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# Contact angle and detachment energy of shape anisotropic particles at fluid-fluid interfaces

Thriveni G. Anjali, Madivala G. Basavaraj *

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

HIGHLIGHTS

- The effect of size, shape and surface properties of particles on the contact angle is investigated.
- The detachment energy calculation for cuboidal and spherocylindrical particles is carried out.
- The surface energy of hematite particles is estimated using the contact angle values at two fluid-fluid interfaces.

GRAPHICAL ABSTRACT
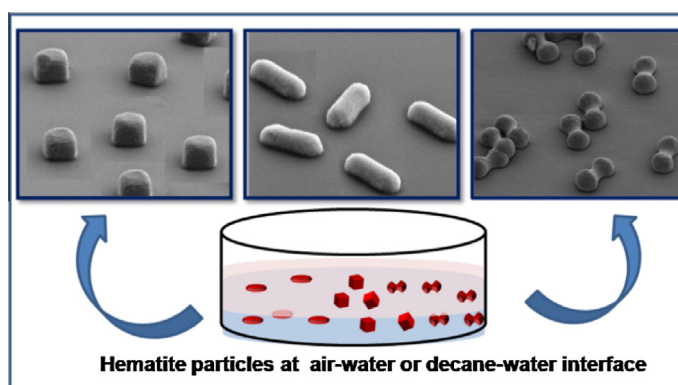
Hematite particles at air-water or decane-water interface

ABSTRACT

The three phase contact angle of particles, a measure of its wettability, is an important factor that greatly influences their behaviour at interfaces. It is one of the principal design parameters for potential applications of particles as emulsion/foam stabilizers, functional coatings and other novel materials. In the present work, the effect of size, shape and surface chemistry of particles on their contact angle is investigated using the gel trapping technique, which facilitates the direct visualization of the equilibrium position of particles at interfaces. The contact angle of hematite particles of spherocylindrical, peanut and cuboidal shapes, hematite-silica core-shell and silica shells is reported at a single particle level. The spherocylindrical and peanut shaped particles are always positioned with their major axis parallel to the interface. However, for cuboidal particles at air-water as well as decane-water interfaces, different orientations namely - face-up, edge-up and the vertex-up - are observed. The influence of gravity on the equilibrium position of the colloidal particles at the interface is studied using the hematite-silica core-shell particles and the silica shells. The measured contact angle values are utilized in the calculations of the detachment and surface energies of the hematite particles adsorbed at the interface.

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1. Introduction

For the past few decades, the self-assembly of colloidal particles adsorbed at fluid-fluid interfaces has received great attention in the scientific community because of the applicability of this concept in the fields of foam and emulsion stabilization, pharmaceutical and food industries, and for the fabrication of functional materials [1–5]. While the spontaneous attachment of colloidal particles at fluid-fluid interfaces was first reported by Ramsden [6] in 1904, Pickering [7] pointed out its technological applicability as emulsion stabilizers. The high attachment energy of colloidal particles at the interfaces makes their adsorption

* Corresponding author.
  E-mail addresses: tganjali@gmail.com (T.G. Anjali), basa@iitm.ac.in (M.G. Basavaraj).

irreversible in contrast to the reversible adsorption of surfactants [8]. The microstructure and mechanical properties of particle laden interfaces depend on many factors such as size, shape, surface roughness, wettability and surface charge of the particles [8–14]. Among these, the wetting properties of the particles, characterized by the three phase contact angle is important to determine the magnitude of their attachment (or detachment) energy, equilibrium position and nature of the interaction between the particles at the interface. For micron sized particles, the value of the attachment (detachment) energy of the particle to (from) the interface is several orders of magnitude greater than the thermal energy, ($k_B T$), making their adsorption irreversible. In the case of the surface active particles, the term contact angle is analogous to the hydrophilic-lipophilic balance [HLB] of the surfactants [8]. When a particle is adsorbed at the fluid-fluid interface, the surface tensions of the three interfaces involved ($\gamma_{f_1 f_2}$, γ_{pf_1}, γ_{pf_2}) are related to the three phase contact angle by the Young's equation [8],

$$\cos \theta_{f_1 f_2} = \frac{\gamma_{pf_1} - \gamma_{pf_2}}{\gamma_{f_1 f_2}} \qquad (1)$$

where $\theta_{f_1 f_2}$ is the particle three phase contact angle at $f_1 - f_2$ interface, γ denotes the surface tension, f_1 refers to fluid 1 – typically either air or oil, f_2 refers to fluid 2 – typically water and p indicates the particle. Depending on the values of the contact angle, particles are classified as, completely hydrophilic ($\theta = 0°$), completely hydrophobic ($\theta = 180°$), neutrally wetting ($\theta = 90°$), partially hydrophilic ($0° < \theta < 90°$) and partially hydrophobic ($0° < \theta < 180°$). While the fluid-fluid interfacial tensions can be measured by a number of experimental techniques, there are no direct methods for the estimation of γ_{pf1} and γ_{pf2}, making the estimation of contact angle using Eq. (1) unfeasible. On the other hand, the contact angle can be obtained directly without the use of any surface tension values, provided their equilibrium positions at the interface are visualized directly. Even though several experimental methods have reported for the measurement of contact angle of the particles, very few methods are successful in direct imaging of the interfacial position of particles and quantification of the wetting behaviour at a single particle level [15,16]. Among these methods, the gel trapping technique (GTT) [17] is widely employed to estimate the contact angle of colloidal particles and to understand the particle adsorption at fluid-fluid interfaces.

In recent years, interest in the studies involving interfacial behaviour of anisotropic colloidal particles is rapidly growing [18–22] as a result of advancements in synthetic chemistry and development of novel methods for the synthesis of anisotropic particles of various shapes. By exploiting the shape and orientation dependent interactions between anisotropic particles adsorbed at the interfaces, it is possible to create different macroscopic structures suitable for diverse applications [23–26]. The unique microstructures and rheological properties of anisotropic colloidal particles at the interface are due to the capillary interactions that originate from the interface deformations around particles. Compared to contact angle measurement of spherical particles at fluid interfaces, the presence of non-planar contact line resulting from the particle anisotropy and the possibility of multitude of particle orientations make the contact angle measurement of anisotropic particles non-trivial and challenging. Regardless of many methods for the contact angle measurement of spherical particles, there are only few reports on the measurement of contact angle and direct visualization of equilibrium position of anisotropic particles at the interface. Moreover, the electrostatic interaction between the particles trapped at interfaces can be estimated from the knowledge of their equilibrium

positions at the interface [27]. In most of the literatures related to the interfacial assembly of anisotropic particles, the role of interface-mediated interactions is discussed; however, the importance of the electrostatic interactions that are known to be of significant importance is not yet explored [28]. To this end, an accurate estimation of contact angle data for anisotropic particles is very crucial in predicting the particle-particle interactions and the stability of such particles at the fluid-fluid interfaces. Interferometry [29], GTT [30] and the Freeze-fracture shadow-casting (FreSCa) cryo-SEM [31,32] are the direct methods that have been applied to measure the contact angle of anisotropic particles at the interfaces. A combination of the interferometry and optical trapping techniques is used to investigate the effect of particle aspect ratio on the contact angle and three phase contact line of the ellipsoidal particles [29]. FreSCa cryo-SEM has been applied to study the wetting behaviour of dumbbell particles [31] and to study the effect of surface chemistry, size and shape of the ellipsoidal particles on their contact angle [32]. The adsorption and orientation of shape anisotropic porous particles at air-water and decane-water interface is directly observed using the GTT [30].

In the present paper, GTT is used to determine the contact angle of micron sized shape anisotropic particles – peanut, cuboidal and spherocylindrical particles, hematite-silica core-shell particles and silica shells - at air-water and decane-water interface. While this method has been widely used for the measurement of contact angle of various particles, an additional care has to be taken if the particles under consideration are temperature sensitive or if particles used tend to swell in the oil medium (for example polystyrene in decane). However, for inorganic particles, such issues do not arise. The easy and high yield synthesis of shape anisotropic hematite particles of uniform surface properties makes them a good model system in the field of colloidal science. The wettability of these particles at an individual particle level will be of great use in estimating the attachment (detachment) energy of the particles and tuning their self assembly at the liquid interfaces. The previous works on the wettability of hematite particles have employed the drop shape technique and reported an average value of their contact angle [26,33]. Here, the effects of particle size, shape and surface properties on the three phase contact angle are systematically investigated by employing hematite particles of different shapes and hematite-silica core-shell particles. The negligible effect of gravity on the equilibrium position of the particles at the interface is inferred from the similar contact angle values of hematite-silica core-shell particles and the silica shells. The influence of the nature of the interface on the particle contact angle is analyzed by comparing the contact angle of the particles at the air-water and the decane-water interface. The particle orientations at the interface are directly imaged by using the SEM. The spherocylinders and the peanut shaped particles orient with their long axis parallel to the interface, where as cuboidal particles exhibit three multiple orientations – face-up, edge-up and vertex-up – consistent with the prior literature [34,35]. and a statistical analysis is done on the percentage occurrence of the three orientations. Since the conventional way of obtaining particle contact angles is not possible for cuboidal particles, the particle wettability is represent in terms of the fractional height (fractional particle surface area) of the particles exposed to the water phase, similar to the previous approaches used for the contact angle calculations of anisotropic colloidal particles [35,36]. The obtained results for all types of particles are consistent with the partial hydrophilic nature of the particles. Moreover, the measured contact angle values are used to calculate the surface energy components of the hematite particles and the detachment energies of the spherocylindrical and cuboidal particles from the air-water interface.