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Detachment of particles and particle clusters from liquid/liquid interfaces

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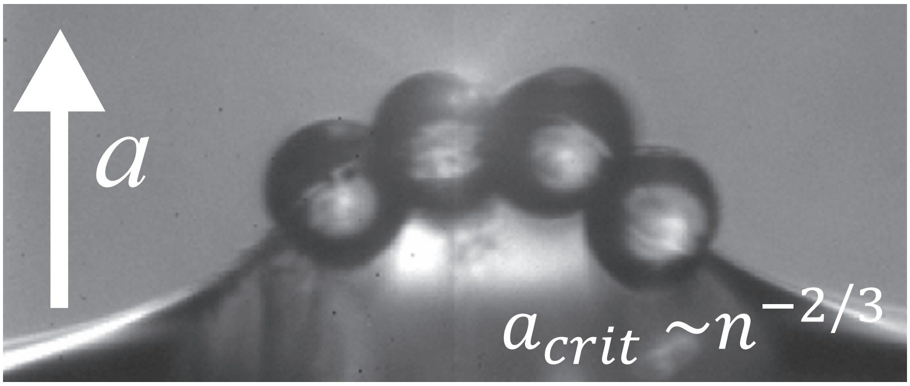
GRAPHICAL ABSTRACT



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ABSTRACT

The detachment of microspheres from a liquid/liquid interface triggered by body forces is studied experimentally, both for the case of single particles and for particle clusters. The values of the critical force required to detach particles from the interface are in agreement with the maximum values of the wetting force keeping a particles at the interface. In the case of particle clusters, a rearrangement of the cluster configuration from a raft to a more compact structure is observed when the body force is increased. Clusters detach from the liquid/liquid interface at smaller acceleration values than single particles. The critical accelerations required to detach particle clusters are consistent with models assuming that the wetting force acts at the circumference of a spherical or hemispherical densely packed particle cluster. These models predict that the critical acceleration for particle clusters scales as $n^{-2/3}$, where n is the number of particles in a cluster.

1. Introduction

Many types of micro- and nanoparticles readily attach to interfaces between two immiscible fluids where they lower their free energy compared to one of the bulk phases [1]. In the past decades, particles attached to fluid interfaces have attracted considerable attention. It has been shown that particles at fluid interfaces can self-organize, forming regular, usually hexagonal patterns [2–5]. Recently, droplets whose surface is covered with particles, so-called liquid marbles, have been studied quite extensively [6–8]. Last but not least, flotation, a well-established separation technology, is based on small particles getting attached to the gas/liquid interface [9]. These examples underpin the need to

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better understand the physics of particle attachment or detachment at fluid interfaces.

When a microscopic particle approaches the interface between two immiscible fluids slowly enough, at a certain point it "snaps in", i.e. it attaches to the fluid interface, and a three phase contact line is formed between the fluid interface and the solid surface. In the reverse process a particle is pulled away from the interface, still being attached to it up to a certain distance, followed by a sudden "snap back" of the interface and a detachment of the particle. Much of our current understanding of the dynamics of particle attachment and detachment is based on the colloidal probe technique [10,11]. This method relies on a small (usually spherical) particle attached to a beam that can be displaced relative to the fluid interface. Measuring the deflection of the beam provides information about the forces acting on the particle when it moves normal to the fluid interface, attaches to it or detaches from it.

In early experiments, the hysteresis-like force–displacement curves obtained when a particle first attaches to a fluid interface and is then pulled away from it were measured [12,13]. Later on, the dynamics of attachment (snap in) or detachment was studied in more detail. When a particle with a diameter of the order of 100 μm snaps in at the interface of a low viscosity-liquid such as water and a gas, its dynamics is usually governed by the interplay of capillary and inertial forces [14]. For particles attaching to liquid/liquid interfaces, the fast initial dynamics may be followed by an extremely slow process (on a time scale of days or even months) during which the particle assumes its final configuration at the interface. The slow dynamics may be attributed to the relaxation of the three-phase contact line [15]. For the reverse process (particle detachment) the work of detachment was compared to theoretical predictions [16]. A good agreement is achieved if contact-angle hysteresis is properly accounted for. It was also shown that the force required to detach a particle from a gas–liquid interface receives significant contributions from viscous drag forces if a constrained geometry is considered. This is the case when detaching a particle from the surface of a liquid film whose thickness is comparable to the particle diameter [17].

The main purpose of the present article is to provide insights into the detachment of particle clusters (as opposed to a single particle) from fluid interfaces. Particles attached to fluid interfaces often form clusters [18–20], therefore the information about the detachment of single particles may often be of limited relevance in a practical context. Naturally, the colloidal probe technique is not well suited to analyze the detachment of particle clusters whose structure can evolve dynamically. By contrast, the method presented in this article is geared towards studying particle clusters, while for the single-particle case its accuracy is most likely not on the same level as the colloidal probe technique.

2. Experimental setup and methods

The experimental setup is illustrated in Fig. 1. It is composed of three different parts: a rotating wheel, an imaging system and a data acquisition system. The wheel is driven by an AC motor and serves the purpose of providing strong centrifugal forces to a small vessel mounted on it. Two similar cuvettes containing the liquid samples are symmetrically attached to the wheel to balance the centrifugal forces due to the additional mass. The imaging system comprises a long-distance microscope connected to a high-speed camera and a high-power flash light. The high-speed camera takes pictures of the interface between two immiscible liquids inside the rotating cuvette at a high frame rate. The high-power flash light ensures sufficient light intensities at short exposure times.

2.1. Rotating wheel and imaging equipment

A Siemens AC motor (1LA7090-2AA10-Z) is used to drive the wheel. The speed control is provided by a frequency converter (SINAMICS G120) which operates from 5 Hz to 50 Hz. A 700C road bicycle wheel with 622 mm diameter is connected to the AC motor. The two immiscible liquids are contained in a glass cuvette (1-G-2, Starna GmbH, Pfungstadt, Germany) mounted at a distance of approx. 35 cm away from the axis of rotation. That way, centrifugal accelerations of up to 3600*g* (corresponding to a rotation frequency of 50 Hz) are achievable. For safety reasons the maximum acceleration in the experiments was 905 g (corresponding to 30 Hz). As the opening of the cuvette is only 2 mm wide, the Bond number (based on the gravitational acceleration) for the considered systems of immiscible fluids (nitromethane/water and water/air) is below 1. Therefore, the interface between the fluids stays intact even during short time intervals of reversed acceleration, e.g. when the wheel stops and the gravitational acceleration dominates.

The imaging system is based on a Shimadzu HPV-2 high-speed camera which is capable of capturing images with up to one million frames per second (fps). The camera operates with a constant pixel resolution of 312×260 at all frame rates ranging from 30 fps to 10^6 fps. To image small spatial scales, the camera is connected to a QuestarQM100 long-distance microscope. The working distance of this microscope is between 150 mm and 350 mm, and the corresponding aperture ranges from 3.5 to 6.0. Moreover, it has different zoom lenses for increasing the magnification. The maximum spatial resolution that can be achieved is 1.9 μm/pixel.

Positioning of the optical system comprising the long-distance microscope and the camera is achieved by a 3D translation stage comprising three actuators (types x.act LT 100-1 and x.act XY50-1 ST, LINOS Photonics GmbH, Göttingen, Germany). The vertical positioning is important to find the fluid interface with the camera, while the depth positioning is used for focusing.

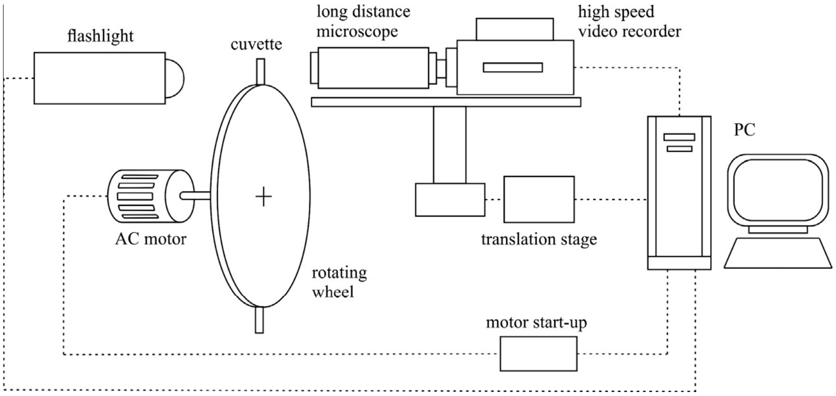

Fig. 1. Schematic of the experimental setup.