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Effect of Aggregation on Thermal Conduction in Colloidal Nanofluids

R Prasher, W Evans, J Fish, P Meakin, P Phelan and P Keblinski

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Ravi Prasher,

Intel Corporation, 5000 W. Chandler Blvd, Chandler, AZ 85226

William Evans,

Lockheed Martin Corporation, Niskayuna, New York 12301 and Mechanical Engineering Department, Rensselaer Polytechnic Institute, Troy, New York 12180

Jacob Fish,

Mechanical Engineering Department, Rensselaer Polytechnic Institute, Troy, New York 12180

Paul Meakin,

Idaho National Laboratory, Center for Advanced Modeling and Simulation, P.O. Box 1625, Mail Stop 2211, Idaho Falls, ID 83415

Patrick Phelan

Department of Mechanical and Aerospace Engineering, Arizona State University, Tempe, AZ 85287

Pawel Keblinski

Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, New York 12180

Using effective medium theory we demonstrate that the thermal conductivity of nanofluids can be significantly enhanced by the aggregation of nanoparticles into clusters. The enhancement is based purely on conduction and does not require a novel mechanism. Predictions of the effective medium theory are in excellent agreement with detailed numerical calculations on model nanofluids involving fractal clusters and show the importance of cluster morphology on thermal conductivity enhancements.

The mechanism behind the enhanced thermal conductivity (k) of nanoscale colloidal solutions (nanofluids) is a hotly debated topic[1,2]. For example a number of authors have proposed that Brownian motion induced nanoscale convection is a significant factor[3-5], while others have argued to the contrary[6-7]. The debate behind the mechanism was largely fueled by limited experimental characterization of the nanofluid systems. However, a number of recently reported experimental studies strongly suggest that nanoparticle aggregation plays a significant role in thermal transport in these nanofluids[8-12]. Yang and collaborators[11] demonstrated by light scattering measurements that Fe nanoparticles aggregate into micron size clusters. Kwak and Kim[12] demonstrated that large thermal conductivity enhancements are accompanied by sharp viscosity increases at low (<1%) nanoparticle volume fractions, which is indicative of aggregation effects. Lee *et al.*[10] demonstrated the critical importance of particle surface charge in nanofluids thermal conductivity. The surface charge is one of the primary factors controlling nanoparticle aggregation. Furthermore, Cahill and collaborators[13] demonstrated that nanofluids exhibiting good dispersion do not show any unusual enhancement of thermal conductivity.

In this letter, building upon recent work of Wang *et al.*[8] and Prasher *et al.*[14] on the effects of aggregation and its kinetics on thermal conductivity, we present a three-level homogenization theory to evaluate the effective thermal conductivity of colloids containing fractal clusters. In particular, our treatment allows the effect of cluster morphology to be evaluated in terms of the average radius of gyration, R_g, of the aggregates and the fractal and chemical dimension of the aggregates (d_f, and d_l,

respectively). We demonstrate that the presence of such fractal aggregates leads to a thermal conductivity enhancement that can be significantly higher than that predicted using homogenization theories of well-dispersed composites. The thermal conductivity enhancement is mainly attributed to the ability of the heat to move rapidly along the backbone of the cluster. The presented three-level homogenization model is validated by comparison to Monte Carlo (MC) numerical calculations of thermal conductivity of structures obtained by diffusion-limited cluster-cluster aggregation (DLCCA) algorithms. The three-level homogenization model's predictions match very well with the MC simulation results.

Following well-established understanding of the fractal morphology of nanoparticle clusters in colloids[15], we built our three-level homogenization analysis based of the model depicted in Fig. 1. As shown in Fig. 1, a fractal cluster is embedded within a sphere of radius equal to R_g and is composed of a few approximately linear chains, which span the whole cluster (aggregate) and side chains. The linear chains which span the whole cluster are called the backbone[15]. The other particles, which do not span the whole cluster, are called dead ends[15]. The backbone plays a significant role in the rheology of colloids because it is the only structure that can transfer elastic forces between clusters [15]. Due to its connectivity, the backbone is also expected to play a crucial role in thermal conductivity. In a previous study Prasher *et al.*[14] assumed that all particles were dead ends, i.e., that no linear chains were present.

Following the definition of the fractal dimension d_f, the number of particles in the cluster is given[14] by $N_{\text{int}} = (R_g / a)^{d_f}$ where a is the radius of the primary nanoparticle. Due to number conservation of the particles, $\phi_p = \phi_{int}\phi_a$, where ϕ_p is the volume fraction

of the nanoparticles, ϕ_{int} is the volume fraction of the nanoparticles in the aggregate or the cluster, and ϕ_a is the volume fraction of the aggregates. It can be shown that[14] $\phi_{\text{int}} = (R_g / a)^{d_f - 3}$ and[15] $(R_g / a)_{\max} = (\phi_p)^{1/(d_f - 3)}$ for which ϕ_a=1. The number of particles belonging to backbone, N_c, is defined by the chemical dimension, d_l, and is given by[15] $N_c = (R_g / a)^{d_l}$. d_l ranges between one and d_f. When $d_l = d_f$, all of the particles belong to the backbone and there are no dead ends. Therefore, the volume faction of backbone particles (ϕ_c) in the aggregate is given by $\phi_c = (R_g / a)^{d_l - 3}$. The volume fraction of the particles belonging to dead ends, ϕ_{nc}, is given by $\phi_{nc} = \phi_{\text{int}} - \phi_c$.

In the thermal model, the first level of homogenization is performed with only the particles belonging to the dead ends as shown in Fig. 1. The thermal conductivity of the aggregate due to dead end particles is calculated using the Bruggman model, which is preferable when high volume fractions of highly conductive particles are involved. This model is given by [14]

$$(1-\phi_{nc})(k_l - k_{nc})/(k_l + 2k_{nc}) + \phi_{nc}(k_p - k_{nc})/(k_l + 2k_{nc}) = 0 \qquad (1)$$

where k_{nc} is the effective thermal conductivity of the aggregate sphere in the presence of the dead-end particles only, k_p is the thermal conductivity of the nanoparticle, and k_l is the thermal conductivity of the liquid.

The effective thermal conductivity of the aggregate including the particles belonging to the backbone is calculated by assuming that the backbone is embedded in a medium with an effective conductivity of k_{nc}. Since the aspect ratio of the chains is significantly larger than one, we use the model by Nan et al.[16] for randomly oriented

cylindrical particles. Using Nan's model, the effective thermal conductivity of the aggregate sphere, k_a, with both the chains and dead ends (Fig. 1) is given by

$$k_a = k_{nc}\frac{3+\phi_c[2\beta_{11}(1-L_{11})+\beta_{33}(1-L_{33})}{3-\phi_c[2\beta_{11}L_{11}+\beta_{33}L_{33}]} \quad (2)$$

where $L_{11} = 0.5p^2/(p^2-1) - 0.5p\cosh^{-1}p/(p^2-1)^{1.5}$, $L_{33} = 1-2L_{11}$ and $\beta_{11} = (k_{nc}-k_l)/[k_l + L_{11}(k_{nc}-k_l)]$. p is the aspect ratio, which for the cluster spanning chain is given by $p = R_g/a$. Finally, following Prasher et al.[14] and Wang et al.[8] the effective thermal conductivity of the whole system is calculated using the Maxwell-Garnet (M-G) model, where the volume fraction and the thermal conductivity of the aggregates are used. Therefore, the effective thermal conductivity of the whole system is given by [14]

$$k/k_l = ([k_a + 2k_l] + 2\phi_a[k_a - k_l])/([k_a + 2k_l] - \phi_a[k_a - k_l]) \quad (3)$$

To provide a test bed for the homogenization procedure described above and to connect with well-known fractal nature of clusters observed in many colloidal suspensions of nanoparticles, we determined the thermal conductivity of model fractal aggregates obtained by diffusion controlled cluster-cluster aggregation. Cluster-cluster aggregation algorithms have been described in detail in the past[17]. In short, we randomly filled 10,000 sites on a cubic lattice to represent the nanoparticles. The remaining sites on the cubic lattice represent the volume occupied by the fluid. The overall size of the lattice was varied such that structures with particle volume fraction of 0.5%, 1.0%, 2.0%, and 4.0% were generated. Starting from the initial structures, particles were allowed to diffuse and form clusters upon contact followed by cluster diffusion and cluster aggregation. For each volume fraction, we prepared several independent sets of

aggregates at various aggregation states. We characterized the aggregates by the average radius of gyration, R_g, where the average is weighted by the number of particles in each aggregate. The inset in Fig. 2 shows a typical structure consisting of 30 aggregates. As described extensively in the literature[17], such an algorithm leads to fractal structures with $d_f \approx 1.8$ and $d_l \approx 1.4$. These values match the experimental data on diffusion controlled cluster aggregation well[15,17,18].

The effective thermal conductivity of model fractal colloids was obtained using a random walker Monte-Carlo (MC) algorithm[19]. In the simulations we selected the particle thermal conductivity to be 100 times larger than that of the fluid. Each MC simulation involved about 0.5 million MC steps, which is sufficient for adequate statistical accuracy.

Figure 2 shows the effective thermal conductivity as a function of the average radius of gyration obtained both from homogenization theory and from the MC. For homogenization theory, we used parameters matching the characterizing model fractal aggregates including; d_l = 1.4, d_f = 1.8 and k_p/k_l = 100. Figure 3 shows that the homogenization model matches the numerical Monte Carlo simulation well, and in both cases the effective thermal conductivity increases rapidly with initial increase of the aggregate size.

Figure 3 shows the thermal conductivity of a fully aggregated systems i.e for $(R_g / a)_{\max} = (\phi_p)^{1/(d_f - 3)}$ for different values of d_l. Figure 3 also shows the M-G model for well-dispersed particles. For randomly oriented long cylindrical objects for $k_p / k_l \to \infty$, k can be written as[16]

$$k / k_l = 1 + \phi_p k_p / (3k_l), \tag{4}$$

which represents an upper limit for conductivity enhancement within our model. Figure 3 shows that Eq. (4) matches well with the homogenization model for $d_l = d_f$ (all the particles belong to the backbone) for small volume fractions. This is because in this regime $(R_g/a)_{\max}$ is large, which makes the aspect ratio of the chains large. As we observed from the MC results, Eq. (4) is also applicable to larger volume fractions when a single cluster spanning the whole volume is present. In this case, however, the system is not, strictly speaking, fluid as it can support elastic load. Figure 3 also shows that with a typical value of d_l (1.4) the conduction is significantly enhanced in comparison to that predicted for a random dispersion.

In summary, by using three-level homogenization theory, as validated by MC simulations of heat conduction on model fractal aggregates, we have shown that the thermal conductivity of nanofluids based purely on conduction phenomenon can be significantly enhanced as a result of aggregation of the nanoparticles. The conductivity enhancement due to aggregation is a strong function of the chemical dimension of the aggregates and the radius of gyration of the aggregates. The model developed in this paper accounts for aggregation kinetics and the impact of chemistry of the system through their dependence of the radius of gyration[14].

References

1 P. Keblinski et al., Int. J. Heat and Mass Transfer **45**, 855 (2002);

2. P. Keblinski, J. A. Eastman, and D. Cahill, Materials Today, **8**, 23 (2005).

3. S.P Jang and S.U.S. Choi, Appl. Phys. Lett. **84**, 4316 (2004);

4. J. Koo, and C. Kleinstreuer, J. Nanoparticle Research **5**, 577, 2004;

5. R.S. Prasher et al., Phys. Rev. Lett. **94**, 025901 (2005);

6. W. Evans, J. Fish and P. Keblinski, Appl. Phy. Lett. **88**, 093116, (2006)

7. M. Vladkov and J-L Barrat, Nano Letters **6**, 1224, 2006

8 B-X. Wang et al., Int. J. Heat and Mass Transfer **46**, 2665 (2003);

9 Y. Xuan and W. Hu., AIChE Journal **49**, 1038, (2003);

10 D. Lee et al., J. Phys. Chemistry B. **110**, 4323 (2006)

11 K.S. Hong T.K. Hong and H.S Yang, Appl. Phy. Lett. **88**, 031901 (2006).

12 K, Kwak and C. Kim, Korea-Australia Rheology Journal **17**, 35 (2005).

13 A. Putnam et al., J. Appl. Phys. **99** 084308 (2006).

14 R.S. Prasher, P. E. Phelan, and P. Bhattacharya, Nano Letters 2006 (in press, available online)

15 W-H. Shih et al., Phys. Rev. A. **42**, 4772 (1990); R. de Rooji et al., J. Chem. Phy. **99**, 9213 (1993)

16 C-W. Nan et al., J. Appl. Phy., 81, 6692 (1997).

17 P. Meakin, Phys. Rev. Lett., 51, 1119 (1982); M. Kolb, R. Boter and R. Jullien, Phys Rev. Lett., 51, 1123 (1982); P. Meakin, Adv. Colloid Interface Sci. 28, 249 (1988), P. Meakin, I. Majid, S. Havlin and H. E. Stanley, J. Phys A: Math. Gen. 17, L975, (1984) .

18 W.B. Russel et al., Colloidal Dispersion, (Cambridge University Press, Cambridge), R.J. Hunter, Foundations of Colloid Science (Oxford University Press, New York)

19 C. DeW. Van Siclen, Phys. Rev. E. **59**, 2804 (1999).

List of figures

Figure 1: Schematic of the a single aggregate consisting of the backbone (black circles and dead ends (grey circles). The aggregate is decomposed into dead ends with the fluid and the backbone. Thermal conductivity of the aggregate with only particles belonging to the dead ends, k_{nc}, is calculated using the Bruggeman model. Linear chains are embedded inside a medium with effective conductivity of k_{nc}. The inset shows an example of an aggregate structure obtained by cluster-cluster aggregation algorithm with 30 aggregates at 1% volume fraction.

Figure 2: Comparison between the three-level homogenization model and Monte Carlo simulation for different values of particle volume fraction. The lines are the results of the effective medium model and the symbols are the results of the Monte Carlo simulation. The thermal conductivity of composites with well-dispersed particles is independent of the radius of gyration whereas for aggregated system it is a strong function of the radius of gyration.

Figure 3: Thermal conductivity of the nanofluid for a fully aggregated system for different values of chemical dimension (d_l). Thermal conductivity is a strong function of d_l and can be significantly higher than that of a composite made of well dispersed particles.

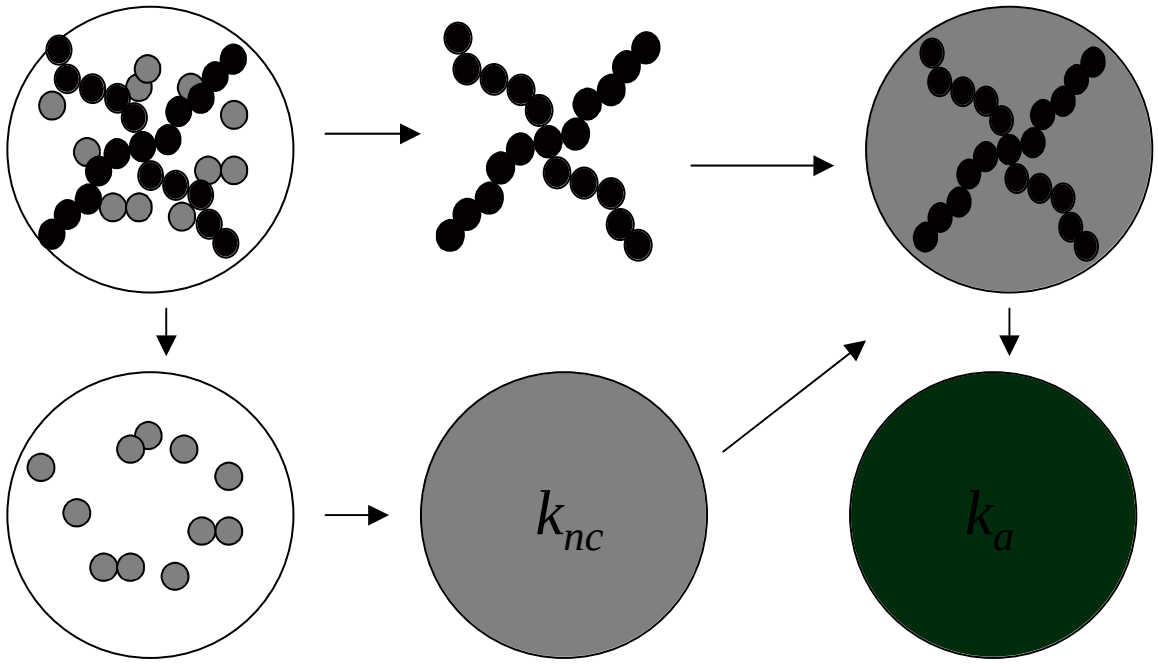

Figure 1

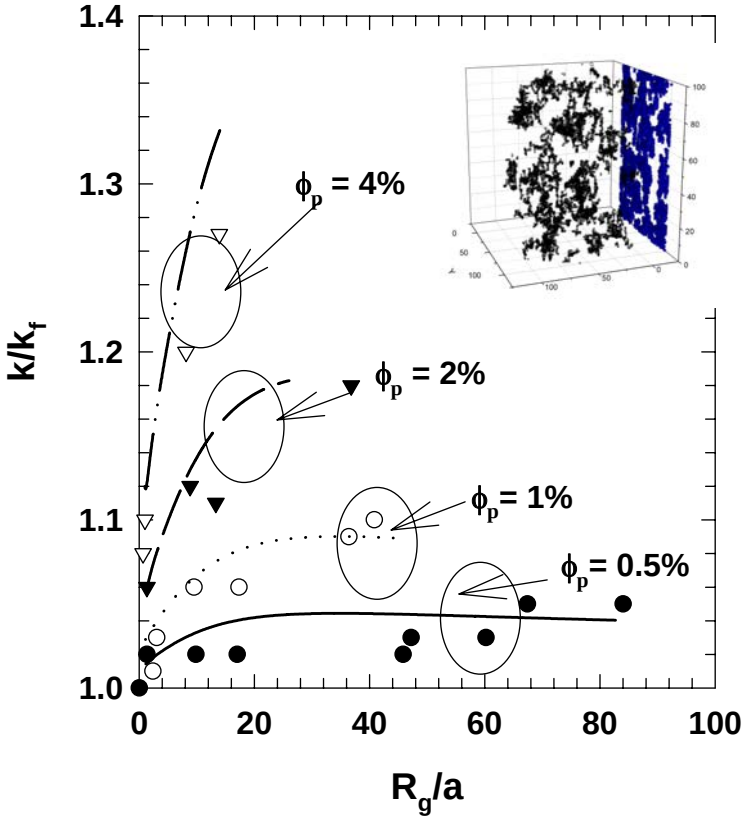

Figure 2

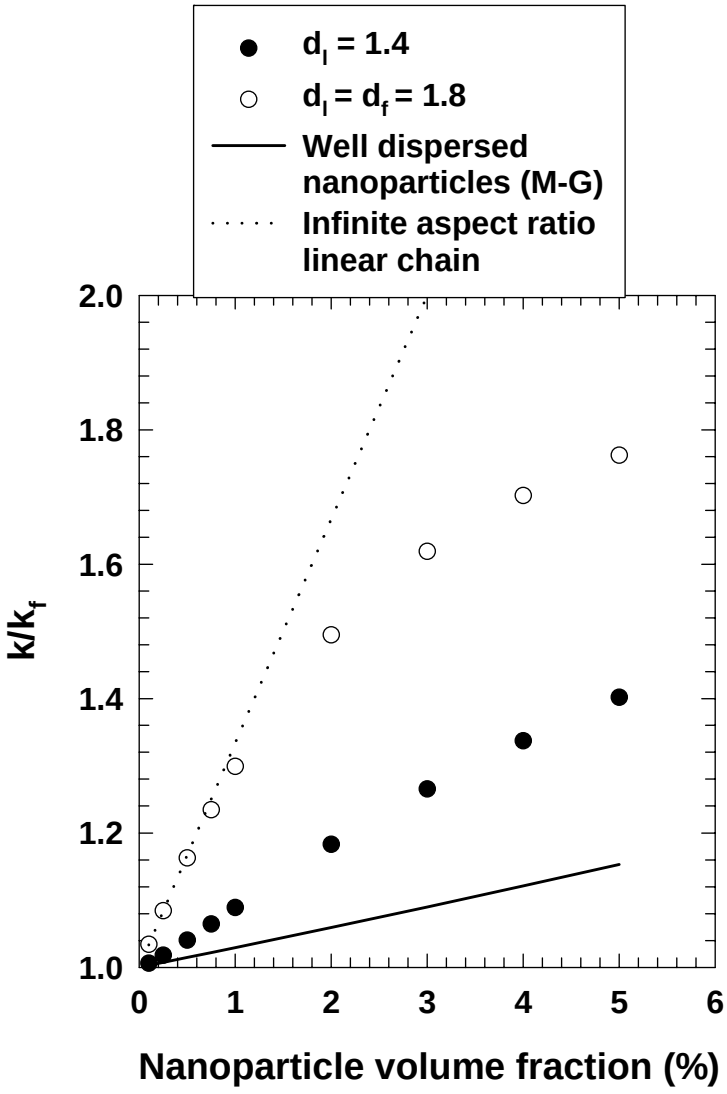
d_l = 1.4
$d_l = d_f$ = 1.8
Well dispersed nanoparticles (M-G)
Infinite aspect ratio linear chain
2.0
1.8
1.6
1.4
1.2
1.0
k/k_f
0
1
2
3
4
5
6
Nanoparticle volume fraction (%)

Figure 3