Self-Propulsion of Liquid Marbles: Leidenfrost-like Levitation

Driven by Marangoni Flow

Edward Bormashenko,[*a,b] Yelena Bormashenko,[b] Roman Grynyov,[a] HadasAharoni,[b]

Gene Whyman[a] and Bernard P. Binks[c]

[a]*Ariel University, Physics Department, P.O.B. 3, 40700, Ariel, Israel*

[b]*Ariel University, Chemical Engineering and Biotechnology Department , P.O.B. 3,*

40700, Ariel, Israel

[c]*Surfactant & Colloid Group, Department of Chemistry, University of Hull,*

Hull. HU67RX. UK

[*]Corresponding author:

Edward Bormashenko

Ariel University, Physics Department, Chemical Engineering and Biotechnology

Department

P.O.B. 3, Ariel 40700, Israel

Phone: +972-3-906-6134

Fax: +972-3-906-6621

E-mail: edward@ariel.ac.il

Contains ESI (1 movie):

ABSTRACT

Self-propulsion of liquid marbles filled with aqueous alcohol solutions and placed on a water surface is reported. The characteristic of velocity of the marbles is *ca.* 0.1 m/s. The phenomenon of self-propulsion is related to the Marangoni solutocapillary flow caused by the condensation of alcohol, evaporated from the liquid marble, on a water surface. The Marangoni flow in turn enhances the evaporation of alcohol from marbles. Addition of alcohol to the water supporting the marbles suppresses the self-propulsion. The propulsion of liquid marbles is mainly stopped by water drag. The velocity of the center of mass of the marbles increases with an increase in the concentration of alcohol within the marble. The self-propulsion velocity of marbles is independent of their volume. Self-propulsion was not observed when marbles were placed on a glycerol surface.

INTRODUCTION

Autonomous locomotion (self-propelling) of droplets driven by various physico-chemical mechanisms attracted widespread attention of researches in the last decade.[1-9] Various mechanisms of self-propelling have been introduced including the use of gradient surfaces[1-3], involving the Leidenfrost effect[5-7] or exploiting micro-structured surfaces[5-7]. Self-propelling of micro-scaled objects[10] and macroscopic bodies such as a camphor boat[11-13] was investigated. Self-propelling supported by solid[1-3] and liquid[14-15] surfaces was reported. An interest in self-propelling systems arises from the numerous applications, including lab-on-chip systems, targeted drug delivery and microsurgery.[16-17]

This paper reports the self-propulsion of liquid marbles filled with aqueous alcohol solutions deposited on a water surface. Liquid marbles are non-stick droplets coated with colloidal particles. When attached to the surface of a liquid droplet, colloidal particles allowed the manufacturing of so-called liquid marbles, presenting an alternative to the lotus-inspired superhydrophobicity.[18-20] Liquid marbles demonstrated a diversity of promising applications, including in encapsulation, microfluidics, cultivation of microorganisms, gas-sensing, miniaturized synthesis and water storage.[21-34] Liquid marbles could be actuated by various stimuli including chemical actuation[21-22] and electrical and magnetic fields.[24,28,29] Our paper relates the effect of self-propelling to the interplay of the Leidenfrost effect (taking place when a droplet is separated from a support by a vapor layer) and the Marangoni solutocapillary flow, arising from non-uniformity of the surface tension of the liquid support in the vicinity of the marble. The Marangoni solutocapillary flow is responsible for a diversity of phenomena, including the self-motion of camphor

boats[11-13] and the fascinating effect of wine tears.[35] The reported results open a way for micromanipulation of small quantities of liquids supported by liquid surfaces.

EXPERIMENTAL METHODS

Liquid marbles containing aqueous ethanol (absolute, max. water 0.2% w/w, Bio-Lab Ltd, Israel) solutions were manufactured with the extremely hydrophobic fumed fluorosilica powder used to prepare oil liquid marbles reported earlier.[36] The primary diameter of these particles is 20-30 nm and they originate from hydrophilic silica after reaction with tridecafluoro-1,1,1,2-tetrahydrooctyltrimethoxysilane. The residual silanol content on their surfaces is 50% and the fluorine content is 10.9%.

Aqueous ethanol droplets of volume between 10 and 50 µL were spread on a layer of fumed fluorosilica powder situated on a glass slide. The slide was vibrated slightly, giving rise to the formation of liquid marbles. The maximum volume concentration of alcohol in water allowing manufacturing of liquid marbles was established as 85 vol.%. A typical marble containing 70 vol.% ethanol in water, resting on a glass slide, is depicted in Figure 1. A larger concentration of alcohol promoted the Cassie-Wenzel wetting transition and marbles were not formed, as discussed in ref. 37. The marbles are not hermetically coated by powder; they evaporate as discussed in detail in ref. 23. The lifetime of marbles enabling self-propulsion is *ca*. 2 min.

Marbles were placed on the surfaces of bi-distilled water (resistivity 2 MΩ cm as measured with LRC-meter Motech MT 4090), aqueous alcohol solutions, silicone (PDMS) oil (M_n = 5600, Aldrich) and glycerol (analytical grade, Frutarom) under the following procedure. Marbles were placed on the bottom of glass Petri dishes of diameters 5 and 25 cm, and a liquid was gently added to the dish. This procedure

avoided supplying the initial velocity to highly mobile liquid marbles. The motion of liquid marbles was registered from above with a rapid camera, Casio EX-FH20. The velocity of marbles was established by the frame-by frame analysis of their motion registered with a rapid camera. Use of Petri dishes with a diameter of 25 cm enabled excluding of boundary effects, due to the meniscus formed in the vicinity of the dish skirting. The experiments performed with marbles containing various concentrations of ethanol were repeated 10 times for every concentration of ethanol. The established velocities of rectilinear motion were averaged.

In some experiments, the marbles contained a 0.1 wt.% solution of phenolphthalein and NaOH was added to the water supporting the liquid marbles at a concentration of 0.1 wt.%. This was to detect if any of the marble contents entered the supporting water phase. All the experiments were performed under the ambient temperature of 23-24 ºC.

RESULTS AND DISCUSSION

Liquid marbles containing aqueous ethanol solutions were placed on the surface of various liquids contained in a Petri dish, as described in the Experimental Methods Section. The marbles did not survive on the surface of the silicone oil and immediately burst, as discussed in ref. 38. They survived and floated motionlessly on the surface of glycerol as shown in Figure 2, but moved rapidly rectilinearly when placed on a water surface, periodically bouncing from the skirting of the Petri dish as depicted in Figure 3. The same type of motion, continuing for *ca*. 10 s displayed in Figure 3, was observed on Petri dishes with diameters of 5 and 25 cm. After this, marbles rotated along the skirting of the Petri dish during *ca*. 1-2 min. and then stopped.

5

The surface tensions γ of water and glycerol are close, whereas their viscosities η differ markedly: $\gamma_w = 72\,\text{mJ/m}^2$, $\gamma_{gl} = 63\,\text{mJ/m}^2$, $\eta_w \cong 10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1}$, $\eta_{gl} \cong 1.5\,\text{kg m}^{-1}\,\text{s}^{-1}$, where γ_w and γ_{gl} are the surface tensions of water and glycerol respectively and η_w and η_{gl} are their viscosities. Thus very different behavior of marbles placed on water and glycerol surfaces may be at least partially related to the different viscosities of the supporting liquids, as will be discussed below.

The velocity of the motion on water established at straight sections of the displacement with the rapid camera is illustrated in Figure 4. It is noted that the collisions of the marbles with the skirting of the Petri dish are elastic and the velocity of a marble remains constant after dozens of collisions (see the movies supplied in the ESI). The total time of the rectilinear motion decreases with an increase in the concentration of alcohol within the marble, as shown in Figure 5. This result is quite understandable; marbles containing a larger concentration of alcohol evaporate faster.

It should be emphasized that aqueous alcohol solutions filling the marbles did not touch the supporting liquid surface. This was proved by placing a marble containing phenolphthalein on water solutions of NaOH (see also ref. 39). No coloring of water below was observed during the self-propulsion of marbles meaning that moving marbles are isolated from the supporting liquid by a vapor layer, as occurs in the Leidenfrost effect.[40-42] The complicated geometry of the vapor layer, depicted schematically in Figure 6(a) was treated in detail in ref. 42. However, the typical value of the velocity of the center of mass of marbles was $v_{cm} \approx 0.1 - 0.15\,m/s$ which is an order of magnitude lower than the velocity observed for Leidenfrost water droplets.[40-41] We relate this observation to the action of a water drag as will be discussed in detail below.

What is the physical mechanism of the self-propulsion of liquid marbles? Remarkably self-propulsion occurs under breaking the spherical symmetry of marbles, *i.e.* the liquid marble, whose evaporation is spherically symmetric, has no inherent reason for movement. Consider the spontaneous increase in evaporation of alcohol from the marble in the direction of $-x$ (recall that alcohol evaporates from a marble much faster than water), depicted in Figure 6(a). This increase will not only drive the marble in the direction of $+x$ but also will give rise to a fascinating instability, driving marbles. Indeed, alcohol condensed on a water surface (as shown in Figure 6(a)) will decrease its surface tension, resulting in the Marangoni solutocapillary flow[43-46] in the direction of $-x$ (towards the left of the zone where alcohol has condensed). This flow in turn enhances the evaporation, withdrawing vapor from the layer separating the marble from the supporting liquid (as shown with a green arrow in Figure 6(a)). The introduced instability displaces a marble in a direction of $+x$ (the displacement of a marble necessarily arises from the total momentum conservation). It seems plausible to suggest that the non-stick pseudo-Leidenfrost contact of marbles with the water surface, providing the rapid evaporation of alcohol below the marble, combined with the Marangoni solutocapillary flow results in the self-propelling effect. The velocity of the Marangoni flow was estimated in ref. 41 for Leidenfrost droplets as *ca*. 0.1 m/s", informing the reader the idea about the order of magnitude of velocity of Marangoni flow inspired by the Leidendfrost-like situation.

If the self-propulsion of marbles is related to the evaporation of alcohol resulting in Marangoni flow, it is reasonable to suggest that an increase of the alcohol concentration in the marble will give rise to larger velocities of their locomotion. This tendency was observed experimentally, as shown in Figure 7, representing the

velocity of the center of mass of marbles as a function of the alcohol concentration within the marble.

If it is supposed that a marble is driven by a solutocapillary Marangoni flow, the driving force may by qualitatively written as $F_{dr} \approx |\Delta\gamma| 2\pi a = \beta |\Delta\gamma| a$, where $|\Delta\gamma|$ is the modulus of the lowering of the surface tension due to the condensation of alcohol on the water surface, a is the radius of the contact area (see Figure 6(b)), and β is the dimensionless coefficient. Thus, the motion of the marble may be described by the following equation:

$$m\ddot{x}_{cm} = \beta |\Delta\gamma| a - F_{fr},$$
(1)

where $\ddot{x}_{cm}$ is the acceleration of the center of mass of a marble, m is its mass, and F_{fr} is the total friction force acting on a marble, made up of three components: $F_{fr} = F_{air} + F_{vapor} + F_{water}$, where F_{air} is the friction exerted on a marble by air, F_{vapor} is the friction due to the viscous dissipation taking place in the vapor layer separating the marble from the liquid below and F_{water} is the viscous drag due to the water under the marble motion.[41] Eq. 1 implies the rectilinear displacement of the center of mass of the marbles, whereas more complicated, curvilinear self-propelling motion of droplets was observed and discussed.[47-48] We restrict our treatment to the rectilinear self-propulsion, actually observed in our experiments.

Consider the components of the friction. F_{air} scales as $\rho_{air} v^2_{cm} R l_{ca}$, where $\rho_{air} = 1.2 kg \cdot m^{-3}$ is the density of air, $R \sim 1$ mm is the radius of the marble, $v_{cm} \cong 0.1 m/s$ and $l_{ca} \cong 2.7 mm$ is the so called capillary length.[46,49] For a realistic estimation of F_{air} we have $F_{air} \approx 3 \cdot 10^{-8} N$. The viscous dissipation occurring in the vapor layer scales as $F_{vapor} \cong \frac{\eta_v v_{cm}}{h} R^2$, where $\eta_v \approx 1.7 \cdot 10^{-5} \frac{kg}{m \cdot s}$ is the viscosity of the

8

vapor layer and $h \approx 100 \mu m$ is its thickness.[41] Thus, the estimation of this component

of friction is $F_{vapor} \cong 1.7 \cdot 10^{-8} N$. The viscous drag of water may be estimated roughly

as $F_{water} = N f_{stokes}$, where N is the number of solid beads of powder in contact with

water and f_{stokes} is the Stokes drag acting on a single bead. N may be estimated as

$N \approx \dfrac{\pi a}{2b}$ (b is the radius of a bead, see Figure 6(b)), and the Stokes drag scales as

$f_{stokes} \approx \xi \eta_w b v_{cm}$, where $\eta_w \cong 10^{-3} \dfrac{kg}{m \cdot s}$ is the water viscosity and $\xi \approx 10$ is the

dimensionless coefficient. Thus, the plausible estimation of the water viscous drag is

$F_{water} \cong \xi a \eta_w v_{cm} \cong 10^{-6} N$. The comparison of the components of the friction leads to

the expected conclusion that the friction is mainly governed by the viscous drag of the

liquid. This explains why marbles are motionless when placed on glycerol as the high

viscosity of glycerol prevents their motion. This situation is quite different from the

motion of Leidenfrost droplets, decelerated mainly by F_{air}.[41]

    If marbles are driven by the Marangoni solutocapillary flow[42-45] their

movement will be suppressed if alcohol is added to water supporting the marbles.

This hypothesis was validated by a series of experiments performed with different

concentrations of alcohol c_s added to water supporting the marbles. Indeed, addition

of alcohol decreased the velocity of marbles dramatically, as shown in Figure 8.

    Considering Eq. 1 and the aforementioned analysis of the friction force yields

the following expression for the stationary velocity of the center of mass of the

marble:

$$\beta |\Delta \gamma| a - \xi a \eta_w v_{cm} = 0. \qquad (2)$$

Thus, the scaling law for the stationary velocity of the center of mass of the marble is

given by:

$$v_{cm} \cong \frac{|\Delta\gamma|}{\eta_w} \quad , \tag{3}$$

and it turns out that the velocity of the center of mass of the marble is independent of its volume. This prediction was checked experimentally for liquid marbles in which their volumes varied from 10 to 50 µL. Figure 9, presenting the dependence of the stationary velocity of marbles on their volume, demonstrates that their velocity is more or less independent of volume, justifying the scaling law given by Eq. 3. It seems instructive to estimate the value of $|\Delta\gamma|$ giving rise to the velocities of liquid marbles observed in our experiments. According to Eq. 3 we have for the sake of a very rough estimation: $|\Delta\gamma| \approx v_{cm}\eta_w \cong 10^{-4}$ J/m². It is seen that a relatively small change in the surface tension of the supporting liquid brings about a velocity of a marble as high as 0.1 m/s. This makes possible the use of marbles for the effective, rapid, frictionless transport of micro-cargo at liquid surfaces.[50] Vapour-driven self-propulsion of water induced by the Marangoni effect was reported recently b Jin *et al.*[51]

It is noteworthy, that the marbles did not roll (rotate) when moved. This was demonstrated with experiments performed with 20 µL Janus-coated marbles, in which hemispheres are coated by both fumed fluorosilica powder and carbon black powder, as depicted in Figure 10(a). The Janus-coated marbles were prepared as described in detail in ref. 24. They moved rectilinearly when placed on a water surface as discussed above. The carbon black coated hemisphere served as a tracer (see Figure 10(b)), indicating the absence of rotation of marbles under their self-propulsion.

CONCLUSION

We report the self-propulsion of liquid marbles containing aqueous ethanol solutions placed on a water surface. Use of very low surface energy fluoroparticles enabled manufacturing of marbles containing concentrated aqueous ethanol solutions. The marbles were at rest when placed on solid surfaces and on glycerol and demonstrated self-propelling rectilinear motion with a velocity of 0.12-0.15 m/s during *ca*. 10s, when put on water bouncing elastically from the skirting of the Petri dish. The rectilinear motion was followed by rotation of marbles along the skirting of the Petri dish during *ca*. 1-2 min. The self-propelling occurs under breaking of the spherical symmetry of marbles. We relate the effect to the instability involving the spontaneous increase of evaporation of alcohol from a marble leading to the Marangoni solutocapillary flow. The Marangoni flow in turn enhances evaporation of alcohol from the marble, by withdrawing vapor from the layer separating the marble from the liquid support. Introducing alcohol into the underlying water suppressed the self-propulsion phenomenon. The velocity of the center of mass of marbles increases with an increase in the concentration of alcohol in the marble. The mechanism of motion of liquid marbles is analyzed. Marbles are stopped mainly by the water drag, which is much larger than the other components of friction including the air friction. The stationary velocity of marbles is independent of their volume.

authors are indebted to Mrs. Al. Musin and Mrs. E. Shapiro for their kind help in preparing this paper.

SUPPORTING INOFORMATION AVAILABLE

The movie presenting self-propulsion of 10 µl liquid marble coated with low surface energy fluoroparticles, containing70 vol.% aqueous ethanol solution is supplied.

AUTHOR INFORMATION

Corresponding Author: *E-mail: edward@ariel.ac.il.

REFERENCES

(1)   Daniel, S.; Chaudhury, M. K.; Chen, J. C. Fast drop movements resulting from the phase change on a gradient surface. *Science* **2001**, *291*, 633-636.

(2)   Daniel, S.; Sircar, S.; Gliem, J.;Chaudhury, M. K. Ratcheting motion of liquid drops on gradient surfaces. *Langmuir* **2004**, *20*, 4085–4092.

(3)   Zheng, X.-P.; Zhao, H.-P.; Gao, L.-T.; Liu, J.-L.; Yu, Sh-W.; Feng, X.-Q. Elasticity-driven droplet movement on a microbeam with gradient stiffness: A biomimetic self-propelling mechanism. *J. Colloid Interface Sci.* **2008**, *323*, 133–140.

(4)   Bico, J.; Quere, D. Self-propelling slugs. *J. Fluid Mech.* **2002**, *467*, 101- 127.

(5)   Agapov, R. L.;Boreyko, J. B.; Briggs, D. P.; Srijanto, B. R.; Retterer, S. T.; Collier, C. P; Lavrik, N. V. Asymmetric wettability of nanostructures directs Leidenfrost droplets. *ACS Nano* **2014**, *8,* 860–867.

(6)   Agapov, R. L.; Boreyko, J. B.; Briggs, D. P.; Srijanto, B. R.; Retterer, S. T.; Collier, C. P; Lavrik, N. V. Length scale of Leidenfrost ratchet switches droplet directionality. *Nanoscale* **2014**, *6,* 9293-9299.

(7)   Lagubeau, G.; Le Merrer, M.; Clanet C.; Quéré, D. Leidenfrost on a ratchet. *Nature Phys.* **2011**, *7*, 395–398.

(8)   Gunji, M.; Washizu, M. Self-propulsion of a water droplet in an electric field. *J. Phys. D: Appl. Phys*. **2005**, *38*, 2417.

(9)   Ismagilov, R. F.; Schwartz, A.; Bowden, N.; Whitesides G. M. Autonomous movement and self-assembly. *Angew. Chem*. **2002**, *114,* 674-676.

(10)   Paxton, W. F.; Sundararajan, Sh.; Mallouk, Th. S.; Sen, A. Chemical Locomotion. *Angew. Chem*. **2006**, *45,* 5420–5429.

(11)   Nakata, S.; Matsuo K. Characteristic self-motion of a camphor boat sensitive to ester vapor. *Langmuir* **2005**, *21*, 982–984.

(12)   Kohira,M. I.; Hayashima, Y.; Nagayama, M.; Nakata, S. Synchronized self-motion of two camphor boats. *Langmuir* **2001**, *17*, 7124–7129.

(13)   Hayashima, Y.; Nagayama, M.; Nakata, S. A Camphor grain oscillates while breaking symmetry. *J. Phys. Chem. B* **2001**, *105*, 5353–5357.

(14)   Neitzel, G. P.; Dell'Aversana, P. Noncoalescence and nonwetting behavior of liquids. *Ann. Rev. Fluid Mech*. **2002**, *34*, 267-289.

(15)   Snezhko, A.; Ben Jacob, E.; Aranson, I. S. Pulsating–gliding transition in the dynamics of levitating liquid nitrogen droplets. *New J. Phys*. **2008**, *10*, 043034.

(16)   Ghosh, A.; Fischer, P. Controlled propulsion of artificial magnetic nanostructured propellers. *Nano Lett*. **2009**, *9,* 2243–2245.

(17)   Wang, J. Can man-made nanomachines compete with nature biomotors? *ACS Nano* **2009**, *3*, 4–9.

(18)   Aussillous, P.; Quéré, D. Liquid marbles. *Nature* **2001**, *411*, 924–927.

(19)   Binks, B. P.; Murakami, R. Phase inversion of particle-stabilized materials from foams to dry water. *Nature Mater*. **2006**, *5*, 865-869.

(20)   Zang, D.; Chen, Zh.; Zhang, Y.; Lin, K.; Geng, X.; Binks, B. P. Effect of particle hydrophobicity on the properties of liquid water marbles. *Soft Matter* **2013**, *9*, 5067–5073.

(21) Tian, J.; Arbatan, T.; Li, X.; Shen, W. Liquid marble for gas sensing. *Chem. Commun*. **2010**, *46*, 4734–4736.

(22)   Dupin, D.; Armes, St. P.; Fujii, S. Stimulus-responsive liquid marbles. *J. Am. Chem. Soc*. **2009**, *131*, 5386–5387.

(23)   Dandan, M.; Erbil, H. Y. Evaporation rate of graphite liquid marbles: comparison with water droplets. *Langmuir* **2009**, *25*, 8362–8367.

(24)   Bormashenko, Y.; Pogreb, R.; Gendelman, O. Janus droplets: liquid marbles coated with dielectric/semiconductor particles. *Langmuir* **2011**, *27*, 7–10.

(25)   Bormashenko, E. Liquid marbles: Properties and applications. *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 266–271.

(26)   Bormashenko, E. New insights into liquid marbles. *Soft Matter* **2012**, *8*, 11018–11021.

(27)   Venkateswara Rao, A.; Kulkarni, M. M.; Bhagat, Sh. D. Transport of liquids using superhydrophobic aerogels. *J. Colloid Interface Sci*. **2005**, *285*, 413–418.

(28)   Bormashenko, E.; Pogreb, R.; Bormashenko, Y.; Musin, A.; Stein, T. New investigations on ferrofluidics: Ferrofluidic marbles and magnetic-field-driven drops on superhydrophobic surfaces. *Langmuir* **2008**, *24*, 12119–12122.

(29)   Zhao, Y.; Hu, Z.; Parhizkar, M.; Fang, J.; Wang, X.; Lin, T. Magnetic liquid marbles, their manipulation and application in optical probing. *Microfluid. Nanofluid.* **2012**, *13*, 555–564.

(30)   Tian, J.; Fu, N.; Chen, X. D.; Shen, W. Respirable liquid marbles for the cultivation of microorganisms. *Colloids Surf. B* **2013**, *106*, 187–190.

(31)   Matsukuma, D.; Watanabe, H.; Minn, M.; Fujimoto, A.; Shinohara,T.; Jinnaia, H.; Takahara, A. Preparation of poly(lactic-acid)-particle stabilized liquid marble and the improvement of its stability by uniform shell formation through solvent vapor exposure. *RSC Adv.* **2013**, *3*, 7862–7866.

(32)   Chu, Y.; Wang, Zh.; Pan, Q. Constructing robust liquid marbles for miniaturized synthesis of Graphene/Ag nanocomposite. *ACS Appl. Mater. Interf.* **2014**, *6*, 8378–8386.

(33)   Bhosale, P. S.; Panchagnula, M. V. On synthesizing solid polyelectrolyte microspheres from evaporating liquid marbles. *Langmuir* **2010**, *26*, 10745-10749.

(34)   Bhosale, P. S.; Panchagnula, M. V. Sweating liquid micro-marbles: dropwise condensation on hydrophobic nanoparticulate materials. *Langmuir* **2012**, *28*, 14860-14866.

(35) Fournier, J. B.; Cazabat, A. M. Tears of wine. *Europhys. Lett*. **1992**, *20*, 517-522.

(36)   Binks, B. P.; Tyowua, A. T. Influence of the degree of fluorination on the behavior of silica particles at air-oil surfaces. *Soft Matter* **2013**, *9*, 834-845.

(37)   Bormashenko, E.; Balter, R.; Aurbach, D. Formation of liquid marbles and wetting transitions. *J. Colloid & Interface Sci.* **2012**, *384*, 157–161.

(38)   Bormashenko, E.; Musin, A. Revealing of water surface pollution with liquid marbles. *Appl. Surf. Sci*. **2009**, *255*, 6429-6431.

(39)   Bormashenko, E.; Bormashenko, Y.; Musin, A.; Barkay, Z.   On the mechanism of floating and sliding of liquid marbles. *ChemPhysChem.* **2009**, *10*, 654-656.

(40)   Biance, A-L.; Clanet, C.; Quéré, D. Leidenfrost drops. *Phys. Fluids* **2003**, *15*, 1632.

(41)   Quéré, D. Leidenfrost dynamics. *Ann. Rev. Fluid Mech*. **2013**, *45,* 197-215.

(42)   Burton, J. C.; Sharpe, A. L.; van der Veen, R. C.; Franco, A. Nagel, S. R. The Geometry of the vapor layer under a Leidenfrost drop. *Phys. Rev. Lett*. **2012**, *109*, 074301.

(43)   Nepomnyashchy, A. A.; Velarde, M. G.; Colinet, P. *Interfacial Phenomena and Convection*; Boca Raton & London. Chapman & Hall/CRC Press, 2002.

(44)   Colinet, P.; Legros, J. C.; Velarde, M. G. *Nonlinear Dynamics of Surface-Tension-Driven Instabilities*; Wiley: Berlin, 2001.

(45)   Pereira, A.; Trevelyan, P. M. J.; Thiele, U.; Kalliadasis, S. Interfacial instabilities driven by chemical reactions. *Europ. Phys. J*. **2009**, *166*, 121-125.

(46)   de Gennes, P. G.; Brochard-Wyart, F.; Quéré, D. *Capillarity and Wetting Phenomena*; Springer: Berlin, 2003.

(47) Nagai, K. H.; Takabatake, F.; Sumino, Y.; Kitahata, H.; Ichikava, M.; Yoshinaga, N. Rotational motion of a droplet induced by interfacial tension. *Phys. Rev. E* **2013**, *87*, 013009.

(48) Ohta, T.; Ohkuma, T. Deformable self-propelled particles. *Phys. Rev. Lett*. **2009**, *102*, 154101.

(49) Bormashenko, E. Y. *Wetting of Real Surfaces*; De Gruyter, W.: Berlin, 2013.

(50) Hashmi, A.; Xu, Y.; Coder, B.; Osborne, P. A.; Spafford, J.; Michael, G. E.; Yu, G.; Xu, J. Leidenfrost levitation: beyond droplets. *Scientific Reports* **2012**, *2*, 797.

(51) Jin, H.; Marmur, A.; Ikkala, O.; Ras, R. H. A. Vapour-driven Marangoni propulsion: continuous, prolonged and tunable motion. *Chem. Sci*., **2012**, *3*, 2526.
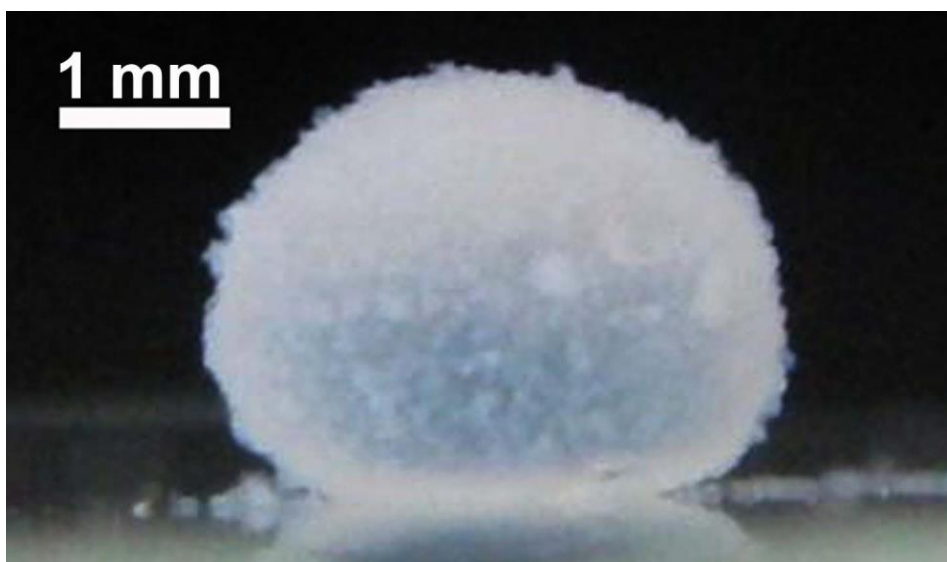
Figure 1. 10 µL liquid marble containing 70 vol.% aqueous ethanol solution resting

on a glass slide.
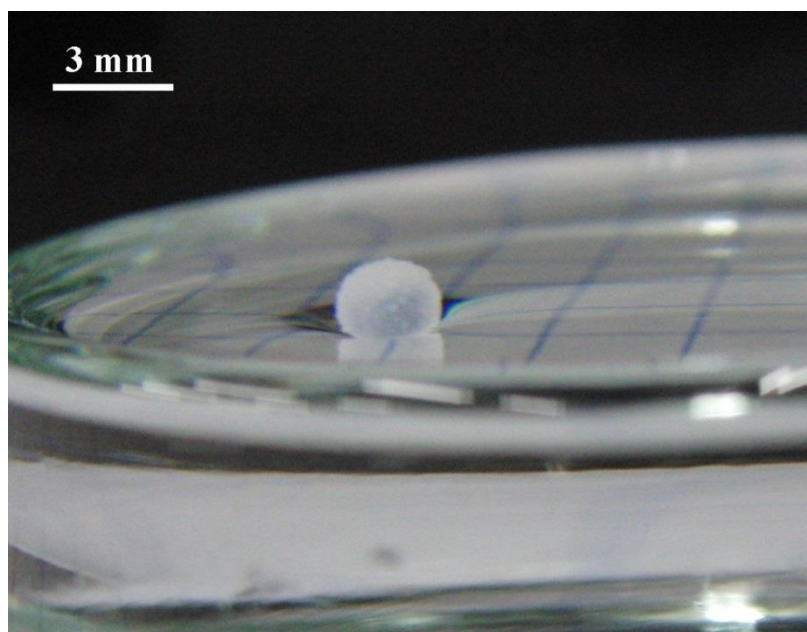
Figure 2. 10 µL liquid marble containing 70 vol.% aqueous ethanol solution floating

on the surface of glycerol.

| 0 s | 0.60 s | 0.70 s | 0.90 s |
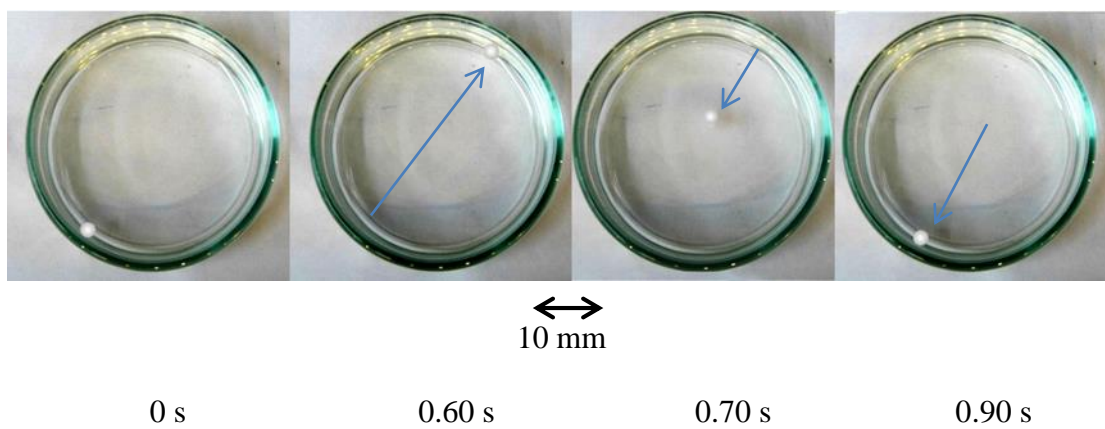
Figure 3. Sequence of images demonstrating the motion of a10 µL liquid marble coated with fumed fluorosilica particles containing 70 vol.% aqueous ethanol solution placed on water.
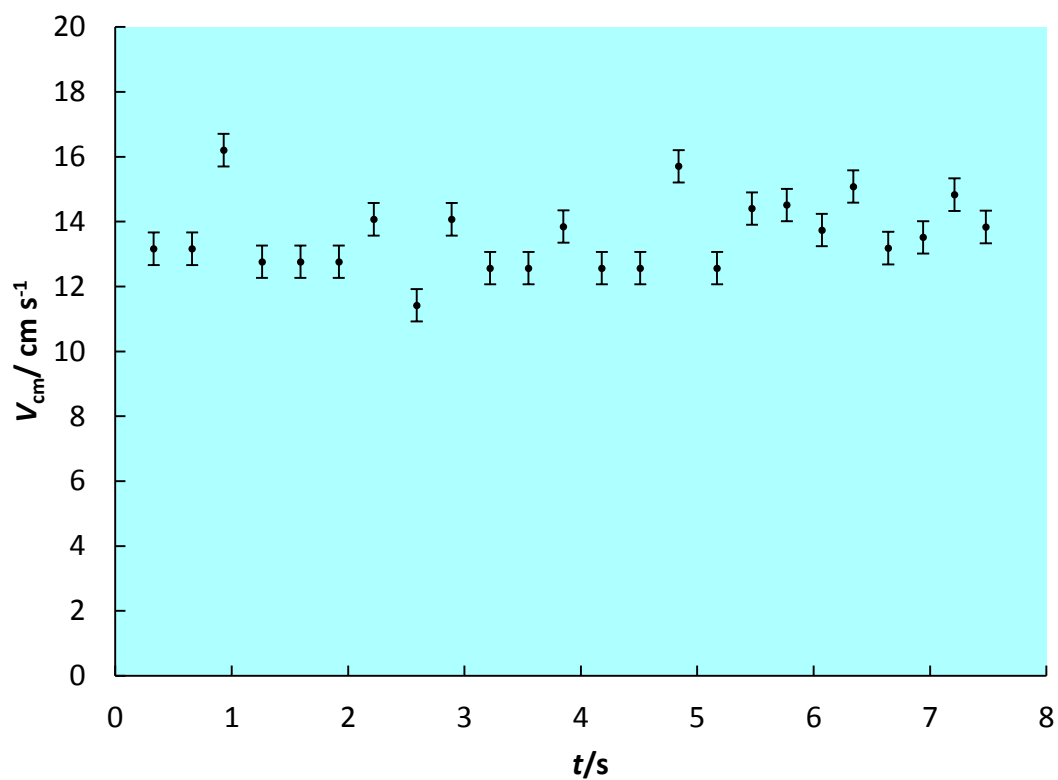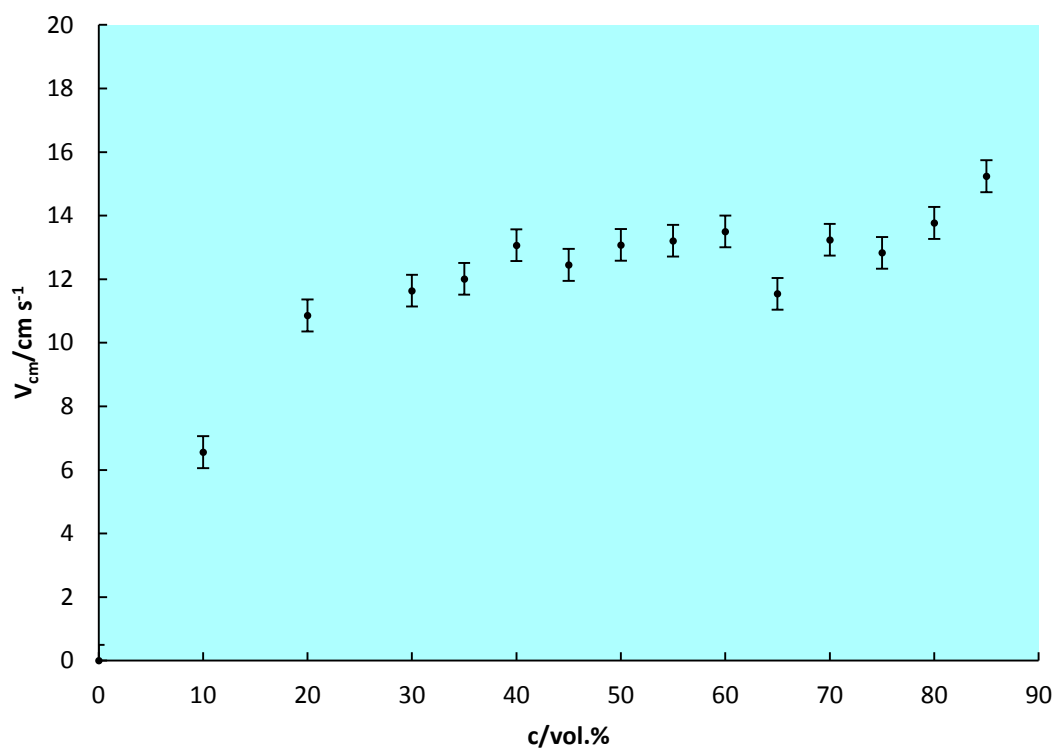
Figure 4. The velocity of the center of mass, v_{cm}, of a 10 µL liquid marble coated with fumed fluorosilica particles containing 70 vol.% aqueous ethanol solution as a function of time. Every point corresponds to the bouncing of the marble with the skirting of the Petri dish.
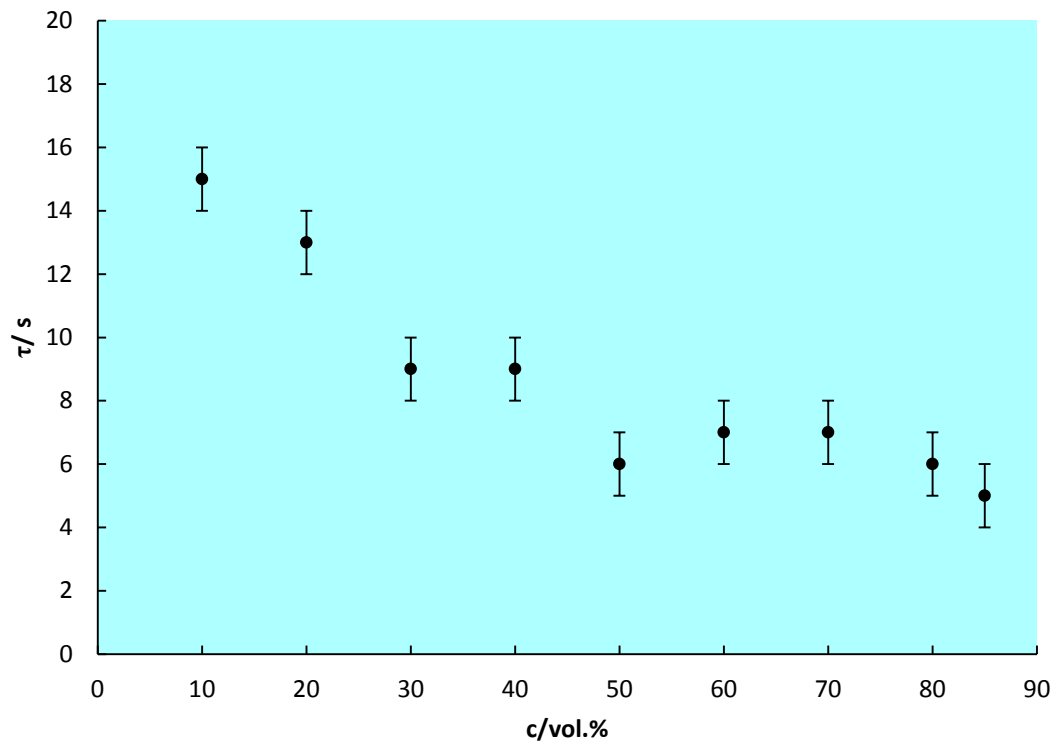
Figure 5. The total time of rectilinear motion of marbles on water, τ, *versus* the
concentration of alcohol in a marble, c.
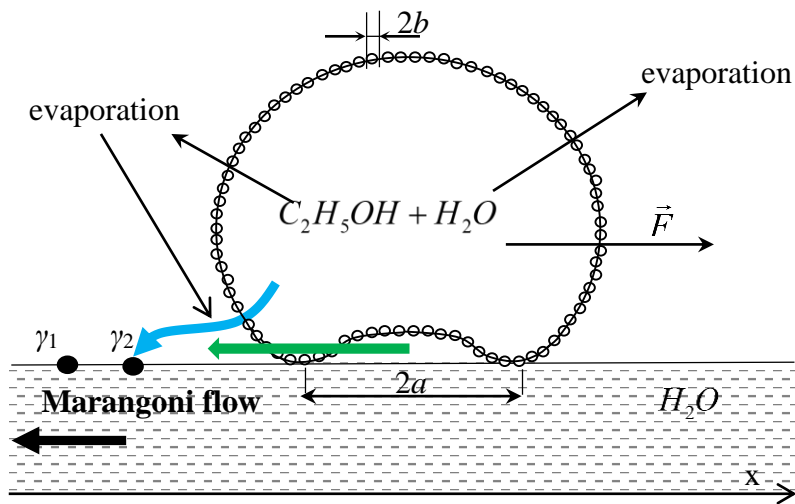
Figure 6(a). Scheme illustrating the origin of the instability driving liquid marbles containing aqueous alcohol solution deposited on a water surface. The blue arrow shows the spontaneous increase of the alcohol evaporation from a marble. The black arrow indicates the direction of the Marangoni flow, increasing in turn the evaporation of alcohol from the area beneath a marble shown by the green arrow; $\gamma_1 > \gamma_2$ for two points shown on the water surface.
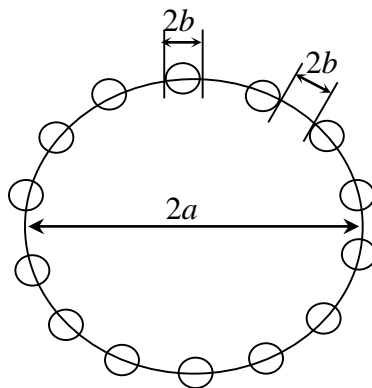
Figure 6(b). Scheme of the contact area of a marble. Solid particles are separated by clearings of *2b*.

Figure 7. The velocity of the center of mass, v_{cm}, of 10 µL liquid marbles coated with

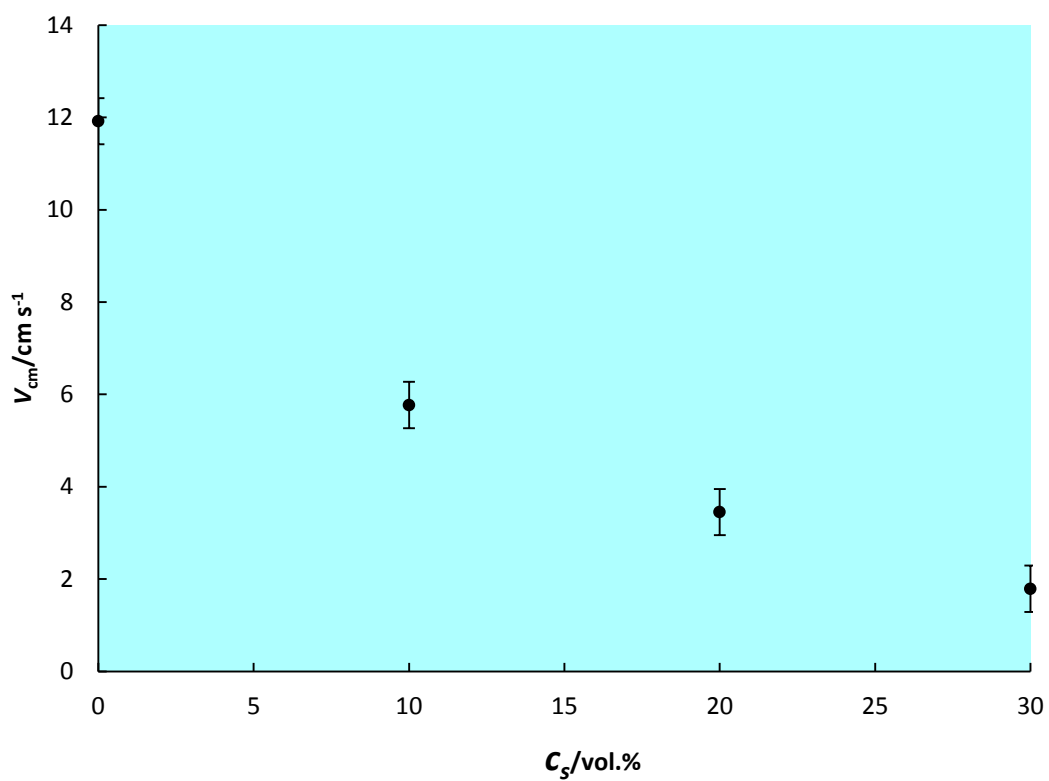fumed fluorosilica particles *versus* the concentration of alcohol within the

marble.

Figure 8. Initial velocity of 10 µL marbles containing 70 vol.% aqueous ethanol solution placed on the surface of aqueous ethanol solutions *versus* the volume concentration of alcohol in the supporting solution, c_s.
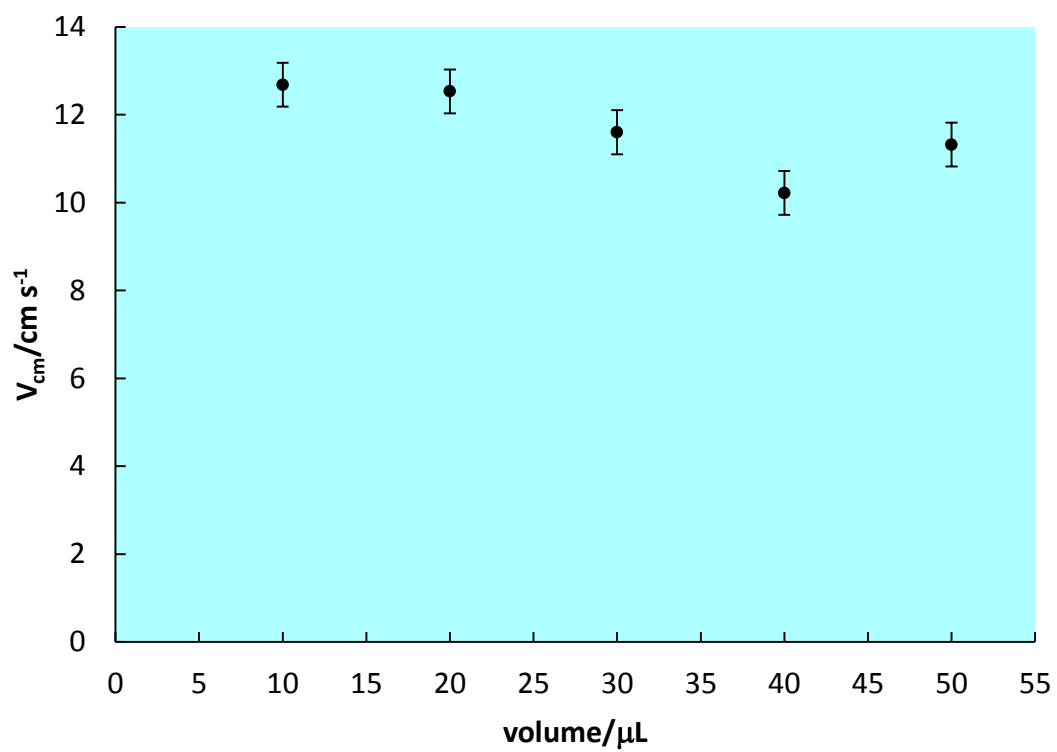
Figure 9. Stationary velocities of the marbles containing 70 vol.% aqueous ethanol solution established for marbles of various volumes.
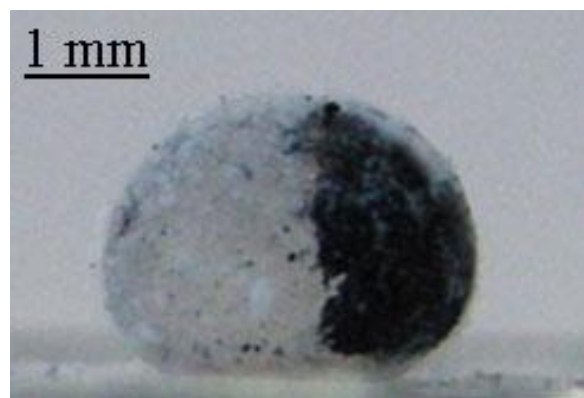
Figure 10(a). 20 µL Janus marble coated with fumed fluorosilica powder and carbon

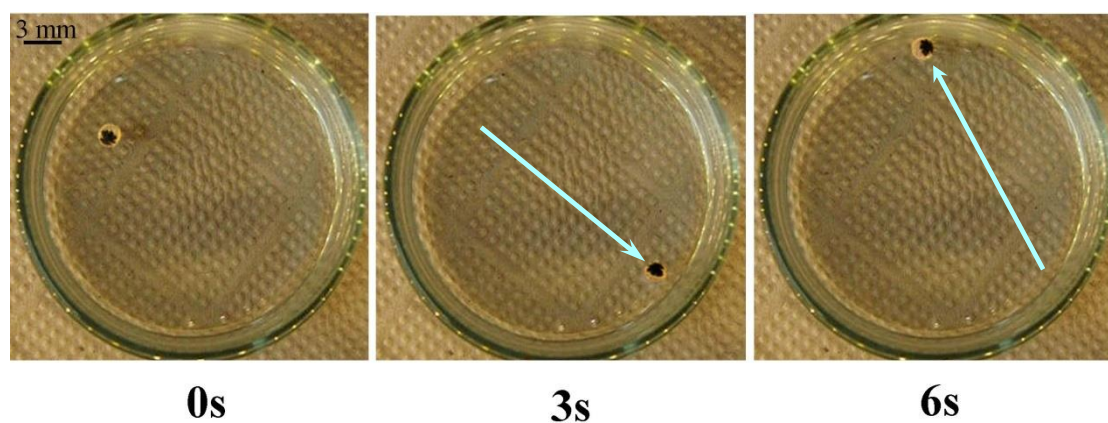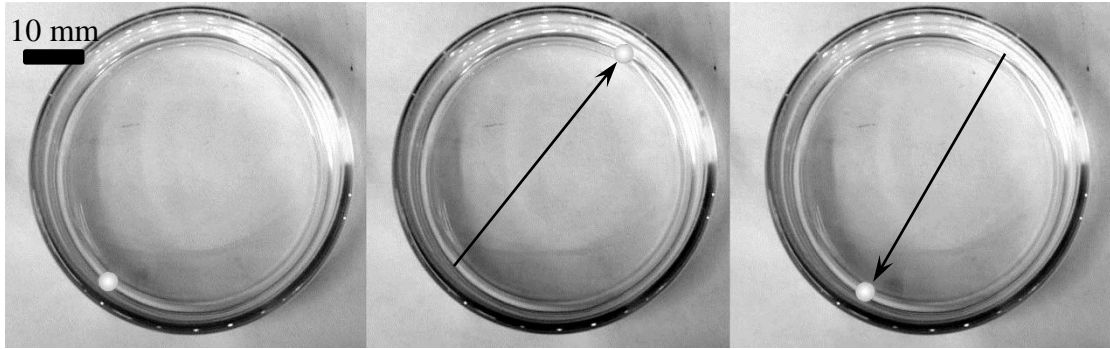black powder. The marble contains 37.5 vol.% aqueous ethanol solution.

Figure 10(b). Sequence of images demonstrating the self-propulsion of the 20 µL

Janus-coated marble in (a). The carbon black-coated hemisphere works as a

tracer.

TOC IMAGE

0 s   0.60 s   0.90 s