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Energy Procedia 00 (2015) 000–000

Energy Procedia

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SHC 2015, International Conference on Solar Heating and Cooling for Buildings and Industry

Towards a multiscale simulation approach of nanofluids for volumetric solar receivers: Assessing inter-particle potential energy

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Abstract

A modern concept for solar thermal collectors is based on volumetric absorption of sunlight, where nanoparticles suspended in liquids directly receive the incident radiation. Suspending nanoparticles in traditional fluids can drastically enhance their optical properties and improve thermo-physical performances, thus leading to highly efficient volumetric solar receivers. Several studies have been addressed on the physical understanding of such nanosuspensions; however, the relation between nanoscale effects and macroscopic properties is far from being fully understood. The present work represents a first step towards a multiscale modeling approach for relating nanoscale properties to macroscopic behaviour of nanofluids. In particular, a suitable Coarse-Grained (CG) method for nanofluids is described. By means of Molecular Dynamics (MD) simulations, the pair Potential of Mean Forces (pPMF) between CG beads of nanofluid is evaluated. A complete CG force field can be then defined by including the effects of water adsorbed at solid-liquid interface, nanoparticle surface charge and solution pH. Our multiscale model is intended to permit a future study of the complex mechanisms of nanoparticle clustering, which is known to affect nanofluids stability and properties. We hope that this multiscale approach may start the process of rational design of nanofluids thus facilitating technology transfer from lab experiments to large-scale industrial production.

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Keywords: Direct absorption; Solar energy; Nanofluids; Coarse-graining; Molecular dynamics; Multiscale modeling

1. Introduction

The majority of current solar thermal technologies exploits absorbing surfaces for converting solar radiation into thermal energy, which is in turn transferred to a carrier fluid by conduction. Such surfaces are designed to have both

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Peer-review by the scientific conference committee of SHC 2015 under responsibility of PSE AG.

high absorptivity in the solar spectrum and low emissivity in the infrared. However, the thermal resistance between heat transfer fluid and absorbing surface may induce large temperature differences between fluid and absorber, therefore leading to significant emissive losses and thus reducing the overall solar energy conversion efficiency [1]. These thermal re-radiation losses are particularly evident at high levels of solar concentration, as in Concentrated Solar Power (CSP) plants.

On the other hand, volumetric solar receivers are based on fluids directly absorbing the incident radiation, which leads to decreased temperature differences between absorber and carrier fluid [2]. Nanofluids are engineered suspensions of nanoparticles, which show peculiar optical, heat and mass transport properties in both engineering [3-6] and biomedical applications [7-9]. Because of these characteristics and of the large surface to volume ratio, nanoparticle suspensions have been investigated as solar absorbing fluids for highly efficient volumetric receivers [10, 11]. However, the multiscale nature of nanofluids makes difficult to relate nanoscale characteristics with resulting macroscopic properties. In particular, the complex mechanism of nanoparticle clustering is known to rule nanofluids stability as well as effective optical and thermal properties [12, 13]. In order to properly take into consideration nanoscale effects in nanofluids, multiscale simulation methods are needed to guide their accurate prediction and rational design in the near future.

Coarse-Grained (CG) is a modelling technique able to bridge Molecular Dynamics (MD) simulations from atomic scale to mesoscale. The basic idea of coarse graining is to combine several atoms into homogeneous groups (CG beads), which interact each other by means of bonded and nonbonded interaction potentials. Numerous coarse-grained techniques have been proposed in the last decades, and they can be classified into top-down or bottom-up methods. In the former, many-body potentials are parameterized in order to reproduce the thermodynamic properties observed at larger scales. For example, Martini Coarse-Grained force field and its further extensions follow the top-down philosophy and are widely used to study complex biomolecular systems [14]. In the bottom-up approach, instead, the effective potentials between CG beads are developed to represent atomistic features. Among the bottom-up techniques, effective CG potentials can be defined by iterative processes with the aim to reproduce a target radial distribution function [15-17] or force distribution in the atomistic system [18-20]. Although these methods are largely employed and provide accurate descriptions for several physical systems, unphysical CG potentials could result from these optimization approaches. Therefore, some novel CG methods have been recently designed for condensed matter systems. Such non-iterative methods include the pair Potential of Mean Forces (pPMF) [21], the Effective Force Coarse Grained (EFCG) [22] and the Conditional Reversible Work (CRW) [23].

Here, a suitable bottom-up CG model for nanofluids is employed for directly evaluating the pPMF from MD simulations. In particular, a couple of alumina nanoparticles (NPs) solvated in water is chosen as an exemplificative building block for nanofluids for volumetric solar receivers [24]. Preliminary analyses about the interaction energies between the NPs clarify the role of Coulomb and Lennard-Jones potentials in the resulting inter-particle energy.

2. Methods

To evaluate the pPMF between suspended Al_2O_3 nanoparticles (NPs) in water, MD simulations are carried out by using GROMACS package [25]. The following steps describe the adopted simulation protocol ("pulling procedure").

First, the atomistic model of Al_2O_3 NP is prepared by defining the particle geometry and atomistic force field. Specifically, a 2 nm alumina sphere is functionalized by adding OH terminal groups on the surface. All bonds, angles and dihedral within the NP core are modeled with a harmonic potential; instead, Lennard-Jones and Coulomb potentials are imposed for mimicking nonbonded interactions. The CLAYFF force field is adopted for distributing partial charges on the NP surface, which is overall neutral [26].

Second, two alumina nanoparticles are considered. The NPs couple is placed in a box (22x8x8 nm) made of SPC/E water molecules [27]. After the energy minimization, the whole system is equilibrated at T = 300 K in canonical ensemble (NVT), by applying Nosè-Hoover thermostat [28]. A second equilibration step is performed in isothermal-isobaric ensemble (NPT, 300 K and 1 bar), by means of Parrinello-Rahman barostat [29]. In the first configuration, the distance between NPs center of mass is set to 2 nm. Then, by restraining one particle (reference group) while pulling the second one (pull group) along a reaction coordinate *r*, a series of configurations is

generated as shown in Fig. 1a. Specifically, the pull velocity is kept constant ($v_{pull} = 0.01\ nm/ps$) in order to guarantee a linear uniform motion of the pulled particles (Fig. 1b). Each configuration, which corresponds to a precise separation distance between the NPs, is taken into account for an independent 2 ns MD simulation.

Third, the pPMF is calculated by numerically integrating the interacting forces between NPs, and it is corrected by adding an entropy term taking into account the center-of-mass distance constraint:

$$pPMF\ (r) = \int_{r_{max}}^{r} F(r)dr - 2k_B T ln(r), \quad (1)$$

where r_{max} is the maximum distance between the two simulated NPs with $pPMF(r_{max}) \cong 0$, k_B is the Boltzmann constant and T is the temperature.

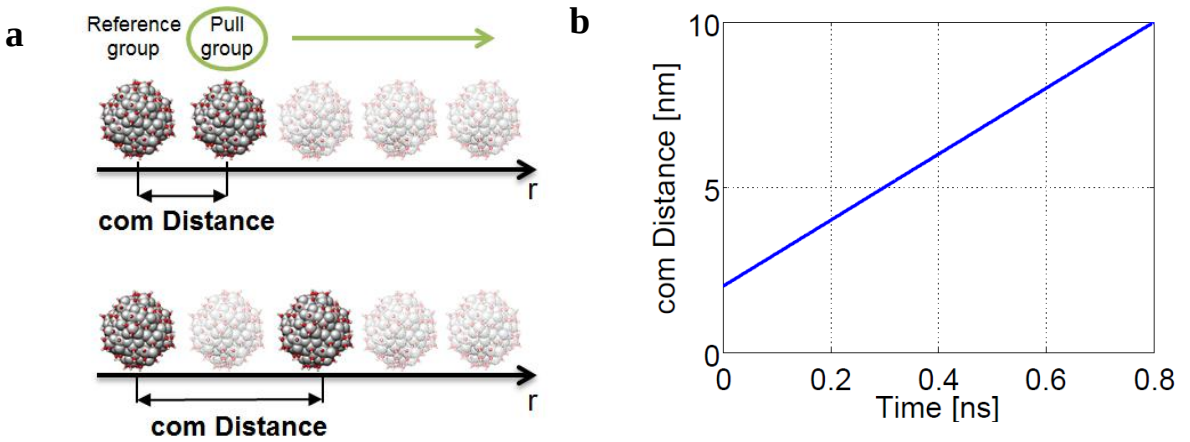

Fig. 1: a) Pulling procedure to create the simulated configurations for a couple of $\alpha - Al_2O_3$ NPs located at different com distances. b) Distance between the center of mass (com) of NPs as a function of time during the pulling procedure.

3. Results

3.1. Interaction energy in constrained configurations

The pulling procedure allows generating several configurations at multiple NP-NP separation distances. Each configuration is then simulated by independent MD runs, where the nanoparticles are constrained in a certain reciprocal position.

Some exemplificative configurations are selected to carry out preliminary analyses on the interaction energy (E_{NPs}) between NPs. Such inter-particle energy is calculated as a sum of the nonbonded interactions (van der Waals, U_{vdw}; Coulomb, U_C) between the atoms belonging to "reference" and "pull" particles, namely $E_{NPs} = U_{vdw} + U_C$. Specifically, the van der Waals interaction between a generic couple of atoms i and k is here mimicked by a 12-6 Lennard-Jones (LJ) model:

$$U_{vdw} = 4\epsilon_{ik}[(\sigma_{ik}/r_{ik})^{12} - (\sigma_{ik}/r_{ik})^{6}], \quad (2)$$

where ϵ_{ik} and σ_{ik} are the LJ parameters obtained by Lorentz-Berthelot combination rules and r_{ik} is the inter-atomic distance. Instead, the Coulomb potential is modelled by:

$$U_C = 1/4\pi\varepsilon_0\,[q_i q_k/(\varepsilon_r r_{ik})], \quad (3)$$

where ε_0 and ε_r are the vacuum and relative permittivity ($\varepsilon_0 = 8.854 \cdot 10^{12}\ F/m$, $\varepsilon_r = 1$), and q_i and q_k are the

partial charges of the *i*-th and *k*-th atom, respectively. The particle-mesh Ewald (PME) algorithm is then implemented to take into account the long range Coulomb potential [30].

The interaction energies corresponding to the initial configuration (center of mass distance = 2 nm) are shown in Fig. 2a. The pie chart highlights the different contributions to E_{NPs}: only 13% of the inter-particle energy can be attributed to van der Waals interactions, while the remaining 87% is due to Coulomb potential. Moreover, the reported negative energy values underline that the superposition of atomic nonbonded interactions leads to a resulting attractive energy between the NPs couple. Note that the energy values shown in Fig. 2a are time averaged over the whole MD trajectory. In Fig. 2b, it is possible to compare the interaction energy in the case of maximum and minimum simulated center of mass distances: the strong adhesive potential (≈ -161±80 kJ/mol) at 2 nm distance completely vanishes at 7.2 nm. The intermediate configurations are then systematically investigated by evaluating the pair Potential of Mean Forces.

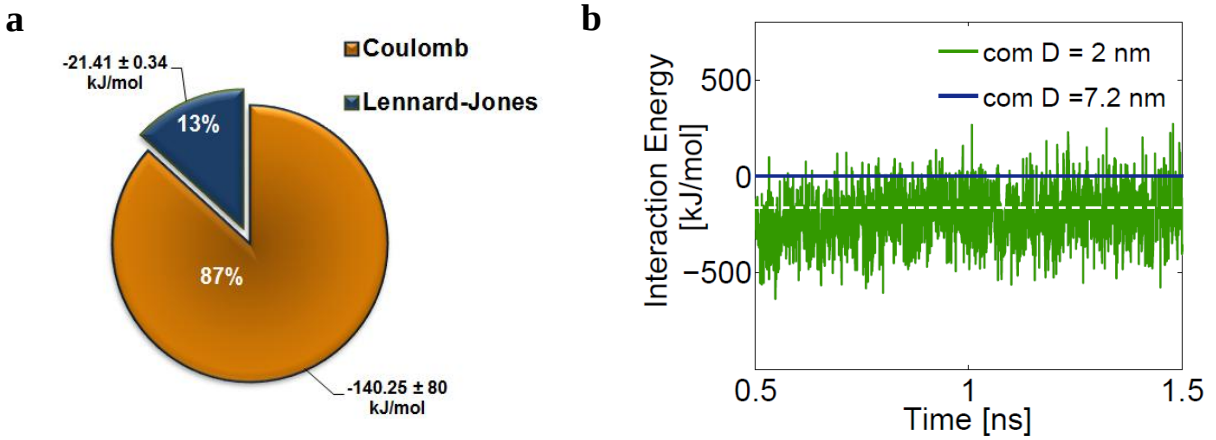

Fig. 2: a) Coulomb and Lennard-Jones contributions to the total interaction energy between two $\alpha - Al_2O_3$ NPs at 2 nm com distance. b) Interaction energy between a couple of NPs in two different configurations: com distance = 2 nm (green solid line) and 7.2 nm (blue solid line). The white dashed line is the time average in the 2 nm configuration.

3.2. Pair Potential of Mean Forces and DLVO theory

The pPMF is therefore calculated by integrating the total interaction forces obtained from the MD runs of each constrained configuration, and results are plotted in Fig. 3 (red dots). As shown, the minimum energy between nanoparticles is achieved at the shortest center of mass distance simulated, namely 2 nm. This confirms the strong attractive potential at 2 nm distance in Fig. 2, which represents the pPMF minimum. As the distance between Al_2O_3 NPs increases, the mutual attractive interaction tends to zero. Numerical results can be best-fitted by:

$$PMF(r) = -F/(r - 2R), \tag{4}$$

where r is the center of mass distance between $\alpha - Al_2O_3$ particles, R=0.9 nm is the particle radius and $F = 22.32\ kJ/mol$ is the optimized fitting parameter.

The resulting fitting curve in Fig. 3 is then compared with DLVO theory, which was first introduced by Derjaguin, Landau [31, 32], Verwey and Overbeek [33]. This theory is current the milestone to model interactions between colloidal particles and their aggregation behavior. Specifically, the DLVO theory assumes that the interaction energy between particles can be approximated by two additive contributions: an attractive term, deriving from van der Waals potential, and a repulsive, electrostatic double-layer interaction. The latter becomes significant when two charged particles approach each other, and their electrical double layers begin to interfere. Since we are

here dealing with uncharged nanoparticles, only the attractive contribution of DLVO model should be considered, namely:

$$U_{vdw}(r) = -A/6 \cdot [2R^2/(r^2-(2R)^2) + 2R^2/r^2 + \ln((r^2-(2R)^2)/r^2)], \quad (5)$$

where A is the Hamaker constant (31.3 kJ/mol for alumina particles in water [34]).

The discrepancy between MD results and DLVO theoretical framework (Fig. 3) could be due to the presence of partial charges (i.e. dipoles) on the functionalized alumina surface. While such interactions are taken into account in the MD simulations, they are generally neglected in the attractive term of DLVO theory. Moreover, the predicted inter-particle potential by DLVO theory may fail because of the additional forces associated with the solvent structure [35, 36]. Figure 4 highlights a possible source of such extra forces: the graph shows the density profile of water between a couple of constrained NPs (center of mass distance: 7.2 nm), where the water density increases in the proximity of solid-liquid interface because of water layering and thus reduced mobility [37]. This could lead to extra repulsive forces known as hydration forces, which manifest at short NP-NP distance.

Although these preliminary results do not reproduce all constituents typically present in nanofluids (e.g. surfactants, pH, ions and counterions), they are explicative for understanding the main issues concerning clustering phenomena in colloidal nanosuspensions. However, the procedure suggested in this work to evaluate the pPMF for a couple of uncharged, alumina nanoparticles in water could be easily extended to different geometrical and chemical configurations.

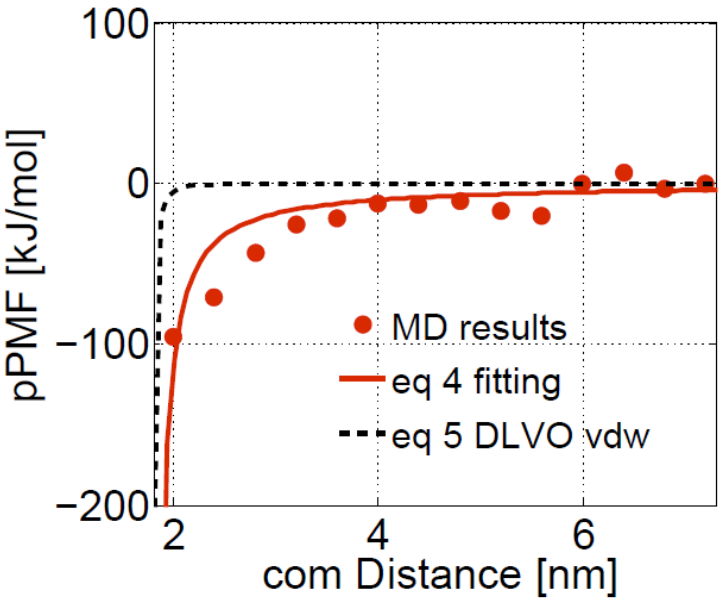

Fig. 3: Pair Potential of Mean Forces (pPMF) between the $\alpha - Al_2O_3$ NPs at different com distance. Eq. 4 (red solid line) fits MD results with $R^2 = 0.76$; Eq. 5 (black dashed line) shows the Van der Waals attractive term in DLVO theory.

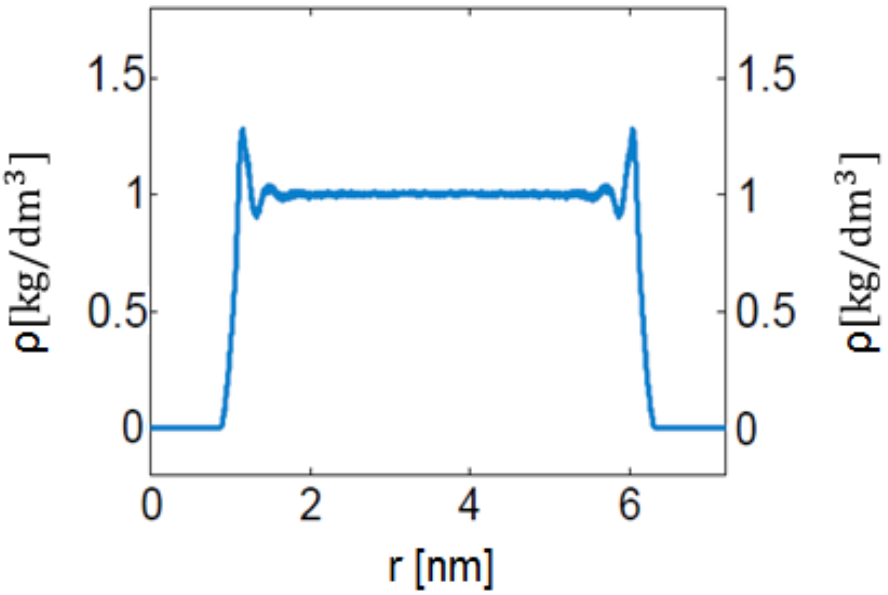

Fig. 4: Water density profile between a couple of constrained $\alpha - Al_2O_3$ NPs centered at r = 0 and 7.2 nm, respectively.

4. Conclusions

The use of nanofluids in volumetric solar receivers have shown promising potential in the last decades. However, the multiscale nature characterizing these nanoparticle suspensions makes difficult their modeling and, consequently, clear guidelines for designing nanofluids are still missing. A multiscale model for nanofluids may allow to study the main physical aspects governing the agglomeration phenomena, and thus to guide a more rational design of nanoparticle suspensions for solar applications.

Here, as an example, the pPMF between alumina nanoparticles in water is evaluated by MD simulations. Due to the generality of the proposed procedure, also other nanofluids as for instance those based on carbon nanoparticles [38, 39] and those utilized in optically black nanofluids [3] can be treated in a similar manner.

The results mechanistically demonstrate the adhesion energy between uncharged particles. According to the well-known DLVO theory, the reason of such attractive interaction is mainly attributed to London-Van der Waals forces. However, the present work underlines the non-negligible role of attractive Coulomb interactions arising from surface functionalizations.

Currently, two main techniques have been investigated and experimentally employed to avoid the formation of nanoparticle aggregates: on one hand, the use of electrolyte solutions to increase the repulsion between double layers of charged nanoparticles; on the other hand, the addition of chemical surfactants introducing steric repulsive interactions between nanoparticles. Hence, future perspectives of the present work may include the extension of the calculation of pPMF to suspension of charged nanoparticle in electrolyte solutions. Moreover, a systematic investigation of the role of hydration forces would allow defining a complete Coarse-Grained model of nanofluids for volumetric solar receivers.

Acknowledgements

Authors would like to acknowledge NANO-BRIDGE project (PRIN 2012) and CINECA (COGRAINS).

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