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Estimation of zeta potentials of titania nanoparticles by molecular simulation

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Non-equilibrium molecular dynamics (NEMD) simulations have been performed in static electric fields for a range of positively-charged spherical rutile-titania nanoparticles with radii of 1.5 to 2.9 nm for two different salt concentrations in water, in order to simulate directly electrophoresis. Using the observed limiting drag velocities, Helmholtz-Smoluchowski (HS) theory was used to estimate their ζ potentials. These estimates were compared to values from numerical solution of the non-linear Poisson-Boltzmann (PB) equation about representative configurations of the nanoparticles, in addition to idealised analytic and Debye-Hückel (DH) solutions about spherical particles of the same geometry and charge state, for the given salt concentrations. It was found that reasonable agreement was obtained between the various approaches, with the NEMD-HS results some 15-15% smaller than the numerical PB results for more highly-charged nanoparticles.

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1. Introduction

Zeta potentials are an important property in characterising the interactions of a wide variety of charged particles, from colloids to nanoparticles, with their environment. They are measured directly from experiments performing electrophoresis, and have important ramifications in processes employing electrophoretic deposition (EPD) [1, 2]. In electrolyte solutions, the electrostatic interactions between charged particles and their surrounding electric double layer determines the kinetics of aggregation, flocculation, coalescence, coagulation, as well as interactions with surfaces which may lead to deposition or adsorption. Titania is an important technologic material, and studies of the interaction of titania nanoparticles with biological systems and the environment are of increasing interest [3]. The electrostatic properties of the double layer are highly influential on these interactions, for instance in determining the ‘biological identity’ of nanoparticles through the protein ‘corona’ adsorbed on their surfaces [4]. The possibility of using computational methods to estimate electrostatic properties of nanoparticles, in particular the ζ potential and the electrostatic potential (ESP) distribution, is clearly attractive.

The motivation of this study is to use a variety of methods to estimate the ζ potential and ESP distribution of a variety of representative titania nanoparticles. One of the main topics in the physics of charged particles relates to charge screening, which affects the ESP directly. The numerical solution of the non-linear Poisson-Boltzmann equation generates the ESP directly about particles, and this may be gauged as the ‘definitive’ solution, but useful analytic approaches are available for ESP distributions, via solution of either the linear PB equation, *e.g.* Debye-Hückel, Deryaguin-Landau [5] or Verwey-Overbeek [6] approaches, or the non-linear form for spherical geometries by Wang *et al* [7-10] and D’yachkov [11]. The use of the

Gouy-Chapman-Stern model may then be used to estimate the ζ potential at the Debye length, κ^{-1} . A further question addressed by this study is the direct NEMD simulation of electrophoresis in a static electric field and use of the Helmholtz-Smoluchowski (HS) approach [12] to estimate the ζ potential based on the drag velocity of the centre of mass of the charged nanoparticle.

2. Simulation Methodology

The relatively large system sizes required to model the spherical nanoparticles in simulation boxes with water (*i.e.*, tens of thousands of atoms) required the use of empirical TiO_2 and water potential models for use in conjunction with classical MD and numerical PB calculations. Several force field models for lattice energy minimization or MD have been reported for TiO_2 polymorphs [13-25]. In a detailed analysis of available potentials, Collins and Smith [21] concluded that the Matsui-Akaogi potential [18] is the most suitable for classical simulation. Ogata et al. [24] and Swamy et al. [25] have developed variable charge models, but Swamy et al. [26] have found that the Matsui-Akaogi potential performs better in some cases than their previous variable charge model [25]. The Matsui-Akaogi potential [18] was used in this study; it is not within the scope of this study to develop or apply a variable charge potential for TiO_2 . This consists of a Buckingham potential and Coulombic interactions between each ion, and the charges allocated to the titanium and oxygen ions are $+2.196 e$ and $-1.098 e$, respectively, where e is the absolute value of the charge on an electron. The rigid SPC/E model was employed for water [27]. This potential affords a satisfactory description of phase behaviour of bulk water, as well as liquid water structure, diffusivity, and dielectric properties over a wide range of temperature and density conditions [28, 29]. Chlorine ions (Cl^-) were also dissolved in the water to keep the overall solvated nanoparticle systems electroneutral. Potential

parameters for these ions, and their interaction potentials with SPC/E water were taken from the study of Palmer *et al* [30]. The titania-SPC/E water interaction parameters of Prědota *et al* [31] were adopted, based on their fits of forcefield forms on *ab initio* calculations. As it was found in this study, as in that of Prědota *et al* [31], the titania surface was shielded from chlorine ions, and therefore only electrostatic interactions between the titania and chlorine were computed.

The rutile form of TiO_2 was used in the construction of the nanoparticles. It has a tetragonal unit cell (D_{4h}^{14} , $P4_2/mnm$) with six atoms per unit cell. Ti atoms occupy the corners and center of the unit cell while the positions of O atoms are generated by applying space group operators upon the set of fractional coordinates $(u, u, 0)$ with $u = 0.3053$. At 298 K, the unit cell dimensions are $a = b = 4.59373 \text{ \AA}$ and $c = 2.959 \text{ \AA}$ [32]. From a large $20 \times 20 \times 31$ defect-free supercell, which had been relaxed without restraints in the NPT ensemble for 0.5 ns at 298 K and 1 bar using the MD strategy specified below, seven spherical nanoparticles of increasing radius were constructed by removal of increasing number of atoms from the centre of the simulation box. These had radii of approximately 1.5, 1.8, 2, 2.2, 2.5, 2.75 and 2.9 nm, such that they contained a stoichiometrically appropriate number of ions. Each nanoparticle so constructed was placed at the centre of a cubic periodic box, and SPC/E water molecules were added to the system from a relaxed liquid configuration at 298 K and 1 bar, such that their oxygen atoms were greater than $2.8 \text{ \AA}$ in distance from the nanoparticles' outer layer of atoms. Each nanoparticle was given a surface charge of $+2e$ and $+6e$, distributed uniformly across the surface layer of Ti atoms in equal positive increments to their forcefield charge. This was done so as to allow electrophoresis to take place (see below), and the uniform distribution was adopted to conform to the Gouy-Chapman-Stern model of the electric double layer and to mimic

the scenario of model solutions to the PB equation used for such purposes. It was desired to carry out NEMD simulations of electrophoresis at salt concentrations of 0.005 and 0.015 mol/l, and to compare HS estimates of the ζ potential with those of model and numerical PB approaches at these concentrations. To maintain electroneutrality of the simulation boxes containing the $+2e$ and $+6e$ - charged nanoparticles, 2 and 6 Cl^- ions were placed in the water, at least 1 nm from the edge of the nanoparticle and from each other. For these 2 and 6 Cl^- ions, the respective salt concentrations of 0.005 and 0.015 mol/l required the presence of approximately 22,200 water molecules; in this way, none of the nanoparticle's surface layer of atoms were lying within less than 1.5 nm from the edge of the simulation box, and the box lengths were 9-10 nm for each system. For the smallest (1.5 nm radius) nanoparticle, the 'clearance' vis-à-vis the box side was almost 3 nm.

The cut-off radius for van der Waals interactions (either Buckingham or Lennard-Jones) was 12 Å, as this was found to lead to satisfactory convergence in these force and energy terms. The smooth particle mesh Ewald (SPME) method [33] was used to handle long-range electrostatics, with a real-space screening parameter for each system of around $0.24 \text{ V}\text{\AA}^{-1}$ and a cut-off radius of 14 Å, in conjunction with an FFT grid spacing of approximately 1.2 Å. This led to a relative error in the Ewald energy summation of less than 1×10^{-6} for each different system. For MD, the velocity Verlet scheme was used [34], and the RATTLE method used to impose holonomic constraints in water molecules [35], using a time step of 1 fs. For relaxation by extended system dynamics in the NVT ensemble, a light coupling to a Nosé-Hoover thermostat was used, with a thermostat relaxation time of 1 ps [36]. For initial NPT relaxation, a light coupling was applied with Melchionna's modified form of the Hoover barostat using isotropic cell fluctuations [37], with thermostat and barostat relaxation times of 1 and 2.5 ps, respectively.

Prior to equilibrium MD to relax the systems, energy minimization was carried out from the initial structures with a composite protocol of steepest descent, conjugate gradient and truncated Newton steps, using termination gradients of 500, 100 and 10 kcal/mol·Å, respectively. All of the atoms in the nanoparticles were restrained with a harmonic restraint force of 50 kcal/mol·Å² for displacements greater than 0.1 Å from their initial position. Each system was then relaxed in the NVT ensemble at 298 K for 0.5 ns, and a further 1 ns at 298 K and 1 bar in the NPT ensemble, maintaining the above constraints on the nanoparticle atoms, during which the total system energy and the nanoparticle-water interaction energy were found to stabilise.

To simulate directly electrophoresis, a uniform external electric field $\mathbf{E}$ was applied in the z -direction, *i.e.* by

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i + q_i \mathbf{E} \quad (1)$$

where q_i denotes the charge and $\mathbf{f}_i$ the force on site i due to the intermolecular potential. Given the net positive surface charges of the nanoparticles, this leads to motion in the direction of the applied field, while the water molecules' dipoles align along the field direction [38]. However, given the presence of only charge and Buckingham interactions in the Matsui-Akaogi potential, it becomes necessary to impose additional restraint forces for O and Ti field-induced motion in opposite directions (cf. eqn. 1), to maintain structural stability of the nanoparticle. This was done by imposing harmonic restraint forces on the nanoparticle atoms (50 kcal/mol·Å²), as previously, for displacements greater than 0.1 Å from their reference position, but by updating the reference position in the direction of field-induced motion by 0.02 Å at each point when the centre of mass had moved by 0.02 Å in that direction. The applied field was 0.04 V/Å in intensity. It has been found from equilibrium MD simulation that electric field intensities in condensed water phases

are in the range of approximately 1.5 to 2.5 V/Å [39], giving rise to *de facto* ‘signal-to-noise’ ratios of between around 60:1 and 40:1 for the intrinsic to applied fields in the present work. The external fields were applied in conjunction with NPT coupling, and are referred to as non-equilibrium NPT (NNPT) simulations [39].

3. Modelling

The nanoparticle with net charge $+q$ is subject to a constant acceleration from the static field $a_E \mathbf{k}$ (*i.e.*, acting along the $+z$ -direction, since the net charge is positive in this case). Given that the nanoparticles have no overall dipole moment, their motion is determined as a function of the field force acting on it (or, effectively, its centre-of-mass) and a retarding force due to friction. Provided that the Reynolds number, given by $\rho v_t a / \mu$, is less than around 0.1, in which limiting (translational) velocity is $v_t \mathbf{k}$, the radius is a and the (mass) density of the medium (water) is ρ , then laminar flow conditions prevail, and one may invoke Stoke’s law for the frictional force [40], *i.e.*

$$\mathbf{a}_E = \left[(qE - 6\pi\mu a v_t) / m \right] \mathbf{k} \quad (2)$$

Here, $v \mathbf{k}$ is the instantaneous velocity of the centre-of-mass, which reaches a ‘terminal’ value $v_t \mathbf{k}$. The electrophoretic motion is essentially laminar for the electric field intensity considered (cf. Results), so this simple treatment is reasonable, and the limiting speed v_t is reached within 10-20 ps, depending on the nanoparticle size. Integrating to obtain $v(t)$, with an initial center-of-mass velocity of zero, one obtains

$$v_t = qE / B \quad (3)$$

where B denotes $6\pi\mu a$. Using the observed value for the terminal velocity v_t , one may use the HS approach to determine the ζ potential directly [12]

$$v_t = \varepsilon E \zeta / \mu \quad (4)$$

using values for the coefficient of viscosity, μ , and the dielectric constant, ε , of SPC/E water.

According to the Gouy-Chapman-Stern model of the electric double layer, the ζ potential of a particle with surface charge may be determined from the value of the ESP at the Debye length, κ^{-1} , from its surface [12, 40], where

$$\kappa^2 = 2e^2 n_0 z^2 / \varepsilon k_B T \quad (5)$$

Here, z is the charge number on the salt ions in solution, while n_0 is the ionic concentration of salt per unit volume. The ESP field, $u(\mathbf{r})$, may be derived from solution of the PB equation applied to n ions of charge q (including those of the charged particle)

$$\nabla \cdot [d(\mathbf{r}) \nabla u(\mathbf{r})] + \sum_{i=1}^n q_i C_i \exp(-q_i u(\mathbf{r}) / kT) + f(\mathbf{r}) = 0 \quad (6)$$

where C are the ion concentrations and f is the charge density. Here, the relative dielectric field d is treated as a sum of Gaussians to describe the variation between the solute and bulk solvent dielectric constants. In the solution of the PB equation in this study, a series of NEMD snapshots of (water-free) nanoparticle configurations during electrophoresis were used with their Matsui-Akaogi and positive surface incremental charges. The interior and solvent (relative) dielectric constants were both set to 78, respectively; the experimental value of 78 at 298 K was used here, as it was desired to compare PB and HS approaches using typical practices employed by the community, and the analytic approaches to be discussed below assume that the nanoparticle's interior dielectric constant is the same as that of the medium. In any event, the experimental value of the static dielectric constant for bulk rutile at room temperature is around 85 [41], but there is no certainty that the static dielectric constant of the nanoparticles would be the same as that of the bulk. It was observed that ESP results

did not display a great dependence on the interior dielectric constant to values as low as around 30 (less than 10 %), so the same interior dielectric constant was used as for the solvent. The full non-linear form of the PB equation was solved numerically by the method of Grant *et al* with a multi-grid preconditioned gradient algorithm [42, 43] on a $(129)^3$ grid constructed with a spacing of 1.2 Å, such that the extent was at least 45 Å in each Cartesian direction from the extremities of the nanoparticle. The value of the ζ potential was then determined via surface integration at the Debye length from the interface of the nanoparticle, as well as the radial (approximately spherically symmetric) ESP profile over the distance range from the centre of the nanoparticle. NaCl salts were specified at 0.005 and 0.015 M concentrations in the solution of the PB equation.

Idealised solutions to the PB equation for particles with uniform surface charge may be obtained for a linearised form, *e.g.* in the Debye-Hückel (DH) approximation, an analytic solution for the ESP outside a sphere of radius a is given by the form proposed in the Derjaguin, Landau, Verwey and Overbeek (DLVO) framework [44]:

$$u(r) = \frac{q}{\epsilon r} \frac{\exp(\kappa a)}{1 + \kappa a} \exp(-\kappa r) \quad (7)$$

where q is the net charge on the particle, r is the radial distance from the centre and ϵ is the dielectric constant of the medium. Here, the dielectric constant of the particle is assumed to be identical to that of the medium, and the relative value was taken as 78. In this study, we obtained the DLVO solution and the analytic solution of the non-linear form of Wang *et al* [7-10] for spherical geometries. Although the latter form diverges from the DH and numerical solutions at short distances, it was found to be useful in this study, as the distance range on interest was larger than the nanoparticle radius.

4. Results and Discussion

As a typical example of the radial ESP distribution, results are shown in Fig.1 from the centre of the 1.5 nm radius nanoparticle of charge $+2e$ in 0.005 M salt solution for the numerical PB solution, and DH and Wang solutions. Although the Wang solution disagrees with numerical data at smaller separations, it is in essential agreement with the DH approach in the region of interest; the Debye length in this case is 4.3 nm, while it was 2.5 nm in the 0.015 M salt solution. The numerical PB and analytic solutions are in good agreement beyond around 6 nm from the centre of the nanoparticle, and similar observations were made for the other nanoparticles and salt concentrations.

[insert Fig 1 here]

The Reynolds number was found to be approximately 0.03 and 0.09 for the $+2e$ and $+6e$ -charged particles, and were similar for each size, as one would expect from eqns. 2 and 3; therefore, this corresponds to laminar flow. The SPC/E water relative dielectric constant at 298 K is 65 [29], while the coefficient of viscosity is 0.65×10^{-3} Ns/m² [45]. Using the HS approach of eqn. 4, the ζ potential was determined directly from the NEMD electrophoresis simulations, and these results are shown in Fig. 2 along with the numerical PB and Wang (analytic) approaches. It can be seen that there is reasonable agreement between the various approaches, with the HS results some 15-15% smaller than the numerical PB results for the $+6e$ -charged particles; this may be because this nanoparticles' motion was closer to the limit of laminar flow. Had the experimental value of the (relative) dielectric constant (78) been used in the HS approach, rather than the SPC/E value (65), those ζ potential values would have been

correspondingly smaller (cf. eqn. 4). These results are in the range of experimental measurements at titania-water interfaces [46]. In particular, recent experimental measurements of zeta potentials of (non-spherical) titania nanoparticles with characteristic diameters of 30-40 nm in ultra-pure water at room temperature were 34 mV in magnitude [47], and the current estimated values are also in that range. Although it was attempted to estimate the ζ potential from equilibrium MD simulation based on the water structure in the electric double layer about the (essentially stationary) nanoparticles, it was found to be difficult to distinguish between mobile and immobile layers, as Prědota et al noted [31]. Attempts to locate the location of a slip plane by consideration of local water mobility with increasing radial separation from the surface proved inconclusive. For this reason, the direct NEMD-HS approach was adopted in this study.

[insert Fig 2 here]

Conclusions

NEMD simulations of electrophoresis for a range of spherical rutile-titania nanoparticles with radii of 1.5 to 2.9 nm and net positive surface charges of $+2e$ and $+6e$ have been carried out for 0.005 and 0.015 M salt concentrations in water. There was reasonable agreement between HS estimates of the ζ potentials and those from solution of the non-linear PB equation about representative configurations, and an idealised analytic solution about spherical particles of the same geometry and surface charge state.

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Captions for the Figures

Figure 1: Electrostatic potential as a function of radial distance from the centre of the 1.5 nm radius nanoparticle of charge $+2e$ at 298 K in 0.005 M salt solution. The DLVO and Wang solutions are ‘extrapolated’ as dotted inside the nanoparticle surface (although a different form of the DLVO expression is applicable inside the nanoparticle), while the numerical PB solution based on NEMD configurations was only computed from the particle surface. Although the Wang solution disagrees with numerical data at smaller separations, it is in essential agreement with the DLVO approach in the region of interest; the Debye length in this case is 4.3 nm.

Figure 2: Zeta potentials for the various nanoparticles of charge (a) $+2e$ and (b) $+6e$ at 298 K in 0.005 and 0.015 M salt solutions, respectively, showing the Helmholtz-Smoluchowski, numerical PB and Wang (analytic) results.

Figure 1

Figure 2.