Particles in thin liquid films and at interfaces

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A R T I C L E   I N F O

A B S T R A C T

The behaviour of small particles at interfaces and in thin liquid films has been studied for many years and recent advances in experimental and numerical techniques have allowed a wealth of new research to be conducted. This manuscript reviews the last five years of work investigating the effect of particle shape and packing density on their behaviour when attached to a thin liquid film or at an interface between two immiscible fluids. We discuss advances at the individual particle scale, covering shape and surface heterogeneity, as well as breakthroughs in experimental and numerical modelling of larger scale systems.

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1. Introduction

The presence of small particles at the surface of thin liquid films can either stabilise or destroy them depending on the specific properties of the particles. This behaviour has long been established and much research has focused upon the interaction of spherical particles with liquid–vapour (LV) or liquid–liquid (LL) interfaces. More recently, with the availability of powerful imaging and numerical modelling techniques, this has been expanded to non-spherical and non-uniform particles.

A previous review by Horozov [1**] discussed many of the advances in the understanding of particle stabilised films up to 2008. This review of more recent literature is similarly concerned with the interaction between particles and thin liquid films, but also highlights publications that investigate the behaviour of particles at the interface between two immiscible fluids. It is contended that the two topics are related so closely that advances in experimental or theoretical techniques in one is of relevance to the other.

The structure of this review has been laid out to discuss advances in one area at a time, however many of the publications cited do fall under a variety of headings. We shall begin with a look at work that has focused on the behaviour of a single particle in a film or at an interface, the most exciting advance being the expansion of models from two to three dimensions. There have also been several papers published that investigate the behaviour of non-spherical particles. The discussion will then move to particles with surface heterogeneity, including Janus particles, an area that has received considerable attention. We shall then move into the area of multiple particles on a film and their

stabilisation effects in the static case, before expanding this to cover work that has looked at the dynamics of particle–particle interaction. Finally the review finishes with a look at the new experimental and numerical techniques that have been developed to measure particle–film interaction.

2. Non-spherical particles

Whilst the simplified two dimensional system of a spherical particle in a film has been well covered, workers are now investigating more realistic and less perfect systems, both through numerical modelling and experimental investigation. Here we discuss the advances that have been made in the area of single particles interacting with a film or interface. Many industrial applications involve non-spherical particles with sharp edges and irregular shapes. These properties have a profound effect on the particle–film interaction and if we are to gain insight into the fundamental behaviour of these systems it is important to move away from the standard two dimensional, idealised spherical particle in film. Advances in experimental techniques also offer us the opportunity to revisit classic work and gain further insight.

In the early 1980s a very elegant study by Dippenaar [2] investigated the mechanisms through which a thin film can be ruptured or stabilised by an orthorhombic particle. Dippenaar experimentally confirmed the theory that the three-point contact lines of a film are drawn together at one of the sharp edges of the particle [3]. These experiments have recently been duplicated [4**] with modern high speed cameras and numerical modelling. Using these previously unavailable resources, it was possible to capture the position and moment that the film rupture occurs. It was found that the interpretation of the data available to Dippenaar was valid, but that significant information was lost between successive video frames. Using 200 μm cubic galena, Morris and Cilliers

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[4**], found that the particle can cause such distortion in the two oppos-ing liquid–vapour interfaces that they are forced together a small distance away from the particle's edges, instead of at the three point contact (TPC). This behaviour had not previously been observed or postulated, and illustrates the value of revisiting such seminal works with newer technology.

If the particles attached to a film or interface are not spherical an additional factor in film stability must be considered; their orientation at the liquid–vapour (LV) interface. As their orientation affects the topology of the LV interface it will alter the film stability and the interaction between the particles. The orientation the particle(s) adopt is, in turn, dependent upon shape and contact angle. In the past it has been difficult to capture the shape of the meniscus surrounding non-spherical particles but with recent improvements in both numerical modelling and experimental techniques it is now possible to do so. Morris et al. [5,6] presented a method that uses the superquadric family of equations to represent the particle(s) in the Surface Evolver program [7] allowing the visualisation of the meniscus as well as the calculation of the forces acting on the particle. Their approach differs to that of Morgan et al. [8] in that it takes into account the deformation of the interface surrounding the (cubic) particle. Whilst the results obtained for a single particle are comparable, the approach used by Morris et al. [5,6] is easily scalable for use with multiple particles. Energetically stable orientations of non-spherical particles (shown in Fig. 1) can be found by identifying the orientations that form the topology with a global or local minimum in total surface energy. These orientations are easily identifiable if the energy associated with each orientation is plotted as an 'energy surface' [6,8]. Local or global minima on the energy surface represent stable orientations of the particle.

Chatterjee and Flury [9] used 3D printing to fabricate particles with various geometric shapes (cylinder, cone, sphere, tetrahedron) which they then passed through the interface whilst measuring the capillary forces on them. The particles used were roughly 5 mm in diameter and thus much larger than those traditionally studied at interfaces and in thin liquid films, but their minimum size was limited by the accuracy of the 3D printer. At the scale used they were able to observe the pinning of the air–water interface at the sharp edges of the particles, as well as the effects of surface roughness on contact angle. Even at this large scale capillary forces were found to dominate over DLVO and gravity forces. Whilst the particle size was limited by the accuracy of the 3D printer, as that technology matures it will allow these types of experiment to be revisited on a smaller scale. At a much smaller scale Morgan et al. [8] fabricated superellipsoidal particles (1.36 μm)
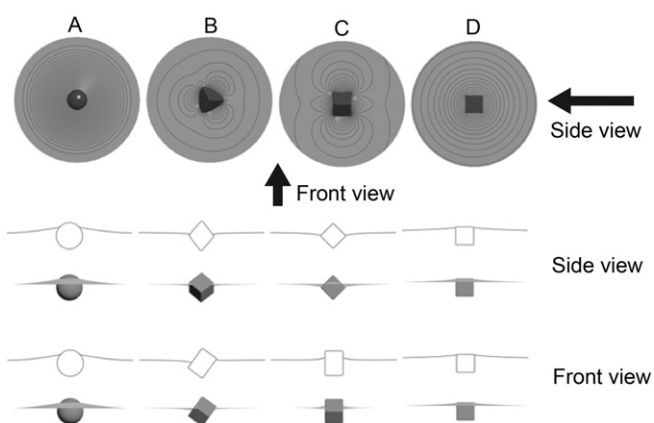
using hematite and studied their orientations at a hexadecane–water interface. They found that the particle adopted three different orienta-tions at the interface (Fig. 1B, C and D), one of which was much less frequent than the others. These findings were verified with simulations showing two energy minima (one local, one global) corresponding to the more popular orientations and one energy plateau corresponding to the less frequent one. However, there is no mention of the contact angle of the particle, a variable that has a considerable effect on the stable orientations of non-spherical particles [6].

There has been a lot of work investigating the stable orientations of non-spherical particles but relatively little covering how the orienta-tions affect film stability. Morris et al. [6,10**] reported that the orienta-tion of particles has a large effect on the stability of the thin liquid films they are attached to. A cubic particle with a contact angle of ~65° has two stable orientations (referred to as *flat* and *rotated*), one of which (*flat*, Fig. 1D) requires a capillary pressure 4 times greater than the other (*rotated* Fig. 1B) to rupture the film. The flat orientation can be described as one in which two of the orthorhombic particle's faces are parallel to the interface, whilst the rotated orientation has three of the orthorhombic faces bridging the interface, with their face normals all at an angle of 55° to the Z-axis. This pattern of orientation behaviour, whilst less prominent is present for contact angles up to 80° at which point the flat orientation becomes energetically unstable. Below a contact angle of 65° the rotated orientation is not energetically stable. The behaviour is also seen across a range of particle aspect ratios [10**], with a third orientation (*diagonal* Fig. 1C) also becoming stable for more oblong particles. He et al. [11] also developed an approach to calculating the interaction of superellipsoidal particles over short length scales at the interface although they neglected the effects of contact angle and thus particle orientation in the film. The work presents a useful method of calculating particle–particle interaction, providing particle orientation is not of importance to the end results.

On a larger experimental scale, de Folter et al. [12] used cubic (superellipsoidal) and peanut shaped hematite particles to make ultra stable Pickering emulsions that lasted more than a year. This was attrib-uted to the packing density achieved with cubic particles that could approach up 90%. It was reported that the particles adopted orientations with one face parallel to the interface, this is the orientation that has been shown to provide the most stability to a film, hence the stability of the emulsions.

When spherical particles are considered on a film, the established thinking is that film stability is a function of both packing density and contact angle. Particles with high contact angles do not stabilise a film as well as those with low contact angles but particles with low contact angles do not attach to the films as readily, resulting in a lower surface coverage. The optimum contact angle for particle stabilised foams seems to lie somewhere in the range of 60–70° [13], which is also the range over which the *rotated* orientation for an orthorhombic particle becomes more stable than the *flat*. It is clear that the interplay between contact angle and packing density is more complex than originally thought and also requires the orientations of the particles to be taken into account. The energetically stable orientation of a particle is a function of both contact angle and shape, so depending on whether film stability or rupture is desired, if the particle shape can be controlled, so too can the film stability. However the interaction between two particles of differing property has yet to be thoroughly investigated, for instance under what circumstances would a *rotated* particle cause a *flat* particle to change its orientation and vice versa?

Fig. 1. Particles at an interface (spherical — A and cubic — B, C, D). The energetically stable orientations of the cubic particles are shown with B — *rotated*, C — *diagonal* and D — *flat*. The top row shows a top-down view of the particles at the interface, the second and third rows are the side and front views, labelled accordingly. The black lines on the inter-face in the top row of images denote contours of equally height and highlight the complex topology that arises on the interface with the diagonal and rotated orientations of a cubic particle.

3. Effects of surface heterogeneity

Recently there has been an increase in the amount of work done on particle heterogeneity. Most of this has focused on Janus particles (Fig. 2, top), which have one hydrophobic hemisphere and one hydrophilic. However patterning of individual micro-particles surfaces has also