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GREEN-KUBO ASSESSMENTS OF THERMAL TRANSPORT IN NANOCOLLOIDS BASED ON INTERFACIAL EFFECTS

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Abstract

Thermal transport in a water-Cu nanocolloid system was investigated using equilibrium molecular dynamics. A systematic analysis of the Green-Kubo calculations is presented to clarify the effect of simulation parameters. Several sources of error were identified and quantified for the thermal conductivity estimations, and the effect of the base fluid potential was investigated. Simulations were carried out with a single copper particle for different diameters and water potentials, and thermal enhancements exceeding both theoretical and experimental results were observed in parallel with some other studies in the literature. The anomalous Green-Kubo thermal enhancement results could be explained by the interfacial dynamics and the neglect of calibrating the interaction potential to satisfy the physically-observed energy flow at the interface.

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I. INTRODUCTION

Colloidal suspensions have recently been the focus of numerous scientific studies due to their potential engineering applications [1]. Studies of particulate systems can involve rheology, interface science and colloidal chemistry [2], and could lead to advances in foams, gels, paints, coatings and wetting-dispersing agents [3]. One recently-developed colloidal system is known as a *nanofluid*, and is a suspension of nanoparticles designed for enhanced heat transfer [4]. The physics of thermal transport in these systems requires further study, and simulations are frequently used for this purpose because of experimental limitations at the relevant length scale.

Molecular Dynamics (MD) is a powerful approach to investigate nanoscale dynamics where interatomic forces govern the system behaviour. There are two different schemes that can be used to measure the heat transport properties in MD simulations: Non-equilibrium Molecular Dynamics (NEMD) [5] and Equilibrium Molecular Dynamics (EMD) [6]. A heat flux is imposed on the system in NEMD and the thermal conductivity is calculated based on the resulting temperature gradients. However, finite size effects are severe as a result of very high temperature gradients, and careful consideration is required to obtain reliable temperature profiles [7]. Equilibrium Molecular Dynamics instead calculates thermal conductivity from the time decay of heat flux fluctuations based on the fluctuation-dissipation theorem. While this requires more computational power, the method does not suffer from the drawbacks of NEMD and is widely used in the literature.

The thermal conductivities of Lennard-Jones liquids [8], water [9–11], methane hydrate [12], Ar-Cu nanofluids [13–15], and a water-platinum nanofluid [16] have been estimated with EMD, though most of these studies do not include a detailed error analysis. This is significant because the fluctuation-dissipation theorem is based on the chaotic movements of particles or atoms, which introduces statistical noise into the calculation of the autocorrelation function (ACF). Porter and Yip [17] and Chen *et al.* [18] proposed to truncate the integration time of the heat current autocorrelation function (HACF) to minimize the statistical noise. Other approaches include curve fitting [19], block averaging [20], random walk modelling [21], and spectral analysis of time series [22]. These studies provide fundamental insights about the statistical nature of the EMD method, and should be carefully considered to estimate the errors associated with Green-Kubo (GK) calculations.

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In most nanofluid studies, Maxwell's relation [23] is used as a reference for the effective thermal conductivity of a simulated system. The Maxwell model neglects Brownian motion, nanolayering and agglomeration [24] as possible heat transfer enhancement mechanisms for nanofluids, but provides a lower limit by only considering the thermal conductivity of the mediums. Anomalous thermal enhancement values with respect to the Maxwell limit have been reported in some nanofluid studies that use the GK method, where the contribution of various mechanisms to this enhancement has been investigated by comparing simulations and theoretical calculations [15, 16, 25–27]. However, inconsistent results and recent developments [18, 19, 22] concerning GK calculations in the literature indicate that there is no generally accepted GK algorithm, and that the effect of the GK parameters on the thermal transport has not yet been fully understood.

The anomalous thermal conductivity of nanofluids as found by GK calculations has been hypothesized to be the effect of Brownian motion [15] or nanolayering [26]. Recent studies have found an insignificant contribution of Brownian motion of the nanoparticles to the heat transfer enhancement of nanocolloids [28, 29]. As for the nanolayering effect, both experimental and theoretical investigations have tried to quantify the thermal conductivity of the adsorbed liquid layer [30–32]. However, investigating nanolayering with MD simulations can be difficult since the interface potential is expected to have a considerable effect on the thermal transport at the solid-liquid surface. Most EMD studies use the Lorentz-Berthelot rules at the interface for lack of an alternative without adequately studying the effect of the surface parameters, even though the Lorentz-Berthelot rule has no physical justification. It has been recently shown that Lorentz-Berthelot can lead to an overestimation of the interfacial thermal resistance for a hBN-water system [33], and an optimization process carried out by fitting potential parameters is required to accurately represent the interface.

This study presents a comprehensive evalution of the Green-Kubo approach by considering the thermal transport in a nanocolloid system, where several inconsistencies and anomalous thermal conductivity results have been reported in the literature. Using a standard force-field as the interatomic potential and a common modeling scheme for interface interactions, possible sources of the observed anomalies are revealed. A statistical assessment of several sources of error is presented and the effect of different water potentials on the thermal transport calculations is tested. The effect of the interface parameters on the thermal conductivity calculations is investigated. Finally, thermal resistances at the solid-

liquid interfaces are quantified to further investigate interfacial effects. We believe that the presented results clarify the contributions of surface phenomena and the associated interfacial thermal resistance to the anomalous thermal enhancement found with Green-Kubo calculations.

II.   METHODOLOGY

A.   Green-Kubo Relations

The Green-Kubo method relies on the fluctuation-dissipation theorem and linear-response theory [6], and describes the system behavior using time autocorrelation functions (ACF). Integrating an ACF in time allows transport properties in the equilibrium state to be extracted [34]. The thermal conductivity is given in the GK formalism as:

$$k = \frac{1}{3k_B V T^2} \int_0^\infty \left\langle \bar{J}(0) \cdot \bar{J}(\tau) \right\rangle d\tau \tag{1}$$

where k_B is Boltzmann's constant, T is the absolute temperature, V is the system volume, $\bar{J}$ is the heat current vector, and the integrand is the heat autocorrelation function (HACF). The HCAF is an ensemble average, which relates the thermal conductivity to the heat current in an equilibrated system. Equation (1) involves integrals in the continuous case, but since time is discrete in MD simulations, the integral is replaced by a summation in practice. The heat current vector is defined as:

$$\bar{J} = \frac{1}{V} \left\{ \sum_i e_i \bar{v}_i + \frac{1}{2} \sum_{i<j} \left[\bar{f}_{ij} \cdot (\bar{v}_i + \bar{v}_j) \right] \bar{r}_{ij} - \sum_\alpha h_\alpha \sum_i \bar{v}_i \right\} \tag{2}$$

where $\bar{v}_i$ is the velocity of atom i, $\bar{r}_{ij}$ and $\bar{f}_{ij}$ are distance and force vectors between atoms i and j, α is the atomic species, and h_α is the enthalpy of that species. The total energy e_i is the sum of the kinetic and potential energies which can be expressed as:

$$e_i = \frac{1}{2} m_i \bar{v}_i^2 + \frac{1}{2} \sum_j \Phi(\bar{r}_{ij}) \tag{3}$$

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where $\Phi(\bar{r}_{ij})$ is the interatomic potential energy.

The enthalpy exclusion in the last term of Equation (3) for multi-phase systems was introduced by Babaei *et al.* [35] who studied a methane-Cu colloidal system using EMD, and was not common in earlier GK studies [15, 16, 27]. This term is subtracted from the heat flux because it represents the energy carried by the mediums but not transported between them. The species enthalpy is defined as:

$$h_\alpha = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \left[e_i + \frac{1}{3} \left(m_i \bar{v}_i^2 + \frac{1}{2} \sum_{j=1}^{N_\alpha} \bar{r}_{ij} \cdot \bar{f}_{ij} \right) \right] \tag{4}$$

where N_α is the number of atoms of species α.

B. Problem and Simulation Details

Pure water and water-Cu models with a single copper nanoparticle (diameter 1.3 or 1.8 nm) in the middle of cubic simulation domains with a side length of 2.8 nm and 4 nm were generated as shown in Fig. 1. Volume fraction calculations are not trivial at the nanoscale, considering that the clearence at the solid-liquid interface is not well-defined. We calculated the volume fraction to be 5% using mass fractions and the bulk densities of the phases, and 4.5% using the sum of volumes of the Voronoi polyhedra. This was kept fixed for all nanofluid systems, and is reported as 5% throughout the text. TIP3P (flexible) [36], TIP4P/2005 (rigid) [37] and SPC/E (rigid) [38] potentials were used to define the water interactions. Pure water systems of the same dimensions were used to estimate the thermal conductivity of the base fluid. The SHAKE algorithm [39] was used to enforce the bond and angle constraints in the rigid water models, and long-range Coulombic interactions were solved using particle-particle-particle-mesh (PPPM) summations [40]. Atomic interactions within a copper nanoparticle were defined using a Lennard-Jones 6-12 potential with ϵ_{Cu-Cu} = 9.4353 kcal/mole and σ_{Cu-Cu} = 0.2338 nm [41]. The Lorentz-Berthelot rule was used for interactions between oxygen atoms and copper atoms, and the timestep was set to 1 fs. Periodic boundary conditions were applied in all directions.
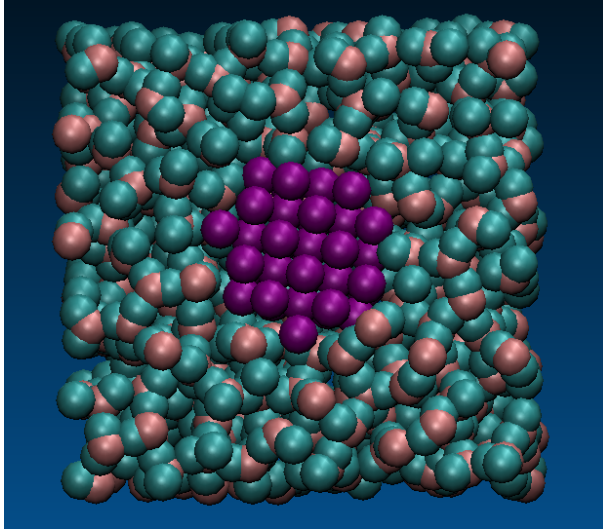
FIG. 1: Cross-section of water-Cu model with 5% volume fraction, 2.8 nm side length and 1.3 nm particle diameter.

Each model was first equilibrated for 100 ps in the isobaric-isothermal (NPT) ensemble, followed by a further 2 ns in the microcanonical ensemble (NVE) at 300 K. The GK calculations were performed in 5-8 ns production runs (depending on the simulation) with HACFs calculated in 20 ps intervals, and the reported results are the average of 20 independent simulations with different initial velocity seedings. All simulations are carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [42], and Fig. 1 was generated using Visual Molecular Dynamics (VMD) [43].

## III.   RESULTS AND DISCUSSION

A.   Green-Kubo Error Analysis

The confidence interval usually reported in the literature is for a single ACF, and corresponds to the fluctuations in the thermal conductivity within a single MD simulation. We denote this type of error as 'short-time error' in this study. Another source of error is denoted as 'long-time error', and can be observed in the scatter of calculated thermal conductivities for different velocity seedings. The heat flux fluctuations are governed by the local properties of the potential energy surface (PES), and a single MD simulation explores a relatively small part of this surface over a period of ns. This effectively introduces a random error that depends more on the initialization, or where the system begins on the PES, than

on the fluctuations of a single ACF. While in principle a single very long MD simulation would explore a sufficiently large region of configuration space, in practice the computational requirements are reduced by changing the initial velocity distribution of the atoms to obtain different trajectories and molecule orientations. This procedure is also followed in several other studies that average the thermal conductivities of independent simulations [25, 44, 45], yet is not the standard procedure in the literature.

The short-time errors occur because of the statistical noise in an ACF, and can be minimized by following the decay of the ACF. The time evaluation of the normalized HACF for pure water with the SPC/E potential (2.8 nm simulation cell in one dimension) is presented in Fig. 2a as a function of the correlation time τ, which represents the time interval within which the ACFs are calculated and integrated, and of the simulation time t, which is the point in the simulation at which the integration begins. A single HACF converges to zero over a 20 ps interval [11], and smoother overall HACF behavior is achieved by beginning the calculation after a short interval of simulation time (200 ps). The effect of the HACF decay can be also observed in Fig. 2b, where the estimated thermal conductivity for a total simulation time of 8 ns is presented. Each data point is obtained by integrating the HACF over a 20 ps interval. The convergence of the integration can be observed by comparing the two inset figures at 200 ps and 5 ns, and the short-time error is reported as the standard error of the mean for the converged region of Fig. 2b between 5-8 ns. The value of this quantity is 0.002 W/mK, which is insignificant compared to the long-time error discussed below. The total production run is therefore set to 5 ns to save computation time.

The long-time error is calculated by sampling some number of relatively short GK results with different velocity initializations instead of performing one long simulation which would require more computation time. Green-Kubo results of the thermal conductivity of independent simulations with different initial velocity seedings for the SPC/E water model (2.8 nm simulation cell in one dimension) are shown in Fig. 3, where the thermal conductivity is seen to change significantly with different velocity initializations. The standard error of the mean $\sigma_{\bar{k}}$ for the long-time error is 0.03 W/mK, significantly larger than the standard error of the mean for short-time-error given above (0.002 W/mK). Therefore, the confidence interval of the thermal conductivity results reported below is constructed based on the long-time error.

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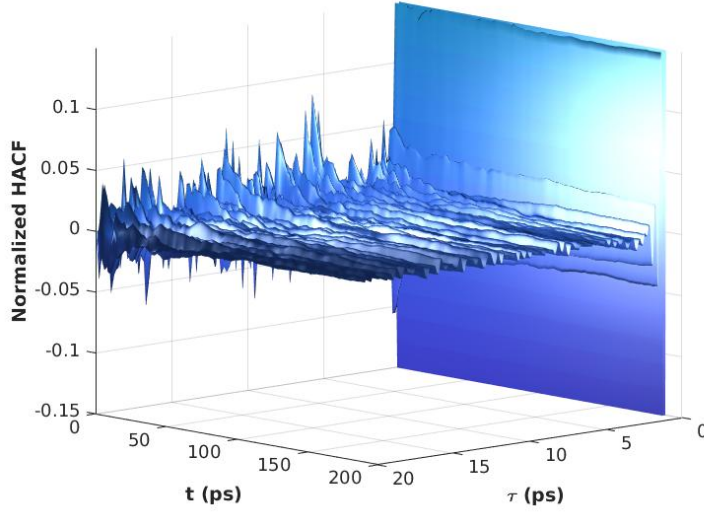
(a)
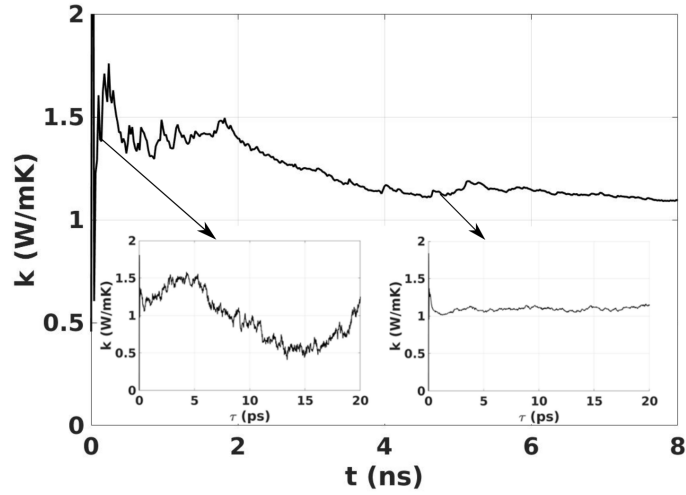
(b)

FIG. 2: a) Surface of HACF behavior for correlation time (τ) and for total simulation time (t) of a pure SPC/E water model. b) Thermal conductivity of a pure SPC/E water model for a total simulation time of $8 \ ns$. Inset figures are representing the thermal conductivities at $200 \ ps$ and $5 \ ns$, respectively. They are produced by integration of individual ACFs within a correlation time interval τ.

B. Thermal Conductivity Calculations

The thermal conductivities of pure water and water-Cu nanocolloid systems are calculated following the procedure described in Section II A. The results for different water potentials, particle diameters and number of particles are presented in Table I. The thermal
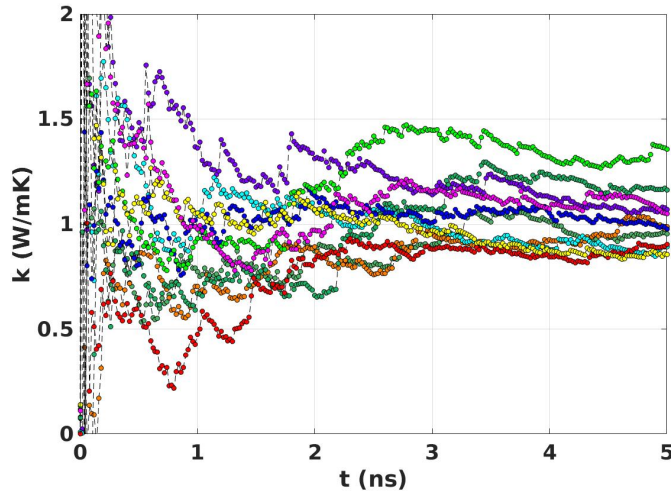
FIG. 3: Thermal conductivity results of 10 different initial velocity seeding for pure SPC/E water.

conductivities of pure water (Simulations 1-3) are in agreement with the reported results in the literature [46]. The thermal conductivity enhancements (thermal conductivity of the nanofluid divided by that of pure water) of a water-Cu nanofluid with a rigid water model (Simulations 5 and 6) are in agreement with the findings of Muraleedharen *et al.* [25] who used the rigid SPC/E water model. It is significant that the same trend is not observed with the flexible TIP3P model (Simulation 4).

The anomalous thermal enhancement observed with rigid water models exceeds both theoretical and experimental results, and has been attributed to an artificial particle correlation effect arising from the use of a single particle with periodic boundary conditions [25]. The suggested solution is to use multiple nanoparticles to break the symmetry of the system. This was tested for the rigid SPC/E water model using a three-nanoparticle system with the same volume fraction and particle diameter. Contrary to the hypothesis that artificial particle correlations are responsible for the anomalous enhancement, a further increase in the thermal conductivity was observed for the rigid SPC/E water model (Simulation 8). Moreover, an insignificant difference was found between the one- and three-nanoparticles cases with the flexible TIP3P model (Simulations 4 and 7), suggesting that there may be some other effects responsible for the observed anomalous increase. The difference between water models persists and is even exacerbated for larger system sizes at a fixed volume fraction, with the larger single particle system having a slightly higher thermal conductivity for the TIP3P model (Simulations 4 and 9) and more than double the thermal conductivity for

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the SPC/E model (Simulations 5 and 10). The abnormal thermal conductivity values associated with SPC/E models tend to increase with increasing particle surface area within the system as additional particles are introduced or particle size is increased (Simulations 8 and 10). Given the reasonable thermal conductivities of the pure water models, these findings suggest that the interfacial interactions that obey the Lorentz-Berthelot rules and that are different for each system are the cause of observed anomalous thermal conductivities.

This argument is supported by the results presented in Table II, where the estimated thermal conductivities for the three different water models are compared with the Maxwell limit [23] and experimental results of Xuan and Li [47] at the same volume fraction. The significant difference between our simulations and experiment regarding the particle size could be interpreted based on the findings of the experimental studies that investigate the effect of particle size to the nanofluid thermal conductivity. It has been showed that the thermal conductivity is increased with smaller size of nanoparticles due to the effect of enhanced Brownian motion [48, 49]. Considering the larger particle diameter in the experiment, our effective thermal conductivity result with TIP3P model is quite reasonable. However, switching the water potential to SPC/E or TIP4P results in anomalous thermal conductivity ratios exceeding both experiment and theory, implying that the parametrization of the system dynamics is responsible for the overestimation rather than any physical mechanism. When the results in Table I and Table II are considered together, our conclusion is that the surface interactions of solid-liquid interfaces in nanocolloids need to be accurately represented to avoid any unphysical interfacial thermal transport.

C. Interfacial Effects

The effect of surface interaction parameters on the effective thermal conductivity of solid-liquid systems has been investigated before in several NEMD studies [33, 50], but the effect of these parameters on GK calculations has not been studied to our knowledge. Our earlier NEMD study [33] showed up to a 12% change in thermal conductivity using an interface coupling tuned to satisfy the experimentally observed contact angle as compared to Lorentz-Berthelot. Surface interactions could have an even larger effect for EMD calculations since GK considers the energy flow associated with the motion of each atom at each time step by means of Equation (2), whereas NEMD uses an average temperature calculated by means

TABLE I: Green-Kubo estimations of the thermal conductivity of water-Cu nanosuspensions with a single nanoparticle. $\bar{k}$ is the mean and $\sigma_{\bar{k}}$ is the standard error of the mean for different water models (Model), volume fractions (ϕ), number of particles (N_p), and particle diameter (D_p). Simulations 1-3 are pure water. Standard error of the means are calculated based on the long-time errors as mentioned above. σ_r in the last column is the ratio of $\sigma_{\bar{k}}$ to $\bar{k}$.

Simulation	Model	$\phi(\%)$	N_p	$D_p(nm)$	$\bar{k}(W/mK)$	$\sigma_{\bar{k}}$	σ_r
1	TIP3P	-	-	-	0.86	0.03	0.03
2	SPC/E	-	-	-	1.02	0.03	0.03
3	TIP4P/2005	-	-	-	1.05	0.03	0.03
4	TIP3P	5	1	1.3	1.12	0.04	0.04
5	SPC/E	5	1	1.3	3.73	0.12	0.03
6	TIP4P/2005	5	1	1.3	3.29	0.11	0.03
7	TIP3P	5	3	1.3	1.19	0.04	0.03
8	SPC/E	5	3	1.3	5.31	0.2	0.04
9	TIP3P	5	1	1.8	1.31	0.04	0.03
10	SPC/E	5	1	1.8	7.78	0.22	0.03

TABLE II: Comparison of the Green-Kubo thermal conductivity estimations with the theoretical Maxwell limit and experimental result for water-Cu nanosuspension at the same volume fraction [47]. N_p, D_p and ϕ are the number of particles, particle diameter and volume fraction, respectively. k_{eff} is the thermal conductivity ratio of the nanosuspension, which is the ratio of nanofluid thermal conductivity to base fluid thermal conductivity.

	$\phi(\%)$	N_p	$D_p(nm)$	k_{eff}
Maxwell [23]	5	-	-	1.15
Xuan and Li [47]	5	1	100	1.55
This study (TIP3P)	5	1	1.3	1.3
This study (SPC/E)	5	1	1.3	3.66
This study (TIP4P/2005)	5	1	1.3	3.13

of kinetic theory.

A Lennard-Jones 6-12 function is employed for the interfacial interactions:

$$\Phi(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] \tag{5}$$

where ϵ is an energy scale and σ is a characteristic length. Ideally, ϵ and σ should be derived

TABLE III: The thermal conductivities ($\bar{k}$) of water-Cu nanosuspensions with a single nanoparticle for different water models. ϵ is the interfacial energy parameter between oxygen and copper. D_p is the nanoparticle diameter.

Simulation	Model	$\epsilon(kcal/mole)$	$D_p(nm)$	$\bar{k}(W/mK)$
1	SPC/E	1.21	1.3	3.73
2	SPC/E	1.21	1.8	7.78
3	SPC/E	0.98	1.3	0.91
4	SPC/E	0.98	1.8	0.99
5	TIP3P	0.98	1.3	1.11
6	TIP3P	0.98	1.8	1.31

from experimental findings or first principle calculations; however, in most of the nanofluid studies they are calculated based on Lorentz-Berthelot mixing rules. Our intention is to identify whether this could be the source of the anomalous thermal conductivity rather than some other simulation input. Existing investigations consider the effects of varying ϵ [50–52] and the same procedure is followed here. The effect on the thermal conductivity of varying ϵ at the water-Cu interface is reported in Table III, indicates that the interfacial energy parameter would easily be able to account for the overestimation of the thermal conductivity in Table I. Specifically, changing ϵ from the 1.21 kcal/mole given by the Lorentz-Berthelot rule for the SPC/E potential to the 0.98 kcal/mole for the TIP3P potential (Simulations 1 and 3) significantly decreased the thermal conductivity. Although these values of ϵ do not have any particular pyhsical basis, they do establish that the thermal conductivity is very sensitive to surface ϵ, and that using the values predicted by the Lorentz-Berthelot rule is likely a significant source of error. This reinforces the necessity of calibrating the interface potential based on experimental findings before using the Green-Kubo method to quantify thermal transport in nanocolloids.

Another observation is that the anomalous thermal conductivity values observed with both rigid models in Tables I and II were not observed with the flexible TIP3P model. While this could appear as a possible reason for the abnormally high thermal conductivites, this conclusion is not supported by the reasonable thermal conductivities of the base fluids in Table I. Moreover, Table III provides direct evidence that an inaccurate interfacial potential could be responsible for the anomalous thermal conductivities.

The significance of the interface to the observed dependence of thermal transport on
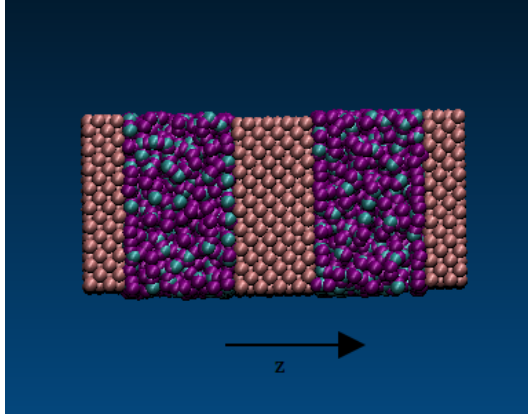
FIG. 4: Two water blocks have been created in between three copper blocks to apply NEMD.

the water model could also be expressed in terms of interfacial thermal resistance. Based on prior work [53], this is measured using the NEMD method. Three different water-Cu systems were generated with the geometry shown in Fig. 4, and the Muller-Plathe algorithm [5] was applied to create a heat flux in the system in the z-direction. The temperature was calculated using a methodology presented elsewhere [53]. The interfacial thermal resistance was calculated as $R = \Delta T/q''$ where R is the thermal resistance, ΔT is the temperature difference at the water-Cu interface, and q'' is the heat flux. Each system was equilibrated for 100 ps in the NPT ensemble, followed by a 1 ns production run in the NVE ensemble. The thermal resistance results were obtained by averaging the results of 100 independent runs, and are presented in Table IV. A higher thermal resistance was found for the TIP3P model compared to the rigid models, and is consistent with our thermal conductivity results. The discrepancy between the relative difference in the thermal resistances (around 60 %) and the thermal conductivities (more than 200 %) could be due to the fact that the thermal resistances were calculated using the NEMD Muller-Plathe algorithm, whereas the thermal conductivities were calculated using the EMD Green-Kubo algorithm. A second contributing factor could be the difference in geometry: whereas the nanocolloid contains highly curved surfaces, the thermal resistances are calculated for flat surfaces.

IV. CONCLUSIONS

The thermal conductivity of a water-Cu nanocolloid system was studied using the Green-Kubo method, with the intention of identifying the source of the anomalously high nanofluid

TABLE IV: The thermal resistivities (R) at water-Cu interface with for different water potentials. σ_R is the associated error in the measurement.

Model	$R[Km^2/W \times 10^{-9}]$	σ_R
TIP3P	2.73	0.06
SPC/E	1.94	0.06
TIP4P/2005	1.68	0.05

thermal enhancements in the literature. This is crucial for the validity of the conclusions drawn on the basis of such simulation results. A detailed error analysis identified different sources of statistical errors, denoted as short-time errors and long-time errors. The magnitude of the error was estimated for both, and the long-time error associated with differences in velocity seeding was found to be larger than the short-time error associated with the fluctuations of a single autocorrelation function.

The anomalous thermal enhancement in the literature was reproduced using rigid SPC/E and TIP4P/2005 water models, but was not observed for the flexible TIP3P water model. Although the rigidity of the water model has appeared to be a possible reason for the observed anomalies, further simulations revealed that the discrepancy is related to the difference in the interfacial potential, pointing to the unsuitability of the Lorentz-Berthelot rules when calculating thermal conductivity with the Green-Kubo formulation. We conclude that the interfacial potential parameters should be carefully optimized to correctly simulate heat transport for solid-liquid systems when using the Green-Kubo method.

[1] William Bailey Russel, Dudley Albert Saville, and William Raymond Schowalter. *Colloidal dispersions*. Cambridge university press, 1989.

[2] Ahn Nguyen and Hans Joachim Schulze. *Colloidal science of flotation*, volume 118. CRC Press, 2003.

[3] Tharwat F Tadros. *Handbook of Colloid and Interface Science: Industrial Applications-Agrochemicals, Paints, Coatings and Food Systems*. Walter de Gruyter GmbH & Co KG, 2017.

[4] Ravi Prasher, Prajesh Bhattacharya, and Patrick E Phelan. Thermal conductivity of nanoscale colloidal solutions (nanofluids). *Physical review letters*, 94(2):025901, 2005.

[5] Florian Müller-Plathe. A simple nonequilibrium molecular dynamics method for calculating the thermal conductivity. *The Journal of chemical physics*, 106(14):6082–6085, 1997.

[6] R Kubo. The fluctuation-dissipation theorem. *Reports on progress in physics*, 29(1):255, 1966.

[7] Patrick K Schelling, Simon R Phillpot, and Pawel Keblinski. Comparison of atomic-level simulation methods for computing thermal conductivity. *Physical Review B*, 65(14):144306, 2002.

[8] R Vogelsang, C Hoheisel, and G Ciccotti. Thermal conductivity of the lennard-jones liquid by molecular dynamics calculations. *The Journal of chemical physics*, 86(11):6371–6375, 1987.

[9] F Bresme, JW Biddle, JV Sengers, and MA Anisimov. Communication: Minimum in the thermal conductivity of supercooled water: A computer simulation study, 2014.

[10] Timothy W Sirk, Stan Moore, and Eugene F Brown. Characteristics of thermal conductivity in classical water models. *The Journal of chemical physics*, 138(6):064505, 2013.

[11] Niall J English and John S Tse. Thermal conductivity of supercooled water: An equilibrium molecular dynamics exploration. *The journal of physical chemistry letters*, 5(21):3819–3824, 2014.

[12] Eilis J Rosenbaum, Niall J English, J Karl Johnson, David W Shaw, and Robert P Warzinski. Thermal conductivity of methane hydrate from experiment and molecular simulation. *The Journal of Physical Chemistry B*, 111(46):13194–13205, 2007.

[13] Ling Li, Yuwen Zhang, Hongbin Ma, and Mo Yang. Molecular dynamics simulation of effect of liquid layering around the nanoparticle on the enhanced thermal conductivity of nanofluids. *Journal of nanoparticle research*, 12(3):811–821, 2010.

[14] Kuo-Liang Teng, Pai-Yi Hsiao, Shih-Wei Hung, Ching-Chang Chieng, Ming-Shen Liu, and Ming-Chang Lu. Enhanced thermal conductivity of nanofluids diagnosis by molecular dynamics simulations. *Journal of nanoscience and nanotechnology*, 8(7):3710–3718, 2008.

[15] Suranjan Sarkar and R Panneer Selvam. Molecular dynamics simulation of effective thermal conductivity and study of enhanced thermal transport mechanism in nanofluids. *Journal of applied physics*, 102(7):074302, 2007.

[16] N Sankar, Nithin Mathew, and CB Sobhan. Molecular dynamics modeling of thermal conductivity enhancement in metal nanoparticle suspensions. *International Communications in Heat and Mass Transfer*, 35(7):867–872, 2008.

[17] Ju Li, Lisa Porter, and Sidney Yip. Atomistic modeling of finite-temperature properties of

crystalline β-sic: Ii. thermal conductivity and effects of point defects. *Journal of Nuclear Materials*, 255(2-3):139–152, 1998.

[18] Jie Chen, Gang Zhang, and Baowen Li. How to improve the accuracy of equilibrium molecular dynamics for computation of thermal conductivity? *Physics Letters A*, 374(23):2392–2396, 2010.

[19] Alan JH McGaughey and M Kaviany. Phonon transport in molecular dynamics simulations: Formulation and thermal conductivity prediction. *Advances in Heat Transfer*, 39:169–255, 2006.

[20] Reese E Jones and Kranthi K Mandadapu. Adaptive green-kubo estimates of transport coefficients from molecular dynamics based on robust error analysis. *The Journal of chemical physics*, 136(15):154102, 2012.

[21] Laura de Sousa Oliveira and P Alex Greaney. Method to manage integration error in the green-kubo method. *Physical Review E*, 95(2):023308, 2017.

[22] Loris Ercole, Aris Marcolongo, and Stefano Baroni. Accurate thermal conductivities from optimally short molecular dynamics simulations. *Scientific reports*, 7(1):15835, 2017.

[23] James Clerk Maxwell, William Garnett, and Peter Pesic. *An elementary treatise on electricity.* Courier Corporation, 2005.

[24] P Keblinski, SR Phillpot, SUS Choi, and JA Eastman. Mechanisms of heat flow in suspensions of nano-sized particles (nanofluids). *International journal of heat and mass transfer*, 45(4): 855–863, 2002.

[25] Murali Gopal Muraleedharan, Dilip Srinivas Sundaram, Asegun Henry, and Vigor Yang. Thermal conductivity calculation of nano-suspensions using green–kubo relations with reduced artificial correlations. *Journal of Physics: Condensed Matter*, 29(15):155302, 2017.

[26] Parveen Sachdeva and Ranganathan Kumar. Effect of hydration layer and surface wettability in enhancing thermal conductivity of nanofluids. *Applied Physics Letters*, 95(22):223105, 2009.

[27] Hongbo Kang, Yuwen Zhang, and Mo Yang. Molecular dynamics simulation of thermal conductivity of cu–ar nanofluid using eam potential for cu–cu interactions. *Applied Physics A*, 103(4):1001, 2011.

[28] Hasan Babaei, Pawel Keblinski, and JM Khodadadi. A proof for insignificant effect of brownian motion-induced micro-convection on thermal conductivity of nanofluids by utilizing molecular dynamics simulations. *Journal of Applied Physics*, 113(8):084302, 2013.

[29] Tolga Akıner, Hakan Ertürk, and Kunt Atalık. Prediction of thermal conductivity and shear viscosity of water-cu nanofluids using equilibrium molecular dynamics. In *ASME 2013 International Mechanical Engineering Congress and Exposition*, pages V08CT09A012–V08CT09A012. American Society of Mechanical Engineers, 2013.

[30] W Yu and SUS Choi. The role of interfacial layers in the enhanced thermal conductivity of nanofluids: a renovated hamilton–crosser model. *Journal of Nanoparticle Research*, 6(4): 355–361, 2004.

[31] Yongjin Feng, Boming Yu, Peng Xu, and Mingqing Zou. The effective thermal conductivity of nanofluids based on the nanolayer and the aggregation of nanoparticles. *Journal of Physics D: Applied Physics*, 40(10):3164, 2007.

[32] C-J Yu, AG Richter, A Datta, MK Durbin, and P Dutta. Molecular layering in a liquid on a solid substrate: an x-ray reflectivity study. *Physica B: Condensed Matter*, 283(1-3):27–31, 2000.

[33] Tolga Akıner, Jeremy K Mason, and Hakan Ertürk. Nanolayering around and thermal resistivity of the water-hexagonal boron nitride interface. *The Journal of Chemical Physics*, 147 (4):044709, 2017.

[34] DA McQuarrie. Statistical mechanics. 2000. *Sausalito, Calif.: University Science Books*, 12: 641, 2004.

[35] Hasan Babaei, Pawel Keblinski, and Jay M Khodadadi. Equilibrium molecular dynamics determination of thermal conductivity for multi-component systems. *Journal of Applied Physics*, 112(5):054310, 2012.

[36] WL Jorgensen, J Chandrasekhar, JD Madura, RW Impey, and ML Klein. Comparison of simple potential functions for simulating liquid water. *J. Chem. Phys.*, 79:926, 1983.

[37] Jose LF Abascal and Carlos Vega. A general purpose model for the condensed phases of water: Tip4p/2005. *The Journal of chemical physics*, 123(23):234505, 2005.

[38] HJC Berendsen, JR Grigera, and TP Straatsma. The missing term in effective pair potentials. *Journal of Physical Chemistry*, 91(24):6269–6271, 1987.

[39] Jean-Paul Ryckaert, Giovanni Ciccotti, and Herman JC Berendsen. Numerical integration of the cartesian equations of motion of a system with constraints: molecular dynamics of n-alkanes. *Journal of Computational Physics*, 23(3):327–341, 1977.

[40] Pekka Mark and Lennart Nilsson. Structure and dynamics of the tip3p, spc, and spc/e water

models at 298 k. *The Journal of Physical Chemistry A*, 105(43):9954–9960, 2001.

[41] David E Sanders and Andrew E DePristo. Metal/metal homo-epitaxy on fcc (001) surfaces: Is there transient mobility of adsorbed atoms? *Surface science*, 254(1-3):341–353, 1991.

[42] Steve Plimpton. Fast parallel algorithms for short-range molecular dynamics. *Journal of computational physics*, 117(1):1–19, 1995.

[43] William Humphrey, Andrew Dalke, and Klaus Schulten. Vmd: visual molecular dynamics. *Journal of molecular graphics*, 14(1):33–38, 1996.

[44] Masoud H Khadem and Aaron P Wemhoff. Comparison of green–kubo and nemd heat flux formulations for thermal conductivity prediction using the tersoff potential. *Computational Materials Science*, 69:428–434, 2013.

[45] JE Turney, ES Landry, AJH McGaughey, and CH Amon. Predicting phonon properties and thermal conductivity from anharmonic lattice dynamics calculations and molecular dynamics simulations. *Physical Review B*, 79(6):064301, 2009.

[46] Yijin Mao and Yuwen Zhang. Thermal conductivity, shear viscosity and specific heat of rigid water models. *Chemical Physics Letters*, 542:37–41, 2012.

[47] Yimin Xuan and Qiang Li. Heat transfer enhancement of nanofluids. *International Journal of heat and fluid flow*, 21(1):58–64, 2000.

[48] Seok Pil Jang and Stephen US Choi. Effects of various parameters on nanofluid thermal conductivity. *Journal of heat transfer*, 129(5):617–623, 2007.

[49] Chan Hee Chon, Kenneth D Kihm, Shin Pyo Lee, and Stephen US Choi. Empirical correlation finding the role of temperature and particle size for nanofluid (al 2 o 3) thermal conductivity enhancement. *Applied Physics Letters*, 87(15):153107, 2005.

[50] S Maruyama T Kurashige S Matsumoto and Y Yamaguchi T Kimura. Liquid droplet in contact with a solid surface. *Microscale Thermophysical Engineering*, 2(1):49–62, 1998.

[51] Frédéric Leroy and Florian Müller-Plathe. Solid-liquid surface free energy of lennard-jones liquid on smooth and rough surfaces computed by molecular dynamics using the phantom-wall method. *The Journal of chemical physics*, 133(4):044110, 2010.

[52] Frederic Leroy, Shengyuan Liu, and Jianguo Zhang. Parametrizing nonbonded interactions from wetting experiments via the work of adhesion: Example of water on graphene surfaces. *The Journal of Physical Chemistry C*, 119(51):28470–28481, 2015.

[53] Tolga Akıner, Jeremy Mason, and Hakan Ertürk. Thermal characterization assessment of rigid

and flexible water models in a nanogap using molecular dynamics. *Chemical Physics Letters*, 687:270–275, 2017.