Supplementary Information

Particle-stabilized oscillating diver: a self-assembled responsive capsule

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July 15, 2011

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1 Introduction

In this Supplementary Information we present experimental details, a broader range of results and further discussion that support the main text. An important aspect is four Movies that give a better impression of the time dependent behavior of the particle-stabilized oscillating diver (POD).

An interface between immiscible fluids is energetically expensive and hence will trap particles of sizes from the nanoscale [1] through to large (∼mm) beads [2] which exhibit partial wettability with the fluids. Bubbles [3], droplets [4] and droplets containing bubbles [5] can be permanently stabilized by such interfacial particles. When trapped at the interface, the particles reduce the amount of shared area between the fluids. This results in a local energy minimum of depth:

$$\Delta E = -\pi r^2 \gamma (1 - |\cos \theta|)^2 \qquad (1)$$

where r is the particle radius, γ is the interfacial tension between the two solvents and θ is the three phase contact angle measured through the more polar phase [4].

Compared to conventional surfactants, the interfacial particles often render droplets and bubbles more stable against coalescence with the interfaces themselves becoming semi-solid [6]. These features are a consequence of the fact that the particles are mesoscopic leading to very strong trapping. Another result of the size of the particles is that they have a noticeable influence on the average properties of the droplet. This has been employed to create droplets that can be moved or destabilized by an applied magnetic [7] or electric [8] field.

In this work we have used large glass beads to modify the average mass density of a capsule. How this capsule, which contains a bubble, is created is described next.

2 Experimental details

The particles used in these experiments are glass beads (Polyscience, Inc.). We exploit the interfacial trapping of these particles to create capsules in two liquid-liquid-particle combinations:

System 1: Glass beads ($d \approx 355 - 420 \mu m$); ethanediol (99.8% anhydrous, Sigma-Aldrich); pentane (99%+, Sigma-Aldrich).

System 2: Glass beads ($d \approx 300 - 355 \mu m$) with 1 mM sodium dodecyl sulphate (SDS, >99%, Sigma-Aldrich); distilled water; pentane.

In both cases the capsules are prepared by first putting the immiscible liquids in a vial (See Fig. S1(A)) and subsequently pouring the beads in using a spatula. The behavior described in the main text occurs without further intervention (see Fig. S1(B,C)). For some capsules (one out of three), a shake is required to free them from the bed of particles.

Figs. 1(II & III), 2 and 3 show four different PODs; in all cases the size of the capsule is roughly constant (much smaller PODs can sometimes form: see Fig. S2) while the size of the bubble can vary markedly. The variability demonstrates that the bubble is not pentane vapor alone; equilibrium
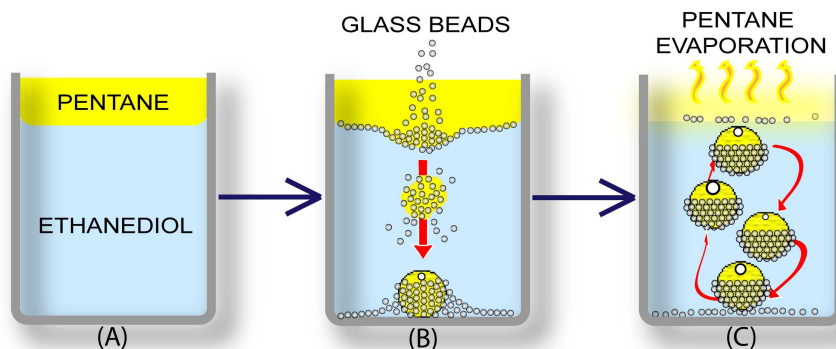
Figure S1. Schematic showing the preparation of a POD. (A) Two immiscible solvents are put in a vial, the top one must be volatile; (B) glass beads are poured in from a spatula leading to air and pentane being dragged to the base of the vial; (C) the rising and falling behavior continues until cooling of the top of the vial ceases.

phase behavior would give a fixed volume of pentane gas for a fixed volume of pentane liquid at a given temperature and pressure. We assume that the remainder of the bubble is filled with air.

Next we confirm that the vertical motion of the POD between 'up' and 'down' states is largely at uniform velocity. Using the POD diameter, $d \approx 2.7\,\mathrm{mm}$, ethanediol viscosity, $\eta = 1.61 \times 10^{-2}\,\mathrm{Pa\,s}$ and density difference between the POD and its surroundings, $\Delta\rho \approx 50\,\mathrm{Kg\,m^{-3}}$, the typical time taken until buoyancy is balanced by viscous drag is $t_T = (\Delta\rho d^2)/\eta \approx 0.02\,\mathrm{sec}$. Journey times are seconds or more so the duration of acceleration is very small compared to the journey time.

Our samples were prepared and filmed using the camera and sample stage from a Krüss Easy Drop DSA20 tensiometer. Images and movies on the millimeter scale (see Figs. 1(III), Fig. 2; Figs. 3a and b; Movies 1, 3 and 4) were recorded using the default optics. A larger (centimeter scale) field of view was achieved with the addition of an Aico auto 3× converter (see Figs. 1(I) and 1(II)a-l; Movie 2; Figs. S2 and S3). Image processing and scene selection was carried out using the ImageJ [9] and VirtualDub [10] packages.

3 Movies and figures

Movie 1 shows the emergence of a buoyant particle-stabilized oscillating diver (POD) at the base of the vial. This movie reveals detail of the droplet containing a bubble rising up through the bed of beads (the bead diameter $\approx 0.4\,\mathrm{mm}$). The droplet is pentane and here the continuous phase is ethanediol. The POD forms as the droplet emerges, some of the beads are shed and others are trapped at the interface.

Movie 2 shows the formation and repeated diving motion of the POD. This movie includes numerous oscillations of the POD. Here we show the capsule travelling up and down the vial on a, more-or-less, vertical trajectory. This and the duration of the pause at the top and bottom of the vial suggest that the POD is not entrained in convection currents. The vial is 2 cm wide.

Movie 3 shows the role of the pentane over-layer. The POD rises and falls repeatedly. In this movie the change in height of the overlying layer of pentane due to its evaporation is visible as the experiment progresses. Once all the pentane has gone then the oscillations cease. The solvent evaporation is cooling the top of the sample creating a temperature gradient. (For the purpose of this demonstration the lid of the vial has been removed to speed evaporation). The bead diameter is ≈ 0.4 mm.

Movie 4 shows the rotation of the POD at the base of the vial. In this movie we see the rotation of the POD about a vertical axis. This behavior occurs at the lowest point of the oscillation when this involves being close to the bed of beads. The origin of this motion is still open to question. The bead size is ≈ 0.4 mm.
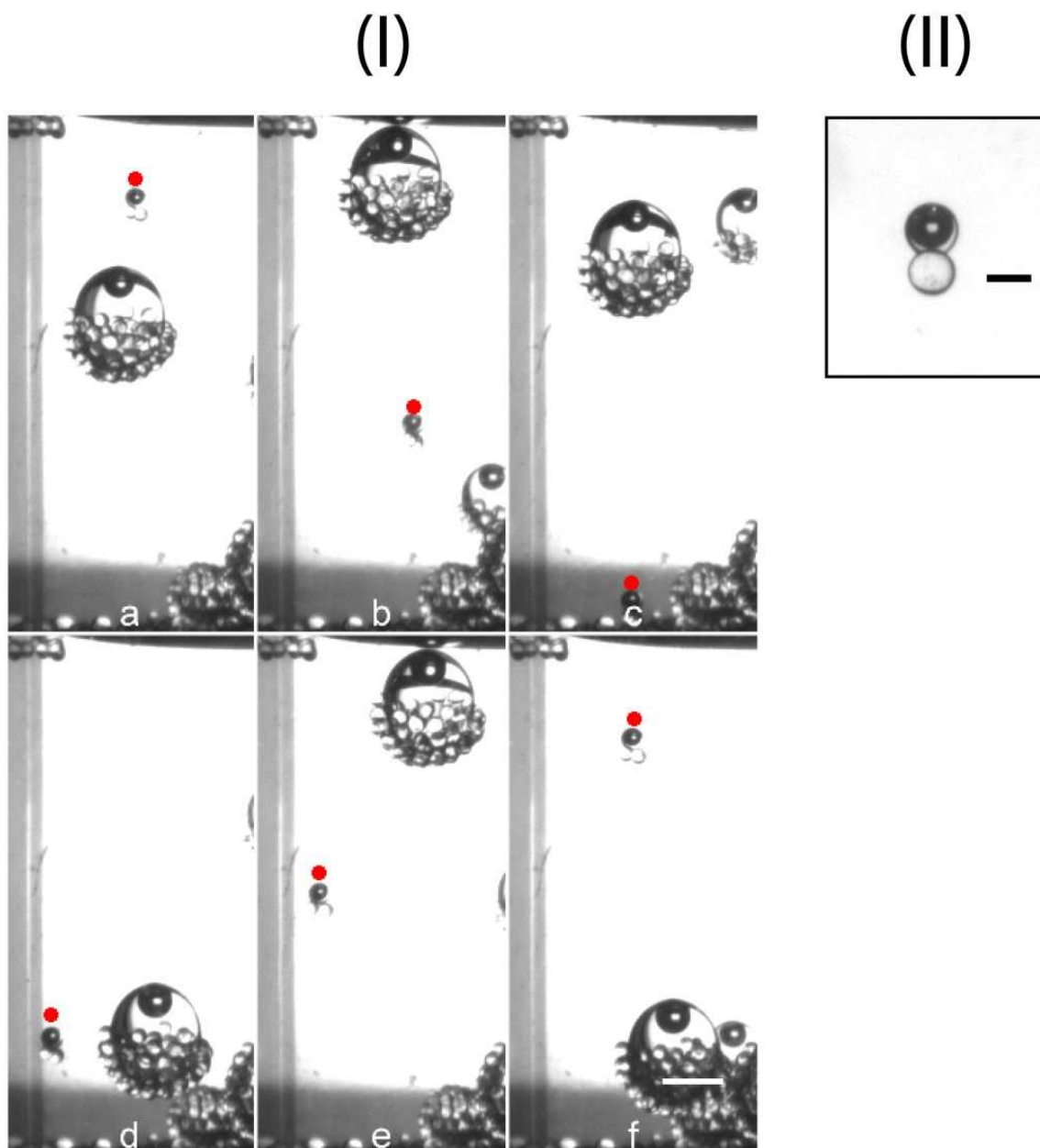
Figure S2. Small scale PODs with the same pattern of motion. (I) Sequence of frames showing the oscillation of a small POD (highlighted with red circle). With only two beads attached, the majority of the dispersed phase is made from air/pentane vapor to achieve near neutral buoyancy. With reference to (a) frames (b) to (f) were captured at 14.5, 19, 25.5, 33 and 51.5 s; the scale bar is 2 mm. (II) A POD with only one bead attached. Here, the encapsulated gas/liquid phase can be more clearly seen. The scale bar is 400 μm.
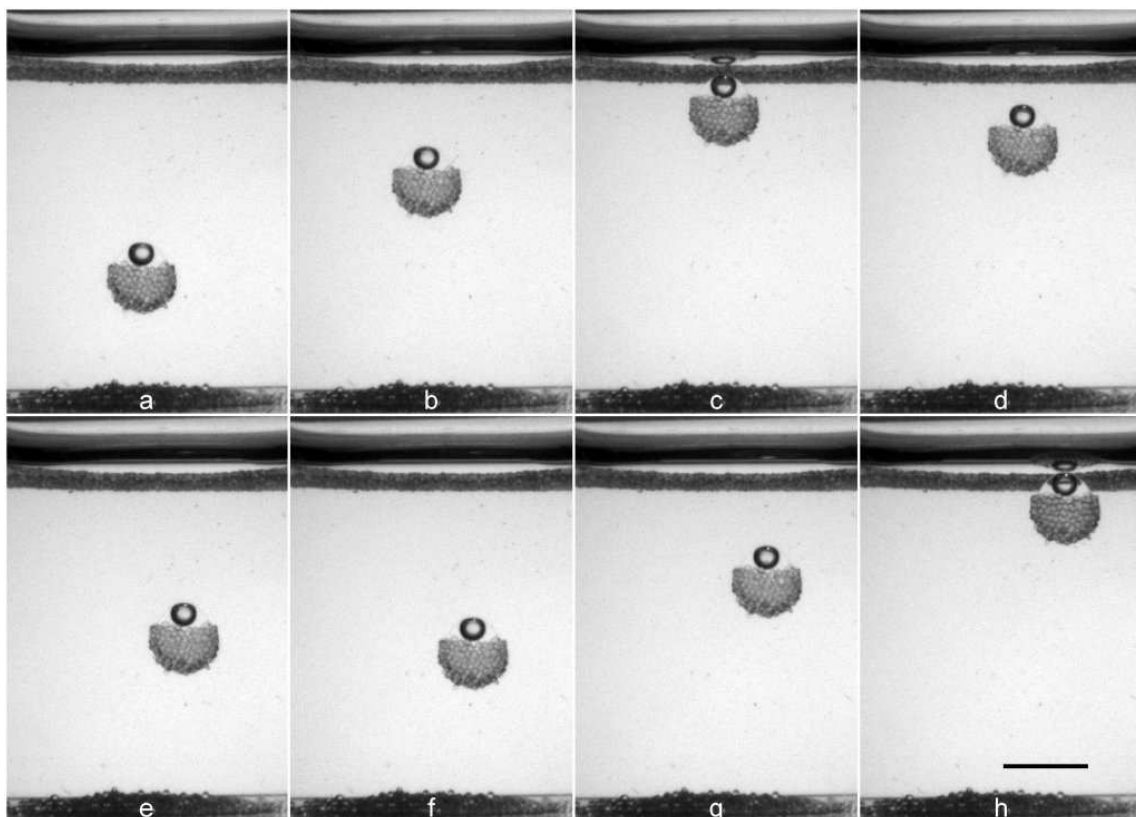
Figure S3. A water based POD showing the versatility of the concept. Here we show a POD oscillating in a continuous phase of water containing $1\,\mathrm{mM}$ SDS (one frame every $3\,\mathrm{s}$; scale bar $3.2\,\mathrm{mm}$). The SDS is used to reduce the capillary length at the pentane-water interface to enable the self assembly of the POD. Without the SDS, many more beads are required to break the interface, leading to large amounts of pentane being entrained, which in turn results in a buoyant 'POD' that rises immediately to the interface (and stays there). The average oscillation period, $\tau_{w,exp}$ taken over 15 cycles is $17\,\mathrm{s}$. Following the procedures outlined in the main text gives a calculated lag time, τ_w, of $5.2\,\mathrm{s}$, a switching time scale, $t_{wJ} \approx 5\,\mathrm{s}$, and hence a complete oscillation period, $\tau_{w,c}$, of $15.2\,\mathrm{s}$; which is in good agreement with the observed oscillation period.

4   Further discussion

The particle-stabilized oscillating diver is an example of an automatic Cartesian diver. This idea was first considered in the context of electrical circuits that perform relaxation oscillations [11]. The relaxation oscillations that we observe are spontaneous as has been seen previously in several fields. In addition to diverse electrical circuits [12], examples include geysers [13], thermal oscillators [14], mechanical systems where a spring and conveyor belt are counterposed [15] and coupled electrical/mechanical oscillators [16]. Droplets have previously been driven to oscillate between two electrodes [17] (or one electrode and another droplet [18], see associated movies) using an electric field. The droplet collects charge at one surface and is then repelled by it; the process is repeated at the opposite surface. Hence, relaxation oscillators have been made from very many constituents, including droplets; however, ours is the first to build itself.

Thermal fluctuations do not play an important role in the self assembly of the POD, which is unusual. The individual constituents observed here are each larger than the colloidal scale. It will be an interesting challenge to create a similar diver where gravity driven movement and diffusion are more equally balanced.

If we broaden the spectrum of dynamical systems we consider beyond oscillators it is curious to compare our central observations with the dynamics seen when glass beads are poured slowly into a pile with no surrounding liquids. In the case of dry beads a 'sand pile' forms with dynamics characterized by a power law distribution of avalanche sizes [19]. During pouring the slope of the sand pile becomes steeper and the system self organizes into a critical state for which the response to a perturbation is independent of the details. Our dynamical system is attracted to a very different state characterized by perpetual oscillations in the vertical plane.

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