

Regulating the self-propulsion of liquid marbles on water pool

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Abstract

Regulating droplet motion, with minimized energy input and adhesion loss, is promising for efficient liquid transportation. One efficient strategy is to design non-sticking droplets that exhibit regulated self-propelling. However, controlling the self-propelling trajectory while keeping a non-sticking property is challenging. Here, we developed a series of non-sticking solvent droplets that self-propelled on the water pool. These droplets are covered with omniphobic nanoparticles to become non-sticking, namely liquid marble. We found that the droplet self-propelling behavior, such as velocity and trajectory (i.e., polygonal, circular, spinning, and random), differed based on the liquid property (surface tension, solubility in water, volatility, etc.) owing to the branched underlying mechanism. The self-propelling driving force is not confined to the solute capillary force but extends to other forces, including the non-solute capillary, vapor-induced recoiling, and electrostatic force. The understanding of the self-propelling dynamics offered a basis for regulating the trajectories of self-propelling droplets of solvents from rectilinear to circular, random, stop-and-go motion, with a modulated transition time. Even liquid selective anti-wetting wettability at the perimeter of the water pool influenced the self-propelling behavior of the prepared liquid marbles. Thereafter, such liquid marbles were successfully explored in cargo transportation.

Introduction

Transport of a small amount of liquid is significant for potential use in microfluidic,^[1] soft robotics^[2,3] and water harvesting.^[4,5] Transportation efficiency increases with the decrease in liquid adhesion loss. Thus, the construction of a transporting system using non-liquid-sticking interfaces is promising.^[6] More favorably, the external energy input required for transportation should be minimized. Thus, the interfacial design of a self-propelling, non-sticking droplet is the most promising.^[7,8]

Liquid marble (LM) is one of the non-sticking droplets,^[9] which is formed by covering the liquid droplet with fine, low-wettability particles. The fine particles form the liquid-repellent particle-jammed structures on the droplet surface and prevent the direct adhesion between contacting solid/liquid and the droplet. This state is known as the Cassie-Baxter state.^[10] In this state, LM rolls off from the solid substrate with slight tilting or float on the liquid pool. Unlike droplets covered with continuous solid shell, LMs keep the liquid property such as splitting, coalescing and wetting under mechanical stress,^[11] because the jammed particles on the liquid surface are reconfigurable in response to shear stress. Various attempts to locomote the LM have been reported for liquid transportation. On the one hand, a major strategy is the use of stimuli-responsive LMs. The LMs move on the solid substrate or liquid pool with the trigger of these stimuli, such as magnet,^[12] light,^[13] temperature,^[14] vapor,^[15] electricity,^[16] or ultrasonic,^[17] when the droplet is covered with low-wettability particles that can respond to these stimuli.

On the other hand, reports on self-propelling LMs with modulated trajectories are rare.^[18-22] In the past, mostly water-soluble components, including alcoholic solvents, aqueous solution of camphor and sulfuric acids, were encapsulated in the liquid marbles to examine their self-propulsion behaviours that followed principles of either soluto-capillary Marangoni flow or thermo-capillary Marangoni flows.^[18-22] Typically, such self-propulsion is driven by directional force owing to the symmetry breakage, which makes the self-propelling motion being highly directional.^[23] In the past, they suggest the driving force of the locomotion of aqueous droplet of ethanol, sulfuric acid or camphor is the Marangoni flow near the water pool surface. In principle, Marangoni flow is formed by the difference in surface tension in the continuous liquid phase. For LM, the Marangoni flow is formed by the partial dissolution of the water soluble components into the water pool, which is supplied from particle-covered droplets via evaporation.^[18-21] In the past, the self-propelling velocity increased while the self-propelling time decreased with increase in ethanol concentration and volume, which seems consistent with their suggestion.^[18-19] While the self-propelling LM is attractive for liquid transportation

techniques, the fundamental understanding of self-propelling LM is still not clear. This is because the droplet library in previous works has been limited to aqueous solutions of either ethanol, camphor or sulfuric acids.^[18-21] Our fundamental question is, “What liquid characters decide the self-propelling behaviour of LMs?” According to the suggested mechanism, the difference in ethanol volatility and surface tension between ethanol and water seems critical. However, a comprehensive understanding of the droplet effect on self-propelling behaviour is lacking.

Here, we designed LMs by covering a variety of solvent droplets with omniphobic nanoparticles and floating them on the water pool. We studied how the solvent solubility to the water pool, volatility and surface tension influence the self-propelling behaviour. The main findings can be summarised as: (1) The self-propelling is observed regardless of the droplet solubility to the water pool, even for immiscible droplets; (2) Self-propelling trajectories are bifurcated depending on the solubility; and (3) There is the case that the self-propelling velocity can increase with the decrease of the droplet volatility. In (1), LM using low water solubility solvents such as toluene or butanol exhibits self-propelling behaviour, with a velocity comparable to LM using ethanol. This indicates that the evaporated solvent doesn't need to be the solute of the water pool and that a different self-propelling mechanism from the previous works exists.^[18,19] In (2), we find the self-propelling LM using the solvent with water solubility less than 6.02 wt.% draws the random trajectory and *vice versa*. The experiment suggested that the evaporated low-water solubility solvent makes the localized solvent domain in the water pool, which disturbs the LM motion. Based on these findings, we regulated the solvent localization to control the LM trajectory, including stop-and-go, long-lasting rectilinear, or spontaneous stopping motions. In (3), we systematically studied the origin of the self-propelling force, where a parameter variation experiment is designed by mixing various solvents to alter target droplet parameters while maintaining other conditions constant. We finally show that the assembled LMs exhibit different motion trajectories as the result of the centre of gravity control. Since most self-propelling objects exhibit monotonic motion, our findings contribute to advancing the fundamental understanding of the self-propelling phenomenon. Moreover, the methodology to regulate the self-propelling trajectory would develop efficient liquid transportation technology.

Results and Discussions

LMs derived from liquid-repellent nano/microparticles provided a protective and non-sticky environment on solid and liquid interfaces.^[24-30] Classically, LMs are formed by covering water with hydrophobic particles; however, omniphobic particles are required to study the effect of

various solvents having a wide range of surface tensions on the trajectory of self-propelling LMs. The omniphobic particles are designed by 1,4-conjugate addition reaction between amine and fluoroacrylate moieties at ambient conditions (Fig. S1). The chemical modification of the prepared silica nanoparticle (~ 100 nm) with fluorinated moiety was characterized with FTIR (Fig. S2), where a characteristic IR signature for C–F stretching appeared at 1417 cm^{-1} . While this, another IR peak for carbonyl stretching at 1750 cm^{-1} indicated the formation of β -amino ester bond through 1,4-conjugate addition reaction (Fig. S2). Owing to its ability for repelling a wide range of solvents (surface tension: 22.10 to 72.80 mN m^{-1} ; Fig. S3a-b), LMs of various polar and non-polar organic solvents—having high (acetonitrile, dimethyl sulphoxide (DMSO), ethanol) or low (dodecane, ethyl acetate, toluene) water solubility were successfully prepared (Fig. 1b and Fig. S3c-d) to investigate their self-propelling behaviour when they were placed on a water pool. Interestingly, different motion profiles were observed depending on the water-solubility of the selected inner solvent of the respective LMs, as schematically depicted in Fig. 1c-d. Highly water-soluble solvents depicted a geometry-mediated change in motion profile, where initially, the motion started as polygonal, transitioned to circular, and finally ended with spinning motion at the center of the water pool. However, for solvents with low water solubility, a vapour-mediated random motion was observed in addition to polygonal and circular motions (Fig. 1c-d).

To understand the motion modes of LMs on the water pool, we defined the LM trajectory with coordinated position (x (cm), y (cm)) as a function of time t (Fig 2a). The water pool is surrounded by a glass dish with a diameter of 6.0 cm, and the coordinate origin $(0, 0)$ is set to the center of the dish. Thus, the boundary condition is $x^2 + y^2 < 6^2$. Moreover, we obtain the LMs' velocity V and acceleration A to be $V = ((dx/dt)^2 + (dy/dt)^2)^{0.5}$ and $A = ((d^2x/dt^2)^2 + (d^2y/dt^2)^2)^{0.5}$, respectively. We also defined the bouncing angle θ_N in LM's collision to the dish wall, where N is the number of the collision = $1, 2, \dots$. Here, as shown in Fig. 2b, the bouncing is the sum of the incident and reflection angles ($\theta_N = \theta_N + \theta_{N+1}$) that can be estimated from the infinitesimal velocity vector of the LM before and after the collision since the LM size ≈ 2.7 mm is negligibly smaller than the water pool one = 6 cm. We further divided the velocity vector just before the collision into the dish tangential and normal directions (dV_ψ and dV_r) as shown in Fig. 2c. In this case, the wall bouncing effect only affects the normal direction. Thus, the velocity vector just after the collision would be dV_ψ for tangential and $e dV_r$ for normal directions, where $e < 1$ is the bouncing coefficient. Thus, the incident and reflection angles can be written as $\tan\theta_{N+1} = \tan\theta_N/e$. Since the reflection angle is equal to the incident angle in the subsequent collision at the linear motion, we can predict the bouncing angle $\theta_N = \theta_N + \tan^{-1}[\tan\theta_N/e]$ by

integrating the geometric progression. This model predicts that θ_N increases with N and finally transitions to circular motion ($\theta_N \rightarrow 90^\circ$ and $V_r \rightarrow 0$).

On placing a LM of ethanol on the water pool, a self-propulsion with three distinct motion trajectories (that is, polygonal, circular, and spinning) was observed over time as shown in Figure 2d-g and Movie S1. The evaporation of ethanol from the LM and its asymmetric condensation, followed by diffusion into the water pool locally altered the surface tension on top of the water pool, resulting a gradient in surface tension—which caused the actuation of the LM. The origin of the symmetry breakage of surface tension around the actuating LM on water pool is the asymmetric coverage of hydrophobic particles around it. Further, the external addition of the entire 10 μL ethanol (i.e. 0.01 vol.%) into the water pool of 100 ml at a time failed to alter the surface tension of the whole water pool (Fig. S4). Hence, local and asymmetric change in surface tension on the water pool around LM contributes to its self-propulsion. In a control study, we have captured image of a self-propelling LM with IR camera as presented in Fig. S5, where the change in temperature between water pool and LM is observed to be very low ($< 1.5^\circ\text{C}$), eliminating the possibility for temperature-gradient-induced Marangoni flow. Temperature of LM is slightly lower than the water pool due to evaporation of encapsulated solvent from LM. We will discuss this mechanism in detail in Fig. 3. The ethanol LM started actuating on the water pool following different trajectories, where the motion of LMs in individual trajectories is represented as the % of observed motion time/total motion time, denoted as Φ . The ethanol LM displayed a short polygonal motion with $\Phi = 7 \pm 1\%$, whereas circular and spinning motions were noticed with $\Phi = 65 \pm 4\%$ and $28 \pm 3\%$, respectively, before it became stagnant, as shown in Fig. 2d. As we have expected in the model, the LM in the polygonal motion transitioned to circular motion after the increase in bouncing angle (Fig. 2h). According to the model fitting, we obtained $e = 0.87 \pm 0.01 < 1$, which indicates that the LM kinetic energy is slightly dissipated in bouncing. The energy dissipation is mainly the viscous dissipation from the water pool, because the e was not differed with the inner solvent of LMs (Fig. S6).

Here, the motion trajectory of the LM transitioned from polygonal to circular when $\theta_N > 80^\circ$ (Fig. 2h). It is important to note that acceleration A of self-propelling LMs also gradually altered (Fig. 2i). Eventually, the LM transitioned to spinning motion at the center of the water pool and finally stopped the motion. The transition of motion trajectory of LMs from circular to spinning occurs because of its deceleration. It is mechanistically clear that the kinetic energy of the LM gradually decreases; spin motion is observed when the kinetic energy of the LM falls below a certain level, as quantified by the 3D trajectory of the LM in Figure 2d. During Spin motion,

the momentum of the LM is not zero, but it cannot move its position. In other words, the momentum of the LM is not significant enough to move its position. The energy barrier required to move its position cannot be considered other than the change in potential energy and/or dissipation due to the deformation of the water surface. On the other side, when ethanol is replaced with a water insoluble and volatile solvent toluene, the LM also displayed self-propelling behavior—but with a distinct pattern of motion trajectories on water pool, as shown in Fig. 2j-m and Movie S2. It shows an initial polygonal motion (Fig. 2k; $\Phi = 30 \pm 4\%$), followed by a short ($\Phi = 17 \pm 4\%$) circular trajectory (Fig. 2l). In this scenario, a relatively fast rise in bouncing angle was noticed with initial collision between LM and wall of the water pool (Fig. 2n). However, a sudden decrease in bouncing angle leads to a random motion time for $\Phi = 53 \pm 8\%$ with respect to a total actuation time of LM (Fig. 2m). While, a highly water-soluble volatile solvents (e.g. ethanol) loaded LMs followed a solute-capillary Marangoni flow and provided self-propulsion with three distinct trajectories (polygonal, circular, spinning), a water-low soluble solvents (e.g. toluene) loaded liquid marbles provided a dominated random motion trajectory because of non-solution-capillary anisotropy. Here, the toluene evaporation speed is slower than ethanol (Fig. S7). Thus, we expected the lifetime in the self-propulsion to be larger for toluene LM than for ethanol. However, due to the difference in diffusivity to the water pool and its life time, the ethanol LM exhibited the longer lifetime than toluene one (see Figure 2i and 2o). Explaining the conclusion in advance, random motion of LMs appears only for water-immiscible and volatile solvents (i.e. toluene). This is because condensed toluene from LM failed to diffuse; rather, it is likely to form multiple isolated domains on the air/water interface, as observed for externally added toluene in the water pool (Fig. S8). The floating isolated domain of toluene will likely contribute to the random motion of actuating LMs. This aspect is discussed in the following section. A decrease in velocity and acceleration was observed for toluene LM as shown in Fig. 2o. Thus, gradual diffusion of water-soluble solvents (Fig. S9) is likely to locally alter the surface tension of the water pool in a controlled manner and provide a definite pattern for motion trajectories, and the condensed and isolated domains of water-immiscible solvents from LMs on the water pool lead to the random motion for LMs. In the following section, a detailed analysis is provided for a deeper understanding of such solvent-based differences in motion trajectories of self-propelling LMs.

In this section, a series of experiments were performed with typical solvents having different physical properties, including i) highly volatile and water-soluble ethanol,^[31, 32] ii) highly volatile and low water-soluble ethyl acetate,^[31, 32] iii) sparingly water-soluble, non-polar and highly volatile toluene,^[31, 32] iv) polar, non-volatile DMSO,^[31, 32] and v) non-polar, non-volatile

dodecane^[31, 33] to further identify the specific roles of solvents and their associated physical properties towards motion trajectory. Different motion trajectories obtained based on the choice of selected solvents are classified into three distinct scenarios (Fig. 3a). In scenario I, LMs using highly volatile solvents with low or high-water solubility displayed self-propelling behavior with three distinct motion trajectories—including polygonal, circular and spinning motions, where circular motion is dominated over other motions. In scenario II, the self-propulsion of LM encapsulated with a non-polar or low water-soluble solvent like toluene included a dominant random motion after the sequential transition of polygonal and circular motions. In scenario III, both the highly water-soluble (DMSO) and low water-soluble (dodecane) non-volatile solvents failed to display self-propelling behavior.

From the relationship between the solvent properties and observed motion, we proposed the possible solvent mass transportation behavior. On the one hand, in scenario I, highly water-soluble solvent molecules evaporated out from LMs would diffuse and distribute inside the water pool resulting in the alteration of interfacial surface tension anisotropy around the LM at the air–water interface as shown in Fig. 3b (left). Here, the solvent does not distort the LM motion and the motion is rectilinear. Eventually, random motion was not observed. On the other hand, in scenario II, low water-soluble and volatile solvent molecules are used. Such solvents have limited ability to diffuse into the water pool. Thus, the evaporated molecules from respective LM are condensed at the water pool surface to form localized solvent domains. As a result, an irregular interfacial surface tension anisotropy at air–water interface was developed around the LM as depicted in Fig. 3b (right), leading to the appearance of random motion trajectory.

To validate the inference, we have performed additional experiments with co-solvents to gradually change some key physical parameters of selected solvents — water solubility and volatility to identify the specific roles of inner solvents of LM towards its random motion. A series of LMs of two solvent mixtures are prepared where the content of ethyl acetate in toluene was gradually varied from 0 to 100 vol.% with an intention to vary the water solubility of co-solvent in water (Fig. 3c and Fig. S10). It is worth mentioning that LMs made up of only ethyl acetate remained incapable of displaying random motion (Fig. 3c and Fig. S11). On increasing the content of ethyl acetate in toluene, the percentage of random motion of LMs was gradually decreased, and the threshold amount of ethyl acetate in toluene that resulted random motion was observed to be 90 vol.% (Fig. 3c and Fig. S10). Thus, the threshold of the water solubility for random motion exists between that for the 90 and 100 vol.%. Furthermore, LMs of other co-solvents, where the amount of a non-volatile solvent, dodecane, is gradually increased in a

volatile solvent — toluene to decrease the volatility of the mixture of co-solvent. With an increment in the content of dodecane in toluene, the percentage of random motion depleted and no random motion was observed for LMs when the content of dodecane in toluene exceeded 60 vol.% (Fig. 3d and Fig. S12). It is worth to mention that the LM made of solely dodecane is incapable of displaying a noticeable actuation (Fig. S13). Random motion is decreased with the increase of dodecane ratio in toluene. This is because of the size of the localized solvent domain—which decreases with the solvent volatility and so with the dodecane ratio, as shown in Fig. 3e. These comprehensive observations of the possible random motion appearance support our hypothesis. Moreover, water solubility and volatility of selected solvents played an important role in controlling the motion trajectory of a self-propelling LM.

We then reconsider the mechanism of the self-propulsion of LMs. Previously, the self-propelling behavior of LMs was limited to ethanol, which is volatile and water-soluble solvent.^[18, 19] In these works, the Marangoni solutocapillary flow was considered as the primary force behind LM self-propulsion. However, the LM self-propulsion is observed even for low water solubility solvent, which is not a “solute” of the water pool. In this study, we designed a series of experiments to investigate how different forces, including Marangoni solutocapillary anisotropy force (denoted as Force 1; Fig. 4a), non-solutocapillary anisotropy force (referred to as Force 2; Fig. 4b), vapor-induced recoiling force (recognized as Force 3; Fig. 4c) and triboelectrification^[31] between prepared particles and water pool (labelled as Force 4; Fig. 4d) towards the self-propulsion of non-sticking solvent droplets. Force 1 arises due to surface tension anisotropy, where the solvent evaporates from liquid marble and subsequently condensed and diffused into the water pool. It creates a surface tension gradient and propels the LMs on the water pool. Force 1 is solely responsible for scenario I of self-propulsion, where LMs of volatile and water-soluble solvents provide polygonal, circular, and spinning motions. Meanwhile, Force 2 acts at the particle-water pool contact line and mostly contributes to scenario II, where LMs predominantly exhibit random motion along with polygonal and circular trajectories. Force 3 and 4 with respect to the other two forces, are considered to be negligible. While, Force 1 is only applicable for water-soluble solvents, Force 2 would act for both water miscible and immiscible volatile solvents; however, it becomes more relevant in the case of water immiscible solvents.

To analyse the contribution from each of the above-mentioned forces in relation to the physical properties of the selected solvents, further experiments were performed using different binary solvent mixtures. The ratio of each component of the selected solvent mixture was systematically varied from 0 to 100 vol.% to assess their individual effects. Fig. 4e shows the

LM velocity by varying a water–ethanol mixture ratio. As the ethanol ratio is increased, the volatility of the mixture is increased, and its surface tension decreases. The tendency is consistent with the previous observations.^[18, 19] As the LM is driven by condensation of solvent on water pool creating a surface tension anisotropy, both Force 1 and Force 2 are expected to contribute more with increasing ethanol content in the LMs, leading to a faster marble propulsion speed as shown in Fig. 4e. The motion trajectory was not significantly different for ethanol/water mixtures (Fig. S14 and Fig. S15). Thereafter, we study how the solvent volatility of water-immiscible solvents affects the motion of LMs prepared with a binary mixture of toluene and dodecane. While dodecane is non-volatile, toluene remains highly volatile. The difference between the surface tension of these two selected solvents is low ($\sim 3 \text{ mN m}^{-1}$). The gradual elevation in the content of dodecane in the selected binary mixtures of toluene and dodecane decreases the speed of prepared LMs, as shown in Fig. 4f. While motion trajectory depends on water solubility, speed of LMs depends on volatility and surface tension, where Force 2 is likely to be dominated. It is worth mentioning that the alteration of solvent composition also influenced the motion profiles of the self-propelling LMs.

Thereafter, another binary mixture of ethyl acetate in ethanol was selected to study the self-propulsion behaviour of LMs, as shown in Fig. 4g, Fig. S16 and Fig. S17, where the water miscibility is gradually reduced with increasing the content of ethyl acetate in ethanol—maintaining a similar surface tension and volatility. On gradually elevating the ethyl acetate content in the binary solvent mixture, a slight improvement in the speed of LMs was observed (Fig. 4g). This result indicates that the magnitude of Force 1 is reduced as the content of ethyl acetate is increased, but Force 2 dominantly contributes to the self-propulsion of LMs with a slightly improved speed.

Finally, a binary solvent mixture of butanol-ethanol enabled the gradual decrease of both solvent volatility and water solubility by increasing the content of butanol in the binary mixture. However, a slight change in surface tension $\sim 3 \text{ mN m}^{-1}$ is expected. Thus, the LMs show a slight increase in propulsion speed when the content of butanol is high in the binary solvent mixture as shown in Fig. 4h. A change in motion profiles of the LMs was also observed with the variation of content of butanol in ethanol (Fig. S18 and Fig. S19).

Thus, the self-propulsion speed of LMs on a water pool is not monotonic but the interplay of various forces originated because of solutocapillary anisotropy, non-solutocapillary anisotropy, vapor-induced recoiling and triboelectrification^[34] (Fig. S20) between prepared particles and water pool. This current study suggested that volatility, water solubility, and low surface tension of solvent contribute to self-propulsion of LMs. Thereafter, Reynolds number (Re) = $\rho VL/\mu$

(ρ : density of the fluid, V : velocity, L : characteristic length $\sim$ droplet size, μ : dynamic viscosity of the fluid), capillary number (Ca) = $\mu V / \gamma$ (γ : fluid surface tension), and Marangoni number (Ma) = $\Delta\gamma L / \mu D$ ($\Delta\gamma$: Surface tension difference between droplet and water pool and D : diffusion constant and the characteristic length (L) ranges from droplet to water pool sizes.) were calculated for self-propelling liquid marbles that were loaded with different organic solvents (see Supporting information Table S1-3). We found $Re \sim 10^1$ to 10^2 for all the solvent LMs. This means the inertia force dominates LM motion rather than the viscous forces. Ca was found to be $\sim 10^{-4}$ to 10^{-2} for all the solvent LMs. This means the solvent LM motion is dominated by capillary force rather than viscous one. Ma was estimated to be $\sim 10^8$ to 10^{10} for actuating LMs irrespective of encapsulated solvents. It indicates the origin of LM actuation is not due to the thermal-marangoni flow.

The fundamental studies in the previous section offered us the method to control the self-propelling of LMs; that is the external addition of selected fluids on the water pool. The motion of self-propelling LMs made up of ethanol can be permanently or temporarily quenched based on the addition of a water-soluble and volatile solvent (ethanol) into the water pool during the course of self-propulsion of LMs encapsulated with ethanol, as depicted in Fig 5a-c. Force 1, because of solutocapillary anisotropy, contributes to the self-propulsion of LMs of ethanol, as shown in Fig. 2d. However, an external addition of a 10 μ L ethanol droplet on the water pool perturbed the Force 1 mentioned in Fig. 4a through its rapid diffusion into water pool as demonstrated in Fig 5a. Thus, the self-propulsion of LM was immediately and permanently quenched (Fig. 5b-c and Movie S3) after the external addition of ethanol. It completely failed to regain the self-propulsion; rather, the buckling of the stationary LM at water pool was noticed. While this, the addition of low water-soluble volatile solvent, toluene, in the water pool resulted in a temporary quenching of self-propulsion as demonstrated in Fig. 5d-f and Movie S4. On addition of a 20 μ L toluene droplet in the water pool with a self-propelling LM of ethanol, the Force 1 (because of solutocapillary anisotropy) is disrupted, and the self-propulsion of the LM is quenched. As the externally added toluene has limited diffusion in the water pool and evaporates out relatively faster (Fig. 5d), after a few seconds, the same LM regained its self-propulsion ability with circular motion trajectory on the water pool, as shown in Fig. 5e-f. Moreover, the volume of added toluene controls the motion quenching duration, as accounted in Fig. 5g and Fig. S21. A small difference (from ~ 9 cm s $^{-1}$ to ~ 13 cm s $^{-1}$) in velocity of LMs was noticed while compared between two states of the LM: before addition of toluene and just after regaining its self-propulsion as shown in Fig. 5h. It is likely due to condensation of

externally added toluene to the LM. However, the amount of toluene added into the water pool has merely any impact on the velocity of LM after restoring its self-propulsion ability (Fig. 5h). In fact, self-propulsion of a single LM can be temporarily quenched multiple times by sequential addition of toluene (5 μ L) at regular time interval as demonstrated in Fig. 5i, Fig. S22 and Movie S5.

Thereafter, we examined the other external factors that dictate the self-propulsion of LMs. In the earlier demonstrations, the self-propelling LMs collided with the bare glass of the container used to prepare the water pool. In this current experimental setup, the circumference of the water pool was separately decorated with superhydrophobic/superoleophilic wall and superomniphobic wall prior to examining their impact on the motion trajectory of the self-propelling LMs. Interestingly, LM of ethanol lost its motion on the water pool after reaching the vicinity of the superhydrophobic/superoleophilic wall of the container (Fig. 6a-c and Movie S6), where superhydrophobic interface having hydrocarbon modification displayed extreme repellence to water with the contact angle (CA) of $> 150^\circ$ —but liquids with low surface tension readily soaked with CA $\sim 0^\circ$ as shown in Fig. S23. No physical contact between LM and superhydrophobic wall was noticed (Fig. 6d and Movie S6). As a consequence, no distortion of LM was observed as shown in Movie 6 and Fig. 6e. We guess the indirect contact between the LM and the superhydrophobic wall is owing to the lubrication of the ethanol to the wall owing to its high wettability (Fig. S23). The lubricated wall highly dissipates the LM kinetic energy. Moreover, the lubrication may also influence the ethanol distribution condensed around LM which can perturb the solutocapillary anisotropy around LM, resulting in a decelerated motion. On the contrary, superomniphobic walls decorated with fluorinated modification provide a repulsive environment for both water and ethanol (Fig. S23). In such an environment, the LM of ethanol displayed only polygonal motion without having any transition of motion trajectory even after 60 s (Fig. 6g-h and Movie S7). Whereas, in the absence of such a superomniphobic wall, the same LM experienced a transition of motion trajectory from polygonal to circular after ~ 20 s (Fig. S24). In the case of an omniphobic wall, the self-propelling LM came in contact with superomniphobic wall and resulted in a distortion of LM (Fig. 6i-j). Such elastic collision between self-propelling LM and the omniphobic wall distorted the LMs (Fig. S25). In addition to this, other external conditions, including the viscosity of the water pool and temperature of the water pool significantly affect the self-propulsion behavior of the LMs, as demonstrated in Fig. S26. On low temperature (5 $^\circ$ C) or at high viscosity (2.28 cP) water pool, the self-propulsion behavior is compromised because of limited evaporation of ethanol from LM or high drag force at viscous water pool. Thus, the current study systematically revealed the

various critical factors that control self-propelling behavior of non-sticking organic solvent droplets on water pool, which enabled the programming of the motion of LMs.

Finally, we demonstrate the ability of self-propelling LM in cargo transportation. In this relevance, LMs of water were used as cargo, and LM of ethanol was denoted as carrier. On placing a single carrier LM on the water pool having two cargo LMs, the carrier LM readily attached to the middle of two cargo LMs and displayed a circular motion (Fig. 7a-d). It continues to propel for more than 500 s with a circular trajectory—and it pulls the other two cargo LMs while moving on a circular path, as shown in Fig. 7g and Movie S8. Even a single carrier LM remained efficient in pushing three other cargo LMs for 400 s, as shown in Fig. S27. However, a single carrier LM failed to display self-propelling behavior in the presence of four cargo LMs, as shown in Fig. 7b, e, h and Movie S9 likely due to the inefficient power for pulling four cargo LMs. However, on the addition of two carrier LMs on the same experimental setup, a rotational motion with a smaller circumference was noticed, as shown in Fig. 7c, f, I and Movie S10. Thus, the current study not only demonstrated the programming of the self-propulsion behavior of LMs, but the transport of cargo is also successfully demonstrated using self-propelling LMs.

Conclusion

We discuss the effect of the solvent character on LM self-propulsion by summarizing our findings. This work studied the effect of the LM solvent on the self-propelling trajectory on a water pool. We first modelled the trajectory based on the linear bouncing model, which explains the dynamics of the LM's polygonal and circular motion. However, the trajectory was not monotonic – the self-propelling trajectory is bifurcated, whether random motion appears or not, depending on the water solubility of the solvent. The water solubility decides whether the condensed solvent diffuses into or remains on the water pool.

Moreover, the self-propelling driving force is not confined to the solute capillary but also extended to the non-solute capillary and electrostatic forces. The possible vapour-induced recoiling force cannot be neglected in this work. These mechanisms offered the idea of regulating the self-propelling trajectory by introducing the other solvents mixing to the inner liquid or water pool. Further, we found that the wall wettability also affects the trajectory. Classically, self-propelling trajectories are controlled by the “geometry” of the boundary.^[35] Thus, the wall wettability effect may potentially develop further regulation of the self-propelling materials. Overall, this work advances the fundamental understanding of self-propelling materials in terms of interface science and fluid mechanics.^[36-38]

Materials and Methods

The details of materials and experimental sections of this work are provided in SI Appendix.

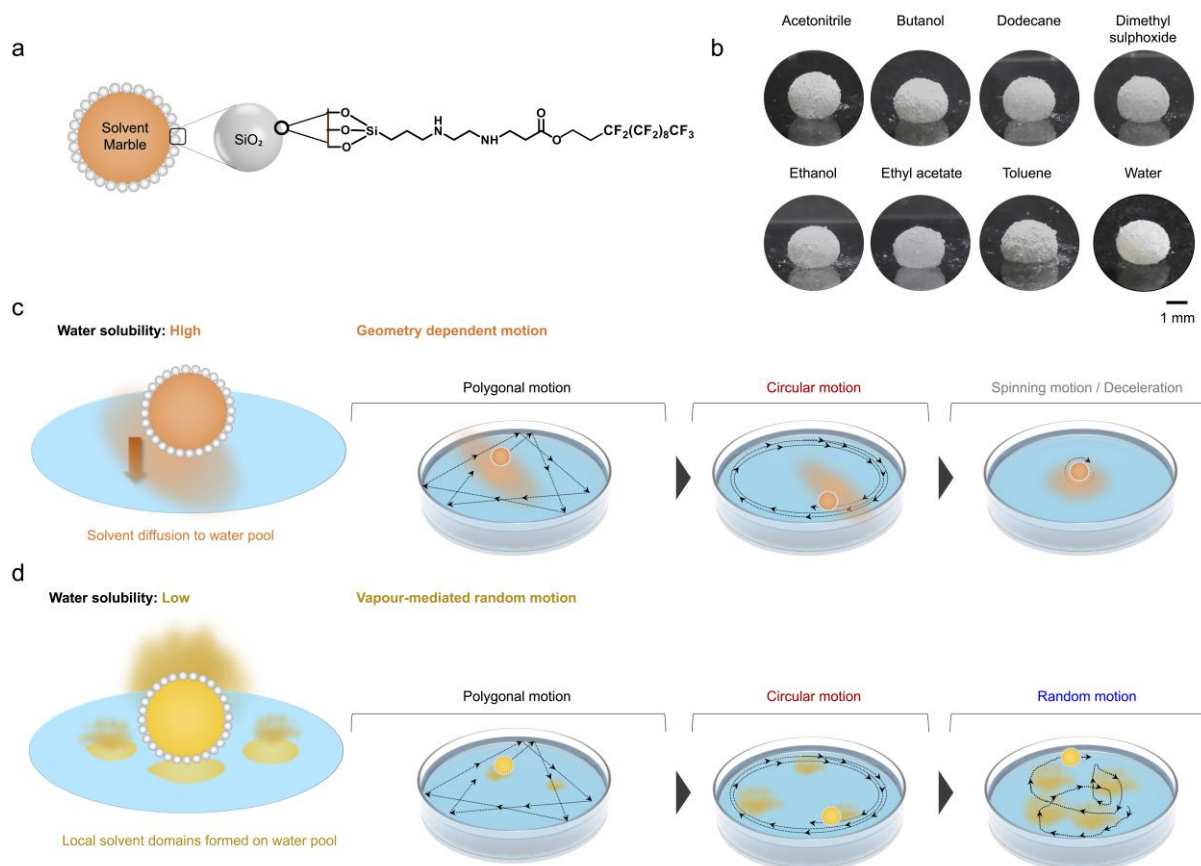


Figure 1. Self-propulsion of liquid marbles. a) Schematic illustration of liquid marble (LM) derived from omniphobic silica nanoparticles decorated with fluoroalkyl moiety through β -amino ester linkage. b) Digital images of LMs for encapsulated various aqueous and organic solvents. c-d) Schematic illustrating the trajectory of LMs propulsion on water pool depending on the selection inner liquids—that are either miscible (c) and immiscible (d) with water pool. Miscibility and diffusion of encapsulated solvents in water pool results in uniform and well-defined trends in motion trajectories—including polygonal, circular and spinning, whereas water immiscibility of inner solvent provides local solvent domains on water pool resulting in non-uniform motion trajectories.

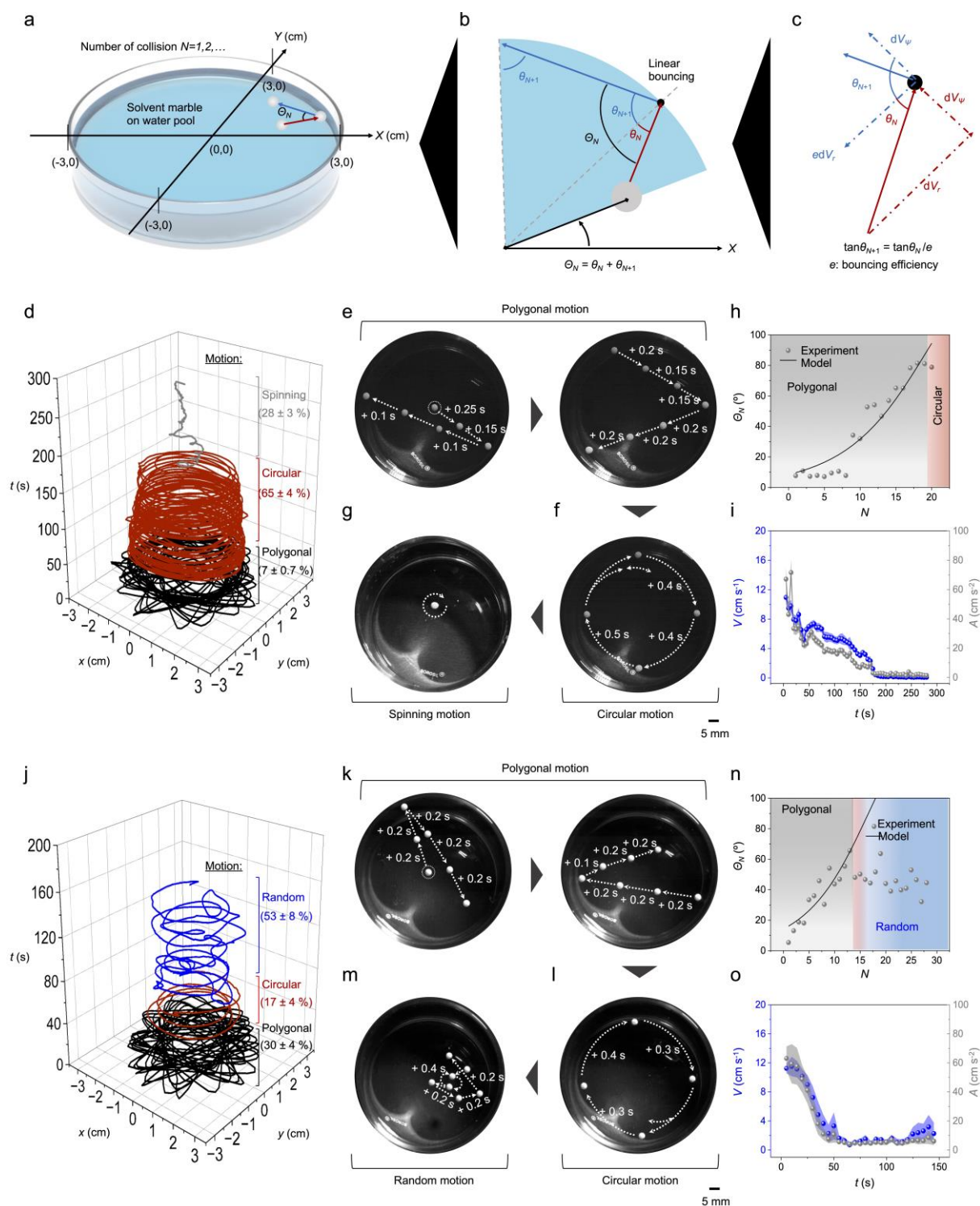
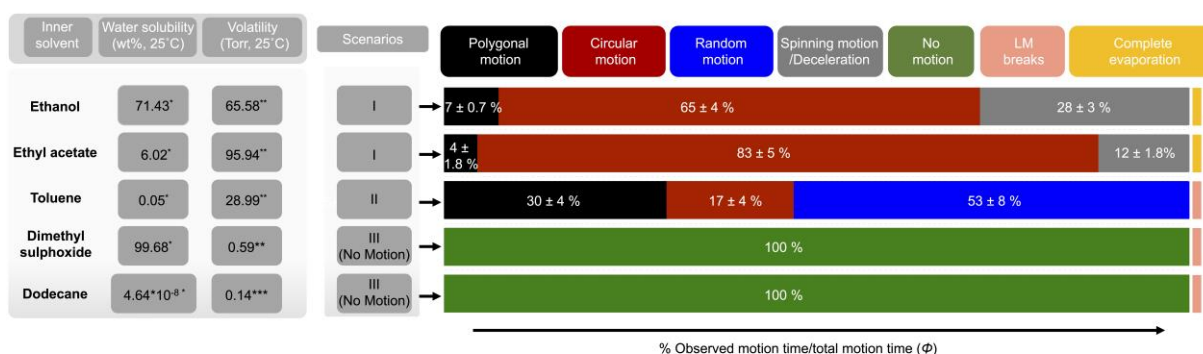


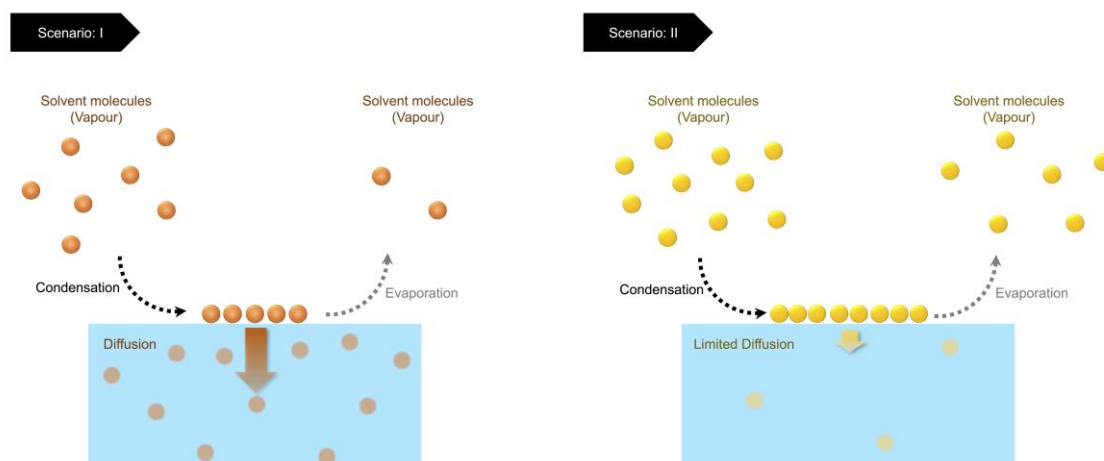
Figure 2. Kinetics and trajectory of LM propulsion. a-c) Schematic diagram depicting LM coordinates and bouncing angle (Θ_N) in relation to dimensions of the water pool. d,o) The three-dimension (3D) spatial reconstruction of change in LMs position with time for accounting polygonal (black), circular (red), spinning (grey) and random (blue) motion profiles for ethanol (d-i) and toluene (j-o) loaded LMs. e-g, k-m) Time lapsed high-speed digital images depicting the evolution in LM trajectory from polygonal (e) to circular (f) to spinning motion (g) for ethanol LM (e-g) and polygonal (k) to circular (l) to random (m) for toluene (k-m) LM (Volume

= 10 μ L). h, n) Graphs representing the change in bouncing angle (Θ_N) with each collision number for ethanol (h) and toluene (n) LMs on water pool (Volume = 10 μ L). i, o) Illustrating the alteration in speed (V) and acceleration (A) with time for ethanol (f) and toluene (o) LMs on water pool (Volume = 10 μ L). The error bar indicates the standard deviation with number of measurements, n=3 for each data point.

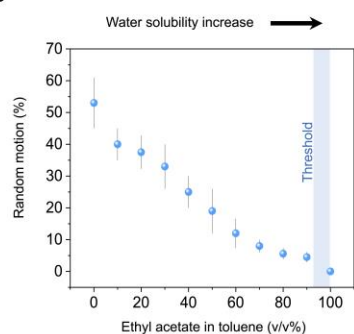
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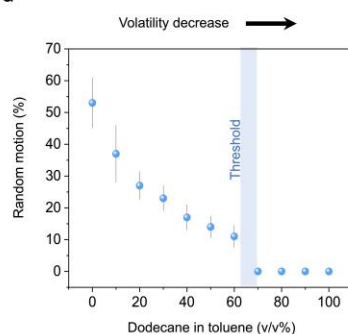
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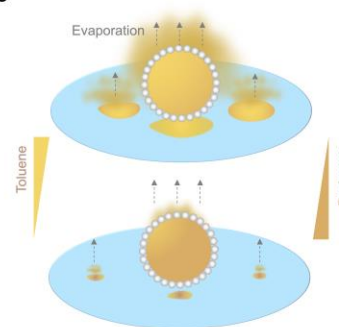


Figure 3. Influence of encapsulated solvents on LM motion trajectory. a) Accounting different scenarios for LM motions and related timescales of different motion trajectories adopted by different LMs depending on the physical properties of encapsulated solvents, where *, ** and *** indicate the data obtained from reference number 28, 29 and 30 respectively. b) Schematic depicting different scenarios of encapsulated solvent on water pools depending on the selection of solvents. While in the scenario I, water miscible volatile solvents molecule is likely to undergo condensation and followed by its subsequent diffusion into water pool, the water immiscible volatile solvents in the scenario II forms liquid domain on condensation because of its limited diffusion in the water pool. c-d) Graph depicting effect of solvent solubility in water (c) and volatility (d) on random trajectory in LM propulsion, where volume %

of ethyl acetate in toluene and volume % dodecane in toluene are gradually increased in respective binary solvent mixture to examine impact of water solubility and volatility on the time percent of observed random motion. e) Schematic illustrating the variation in solvent domains on water pool depending on composition of toluene and dodecane in their binary mixture. The error bar indicates the standard deviation with number of measurements, $n=3$ for each data point.

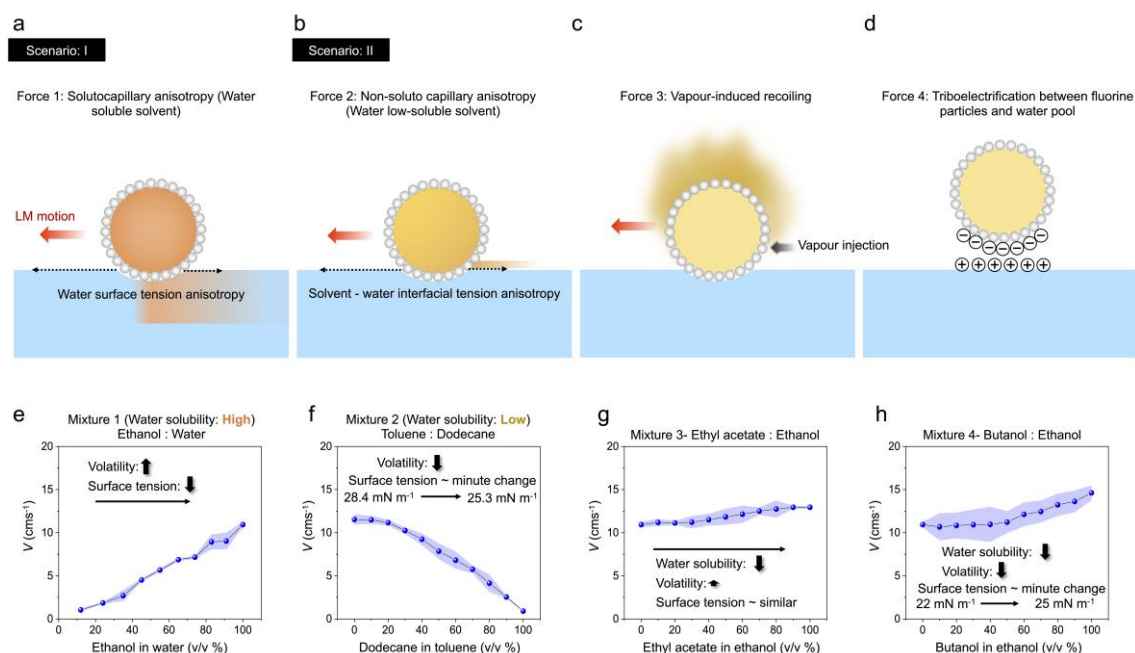


Figure 4. Plausible forces involve in self-propulsion of LM. a-d) Schematic depiction of different forces; solutocapillary force (a), non-solutocapillary force (b), vapour induced recoiling force (c) and Triboelectric force (d) acting on LM placed on water pool. e-h) Plots accounting the speed of self-propelling LMs encapsulated with different binary solvent mixture—including water: ethanol (e), toluene: dodecane (f), ethanol: ethyl acetate (g), and ethanol: butanol (h), where % of volume of selected solvents in their respective binary mixtures alters gradually. (Volume = 10 μ L). The error bar indicates the standard deviation with number of measurements, $n=3$ for each data point.

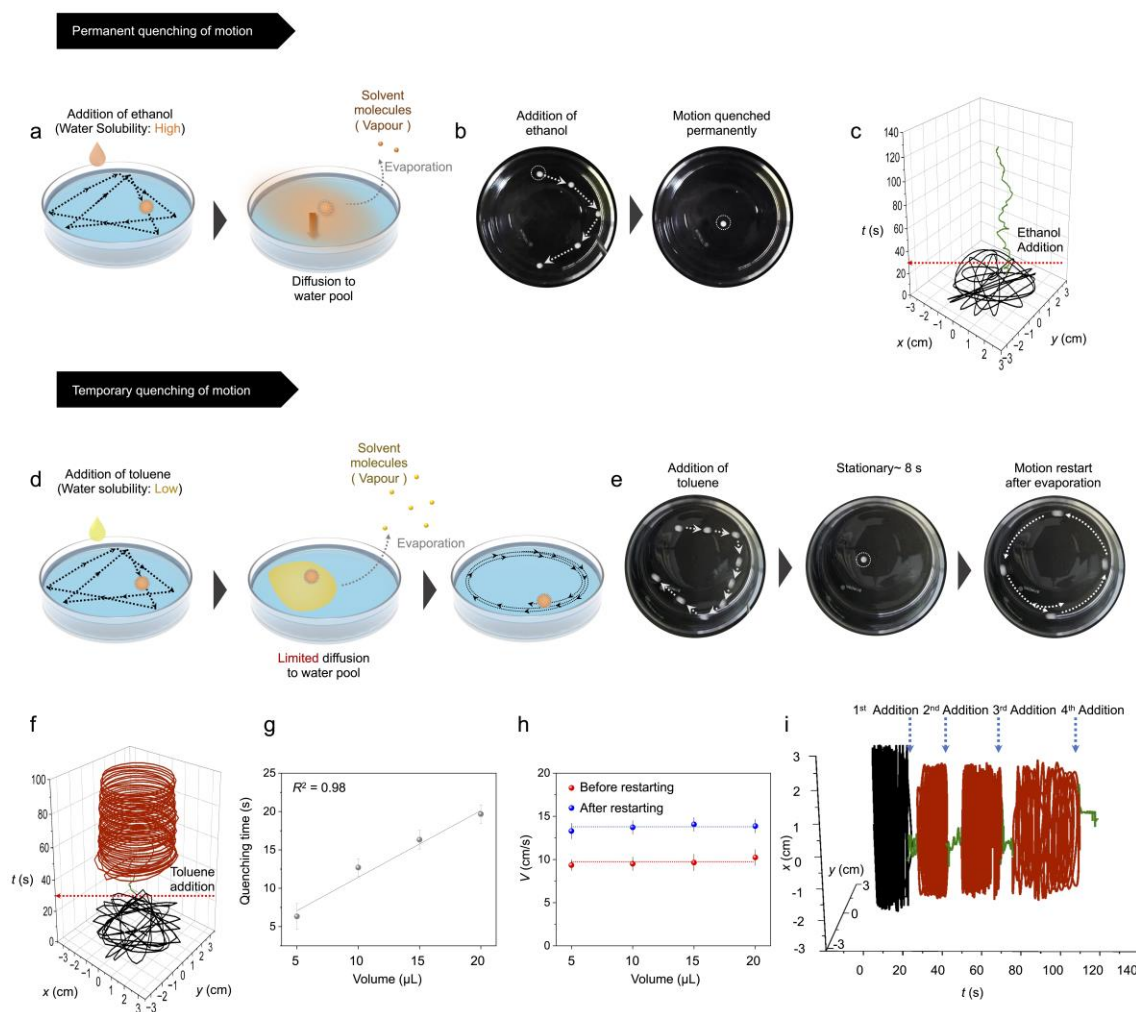


Figure 5. Programming the self-propulsion of LM. a) Schematic illustrating a permanent quenching of LM propulsion through external addition of ethanol to the water pool. Fast diffusion and distribution of ethanol across the water pool lowers the surface tension gradient, disrupting marble propulsion. b-c) Digital images (b) and 3D reconstruction of motion trajectory (c) accounting a permanent halting of LM propulsion after addition of ethanol externally to the water pool. The time of addition of ethanol is indicated by red dotted arrow. d) Schematic depicting a temporary quenching of ethanol-loaded LM propulsion by addition of toluene externally to the water pool. Toluene being water immiscible doesn't diffuse into water pool, rather forms a thin layer on air-water interface, disrupting LM propulsion temporarily. As this toluene evaporates, LM regains its motion. e) Digital images showing temporary halting of LM propulsion after a droplet of toluene is added externally to water pool. f) 3D reconstruction of motion profile for LM before toluene addition (black), immediately after addition (green) and after toluene evaporation (red). The red dotted arrow indicates the time of addition of toluene to the water pool. g) The plot accounting the gradual change in quenching time of LM

propulsion with different volumes of toluene added. h) Illustrating the speed of LM before quenching and after resuming its motion. i) The 3D plot depicting the motion trajectory for LM with sequential additions of toluene to the water pool. The error bar indicates the standard deviation with number of measurements, $n=3$ for each data point.

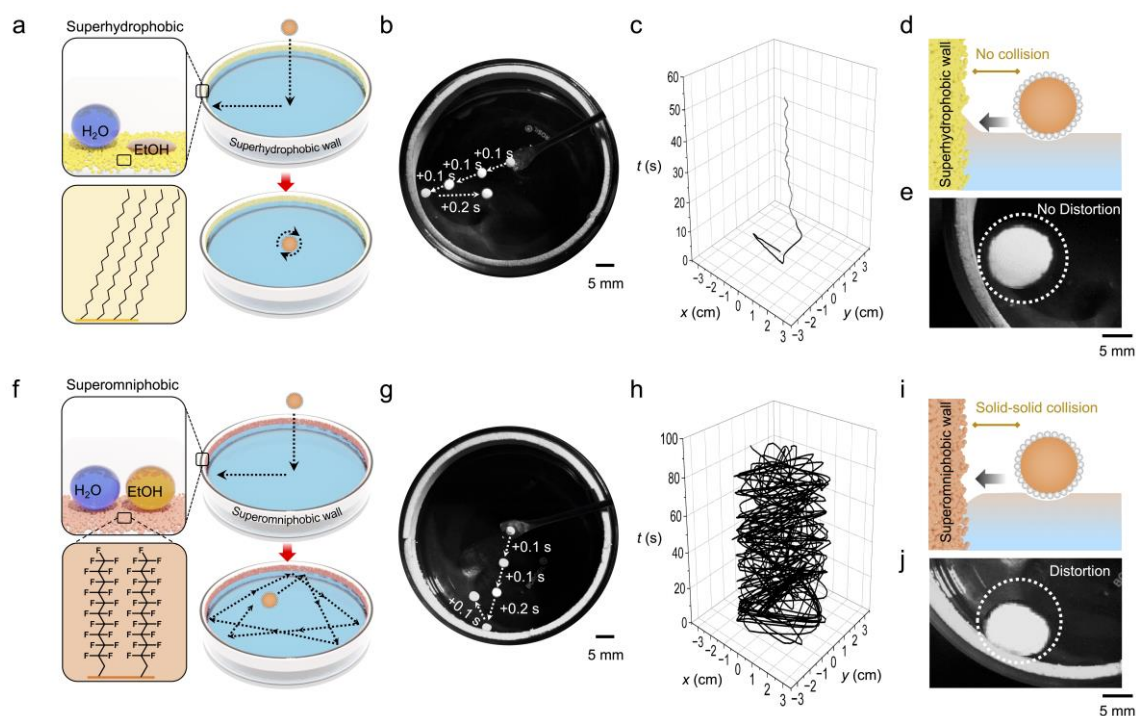


Figure 6. Effect of liquid wettability on LM propulsion. a) Illustrating the impact of superhydrophobic/superoleophilic walls on the water pool towards LM propulsion. b-c) Digital images (b) and motion trajectory (c) of LM on a water pool decorated with superhydrophobic/superoleophilic walls. d-e) Schematic (d) and digital image (e) showing no distortion of LM on collision with superhydrophobic/superoleophilic. f) Schematic illustration of superomniphobic walls for water pool to account motion of LMs. g-h) Digital image (g) and motion trajectory (h) of LM on water pool having superomniphobic walls. i-j) Schematic (i) and digital image (j) depicting distortion of LM on collision with omniphobically modified wall of the water pool.

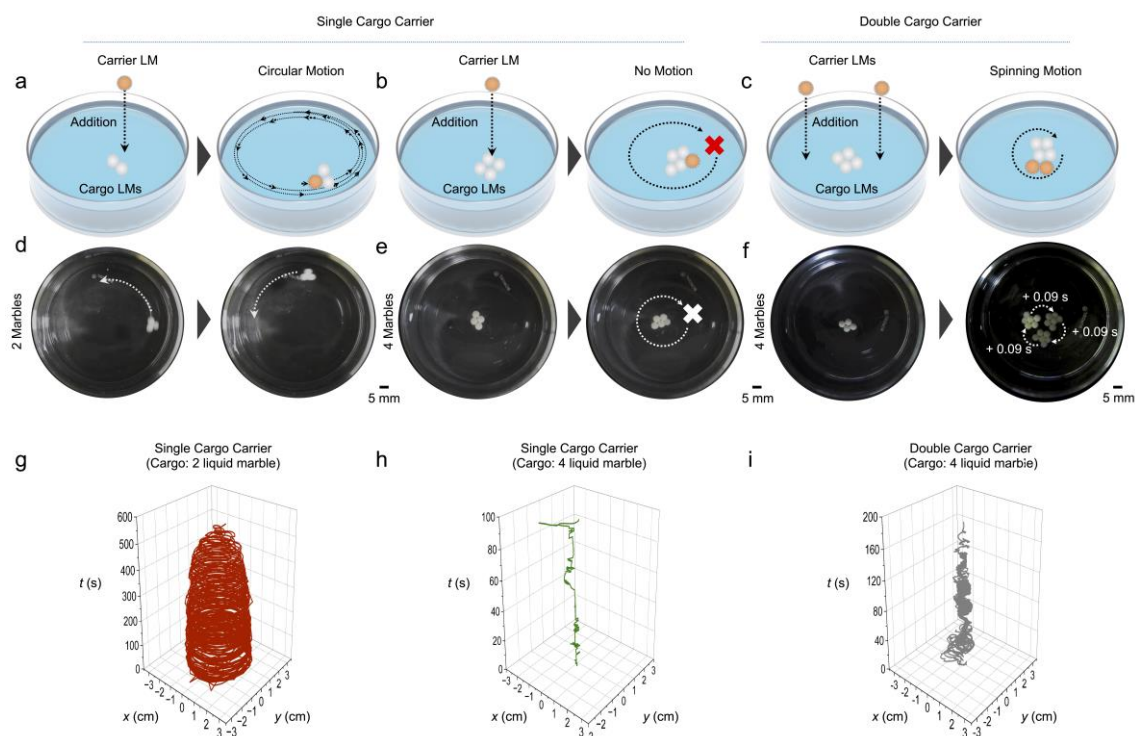


Figure 7. Self-propelling LM in cargo transportation. a-f) Schematic (a-c) and digital images (d-f) illustrating the cargo carrying ability by single (a-b) and double (c) self-propelling LMs (denoted as cargo carrier, encapsulated with ethanol). While single cargo carrier fails to carry four non-propelling LM (encapsulated with water), two cargo carrier displayed ability to displace four non-propelling LM. g-h) Motion trajectories of single (g-h) and double (i) cargo carriers with two (g) and four (h, i) non-propelling LM.

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Data availability

The data presented in this article are available from the corresponding authors on reasonable requests.

Competing interests

The authors have no competing interests to declare.

Supplementary information

The online version contains supplementary material.