Electrophoresis without charge: Mobility of nanometer-size solutes in water

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We investigate the mobility of nanometer-size solutes in water induced by a uniform external electric field. General arguments are presented to show that a closed surface cutting a volume from a polar liquid will carry an effective non-zero surface charge density when preferential orientation of dipoles exists in the interface. This effective charge will experience a non-vanishing drag in an external electric field even in the absence of free charge carriers. Numerical simulations of model solutes are used to estimate the magnitude of the surface charge density. We find it to be comparable to the values typically reported from the mobility measurements. Hydrated ions can potentially carry a significant excess of the effective charge due to over-polarization of the interface. As a result, the electrokinetic charge can significantly deviate from the physical charge of free charge carriers. We propose to test the model by manipulating the polarizability of hydrated semiconductor nanoparticles with light. The inversion of the mobility direction can be achieved by photoexcitation, which increases the nanoparticle polarizability and leads to an inversion of the dipolar orientations of water molecules in the interface.

I. INTRODUCTION

Electrophoretic mobility of oil drops and air bubbles in water has traditionally been linked to the preferential adsorption of ions. Their counterions form the diffuse double layer. In this view, the overall charge measured by mobility is determined by incomplete compensation between the charge of the adsorbed ions and the part of the diffuse layer within the shear surface. The latter encircles the stagnant layer of the electrolyte moving together with the dissolved particle. The excess of the adsorbed charge over the diffuse-layer charge is reflected in the sign of the ζ-potential at the shear surface.[1] A negative ζ-potential, typically recorded for oil drops and air bubbles in water, is attributed to the excess of the adsorbed negative charge, with the hydroxide anion being a long-time favorite.[2–5]

Recent calculations[6] and measurements by surface-sensitive second-harmonic generation techniques[7,8] do not support excessive adsorption of hydroxide to the oil-water[7] and air-water[8] interfaces. In addition, the total X-ray reflection fluorescence spectroscopy[9] provides the upper estimate for the free surface charges at the air-water interface at the level of 0.002 (e/nm^2). This estimate is much below the surface charge density of $0.04 - 0.5$ (e/nm^2) extracted from mobility.[4] It seems clear that either the formalism of estimating the surface charge density from mobility requires modification or models of mobility not involving ion adsorption need to be advanced.

The possibility of charge-free electrophoretic mobility in water has been discussed in the literature,[7,10–14] but has not received general acceptance so far.[15] The main idea here is that the microscopic structure of the interface, allowing molecular order within the hydration layers, can produce an effective electrokinetic charge. This proposal has faced two difficulties. From the theoretical side there is no established framework of how to translate the microscopic structure of the interface, captured by atomistic numerical simulations, into the macroscopic current. Care is required in implementing correct cut-off/boundary conditions[16] and statistical ensembles adequately representing the conditions of the mobility measurements (as discussed briefly below). From the experimental side, it is not clear how to connect the results provided by surface-sensitive spectroscopies, which directly report on the polarization structure of the interface, with measured mobilities. Here we present a formalism that connects the effective mobility charge to the interfacial structure and casts the problem in terms of parameters accessible by laboratory and computer experiments. It allows both to alter the charges of free carriers into effective electrokinetic charges and explains mobility without charge.

We do not directly calculate the current produced by applying the external field, but derive the equation for the effective charge of the hydrated solute in terms of the orientational order of water dipoles in the interface. By doing this we show that the effective charge of the solute responding to the uniform external field is not equal to the charge of the free carriers. It is therefore possible that the effective charge reported by mobility measurements significantly overestimates the charge of the adsorbed ions. The orientational structure of the interfacial dipoles is the key in understanding these differences. Since the interfacial structure and the dipolar orientations in the interface can be altered by modifying the solute/substrate,[7,17] one gains the means to experimentally test both the effect of the interface on the effective charge and the hypothesis of charge-free mobility. In particular, we suggest that changing the polarizability of a (semiconductor) nanoparticle by exciting

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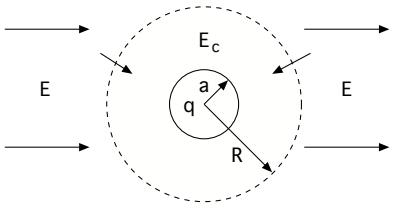

Figure 1. Ion with the charge q and the radius a immersed in a polar liquid in the uniform macroscopic (Maxwell) field E. R indicates the radius of the shear sphere incorporating the stagnant layer of the liquid dragged by the field along with the solute. E_c is the cavity field of the uniformly polarized liquid created inside the shear sphere. The arrows on the opposite sides of the spherical cavity indicate water dipoles oriented favorably (left) and unfavorably (right) along the external field. The difference in the chemical potential between right and left is positive. It creates an osmotic pressure pushing the particle in the direction opposite to the field and corresponding to an effective negative charge.

electron-hole pairs can invert the sign of the mobility. This effect is driven by the relation between orientations of dipoles in the hydration layers with the nanoparticle polarizability,[18] which can be manipulated by light.[19]

II. INTERFACIAL STRUCTURE AND PARTICLE MOBILITY

We start with general arguments applicable to the standard picture of electrophoretic mobility in a uniform external field as illustrated in Fig. 1. A spherical ion with the charge q at its center and with a (cavity) radius a is placed in a polar solvent with the bulk static dielectric constant ϵ_s. The hydrodynamic mobility of the ion is determined by the shear surface of the radius R. Electrostatics suggests that the force acting on the ion and its stagnant layer is the product of the average charge $\langle Q_R\rangle$ within the shear surface with the field acting on these charges. This field is the cavity field E_c[20] combining the field from external charges with the field of the polarized dielectric outside of the shear surface

$$\langle F\rangle = \langle Q_R\rangle E_c. \tag{1}$$

In dielectric theories, the cavity field inside a sphere is related to the macroscopic Maxwell field E by the equation[20]

$$E_c = \frac{3\epsilon_s}{2\epsilon_s+\epsilon_p}E, \tag{2}$$

where ϵ_p the dielectric constant of the particle.

The steady flow of dissolved particles with the speed u is reached when the electrostatic drag is counterbalanced by hydrodynamic friction, $\langle F\rangle = 6\pi\eta u R$, where η is the bulk viscosity. The resulting mobility $\mu = u/E \simeq \langle Q_R\rangle/(4\pi\eta R)$ [$\epsilon_s \gg \epsilon_p$, $\epsilon_s \gg 1$ in Eq. (2)] gives direct access to the total charge $\langle Q_R\rangle$. Smoluchovski's equation typically used in the literature re-writes this relation in terms of the ζ-potential defined as the electrostatic potential at the shear surface $\zeta = \langle Q_R\rangle/(\epsilon_s R)$.[21] The result is the equation for the mobility[1]

$$\mu = \frac{\epsilon_s\zeta}{4\pi\eta}. \tag{3}$$

This formalism is well established and the results of mobility measurements are often cast in terms of the effective surface charge density[4] $\sigma_{\rm eff} = \langle Q_R\rangle/S$, where S is the surface area of the particle. We follow this established practice and focus mostly on $\langle Q_R\rangle$ and the corresponding $\sigma_{\rm eff}$. The arguments given here need to be modified with the account for the diffuse potential of the electrolyte[21] not considered here. We focus instead on a charged or uncharged particles dissolved in a polar molecular solvent establishing a microscopic multipolar structure in the interface. The main outcome of this perspective is the modification of the effective charge $\langle Q_R\rangle$ by the dipolar order of the interface expressed in terms of the average cosine of the interfacial dipoles (order parameter) p_1.

The overall charge within the shear sphere, which enters Eq. (1), is given as the integral of the charge density of the ion $\rho_i = q\delta(\mathbf{r})$ and the density of bound charges in the polar liquid $\rho_b = -\nabla\cdot\mathbf{P}$, where $\mathbf{P}$ is the polarization density which can include higher multipoles (quadrupole, etc)[20]

$$\langle Q_R\rangle = \int_{\Omega_R}\left[\rho_i - \nabla\cdot\langle\mathbf{P}\rangle\right]d\mathbf{r}. \tag{4}$$

The integral is over the volume Ω_R enclosed by the shear surface. The result is obviously

$$\langle Q_R\rangle = q + 4\pi\left[a^2P_a - R^2P_R\right], \tag{5}$$

where P_a and P_R are the average radial projections of the polarization density, $P_r = \langle\hat{\mathbf{r}}\cdot\mathbf{P}\rangle$, $\hat{\mathbf{r}} = \mathbf{r}/r$ taken at $r = a$ and $r = R$, respectively.

It is useful to stress here that the density of bound charge ρ_b and the corresponding polarization field $\mathbf{P}$ are microscopic scalar and vector fields corresponding to an instantaneous configuration of the liquid.[22–24] No continuum approximation is applied here, and the representation $\rho_b = -\nabla\cdot\mathbf{P}$ is based solely on the conservation of charge.[25] One gets for the charge density $\rho_b(\mathbf{r}) = \sum_j q_j\delta(\mathbf{r}-\mathbf{r}_j)$, where q_j are the atomic partial charges located at the coordinates $\mathbf{r}_j$. Correspondingly, the polarization field becomes[20,26]

$$\mathbf{P}(\mathbf{r}) = \sum_j \mathbf{m}_j\delta(\mathbf{r}-\mathbf{r}_j) - \tfrac{1}{3}\nabla\cdot\sum_j\mathbf{Q}_j\delta(\mathbf{r}-\mathbf{r}_j) + \ldots, \tag{6}$$

where $\mathbf{m}_j$ denotes the molecular dipole, $\mathbf{Q}_j$ is the molecular quadrupole (defined according to Ref. 26), and the dots refer to the higher-order multipolar terms. The vector field $\langle\mathbf{P}\rangle$ in Eq. (4) is then the statistical average of the instantaneous $\mathbf{P}$ over the microscopic configurations consistent with a given statistical ensemble.

There are two radial polarization projections, P_a and P_R, entering Eq. (5). We show below that $a^2P_a = R^2P_R$ in the standard dielectric theories, and they cancel out in Eq. (5). As expected, one has the equality between the electrokinetic charge $\langle Q_R\rangle$ and the electrostatic charge q in this case. This cancellation does not occur for nanometer-scale interfaces and, perhaps, at larger scales as well. This is what we intend to show in the following discussion.

One can proceed in two steps and first apply some reasonable approximation to the surface charge density at the shear surface. The surface charge density at the actual physical surface of the solute then becomes our main focus. Since the shear surface does not involve any physical disruption of the liquid structure, it is reasonable to assume that P_R can be related to the field of the ion charge by the rules of continuum electrostatics[20] $4\pi R^2P_R = q(\epsilon_s - 1)/\epsilon_s$. We stress that this assumption does not affect the main points of our reasoning, as will be clear from the discussion below. With the continuum polarization at the shear surface one gets in Eq. (5)

$$\langle Q_R\rangle = q\epsilon_s^{-1} + S\sigma_q, \tag{7}$$

where $S = 4\pi a^2$ is the surface area of the solute and $\sigma_q = P_a$ is the surface charge density. It is produced by the interfacial dipoles oriented in the interface by the combination of their mutual microscopic interactions and the field of the ion charge q.

If the interface is polarized by the ion charge according to the rules of continuum dielectrics, one gets

$$S\sigma_q = q(1 - \epsilon_s^{-1}) \tag{8}$$

and $\langle Q_R\rangle = q$ in Eqs. (5) and (7). As mentioned above, no deviation of the charge coupled to the external field from the ionic charge q occurs in this case, in accord with the standard equations of electrophoretic mobility based on dielectric continuum as the solvent.[16,21,27] However, the microscopic susceptibility of the nanometer interface significantly deviates from the rules of macroscopic continuum electrostatics[22,24,28] and, therefore, σ_q is left unspecified in Eq. (7). The simple and general message delivered by Eqs. (5) and (7) is that asymmetry in the water susceptibility between the shear and solute dividing surfaces leads to a modification of the standard result $\langle Q_R\rangle = q$.

The surface charge density σ_q in Eq. (7) is proportional to the ion charge q in the dielectric models, as in Eq. (8). The effective charge $\langle Q_R\rangle$ is different from q if the susceptibilities at the solute and shear surfaces are unequal, but $\langle Q_R\rangle = 0$ if $q = 0$. On the other hand, if the polar liquid is spontaneously polarized in the interface, i.e., the interfacial dipoles possess preferential non-random orientations, $\langle Q_R\rangle \neq 0$ even at $q = 0$. What is required is a nonzero radial projection of the dipolar polarization density at the solute surface. Note that the same result follows from the asymmetry of the solvent response to positive and negative ions adsorbed to the solute, but adding up to the overall zero charge.

The dipole ordering in the interface can be described by the orientational order parameter $p_1 = \langle \hat{\mathbf{m}} \cdot \hat{\mathbf{r}}\rangle_a$, which is the average cosine of the water dipole moment projected on the radial direction and calculated in a narrow layer at the solute surface $r = a$.[28] The surface charge density can be written in terms of the water dipole moment m and the order parameter, $\sigma_q = (mp_1/S)(dN_s/dr)\big|_{r=a}$. Here, $N_s = N_s(r)$ is the number of water molecules within the shell of the radius $r > a$. By using the definition of the number of water molecules in the shell in terms of the solute-solvent radial distribution function (RDF) $g_{0s}(r)$, one can re-write σ_q as

$$\sigma_q = \rho m p_1 G, \tag{9}$$

where $G = g_{0s}(a)$ is the contact value of the solute-solvent RDF and ρ is the number density of bulk water. Equation (9) is written for an arbitrary value of q, which means that p_1G should be calculated in the presence of the ion charge q; σ_0 corresponds to $q = 0$.

The value of σ_q for large particles can be estimated from the $a \to \infty$ asymptote for the hard-sphere (HS) solute[29] $G_{\rm HS} \to \beta P/\rho$, which results in $\sigma_q \to \beta m p_1 P$, where P is the hydrostatic pressure. This gives for water at ambient conditions $\sigma_q \simeq 10^{-3} p_1 (G/G_{\rm HS})(P/\text{atm})$ e/nm^2, where $G/G_{\rm HS} \simeq \exp[-\beta\Delta\mu_w]$ defines the affinity of water toward the solute $\Delta\mu_w$ beyond simple HS packing preferences.

Equation (9) establishes the effective charge of a closed spherical interface within a polar liquid. Its sign is fully defined by the orientational order parameter p_1: it is negative when the water dipoles preferentially orient toward the solute/cavity and is positive when they point toward the bulk. This equation clearly shows that any closed dividing surface cutting a volume from a polar liquid will be dragged by an external electric field if a preferential orientation of dipoles in the interface is established. This result is independent of the presence of the electrolyte since bound charges are not screened by the ions. We do not consider the polarizability of the interface here, i.e., the change in dipolar orientations in response to the applied field. Macroscopic fields used in experiment are typically weak compared to microscopic interfacial fields[23] and do not significantly alter dipolar orientations. Additionally, this contribution to the force in Eq. (1) is quadratic in the external electric field and is usually excluded from mobility.

It is clear from the derivation that the force on the closed surface surrounding the solute is related to the inhomogeneous, divergent polarization field with $\nabla \cdot \mathbf{P} \neq 0$; no force will appear for a uniformly polarized dielectric.[20,30] It is useful to provide additional physical arguments explaining why a non-zero net force can be associated with this situation. We illustrate our arguments in Fig. 2, where a polar material with a spherical cavity is placed in the (vacuum) field E_0 created by external charges. We assume that the dipoles of the molecular liquid interfacing the cavity are polarized in the radial orientation and the field E_0 is too weak to dis-

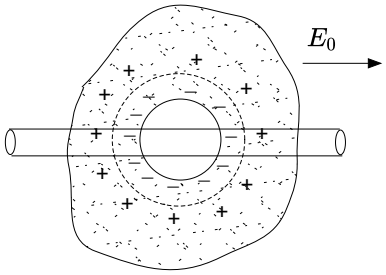

Figure 2. Illustration of the net charge produced in the polarized interface of a spherical cavity. The molecular dipoles in the interface are oriented radially outward from the cavity; "+" and "−" indicate the positive and negative ends of the molecular dipoles. The dashed line is drawn through the middle of molecular dipoles in the first hydration shell to indicate the non-uniform distribution of the molecular charge. As an example, the total charge calculated within an infinitely long cylinder is non-zero. This non-zero net charge interact with the field of external charges E_0, which is assumed to be weak and not perturbing the order of the interface (zero interface polarizability). The resulting force is given by Eq. (10) for a radially decaying interfacial polarization $P_r \propto r^{-\alpha}$.

rupt this preferential order established by much stronger intermolecular forces.

The radially polarized solvent will create a non-uniform density of the molecular charge, which is indicated in the figure by the positive and negative ends of the molecular dipoles. In order to understand the origin of a non-zero effective charge, one can consider a cylindrical region of the liquid oriented along the field E_0. It is clear that there will be more negative charges contributed by the first layer of charges than the positive charges contributed by the second layer (they are separated by a dashed line in the figure). This rule applies to every consecutive pair of layers added to calculate the total charge within the cylindrical volume. The overall charge will add up to a nonzero value. The sign of the charge is defined by the projection of the polarization field on the normal outward to the dielectric at the dividing surface.[20,25]

This physical arguments are supported by direct mathematical manipulations. Assume the polarization field decays radially as $P_r(r) \propto r^{-\alpha}$ with $\alpha > 2$. One then calculates the net force acting on the polar material as

$$\langle F \rangle = -E_0 \int_\Omega \nabla \cdot \langle \mathbf{P} \rangle d\mathbf{r} \propto a^{-\alpha} E_0, \qquad (10)$$

where the integral is extended to a macroscopic volume Ω outside the cavity with the radius a. Note that one has to require the polarization field to decay faster than $\alpha = 2$ prescribed by the linear susceptibility to the electric field of a charge inside the cavity. This prescription is an alternative mathematical form for the different polarization susceptibilities at the solute and shear surfaces required to produce $\langle Q_R \rangle \neq q$ in Eqs. (5) and (7).

While our focus here is on a particle dissolved in a polar solvent, the proposed formalism can be extended to the

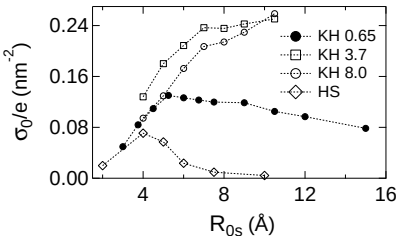

Figure 3. Surface charge density of hard-sphere (HS) and Kihara (KH) solutes of varying solute size R_{0s} in SPC/E water[28] (solid points) and TIP3P water (open points). The LJ energy ϵ_{0s} in Eq. (11) was varied in the simulations: 0.65, 3.7, and 8.0 kJ/mol. The dotted lines connect the points to guide the eye.

problem of a water drop in a nonpolar solvent (oil).[13] Equation (9) still defines the surface charge density with the convention that the orientational order parameter is calculated by projecting the surface water dipoles on the radial direction pointing toward water (inward in the case of a drop). To make our assignment clear, the water-oil interface with water's hydrogen pointing toward the oil phase[7,31,32] will, according to Eq. (9), produce a negative charge of the water drop.

The drag experienced by a closed surface can be viewed as a specific form of osmosis. The gradient of the chemical potential of interfacial waters at the opposite sides of the surface is created by the external field. It is the consequence of the favorable orientation with the field of the molecules on one side of the surface compared to the unfavorable orientation on the opposite side[33] (surface arrows in Fig. 1). The chemical potential gradient will result in the osmotic pressure difference on the opposite sides of the surface. This physical interpretation of the non-zero mobility implies that direct numerical simulations of this effect will require the μVT ensemble,[29,33] keeping the chemical potential of water constant. Since these results are presently not available, we use more conventional NVT and NPT simulations of nonpolar solutes in water to estimate the interfacial charge density σ_0 in Eq. (9) from the computed $p_1 G$ parameter.

III. COMPUTER SIMULATIONS

We have considered HS and Kihara (KH) solutes dissolved in force-field water. The Kihara potential is the HS core modified with the Lennard-Jones (LJ) layer at its surface.[34] Specifically, the solute-solvent potential is given as

$$\phi_{0s}(r) = 4\epsilon_{0s} \left[\left(\frac{\sigma_{0s}}{r - R_{\rm HS}} \right)^{12} - \left(\frac{\sigma_{0s}}{r - R_{\rm HS}} \right)^{6} \right], \qquad (11)$$

where ϵ_{0s} in the LJ energy and σ_{0s} is the distance between the solute HS core with the radius $R_{\rm HS}$ and water's oxygen. $\sigma_{0s} = 3$ Å was kept constant in the simulations, while $R_{\rm HS}$ and ϵ_{0s} were varied.

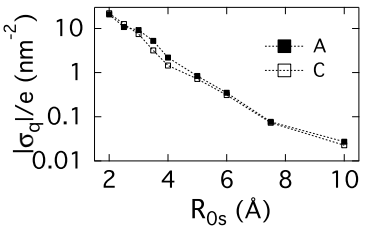

Figure 4. Surface charge density of HS cations (C) and anions (A) in TIP3P water. The calculations are done according to Eq. (9); the dotted lines connect the points. σ_q is positive for cations and negative for anions.

The molecular dynamics (MD) and Monte Carlo (MC) simulations presented here address the question of whether the product p_1G characterizing water interfacing these solutes will produce σ_q comparable to experiment. The details of the simulation protocols have been discussed elsewhere[18,28,35] and are given in the Supplementary Material.[36] Here we focus only on the results.

Figure 3 shows σ_0/e ($q = 0$, e is the elementary charge) from the simulation data changing with the size of the HS and KH solutes in TIP3P and SPC/E water models.[37] The size of the KH solute is measured as $R_{0s} = R_{\rm HS} + \sigma_{0s}$ [Eq. (11)]. It approximates well the position of the first peak of the solute-solvent RDF. The size of the HS solute R_{0s} is defined as the distance of the closest approach of the water oxygen to the solute. It gives the exact position of the RDF's first peak.

The sign of the surface charge density is positive for both HS and KH solutes, reflecting the preferential orientation of the surface water dipoles into the bulk. Increasing the solute-solvent LJ attraction makes the hydration shell denser, as reflected by a higher σ_0. The fast drop of σ_0 for the HS solute is caused by its partial dewetting[38] when $R_{0s} \geq 5$ Å. The magnitude of σ_0 is somewhat higher than the values typically reported from mobility measurements (~ -0.04 (e/nm^2) for hexadecane in 0.2 mM NaCl[4]). Our solutes are of course significantly smaller in size than oil drops used in mobility measurements ($\sim 200 - 300$ nm in Ref. 7) and have a smooth surface, in contrast to the corrugated surface of oil emulsions.[32]

The potential situation with hydrated ions is illustrated in Fig. 4, where σ_q is calculated from Eq. (9) for HS cations and anions of varying size in TIP3P water in the absence of counterions.[35] The main observation here is that σ_q significantly exceeds in the absolute magnitude the prediction of the continuum electrostatics in Eq. (8). This means $\langle Q_R \rangle \gg q$ in Eq. (7), which should lead to overestimates of the number of adsorbed ions when the standard equations for the screening of free charge carriers in electrolytes are applied to the analysis of the mobility data.[21]

The overpolarization of the water dipoles attached to the surface ions might have significant implications for the interpretation of the mobility data. Figure 4 indicates that the microscopic orientational order of the water dipoles next to a positive ion will significantly enhance its effective electrokinetic charge determined from the mobility measurement. Correspondingly, a negative adsorbed ion will appear more negative in the particle mobility. Therefore, the actual concentration of adsorbed ions can be significantly lower than estimated from mobility. This observation might help to explain the disagreement between the electrokinetic measurements[4] and surface-sensitive spectroscopies[7,8] regarding the concentration of the surface adsorbed ions. The actual extent of overpolarization requires more extensive simulations in realistic electrolytes. One also should not underestimate the potential effect of corrugation of any real water-oil interface,[32] which will affect the average contact RDF G in Eq. (9).

Figure 4 indicates that surface charge densities of large positive and negative ions with $|q| = 1$ charge at the center are close in magnitude. However, this outcome might not hold for small ions adsorbed at the surface of a large particle. The product p_1G is generally asymmetric between cations and anions because of the asymmetry in the charge distribution of the water molecule.[39] In that case, the orientational order and the corresponding surface charge density will not compensate between the oppositely charged adsorbed ions and a non-vanishing σ_q will follow even at the total zero charge. The observable consequence of this asymmetry would be a shift between the iso-electric point of electrokinetic mobility and the point of zero charge, as reported for some systems.[40] Overall, the main results of the general formalism summarized by Eq. (7) and simulations performed here is that the charge of free carriers and the effective electrokinetic charge incorporating the interfacial dipolar order can be significantly different.

IV. EXPERIMENTAL TESTING AND CONCLUSIONS

In conclusion, we have derived a simple equation [Eq. (9)] relating the effective charge of a hydrated nanoparticle to the orientational order in the interface and the water density in contact with the solute. Both parameters carry asymmetry between positive and negative charges. Therefore, the surface charge density σ_q induced by the positive and negative free carriers will not compensate and produce an overall nonzero value even when the total charge is zero. The electrokinetic charge can be substantially enhanced by the dipolar order in the interface and the theory predicts a non-zero effective charge when the interface is spontaneously polarized in the absence of free charge carriers (charge-free mobility). The values of the surface charge density derived from simulations of uncharged nanometer-size solutes are consistent with those typically reported from mobility measurements.

The direct connection of the mobility of nanoparticles in water to the orientational order of the water dipoles in the interface offers opportunities to testing this pre-

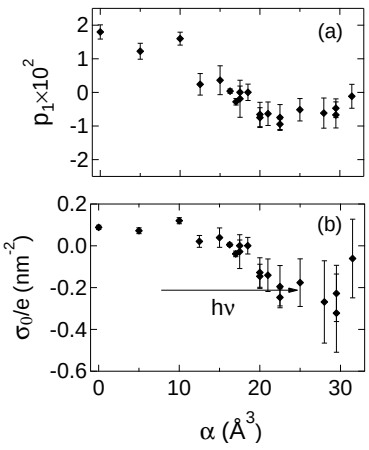

Figure 5. The order parameter p_1 (a) and the surface charge density σ_0 (b) vs the polarizability of a polarizable HS solute, carrying the isotropic polarizability α and dipole moment $m_0 = 5$ D, in TIP3P water[18] (error bars show the uncertainties of calculations). The horizontal arrow indicates the photoinduced alteration of the polarizability that inverts the mobility of the nanoparticle.

diction by experiment. One possible direction is the modification of the surface with chemical groups (surface dipoles) altering the interfacial order.[41] We, however, recently discovered another property dramatically affecting the interfacial dipoles: the polarizability of the solute. Increasing the solute polarizability drives the solute-water system to the point of instability of harmonic fluctuations expressed in terms of the solvent electric field inside the solute as the order parameter. Reaching the point of global instability toward fluctuations drives a structural transition of the hydration layer, which reorients the water dipoles and creates a high density of dangling OH bonds.[18] The emergent new structure of the interface also suggests, according to Eq. (9), the alteration of the sign of σ_0 ($q = 0$).

The results of MC simulations of HS solutes with changing isotropic dipolar polarizability α at the solute's center are presented in Fig. 5. The size of the solute is maintained constant and only the polarizability is varied. One observes a switch from a positive to a negative surface charge with increasing polarizability. In other words, the isoelectric point of electrophoretic mobility can be reached, and crossed, by manipulating the polarizability of the solute. This observation opens the door to experimental testing of the model. Polarizability of semiconductor nanoparticles can be dramatically increased by photoexcitation,[19] which is predicted to invert the nanoparticles' mobility (horizontal arrow in Fig. 5b).

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