Enhanced Heat Transport via Collective Modes in Confined Nanofluids

Philippe BEN-ABDALLAH Laboratoire de Thermocinétique, CNRS UMR 6607 Ecole Polytechnique Université de Nantes Rue Christian Pauc, 44 306 Nantes cedex 03 FRANCE

Abstract: - The collective transport of heat in nanofluids confined between two soft parallel walls is studied by extensive Brownian-dynamics simulations. We show that the particle interactions mediated by the walls improve the spatial order and drastically enhance heat transport.

Key-Words: Colloid, Brownian dynamics, Thermal properties of condensed matter, Nanoparticle, Cooling, Micro- and nano-electromechanical system.

1 Introduction

Nanofluids [1-2] are liquids containing suspended nanometer-size solid particles. Many of these colloidal suspensions have displayed [1,3-4] an abnormally high thermal conductivities that the classical theory of effective media [5] fails to explain. These observations have caused a strong interest in the scientific community (see refs. 6 and 7 for a recent review) because it paved the way to a wide variety of applications ranging from the transportation and energy production to promising fluidic cooling technologies. Considerable efforts have been, since then, devoted both theoretically and experimentally, to understand the origin of this unexpected result. Today, this remains a challenging problem and only partial conclusions have been reached. However, in a recent work Vladkov and Barrat [8] have shown that the collective motion of particles plays a predominant role in the transport of heat.

In a numerical work Battacharya et al. [9] used Brownian dynamic simulations to investigate heat transport in unconfined nanofluids from the self-ordered motion of particles. Their model was shown to predict qualitatively well the concentration and size dependence of the thermal conductivity. In the present paper we focus on the collective transport of heat in nanofluids confined in quasi-two-dimensional geometries. In such configurations, the heat transport mechanisms are more complex than in unconfined colloids since the motion of particles is also coupled to confining walls. We by extensive Brownian demonstrate dynamics simulations that the heat transport throughout the selfordered motion of particles is more important in these geometries than in unconfined nanofluids. We show also that this enhancement results from the coupling of particles with the walls which considerably increases the

spatial order of colloids at short range and so promotes collective modes.

2 Brownian motion model

Let us start by describing the system we consider in this study. It consists on N identical, spherical, Brownian particles of radius R dispersed at positions $(r_1, r_2, ..., r_N)$ between two parallel walls (fig.1) in a viscous incompressible solvent made with infinitely smaller molecules (i.e. $r_{fluid} \ll R$).



Fig. 1 : Snapshot after equilibration of an instantaneous configuration for a LJ nanofluid (d = 80 nm) in a quasi-2D channel of height h = 240 nm. Lengths have been rescaled for readability reasons.

In this system, the short-range repulsive interaction and the van der Waals (vdW) attraction between particles i and j are modeled by a truncated shifted and smoothed Lennard-Jones (TSSLJ) potential

$$u(r_{ij}) = \begin{cases} V_{LJ}(r_{ij}) - V_{LJ}(r_c) - \left(\frac{dV_{LJ}}{dr_{ij}}\right)_{r_{ij}=r_c} (r_{ij} - r_c) & r_{ij} \le r_c \\ 0 & r_{ij} > r_c \end{cases}$$
(1)

where $V_{LJ}(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$ is a 12-6 LJ potential,

 $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ stands for the interparticle distance while r_c , ε and σ represent the cutoff radius of TSSLJ potential and the LJ parameters, respectively.

All particles interact also with the walls $z = \pm h/2$ via the purely repulsive soft potential (sticking on these walls is prohibited)

$$u_{wall}(z) = \begin{cases} \alpha \widetilde{\varepsilon} \left[\left(\frac{\widetilde{\sigma}}{h/2 - |z|} \right)^{10} - \left(\frac{\widetilde{\sigma}}{h/2 - |z|} \right)^4 \right] - \widetilde{\varepsilon} & |z| \le \gamma \\ 0 & |z| > \gamma \end{cases}$$
(2)

where $\gamma = \frac{h}{2} - (\frac{5}{2})^{1/6} \tilde{\sigma}$. Here h is the separation distance between the upper and lower surfaces, $\alpha = (\frac{1}{z_{\min}})^{10} - (\frac{1}{z_{\min}})^4$ and $z_{\min} = (5/2)^{1/6} \tilde{\sigma}$ is the position where μ is minimum. The translational

position where u_{wall} is minimum. The translational dynamic of particles in the host fluid is then described by the N-body Langevin equation

$$m\dot{\boldsymbol{v}}_{i} = -\overline{\overline{\boldsymbol{\xi}}}_{ij} \boldsymbol{v}_{j} + \boldsymbol{F}_{i} + \overline{\overline{\boldsymbol{a}}}_{ij} \boldsymbol{f}_{j}, \qquad (3)$$

where \mathbf{v}_i is the linear velocity of the particle i, $\overline{\boldsymbol{\xi}}$ is the $(3N \times 3N)$ friction tensor, F_i is the sum of interparticle and wall-particle forces acting in the i th particle while f_j represents here a Gaussian field with zero mean and covariance $\langle f_i(t)f_j(t')\rangle = 2\delta_{ij}\delta(t-t')$. According to the fluctuation disipation theorem [10], the random force $\overline{\boldsymbol{\alpha}}_{ij}f_j$ exerted on the particle by the surrounding fluid is related to the friction tensor by the relation $\xi_{ij} = (k_B T)^{-1} \sum_{l} \alpha_{il} \alpha_{jl}$. The system of coupled equations (3) might be solved using the Ermak and McCammon algorithm [11]

$$\mathbf{r}_{i}(t+\delta t) = \mathbf{r}_{i}(t) + \frac{1}{k_{B}T} \sum_{j=1}^{N} \mathbf{D}_{ij}(t) \mathbf{F}_{j}(t) + \delta \mathbf{\hat{r}}_{i}$$
(4)

where $\delta \hat{\mathbf{r}}_i$ denotes the N-correlated displacement vector and $\overline{\mathbf{D}}_{ij}$ is the Kirkwood diffusion tensor which describes the hydrodynamic interactions in the host fluid is related to the friction tensor by the simple relation $\sum_j D_{ij} \xi_{jl} = k_B T \delta_{il}$. In order to satisfy the assumptions of Ermak and McCammon algorithm, a time step δt is chosen much smaller than the Brownian time (i.e. time necessary for a nanoparticle to move through a distance equivalent to its diameter) and much greater than the momentum relaxation time (i.e. time interval Δt beyond which the velocity $v_i(t + \Delta t)$ of a particle is uncorrelated with the velocity $v_i(t)$). In our simulations, this condition is always fulfilled because there is at least two orders of magnitude between both characteristic times. In our simulations, the diffusion tensor is approximated by the (positive-definite) Rotne-Prager expression [12]

$$\boldsymbol{D}_{ij} = \begin{cases} \frac{k_B T}{6\pi\eta R} \overline{\mathbf{I}} & (i=j) \\ \frac{k_B T}{6\pi\eta r_{ij}} [(\overline{\mathbf{I}} + \frac{\boldsymbol{r}_{ij} \otimes \boldsymbol{r}_{ij}}{r_{ij}^2}) + \frac{2R^2}{r_{ij}^2} (\frac{1}{3} \overline{\mathbf{I}} - \frac{\boldsymbol{r}_{ij} \otimes \boldsymbol{r}_{ij}}{r_{ij}^2})] & (i \neq j) \end{cases}$$

In this expression η represents the viscosity of host fluid, $\overline{\overline{\mathbf{I}}}$ is the unit dyadic tensor and \mathbf{r}_{ij} is the vector which relates the center of particle j to the center of particle i. In order for the dynamics to satisfy the fluctuation-dissipation theorem, the stochastic displacement vector in relation (4) must verifies the supplementary constraints $\langle \delta \hat{\mathbf{r}}_i \rangle = 0$ and

$$\left< \delta \hat{\boldsymbol{r}}_i \delta \hat{\boldsymbol{r}}_j \right> = 2 \boldsymbol{D}_{ij} \delta t$$

All our simulations are started with an fcc configuration and the system is equilibrated with at least 30000 time steps. The duration of this equilibration phase is a posteriori checked from the relaxation curve of the cohesion energy (not plotted here). The transport properties are calculated using the linear response theory with 1000 supplementary time steps while the static structural properties i.e. the pair distribution functions, are calculated with at least 50 000 time steps. Periodic boundary conditions were applied in the x and y directions (Fig.1) and calculations are carried out with adimensioned variables built from the following references quantities : length $r^* = 2R$, temperature $T^* = \varepsilon / k_B$, mass of particles $m^* = m$, dynamic viscosity $\eta^* = (m\varepsilon)^{1/2} / (4R^2)$, time $t^* = 2(mR^2)^{1/2} / \varepsilon$ and diffusion $D_{ij}^* = 2(\varepsilon R^2 / m)^{1/2}$. The values of the dynamic viscosity, of the temperature, of the mass density of particles and the volume fraction of nanoparticles used in our simulations are $\eta = 159 \times 10^{-4} N.s.m^{-2}$ (ethylene glycol viscosity), T = 300K, $\rho = 3970 kg.m^{-3}$ (aluminum density) and $\phi = 1\%$, respectively. The potential parameters used in the present work are $\varepsilon = 5k_{\scriptscriptstyle R}T$, $\tilde{\varepsilon} = 0.01\varepsilon$, $\sigma = \tilde{\sigma} = d$ and $r_c = 1,5\sigma$ while the number N of particle is fixed to 108.

3 Lattice thermal conductivity

We now focus our attention on the transport of heat from the collective modes of particles, i.e. natural phonons, caused by their self-ordered motion in the host fluid. In quasi-2D geometries only the longitudinal modes are meaningful. Therefore we restrict ourselves to the investigation of transport from the longitudinal (i.e. in the x-y plane) modes. The longitudinal lattice thermal conductivity (LTC) $\kappa_L^{\prime\prime}$ is calculated from the autocorrelation function $C_{\prime\prime}(t) = \langle \mathbf{Q}_{\prime\prime}(0).\mathbf{Q}_{\prime\prime}(t) \rangle$ of parallel heat flux vector $\mathbf{Q}_{\prime\prime}(t) = [Q_x(t), Q_y, 0]$ using the Green-Kubo formula [13]

$$\kappa_{L}^{\prime\prime}(T) = \frac{V}{2k_{B}T^{2}} \int_{0}^{\infty} C_{\prime\prime}(t) dt , \qquad (6)$$

where V represents the volume of the simulation box. The brackets in this expression stand for the statistical average of the autocorrelation function. Without metastable state (here ergoticity is assured by the weakness of short-ranged attractive interactions) the statistical averages is identified to the time average over the duration of the experiment i.e. $\langle O \rangle \equiv \langle O \rangle_{time} = \lim_{\tau_{obs} \to \infty} \frac{1}{\tau_{obs}} \sum_{\tau=0}^{\tau_{obs}} O(j(\tau))$ where τ_{obs} is

the duration of a numerical run. As for the heat flux operator, it is calculated from the x-y projection \mathbf{v}_i'' of the particles velocity $\mathbf{v}_i = [\mathbf{r}_i(t+\delta t) - \mathbf{r}_i(t)]/\delta t$, the

particles energy $e_i = \sum_j u(r_{ij}) + \frac{1}{2}mv_i^2$ and the

interparticle forces \mathbf{F}_{ij} according to [14]

$$\boldsymbol{Q}_{\prime\prime\prime}(t) = \frac{1}{V} \left[\sum_{i} \mathbf{v}_{i}^{\prime\prime} \boldsymbol{e}_{i} + \frac{1}{2} \sum_{i} \sum_{l \neq i} (\mathbf{F}_{il} \cdot \mathbf{r}_{il}) \mathbf{v}_{i}^{\prime\prime} \right].$$
(7)

In figure 2, we present the evolution of $\kappa_L^{\prime\prime}$ versus the separation distance h for different nanoparticle sizes. Below a threshold distance (~20 particle diameters), $\kappa_L^{\prime\prime}$ exponentially increases. We see that the LTC under confinement is in essential contrast with that unconfined nanofluids. An enhancement of one order of magnitude is observed when $h/d \approx 3$. Ultraconfinement (colloidal monolayer) has not been considered in this work for numerical stability reasons. However a linear extrapolation of our results plotted in Fig.2 shows that an enhancement of at least 2 orders of magnitude can be reached in these configurations. It is obviously a direct consequence of particles coupling with the channel walls.



Fig. 2 : Lattice thermal conductivity enhancement of LJ nanofluids versus the inter-plate separation distance h. Symbol shapes correspond to different particles diameter : 20 nm (deltas), 50 nm (circles), 80 nm (squares).

4 Structural order

In order to explain the thermal conductivity enhancement highlighted above let us now analyze in details the static structure of nanofluids under confinement. Based on the simulation data, the pair distribution function

$$g(\mathbf{r}^{xy}) = \frac{V}{N^2} \left\langle \sum_{i} \sum_{i \neq j} \delta(\mathbf{r}^{xy} + \mathbf{r}_j^{xy} - \mathbf{r}_i^{xy}) \right\rangle \Big|_{|\Delta z| < \frac{1}{2}\sigma}$$
(8).

restricted to the particle position $\mathbf{r}^{xy} = \mathbf{r} - \mathbf{z}$ in the x-y plane is calculated. In homogeneous and unconfined nanofluids, the pair distribution function $g(\mathbf{r}^{xy})$ is related to its 3D counterpart $g(\mathbf{r}) = \frac{V}{N^2} \left\langle \sum_{i \ i \neq j} \delta(\mathbf{r} - \mathbf{r}_i - \mathbf{r}_j) \right\rangle$ by the simple relation $\lim_{|\Delta z| \to 0} g(\mathbf{r}^{xy}) = g(\mathbf{r})$, since all directions of space are statistically equivalent.

In figure 3 the calculated values of $g(\mathbf{r}^{xy})$ shows that, the confinement affects the spatial correlation of particles both at short and long distance. Close to contact ($\mathbf{r} \sim d$), the height of the first peak of correlation increases compared to that observe in the bulk system (i.e. periodic boundary conditions in the three directions of space) meaning so that the presence of solid walls improves the structural order at short distance. At long range an another interesting structural order appears in many situations. For sufficiently large particle sizes, $g(\mathbf{r}^{xy})$ slightly oscillates with a period approximately twice equals to the inter-plate separation distance. Moreover, $g(\mathbf{r}^{xy})$ decays to approximately 1,4 at large distance. This is a clear indication of the formation of a high density in the x-y plane under the action of wall forces. In contrary, the pair distribution function along the z axis (not plotted here) goes below 1 sufficiently large distances (close to the walls) in agreement with the strong inhomogeneity in the transversal distribution of particles.

In addition, because the LTC enhancement takes place for any particles size and even it is maximum with the smallest particles we may conclude that the magnification process highlighted above is closely related to short ranged correlations.



Fig. 3 : Pair correlation function in the x-y plane in quasi-2D channel (h/d = 3) for different particle diameter d. Symbol shapes correspond to different diameters : d = 20 nm (deltas), d = 50 nm (circles), and d = 80 nm (squares). The solid line represents the pair correlation function of bulk nanofluids (i.e. periodic boundary conditions are applied in the three directions of space) with particle sizes of 20 nm.

These can be analyzed as follow. First of all note that the first peak of correlation increases significantly (compared to the first peak in the bulk) with the particle size meaning that the interactions mediated by the confining walls are more positive (i.e. particles drag more a given particle in the same direction) when the particles size decreases. Such an effect promotes the self ordered motion (collective modes) of particles while a dual mechanism, i.e. an anti-drag-like mechanism [15], would inhibited the collective motion of particles. In addition to the evolution of the magnitude of first peaks, we see also that, they spread out, under confinement. This effect is more marked when the particle size is small and it increases the range of short correlations. This clearly tends to dope the thermal conductivity and explains qualitatively well the results observed in Fig. 2.

5 Conclusion

In summary, the confinement has been observed to strongly enhance the lattice thermal conductivity of nanofluids. This unexpected behavior is due to short ranged interactions mediated by the confining walls that increase the structural order and improve the self ordered motion of particles. These results open interesting prospects for the thermal management of micro and nanoscales systems.

However the consequences of confinement on the apparent viscosity of nanofluid should be estimated before considering furthermore nanofluidic cooling devices at these scales.

The influence of wetting properties on the transport of heat in confined systems seems also a promising area for future research.

References:

- [1] J. A. Eastman, S. U. S. Choi, S. Li, W. Yu, and L. J. Thompson, anomalously increased effective thermal conductivities of ethylene glycol-base nanofluids containing copper nanoparticles, Appl. Phys. Lett., Vol. 78, 2001, pp. 718-720.
- [2] J. A. Eastman, S. R. Phillpot, S. U. S. Choi and P. Keblinski, Thermal transport in nanofluids, Annu. Rev. Mater. Res., Vol. 34, 2004, pp. 219-246.
- [3] S. Lee, S. U. S. Choi and J. A. Eastman, Measuring thermal conductivity of fluids containing oxide nanoparticles, J. Heat Transfer, Vol. 121, 1999, pp. 28-289.
- [4] S.K. Das, N. Putra, P. Thiesen and W. Roetzel, Temperature Dependence of Thermal Conductivity Enhancement for Nanofluids, J. Heat Transfer, Vol. 125, 2003, pp. 567-574.
- [5] R. L. Hamilton and O. K. Crosser, Thermal conductivity of heterogeneous two-component systems, Ind. Eng. Chem. Fundam., Vol. 1, 1962, pp. 187-191.

- [6] P. Keblinski, J. A. Eastman and D. G. Cahill, Nanofluids for thermal transport, Materials Today, Vol. 8, 2005, pp. 36-44.
- [7] R. Prasher, P. Bhattacharya and P. E. Phelan, Thermal conductivity of nanoscale colloidal solutions (nanofluids), Phys. Rev. Lett., Vol. 94, 2005, 025901.
- [8] M. Vladkov and J. L. Barrat, Modelling transient absorption and thermal conductivity in a simple nanofluid, preprint cond-mat/0603704 (2006).
- [9] P. Bhattacharya, S. K. Saha, A. Yadav, P. E. Phelan, and R. Prasher, Brownian dynamics simulation to determine the effective thermal conductivity of nanofluids, J. Appl. Phys., Vol. 95, 2004, pp. 6492-6494.
- [10] H. B. Callen and T. A. Welton, Irreversibility and generalized noise, Phys. Rev., Vol. 83, 1951, pp.1.
- [11] D. L. Ermak and J. A. McCammon, Brownian dynamics with hydrodynamic interactions, J. Chem. Phys., Vol. 69, 1978, pp. 1352.
- [12] J. Rotne and S. Prager, Variational treatment of hydrodynamic interaction in polymer, J. Chem. Phys., Vol. 50, 1969, pp. 4831.
- [13] R. Kubo, M. Toda and N. Hashitsume, Statistical Physics, Berlin, Springer, 1985.
- [14] Y. H. Lee, R. Biswas, C. M. Soukoulis, C. Z. Wang, C. T. Chan, and K. M. Ho, Molecular dynamics simulation of thermal conductivity in amorphous silicon, Phys. Rev. B, Vol. 43, 1991, pp. 6573-6580.
- [15] B. Cui, H. Diamant, B. Lin and S. Rice, Anomalous hydrodynamic interaction in a quasitwo-dimensional suspension, Phys. Rev. Lett., Vol. 92, 2004, 258301.