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Particle-assisted wetting

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Abstract

Wetting of a solid surface by a liquid is dramatically impeded if either the solid or the liquid is decorated by particles. Here it is shown that in the case of contact between two liquids the opposite effect may occur; mixtures of a hydrophobic liquid and suitable particles form wetting layers on a water surface though the liquid alone is non-wetting. In these wetting layers, the particles adsorb to, and partially penetrate through, the liquid/air and/or the liquid/water interface. This formation of wetting layers can be explained by the reduction in total interfacial energy due to the replacement of part of the fluid/fluid interfaces by the particles. It is most prominent if the contact angles at the fluid/fluid/particle contact lines are close to 90°.

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

1. Introduction

The wetting of an interface is generally governed by the interplay of short-range and long-range forces. If both are in favour, the formation of infinitely thick wetting layers is obtained. In the case of unfavourable short-range forces, one usually observes the formation of lenses with a finite contact angle that coexist with the bare interface. In contrast, the competition between favourable short-range forces and unfavourable long-range forces will give rise to a liquid layer of limited thickness that coexists with lenses, formed by the excess of the liquid [1, 2]. In the case of smooth interfaces, these principles are the same on fluid interfaces as on solid interfaces. For the wetting of water, the long-range forces across a wetting layer on top of the water surface are very often unfavourable and—besides a few exceptions [3–6]—the formation of lenses is generally observed [1]. On solid surfaces, wetting is further influenced by

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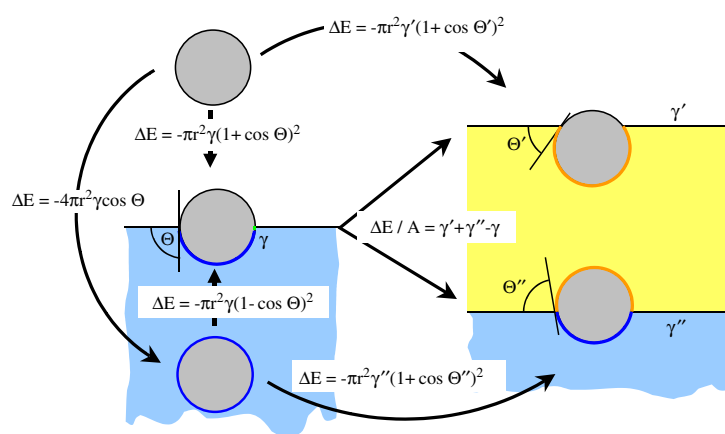


Figure 1. Elemental steps in the construction of various scenarios of particle-assisted wetting.

the roughness of the interfaces. The most prominent examples are the hydrophobic surfaces of plant leaves or artificial ‘super’-hydrophobic surfaces. In these cases, a solid surface is roughened [7] or decorated with hydrophobic solid particles [8]. The increased roughness of the solid surface yields an increased interaction between the liquid and the surface. Thus, the apparent contact angle of water, observed at length scales exceeding the length scales of the particles or protrusions, is considerably higher (if the surface is hydrophobic) or lower (if the surface is hydrophilic) than the local contact angle at the air/water/solid contact line [9]. In the case of high local contact angles, the liquid retracts further from the grooves and dimples in the surface and only covers the elevations, in effect placing the protrusions or particles on the solid surface into a liquid/air interface [10, 11]. The position of the protrusions or particles within this interface is given by the shape of the protrusion and the contact angle between the solid particle and the liquid/air interface.

Related situations can arise if particles are not bound to a *solid* surface, but are allowed to adsorb to a liquid/air or liquid/liquid interface. Solid particles have a strong tendency to adsorb to such fluid interfaces. The major driving force for this adsorption results from the fact that part of the fluid interface is replaced by the particle. Particles can be used to stabilize emulsions (e.g. oil in water or water in oil) [12–14] and at the same time prevent the coalescence or adhesion of droplets or bubbles either dispersed in a liquid medium or in air [15, 16]. On the other hand, at a low surface coverage, particles can bridge a thin liquid lamella between two liquid/liquid interfaces and lead to strong adhesion between two bulk liquid phases adjacent to this lamella [17].

As will be illustrated below, particles can also be used to promote the wetting of liquids on surfaces. In this so-called particle-assisted wetting, a liquid (for simplicity from now on called ‘oil’), which normally does not wet the surface of another liquid (from now on called water), can form a wetting layer if suitable particles are added. This effect can be interpreted in line with the phenomena described above.

2. Theory

If a liquid surface is covered by a layer of a second liquid, the change in energy ΔE per unit area A is given by subtracting the interfacial tension of the liquid without the layer from the sum of interfacial tensions of the newly generated interfaces (see figure 1); the negative value

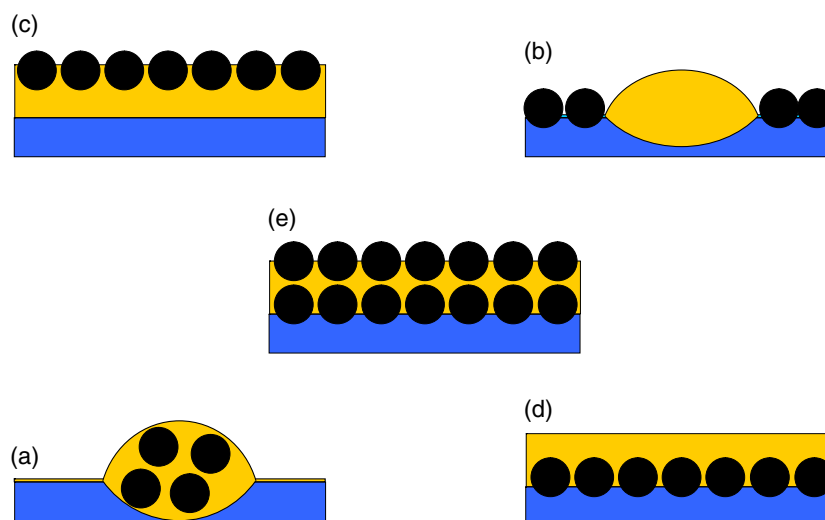


Figure 2. Several possible scenarios of arrangement of oil and particles on a water surface.

of this change in energy per area is called the equilibrium spreading coefficient $S = -\Delta E/A$. On a water surface, however, the formation of a wetting layer is more the exception than the rule. Most oils applied to a water surface form lenses instead of a thin layer. The value of $\Delta E/A$ calculated for a hypothetical layer of oil on water is positive and hence the equilibrium spreading coefficient is negative. Whereas the surface tension of water is not affected by the presence of non-polar oils like paraffin or perfluoropolymers, more polar compounds like triglycerides, aromatic compounds or acrylate based monomers usually form a monolayer on the water surface, which lowers its interfacial tension to such a degree that the equilibrium spreading coefficient has a barely measurable—though still negative—value [18]. Thus, in the following all phases and interfaces are considered to be in equilibrium and saturated with each other, regardless of whether this equilibrium can be reached by transport through the bulk phases or along the interface.

On the other hand, placing a particle from one of the adjacent phases into the fluid interface is associated with a negative change in interfacial energy per particle. This gain in energy is due to the fact that part of the fluid/fluid interface is replaced by the particle and is equal to $\Delta E = -\pi r^2 \gamma (1 - \cos \Theta)^2$ [14, 19], where r is the radius of the particle, γ is the interfacial tension of the interface and Θ is the angle between the liquid/liquid interface and the interface between the particle and the phase in which the particle was initially incorporated⁵. One can assume that a mixture of oil and particles applied to a water surface can adopt the five scenarios schematically depicted in figure 2 (formation of lenses with (a) complete incorporation of the particles or (b) complete separation between particles and oil, or the formation of a laterally uniform mixed layer with the particles adsorbed to (c) the top, (d) the bottom or (e) both interfaces of the layer).

One can use the above equations to calculate the total interfacial energies of all these scenarios at given interfacial tensions, contact angles and area per particle and determine which of these scenarios is most favourable. Since the contact angles and interfacial tensions

⁵ Θ is defined as the angle between the fluid/fluid interface and the interface between the particle and the phase in which the particle was initially incorporated. If the particle approaches the interface from the other side, the term $-\cos \Theta$ changes sign as indicated in figure 1 on the left side.

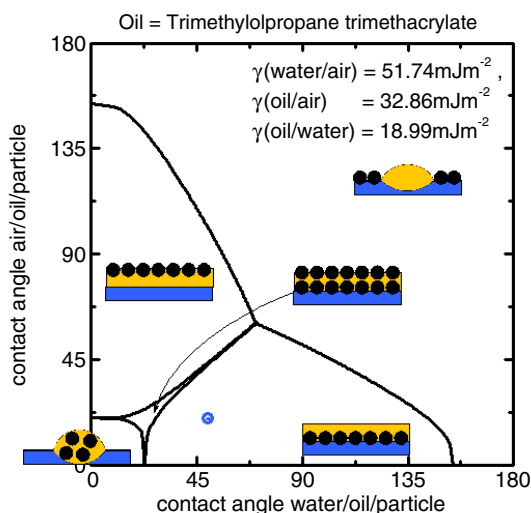


Figure 3. Theoretical phase diagram of particle-assisted wetting of the polymerizable non-volatile liquid trimethylolpropane trimethacrylate. The blue circle indicates the contact angles corresponding to the experiment shown in figure 7(c).

are correlated through the Young equation, actually only five independent parameters are needed to calculate the total interfacial energy of the system (the area per particle, two contact angles and e.g. the ratio of two interfacial tensions to the third one) and finally ‘phase diagrams’ of the particle-assisted wetting can be constructed.

Figure 3 depicts as one example the ‘phase diagram’ of particle-assisted wetting of the polymerizable non-volatile organic liquid trimethylolpropane trimethacrylate, TMPTMA (for the chemical structure see figure 7(a)). Each of the continuous lines depicts the coexistence conditions between one pair out of the five scenarios in figure 2. The areas enclosed by the lines define the stability regime for the indicated scenarios. At very high or very low contact angles between the particles and the interfaces of the oil, no particle-assisted wetting is expected; instead, the formation of lenses is predicted, which either are separated from the particles (high contact angles) or completely engulf them (low contact angles). Around contact angles of 90° , one expects particle-assisted wetting to occur, the particle being preferentially adsorbed to the interface with the contact angle closer to 90° , or adsorbed to both interfaces if the contact angles at both interfaces are comparable.

The diagram in figure 3 is of most relevance for the experiments conducted with this liquid that are described in more detail below. To highlight general trends, it is further instructive to discuss the hypothetical scenarios shown in figures 4–6.

Figure 4 depicts ‘symmetric’ cases in which the interfacial tension of the upper surface of the oil layer is identical to the lower one and the particles are closely packed at the interface. From figures 4(a)–(d), the interfacial tensions of the upper and lower interface of the oil layer increase from $0.5 \times$ to $1 \times$ the value of the interfacial tension of the air–water interface. As the interfacial tensions increase, the regions of particle-assisted wetting gradually decrease.

In figure 5 the sum of both interfacial tensions (and hence the spreading coefficient) is kept constant, but the interfacial tension of the lower interface is increased at the expense of the upper one. With increasing dissymmetry between the two interfacial tensions, the particles preferentially adsorb to the interface with the higher interfacial tension.

Figure 6 shows the effect of increasing the area per particle, starting at dense two-dimensional packing in figure 6(a) and ending at an area per particle 20 times the value of

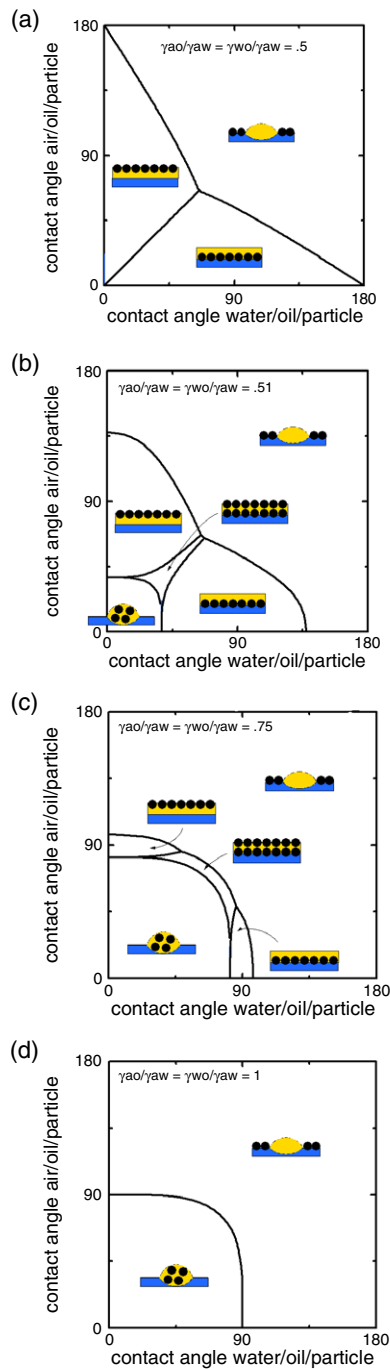


Figure 4. Phase diagram of particle assisted wetting, the spreading coefficient S decreasing from $S = 0$ (a), $S = 1 \times$ the interfacial tension of the air water interface (d).

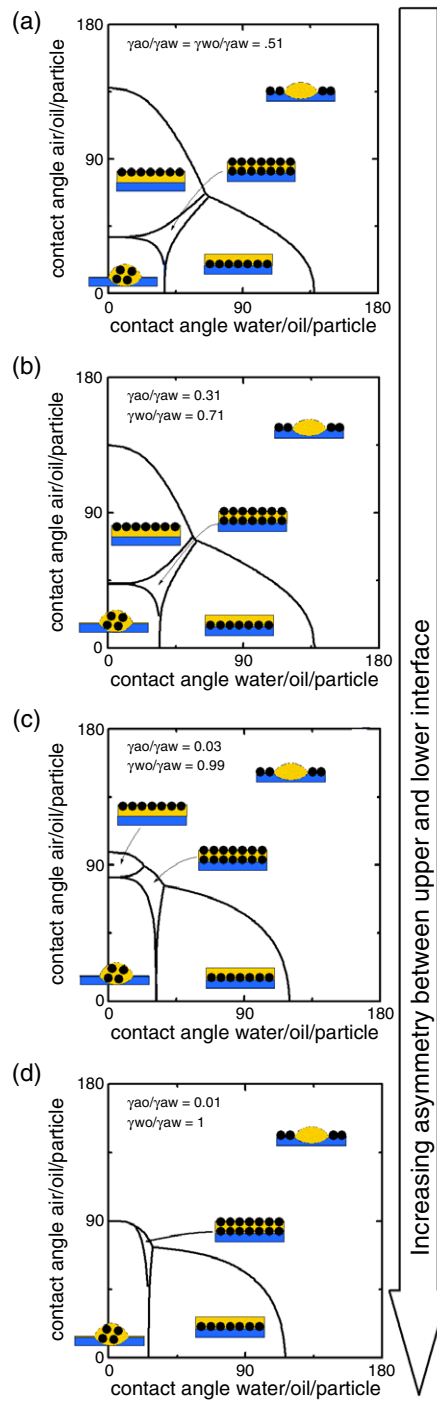


Figure 5. Phase diagram of particle assisted wetting, the ratio between the interfacial tension of the 'upper' interface to the 'lower' interface of the oil layer decreasing from 1 to 0.01 from (a) to (d).

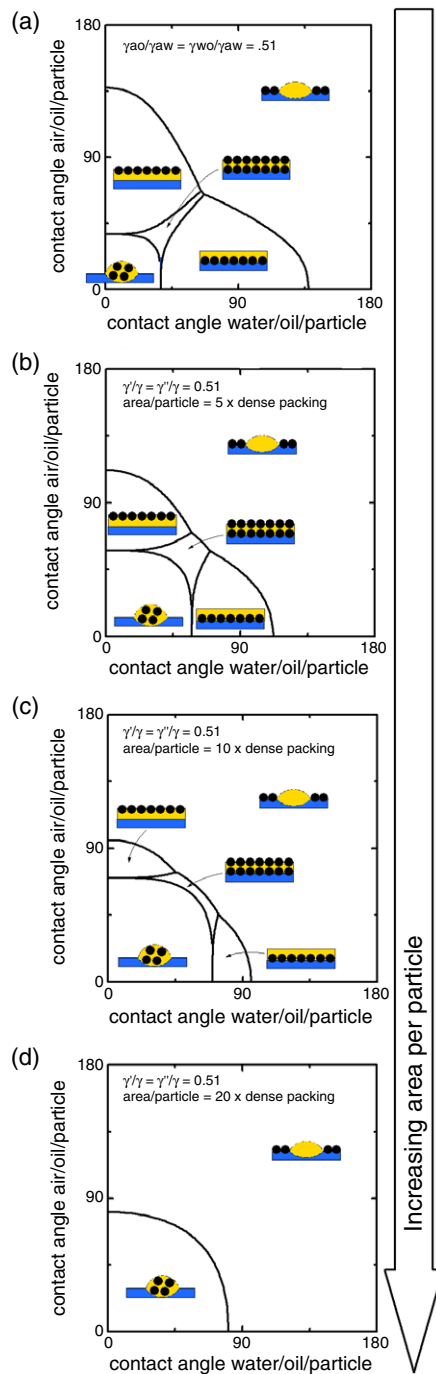


Figure 6. Phase diagram of particle assisted wetting, the area per particle increasing from $1\times$ (a) to $5\times$ (b), $10\times$ (c) and $20\times$ (d) the value of dense two-dimensional packing.

dense packing in figure 6(d). With increasing area per particle, the predicted regions of particle-assisted wetting gradually decrease and finally vanish completely, but even at an area per particle of ten times the value corresponding to dense packing, particle assisted wetting is still expected to occur. One has to note, however, that the diagrams are based on the

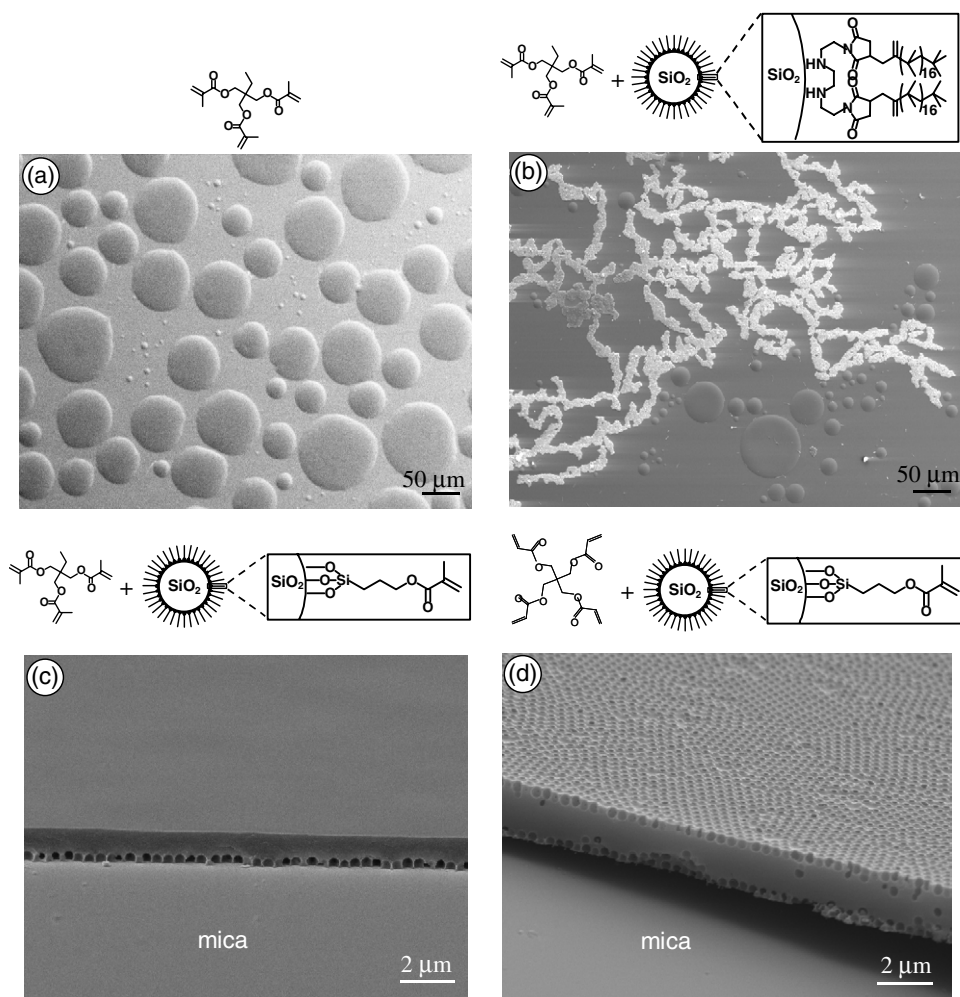


Figure 7. Scanning electron microscopy images of the oil and their mixtures with silica colloids after application to a water surface, UV irradiation and transfer to mica substrates (the chemical structures are depicted above each panel). (a) Lenses formed by the oil TMPTMA. (b) Structures formed by a mixture of TMPTMA and silica colloids that are coated with oligoisobutene chains. (c) Side view of a wetting layer formed from methacrylate-coated silica particles and the oil TMPTMA. (d) Wetting layer formed from a mixture of methacrylate-coated silica particles and the oil PETA. For the sake of image contrast, the particles were removed by etching with hydrofluoric acid.

assumption of uniform distribution of the particles across the water surface. If the particles form two-dimensionally densely packed aggregates instead of being evenly distributed, it is energetically favourable to cover only these aggregates with the oil, while the remaining part of the water surface is void of oil.

3. Experiments

Particle-assisted wetting has been investigated by applying mixtures of two types of hydrophobized silica particles and the non-volatile polymerizable oils trimethylolpropane trimethacrylate, TMPTMA, and pentaerythritol tetraacrylate, PETA (the chemical structures of

the two liquids are shown above figures 7(a) and (d), respectively). The use of a polymerizable oil has the advantage that one can solidify the oil, transfer it to solid substrates and image it with electron microscopy.

The oils alone do not form mesoscopic wetting layers on a water surface but retract into liquid lenses (as shown in figure 3(a) for the oil TMPTMA), which coexist with an Angstrom-scale monomolecular layer. If silica colloids coated with polyisobutene chains (Si-PIB) are mixed with the same oil and applied to a water surface, one immediately notes the formation of small lenses by the unaided eyes. In this case, the particles form irregular three-dimensional aggregates on the surface that coexist with oil lenses (figure 3(b)). However, mixtures of the same oils with silica colloids that are coated with methacrylate-terminated silanes (Si-TPM) spread evenly on the water surface without forming lenses. Close-ups of cross-sections of these layers are shown in figures 3(c) and (d); for the sake of image contrast and sample preparation, the particles were removed via etching with hydrofluoric acid before cutting.

As discussed before, the formation of wetting layers is expected to be a function of the contact angles at the oil/particle interfaces. It was possible to measure these contact angles by embedding the particles in the relevant interfaces, photo-cross-linking the oil and analysing the height traces of AFM pictures of the protruding parts of the embedded particles. In the case of the methacrylate-coated particles embedded in a layer of TMPTMA, the measured contact angles are included as a blue circle in the corresponding phase diagram in figure 2(d). The position of the circle in the diagram is in agreement with the prediction of the formation of a mixed wetting layer with the particles adsorbed to the bottom interface of the layer. It is instructive to compare the contact angles at the upper and lower interfaces for the system TMPTMA/methacrylate-coated particles (25° and 50° at the upper and lower interface, respectively) with those of the system PETA/methacrylate-coated particles (23° and 20° at the upper and lower interface, respectively). The asymmetry of the contact angles in the former case is in agreement with the location of the particles at the bottom interface, while the symmetric condition in the latter case is in agreement with the observed adsorption of the particles at both interfaces.

The above experiments were conducted at a surface coverage of the particles near to close packing of the particles. The mathematics depicted above in principle allow any area per particle larger than the value corresponding to dense packing. As can be seen from figure 6(c) even at areas per particle considerably larger than close packing one can still expect particle-assisted wetting, provided that the particles are distributed evenly across the water surface. In reality, however, particles embedded in a thin layer of oil are subject to comparatively strong and long range attractive capillary forces [20, 21]. At larger areas per particle than dense packing, one obtains therefore patches of close-packed particles that are embedded in oil lenses and coexist with a non-covered water surface (see figure 8(a)). Thus, if one is interested in covering a water surface evenly with particles and oil, repulsive forces are needed to overcome this capillary attraction. These forces could in principle be electrostatic repulsion between highly charged particles [22, 23]. However, addition of high charges to the particle surface will change the contact angles as well. Thus the influence of inter-particle forces on particle-assisted wetting cannot be clearly separated from other effects. We therefore chose to use paramagnetic particles and induce repulsive forces by applying an external magnetic field perpendicular to the water surface [24]. This allows investigation of the differences between attractive and repulsive particles without altering any other properties of the system. Figure 8 shows a mixture of the polymerizable oil TMPTMA and $\sim 2 \mu\text{m}$ diameter polystyrene particles containing 22% of magnetic iron oxide (Merck Chimie, France) with a volumetric susceptibility of 0.052 ± 0.003 and a saturation magnetization of $21.1 \text{ A m}^2 \text{ kg}^{-1}$, applied at sub-monolayer coverage to a water surface. To facilitate the observation, the amount of oil

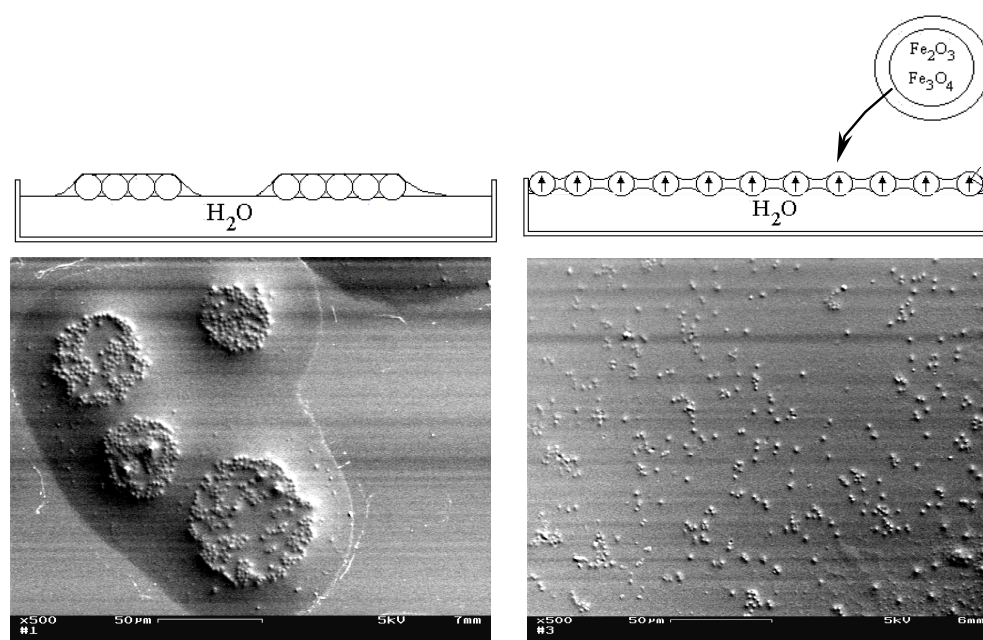


Figure 8. Mixtures of the polymerizable oil TMPTMA and paramagnetic particles, applied to a water surface (and subsequently photo-cross-linked and transferred to a mica substrate) (a) in the absence of an external field, (b) in the presence of a magnetic field perpendicular to the water surface.

was chosen in such a way that the particles penetrate both interfaces of an assumed oil layer and thus are visible in top view. Without an external field (figure 8(a)) the particles form two-dimensional, comparatively dense-packed aggregates, which do not evenly cover the water surface. An external magnetic field of $16 \times 10^3 \text{ A m}^{-1}$, applied perpendicular to the water surface, induces magnetic dipoles within the particles and thus renders them repulsive. This repulsion is large enough to break up the islands of particles and to spread them over the water surface, taking the oil with them in a thin layer (figure 8(b)). The oil layer in figure 8(b) is almost featureless and therefore barely visible in the electron microscopy image.

The principle of particle-assisted wetting is also useful for the preparation of advanced materials. As shown in figure 7(c), the mixed wetting layers can be prepared with an amount of oil large enough that the layer thickness is considerably larger than the dimensions of the particles. If the amount of oil is reduced as shown for example in figure 9, one can obtain mixed layers in which the particles protrude at the top and the bottom of the interface. If in these layers the particles are selectively removed after cross-linking of the oil, one obtains thin solid membranes, bearing dense arrays of uniform holes. The resulting porous membranes can be easily transferred to any desired substrate such as mica, silicon wafers, and even macroporous supports like electron microscopy grids with $100 \mu\text{m}$ wide openings. Figures 9(a) and (b) show such a solidified layer from top and bottom views after cross-linking. Figure 9(c) depicts a side view of a resulting porous membrane transferred to a mica plate. In order to expose a cross-section as well as the top surface, part of the membrane was peeled off by a Scotch tape. A top view of a freely suspended porous membrane that spans the openings of an electron microscopy grid is shown in figure 9(d). The membrane covers the openings of the grid completely. The pores are visible from the top and the bottom of the membrane and one can see the underlying grid through the pores (bottom view not shown here).

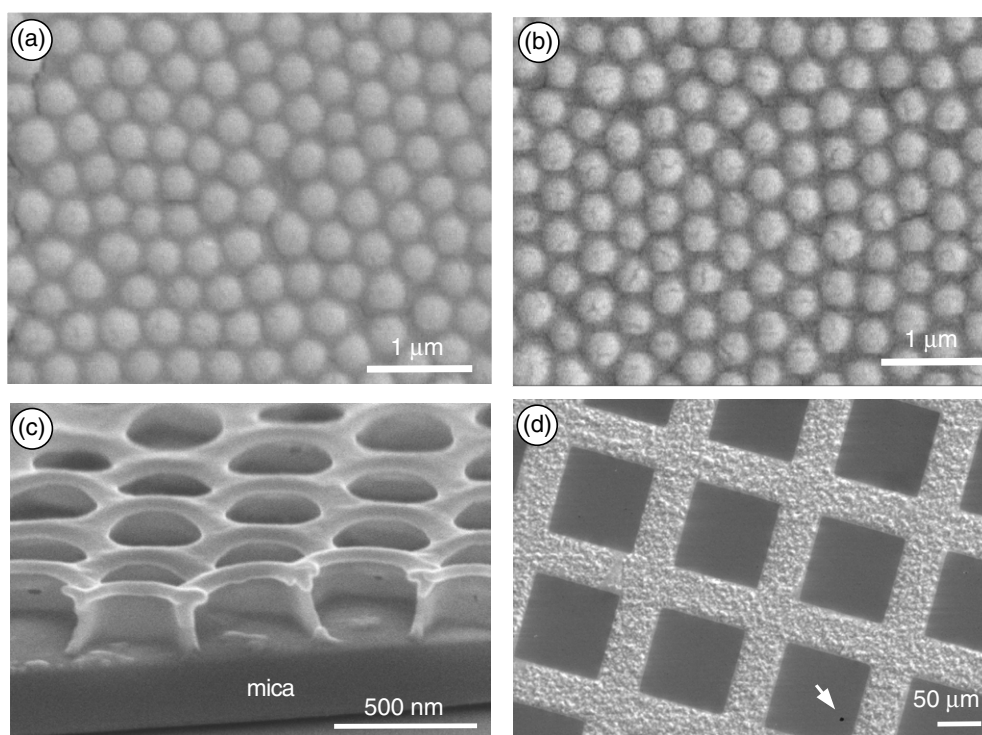


Figure 9. Bottom view (a) and top view (b) of a composite membrane obtained from mixed layers with a mixing ratio between the photo-cross-linkable oil TMPTMA and the silica particles low enough to allow the particles to penetrate through both interfaces of the oil layer. (c) A porous layer obtained from the photo-cross-linked oil after removal of the particles. (d) A freely suspended porous membrane transferred to a microscopy grid. The dark dot at the bottom of the image is a defect, showing the contrast between a covered and a non-covered area.

The size of the pores is given by the size of the particles used as templates. It is therefore possible to tune the pore size by using particles of appropriate sizes. Figure 10 shows examples of porous membranes obtained by the method described above with pores in the size range from several micrometres to several nanometres. It has to be noted that not only the pore size, but as well the membrane thickness and hence its mechanical stability, decreases with the size of the particles. The membranes with micrometre pore sizes can be handled without any support, whereas the membranes with sub-micrometre pores need to be supported by a grid or other (porous) substrates.

4. Conclusions

In summary, particle-assisted wetting is a new phenomenon, which can be described by rather simple mathematics and enables us to fulfil the usually impossible task of forming wetting layers on a water surface. The experiments reported here have exclusively been conducted at planar air/water interfaces. The underlying principle, however, is more general and might be applicable to various three-phase systems. Such systems can include those involving curved surfaces like flotation problems or enhanced oil recovery or non-aqueous systems like complex alloys or polymer blends. Furthermore, particle-assisted wetting opens up new and

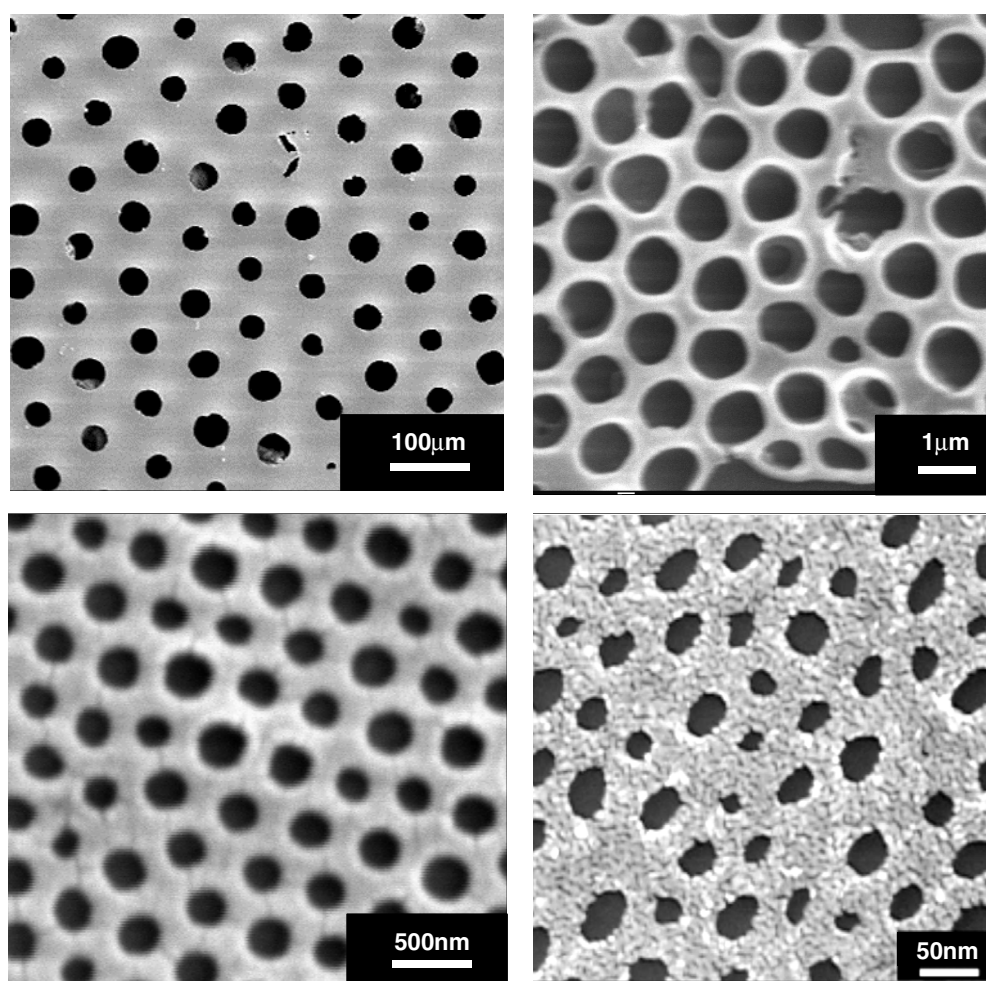


Figure 10. Freely suspended porous membrane of various pore sizes, obtained via particle-assisted wetting of an oil on the water surface, photo-cross-linking of the oil, removal of the particles and transfer to a support with openings.

technologically interesting applications like switching wettability by external fields and the preparation of regular surface structures and membranes of controlled and uniform pore sizes.

Acknowledgments

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