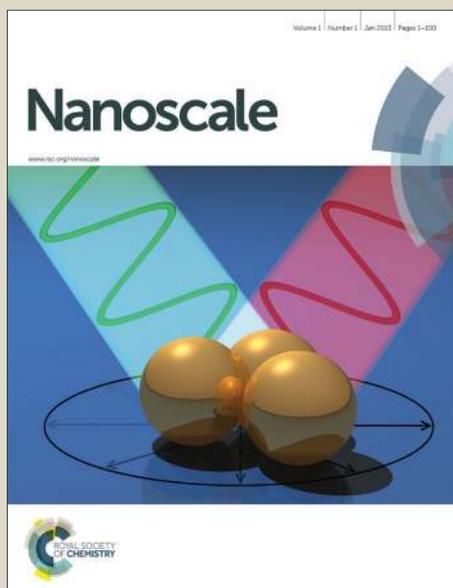


Nanoscale

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: M. Sabapathy, V. Kollabattula, B. Madivala and E. Mani, *Nanoscale*, 2015, DOI: 10.1039/C5NR03369A.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/xxxxxxxxxxx

Visualization of equilibrium position of colloidal particles at fluid-water interfaces by deposition of nanoparticles †

Manigandan Sabapathy, Viswas Kollabattula, Madivala G. Basavaraj and Ethayaraja Mani*

Received Date

Accepted Date

DOI: 10.1039/xxxxxxxxxxx

www.rsc.org/journalname

We present a general yet simple method to measure contact angle of colloidal particles at fluid-water interfaces. In this method, the particles are spread at the required fluid-water interface as a monolayer. In the water phase a chemical reaction involving reduction of a metal salt such as aurochloric acid is initiated. The metal grows as a thin film or islands of nanoparticles on the particle surface exposed to water side of the interface. Analyzing the images of particles in high resolution scanning microscopy (HRSEM), we trace the three phase contact line upto which deposition of metal film occurs. From geometrical relations, the three phase contact angle is then calculated. We report measurements of contact angle of silica and polystyrene (PS) particles at different interfaces such as air-water, decane-water and octanol-water. We also apply this method to measure contact angle of surfactant treated polystyrene particles at air-water interface, and we find a non-monotonic change of contact angle with concentration of surfactant. Our results are compared with the well-known gel trapping technique and we find good comparison with previous measurements.

1 Introduction

Adsorption of particles at fluid-fluid interfaces is of fundamental importance in soft matter and colloid science from the perspectives of interactions between particles, kinetics of adsorption and structural properties of monolayer of particles.^{1,2} Further, adsorption of particles helps stabilize drops, bubbles and foams, wherein particle-laden interfaces offer kinetic barrier for coalescence and provides better stability against phase separation.³ In general, micron-sized particles irreversibly adsorb at fluid-fluid interfaces due to high adsorption energies. The adsorption energies depend on the particle-fluid interfacial tensions, size and three phase contact angle (θ) of the particles.⁴ Of these parameters, contact angle dictates the type of emulsion (w/o or o/w) that can be stabilized. For instance, particles with contact angle $< 90^\circ$ stabilize o/w emulsion while particles with contact angle $> 90^\circ$ stabilize w/o emulsion.⁵ Therefore, accurate measurement of θ of particles is important as it directly relates to the formation and stabilization of emulsions and foams.

The search for an unified method for determination of contact angle of colloidal particles at various kinds of interfaces has been

on-going over many years. Several methods for measuring contact angle, although limited in scope, have been reported. The easiest but indirect method of measuring θ is based on sessile drop.⁶ In this method, a thin continuous film of the material of the particle is coated on a substrate. This is possible only if the particles can be dissolved in a suitable solvent. Therefore this method is suitable for latex particles such as polystyrene, PMMA and so on. The substrate is placed in the lighter (low density) fluid and a fine drop of the heavier (high density) liquid is placed on the substrate. Scheme 1a shows a schematic of the sessile drop method. By imaging equilibrium shape of the liquid drop on the substrate, the contact angle can be calculated using Young-Dupre equation (see Scheme 1a). This method lacks accuracy due to the effect of film thickness, roughness, degree of dissociated charges (in case of charged particles), and often gives large inconsistencies in the measurement of θ . Moreover, inorganic particles such as silica, which is often studied as a model system, can not be made as a film directly. For such cases, a close packed monolayer of particles is coated on a substrate.⁷ The contact angle of a liquid drop is determined by placing a liquid drop on the substrate followed by the drop shape analysis. This contact angle is assumed to be the contact angle of the particle at the liquid-air interface. However, the effect of particle roughness and line tension limit the accuracy of the measured contact angle.

Indirect measurement of contact angle of particles at fluid-fluid

Polymer Engineering and Colloid Science Laboratory, Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai -600 036, India

* Email: ethaya@iitm.ac.in

† Electronic Supplementary Information (ESI) available

interface was first suggested by Clint and Taylor.⁸ The monolayer of particles in a Langmuir trough is compressed until it collapses and the corresponding collapse pressure (Π_c) is measured. Π_c is equal to the Gibbs free energy of detachment of particles from the interface. By assuming the particles are close-packed, contact angle is calculated. This method relies on the accurate measurement of collapse pressure. However, due to relaxation time associated with rearrangement of particles in the monolayer near collapse, the measured collapse pressure is subjected to significant variability leading to inaccurate measurement of contact angle.⁹

The pursuit of in-situ measurements of contact angle of particles has significantly increased because of limitations of the existing techniques and advances in the development of novel experimental tools. Mohammadi and Amirfazli reported a method to measure contact angle, wherein a confocal laser scanning microscope is used to obtain cross sectional images of the particles in the plane perpendicular to the interface when it is in equilibrium position. Based on change in the background intensity, the cross sectional area of the particle at the interface is calculated to obtain the contact angle of the particles.¹⁰ Further, Snoeyink *et al.* had very recently reported a method for measuring the contact angle of polystyrene particles using Bessel beam microscopy.¹¹ By probing the particle height at the interface through the image analysis over hundreds of particles, the contact angle of particles is measured in-situ at interface.

In the recent past, the methods based on freezing,^{12,13} or gel trapping (GTT)^{14,15} of particles at liquid interfaces have been demonstrated to show direct measurement of contact angle. The state of particles trapped at interface is examined through microscopic techniques such as scanning electron microscope (SEM) or atomic force microscope (AFM), which detect particle's immersion depth. The depth of immersion is related to the three phase contact angle. However, the gelling and freezing of particles during the process may affect particle location, particles shape, or chemical composition of the system¹¹. Additionally, in the case of freezing technique, the methodology reported by the author works only for oil that is freezable at moderate cooling.

In this article, we demonstrate a simple method to measure θ in-situ at various kinds of fluid-water interfaces. A fluid-water interface is created by considering water containing a mixture of a metal salt such as HAuCl_4 and a reducing agent such as NaBH_4 , sodium citrate and a suitable oil/air. The particles are then spread at the interface so as to create particle monolayer. The reduced metal atoms nucleates and grow on the part of the particle that is immersed in water side. After completion of the reaction, a thin film of gold deposits on the particle surface in contact with aqueous phase enabling the tracing of three phase contact line. The particles are removed carefully from the interface by dip coating. Scheme 1 b shows the schematic of the method. The particles are imaged in high resolution scanning electron microscope (HRSEM) to trace the equilibrium contact line of particles. By measuring the two dimensional projection of the uncoated region and particle diameter, θ can be calculated (refer Scheme1b). In this method, one can also use other metallic/in-organic coating instead of gold deposition as long as the deposition of nanoparticles/nanofilm on the adsorbed parti-

cle provides enough contrast during SEM analysis. Unlike sessile drop method, the proposed method is not limited for a particular kind of particles. Our method can be used at room temperature unlike GTT which requires moderate temperature for the gellan to remain in water-like liquid. In what follows, we describe experimental details in Section 2 and present results for PS, silica and surfactant treated PS particles and finally provide some general remark of the proposed method.

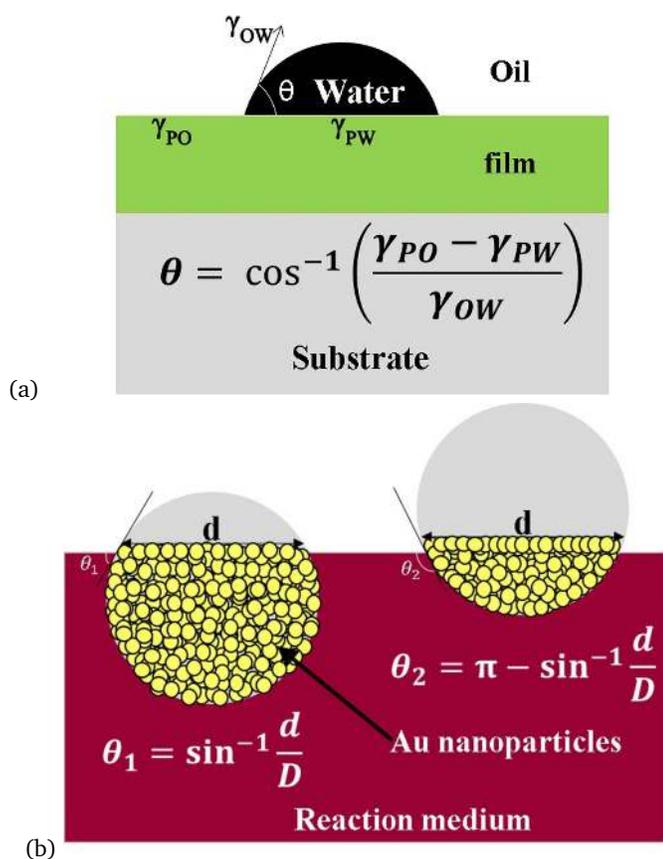
2 Experimental Section

2.1 Materials and Methods

The amidine functionalized positively charged polystyrene (PS) particles of diameter $2.2 \mu\text{m}$ are purchased from Interfacial Dynamics Corporation. The 3-Amino propyl trimethoxysilane (APTES, 97%) is procured from Alfa Aesar, USA and is used as received. The positively charged APTES treated silica particles are prepared starting from monodispersed silica (SiO_2) particle of size $1 \mu\text{m}$ obtained from Fiber Optic Centre, Inc., USA. The surface treatment leads to amine groups on the silica particles surface. Initially, silica particles of 4 wt % suspended in 1 ml of ethanol is mixed with $100 \mu\text{l}$ APTES and left undisturbed for 3 hrs. The particles are then separated from APTES mixture by centrifugation and washed with DI water for at least four washing cycles to remove any excess APTES. The zeta potential of bare silica ($1 \mu\text{m}$) and polystyrene ($2.2 \mu\text{m}$) measured using electrophoretic dynamic light scattering (DLS) are 29 ± 2 , 81 ± 3 mV, respectively. Aurochloric acid, a common precursor for gold, is obtained from Sigma Aldrich, USA. The reducing agents such as sodium borohydride (NaBH_4), tri sodium citrate are received from Merck, Germany. 1-Octanol and n-decane received from Alfa Aesar, USA and Merck, Germany, respectively, are used as oil phase. Sodium dodecyl sulfate (SDS), Merck, Germany is used to functionalize particles prior to spreading at the interface in one set of experiments. Ethanol used to aid spreading is supplied by Merck, Germany. The gellan which is used to gel aqueous phase in gel trapping technique is gifted by CP Kelco, USA. Poly dimethylsiloxane (PDMS) and curing agent (Sylguard[®] 184) purchased from Dow Corning, USA are used as cross-linked elastomer to transfer the particles from the gellan surface on to the PDMS. For all process requirements, MilliQ[®] de-ionized water (DI) is used.

2.2 Measurement of equilibrium contact angle of colloidal particles

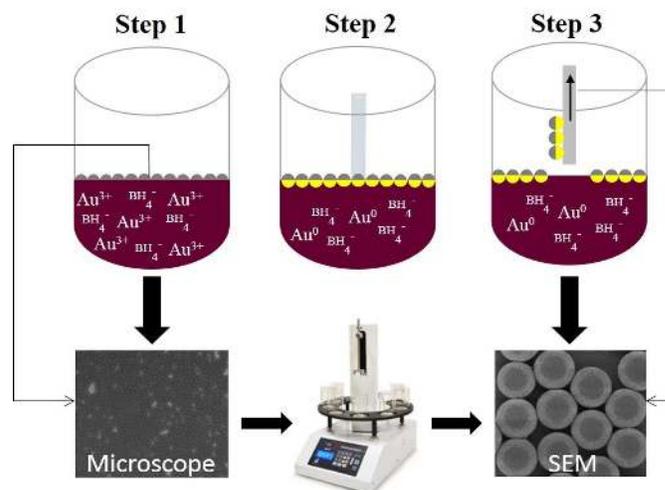
In the proposed method, equilibrium contact angle of PS and SiO_2 particles is measured by depositing a thin film of gold selectively on particle surface exposed to water side of the fluid-water interface. The deposition of gold produces a clear and distinguishable surface contrast when imaged using HRSEM and therefore the method offers a way to measure the contact angle directly. As described in Scheme 2, the aqueous phase used contains aurochloric acid and sodium borohydride (reducing agent). Here after, we denote the aqueous reaction mixture as "water" phase. These reagents are mixed such that the molar ratio between reducing agent/gold is 20% more than the stoichiometric requirement, so that NaBH_4 is always present in excess quantities. Typically we



Scheme 1 Schematic showing calculation of contact angle measurement from a) sessile drop technique (γ_{PO} - Surface energy of particle-oil, γ_{PW} - Surface energy of particle-water, γ_{OW} - Surface energy of oil-water; unit of surface energy is given in mJ/m^2), b) proposed technique (θ - Contact angle, d - diameter of the circle obtained by two dimensional projection of uncoated region of the particle, D - diameter of particle).

use aurochloric acid concentrations in the range of 0.2 - 0.5 mM. Subsequently, a 55 μL ethanol-water suspension (2:1 volume ratio) containing known concentration of particles is spread at the air-water or oil-water interface. The surface coverage of particles at the interface is typically close-packed. This is confirmed from microscopic observations (refer Figure S1). Then, a substrate, usually glass, held in dip coater port (APEX instruments, India) is immersed in the reaction mixture. The desired area of substrate to be coated can be varied by changing the dipping length. Prior to dipping, the substrate is cleaned by immersing it in a piranha bath containing hydrogen peroxide and sulphuric acid in the volume ratio of 1:3. The reaction leading to the deposition of gold on the particle surface is allowed to continue for 2 hrs. The substrate is then pulled from the mixture at a constant lifting speed of 2 mm/min and suspended for 5-10 min in air to evaporate residual reaction mixture from the film (monolayer) of particles. Finally, the particles are imaged in HRSEM to demark the gold coated part from bare surface. For comparison, we also evaluate the contact angle of particles using another reducing agent such as tri sodium citrate. The reaction mixture containing aurochloric acid and sodium citrate solution are mixed and kept at 80°C. The

molar ratio between reducing agent/gold is 20% more than the stoichiometric requirement. Since a higher temperature of 80°C is required when sodium citrate is used, we choose to use NaBH_4 in most of the experiments.



Scheme 2 Schematic representation of experimental steps describing deposition of gold nanoparticles on the particle surface at the interface.

2.3 Surfactant treated PS particles

It is known that the contact angle of particles can be modified by treating the particles with oppositely charged surfactants.¹³ We show that our method can be used to study the variation of contact angle of surfactant-treated particles. The deposition of gold film is not affected by this additional functionalization as we will show later. In one set of experiments, the PS particles are pre-treated with SDS before spreading at the air/water interface. For treatment, equal volume of PS particles (4w/v%) and SDS of various concentration are mixed and sonicated for 5 min before leaving it undisturbed for an hour. It is expected that negatively charged SDS will bind electrostatically with positively charged PS particles. After this treatment, the mixture is centrifuged and sedimented particles are re-dispersed in DI water using ultrasonicator. This procedure is repeated four times to remove free surfactant molecules. Further, the conductivity of supernatant solution is monitored after every wash in order to confirm the absence of free surfactants. The results obtained from the conductivity meter show that there is no significant variation after the second wash onwards. The values of conductivity after every washing steps are 0.15, 0.1, 0.1, 0.1 $\mu\text{S/cm}$. Thorough washing to remove free surfactant is essential because, free surfactant present may reduce fluid-fluid interfacial tension and change the actual θ . Thereby we make SDS functionalized PS particles with various degrees of functionalization.

2.4 Gel trapping

Contact angles measured based on the proposed method is validated using gel trapping technique (GTT). GTT is performed by spreading the particles on an air-water or oil-water surface followed by gelling of the water phase containing a nonadsorbing

polysaccharide such as gellan.¹⁴ The gellan mixture is prepared by dispersing 1.5 wt% of gellan (CP Kelco, USA) in DI water. The mixture is heated to 90°C in a water bath for 15 min to dissolve and hydrate the gellan. After the gel trapping procedure, the air or oil phase is replaced with a small amount of poly (dimethylsiloxane) (PDMS) elastomer. For this modification, PDMS mixed with curing agent in 1:10 wt ratio (Sylgard[®] 184, Dow Corning, USA) is used. The PDMS spread on the particle monolayer at the solidified gellan surface is allowed to cure slowly for 48 hrs so that the particle region exposed to air/oil is embedded into the curing PDMS elastomer. This makes the calculation of equilibrium contact angle of particles easier as the part exposed from the PDMS base can be directly viewed using HRSEM.

2.5 Characterization

The structural morphology and contact angle measurement of particles are studied using HRSEM (Hitachi S-4800) with operating voltage from 1-3 kV. For better image quality, a thin layer of gold is sputter coated on the sample to render them electronically conductive. Energy dispersive X-ray spectroscopy analysis (EDS) is made using the HRSEM to quantify the surface composition of particles. EDS analysis of the particles are carried out without sputter coating. Inverted microscope (Model: DMI3000B, Leica Microsystems, Germany) is used to characterize the particle monolayers prior to dip-coating and to observe structural morphology. Ultrasonicator (500GTI, Martin Walter Powersonic, Germany) is used for the separation and re-dispersion of surfactant treated particles into required liquid medium at an operating frequency of 132 KHz for 10 min. Conductivity of supernatant solution containing surfactants is monitored using conductivity probe (GA instruments, India). Dynamic light scattering, DLS (Horiba SZ-100) is performed to measure the zeta potential of particles used. The surface tension analysis for reaction mixture-air and reaction mixture-decane is carried-out using a goniometer (GBX instruments, France).

3 Results and Discussions

3.1 Contact angle of PS particles at air-water interface

Since the three phase contact angle of a particle at an interface is influenced by the fluid-fluid interfacial tension, we first establish that the presence of metal salt and the reducing agent does not affect the air-water and oil-water interfacial tension (see Fig. S1 in Supplementary Information). Further it is also confirmed based on control experiments with flat interfaces that the true contact angle of particle is not affected by the in-situ deposition of gold nanoparticles on the colloidal particle surface (see Fig. S2 in Supplementary Information). As a result of the chemical reaction in the bulk, the gold salt is reduced to gold metal. Since the particles are already adsorbed at the interface, the metal atoms that nucleate in the bulk grow as nanoparticles on the surface of the particle in contact with the aqueous phase. As the part of the particle exposed to water side is available for gold to grow, one can expect the formation of either thin gold film or islands of gold nanoparticles. Figure 1 shows a representative HRSEM image of regular hexagonal arrangement of particles with gold metal nanoparticles

on the surface for two different reducing agents. After scanning the entire region of substrate, we observed that there is a thin layer of gold on the surface of particles immersed in the reaction medium while there is no sign of gold deposition on the part exposed to air. The EDS mapping analysis using HRSEM confirms the presence of gold on the particle surface exposed to water side and absence in the air side (insets Figure 1). From the image analysis based on 100 representative particles, the diameter of circle (d) obtained from two dimensional projection of uncoated part of the particle (part exposed to air) and D (particle diameter) were measured individually for all particles. Dip coating allows to retain the orientation of the particles intact as in they were at the interface. From geometry, θ can be calculated from the values of d and D .

For contact angle $< 90^\circ$, we use the equation¹⁴

$$\theta = \sin^{-1} \left(\frac{d}{D} \right) \quad (1)$$

and for contact angle $> 90^\circ$,

$$\theta = 180 - \sin^{-1} \left(\frac{d}{D} \right) \quad (2)$$

Based on equation 1, the contact angle measured for the PS particles at water-air interface system using sodium citrate and NaBH_4 are $39 \pm 1^\circ$ and $38.5 \pm 1^\circ$, respectively, showing the choice of the reducing agent has no effect on the measured contact angle.

We note that there is no significant variation in the apparent contact angle obtained for reaction times of 10 min, 60 min and 120 min, although the quality of gold film strongly depends on reaction time (see Fig. S3 in Supplementary Information). However, film quality in turn affects the accuracy of measurement of contact angle. Of the three reaction times studied in our experiments, 60 min gives good demarcation of the contact line.

3.2 Contact angle of surfactant treated-PS particles at air-water interface

Recently there has been growing interest in using a combination of charged colloidal particles and oppositely charged surfactant to stabilize Pickering emulsions or foams.¹⁶ The synergistic interaction between particles and surfactant molecules is found to offer better stabilization. This combination can be used to alter contact angle of a particle at the same interface. A monotonic increase of contact angle as a function of added surfactant has been reported earlier.¹³ However, in this case surfactant molecules are present both on particle surface (via electrostatic) and in bulk water as free surfactant molecules. Therefore the increase in θ can be due to the decrease in oil-water interfacial tension because of the free surfactant. It is not clear whether increase in θ is due to free surfactant or due to particle-surfactant complex or both. In another study where excess surfactant molecules were thoroughly removed and only the surfactant molecules bound to particle surface were present, it was shown that the contact angle did not depend on the initial concentration of the surfactant.¹⁷ It can be argued that in these range of surfactant concentrations, the par-

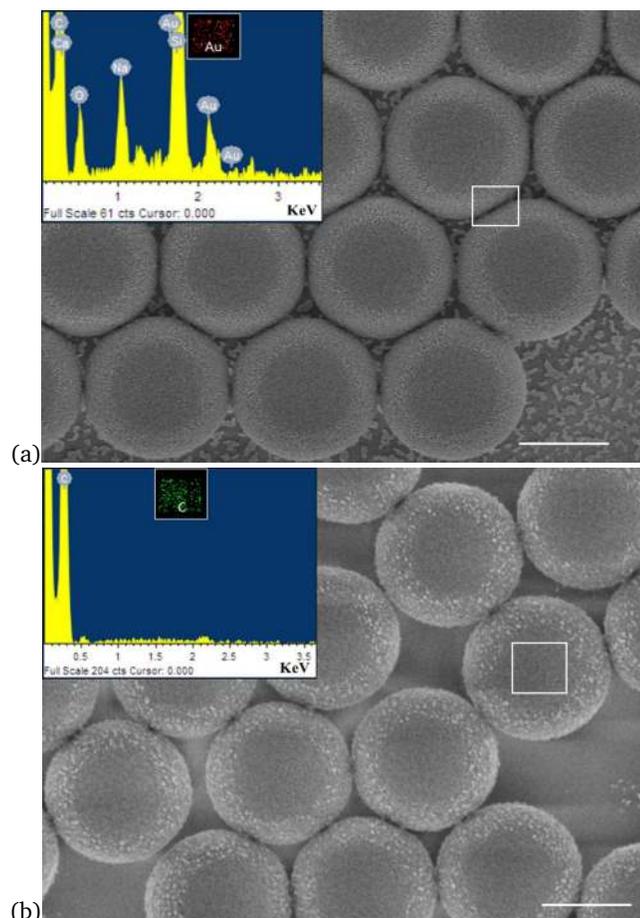


Fig. 1 HRSEM images showing gold nanoparticles on particle surface using reducing agent: A) sodium citrate, and B) sodium borohydride. Insets show EDS analysis showing the presence of gold. The scale bar corresponds to 2 μm .

ticles were highly charged. On one hand the charged particles like to maximize the area exposed to water and decrease the contact angle and on the other hand, surfactants adsorbed on the particle surface can impart hydrophobicity leading to an increase in contact angle. Therefore one might expect constancy in contact angle with surfactant concentration where electrostatic contribution is dominant, followed by an increase in contact angle as hydrophobicity becomes dominant. If surfactant concentration is increased further, contact angle should decrease again. Because of charge reversal, as discussed below, one is expected to see this nonmonotonic change in contact angle as a function of surfactant concentration. We verify this hypothesis by functionalizing the particles with oppositely charged surfactants and use our contact angle measurement technique to investigate this hypothesis.

Figure 2 a shows the variation of zeta potential and contact angle of PS particles (2.2 μm) with SDS surfactant (anionic) concentration. In the plot, the SDS concentration is expressed as c/cmc , where c is the concentration of surfactant and cmc is the critical micellar concentration (8.2 mM at 20°C). As the surfactant concentration increases, the charge of the particles reverses from positive to negative. This is because initially SDS binds with PS particles by electrostatic attraction thus screens the charge on the

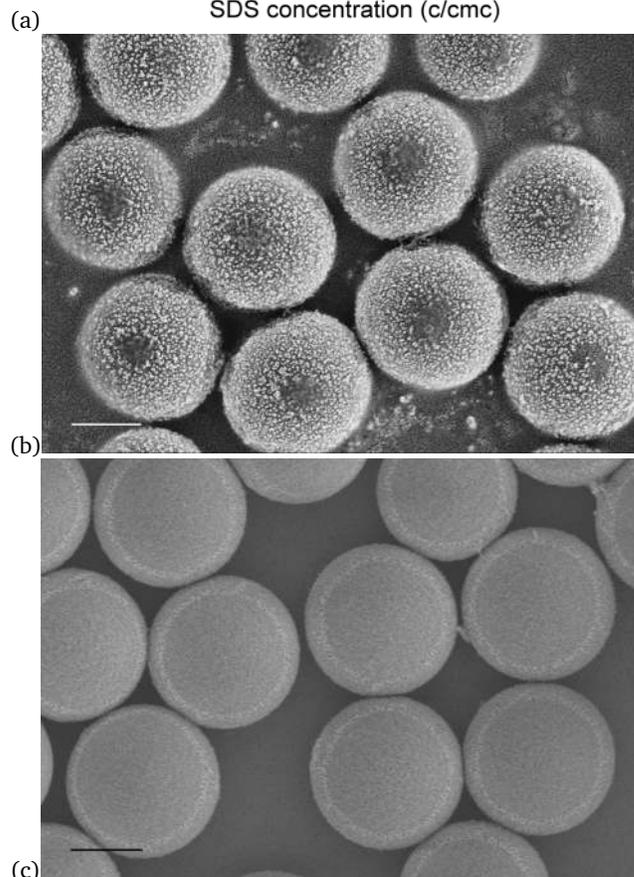
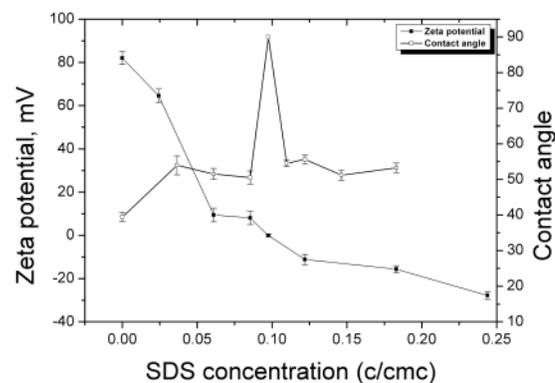


Fig. 2 Effect of surfactant concentration on contact angle of PS particles, a) Dependence of zeta potential and contact angle with SDS concentration, b) Bottom morphology of particles shows gold deposition upto one half of the particle surface (i.e., contact angle 90°) for SDS concentration of 0.097, c) Top morphology of particles showing gold deposition for SDS concentration of 0.036 corresponding to contact angle $\approx 53^\circ$. The scale bar corresponds to 1 μm .

particle. At certain concentration, the charges on the particle is completely screened by a monolayer of surfactant molecules. As we increase surfactant concentration further, a bilayer of surfactant begins to form via tail-tail interaction, where the head group of the outer surfactant layer is exposed to water. In such a scenario, the particles acquire a net negative zeta potential. Next we discuss how this charge reversal affects the contact angle. When little surfactant (0.036) is present, there is an increase in contact

angle from 39° to 53° . With further increase in surfactant concentration upto 0.085, no appreciable change in θ is observed. However at 0.097, a sharp increase in θ of 90° is observed. Interestingly at this concentration, the zeta potential of the particle is close to zero. Hence the hydrophobic nature of the surfactants on the particle surface leads to higher θ value. Further increase in surfactant concentration leads to reversal of the sign of zeta potential and electrostatic effect reappears leading to a decrease in θ . Figures 2 b-c show the representative HR SEM images of bottom and top morphology of surfactant treated particles at two instances, 1) contact angle 90° and 2) contact angle 53° , respectively. For contact angle measurement, each and every data points have been plotted based on average values from three different repeated experiments (totally three hundred measurements have been done for each data points). The structure of particles at the interface under fully charged state and neutral state is given in Supporting Information (Fig. S5 in Supplementary Information).

3.3 Contact angle of PS particles at oil-water interface

Next, we apply our method to measure contact angle of particles in two different oil-water interfaces, namely decane-water and octanol-water. In these experiments, we used sodium borohydride as reducing agent. When imaged using HRSEM, the top view of the particles i.e., portion of the particle exposed to oil did not show any gold deposited regions (Fig. S6 in Supplementary Information). Therefore, we investigated the bottom side of the particles by transferring the particles using carbon tape. Figure 3 shows the bottom view of particles i.e., portion of the particle exposed to aqueous phase. From Figure 3 a, it appears that $\theta > 90^\circ$, and therefore we apply Eq. 2 to estimate contact angle. We measured for decane-water $\theta = 111 \pm 5^\circ$ and for octanol-water $\theta = 158 \pm 1^\circ$. The value of contact angle of particles increased drastically when the type of interface is changed from air-water ($\theta = 39 \pm 1^\circ$) to decane-water and octanol-water. The drastic change of equilibrium contact angle is attributed to change in interfacial surface tension of water-decane (52 mN/m), water-octanol (8 mN/m) interface and distribution of charges. The higher values of θ implies that the particles are immersed more into the oil phase. Similar range of contact angle values are observed, when sodium citrate is used as a reducing agent (Figure 3 c). The measured contact angle at decane-water is $124 \pm 1^\circ$ with citrate as reducing agent.

3.4 Contact angle of silica particles at air-water and oil-water interfaces

In order to show that the technique can be extended to other type of particle as well, contact angle of silica particles is measured at different interfaces using NaBH_4 as reducing agent. Figure 4 represents HRSEM images showing top morphology of silica particles deposited on the glass substrate. From the analysis of SEM images, the contact angle measured at air-water and decane-water interface is found out to be $62 \pm 3^\circ$ and $39 \pm 3^\circ$. We note in the case of silica particles, the gold is deposited as a distinct ring along the three phase contact line, different from what was observed in PS particles. This may be due to low charge density on

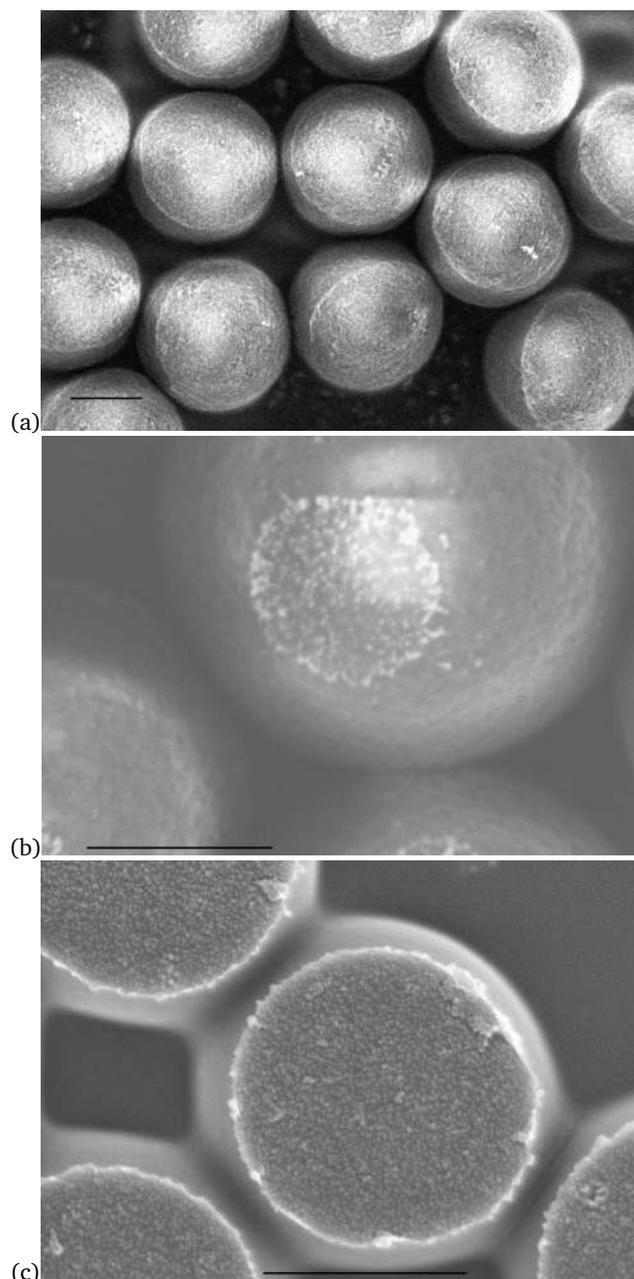


Fig. 3 HRSEM images showing gold deposition on polystyrene particles adsorbed at water-oil interface a) decane-water (NaBH_4), b) octanol-water (NaBH_4), c) decane-water (citrate). The scale bar corresponds to $1 \mu\text{m}$.

silica particle surface. However, our method of measuring contact angle requires only the contour of the three phase contact line and its projection. Our method is not limited by the quality of the deposited film as long as the contact line is traceable.

3.5 Comparison of measured contact angle with gel trapping technique

To compare our measurements, we carried out gel trapping technique to measure contact angles of PS at air-water and octanol-water interfaces. Figure 5 shows HRSEM image of polystyrene

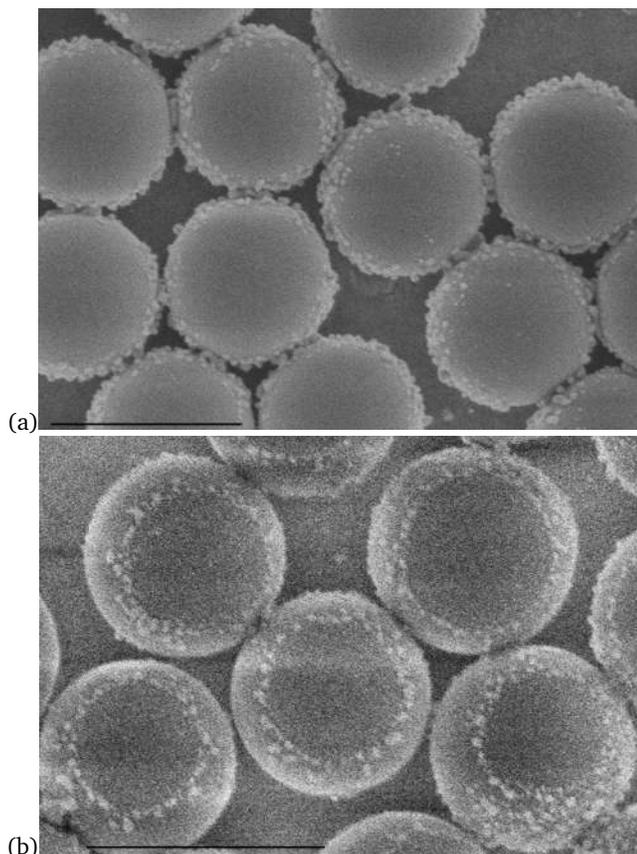


Fig. 4 HRSEM images showing gold deposition on silica particles adsorbed at water-fluid interfaces, a) water-air, b) decane-water. In both cases NaBH_4 is used as a reducing agent. The scale bar corresponds to $1 \mu\text{m}$.

particles embedded in PDMS block at air-water and oil-water interface. Based on image analysis, the contact angle measured for water-air system (Figure 5 a) is $50 \pm 3^\circ$, while, contact angle of particles at octanol-water interface is $150 \pm 1^\circ$ (Figure 5 b). Based on the chemical deposition of gold methodology proposed by us, the contact angle values correspond to $38.5 \pm 1^\circ$ and $158 \pm 1^\circ$, respectively. We find that a deviation of 5% is observed for octanol-water and 22% for air-water interfaces. These differences can be due to solidification of the gellan and reduction in the charge density of the particles. The surface charge density of the particles plays an important role in the contact angle. Increasing the surface charge density of the particles by a factor of 2 decreases the contact angle by a factor $2/3$.¹⁸ The adsorption of gellan on particle surface may affect the accurate measurement of contact angle by GTT, which we have not investigated in detail. In some of our GTT experiments with PS particles at aqueous gellan-decane interface, particle swelling is observed. Moreover, while using PS particles, if temperature of gellan is slightly above what is reported, we observed a shape transformations, similar to the report of Park and Furst.¹⁹ These effects associated with GTT may explain the deviation from true contact angle values.

Based on all our measurements, the contact angles obtained from different methods and interfaces are summarized in Table 1.

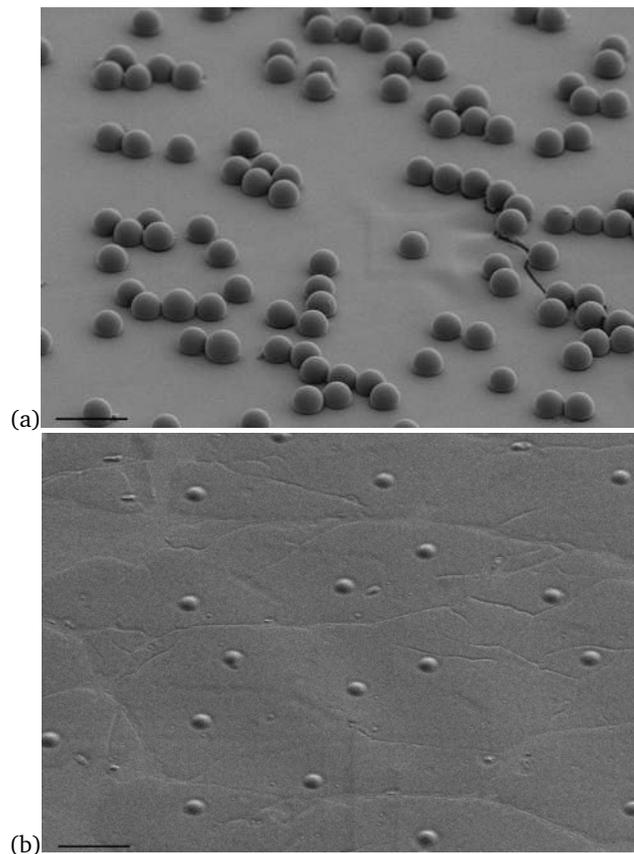


Fig. 5 HRSEM images of polystyrene trapped in PDMS film obtained from gel trapping technique for interfaces a) air-water system, b) octanol-water system. The images were obtained using HRSEM operated in tilted mode with an observation angle of 60° . The scale bar corresponds to $5 \mu\text{m}$.

The data shows that there is considerable agreements in contact angle values measured between existing GTT and our technique. The method proposed by us in this article can be considered as yet another technique which is simple and robust in application and can be used to calculate contact angle of particles in-situ at fluid-water interfaces.

3.6 Some general remarks on proposed technique

We have shown the generality of the proposed method to measure contact angle by using two different kinds of particles at three different kinds of interfaces. Here we highlight some general remarks on the method. One of requirements in this method is to assemble particles as a monolayer at the interface. This can be easily achieved for micron or sub-micron sized particles due to irreversible adsorption at the interface. However, for very small nanoparticles ($< 10\text{nm}$), the desorption energies can be comparable to thermal energy leading to exchange of particles from the interface to bulk and vice versa. In such scenario, the deposition gold might occur on the whole particle surface. Further, imaging the nanoparticles in HRSEM after coating will give rise to uncertainty in the measurement of contact angle. This method works well for particle sizes more than $1 \mu\text{m}$. Since our method involves

Table 1 Summary of measurements of contact angle from different techniques

Type of particles	Type of interface	GTT	Proposed method
Polystyrene	air-water	$50 \pm 3^\circ$	$38.5 \pm 1^\circ$
	decane-water	122° ¹⁰	$111 \pm 5^\circ$
	octanol-water	$150 \pm 1^\circ$	$158 \pm 1^\circ$
Silica	air-water	70° ¹⁰	$65 \pm 2^\circ$
	decane-water	33° ²⁰ (freeze technique)	$39 \pm 3^\circ$

a chemical reaction in aqueous phase, one of the fluids should be water. Therefore our method may not be applicable for oil-air interface. We note that the quality of the deposited gold film to demark the interface is important for accurate measurement of contact angle. We found that if the particles are positively charged, the quality of gold film is better. For negatively charged particle, the film is discontinuous and often we observed either islands of gold nanoparticles or a thin layer of gold around the contact line. A detailed study in improving the quality of the film by optimizing reaction conditions or metal salt is required to fully realize the generality of the method. In other words, the mechanism by which gold nanoparticle adsorb on the particle surface needs further investigation. Although it has been cited in many articles that the gold nanoparticles bind to the surface via electrostatic attraction followed by nucleation and growth, the role of the nature of the charge is not completely understood. For instance, Bao *et al.* indicated that the metals with negatively charged precursor ions would nucleate on cationic particles whereas those with positively charged precursor ions would prefer anionic particles.²¹ However, as described in Section 3.2, it is not clear as to why would a negative precursor metal (gold) ions grow on a surface of surfactant treated particles, pertaining to a zeta potential value of -28.0 mV, which is effectively an anionic particle. In this method, one can also use deposition of other kinds of nanoparticles instead of gold, as long as the deposition of nanoparticles/nanofilm on the adsorbed particle provides enough contrast during SEM analysis. To this end, 15 nm sized negatively charged silica nanoparticles are deposited on positively charged PS particle at air-water interface. The contact angle of particles obtained in this method ($36 \pm 0.8^\circ$) is in agreement with the gold deposition method ($39 \pm 1^\circ$). For more details, see Fig. S4 in Supplementary Information. The study of the role of charge on adsorption of metal nanoparticles on cationic or anionic surfaces is currently being investigated. The effect of shape of particles on adsorption at fluid-water interfaces have been reported both theoretically and experimentally.^{22–26} These particles experience strong, and long-ranged attractive capillary interactions that greatly exceed the thermal energy $k_B T$. Further, the combined effect of sharp edges and capillary interaction of particles^{27,28} due to shape anisotropy at fluid-water interfaces tend to show pinning and de-pinning behaviour at the interface.²⁵ These effects give rise to complications in determining equilibrium contact angle of anisotropic particles.

Hence, our method is limited to measure the contact angle of particles of spherical shape. Nevertheless, the promising application of the proposed technique can be finding the equilibrium confirmation or orientation of anisotropic colloids at interfaces. Further this method can be used to synthesize patchy colloids as choice of different interfaces allow a control of the patch size.

3.7 Conclusion

To summarize, we have proposed a new methodology to measure contact angle from real space imaging of particles that are coated with metal nanoparticles on the surface exposed to water side of the interface. The contact angle of pristine PS particles have been found to be unaffected by the type of reducing agent used in the reaction. The generalization of method is shown by measuring contact angles of polystyrene and silica at interfaces such as air-water, decane-water and octanol-water, which are commonly used fluid-water interfaces. In a separate study on a surfactant treated particles, we have shown that the addition of oppositely charged surfactants to the suspension of cationic particles causes change in contact angle as well as charge reversal of the particles. Apart from 90° contact angle corresponding to surfactant concentration of 0.097, the particles showed constancy of measured θ values throughout the range of surfactant concentration studied. A potential extension of this work can be visualization of equilibrium orientation of anisotropic particles at interfaces. Further this method can be used to synthesize single patchy colloids of controlled patch size.

3.8 Acknowledgement

The authors thank Dr. Pijush Ghosh, Applied Mechanics, Indian Institute of Technology Madras, for providing access to Goniometer and dip coater facilities. The authors acknowledge Mrs. Neethu Thomas and Mr. Venkateshwar Rao Dugyala for useful discussion during this study. The use of HRSEM facility (procured through DST-FIST grant) in this work is acknowledged. E.M acknowledges Department of Science and Technology, India for research grant (SR/S3/CE/055/2012).

References

- 1 E. Guzman, E. Santini, L. Liggieri, F. Ravera, G. Loglio, J. Krägel, A. Maestro, R. G. Rubio, D. Grigoriev and R. Miller,

- in *Colloid and Interface Chemistry for Nanotechnology*, ed. P. Kralchevsky, R. Miller and F. Ravera, CRC Press, Boca Raton, 2013, vol. 4, pp. 77–109.
- 2 A. J. Mendoza, E. Guzmán, F. Martínez-Pedrero, H. Ritacco, R. G. Rubio, F. Ortega, V. M. Starov and R. Miller, *Advances in Colloid and Interface Science*, 2014, **206**, 303–319.
 - 3 E. J. Stancik, M. Kouhkan and G. G. Fuller, *Langmuir*, 2004, **20**, 90–94.
 - 4 A. Maestro, E. Guzmán, F. Ortega and R. G. Rubio, *Current Opinion in Colloid & Interface Science*, 2014, **19**, 355 – 367.
 - 5 B. P. Binks, *Current Opinion in Colloid & Interface Science*, 2002, **7**, 21 – 41.
 - 6 Y. Rotenberg, L. Boruvka and A. Neumann, *Journal of Colloid and Interface Science*, 1983, **93**, 169 – 183.
 - 7 Y. Guo, D. Tang, Y. Du and B. Liu, *Langmuir*, 2013, **29**, 2849–2858.
 - 8 J. H. Clint and S. E. Taylor, *Colloids and Surfaces*, 1992, **65**, 61 – 67.
 - 9 S. Pradhan, L. Xu and S. Chen, *Advanced Functional Materials*, 2007, **17**, 2385–2392.
 - 10 R. Mohammadi and A. Amirfazli, *Journal of Dispersion Science and Technology*, 2005, **25**, 567–574.
 - 11 C. Snoeyink, S. Barman and G. F. Christopher, *Langmuir*, 2015, **31**, 891–897.
 - 12 L. Isa, F. Lucas, R. Wepf and E. Reimhult, *Nature Communications*, 2011, **2**:438, 1–9.
 - 13 S. Jiang and S. Granick, *Langmuir*, 2008, **24**, 2438–2445.
 - 14 V. N. Paunov, *Langmuir*, 2003, **19**, 7970–7976.
 - 15 N. Vogel, J. Ally, K. Bley, M. Kappl, K. Landfester and C. K. Weiss, *Nanoscale*, 2014, **6**, 6879–6885.
 - 16 B. P. Binks, A. Desforges and D. G. Duff, *Langmuir*, 2007, **23**, 1098–1106.
 - 17 R. Deleurence, C. Parneix and C. Monteux, *Soft Matter*, 2014, **10**, 7088–7095.
 - 18 L. N. Arnaudov, O. J. Cayre, M. A. C. Stuart, S. D. Stoyanov and V. N. Paunov, *Physical Chemistry Chemical Physics*, 2010, **12**, 328–331.
 - 19 B. J. Park and E. M. Furst, *Langmuir*, 2010, **26**, 10406–10410.
 - 20 B. P. Binks, L. Isa and A. T. Tyowua, *Langmuir*, 2013, **29**, 4923–4927.
 - 21 H. Bao, T. Bühr, A.-S. Smith and R. N. K. Taylor, *Nanoscale*, 2014, **6**, 3954–3966.
 - 22 M. G. Basavaraj, G. G. Fuller, J. Fransaer and J. Vermant, 2006, **22**, 6605–6612.
 - 23 J. Ally, M. Kappl and H.-J. Butt, *Langmuir*, 2012, **28**, 11042–11047.
 - 24 J. A. Champion, Y. K. Katare and S. Mitragotri, *Proceedings of the National Academy of Sciences*, 2007, **104**, 11901–11904.
 - 25 N. Chatterjee, S. Lapin and M. Flury, *Environmental Science & Technology*, 2012, **46**, 4411–4418.
 - 26 K. D. Danov and P. A. Kralchevsky, *Advances in Colloid and Interface Science*, 2010, **154**, 91–103.
 - 27 H. Lehle, E. Noruzifar and M. Oettel, *The European Physical Journal E*, 2008, **26**, 151–160.
 - 28 E. Van Nierop, M. Stijnman and S. Hilgenfeldt, *Europhysics Letters*, 2005, **72**, 671.