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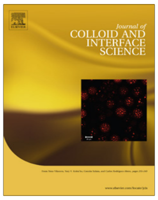

Buckling of particle-laden interfaces

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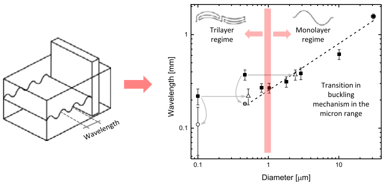
GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, we investigate the buckling of an oil–water interface populated by micron-sized latex particles using a Langmuir trough. In this work, we extend results of buckling of particle-laden interfaces from the millimeter down to the submicron range while investigating the effect of a different capillary length on the resulting wavelength. The experimental data is compared to the existing theoretical framework. An unexpected deviation from the prediction of theory of the dominant wavelength of buckling is observed for particles smaller than one micron. Those observations suggest that there is a transition to a new buckling regime involving the formation of trilayers below one micron. For the first time in particle rafts, cascading of the dominant wavelength similar to that observed in thin polymer films is reported. In addition a series of transitions between wavelengths not observed in thin films is observed within the same particle raft. Lastly, the effect of compression history on the macroscopic arrangement of particles is investigated, along with its effect on the buckling wavelength.

1. Introduction

Particle-laden interfaces have found wide application in modern industry [1]. In particular, particles on interfaces have been widely used in industry, consumer products and foods to stabilize emulsions. This concept was originally proposed in the beginning of the 20th century [2] and is often given the name "Pickering emulsions".

A few factors lead to the ability of particles to stabilize emulsions. First, coalescence between drops is hindered by the presence of solids on the interfaces. Furthermore, Ostwald ripening can stop as the surface coverage ratio of smaller drops becomes higher and the effective surface tension decreases. Thus, a particle-stabilized emulsion tends to an equilibrium state where all the drops are at approximately the same Laplace pressure [3]. It has also been suggested that the elasticity of the particle shell around each drop could also help halt ripening by resisting compression of the drop interface [1]. As a result, particles and surfactant molecules have very similar effects on the behavior of the interface [1].

Besides stabilizing emulsions, it has been shown that particles can be used to create self-assembled capsules, for example by using a liquid jet as a template [4,5]. This opens the possibility of using particle-laden interfaces for encapsulation of active ingredients, such as drugs, by creating small, self-assembled capsules [6].

However, self-assembly is not limited to curved capsules and indeed flat surfaces of different properties can be manufactured this way. It is particularly interesting that using particles of different surface treatments and of different sizes, one can control the way they pack on the interface and thus modify the properties of the resulting solid material [7]. Naturally, that raises the question of how particles interact on the interface. This question is

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fundamental not just for self-assembly, but also to understand the drop in surface pressure due to the presence of particles. In fact, particle–particle interactions is a rich field that gives insight on very interesting physics. On a very simplified level, particles interact through long and short range forces, which can be either repulsive or attractive. Because a number of forces are at play at any given time (gravity, surface tension, Coulombic attraction and repulsion, electrodipping, van der Waals, etc.) and they depend on a number of factors including the distance between the particles [8], it is natural to expect that the nature of these interactions can change as the packing of particles is modified.

Capillary interactions between multiple objects floating on an interface can lead to their self-assembly and the formation of particle rafts [9–13]. For a dense object with a large contact angle floating on the surface of a liquid, the weight of the particle can deform the fluid interface downward in such a way that the gravitation potential energy has been shown to decrease as the objects approach [14]. The result is an attractive force which scales like the inverse of particle separation and causes the floating objects to self-assemble [14]. For colloidal particles, the weight of the particle becomes too small to significantly deform the fluid interface and the gravitational forces become inconsequential. Even in the absence of gravity, however, attractive interactions between particles have been observed [15]. These attractive interactions can originate from interface deformation resulting from the electrostatic forces from a charged particle which can introduce a normal force acting on the oil water interface [9] or alternatively from immersion capillary forces resulting from non-uniform wetting [14–16]. Both these phenomena can result in particle aggregation into dense clusters [16]. In addition, for these small particles suspended on a water–oil or water–air interface, Coulomb interactions tangent to the interface can result in a repulsive force between particles that can often lead to their assembly into well-ordered hexagonal crystalline lattices [17–19].

The end result of such complex interactions is that particle-laden interfaces can have very interesting elastic behavior, particularly in shear and compression. In fact, the elasticity of the interface has been measured in a number of ways, such as by compression of flat interfaces [10] or by measuring surface pressure isotherms in particle-laden droplets [20]. Furthermore, as the interface is compressed the packing density increases and eventually reaches a maximum where particles can no longer rearrange on the interface. At this point, the surface tension goes to zero, as the repulsive and attractive interactions cancel each other [20,21]. Because the particles cannot rearrange, further compression of the interface must either lead to compressive deformation of the particles themselves or out-of-plane deformation, or buckling, of the interface. Whether an interface buckles depends on whether, at a given strain, it is energetically more favorable to accommodate further deformation with additional in-plane strain or through local bending and surface wrinkles. Given that the particles tend to be relatively stiff and the resistance to bending of the interface relatively small, a particle-laden interface will usually buckle given enough strain [10,17]. The phenomena of buckling has been employed in previous work [10] to study the mechanical properties of the particle raft. A theoretical model of the buckling of particle-laden interfaces was presented in the same work [10]. In that model, the particles were assumed to be perfectly rigid when compared to the interface as a whole, the Poisson ratio was derived geometrically by describing the deformation of a rhombic cell, and the bending stiffness was assumed to be equivalent to that of a solid thin film of thickness equal to the diameter of the particles. Planchette et al. [22] recently showed through independent measurements of the bending stiffness of particle laden surfaces that the assumption of Vella et al. [10] capture the right scaling of the bending stiffness with particle size, but over predict its magnitude by a factor of about two. Following Vella et al.'s work [10], an estimate for the buckling wavelength is obtained:

$$\lambda = \pi\left[\frac{4}{3(1-\phi)(1+\nu)}\right]^{1/4}\sqrt{L_c d} \qquad (1)$$

where ϕ is the surface coverage ratio of solids to the entire interface, ν is the estimated Poisson ratio, L_c is the capillary length of the liquid–fluid interface and d is the diameter of the particles. It was shown [10] that the prediction works well for particle diameters in the millimeter range on air–water interfaces. However, to the best of our knowledge the model for wavelength has not been tested on oil–water interfaces, or in the micron or submicron range. Here we will show that Vella et al.'s model holds for particles on an oil–water interface, but that a systematic deviation from the model occurs for particles less than one micron in diameter.

In a related field, it has been shown that the wavelength of wrinkles on a floating thin elastic sheet decays smoothly as one moves from the center of the sheet to its border, in a phenomenon called cascading [23]. Later, theory for cascading was developed based on *wrinklons*, which are defined as the localized transition region from one wavelength to another. It was also shown that the scaling for wavelength as a function of distance into the sheet depends on whether the sheet is under tension or not [24]. For a floating thin elastic sheet the tension was provided by the surface tension of the liquid acting on the edge of the sheet [23]. We will show for the first time that cascading can also occur for particle-laden interfaces and that the variation and complexity of these wrinkle transitions is amazingly rich.

Lastly, while it is known that compression affects the microscopic arrangement of particles on the interface [17], it is unclear what effects this has on the macroscopic arrangement of the particle raft on the interface or the resulting wavelength at buckling. Here we will demonstrate that the strain history of the particle raft can impact not only the uniformity of buckling across an interface, but the critical strain needed to buckle and in some instances the wavelength of the resulting wrinkles.

The objectives of this work, therefore, are manifold: to measure for the first time the buckling wavelength of particle-laden oil–water interface with particles in the sub-micron to micron range and to compare the measurements with theory; to demonstrate for the first time that cascading of wrinkles is possible on particle-laden interfaces and investigate the richness of the observed wrinkling transitions; and to understand how successive compression cycles can alter the wavelength, uniformity and critical strained needed to induce buckling.

2. Experimental setup and data collection

An acrylic Langmuir trough was used for the experiments. As presented in Fig. 1, the trough was composed of three fixed walls and a moving wall, the displacement of which was controlled by hand using a micrometer. Consequently, the strain imposed on the interface was precisely controlled, but not the strain rate. The moving wall and the fixed wall opposite to it were each fitted with a block of acrylic, which reduced the length of the interface at the middle of the raft as seen in Fig. 1. This modification increased the strain along the center of the interface compared to the edges and mitigated the effect of shear from the bounding walls. The total width of the trough was 38.1 mm and the width of the middle section was 12.7 mm. At full extension (0% compressive strain), the sides had a length of 32.0 mm and the middle section 16.0 mm.

The particles were spread on a decane–water interface. The decane was manufactured by Sigma–Aldrich (anhydrous, ⩾99%)