}$ is the relative position between atoms or molecules in the particle, h_{f} is the enthalpy of a fluid molecule and h^i_p is the enthalpy of an atom or molecule in gth nanoparticle. Obviously,

$$\sum_{i=1}^{N_p}\vec{v}^{\,g}_i = 0 \quad\text{and}\quad \sum_{i=1}^{N_p}m^i_p = M \tag{6}$$

here M is the mass of a nanoparticle.

Before evaluating the heat flux autocorrelation function, there are several factors that need to be taken into account:

1. For the purposes of the current application, the nanofluid is assumed to have a low concentration of nanoparticles. Therefore the interaction between nanoparticles may be neglected.
2. The motion of nanoparticles suspended in fluid obeys Langevin equation.

$$M\frac{\mathrm{d}}{\mathrm{d}t}\vec{V}(t) = 6\pi\mu R\,\vec{V}(t) + \vec{F}_{\mathrm{random}}(t) \tag{7}$$

where μ is dynamic viscosity of the bulk fluid, $\vec{F}_{\mathrm{random}}(t)$ is the random force and R is the radius of nanoparticle. The velocity autocorrelation function has the form [19]:

$$\langle \vec{V}^x_g(t+\tau)\vec{V}^x_g(t)\rangle = \frac{kT}{M}\exp\left(-\frac{6\pi\mu R}{M}\tau\right) \tag{8}$$

3. By taking into account the enthalpy definition in [20], Eq. (5) may be written in the following form:

$$\vec{S}_n = \vec{S}_{n1} + \vec{S}_{n2} \tag{9}$$

where

$$\begin{aligned}\vec{S}_{n1} = \sum_{g=1}^{N_n}\sum_{i=1}^{N_p}\Bigg[&\frac{1}{2}m^i_p(\vec{v}^{\,g}_i\cdot\vec{v}^{\,g}_i)\vec{v}^{\,g}_i\\ &+\frac{1}{2}u^{i,g}_p\vec{v}^{\,g}_i + \frac{1}{2}\sum_{i\neq j}^{N_n}\vec{r}^{\,g,p}_{ij}(\vec{f}^{\,g,p}_{ij}\cdot\vec{v}^{\,g}_i)\\ &+\frac{1}{2}\sum_{j=1}^{N_{\mathrm{f}}}\vec{r}^{\,g}_{ij}(\vec{f}^{\,g}_{ij}\cdot\vec{v}^{\,g}_i)\Bigg]\end{aligned} \tag{10}$$

$$\begin{aligned}\vec{S}_{n2} = &\sum_{g=1}^{N_n}\sum_{i=1}^{N_p}\left[m^i_p(\vec{v}^{\,g}_i\cdot\vec{v}^{\,g}_i)\vec{V}_g\right]\\ &+\sum_{g=1}^{N_n}\left[\frac{1}{2}M(\vec{V}_g\cdot\vec{V}_g)\vec{V}_g + U_g\vec{V}_g\right]\end{aligned} \tag{11}$$

here

$$U_g = \sum_{i=1}^{N_p}\frac{1}{2}u^{\mathrm{f}}_{ij} + \sum_{j=1}^{N_{\mathrm{f}}}\frac{1}{6}\vec{r}^{\,\mathrm{f}}_{ij}\cdot\vec{f}^{\,g}_{ij} \tag{12}$$

with u^{f}_{ij} to be the interaction energy between atoms or molecules comprising gth nanoparticle and fluid molecules. For a nanoparticle, U_g is a constant.

Within a nanoparticle, the sum of kinetic energy of all atoms or molecules can be treated as a constant

$$\sum_{i=1}^{N_p}m^i_p(\vec{v}^{\,g}_i\cdot\vec{v}^{\,g}_i) = \frac{3}{2}N_p k_B T \tag{13}$$

It is necessary to mention that we obtain Eqs. (10) and (11) by assuming the total momentum of nanoparticles fluctuates,

$$\vec{S}_{n2} = \sum_{g=1}^{N_n} \left[\frac{1}{2} M(\vec{V}_g \cdot \vec{V}_g)\vec{V}_g\right] + \sum_{g=1}^{N_n} (N_p k_B T + U_g)\vec{V}_g \tag{14}$$

The second term in Eq. (14) represents the heat flux due to the momentum fluctuation of nanoparticles and this term does not contribute to the thermal conductivity due to its random nature.

Finally, the heat flux can be divided into two parts, one contribution is from the microscopic motion of atoms and molecules in both nanoparticles and fluid and the other from the motion of the centers of mass of the nanoparticles.

Since the nanoparticle has a large mass compared with those of fluid molecules, the energy flux of nanoparticles and that of fluid molecules evolve on different time scales; consequently, the correlation between them may be neglected. Finally, Eq. (3) can be decomposed into two parts,

$$\langle \vec{S}(0) \cdot \vec{S}(t) \rangle = \langle \vec{S}_{n1}(0) \cdot \vec{S}_{n1}(t) \rangle + \langle \vec{S}_{n2}(0) \cdot \underset{n2}{\vec{S}}(t) \rangle \tag{15}$$

The first part in Eq. (15) represents the heat flux autocorrelation function without Brownian motion; the other part represents nanoparticles suspended in a homogeneous fluid, whose motion obeys the Langevin equation. The first part of Eq. (15) should contribute to the thermal conductivity predicted by the continuum model [2] and the second accounts for the enhancement beyond the prediction of continuum model.

Therefore, the contribution to the enhancement of thermal conductivity due to the Brownian motion of nanoparticle is

$$\lambda^{\text{excess}} = \frac{1}{3VkT^2} \int_0^\infty \langle \vec{S}_{n2}(0) \cdot \vec{S}_{n2}(t) \rangle \, \mathrm{d}t \tag{16}$$

this expression is what is obtained in [7], and the authors give the analytical result

$$\lambda^{\text{excess}} = \frac{85}{96\pi^2} \frac{\phi k_B^2 T}{R^4 \mu} \tag{17}$$

where ϕ is the volume fraction of nanoparticles, k_B is the Boltzmann constant, T is the system temperature and μ is the dynamic viscosity of fluid.

With the expression in Eq. (17), we may notice the following important properties:

1. The enhancement of thermal conductivity due to the Brownian motion is proportional to the volume fraction of the nanofluid.
2. The dynamic viscosity of a fluid μ decreases as temperature increases, the enhancement should rise as temperature rises.
3. Regarding the third property, the dynamic viscosity μ is not a constant. The detailed discussion on the dynamic viscosity were given in [21–25]. Since, here for nanoparticles with radii greater than 10 nm, it is not vital to the final result, we will not discuss it in detail. The drag force on a spherical nanoparticle suspended in fluid with a slip length L_s is given in [26], from where, the size-dependent dynamic viscosity is written as

$$\mu^{\text{eff}} = \mu \frac{1 + \frac{2L_s}{R}}{1 + \frac{3L_s}{R}}. \tag{18}$$

The reciprocal of effective viscosity is easily seen to have a dependence of $1 + \frac{1}{1+\frac{R}{L_s}}$.For the parameters set above, at temperature of 320 K, we find that λ^{excess} is on the order of $10^{-15} \frac{W}{mK}$. Compared with the value for water, the contribution from the Brownian motion therefore can be neglected. This result agrees with computer simulation of the thermal conductivity of nanofluid [10].

4. Phonon mean path

In [27], the authors observed that when water is in a sea of obstacles, the properties of water might change. When the density of those obstacles is high, they will hinder the formation of the network of water linkages via the hydrogen bond in normal water. However, when the density of those obstacles is low, they will favor increasing the structure order of water, which implies the mean free path of phonon in such case, will increase. Therefore, it is necessary to explore whether the nanoparticle will bring this effect to the nanofluid in the low concentration limit. First we used the density functional theory to determine the effect on the liquid structure due to the insertion of nanoparticles. Since detailed information of interaction of nanoparticles is not very clear, we present a crude estimation via density functional theory. We treat the water molecule as Lennard–Jones spheres with four hydrogen-bonding sites [28,29]. In order to fit the coexistence density around 300 K well, we choose the parameters as follows, $\frac{\varepsilon}{k_B} = 484.21$ K, $\sigma = 3.164$ Å and $\frac{\varepsilon_{HB}}{k_B} = 1534.00$ K. The values above are close to the choice in [30]. The interaction between nanoparticle and fluid molecules takes the form

$$U^{\text{int}}(r) = \varepsilon_{\text{w}} \exp(-\alpha r) \tag{19}$$

where $\frac{\varepsilon_{\text{w}}}{k_B} = 2527.81$ K and $\alpha = \frac{2}{\sigma}$, ε_{w} is the work required to move a water molecule from the surface of a nanoparticle to infinity, which equals the binding energy of a water molecule at the nanoparticle surface. Here, we choose ε_{w} to be the energy of hydrogen bonding, which is the value used in [31] to mimic the hydrogen bond. α is chosen to make sure the interaction is a short-ranged potential. The procedure of the density functional theory to evaluate the density profile of fluid around the nanoparticle follows [32–34]. Fig. 1 is an example of the density distribution for water around a nanoparticle with radius of 30 nm at 320 K. What we would like to stress here is that the hydrogen bond is not the only chemical bond that can be formed between the base fluid molecules and the nanoparticle molecules. Since so far, many molecular dynamic simulations are using the Lennard–Jones model to represent the interaction between

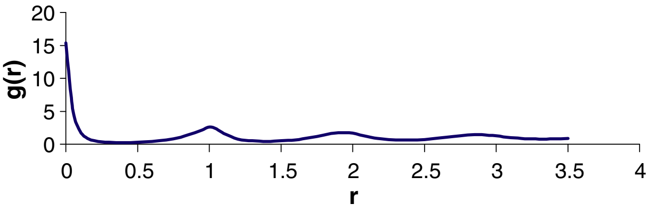

Fig. 1. The density distribution for water around a nanoparticle with radius of 30 nm at 320 K where r is distance from particle surface in nanometers and $g(r)$ is in nm^{-3}.

the base fluid molecules and nanoparticle molecules, for example [10], we think the model used in this work is closer to physical reality.

Through a series of calculations, we found that for nanoparticles ranging from 10 nm to 60 nm, the density distribution changes only slightly. Within a narrow range of temperatures at a given radius, the density distributions are nearly the same. Therefore it is reasonable to assume that the density distribution is always the same as far as our interests here are concerned. It is noticeable that beyond three times the fluid molecular diameter, the layering structure disappears, which means the fluid beyond that distance has the properties of the bulk fluid. We have altered the strength between the wall and fluid molecule and found that only the height of peak changed but the three-layer structure does not change much. This layer structure may account for the second mode of acoustic excitation in [14,15]. For the low volume concentration of nanoparticles, most of the fluid molecules stay in the liquid phase; only a small part of them enter the layer structure, whose thickness is approximately one nanometer according to the current calculation, and we may conclude that the mean free path of phonon does not change much in the nanofluid.

5. Phonon transport speed

In the pure fluid, phonon transport speed is related to the sound speed in the fluid. The sound speed is related to the compressibility and the density of the fluid

$$c = \sqrt{\frac{1}{\rho\kappa_T}} \tag{20}$$

where ρ is the density of the material and κ_T is the compressibility of the material

$$\frac{1}{\kappa_T} = \rho\frac{\partial P}{\partial \rho} \tag{21}$$

where P is the pressure and ρ is the number density. From above, once we know the equation of state, we may evaluate the compressibility and speed of sound.

The properties of a fluid are mainly determined by the repulsive part of the intermolecular potential of the fluid molecules, so the fluid may be modeled as a hard sphere fluid. Here, we assume the nanofluid is a highly asymmetric hard sphere mixture. From [35–37], the compressibility for the simple hard sphere fluid

$$\frac{1}{\kappa_T} = nk_BT\frac{(1+2\eta_1)^2}{(1-\eta_1)^4} \tag{22}$$

here n is the number density, k_B is the Boltzmann constant, $\eta_1 = \frac{\pi}{6}n\sigma^3$ is the packing factor and σ is the hard sphere radius. For the hard sphere mixture,

$$\frac{1}{\kappa_T} = nk_BT\frac{(1+2\eta)^2 - \Delta}{(1-\eta)^4} \tag{23}$$

where

$$\Delta = \frac{3x(1-x)\eta(1-\alpha)^2}{x+(1-x)\alpha^3}\left((2+\eta)(1+\alpha) + 3\eta\alpha\frac{(1-x)\alpha^2+x}{x+(1-x)\alpha^3}\right) \tag{24}$$

x is the number concentration of nanoparticles, and R is the radius of a nanoparticle. $\alpha = \frac{R}{\sigma}$ is the radius ratio of nanoparticles and fluid molecules, $\eta = \frac{\pi}{6}n(1-x)\sigma^3 + \frac{\pi}{6}nxR^3$ is the total packing factor of the system. For the low nanoparticle concentration case, the linear combination approximation is sufficient for the total packing factor.

From the analysis above we find that the single sphere nanoparticle insertion will not change the compressibility of the system. In the following part we will explore the case of the insertion of non-spherical hard bodies, mimicking the non-spherical nanoparticles and the aggregates of spherical nanoparticles. Refer [38–45] discussed mixtures of hard spheres and various hard bodies. Here we adopt the cylinder as the shape of both the non-spherical nanoparticles and the aggregates of spherical nanoparticle by adjusting the length and diameter. According to [44,45], the pressure of the mixture of hard spheres and cylinder is given by

$$P = P_s + P_c\left[\alpha - \eta_s\frac{\partial\alpha}{\partial\eta_s}\right] \tag{25}$$

where P_s is pressure contribution from the fluid molecules

$$P_s = n_sk_BT\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \tag{26}$$

here P_c is pressure contribution from the suspended cylinder

$$P_c = n_ck_BT\left[\frac{1}{1-\eta_c} + \frac{3k\eta_c}{(1-\eta_c)^2} + \frac{k^2\eta_c^2(3-\eta_c)}{(1-\eta_c)^3}\right] \tag{27}$$

in the above equation

$$k = \frac{1}{3}\left(\frac{\pi^2D^3}{16} + \frac{\pi D^2L}{8}(3+\pi)\right) \tag{28}$$

where D is the diameter of the cylinder and L is the length of the cylinder.

α is free-volume fraction, defined as

$$\alpha = (1-\eta_s) \times \exp\left[-\left\{A\frac{\eta_s}{1-\eta_s} + B\left(\frac{\eta_s}{1-\eta_s}\right)^2 + C\left(\frac{\eta_s}{1-\eta_s}\right)^3\right\}\right] \tag{29}$$

A, B, C are quantities related to geometry

$$\begin{aligned} A &= \frac{3}{2}q\left[\frac{\pi}{2} + q + r(1+q)^2\right] \\ B &= \frac{9}{8}q^2\left[\left(\frac{\pi}{2} + r\right)^2 + 4qr\right] \\ C &= \frac{9}{2}q^3 r \\ r &= \frac{L}{D} \\ q &= \frac{D}{\sigma} \end{aligned} \tag{30}$$

the packing factors for hard sphere and cylinder are

$$\begin{aligned} \eta_s &= \frac{\pi}{6}n_s\sigma^3 \\ \eta_c &= \frac{\pi}{4}n_c D^2 L \end{aligned} \tag{31}$$

the compressibility for the system is formally written as

$$\frac{1}{\kappa_T} = n\left[\left(\frac{\partial P_s}{\partial n}\right) + \left(\frac{\partial P_c}{\partial n}\right)\left(\alpha - \eta_s\left(\frac{\partial \alpha}{\partial \eta_s}\right)\right)\right] + P_c\left[\left(\frac{\partial \alpha}{\partial \eta_c}\right) - \frac{\partial}{\partial n}\left\{\eta_s\left(\frac{\partial \alpha}{\partial \eta_s}\right)\right\}\right] \tag{32}$$

Eq. (32) contains zeroth, first order and second order of the derivatives of α. The typical value for the packing factor of fluid, for example water is 0.466.

We found that under the value of the fluid packing factor, all the terms containing α are very small and can be safely treated as zero no matter how the parameters of the suspended cylinder are varied under the low volume concentration assumption.

6. Conclusion

In this work, we have considered several mechanisms that might account for the high enhancement of thermal conductivity observed by many groups. We have given the exact result of enhancement of thermal conductivity due to the Brownian motion and estimated its order of magnitude. Our result indicates that although the enhancement of thermal conductivity is proportional to the volume fraction of nanofluid in the low concentration limit, at a given size of nanoparticle, the enhancement is proportional to $\frac{T}{\mu}$; however, the contribution is so small that it can be neglected. We discussed the possibility of the micro convection in the nanofluid and concluded that this phenomenon cannot happen because of the quick decay of the hydrodynamic field around the Brownian nanoparticles. We also discussed the phonon mean free path and phonon transport speed in nanofluid due to the existence of suspending nanoparticles. We found that only a thin layer of one nanometer may form around the nanoparticle and most of the base fluid molecules will remain unperturbed; hence there is no improvement on the structure of the fluid phase. By exploring the compressibility of the nanofluid with single spherical nanoparticle or aggregates of nanoparticles suspended, we noticed negligible changes in compressibility, which indicates the speed of phonon transport will not be affected due to the existence of nanoparticles in the low volume fraction limit.

Our result leads us to the conclusion that neither the motion of nanoparticles nor the structure of the fluid accounts for the enhancement of thermal conductivity in the nanofluid as observed by many groups. The continuum model and the layer structure model are correct; however, recently proposed models such as translational Brownian model and convective model cannot account for the enhancement of thermal conductivity because the translational Brownian model has been shown to have negligible effect and the convective model is not physically reasonable. Based upon what we analyzed here, the high observed thermal conductivity of nanofluid is questionable, because the continuous model and layer structure model cannot account for the enhancement reported so far and our conclusion here corresponds to the recent simulation work [46] and experimental work [47].

Although, the proposed mechanisms accounting for enhancement of thermal conductivity discussed in this paper do not work, it might not indicate that our conclusion is the final word on the nanofluid thermal conductivity enhancement. On one hand, we have omitted some other promising mechanisms suggested elsewhere, for example, the electrolytic structure of the base fluid plus particle system [48] and the percolation [49]; on the other hand, some recent simulation work such as [11] observed some thermal conductivity enhancement in the mixture of base fluid and subnanometer clusters mixture, though with very different materials. Therefore, both theoretical and experimental works are needed in the future.

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References

[1] C.H. Chon, Kenneth D. Kihm, Shin Pyo Lee, Stephen U.S. Choi, Appl. Phys. Lett. 87 (2005) 153107.
[2] R.L. Hamilton, O.K. Crosser, I & EC Fundam. 1 (1962) 187.
[3] B.X. Wang, L.P. Zhou, X.F. Peng, Int. J. Heat Mass Transfer 46 (2003) 2665.
[4] Q.A. Xue, W.M. X, Mater. Chem. Phys. 90 (2005) 283.
[5] H. Xie, M. Fujji, X. Zhang, Int. J. Heat Mass Transfer 48 (2005) 2926.

[6] P. Bhattacharya et al., J. Appl. Phys. 95 (11) (2004) 6492.
[7] R.K. Shukla, V.K. Dhir, in: Proceedings of IMECE, 2005.
[8] S.P. Jang, S.U.S. Choi, Appl. Phys. Lett. 84 (2004) 4316.
[9] R. Prasher, P. Bhattacharya, P.E. Phelan, J. Heat Transfer 128 (2006) 588.
[10] P. Keblinski, S.R. Phillpot, S.U.S. Choi, J.A. Eastman, Int. J. Heat Mass Transfer 45 (2002) 855.
[11] J. Eapen, J. Li, S. Yip, Phys. Rev. Lett. 98 (2007) 028302.
[12] R. Prasher, P. Bhattacharya, P.E. Phelan, Phys. Rev. Lett. 94 (2005) 025901.
[13] J. Che, T. Cagin, W. Deng, W.A. Goddard III, J. Chem. Phys. 113 (2000) 6888.
[14] R.S. Penciu, H. Kriegs, G. Petekidis, G. Fytas, E.N. Economou, J. Chem. Phys. 118 (2003) 5224.
[15] H. Kriegs, G. Petekidis, G. Fytas, R.S. Penciu, E.N. Economou, A.B. Schofield, J. Chem. Phys. 121 (2004) 7849.
[16] J. Koo, C. Kleinstreuer, J. Nanopart. Res. 6 (2004) 557.
[17] P. Keblinski, J. Thomin, Phys. Rev. E 73 (2006) 010502.
[18] S. Singh, K. Tankeshwar, K.N. Pathak, S. Ranganthan, J. Phys.: Condens. Matter 18 (2006) 1395.
[19] W.B. Russel, Ann. Rev. Fluid Mech. 13 (1981) 425.
[20] D. Macgowan, D.J. Evans, Phys. Lett. A 117 (1986) 414.
[21] S.A. Rice, J.G. Kirkwood, J. Chem. Phys. 31 (1959) 901.
[22] E. Bonaccurso, M. Kappl, H.J. Butt, Phys. Rev. Lett. 88 (2002) 076103.
[23] P.A. Thompson, M.O. Robbins, Phys. Rev. A 41 (1990) 6830.
[24] X. Zhou, D. Andrienko, L.D. Site, K. Kremer, J. Chem. Phys. 123 (2005) 104904.
[25] D. Andrienko, B. Dunweg, J. Chem. Phys. 119 (2003) 13106.
[26] M.T. Mathews, J.M. Hill, Quart. J. Mech. Appl. Math. 59 (2006) 191.
[27] T. Urbic, V. Vlachy, O. Pizio, K.A. Dill, J. Mol. Liquids 112 (2004) 71.
[28] D. Ghonasgi, W.G. Chapman, Mol. Phys. 79 (1993) 291.
[29] J.K. Johnson, K.E. Gubbins, Mol. Phys. 77 (1992) 1033.
[30] A. Galindo, P.J. Whitehead, G. Jackson, J. Phys. Chem. 100 (1996) 6781.
[31] Pavel B. Paramonov, Sergei F. Lyuksyutov, J. Phys. Chem. 123 (2005) 084705.
[32] C.J. Segura, W.G. Chapman, K.P. Shukla, Mol. Phys. 90 (1997) 759.
[33] V. Talanquer, D.W. Oxtoby, J. Chem. Phys. 112 (2000) 851.
[34] F.J. Blas, E.M.D. Rio, E.D. Miguel, G. Jackson, Mol. Phys. 99 (2001) 1851.
[35] J. Jarzynski, J.R. Smirnow, C.M. Davis Jr., Phys. Rev. 178 (1969) 288.
[36] N.W. Ashcroft, D.C. Langreth, Phys. Rev. 156 (1967) 685.
[37] S.B. Yuste, A. Santos, M.L. de Haro, J. Phys. Chem. 108 (1988) 3683.
[38] M. Schmidt, J. Phys.: Condens. Matter 15 (2003) S101.
[39] M.A. Miller, D. Frenkel, J. Phys.: Condens. Matter 16 (2004) S4901.
[40] J. Kumar, T.K. Dey, S.K. Sinha, J. Chem. Phys. 122 (2005) 224504.
[41] A. Estermann, H. Reich, M. Schmidt, Phys. Rev. E 73 (2006) 011407.
[42] P. Bolhuis, D. Frenkel, J. Chem. Phys. 101 (1994) 9869.
[43] L. Harnan, S. Dietrich, Phys. Rev. E 71 (2005) 011504.
[44] G.A. Vliegenthart, H.N.W. Lekkerkerker, J. Chem. Phys. 111 (1999) 4153.
[45] S.M. Oversteegen, H.N.W. Lekkerkerker, J. Chem. Phys. 120 (2004) 2470.
[46] W. Evans, J. Fish, P. Keblinski, Appl. Phys. Lett. 88 (2006) 093116.
[47] X. Zhang, H. Gu, M. Fujii, Exp. Therm. Fluid Sci. 31 (2007) 593.
[48] D. Lee, J.-W. Kim, B.G. Kim, J. Phys. Chem. B 110 (2006) 4323.
[49] R. Prasher, P.E. Phelan, P. Bhattacharya, Nano Lett. 6 (2006) 1529.