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2010


http://hdl.handle.net/10379/5338

http://dx.doi.org/10.1016/j.cplett.2010.06.074
Molecular simulation of nanoparticle diffusion at fluid interfaces

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Abstract

Using molecular dynamics simulations the transport properties of a model nanoparticle in solution are studied. In bulk solvent the translational diffusion coefficients are in good agreement with previous simulation and experimental work, while the rotational diffusion is more rapid than in previous simulations. When the nanoparticle is adsorbed at a liquid-liquid interface it becomes strongly attached to the interface. This leads to highly anisotropic motion with in-plane diffusion being several orders of magnitude larger than out-of-plane diffusion. By contrast the rotational diffusion is only slightly changed when the particle is adsorbed at the interface.

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1 Introduction

Motivated by the long-standing observation that solid particles may adhere to liquid interfaces \[1,2\] the behaviour of nanoparticles at fluid interfaces has, over the past few years, become an area of active interest \[3\]. Much of this interest has been driven by the potential use of liquid interfaces as a template for the formation of dense nanoparticle structures, such as monolayers and membranes. The modification of interfacial properties by the adhesion of nanoparticles may also be used to stabilize the formation of large-scale structures.

It has long been recognized that the dynamic and transport properties of nanoparticles, in the bulk \[4–8\] and at interfaces, may be significantly different to those of larger particles. The translational motion of particles at interfaces is important in understanding the interfacial self-assembly processes and in the use of nanoparticles as tracer particles in micro- and nanorheology \[9,10\]. The orientational dynamics of nanoparticles is also worthy of investigation. In particular functionalization of particles adsorbed on liquid-liquid interfaces has been used as a route to the formation of micron-sized Janus particles \[11\]; the extension of this technique to smaller particles, however, relies on the rotational diffusion of the particles being sufficiently slower than the reaction rates. The orientational motion of nanoparticles also has implications for their use as catalysts \[12\]; as edges and points on nanoparticle surfaces are typically the most active sites for catalysis the orientation of these sites relative to the interface will determine their activity.

Due to the ability of molecular simulations to directly access the nanometre
lengthscales appropriate to nanoparticles, it provides a natural tool for the investigation of these systems. Previous simulations have addressed the stability of nanoparticles at interfaces [13–17], interactions between nanoparticles [18], orientational behaviour of anisotropic nanoparticles [17, 19], and the self-assembly of nanoparticles at fluid interfaces [20, 21]. These simulations have largely focused on the static properties of nanoparticles at interfaces, while only recently has simulation been turned to the dynamic properties of nanoparticles at liquid interfaces [22].

In this paper molecular dynamics simulations are used to examine the transport properties of a nanoparticle in both bulk solvent and at a liquid-liquid interface. Specifically it aims to address the effect of interfacial adsorption on the diffusion of nanoparticles (at low concentration). Understanding the translational diffusion of nanoparticles at liquid interfaces, in particular in relation to particle size, is important in their use as tracer particles; due to the highly inhomogeneous nature of the interfacial region the diffusive behaviour of nanoparticles may be different to that in the bulk. Study of the rotational diffusion of nanoparticles, which has been poorly studied bulk solvents as well as at interfaces, will provide a guide to the applicability of interfacial techniques of particle synthesis [11] to nanoparticles and to nanoparticle catalysis. The applicability of the continuum Stokes-Einstein(-Debye) relations to nanoparticles at interfaces will also be investigated. The simulation methodology and model is outlined in the following section, along with description of the analysis of the the simulation trajectories. The results are then presented in Sec. III before some brief conclusions in Sec. IV.
2 Methodology

2.1 Model and simulation details

The solvent was modelled as a Lennard-Jones fluid, interacting with the potential

\[ V(r) = \begin{cases} 
4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] & r \leq r_{\text{cut}} \\
0 & r > r_{\text{cut}}, \end{cases} \]

with \( r_{\text{cut}} = 2.5\sigma \) for like particles and \( r_{\text{cut}} = \sqrt{2}\sigma \) for unlike particles (i.e. the interaction is cut-off at the potential minima). The nanoparticle was modelled as a rigid cluster of Lennard-Jones sites, constructed from a FCC lattice, containing particles within a distance \( R_c \) of the origin (details of the simulated nanoparticles are presented in Table 1). The interaction between the sites in the nanoparticle and the solvent particles is given by Eqn. 1 with \( r_{\text{cut}} = \sqrt{2}\sigma \).

For simulations of the nanoparticle in bulk solvent, the nanoparticle was initially placed in the centre of the simulation cell and the solvent particles were randomly placed around it, while for the interface simulations, the nanoparticle was placed in the interface between the two liquid components.

The system was studied using constant-\( NVT \) molecular dynamics simulations, using the LAMMPS simulation package [23]. All simulations were performed at temperature \( T^* = k_B T/\epsilon = 1 \) (using a Nosé-Hoover thermostat [24]) and solvent density \( \rho^* = \rho\sigma^3 = 0.69 \). For the single component system this is well within the liquid region for the truncated Lennard-Jones fluid [25] and this density is well above the demixing transition for the two-component mixture. A timestep of \( \delta\tau = 0.005\tau \) was used (\( \tau = \sqrt{m\sigma^2/\epsilon} \)) and the simulations consisted of \( 6 \times 10^6 \) MD steps (\( 10^6 \) MD steps equilibration and \( 5 \times 10^6 \) steps...
2.2 Analysis

The translational motion of the nanoparticle may be analyzed through the usual self-diffusion coefficient

\[ D_t = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \langle |r_c(t) - r_c(0)|^2 \rangle = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \Delta r^2 \]

(2)

where \( r_c(t) \) is the centre of mass position of the nanoparticle at time \( t \) and the angled brackets denote averaging over different time origins. \( D_t \) is extracted from the slope of the mean-squared diffusion at long times. \( D_t \) may also be found from the velocity autocorrelation function \( C_v(t) = \langle v(t) . v(0) \rangle \) from [26]

\[ D_t = \frac{1}{3} \int_0^\infty dt \ C_v(t) . \]

(3)

The orientational motion of the nanoparticle may be quantified in terms of the angular velocity correlation function

\[ C_\omega(t) = \langle \omega(t) . \omega(0) \rangle. \]

(4)

Analogously to translational motion, the integral of \( C_\omega(t) \) may be used to define the rotational diffusion coefficient

\[ D_r = \frac{k_B T}{I} \int_0^\infty dt \frac{C_\omega(t)}{C_\omega(t = 0)} = \frac{k_B T}{I} \tau_\omega \]

(5)

where \( I \) is the particle moment of inertia (as the particles are rigid and approximately spherical \( I = I_{xx} = I_{yy} = I_{zz} \)) and \( \tau_\omega \) is the angular velocity relaxation time. The orientational motion may also be characterized through
the orientational correlation function

\[ C_\ell = \langle P_\ell(\hat{e}(t)\cdot\hat{e}(0)) \rangle \quad (6) \]

where \( P_\ell(x) \) is a Legendre polynomial and \( \hat{e}(t) \) is the vector joining the two atoms farthest apart in the nanoparticle. At long times \( C_\ell(t) \) decays exponentially \( (C_\ell(t) \propto \exp(-t/t_u) \quad [7]) \) and for \( \ell = 1 \) the decay time \( t_u \) may be related to the \( D_r \) via [27]

\[ D_r = -\frac{1}{2} \lim_{t \to \infty} \log C_1(t) = \frac{1}{2t_u}, \quad (7) \]

giving us two routes to the rotational diffusion coefficient. It should be noted that the first route, through \( C_\omega(t) \) is more convenient as it involves the integral of a rapidly decaying function [4].

3 Results

3.1 Nanoparticles in bulk solvent

We first present results for nanoparticles in a one-component bulk solvent. Figure 1 shows the solvent density profile around nanoparticles in a bulk solvent. For the smallest particle considered the surrounding fluid is highly structured, with a number of peaks (spacing \( \sim 1\sigma \)). On increasing the \( R_c \) the fluid structure becomes weaker; for the largest particle \( R_c = 3\sigma \) the density profile tends monotonically to a constant values far from the particle surface.

The centre-of-mass motion of the nanoparticle, as quantified by the mean-squared-displacement \( (\Delta r^2) \) and velocity autocorrelation function \( (C_v(t)) \) are shown in Fig. 2. As may be expected the translational motion of the nanoparticle depends on the particle radius with smaller particles diffusing more
rapidly (Fig. 2(a)). The velocity autocorrelation function (Fig 2(b)) decays more rapidly for the smallest particles. The rotational motion of the particle (Fig 2(c) and (d)) also shows a strong dependence on particle size, with both the orientational correlation function \(C_1(t)\) and angular velocity correlation function \(C_\omega(t)\) decaying more slowly as \(R_c\) increases.

The diffusion coefficients are summarized in Tab. 2. For large particles the \(D_t\) may be given by the Stokes-Einstein (SE) relation

\[
D_t = \frac{k_B T}{n_T \pi R_c \eta}
\]

(8)

where \(\eta\) is the viscosity and \(n_T\) depends on the boundary conditions (for slip boundaries \(n_T = 4\) while for stick boundaries or \(n_T = 6\)). For the present system the viscosity, calculated from RNEMD simulations [28], is \(\eta = 1.1 m \sigma^{-1} \tau^{-1}\), giving \(D_t = 0.032 - 0.016 \sigma^2 \tau^{-1}\) for stick boundary conditions and \(D_t = 0.048 - 0.024 \sigma^2 \tau^{-1}\) for slip, in reasonable agreement with simulation. This is contrary to recent simulation work [8]. This difference may arise due to the lack of attractive interactions between the nanoparticle and solvent particles in this work or differences in viscosity. Despite the lack of attractive interactions the SE relation with stick boundary conditions gives a better agreement with simulation, due to the solvent structure around the nanoparticle. The values of \(D_t\) are in good agreement with previous simulations [4]. The Stokes-Einstein-Debye relation

\[
D_r = \frac{k_B T}{n_R \pi R_c^3 \eta}
\]

(9)

predicts that the rotational diffusion coefficient should scale as \(R_c^{-3}\), which is well reproduced by particles studied in this work. Use of \(n_R = 8\), appropriate for stick boundaries, gives values of \(D_r\) substantially smaller than calculated
from simulation \(D_r \approx 0.010\tau^{-1}\) for \(R_c = 1.5\sigma\) and \(\approx 0.001\tau^{-1}\) for \(R_c = 3\sigma\), while the simulation results are recovered for \(n_r \approx 1.19\). This rescaling has been previously observed in molecular simulations \[29\] and for tracer diffusion in colloidal suspensions \[30\]. The values of \(D_r\) calculated here are somewhat larger than those from previous simulations \[4\]. The orientational \((\tau_u)\) and angular velocity \((\tau_\omega)\) relaxation times are also listed in Tab. 2. \(\tau_u\) is in all cases significantly larger than \(\tau_\omega\) and is in good agreement with previously reported values for similar sized nanoparticles \[4\]. \(\tau_\omega\) is significantly larger; this may be due to the larger density of cluster or the neglect of the cluster’s internal degrees of freedom in this work.

The present results may be compared to those of atomistic simulations and experimental measurements. Taking parameters for liquid argon \((\sigma = 3.395 \text{ Å}, \epsilon/k_B = 116.8 \text{ K}, m = 39.948 \text{ amu}, \text{ and } \tau \approx 2.2 \text{ ps} \[31\])\). The simulated translational diffusion coefficients are then \(D_t \approx 2 \times 10^{-5} \text{ cm}^2\text{s}^{-1} (R_c = 1.5\sigma)\) to \(D_t = 0.5 \times 10^{-5} \text{ cm}^2\text{s}^{-1} (R_c = 3\sigma)\), in good agreement with previous simulations \[22\]. The present results are also in good agreement with experimental measurements, with \(D_t \approx 0.2 \text{ cm}^2\text{s}^{-1}\) for 1 nm dye particles \[32\]. Experimentally the orientational behaviour of nanoparticles is less well characterized; many previous studies have been on ferrofluids in which, for the particle sizes considered in this work, the orientational behaviour is dominated by magnetic interactions \[33\]. For larger particles the reorientation times are typically of the order of 1-100 ns for a 20 nm particle; as the orientational relaxation times scale as \(R_c^3\) this is consistent with the simulated reorientation times of 50-150 ps, which are also in the same range as previous simulation results \[7\].
3.2 Nanoparticles at liquid interfaces

When the nanoparticle is adsorbed at a liquid-liquid interface the solvent structure around the particle becomes highly anisotropic. Two-dimensional maps of the solvent around the nanoparticle (Fig. 3(a)) show a sizeable depletion region between the two solvent components [15], with the interface width being comparable to the nanoparticle size for $R_c = 1.5\sigma$. The width of the interface may be estimated from the density profiles of the individual components, specifically from the distance between the points at which the density of the $A$ component is 90% and 10% of its bulk value [34], yielding an interfacial width $w = 1.97\sigma$. In experimental units this corresponds to a $w \approx 6.7 \, \text{Å}$, which is typical for simple fluid interface. The perturbation in the fluid caused by the nanoparticle may also be seen; in particular the presence of a high density layer near the surface of the particle. The layering of the solvent may be seen more clearly in the normalized density profiles (Fig. 3(b)). It is noticeable that at the interface there is a peak in the density profiles near the particle surface for all $R_c$, whereas for in bulk solvent (in Fig. 1 the peak is absent for larger particle radii).

Due to the presence of the interface, the motion of the nanoparticle becomes anisotropic. It is useful to consider the motion of the nanoparticle parallel and perpendicular to the interface

\[
D_t^\parallel = \frac{1}{4} \langle (x(t) - x(0))^2 + (y(t) - y(0))^2 \rangle 
\]

\[
D_t^\perp = \frac{1}{2} \langle (z(t) - z(0))^2 \rangle,
\]
Similarly the velocity autocorrelation function may be decomposed into

\[ D^\parallel = \frac{1}{2} \int_0^\infty dt \, C^\parallel(t) = \frac{1}{2} \int dt \langle v_y(t) \cdot v_y(0) \rangle \]  
\[ D^\perp = \int_0^\infty dt \, C^\perp(t) = \int dt \langle v_z(t) \cdot v_z(0) \rangle. \]

Shown in Fig. 4(a) is the mean-squared displacement for nanoparticles adsorbed at the interface. The effect of the interface on the nanoparticle diffusion may be clearly seen, with diffusion in the plane of the interface being significantly larger than perpendicular to the interface, consistent with the particle being strongly bound to the interface. This implies that the detachment energy of the particle from the interface is significantly larger the \( k_B T \) even for the smallest particle studied, larger than in previous work [16, 17] due to the larger interfacial tension in this study. The detachment energy may be estimated from [35]

\[ \Delta F = \pi R^2 (1 + \cos \theta) \gamma, \]  
where \( \gamma \) is the interfacial tension and \( \theta \) is the contact angle (which, due to the symmetry between the two solvent components, is \( \theta = \pi/2 \)). In reduced units \( \beta \sigma^2 \gamma = 1.2 \) (which is up to an order of magnitude larger than in Ref. [16]), giving \( \beta \Delta F = 8.5 - 33.9 \), although it has been shown that Eqn. 12 is likely to underestimate the detachment energy, due to the neglect of line tension and capillary waves [16, 17]. Similar conclusions may be drawn from the velocity autocorrelation function (Fig. 4), with \( C^\parallel(t) \) differing markedly from \( C^\perp(t) \). For all \( R_c \), \( C^\perp(t) \) has a negative region, indicating that the particle is oscillating in the vicinity of the interface.

The translational diffusion coefficients for the nanoparticle adsorbed at the interface are presented in Table 3. These are in good agreement with previous
simulations [22] and find that the in-plane diffusion coefficients are larger than the nanoparticle diffusion coefficient in bulk solvent. This increased diffusion may arise due to the lower viscosity of the interfacial region; from RNEMD simulations [28, 36] the viscosity in the interfacial region is found to be approximately four times smaller than in the bulk ($\eta_I \approx 0.25 m \sigma^{-1} \tau^{-1}$); it should be noted the the shear rate in the interfacial region is rapidly varying, so the effective viscosity acting on the nanoparticle is larger than this, though still smaller than in the bulk solvent. Alternatively as the overall diffusion coefficient is largely unchanged when the particle is adsorbed at the interface, the in-plane diffusion coefficient increases due to the lack of diffusion normal to the interface.

Experimental measurements find much smaller (one to two orders of magnitude) diffusion coefficients for CdTe nanoparticles on water-toluene interface [37]. These were performed on nanoparticle monolayers rather than for a single nanoparticle in the present case and are performed in solvents of different viscosities which lead to a lower diffusivity [38].

Adsorption at the liquid-liquid interface may also affect the rotational motion of the nanoparticle. Shown in Fig. 5(a) is the orientational correlation function $C_1(t)$, for nanoparticles at the interface. For the smallest nanoparticles studied there is little difference between the rotational diffusion in the bulk and at the interface with the decay being exponential in both cases. For $R_c = 3\sigma$ there is a difference between $C_1(t)$ at the interface and bulk, which is most noticeable at long times were their appears to be a deviation from an exponential decay for the particle at the interface. The variation in $C_\omega(t)$ is consistent with this (Fig. 5(b)). For $R_c = 1.5\sigma$ $C_\omega(t)$ decays more slowly at the interface, indicating that the rotational diffusion is slightly more rapid. This situation reverses as
$R_c$ increases. Considering separately the correlation functions of the $x$, $y$, and $z$ components of $\omega$ shows only a slight difference between $C_\omega^\alpha(t)$ ($\alpha = x, y, z$), with $C_\omega^x(t) \approx C_\omega^y(t)$ and $C_\omega^z(t)$ showing a slightly slower decay.

The calculated rotational diffusion coefficients and orientational relaxation times are presented in Table 3. Despite the differences in the orientational correlation functions between the bulk and interface, $D_r$ is very similar for both cases. For the $R_c = 1.5 \sigma$ particle $D_r$ and $t_\omega$ are larger and $\tau_u$ is smaller at the interface indicating more rapid orientational motion. This more rapid orientational motion is due to the lower effective viscosity of the interfacial region. As the particle size increases. As $R_c$ increases the difference between the interface and bulk results decreases, with $D_r^{\text{interface}} \approx D_r^{\text{bulk}}$ for the largest particles. The trend towards the bulk values for diffusion coefficients may be understood as the particle becomes larger than the interfacial width and more of its surface is in contact with ‘bulk’ solvent.

4 Conclusions

In this paper the transport properties of spherical nanoparticles have been studied using molecular dynamics simulations. In bulk solvent the translational diffusion coefficients are comparable with previous simulation and experimental studies. The rotational diffusion however is somewhat more rapid than in previous work, which may arise due to the more dense nanoparticles studied in this work.

When the particle is adsorbed at a liquid-liquid interface the translational diffusion becomes highly anisotropic, with $D^\parallel_t >> D^\perp_t$. Indeed due to the strong
attachment of the nanoparticle to the interface, arising due to the decrease in the interfacial free energy between the two solvent components, there is virtually no diffusion perpendicular to the interface. This effective two-dimensional diffusion leads to an in-plane diffusion coefficient that is significantly larger than the diffusion coefficient in the bulk (as the diffusion normal to the interface is negligible the overall diffusion coefficient for the particle at the interface is essentially the same as in the bulk). The in-plane diffusion coefficient is affected by the difference between the viscosities of the two solvent components; the identical viscosities in the present case leads to more rapid in-plane diffusion than if the solvent viscosities were different. This, along with the present simulations being performed on a single nanoparticle (effectively infinite dilution), may explain the difference between the present simulation results and experimental measurements on nanoparticle monolayers (in which the nanoparticle diffusion was slower on the interface).

By contrast the rotational diffusion of the particle is almost isotropic. For the smallest particles studied the diffusion (both translational and rotational) is more rapid at the interface than in bulk solvent as the sit in the low-density region between the two fluid components. On increasing particle size the diffusion coefficients tend towards their bulk values, indicating that the rotational motion of nanoparticles is the same at the interface and in the bulk. This tendency towards bulk-like behaviour may be understood as more of the particle surface is in contact with the bulk solvent. The rotational diffusion may be characterized by taking the ratios of $\tau_u$ and $\tau_\omega$ with $\tau_{rot} = \sqrt{I/k_B T}$ (the time taken for a free rotator to rotate by one radian). 'Small-step' rotational diffusion is indicated by $\tau_{rot} \gg \tau_\omega$ and $\tau_{rot} \ll \tau_u$ [27]. While $\tau_\omega$ is smaller than $\tau_{rot}$ for all $R_c$, only for the largest cluster is $\tau_u$ significantly larger than $\tau_{rot}$.
implying that this model may not be appropriate for the rotational diffusion of smaller clusters. The precise determination of the reorientation mechanism may form the basis for future work.

The translational diffusion coefficients found in this work are comparable to experimental values. Rotational motion of nanoparticles, both in bulk solvent and at interfaces, has not been so well characterized. In particular the orientational relaxation time, which for the particles studied in this work is of the order of 100 ps, provides a guide to the rates of reaction for the patterning of nanoparticle surfaces or nanoparticle catalyzed reactions at interfaces. While the present study was restricted to (approximately) spherical, more complex nanoparticle geometries are of interest for many applications and the method used may be easily applied to these systems.

Acknowledgements

This work was funded by UK EPSRC and ERC and computational facilities were provided by the Centre for Scientific Computing, University of Warwick. The author is grateful to Dr Stefan Bon for useful discussions during this work.

References


URL http://lammps.sandia.gov


Table 1
Summary of principal properties of the nanoparticles studied in this work. $R_c$ is nanoparticle radius, $N_{\text{cluster}}$ is number of atoms in nanoparticle, $\langle R_{g}^2 \rangle = (1/N_{\text{cluster}}) \sum r_i^2$ is the nanoparticle radius of gyration and $I$ is the nanoparticle moment of inertia.

<table>
<thead>
<tr>
<th>$R_c / \sigma$</th>
<th>$N_{\text{cluster}}$</th>
<th>$\langle R_{g}^2 \rangle / \sigma^2$</th>
<th>$I / m\sigma^2$</th>
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<tr>
<td>1.5</td>
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<td>48</td>
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<td>459</td>
<td>5.64</td>
<td>1672</td>
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Table 2

Diffusion coefficients (translational and rotational) and rotational correlation times for nanoparticles in bulk solvent. Figures on parenthesis given errors in last digit.

<table>
<thead>
<tr>
<th>$R_c / \sigma$</th>
<th>$D_i^{MSD} / \sigma^2 \tau^{-1}$</th>
<th>$D_i^{YCF} / \sigma^2 \tau^{-1}$</th>
<th>$D_v^\theta / \tau^{-1}$</th>
<th>$D_v^\omega / \tau^{-1}$</th>
<th>$\tau_u / \tau^*$</th>
<th>$\tau_\omega / \tau^*$</th>
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</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.038(5)</td>
<td>0.037(5)</td>
<td>0.075(1)</td>
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<td>6.7(3)</td>
<td>3.5(4)</td>
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<td>0.024(4)</td>
<td>0.031(3)</td>
<td>0.03(1)</td>
<td>16.1(7)</td>
<td>7.2(4)</td>
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<td>0.013(2)</td>
<td>0.010(2)</td>
<td>0.010(2)</td>
<td>50.5(5)</td>
<td>17.5(6)</td>
</tr>
<tr>
<td>$R_c / \sigma$</td>
<td>MSD</td>
<td>VACF</td>
<td>$D_u$</td>
<td>$D_\omega$</td>
<td>$\tau_u$</td>
<td>$\tau_\omega$</td>
</tr>
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<tr>
<td></td>
<td>$D_t$</td>
<td>$D^\parallel_t$</td>
<td>$D_t$</td>
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<td>0.008(2)</td>
<td>0.010(1)</td>
</tr>
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</table>

Table 3

Diffusion coefficients and orientational relaxation times for nanoparticle at liquid-liquid interface. Figures on parenthesis given errors in last digit.
Figure Captions

Fig. 1. Normalized solvent density profiles around nanoparticle with radius $R_c = 1.5\sigma$ (solid curve, black), $R_c = 2\sigma$ (dotted curve, red), $R_c = 2.5\sigma$ (dashed curve, green), $R_c = 3\sigma$ (dot-dashed curve, blue).

Fig. 2. (a) Mean-squared displacement of uniform nanoparticle with radius $R_c = 1.5\sigma$ (solid curve, black), $R_c = 2\sigma$ (dotted curve, red), $R_c = 2.5\sigma$ (dashed curve, green), $R_c = 3\sigma$ (dot-dashed curve, blue). (b) Normalized velocity autocorrelation function for uniform nanoparticle (symbols as in (a)). Inset shows unnormalized $C_v(t)$. (c) Orientation correlation function $C_1(t)$. Symbols as in (a). (d) Normalized angular velocity correlation function $C_\omega(t)$. Symbols as in (a). Inset shows unnormalized $C_\omega(t)$.

Fig. 3. (a) Solvent density maps around $R_c = 1.5\sigma$ (left) and $R_c = 3\sigma$ (right) nanoparticles. (b) Normalized density profiles (for A-component) around nanoparticle of radius $R_c = 1.5\sigma$ (solid line, black), $R_c = 2\sigma$ (dotted line, red), $R_c = 2.5\sigma$ (dashed line, green), and $R_c = 3\sigma$ (dot-dashed line, blue).

Fig. 4. (a) Mean-squared displacements for nanoparticle of radius $R_c = 1.5\sigma$ (top) and $R_c = 3\sigma$ (bottom) at liquid-liquid interface. Solid line (black) denotes total MSD, dotted line (red) MSD in plane of interface, dashed line (green) MSD perpendicular to interface and dot-dashed line (blue) MSD for nanoparticle in bulk solvent. (b) Velocity ACF for nanoparticle of radius $R_c = 1.5\sigma$ (top) and $R_c = 3\sigma$ (bottom) at liquid-liquid interface. Solid line (black) denotes $C_v(t)$, dotted line (red) $C_{xy}v(t)$, dashed line (green) $C_zv(t)$ and dot-dashed line (blue) $C_v(t)$ for nanoparticle in bulk solvent.

Fig. 5. (a) $C_1(t)$ for nanoparticle of radius $R_c = 1.5\sigma$ (top) and $R_c = 3\sigma$ (bot-
tom). Solid line (black) denotes nanoparticle at liquid-liquid interface and dotted line (red) denotes nanoparticle in bulk solvent. (b) $C_\omega(t)$ for $R_c = 1.5\sigma$ (top) and $R_c = 3\sigma$ (bottom) nanoparticles at liquid-liquid interface. Solid line denotes $C_\omega(t)$, dotted line (red) $C_x^\omega(t)$, dashed line (green) $C_y^\omega(t)$, and dot-dashed line $C_z^\omega(t)$. $C_\omega(t)$ for bulk system shown by double-dot-dashed (magenta) line.
Fig. 2
Fig. 3
Fig. 4
Fig. 5