Reconfiguring droplet interface bilayer networks through sacrificial membranes

Elio J. Challita, Michelle M. Makhoul-Mansour, and Eric C. Freeman^{a)}

*School of Environmental, Civil, Agricultural, and Mechanical Engineering,
College of Engineering, University of Georgia, Athens, Georgia 30602, USA*

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The droplet interface bilayer platform allows for the fabrication of stimuli-responsive microfluidic materials, using phospholipids as an organic surfactant in water-in-oil mixtures. In this approach, lipid-coated droplets are adhered together in arranged networks, forming lipid bilayer membranes with embedded transporters and establishing selective exchange pathways between neighboring aqueous subcompartments. The resulting material is a biologically inspired droplet-based material that exhibits emergent properties wherein different droplets accomplish different functions, similar to multicellular organisms. These networks have been successfully applied towards biomolecular sensing and energy harvesting applications. However, unlike their source of inspiration, these droplet structures are often static. This limitation not only renders the networks unable to adapt or modify their structure and function after formation but also limits their long term use as passive ionic exchange between neighboring droplet pairs may initiate immediately after the membranes are established. This work addresses this shortcoming by rupturing selected sacrificial membranes within the collections of droplets to rearrange the remaining droplets into new configurations, redirecting the droplet-droplet exchange pathways. This is accomplished through electrical shocks applied between selected droplets. Experimental outcomes are compared to predictions provided by a coupled mechanical-electrical model for the droplet networks, and then advanced configurations are proposed using this model. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5023386>

INTRODUCTION

The droplet interface bilayer (DIB) technique has rapidly gained popularity as a platform for studying membrane transport mechanics and for developing biologically inspired smart materials and microdevices.^{1–4} Highly tailorable and robust, this technique allows for the construction of lipid bilayers between aqueous droplets in an oil reservoir with dissolved lipids, providing a self-assembled collection of lipid bilayer membranes at the intersections of lipid-coated droplets.⁵ The droplets gradually acquire a lipid coating once they are immersed in a lipid-oil medium, where the phospholipid molecules form monolayers at the water-oil interfaces. When two lipid-coated aqueous droplets are brought into contact, the oil in the surrounding medium is gradually expelled, and the ordered lipid monolayers adhere together into a lipid bilayer membrane.^{6,7} This bilayer provides a suitable scaffold for the reconstitution of stimuli-responsive biomolecules, thus allowing for applications such as biosensing⁸ and osmotic actuation⁹ through the controlled exchange of fluid and ions between the droplets.

Without transporters, these lipid-based membranes are nearly impermeable to ions. A widely accepted electrical representation for these membranes is the Hodgkin-Huxley model,¹⁰

^{a)}Present address: 137 Riverbend Research North, 110 Riverbend Road, Athens, GA 30605, USA. Electronic mail: ecfreema@uga.edu.

where a single DIB is represented as a capacitor in parallel with a variable resistor representing the selective transport.¹¹ Consequently, any electrical potential applied across a web of DIBs will be divided across multiple membranes governed by the relative dimensions and locations of the bilayer interfaces. These membranes are also dynamic¹² and their equilibrium dimensions are dictated by the balance of monolayer and bilayer tensions at the point of contact as shown in Fig. 1.¹³ This enables a response to mechanical constraints which has been demonstrated in the literature, both for the regulation of the adhered membrane area¹⁴ and the development of biological mechanosensors.^{12,15–17}

While a single bilayer is suitable for biophysical studies of membrane properties and transport,^{17–20} a unique strength of the DIB technique lies in its scalability. By connecting multiple droplets,^{3,4,11,21} larger DIB networks may be formed. These networks exhibit emergent properties,²² where the observed response of the network is controlled by the gradual collective exchange of contents between neighboring droplets within the network. As an example, it is possible to set some initial gradient within the DIB network that powers the network functionality for applications such as osmotic actuation^{3,13} and the creation of biologically inspired batteries.²³ A downside to this methodology is that once the network is formed, diffusion will initiate between the neighboring droplets and the stored energy will begin to gradually dissipate. This introduces complications when developing droplet-based materials for long-term use, since the majority of DIB applications use static architectures that do not change over the material lifespan. Living cellular organisms circumvent this in part by constantly reshaping and adapting their membrane architecture, which has yet to be incorporated into a DIB platform.

A proposed solution for these static DIB network architectures is the use of selective droplet coalescence, where targeted membranes are ruptured to trigger the network reconfiguration. The structure of the adhered network as a whole obeys classical droplet mechanics and will seek new equilibrium configurations once a membrane is removed. This leads to a rearrangement of the droplets and may be used to form or separate existing membranes or complete pathways for transport as shown in Fig. 2. Selective membrane collapse has already been used to facilitate mixing between two droplets¹⁸ for similar applications, but has not been applied towards larger droplet networks.

To study the mechanics of the DIB network reconfiguration through coalescence, clusters of droplets will be created and allowed to adhere into networks. The interfacial membranes within these structures will then be selectively ruptured through an electrical pulse, causing a redistribution of the fluid volume and adjustment of the remaining droplets. A model is proposed based on the minimization of the interfacial energy to capture these reconfiguration events and will be validated against experimental results. The goal of this work is identifying methods for the droplet network reconfiguration to enable on-demand release of the stored internal gradient.

FIG. 1. A lipid membrane can be formed at the interface of two nanoliter lipid-coated aqueous droplets in an oil reservoir. This membrane may be approximated as a capacitor in parallel with a high-impedance resistor whose dimensions are dictated by the balance of surface tensions at the surrounding annulus. At equilibrium, the bilayer tension is balanced by two equal monolayer tensions at the bilayer center-line with an angle θ as shown. When multiple droplets are brought together, more complex DIB structures are formed. This is accomplished through ferrofluids in this work, collecting the droplets together using a permanent magnet and allowing them to adhere. The scale bar is $800\ \mu\text{m}$.

FIG. 2. Cross-sectional schematic of microdroplets with adhered interfaces. Green interfaces indicate lipid membranes with available pores for transport. While “bare” membranes provide an impermeable barrier to most species, restructuring the network by coalescing the rightmost two droplets allows for pore insertion in the remaining membrane. This enables passive diffusion between the remaining adjacent droplets post-coalescence.

MATERIALS AND METHODS

Ferrofluids

A ferrofluid solution was used to easily manipulate the droplets into networks.²⁴ Ferrofluids solutions are stable colloidal suspensions of magnetic nanoparticles coated with a surfactant to prevent aggregation within a carrier fluid.²⁵ Ferrofluid droplet motion may be guided through externally applied magnetic fields. The ferrofluid solutions used in this work consisted of a stable aqueous suspension of magnetite ($\gamma\text{-Fe}_2\text{O}_3$)²⁴ with a nanoparticle concentration of 0.46% by volume. 250 mM Potassium Chloride (KCl, Sigma-Aldrich, St. Louis, MO) and 10 mM 3-(N-morpholino) propanesulfonic acid (MOPS, Sigma-Aldrich, St. Louis, MO) salts were added. Solutions were systematically filtered (Sterile Syringe Filter 0.2 μm PES, VWR) and sonicated prior to each use for a minimum of 20 min to ensure homogeneity. Previous research has established that these ferrofluids are compatible with DIB networks and minimally influence the membrane properties.²⁴

Lipid solutions

The lipid-out technique was used in this work, dissolving the lipids in the oil phase.²⁵ Zwitterionic lipids (1,2-diphytanoyl-sn-glycero-3-phosphocholine (DPhPC), Avanti Polar Lipids, Alabaster, AL) were dissolved in a 1:1 (volume: volume) mixture of silicone oil AR20 and hexadecane oil (Sigma-Aldrich, St. Louis, MO) at a concentration of 0.5 mg/ml throughout all of the experiments. Hexadecane was used as a solvent in order to minimize the amount of oil retained in the bilayer upon membrane formation,²⁶ while silicone oil AR20 was mixed with it to enhance the stability of the bilayer, reduce gravitational effects,³ and reduce the monolayer formation time as shown in the literature.²⁷ All lipid-oil solutions are sonicated (Avanti Sonicator, Avanti Polar Lipids, Alabaster, AL) upon fabrication and before each experiment. Solutions were stored at 2–8 °C when not in use.

EXPERIMENTAL METHODOLOGY

DIB network formation

The tip of a pulled pipette (KWIK-Fil Borosilicate Glass Capillaries, World Precision Instruments, Inc.) filled with the previously described ferrofluid solution was introduced into a Sylgard 184 (Dow Corning Corporation, Midland, MI) Silicone Elastomer Base (PDMS) (13:3 v:v ratio of base to curing agent) dish comprised of a 15 mm diameter circular hole at the center of a 30 mm square surface. Ferrofluid droplets of equal diameter (800 μm) were systematically injected into the solution using a pressure-based injector (FemtoJet 4i, Eppendorf, Hauppauge, NY). After allowing time for lipid monolayer formation at their oil-water interfaces, droplets were collected by a permanent magnet. The droplets were gradually drawn together and bilayers spontaneously formed at their interfaces as they came into contact

creating a simple tightly packed hexagonal-shaped DIB network as shown in Fig. 1. After membrane formation, the magnet was removed, and the droplets retained their connected framework. This approach allowed for the rapid creation of hexagonally packed DIB networks.

The electrical properties of the network were measured using agarose-coated (2% by weight EZ Pack Agarose LE, Molecular Biology Grade, Benchmark Scientific, Sayresville, NJ) silver/silver-chloride (Ag/AgCl) electrodes (125 μm in diameter, GoodFellow, Coraopolis, PA) mounted on three-axis manual micromanipulators (Siskiyou, Grants Pass, OR). Upon network formation and magnet removal, the electrodes were introduced into the desired droplets. Failure in these networks was induced by applying a 1 V electrical impulse to the desired failure locations in the networks causing an instantaneous rupture of select membranes through electroporation.²⁸

DIB NETWORK MECHANICS

The goal of this work is to explore the dynamic reconfiguration of DIB networks when specific droplet pairs coalesce due to the electrical pulse. The coalescence of two previously distinct droplet volumes generates a shift in the network configuration and may be used to study the change in network behaviors. A two-component model is necessary to capture the electrical properties of the DIB network as well as the configuration post-coalescence.

The mechanical properties of emulsive systems are often described as the summation of the interfacial energies, or the product of the total surface areas multiplied by the corresponding surface tension.^{29,30} A classical DIB system is mainly defined by two surface tensions $\gamma_{\text{monolayer}}$ and γ_{bilayer} , where $\gamma_{\text{monolayer}}$ refers to the monolayer surface tension and γ_{bilayer} refers to the bilayer surface tension as shown in Fig. 1. The total interfacial energy in a DIB network may be approximated as the sum of the interfacial tensions and their areas $A_{\text{monolayer}}$ and A_{bilayer}

$$E_{\text{DIB}} = \gamma_{\text{monolayer}} A_{\text{monolayer}} + \gamma_{\text{bilayer}} A_{\text{bilayer}}. \quad (1)$$

The equilibrium configuration may be found as the minimization of the total energy with the volume of the fluid as a constraint. This leads to the formation of the lipid bilayer membranes if the energy of adhesion is positive,^{26,31,32} defined in DIBs as

$$\Delta F = A_{\text{bilayer}} (2\gamma_{\text{monolayer}} - \gamma_{\text{bilayer}}). \quad (2)$$

This equation describes the change in interfacial energy when replacing two lipid monolayers with a single lipid bilayer. According to parametric studies on DIB configurations, this value is optimized in cases with a 1:1 hexadecane/silicone oil AR20 mixture.²⁶

The ratio of the equilibrium bilayer area with respect to those of the monolayers is governed by the contact angle between the droplets (θ_m)¹³ (Fig. 1) resulting from the balance of tensions at the annulus of contact. As the DIB is formed, the monolayers exert a tension on the interfacial membrane, causing it to grow and expand. This continues until the tension in the bilayer reaches its equilibrium value dictated by the monolayer tensions as shown in Eq. (3)

$$2\gamma_{\text{monolayer}} \cos(\theta_m) = \gamma_{\text{bilayer}}. \quad (3)$$

Surface evolver model

Based on the observed properties of the droplet network, the network's equilibrium structure may be approximated by minimizing the interfacial energies with constant volume constraints.³⁰ However, the equations generated for adhered droplets generally do not allow for an analytical solution, so numerical approximations are necessary.

To this end, the open-source computational software Surface Evolver³³ was used to predict the equilibrium shapes of the droplet clusters. An initial approximation of the droplet surfaces is provided, and the software seeks to find the lowest interfacial energy configuration available

TABLE I. Surface evolver model inputs.

Variable	Value	Source
Fluid phase density	1007 kg/m ³	Measured
Oil phase density	890 kg/m ³	Measured
Monolayer surface tension	1.12 mN/m	Calibrated ^{24,26}
Bilayer surface tension	1.825 mN/m	Calibrated ^{24,26}

with the given constraints. DIBs were approximated in this software by defining their adhered interfaces, relative density, fluid volumes, and interfacial tensions. While Surface Evolver provides a suitable platform for studying coalescence events in networks of DIBs, it can only predict the equilibrium state of the system, i.e., it cannot capture the momentum of the droplets or the mechanics of membrane creation. Therefore, the results obtained may be used to guide the development of these membrane clusters with some limitations.

Surface evolver model initialization

In DIB networks, the droplets often adapt a hexagonally packed geometry. Experimental results obtained for seven ferrofluid droplets demonstrated this as shown Fig. 1. Dodecagonal prisms are the most efficient at capturing the final configuration of hexagonal packing and thus were used to present the initial conformation of the droplets. The monolayer and bilayer surface tensions and the specific gravity considered in the model are shown in Table I, and an example of a converged solution is shown in Fig. 3. Monolayer and bilayer surface tensions were determined by comparing the experimental results and model predictions and are well within the expected ranges for this DIB configuration.^{24,26}

Droplet coalescence was simulated by setting the collapsed interface's tension to zero, effectively removing the interface from energy minimization considerations [Eq. (1)]. This allows the interface to deform and expand freely as needed with no cost. The volumes of the coalesced droplet pair are consequently combined, and the zero-tension interface allows the coalesced droplets to form one larger droplet. The surrounding droplets rearrange into a new equilibrium, allowing for the network reconfiguration.

Electrical circuit models for DIB networks

The failure mechanism selected for this study is coalescence through electroporation, or exceeding the voltage threshold necessary for membrane failure. Recall that single DIB membranes without embedded channels may be approximated as a capacitor in parallel with a high amplitude resistor.^{11,34,35} The balance of the resistances in the aqueous phases and across the

FIG. 3. The ferrofluid droplets were modeled as dodecagonal prisms elements in the Surface Evolver. The resulting droplet morphologies after minimization of the interfacial energies match experimental observations.

FIG. 4. The electrical model for a single membrane consists of a capacitor and resistor in parallel. This stencil may be combined into larger networks to produce linear systems of differential equations describing the voltage drop across each membrane with prescribed boundary conditions.

membrane allows for a simplified model at low frequencies of operation where the resistance of the aqueous phases is ignored³⁴ as shown in Fig. 4. The membrane capacitance and conductance both scale with the area of the membrane, and values for the specific capacitance and conductance are obtained from the literature as shown in Table II.

The bilayer dimensions are exported from the Surface Evolver predictions and the membrane dimensions are assumed constant up until failure with no electrowetting,^{26,37} providing an electrical approximation of the DIB network using the per-area values in Table II. The current through the membrane may be calculated using Eq. (4), where G_m is the membrane conductance, C_m is the membrane capacitance, and dV/dt is the change in the transmembrane voltage with respect to time. The voltage values are the voltage drop across the membrane that require the two nodal values on either side of the interface. Kirchhoff's current law is employed for each droplet to write a balance of current thus creating a linear system of differential equations for the nodal voltages, one value for each of the droplets within the cluster [Eq. (4)]. This system of differential equations is solved using ode15s in MATLAB. The model results for the nodal voltages show how the voltage is divided across each individual membrane, predicting the likely path of failure under an electrostatic load

$$[C]\left\{\frac{dV}{dt}\right\} + [G]\{V\} = 0. \quad (4)$$

Current is estimated by calculating the necessary current to charge the membranes to the clamped voltage. Distribution of the voltage across the membrane network is influenced by the location of the electrodes, configuration of the membranes, and their relative interfacial areas. These may be tuned to accomplish selective destruction of the sacrificial membranes, altering the network shape.

TABLE II. Circuit model inputs.

Variable	Value	Source
Bilayer specific capacitance	$0.583 \mu\text{F}/\text{cm}^2$	Ref. 24
Bilayer specific conductance	$0.14 \mu\text{S}/\text{cm}^2$	Ref. 36

Model validation

With the coupled electrical-tension model established, it is possible to predict the most likely chain of failure in a droplet network with the application of a voltage and the network configuration post-failure. Four different cases were examined to test the hypotheses and demonstrate network folding. Each case is built on the seven-droplet structure as seen in Fig. 3, as this structure was easily achieved using the ferrofluid droplets.

The first case is shown in Fig. 5, where the applied voltage impulse spanned across the central droplets. The coupled model predicted that the most likely path of failure occurred between the electrodes, matching the experimental observations. Once the central membranes were ruptured by the voltage impulse, the collection of droplets adapted a new configuration, matching the configuration predicted by the Surface Evolver.

To further compare the model predictions against experimental data, a triangle wave voltage is simulated in the model and the resulting square-wave current is compared against experimental data [Fig. 5(d)]. The tensions are calibrated to provide a match with the experimental data, and the resulting values are shown in Table I. All of these values are appropriate and fall within the expected ranges for ferrofluid DIBs²⁴ in this particular solvent.

This process was repeated for a case where the path of failure was set to occur across the outer ring of the hexagonal-packed droplet structure (Fig. 6). In this particular instance, the rupture pathway was stochastic, alternating between the central droplets and the outer droplets. This prediction was also shared by the model, showing that the voltage drops across the two membrane pathways were equivalent. The configuration post-coalescence matches as well. Interestingly, when failure occurred across the outer droplet ring, the adhesive forces between the droplets caused the outer droplet ring to contract and compress the central droplets. Since the density of the oil mixture is similar to the density of the aqueous droplets and the selected

FIG. 5. Comparison between model predictions and experimental results for failure across the central line of a hexagonally packed structure. (a.1) Initial configuration—electrode locations are marked. (a.2) The application of the voltage spike resulted in the coalescence of the three central droplets. (b.1) The predicted Surface Evolver configuration of the initial set of droplets. (b.2) The predicted configuration after rupturing the membranes. (c) Likely path of failure predicted by the electrical model. (d) Comparison of experimentally measured current (black) and current predicted by the model (red) with the inputs from Tables I and II prior to membrane coalescence. Scale bars are 800 μm .

FIG. 6. Comparison between model predictions and experimental results for failure across the outer ring of a hexagonally packed structure, demonstrating two possible coalescence pathways. (a.1) Initial configuration—electrode locations are marked. (a.2) and (a.3) Configurations after coalescence. (b.1) The predicted Surface Evolver configuration of the initial set of droplets. (b.2) and (b.3) The predicted configuration after rupturing the membranes. (c) Likely paths of failure predicted by the electrical model. Comparison of experimentally measured current (black) and current predicted by the model (red) with the inputs from Tables I and II prior to membrane coalescence. Scale bars are $800\text{ }\mu\text{m}$.

oil mixture maximizes the energy of adhesion,²⁶ the collapsed 2D structure is able to elevate the central droplet to accommodate the ring contraction [Fig. 6(a.3)]. This may provide an opportunity for folding planar DIB structures into 3D structures when gravitational effects are minimized.

The current is compared again in a similar fashion to the procedure described for Fig. 5. The same values (Tables I and II) used for calibration (Fig. 5) are employed as these studies were taken for the same ferrofluid and lipid solutions, and a match is produced between the experimental data and model predictions. This provides further assurance that the Surface Evolver model is appropriate for predicting the equilibrium configurations of DIB networks, and that the membranes formed in the experimental work are similar to membranes produced in the past.

Two additional cases are summarized in Fig. 7. As before, the predicted morphologies post-coalescence and paths of coalescence match the experimental results, illustrating the effectiveness of the Surface Evolver approach for predicting the DIB network configuration.

DISCUSSION OF EXPERIMENTAL COMPARISONS

From the preliminary results, the failure of designated sacrificial membranes results in an intuitive contraction of collapsed droplets. This contraction effectively redistributes the remaining attached droplets and demonstrates the capability to fold a two-dimensional network into a three-dimensional structure as shown in Fig. 6. It should be noted that this behavior is dependent on the DIB composition—if for example hexadecane alone was used as the oil phase, the energy of adhesion would be diminished, gravitational forces will increase, and the droplets would likely separate rather than fold together.²⁶

MODEL EXTENSION

With the model validated against experimental data for both the mechanical (Surface Evolver via equilibrium configurations) and electrical (capacitor-resistor approximation via

FIG. 7. Two additional comparison cases. (a.1) and (a.2) Initial configuration—electrode locations are marked. (a.3) and (a.4) Configuration post coalescence. (b.1) and (b.2). The predicted configurations after rupturing the membranes. (c.1) and (c.2) Likely paths of failure predicted by the electrical model. Scale bars are $800\ \mu\text{m}$.

membrane failures and measured currents) components, the next step is to investigate how these sacrificial membranes may be employed to allow for changes in larger DIB networks.

The mechanics of droplet coalescence are relatively simple for a single DIB as shown in Fig. 8. As the membrane fails, the two spherical caps collapse together, causing a contraction of the droplet heights and an expansion along the formerly adhered interface. The equations for this collapse may be written as a function of the contact angle as shown in Eq. (5), with a necessary assumption that the droplets will behave as spherical caps with a constant volume per droplet Vol . If the droplets coalesce, the contact angle is effectively 90° as predicted by the modified Young's equation [Eq. (3)] and the radius R increases, while the cap height h is reduced, causing simultaneous contraction and expansion as shown in Fig. 8(b)

$$R = \left(\frac{3Vol}{\pi(\cos \theta + 1)^2(2 - \cos \theta)} \right)^{\frac{1}{3}},$$

$$h = \left(\frac{3Vol}{\pi(\cos \theta + 1)^2(2 - \cos \theta)} \right)^{\frac{1}{3}} (1 + \cos \theta).$$
(5)

This coupled contraction-expansion mechanic adequately describes the observed behaviors in the collapsed networks. However, there are limitations to this—these droplets are effectively

FIG. 8. The droplets in a single DIB may be approximated as two spherical caps with a shared interface. It is possible to directly write functions for h and R as functions of θ_m and Vol by assuming this geometry and constant droplet volumes. Setting the contact angle θ_m to 90° produces a coalesced droplet pair as shown in (b).

soft particles and are capable of adapting non-spherical configurations if necessary. The assumption of spherical cap geometry, while useful, is not always valid due to the droplet-droplet adhesion.

This was demonstrated previously in several DIB studies,^{12,17,38} where two droplets were compressed together to regulate the size of the adhered interface. Here, external constraints are provided, forcing the droplets to adapt non-spherical configurations. While equations for compressed droplets have been derived assuming non-wetting conditions,³⁰ these are inappropriate for DIBs and computational methods such as the Surface Evolver are necessary for determining the configurations under these constrained conditions.

Constraining a droplet shows a net increase in the total interfacial energy even as the interfacial tensions remain unchanged (Fig. 9) through increases in the surface area. Transient changes in the monolayer tension upon droplet deformation are expected due to the increase in the area per lipid,^{38–40} but this is also self-correcting and the tension will return to the equilibrium value given enough time. This represents a resistance to the deformation, demonstrating that while the droplet may be deformed it will exert a restitution force towards regaining the equilibrium spherical shape. In addition, if the adhered droplets are pulled apart there is a point where the droplets will separate entirely and regain a spherical shape without the adhesive membranes. This was simulated for three solvents (Hexadecane, Decane, and 1:1 Hexadecane/Silicone Oil AR 20) using values for the interfacial tensions from Taylor and Sarles²⁶ as shown in Fig. 9, plotting the change in interfacial energy for a single droplet with two adhered interfaces as a function of distortion from equilibrium. DIBs in solvents that provide greater adhesion energies show a much greater elasticity and resistance to separation as the droplet is compressed or pulled apart.

While each droplet connection may be loosely approximated as a spring, these springs are also capable of disconnecting once the droplets are sufficiently separated. As the droplets elongate, the total interfacial energy gradually approaches that of a spherical droplet with no adhesive membranes, or $E_{DIB}/E_{sphere} = 1$. Once the interfacial tension reaches the same value as an unattached droplet, separation occurs. Therefore, it is possible to tailor a coalescence event that causes contraction in the droplet network where certain adhesive interfaces or transport bridges are removed, reshaping the surrounding droplets.

This elasticity of the droplets must be considered in the framework of larger networks as well where the entire network adapts a mutually agreeable configuration. Combining the observations from Figs. 8 and 9 predicts that coalescence will generate a combination of forces in the contracting and expanding directions as the coalesced droplet attempts to expand to a spherical configuration. In networks, the balance of adhesive forces between the droplets will restrict

FIG. 9. A single droplet within a DIB chain is constrained uniaxially and the change in energy divided by the energy of a single spherical droplet is plotted for three different solvents as a function of the deviation from equilibrium divided by the spherical radius of the droplet. It is shown that the more favourable the formation of the membrane, the greater the resistance to deformation and the greater range of deformation prior to separation. As the droplets are elongated, the membranes are separated when the total interfacial energy surpasses or equals that of a single unattached droplet, where $E_{DIB}/E_{sphere} \geq 1$.

FIG. 10. While rupturing a single droplet pair is intuitive, larger networks behave as balanced structures and seek the minimum interfacial energy for the entire network. In this new structure, certain droplets are distorted away from equilibrium (red), while others achieve a more favourable configuration (green).

this motion. As shown in Fig. 10, a small coalescence event in the center of a tightly packed DIB network results in a minor change at the outer boundary—while the coalesced droplets do exert a force on their surrounding neighbors, they are not able to resume a spherical shape. The droplets that border the coalesced group are distorted from their ideal shapes, while the deformational impact is diminished as we move further from the center. Figure 10(b) is color-coordinated to reflect which droplets experienced a substantial reduction in their interfacial energies (green, more favorable) or substantial increase (red, less favorable). The outcome is a new droplet configuration which minimizes the overall energy yet still requires distortion of select regions within the droplet cluster. The limits of this distortion is governed by the balance of interfacial tensions according to Fig. 9. If a less favorable solvent is used, separation of the adhered droplets occurs.

Two additional example cases are presented in Fig. 11. Here, the coalescence of a larger collection of monodisperse droplets within the center of the network generates a contraction event. This forces the outer droplets to accommodate the new constraints, causing separation of several membranes as predicted in Fig. 9. In some cases, the resulting droplet motion post-separation allows for the formation of new membranes as droplets come into contact [Fig. 11(b.2)]. These behaviors are capable of initiating the exchange between neighboring droplets on demand, providing a methodology for enabling the DIB network functionality post-formation. As DIB complexity continues to increase, this will allow for dynamic droplet networks that are capable of changing configuration on demand.

CONCLUSIONS

The droplet interface bilayer (DIB) technique is used to form complex networks of aqueous compartments joined by biological membranes. The configuration of such networks is dictated

FIG. 11. Two example cases showing the evolution of a network post formation. Red symbols mark membranes that are selectively ruptured and green symbols indicate locations where new membranes may form after network coalescence—the creation of new interfaces is not feasible in Surface Evolver. These examples demonstrate the ability to fold the network into new configurations through tailored destruction of interfacial membranes.

by the minimization of the interfacial energies present within the adhered droplet morphologies. As a result, any changes in the properties of these networks or in the external mechanical constraints will cause the entire network to shift in search of a new equilibrium. This gives control over the membrane interfacial areas which may be tuned accordingly.

Here, the reconfiguration of droplet networks was examined through a coupled mechanical/electrical framework. The results demonstrated that a DIB network is capable of dramatically changing its transport properties through controlled membrane collapse—changes in one region of the DIB cluster also influence the equilibrium configuration through the adhesive properties of the droplet interfaces. In this study, failure was controlled through an applied voltage shock, but there are many other avenues available for selective collapse. This selective coalescence allows for the reconfiguration of droplet networks, which will allow for on-demand activation of DIB functionalities.

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