

Effect of aggregation on thermal conduction in colloidal nanofluids

Ravi Prasher^{a),b)}

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

William Evans

Lockheed Martin Corporation, Niskayuna, New York 12301

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

Paul Meakin

Idaho National Laboratory, Center for Advanced Modeling and Simulation, Idaho Falls, Idaho 83415

Jacob Fish

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

Patrick Phelan

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

Pawel Keblinski^{a),c)}

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

(Received 20 July 2006; accepted 23 August 2006; published online 6 October 2006)

Using effective medium theory the authors demonstrate that the thermal conductivity of nanofluids can be significantly enhanced by the aggregation of nanoparticles into clusters. Predictions of the effective medium theory are in excellent agreement with detailed numerical calculation on model nanofluids involving fractal clusters and show the importance of cluster morphology on thermal conductivity enhancements. © 2006 American Institute of Physics. [DOI: 10.1063/1.2360229]

The mechanism behind the exceptionally enhanced thermal conductivity (k) of nanoscale colloidal solutions (nanofluids) is a hotly debated topic.^{1,2} For example, a number of authors proposed that Brownian motion induced nanoscale convection is a significant factor,³⁻⁵ while others 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 the thermal transport in nanofluids.⁸⁻¹² In particular, Hong *et al.*¹¹ demonstrated by light scattering measurements that Fe nanoparticles aggregate into micron size clusters. Kwak and Kim¹² 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 nanofluid thermal conductivity. The surface charge is one of the primary factors controlling nanoparticle aggregation. Furthermore, Putnam *et al.*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 dimensions of

the aggregates (d_f and d_l , respectively). We demonstrate that such fractal aggregates lead to 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 homogenization model is validated by comparison with Monte Carlo (MC) numerical calculations of thermal conductivity of structures obtained by diffusion-limited cluster-cluster aggregation algorithms.

Following well-established understanding of the fractal morphology of nanoparticle clusters in colloids,¹⁵ we built our homogenization analysis based on the model depicted in Fig. 1. According to 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 are called

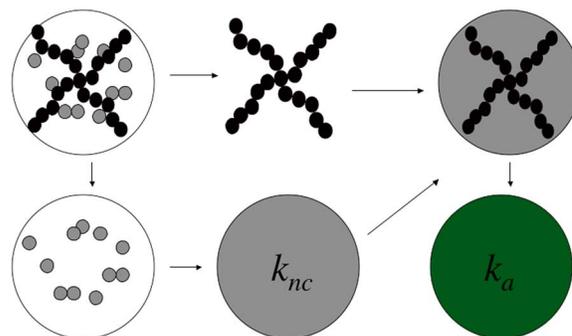


FIG. 1. (Color online) Schematic of a single aggregate consisting of the backbone (black circles) and dead ends (gray circles). The aggregate is decomposed into dead ends with the fluid and the backbone. Thermal conductivity of the aggregate only with particles belonging to the dead ends, k_{nc} , is calculated using the Bruggeman model. Linear chains are embedded inside a medium with effective conductivity of k_{nc} .

^{a)} Authors to whom correspondence should be addressed.

^{b)} Electronic mail: ravi.s.prasher@intel.com

^{c)} Electronic mail: keblip@rpi.edu

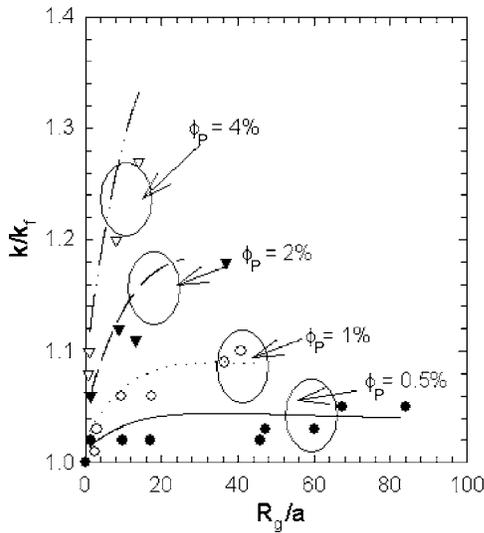


FIG. 2. Comparison between the three-level homogenization model (lines) and Monte Carlo simulation (symbols) for different values of particle volume fraction as a function of the radius of gyration.

the backbone of the cluster, while the other particles are called dead ends.¹⁵ The backbone plays a significant role in the rheology of colloids because it is this 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 the previous studies^{8,14} no linear chains were considered explicitly.

Following the definition of the fractal dimension d_f , the number of particles in the cluster is given¹⁴ by $N_{int} = (R_g/a)^{d_f}$ 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 that¹⁴ $\phi_{int} = (R_g/a)^{d_f-3}$ and¹⁵ $(R_g/a)_{max} = (\phi_p)^{1/(d_f-3)}$ for which $\phi_a = 1$. The number of particles belonging to the backbone, N_c , is defined by the chemical dimension d_l and is given by¹⁵ $N_c = (R_g/a)^{d_l}$. d_l ranges between 1 and d_f . When $d_l = d_f$, all the particles belong to the backbone and there are no dead ends. Therefore, the volume fraction of backbone particles (ϕ_c) in the aggregate is given by $\phi_c = (R_g/a)^{d_f-3}$. The volume fraction of the particles belonging to dead ends, ϕ_{nc} , is given by $\phi_{nc} = \phi_{int} - \phi_c$.

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 Bruggeman model, which is preferable when high volume fractions of highly conductive particles are involved. This model is given by¹⁴

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

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

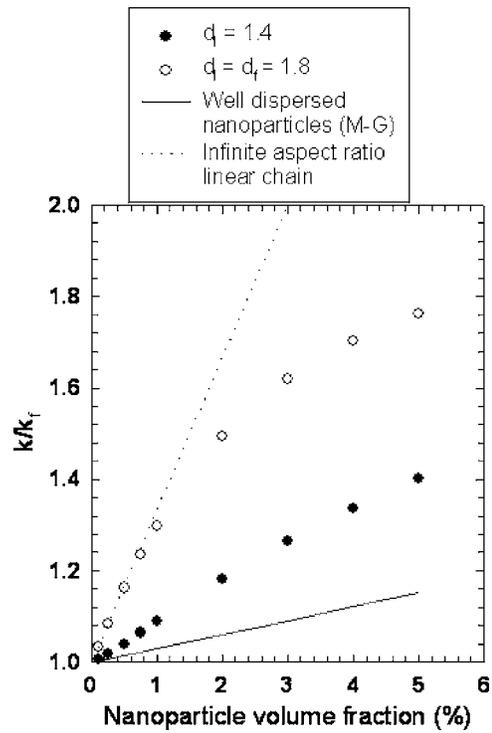


FIG. 3. Thermal conductivity of the nanofluid for a fully aggregated system for different values of chemical dimension (d_l). Thermal conductivity is a strong function of d_l and can be significantly higher than that of a composite made of well-dispersed particles.

with an effective conductivity of k_{nc} . Since the aspect ratio of the chains is significantly larger than 1, we use the model by Nan *et al.*¹⁶ for randomly oriented cylindrical particles. Using the model by Nan *et al.*, the effective thermal conductivity of the aggregate sphere (k_a) with both the chains and dead ends (Fig. 1) is given by

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

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 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 by¹⁴

$$k/k_f = ([k_a + 2k_l] + 2\phi_a[k_a - k_l])/([k_a + 2k_l] - \phi_a[k_a - k_l]). \tag{3}$$

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 algorithm has been described in detail in the past.¹⁷ In short we randomly fill 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 is varied such that structures with particle volume fractions of 0.5%, 1.0%, 2.0%, and 4.0% are 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. As described extensively in the literature,¹⁷ such algorithm leads to fractal structures with $d_f \approx 1.8$ and $d_l \approx 1.4$. These values represent the experimental data on diffusion controlled cluster aggregation very well.^{15,17,18}

The effective thermal conductivity of model fractal colloids was obtained using a random walker (MC) algorithm.¹⁹ In our simulations a random walker attempts to move randomly with equal probability into one of the six directions on a cubic lattice. The probability of a successful move is equal to $k_{in}/(k_{in}+k_{fi})$, where k_{in} and k_{fi} are the conductivities of the cubes at which the walker resides and to which it attempts to move, respectively.¹⁹ Regardless of the success of the move the clock is advanced by the time proportional to $1/k_{in}$. The effective conductivity is calculated from the slope of the walker mean square displacement as a function of time. In the simulations we selected the particle thermal conductivity to be 100 times larger than that of the fluid. Each MC simulation involved about 0.5×10^6 MC steps, 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 MC simulations. For homogenization theory, we used parameters matching those characterizing model fractal aggregates including $d_l=1.4$, $d_f=1.8$, and $k_p/k_l=100$. Figure 2 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 system, i.e., for $(R_g/a)_{\max}=(\phi_p)^{1/(d_f-3)}$ for different values of d_l . For randomly oriented long cylindrical objects for $k_p/k_l \rightarrow \infty$, k can be written as¹⁶ $k/k_l=1+\phi_p k_p/(3k_l)$ which represents an upper limit for conductivity enhancement within our model. Figure 3 shows that at low volume fraction the conductivity characterizing composites of long cylinders matches very well with that obtained by the homogenization model when $d_l=d_f$ (all the particles belong to the backbone). This is because in this regime $(R_g/a)_{\max}$ is large which in turn makes the aspect ratio of the chains large.

Figure 3 also shows that with a typical value of d_l (1.4) the conduction is significantly enhanced by comparison with that predicted for a random dispersion.

In summary, using three-level homogenization theory 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 the letter can easily include the aggregation kinetics and the impact of chemistry of the system, based on dependence of the radius of gyration on these factors.¹⁴ Furthermore, the effect of the thermal interfacial resistance,² which we neglected in the present analysis, can be also incorporated.

¹P. Keblinski, S. R. Phillpot, S. U. S. Choi, and J. A. Eastman, *Int. J. Heat Mass Transfer* **45**, 855 (2002).

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

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

⁴J. Koo and C. Kleinstreuer, *J. Nanopart. Res.* **5**, 577 (2004).

⁵R. S. Prasher, P. Bhattacharya, and P. E. Phelan, *Phys. Rev. Lett.* **94**, 025901 (2005).

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

⁷M. Vladkov and J.-L. Barrat, *Nano Lett.* **6**, 1224 (2006).

⁸B.-X. Wang, L. P. Zhou, and X. F. Peng, *Int. J. Heat Mass Transfer* **46**, 2665 (2003).

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

¹⁰D. Lee, J. W. Kim, and B. G. Kim, *J. Phys. Chem. B* **110**, 4323 (2006).

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

¹²R. Prasher, P. E. Phelan, and P. Bhattacharya, *Nano Lett.* **6**, 1529 (2006).

¹³A. Putnam, D. G. Cahill, P. V. Braun, Z. B. Ge, and R. G. Shimin, *J. Appl. Phys.* **99**, 084308 (2006).

¹⁴R. S. Prasher, P. E. Phelan, and P. Bhattacharya, *Nano Lett.* (in press).

¹⁵W.-H. Shih, W. Y. Shih, S.-I. Kim, J. Liu, and I. A. Aksay, *Phys. Rev. A* **42**, 4772 (1990); R. de Rooij, A. A. Potanin, D. van den Ende, and J. Mellema, *J. Chem. Phys.* **99**, 9213 (1993).

¹⁶C.-W. Nan, R. Birringer, D. R. Clarke, and H. Gleiter, *J. Appl. Phys.* **81**, 6692 (1997).

¹⁷P. Meakin, *Phys. Rev. Lett.* **51**, 1119 (1982); M. Kolb, R. Boter, and R. Jullien, *ibid.* **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* **17**, L975 (1984).

¹⁸W. B. Russel, D. A. Saville, W. R. Schowalter, M. J. Ablowitz, S. H. Davis, E. J. Hinch, A. Iserles, J. Ockendon, and P. J. Olver, *Colloidal Dispersion* (Cambridge University Press, Cambridge, 1992); R. J. Hunter, *Foundations of Colloid Science* (Oxford University Press, New York, 1992).

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