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TOPICAL REVIEW

Understanding voltage-induced localization of nanoparticles at a liquid–liquid interface

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Online at stacks.iop.org/JPhysCM/20/073102**Abstract**

Functionalization of liquid–liquid interfaces is a hot area, driven by aspirations to build self-assembled interfacial structures with unique properties, in particular accessible to light from both sides of the interface. Adsorption of nanoparticles is an example of such functionalization. Interesting new developments take place in electrochemical liquid–liquid systems, consisting of two immiscible electrolytic solutions that form an interface impermeable to ions until a sufficiently high voltage is applied across the interface. The voltage drops across a nanoscale region near the interface due to the formation of two back-to-back electrical double layers on the two sides of the interface. This highly localized voltage drop opens a new possibility for the stabilization and control of interfacial architectures. This appears to be particularly important for metal and even semiconductor nanoparticles, because they are, in turn, ‘functionalized’. They are covered by surfactants with acidic groups, some of which dissociate in water. Coverage with surfactants is required to avoid particle–particle agglomeration in the bulk. An electric field can push such nanoparticles to the interface or move them away, depending on the direction of the field. This, together with the change of the free energy of solvation of nanoparticles when they move from the bulk to the surface, are the two new decisive factors affecting their adsorption and desorption. We discuss these effects together with the more familiar ones that are known to determine interfacial localization of uncharged nanoparticles. The presented critical analysis is qualitative. Although we will try to rationalize the main effects by some simplified formulae, they should not be taken literally: they pave the way towards understanding of nanoparticle localization in these systems, rather than give exact answers. These equations will, however, help us to ‘visualize’ how a properly applied electric field, assisted by the interfacial tension but opposed by the line tension and the change in the free energy of hydration, causes stable localization at the interface. We show that for multiply charged nanoparticles, sustainable potential drops across the interface *can* give rise to deep adsorption wells with adsorption energies much larger than the thermal energy. The fine balance between adsorption and desorption forces, which depends on the particle size and charge, determines whether the particle will be localized at the interface or not and permits reasonable voltages to substantially modify their interfacial concentration.

(Some figures in this article are in colour only in the electronic version)

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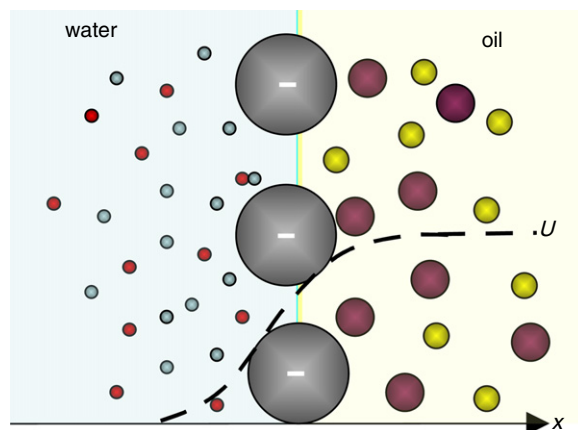


Figure 1. A cartoon of ITIES with nanoparticles adsorbed at the interface (in reality nanoparticles are much larger than the ions). The dashed curve sketches a distribution of electrostatic potential for a given potential drop U across a polarized ITIES in the absence of nanoparticles.

Interest to two-dimensional colloidal crystals at liquid–liquid interfaces has a long history that goes back to Pickering, 1907 [1]. A revival of interest in this area started with Pieranski [2] who has not only observed an ordered layer of micron-size polystyrene particles at a water–air interface but also rationalized the driving forces for building such two-dimensional arrays. Later, similar ideas were applied to form arrays of much smaller particles at liquid–liquid interfaces, including metal nanoparticles and quantum dots [3–6]. The next logical step was to extend this to interfaces of immiscible electrolytic solutions (ITIES) [7–10].

ITIES, sketched in figure 1 are particularly interesting because the potential bias provides an external control of the interface properties and the confining potential for particles. The potential drop is localized in a narrow interfacial region of ‘back-to-back’ ionic double layers on the two sides of the interface [11, 12], leading to very large electric fields. This gives a unique opportunity for easy control over stabilization/destabilization of adsorbed layers of nanoparticles, using the potentiostat. Functionalizing ITIES with metal and semiconductor nanoparticles may lead to interesting optical, electronic and sensing applications. For example, one can foresee the design of addressable liquid-mirror arrays by adsorbing charged nanoparticles at these interfaces [13]. With increased understanding of the particle behaviour even more interesting and promising applications should come.

Formation of sub-monolayers of Au-nanoparticles at ITIES was first reported in a pioneering paper of Cheng and Schiffrin [7], who also studied its kinetic aspects through cyclic voltametry and time evolution of Mie scattering from the interface; later Kontturi’s group have studied various aspects

of ‘electrodeposition’ of Pd nanoparticles [8]. Measuring the adsorption isotherm of Au-nanoparticle the Girault–Samec team has unambiguously shown the effect of the potential drop across the interface on the interface coverage [9]. It was clearly demonstrated that this adsorption is fully reversible with respect to potential variation [9, 14].

The properties of a dense assembly of nanoparticles usually depend on their concentration. Thus voltage control of the concentration of nanoparticles at an interface should lead to voltage control of a variety of physical properties, which could include optical transparency, magnetization and electrical conductivity. All in all, to understand these properties we need a clear picture of the origin of particle localization and its dependence on voltage bias.

Both metal and semiconductor nanoparticles are ordinarily functionalized by ligands in order to prevent particle agglomeration. The ligands, which are attached to the particles by thiol groups, have acidic terminal groups that can dissociate in aqueous phase. This results in a net charge of the particles, which is, however, much smaller than the number of ligands, because of Coulomb repulsion of ionized groups. Equilibrium values of the number of charges per particle are affected by acid ionization constants and depend on pH.

In contrast to uncharged particles, which adsorb spontaneously at liquid–liquid interfaces in order to reduce interfacial energy, multiply charged nanoparticles tend to stay in water, and in order to localize them at the interface between water and oil one needs to apply an electric field. Our estimates below will show that the electric fields available for ITIES can provide sufficiently deep potential wells for a stable arrangement of nanoparticles at the interface and that external variation of the field can reversibly control adsorption–desorption.

In this article we will examine the *main driving forces* that keep metal or semiconductor nanoparticles at the ITIES. We show how the potential energy profile of a nanoparticle at ITIES depends on the properties of the liquids, electrolyte concentrations, the potential bias, the nature of the

nanoparticles and their size. In the end, we also discuss the adsorption isotherms reported in [9] and make conclusions on the range of less-known parameters, such as the three phase contact angle and line tension, that allow us to rationalize experimental data.

The material we present here forms altogether a provocative, discussion-like paper, unusual for topical reviews in this journal. At best this could be qualified as a ‘brief introduction to an emerging area’, rather than a review of an established area. Thus, the readers of this paper should not expect to find in it final answers to their questions: first principle calculations in this area are hardly possible, and even MD simulations are rather difficult due to slowly converging Coulomb forces. But we can promise them some rational and provocative thoughts, which may also provide a useful framework for focusing and interpreting future simulations.

This article may be considered a continuation of a conversation started in a review article by Bresme and Oettel on ‘Nanoparticles at fluid interfaces’ [15], the content of which we have become acquainted with after having finished these notes. To outline the difference: we step here into further unknown territory—localization of nanoparticles at the *ITIES*. As in all the previous papers reviewed in [15], that review itself did not consider the effects of Born-type re-solvation when a charged nanoparticle moves across the interface, nor the effects of an *external* electric field on it. But, generally, Bresme and Oettel present a most valuable, wide exposition and analysis of various effects that nanoparticles may experience; this background will be helpful for the readers of our brief paper, although we composed it to be self-contained.

1. The effects that drive or hamper localization at the interface

The main terms that determine whether a particle will adsorb at the interface or not are discussed below with references to the corresponding expressions in the appendix.

1.1. Competitive wetting

It is well established that the localization of an uncharged nanoparticle at the water–oil interface (figure 1) is driven by the reduction of interfacial energy. The particle pierces the interface when $|\sigma_{p/o} - \sigma_{p/w}|/\sigma_{o/w} < 1$, where $\sigma_{p/o}$, $\sigma_{p/w}$ and $\sigma_{o/w}$ are the surface tensions at the particle–oil, particle–water and water–oil interfaces, respectively. If the particle is hydrophilic but still $\sigma_{p/o} < \sigma_{o/w} + \sigma_{p/w}$, the particle will localize at the interface from the water side in order to remove some contact area between oil and water. If the particle is hydrophobic, but still $\sigma_{p/o} < \sigma_{o/w} + \sigma_{p/w}$, it will localize from the oil side, but again pierce the interface in order to diminish oil/water contact. Both cases, of course, represent the classical phenomenon of *incomplete wetting*, shown in figure 2. The contact angle θ is given by the Young–Laplace equation, $\sigma_{p/o} - \sigma_{p/w} = -\sigma_{o/w} \cos \theta$. The surface tension contribution to the interfacial energy profile is given by equation (A.2) of the appendix.

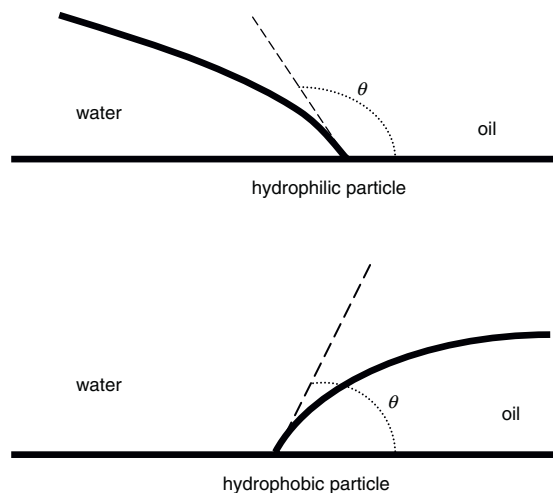


Figure 2. Wetting angle (two cases sketched: (a) hydrophilic particle, (b) hydrophobic particle)⁴.

One may question application of the *laws of macroscopic capillarity* to interfaces with nanoparticles. However, the estimates, using the Uhlig formula [16], based on extrapolation of these laws to the micro-world are known to work empirically well even for smaller objects, e.g. for evaluations of free energies of transfer of large ions between two liquids [17]. MD simulations for nanoparticles have shown that these laws are, in fact, quite instructive at nanoscales [18].

1.2. Solvation of charged nanoparticles

Acidic terminal groups of the ligands coating nanoparticles can dissociate in the aqueous phase, so that at normal pH the particles are negatively charged in the aqueous phase. For instance, the gold nanoparticles of [9] were claimed to bear between four and five negative charges. Water has a higher dielectric constant than any oil; in particular the dielectric constant of 1,2-dichloroethane is 10.7 against 78.8 of water. This leads to a substantial electrostatic contribution to the free energy of a nanoparticle transfer from water to oil, which is quadratic in its charge. This effect is very strong (equation (A.2) of appendix) and, as we will see, it leaves practically no chance for localization at the interface, unless an electric field is applied.

1.3. Shift in external electric field

In an electrochemical cell a large voltage drop between the bulk of the two phases can be maintained. This will create a potential distribution across the interface that may stabilize or destabilize nanoparticle adsorption (see equations (A.4)–(A.7) in the appendix). For instance, if the nanoparticle bears four to five negative charges, as in the experiments of [9], and if the potential drop between water and oil is negative, the particle will be pushed towards oil; whereas the surface tension

⁴ Quite often wetting angles are defined for the aqueous phase, which in the current notation correspond to $\pi - \theta$. For technical reasons we will use the notation employed in figure 2.

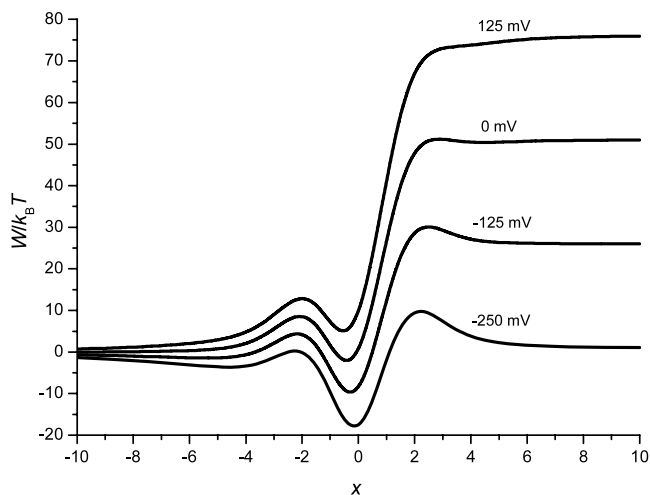


Figure 3. Nanoparticle energy profile at ITIES: the effect of potential drop across the interface between the aqueous and organic phases. Curves correspond to calculations based on equations (A.1)–(A.8) with the following values of parameters: radius of the nanoparticle = 1.5 nm, dielectric constants $\epsilon_w = 78.8$ (water), $\epsilon_o = 10.7$ (1,2-dichloroethane); charge of the nanoparticles, $z = -5$, concentrations of electrolytes in water and 1,2 dichloroethane, $c = 5 \times 10^{-3}$ M (which corresponds to Debye lengths 4.31 nm in water and 1.6 nm in oil); interfacial tension between water and oil: 30 mN m^{-1} ; line tension: 10^{-11} N; three phase contact angle between the particle surface and water–oil interface (cf figure 2) $\theta = 0.55\pi$.

effects and solvation, as discussed above, will impede the particle penetration into the oil phase. Thus, the particle will move closer to the interface and the adsorption minimum will be deeper. Positive polarization will diminish the minimum leading finally to desorption of particles from the interface into the water bulk. Note that with the increase of the voltage drop the potential distribution becomes steeper (due to the effects of nonlinear screening), and the minimum created by the negative polarization will become sharper.

1.4. Polarizability drive

There is another finer and smaller effect of external field on localization of any polarizable particle, which is independent of the charge it bears. This is the attraction of the polarizable sphere within an inhomogeneous field, $E(x)$. The polarizability contribution to the energy of the particle in the electric field, $W_{\text{pol}} = -\alpha[E(x)]^2$, is proportional to the square of the field (α is the particle polarizability) and it favours localization of the particle right at the interface, where the electric field is maximal. However, for highly charged particles with the radius smaller than the thickness of the interfacial double layer this ‘induced dipole-type’ effect can be neglected compared to the direct interaction of the charged particle with the electric field discussed above. The relative contribution of the dipole-type effect decreases, generally with the radius of the particle.

1.5. Line tension

Line tension [19, 20] is a puzzling feature, a concept often referred to, but still poorly understood. It is thoroughly

discussed in the classical book of Rowlinson and Widom [19], but for us it will simply be the term that incorporates all the contributions not taken into account by microscopically described surface tension terms, i.e. it bears information about the molecular interactions very close to the three phase boundary. The contribution of the line tension to the interaction of nanoparticles with liquid–liquid interfaces has been recently addressed in [21] and, as well as in all previous considerations, it was intended to take into account all microscopic effects not incorporated in the macroscopic contact angle theory.

In principle, account for such deviations can give rise to any sign of the line tension. Independence on the radius of the absolute value and the sign of the line tension were disputed by Bresme and Quirk [22]⁵.

For simplicity, hereafter, we will assume the line tension to be constant and positive. As such it acts against piercing the interface, as the energy term associated with this effect is proportional to the three phase perimeter, as given by equation (A.8) of the appendix. The line tension energy term is symmetric with regards to the shift of the nanoparticle position from the interface. For a positive line tension it pushes the particle to slide to either side of the interface.

1.6. Total balance

All these important terms, as calculated using the equations of the appendix, are shown separately in figure A.1. Together they give the energy profile for the particle near ITIES, also shown in figure A.1 and studied in detail in figures 3–5 of the next section.

2. Main lessons

Figure 3 shows the effect of applied potential bias. One can see that in contrast to the case of uncharged particles which adsorb spontaneously at the liquid–liquid interface in order to reduce the interfacial energy, multiply negatively charged particles tend to stay in water in the absence of the applied voltage (and for positive potentials). These calculations demonstrate that the electric fields available for ITIES can provide a sufficiently deep potential well at the interface. For a potential bias of -250 mV the minimum of the energy profile for the charged nanoparticles could be essentially deeper (about one order of magnitude) than that for the uncharged particles. On the contrary, uncharged nanoparticles with sizes smaller than 2 nm

⁵ They found that in order to bring the macroscopic theory in agreement with their MD calculations of the localization energy of small nanoparticles of radius <1.5 nm (at ordinarily liquid–liquid interfaces) they have to add the line tension term to the surface tension term. But in order to reach a good fit they found that the former must increase linearly with the interfacial tension between the liquids. The fit also demanded variation of the line tension with the radius of nanoparticles; moreover, for small particles (smaller than five radii of water molecules) it becomes increasingly negative. If true, the negative line tensions would ask for the largest radius of the three phase line, i.e. the particle will tend to cause the ‘maximal piercing’ of the interface. This problem requires further studies and the answer may be different for different combinations of liquids and different materials that nanoparticles are made of. Due to uncertainty of this situation, we have referred to more traditional views on the line tension; in the plotted figures it was taken to be positive and of the same order of magnitude as obtained by Bresme and Quirk for large nanoparticles.

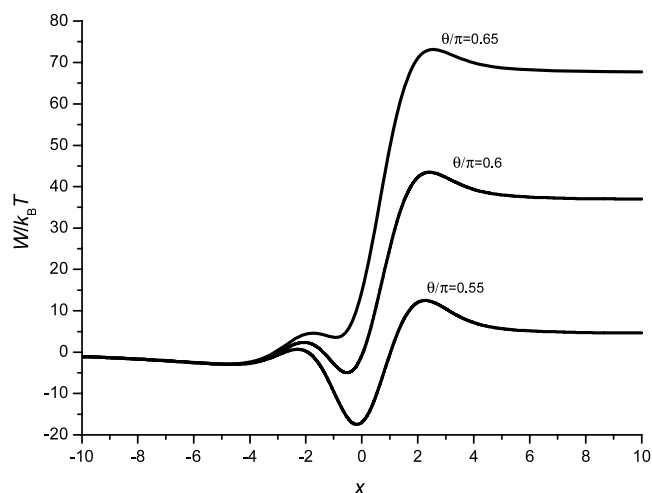


Figure 4. Calculated nanoparticle energy profile at ITIES: effect of the three phase contact angle between the particle surface and water–oil interface (cf figure 2). (Obtuse angle means less wetting by organic phase, i.e. stronger hydrophilicity of the functionalized particle.) Parameters—potential drop across the interface is -250 mV all others as in figure 3.

do not have sufficient drive to get localized at the liquid–liquid interface because the surface tension contribution provides the energy of adsorption of the order of $1\text{--}2 k_B T$ only.

Figure 3 also shows that a variation of the potential bias allows one to control reversibly the depth of the energy minimum and thus change the coverage of the interface by nanoparticles. In addition, the variation of the potential bias shifts the position of the energy minima and thus affects the location of nanoparticles in the interfacial layer. As discussed below this effect could influence interaction between the nanoparticles localized at ITIES and be essential for the description of the adsorption isotherm.

The energy profile for the nanoparticle is strongly sensitive to the value of the contact angle, as shown in figure 4. A pronounced minimum at the interface is possible when the contact angle does not differ much from 90° , otherwise the particle will slide to the phase which better wets its surface.

Figure 5 shows the effect of particle size on the energy profile for a given charge of the particle. The minimum is deeper when the particle is larger (the surface tension effect). Possible (quadratic) increase of the charge of a functionalized nanoparticle with its size does not change this trend.

3. Can particles lose their charge on the oil side when piercing the interface?

So far we have assumed that the charge of nanoparticles does not change when they approach the interface. However, one could expect much lower dissociation of the acidic groups at the nanoparticles in the oil phase compared to that in the aqueous phase, which could reduce the net charge of the nanoparticle when the latter penetrates the interface. This effect can be included phenomenologically assuming that the charge of nanoparticles is proportional to its surface area in contact with the aqueous phase. Having included such a

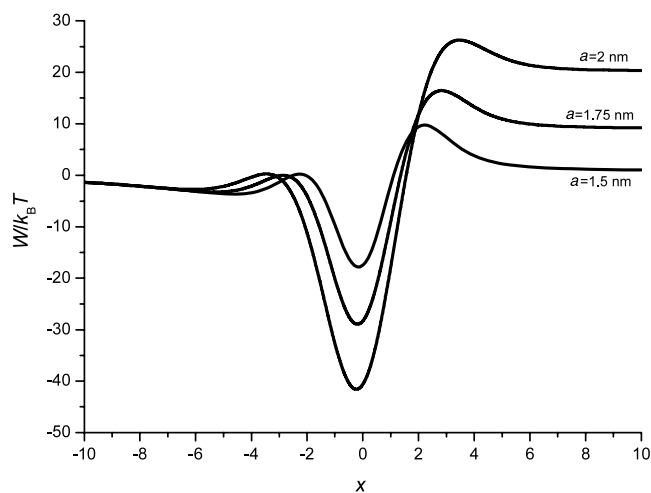


Figure 5. Calculated nanoparticle energy profile at ITIES: effect of particle radius (at constant charge on its surface). Parameters—potential drop across the interface is -250 mV, all others as in figure 3.

correction we found that the required charge reduction of a nanoparticle creates an extremely high energy barrier for its penetration into the oil phase and any reasonable potential cannot help to localize them at ITIES. This suggests that the charge of nanoparticles is not changed substantially when they approach the interface.

This ‘contradiction’ can be resolved if we take into account that the proton equilibrium between acidic groups and water is strongly influenced by the electrostatic repulsion between the charged groups localized at the same nanoparticle, and thus the number of ionized groups is only a small portion of the total number of terminal groups. It may well be true that this number of groups is close to what the dissociation equilibrium in oil demands. As a result the net charge may not change much with the slight embedment of a nanoparticle into the oil phase⁶.

4. Pair interaction potential and adsorption isotherm

Figure 3 shows that a potential drop as small as -100 mV across the aqueous–organic phase interface can effectively localize a negatively charged nanoparticle at the interface. Experiments show that when such particles adsorb at the interface they occupy the sites of a hexagonal two-dimensional (2D) grid, whose lattice constant is determined, roughly, by the minimum in the pair interaction potential between the nanoparticles. This interaction potential is formed by two main forces: (i) electrostatic repulsion of charges on the nanoparticles screened by the electrolyte [23] and (ii) attraction due to capillary forces between particles pinned

⁶ Otherwise, the distribution of charges on nanoparticles will become inhomogeneous, and as was discussed in the literature, these, together with the accumulation of counterions near the charges of nanoparticles may lead to a kind of ‘dipolar forces’ between nanoparticles in the interfacial layer. In fact, when the field caused by the nanoparticle is screened on both sides of the interface, we do not need to invoke dipolar forces, but rather study properly screened charge–charge interactions.

at the interface [24, 25]. Competition between these forces establishes the averaged distance between the particles.

As electrostatic repulsion depends on the Debye screening length and as the latter depends on the voltage drop (in the nonlinear Poisson–Boltzmann approximation) becoming shorter at higher drops, one can achieve shorter lattice constants at higher potential drops. Thus, in the range of negative potentials, where each particle has a warranted deep well at the interface, the above effect will lead to an increase of the limiting value of surface coverage in the adsorption isotherm with an increase of the absolute value of the potential. This effect has been observed experimentally for the case of Au-nanoparticles at ITIES [9]. It should be noted, however, that a variation of the potential may also affect the capillary attraction between nanoparticles through its effect on the interfacial tension and on the particle location relative to the boundary. Thus a quantitative description of the adsorption isotherm requires a more thorough analysis of the potential dependence of both electrostatic and capillary interactions between nanoparticles. It is relatively clear how to develop a theory of this effect within the framework of the discussed models, combining electrostatic interactions with capillary forces using also the experience gained in the studies of Reincke *et al* [26, 27]⁷. However, other terms in the interaction of nanoparticles at the interfaces are much less clear, such as short range hydration forces on the water side and hydrophobic interactions at the oil side. They all may well play greater roles when the particles are close to each other and could give unpredictable effective values of ‘line tension’, etc. Thus, efforts invested in such a theory may not be fully paid back. In this context MD simulations could be more instructive.

5. Influence of nanoparticle charge on sensitivity to applied voltage

Variation of the depth of the energy minimum with potential, which is shown in figure 3, is accessible to direct experimental measurements, for instance through the adsorption isotherm of nanoparticles at low concentrations. It would be therefore particularly interesting to compare this prediction with experimental observations. We are unaware of data that could bring light on this issue in the case of semiconductor nanocrystals (quantum dots). However, experimental data on the adsorption isotherms at different potentials for gold nanoparticles are available [9]. Although the whole isotherm looks Langmuir-like, at low concentrations it is roughly Henry-like. The slope of the Henry isotherm is reciprocal to the

⁷ These works were focused on understanding the self-assembly of charged colloid nanocrystals at the aqueous electrolyte–oil interface, both experimentally and theoretically. The authors studied the dependence of the adsorption isotherm on the surface charge of the nanoparticles, which they could affect by changing the pH of the aqueous phase. As it should be, they found that the interfacial coverage increases with a decrease of the particle charge. In order to explain the data the authors assumed that the particles partially pierce the interface, halfway in water and halfway in oil. Their theory included the (i) electrostatic repulsions between the particles—the direct one through the oil phase and the partially screened one in the aqueous phase, (ii) dipole interactions between the incomplete double layers around the particles and (iii) attractive van der Waals interactions between the colloidal particles adsorbed at the interface. They reached good qualitative agreement of the theory with the experimental data.

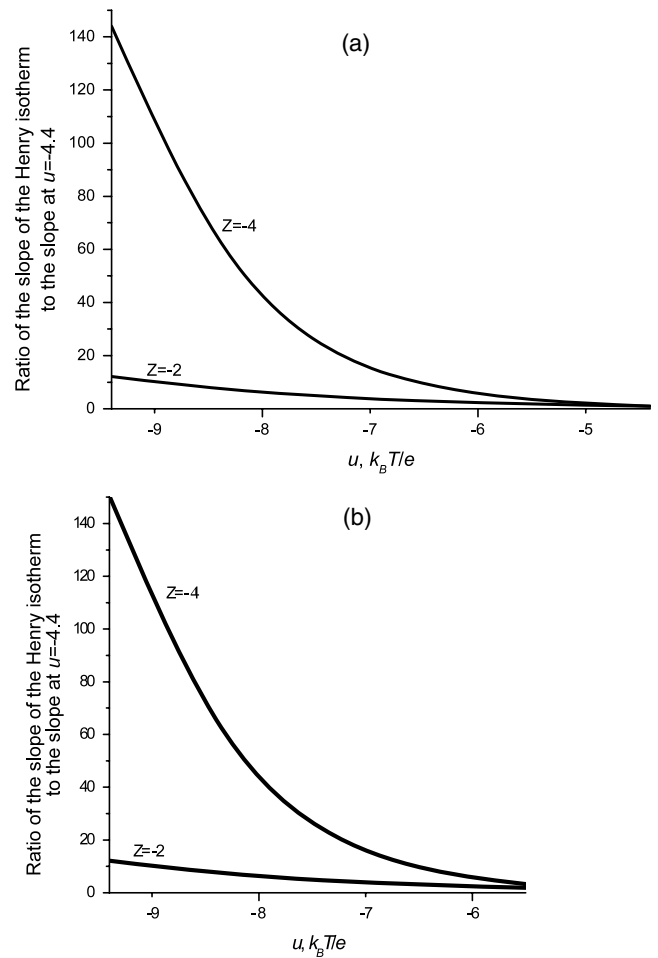


Figure 6. Variation of the slope of the Henry isotherm with potential. (a) Calculated at $\theta = 0.65\pi$ and line tension: 0.5×10^{-11} N for⁸ two indicated values of the net charge on the coated nanoparticles. The rest of the parameters are the same as used in figure 3. (b) The same but for two times smaller radius of nanoparticles, in order to correspond to the data of [9], $\theta = 0.55\pi$ as in figures 3–5 and line tension = 1.7×10^{-12} N (in correspondence with the estimates of [22]). This variation of parameters shows that they have a minor effect on the response to electric field. Whereas the minimum of adsorption energy will certainly be affected by this variation, the Henry constant is affected only slightly.

Boltzmann exponent, $\propto e^{\frac{E_{\text{ads}}}{k_B T}}$, where E_{ads} is the depth of the adsorption potential well. Thereby, if we compare the slopes at two different potentials, considering the ratio of the slope at V_1 to the slope at V_2 we get $e^{\frac{E_{\text{ads}}|V_1 - E_{\text{ads}}|V_2}{k_B T}}$. As we see in figure 3, the potential dependence in the minimum of the potential well is very strong. If we fix V_1 and vary V_2 for the parameters used in plotting figure 3 we will get in the end a 10^4 times enhancement of the slope. This is not seen in the data of [9], where the slope increases at most 10 times when the potential changes from -0.110 to -0.235 V.

⁸ Although the value of line tension does not influence a variation of the slope, a two times smaller line tension, as compared to the one adopted in the previous figures, was used in figure 6. This had to be assumed, because with a new $\theta = 0.65\pi$ and the previous value of line tension, no particles of this size will adsorb at the interface (at least for low negative potentials).

However, we do not have sufficient information about the system parameters to fit the experimental data: (i) we do not know the exact values of surface tension at the oil–particle and water–particle interface, as the particles are not bare gold particles, but are coated with ligands (this could be evaluated with the help of MD simulations, say, similarly to [18]). Next, the exact value of the charge of the coated particle is not known. Therefore, instead of fitting, we ‘simulate’ the results. Namely, we plot the relevant ratio of the slopes for charges -4 and -2 at poorer wetting of the nanoparticle by oil which results in a larger contact angle θ . All these changes of parameters are made to reduce the depth of the potential well and, thereby, the scale of its potential variation.

From figure 6 we see that at a reasonable $\theta = 0.65\pi$ the variation of the scale is still too large for $z = -4$. We need $z = -2$ to bring the results to reasonable scale of the slope variation. Larger θ will also help, then one will not need to assume such small charges to explain the data. So, it may be reasonable to revisit the system studied in [9]. Getting independent information on the Young angle of the coated gold could reduce ambiguity in at least one of the parameters of the model, which has a decisive effect on the depth of the well and its potential dependence. Note that the line tension is also important for the depth of the well, but it has a weak effect on its variation with potential.

6. Conclusion

Localization of nanoparticles at liquid–liquid interfaces induced by an external electric field is an emerging new area with great potential for applied and fundamental research. In order to understand its nature at ITIES one has to consider the following contributions to the particle’s energy: *competitive wetting* at the interface, *solvation* of charged particles, interaction with the *electric field*, the effect of *line tension* and generally speaking the interface deformability.

The presented estimates demonstrate that:

- (1) Nanoparticles with a typical number of charges from the functional groups indeed cannot be spontaneously localized at the interface of water and a low polar organic liquid such as 1,2-dichloroethane, without a stabilizing external electric field. But quite moderate, -100 mV, potential drops can provide sufficiently deep wells for localization.
- (2) For sufficiently charged nanoparticles characterized by small contact angles with oil the variation in nanoparticle concentration with applied electric field can be extremely strong. For nanoparticles with fewer charges and larger contact angles, the effect of the electric field can be much smaller, a situation perhaps seen in [9].
- (3) By exploring systems of nanoparticles with larger numbers of ionized functional groups and using oils that have smaller contact angles with the nanoparticles, a very large variation in the coverage can be achieved with voltages in the range of only a couple of hundred millivolts.

The latter may permit sensitive, voltage controlled tuning of the properties of the interface through changing the coverage of nanoparticles confined to it.

There are a number of effects that we did not pay enough attention to in this first discussion of field-induced localization of nanoparticles. One of them is the intrinsic potential distribution across the unpolarized interface, due to the spontaneous orientation of water molecules at the surface, resulting in spontaneous potential drop across the interface [28, 29]. This may affect the localization of nanoparticles at zero charge of the interface. The potential distribution of this kind extends to both sides of the interface over a distance characteristic of the short range structure of both liquids, but it is currently unclear how this distribution is disturbed by nanoparticles⁹.

Understanding of adsorption isotherms is still very incomplete. The ‘super-sensitivity’ of the slope at low concentrations of the variation of a bias voltage, ‘the mystery of the Henry slope’, is something we need to understand in depth before going any further. Here, joint efforts of theoreticians and experimentalists would be most welcome. The investments will pay back, due to wide areas of new applications that this emerging area can offer.

Localization and assembly of nanoparticles at liquid–liquid interfaces can be additionally manipulated by tuning the particle surface properties, in particular synthesizing amphiphilic (Janus) nanoparticles which have two surface regions of distinctly different wettabilities [30, 31]. The amphiphilic particles can exhibit an interfacial activity several times higher than homogeneous particles with the same radius [30, 31]. However, manufacturing of amphiphilic nanoparticles with desirable surface properties is still a challenging problem [32]. Another rapidly growing field is assembly of organic and bionanoparticles at liquid–liquid interfaces [31] which could play a major role in photo-energy conversion. Compared to inorganic nanoparticles, bionanoparticles have unique advantages, including truly monodisperse size-distribution and a range of versatile surface functionalities available for modification of protein shells.

Acknowledgments

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Appendix. Basic equations

The free energy profile for the nanoparticle at the electrified interface, W , includes four essential terms:

$$W = W_{\text{cap}} + W_{\text{solv}} + W_{\text{ext}} + W_{\text{line}} \quad (\text{A.1})$$

⁹ Furthermore, the potential drop of this kind simply shifts the potential of zero charge of the interface. Therefore, the resulting potential distribution is always determined by the total potential drop between the two phases fixed by the potentiostat.

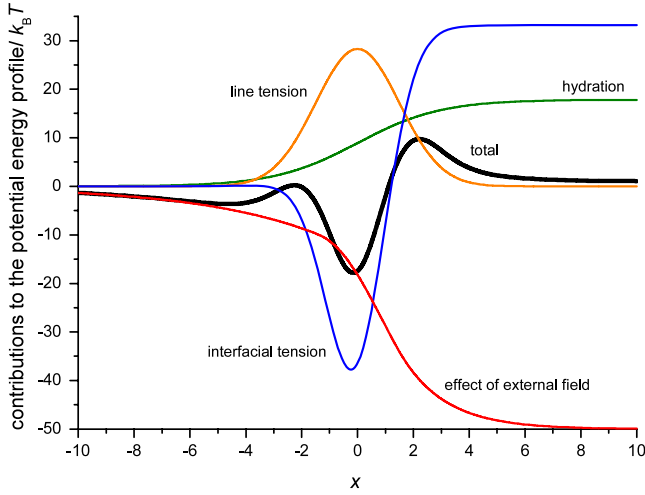


Figure A.1. Different contributions to the nanoparticle energy profile at ITIES, compared to the total profile. Parameters—potential drop across the interface is -250 mV, all others as in figure 3.

where W_{cap} , W_{solv} , W_{ext} and W_{line} describe the energy contributions of surface tension, hydration of charged particles, interaction with the electric field and the effect of line tension, respectively. Below we define these contributions.

Note that in the following equations all contributions to the energy profiles were *smeared over the size of the particle*, in order to include effects of particle nonuniformity, roughness and a finite thickness of the interface and thermal fluctuations. This procedure gives rise to the corresponding a -ranged exponentials. This is not a common procedure, but we introduced it to take into account the mentioned effects. It does not change the discussed effects dramatically but it helps the energy profiles to look smoother (avoid derivative breaks and thereby jumps in the force) which is always the case in reality.

The energy in the bulk of the aqueous phase was taken to be zero. The contributions of these four terms are shown, separately in figure A.1 for a potential drop of -250 mV. Other parameters are described in the caption.

Appendix. A.1. Surface tension [21]

$$W_{\text{cap}} = -\pi a^2 \sigma_{\text{o/w}} \left[\frac{4 \cos(\theta)}{1 + e^{-2x/a}} + e^{-x^2/a^2} \right]. \quad (\text{A.2})$$

Here x is a position of the centre of the particle with respect to the interface (aqueous phase occupies the semispace $x < 0$ and the oil phase occupies $x > 0$), a is the nanoparticle radius, $\sigma_{\text{o/w}}$ is surface tension at the oil–water interface, θ is the contact angle as defined in figure 2.

Appendix. A.2. Solvation [33]

$$W_{\text{solv}} = k_B T \frac{z^2 L_B}{2a} \left[\frac{\varepsilon_1}{\varepsilon_2} \frac{1}{1 + \kappa_2 a} - \frac{1}{1 + \kappa_1 a} \right] \frac{1}{1 + e^{-x/a}}. \quad (\text{A.3})$$

Here, z is the charge number of the nanoparticle, ε_1 and ε_2 are the dielectric constants of water and oil, respectively, $L_B =$

$e^2/(\varepsilon_1 k_B T)$ is the Bjerrum length in water, $k_B T$ is the thermal energy, κ_1 and κ_2 are the inverse Debye lengths in water and oil, respectively. This formula describes electrostatic free energy of re-solvation of a charged nanoparticle, when it moves from the aqueous phase to the oil phase.

Appendix. A.3. Energy in external electric field

$$W_{\text{ext}} = \int_{-\infty}^{\infty} dX \Phi(X) \rho(x - X), \quad (\text{A.4})$$

$$\frac{e\Phi(x)}{k_B T} = 4 \tanh^{-1} \left[e^{\kappa_1 x} f_1 \left(\frac{eV}{k_B T} \right) \right] \Theta(-x) + \left\{ \frac{eV}{k_B T} - 4 \tanh^{-1} \left[e^{-\kappa_2 x} f_2 \left(\frac{eV}{k_B T} \right) \right] \right\} \Theta(x), \quad (\text{A.5})$$

where V is the potential drop between the oil and water

$$f_1(u) = \frac{\sqrt{1 + \tau e^{u/2}} - \sqrt{1 + \tau e^{-u/2}}}{\sqrt{1 + \tau e^{u/2}} + \sqrt{1 + \tau e^{-u/2}}}, \quad (\text{A.6})$$

$$f_2(u) = \frac{\sqrt{\tau + e^{u/2}} - \sqrt{\tau + e^{-u/2}}}{\sqrt{\tau + e^{u/2}} + \sqrt{\tau + e^{-u/2}}}, \quad \tau = \frac{\varepsilon_2 \kappa_2}{\varepsilon_1 \kappa_1},$$

and the factor

$$\rho(x) = \frac{2z}{\pi a^2} \sqrt{a^2 - x^2} \Theta(a^2 - x^2) \quad (\text{A.7})$$

takes care of the fact that the charge is smeared on the surface of the particle (for small particles the effect of smearing on the result of equation (A.4) is not important). Equations (A.5) and (A.6) are based on the Verwey–Niessen [34] expression for the electrostatic potential, $\Phi(x)$, obtained as a solution of the nonlinear Poisson–Boltzmann equation for two back-to-back diffuse double layers (without a compact layer in between). As accounted for by equation (A.4), the action of the field is weighted with a charge number density $\rho(x)$, which corresponds to a homogeneously charged sphere with charge z .

Appendix. A.4. Line tension [19, 21]

$$W_{\text{line}} = 2\pi a \mu \exp\left(-\frac{x^2}{2a^2}\right). \quad (\text{A.8})$$

Here μ is the line tension and again we have included smearing of this effect, approximating the macroscopic formula $2\pi a \mu \sqrt{1 - x^2/a^2}$ by an exponential.

From figure A.1, which shows the contributions of the energy terms described above to the energy profile of the nanoparticles, one can see the important role of the effects of solvation and interaction with the applied electric field. As described they are, of course, present only in the case of charged nanoparticles and they change qualitatively the behaviour of the energy profile at ITIES compared to that for the uncharged nanoparticles. Thus these effects strongly influence partition of charged nanoparticles between the bulk phases and the interface.

References

- [1] Pickering S 1907 *J. Chem. Soc.* **91** 2001
- [2] Pieranski P 1980 *Phys. Rev. Lett.* **45** 569
- [3] Lin Y, Skaff H, Emrick T, Dinsmore A and Russell T 2003 *Science* **299** 226
- [4] Lin Y, Skaff H, Boker A, Dinsmore A, Emrick T and Russell T 2003 *J. Am. Chem. Soc.* **125** 12690
- [5] Dai L L, Sharma R and Wu C 2005 *Langmuir* **21** 2641
- [6] Wang D, Duan H and Moehwald H 2005 *Soft Matter* **1** 412
- [7] Cheng Y and Schiffrin D J 1996 *J. Chem. Soc. Faraday Trans.* **92** 3865
- [8] Johans C, Lahtinen R, Kontturi K and Schiffrin D J 2000 *J. Electroanal. Chem.* **488** 99
- [9] Su B, Abid J-P, Fermin D J, Girault H H, Hoffmannova H, Krtil P and Samec Z 2004 *J. Am. Chem. Soc.* **126** 915
- [10] Su B, Fermin D J, Abid J-P, Eugster N and Girault H H 2005 *J. Electroanal. Chem.* **583** 241
- [11] Girault H H and Schiffrin D H 1989 *Electroanalytical Chemistry* vol 15, ed A J Bard (New York: Dekker) p 1
Girault H H 1993 *Modern Aspects of Electrochemistry* vol 25, ed J O'M Bockris *et al* (New York: Plenum) p 1
- [12] Samec Z and Kakiuchi T 1995 *Advances in Electrochemical Science and Engineering* ed E Gersicher and C W Tobias (Weinheim: VCH) p 297
- [13] Girault H H 2006 *Nat. Mater.* **5** 851
- [14] Abid J-P, Abid M, Bauer C, Girault H H and Brevet P-F 2007 *J. Phys. Chem. C* **111** 8849
- [15] Bresme F and Oettel M 2007 *J. Phys.: Condens. Matter* **19** 413101
- [16] Uhlig H 1947 *Z. Phys. Chem.* **41** 1215
- [17] Kornyshev A A and Volkov A G 1984 *J. Electroanal. Chem.* **180** 363
- [18] Bresme F and Quirk N 1998 *Phys. Rev. Lett.* **80** 3791
Bresme F and Quirk N 1999 *J. Chem. Phys.* **110** 3536
- [19] Rowlinson J S and Widom B 1989 *Molecular Theory of Capillarity* (Oxford: Clarendon)
- [20] Aveyard R and Clint J H 1996 *J. Chem. Soc. Faraday Trans.* **92** 85
- [21] Johans C, Liljeroth P and Kontturi K 2002 *Phys. Chem. Chem. Phys.* **4** 1067
- [22] Bresme F and Quirk N 1999 *Phys. Chem. Chem. Phys.* **1** 2149
- [23] Vorotynev M A, Kornyshev A A and Rubinstein A I 1979 *Dokl. Acad. Sci. USSR* **248** 1321
Vorotynev M A, Kornyshev A A and Rubinstein A I 1980 *Dokl. Acad. Sci. USSR* **255** 1288 (erratum)
- [24] Kralchevsky P A and Nagayama K 2000 *Adv. Colloid Interface Sci.* **85** 145
- [25] Nikolaidis M G, Bausch A R, Hsu M F, Dinsmore A D, Brenner M P, Gay C and Weitz D A 2002 *Nature* **420** 299
- [26] Reincke F, Kegel W K, Zhang H, Nolte M, Wang D, Vanmaekelbergh D and Moewald H 2006 *Phys. Chem. Chem. Phys.* **8** 3828
- [27] Reincke F, Hickey S G, Kegel W K and Vanmaekelbergh D 2004 *Angew. Chem. Int. Edn* **43** 458
- [28] Sokhan V P and Tildesley D 1997 *Mol. Phys.* **92** 625
- [29] Tay K A and Bresme F 2006 *J. Am. Chem. Soc.* **128** 14166
- [30] Brinks B P and Fletcher P D I 2001 *Langmuir* **17** 4708
- [31] Boker A, He J, Emrick T and Russell T P 2007 *Soft Matter* **3** 1231
- [32] Perro A, Reculosa S, Ravaine S, Bourgeat-Lami E B and Duguet E 2005 *J. Mater. Chem.* **15** 3745
- [33] Kornyshev A A 1981 *Electrochim. Acta* **26** 1
- [34] Gavach C, Seta P and d'Epenoux B 1977 *J. Electroanal. Chem.* **83** 225