

Liquid morphologies and capillary forces between three spherical beadsCiro Semperebon,¹ Mario Scheel,^{1,2} Stephan Herminghaus,¹ Ralf Seemann,^{1,3} and Martin Brinkmann^{1,3,*}¹*Max-Planck-Institute for Dynamics and Self-Organization, Am Fassberg 7, D-37077 Göttingen, Germany*²*Synchrotron Soleil, L'Orme des Merisiers, Saint-Aubin, F-91190 Gif-sur-Yvette, France*³*Experimental Physics, Saarland University, D-66123 Saarbrücken, Germany*

(Received 24 December 2015; revised manuscript received 2 May 2016; published 29 July 2016)

Equilibrium shapes of coalesced pendular bridges in a static assembly of spherical beads are computed by numerical minimization of the interfacial energy. Our present study focuses on generic bead configurations involving three beads, one of which is in contact to the two others while there is a gap of variable size between the latter. In agreement with previous experimental studies, we find interfacial “trimer” morphologies consisting of three coalesced pendular bridges, and “dimers” of two coalesced bridges. In a certain range of the gap opening we observe a bistability between the dimer and trimer morphology during changes of the liquid volume. The magnitude of the corresponding capillary forces in presence of a trimer or dimer depends, besides the gap opening, only on the volume or Laplace pressure of the liquid. For a given Laplace pressure, and for the same gap opening, the capillary forces induced by a trimer are only slightly larger than the corresponding forces in the presence of three pendular bridges. This observation is consistent with a plateau of capillary cohesion in terms of the saturation of a wetting liquid in the funicular regime, as reported in the experimental work [Scheel *et al.*, *Nat. Mater.* **7**, 189 (2008)].

DOI: 10.1103/PhysRevE.94.012907

I. INTRODUCTION

Capillary forces and the mechanics of wet granular materials remained an active field of research since the seminal works of Haines [1] and Fisher [2] on soil mechanics. Until to date the majority of models consider capillary forces in the presence of pendular bridges [3–8], and are thus restricted to describe the mechanics at low liquid saturations [9,10]. Recent developments in three dimensional imaging techniques such as fast confocal microscopy [11] and x-ray tomography [12] made it possible to investigate the shape of liquid clusters consisting of coalesced pendular bridges with a resolution well below the scale of a single grain. The growth of these “funicular structures” in disordered packings of disks during condensation, and the corresponding evolution of the cohesive forces have been recently investigated also in Lattice Boltzmann simulations [13].

Despite these advances, only a few attempts have been made to quantify capillary forces between spherical grains in the funicular regime [12,14,15]. It is evident that the magnitude of the cohesive forces at different liquid saturations is intimately linked to the morphology of the interstitial fluids on the scale of single grains [12,16]. A better understanding of the liquid structures emerging in the funicular regime and the capillary cohesion caused by them may help to predict landslides or avalanches [17], and to complement existing models for technological applications in wet granular aggregation or particle coating [18]. Besides the immediate relevance for the mechanics of wet granulates, modeling the cluster morphology of partially wetting liquids will also have repercussions on the theory of fluid transport in wet granular beds [10,16,19–21].

In this article we present the results of a systematic study of fundamental liquid morphologies and corresponding capillary forces in arrangements of spherical beads at saturations above

the regime of pendular bridges. These liquid clusters appear above a threshold saturation corresponding to the transition from the pendular regime to the funicular regime. Considering perfectly wetting liquids and a random close packing of spherical beads, the pendular bridge regime is limited to a range of liquid contents $W < W^* \approx 2.5 \times 10^{-2}$, here expressed with respect to the total sample volume [12,22]. At slightly higher liquid contents $W > W^*$, the lateral extension of a pendular bridge on a bead does not anymore permit the formation of isolated bridges. Consequently, a certain fraction of the pendular bridges coalesces and transforms into a funicular structure, i.e., into liquid clusters that are simultaneously in contact to at least three beads.

The most characteristic cluster morphology found in granular bed of highly wettable spherical beads is a “trimer” of pendular bridges [12]. As can be seen in the three dimensional rendering of x-ray tomography data in Fig. 1(a) [12], three pendular bridges have coalesced around a triangular opening formed by three adjacent beads. In what follows we refer to the center of the opening as a “throat.” Throats are found in large numbers in a disordered assembly of spherical beads [12,23], and it is not surprising that filled throats connecting three adjacent bridges represent the most generic liquid structure beyond isolated pendular bridges. A close inspection of the liquid morphology shown in Fig. 1(c) reveals that this large liquid cluster indeed consists mostly of these trimer units: Any of the three pendular bridges belonging to a certain trimer unit can be part of a least one more trimer unit. The filled throats in a granular assembly can thus form large interconnected chains of pendular bridge “polymers.” Owing to its outstanding importance we will focus our present numerical study on a single trimer.

Capillary forces of pendular bridges between two spherical beads in contact display only small variations with the liquid volume [2,15,17]. This observation readily explains the insensitivity of the mechanical cohesion of a wet granular assembly with respect to the liquid content W in the pendular

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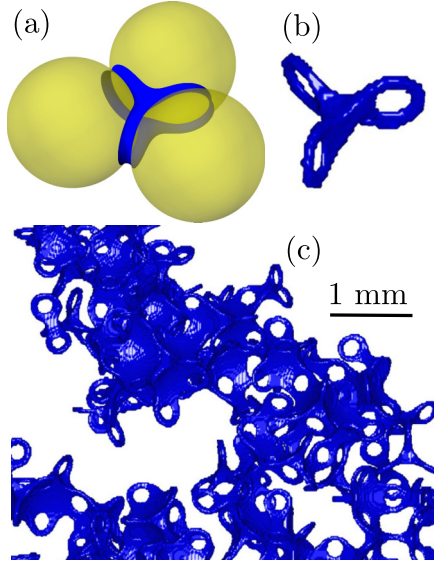


FIG. 1. (a) Trimer morphology computed in our numerical energy minimizations. (b),(c) Renderings of segmented x-ray microtomography images of a wetting liquid between spherical glass beads and a large liquid cluster in a disordered packing from x-ray tomography [12]. Bead radius $R = (355 \pm 35) \mu\text{m}$, wetting liquid aqueous ZnI_2 solution in (b) and (c).

regime $W \lesssim W^*$ [17]. Quite surprisingly, the magnitude of capillary cohesion evolves smoothly while the liquid content is increased from the pendular regime $W \lesssim W^*$ into the funicular regime $W \gtrsim W^*$ [12]. Measurements of capillary cohesion employing the fluidization threshold or the tensile strength [9,12] reveal a plateau in the range of W from approximately 0.03 reaching to values larger than ≈ 0.1 . At higher liquid contents, capillary cohesion gradually weakens with increasing W and vanishes at full saturation of the pore space ($W \approx 0.4$). In the latter case, every bead in the granular bed is completely immersed in liquid and, thus, there are no fluid interfaces that can give rise to capillary cohesion.

An experimental quantification of capillary forces in small ensembles of beads is difficult and *in situ* measurements are hardly feasible with the currently available experimental techniques. To reach a quantitative picture of capillary cohesion between three or more beads, we employ numerical minimizations of the interfacial free energy and obtain the equilibrium morphology of the liquid interfaces along with the magnitude and direction of capillary forces. The respective capillary forces as a function of the surface-to-surface separations can be then employed to formulate a model for the mechanics of wet beads, provided the complete set of rules to transform, merge, or split liquid cluster in response to slow changes of the local bead configuration is known [16].

A statistical analysis of x-tomography images revealed that local triangular configurations with three detectable finite separations between the bead surfaces are extremely rare in random packings of monodisperse beads [12,21]. The majority of these local throats exhibit only one detectable gap between the surfaces of the beads. Beads of the remaining two pairs are in mechanical contact. The other extreme case where all three bead pairs are in contact is equally rare. No significant

differences in the statistics of surface-to-surface separations of adjacent beads between dry and wet assemblies could be detected in the x-ray tomography [12]. In view of the three dimensional parameter space that accounts for the most general configurations of three beads, we will restrict our discussion in this work to the most relevant case, i.e., three bead configurations with two mechanical contacts and one finite gap opening. Local bead configurations where all three pairs are in contact are covered as a special case. To account for the range of experimentally relevant situations we report the results for both the volume controlled case and the pressure controlled case. In a forthcoming work, we will present the results on the general case with two and three finite gap openings, respectively.

This article is organized as follows: In Sec. II we introduce the physical model and give details about the numerical method to compute equilibrium configurations of the liquid interface. In Sec. II, we summarize the fundamentals of theory of capillarity and methods to compute capillary forces between solid bodies in numerical energy minimizations. The appearance of trimers and dimers of pendular bridges in local bead configurations with two contacts are described in Sec. III A and compared to wetting experiments in Sec. III B. Numerically computed capillary forces between beads in the presence of trimers and dimers are presented and discussed in Sec. III C. Finally, we conclude with a summary and outlook in Sec. IV.

II. PHYSICAL MODEL AND NUMERICAL IMPLEMENTATION

Before we address the theory of capillary forces, we will first give a short outline of the framework of capillarity. To this end, we will consider the most general case of N spherical beads in contact to two fluid phases. The position of the N bead centers are given by vectors $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ with Cartesian coordinates $\mathbf{r}_i = (x_i, y_i, z_i)$. For later convenience we denote vectors and tensors by boldface symbols. The fluid phases in contact to the beads may represent two immiscible liquids or a liquid in coexistence with a vapor phase. As we assume the beads to be fixed in space, or allowing only adiabatically slow variations of their positions, any flow inside the fluids has ceased once a mechanical equilibrium of the bulk phases and their interfaces has been reached. In this state, both fluids are at rest relative to the surface of the beads which implies the absence of viscous stresses.

A. Interfacial energies

The shape of the liquid-vapor interface in mechanical equilibrium and the corresponding capillary forces and torques acting on the beads can be obtained from thermodynamic considerations of the interfacial free energy \mathcal{E} . For given positions $\mathbf{r} \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ of the bead centers, the functional

$$\mathcal{E}\{\Sigma^{\text{lv}}\} = \gamma^{\text{lv}} A^{\text{lv}} + (\gamma^{\text{ls}} - \gamma^{\text{vs}}) \sum_{i=1}^N A_i^{\text{ls}} \quad (1)$$

assigns a free energy to every configuration Σ^{lv} of the liquid-vapor interface. The first term on the right-hand side of Eq. (1)

represents the free energy of the liquid-vapor interface with area A^{lv} and interfacial tension γ^{lv} . The second term in Eq. (1) accounts for the free energy related to the surface Σ_i^{ls} of bead i in contact to the liquid with area $A_i^{ls} \equiv |\Sigma_i^{ls}|$ and the liquid-solid and vapor-solid surface tension γ_{ls} and γ_{vs} , respectively.

Liquid-fluid interfaces display a pronounced contact angle hysteresis on virtually all solid materials, including model granulates consisting of submillimetric glass, basalt, or ruby, beads [12,21]. In the case of a finite contact angle hysteresis, the free energy difference $\Delta\gamma \equiv \gamma^{ls} - \gamma^{vs}$ in Eq. (1) has to be replaced by the work per length, $\Delta\gamma_a^s$ and $\Delta\gamma_r^s$, that is necessary to advance or recede, respectively, the contact line of the wetting liquid on the bead surface. Static contact hysteresis implies that $\Delta\gamma_a^s - \Delta\gamma_r^s > 0$ even for asymptotically slow contact line displacements. As a consequence of this “static friction,” the local contact angle θ in mechanical equilibrium depends on the history of contact line motion and can thus assume any value between the receding contact angle θ_r and the advancing contact angle $\theta_a > \theta_r$. To elucidate the relation between capillary forces induced by a liquid cluster and the free energy landscape we will assume a fully reversible displacement of the contact line in this work, i.e. consider idealized surfaces without contact angle hysteresis.

Moreover, we will neglect the influence of gravity and buoyancy, as their effects are typically small in liquid clusters with extensions on the length scale of the grains, which is typically between 1 mm and 100 μm . The capillary length for an air-water interface is in the range of a few millimeters [24]. Expressed in terms of the Bond number $\text{Bo} \equiv \Delta\rho g R^2 / \gamma^{lv}$ with a typical vertical dimension of the interface in the range of the bead radius R , we have $\text{Bo} \ll 1$. Furthermore, we assume that the typical distances between the liquid interface and solid walls are large such that contributions of the disjoining pressure to the normal stress at the interface can be safely excluded.

Under these conditions, any mechanically stable interface configuration Σ^{lv} in contact to the beads with fixed positions $\bar{\mathbf{r}}$, is a local minimum of the free energy Eq. (1). Dealing with nonvolatile liquids, we have to consider minima of the functional (1) under the subsidiary constraint of a fixed volume V of the liquid body. We will refer to this situations as the “volume controlled case.”

In some situations it is justified to assume that the liquid in contact to the beads can be exchanged with a reservoir that fixes the pressure difference $P \equiv P^l - P^v$ between the liquid (l) and vapor (v) phases. The pressure controlled case applies to experimental systems where a liquid transport can proceed either through thin films on the surfaces of the particles [12,21,25,26] or directly through a diffusive flux in the vapor phase; see, e.g., Ref. [27]. If these equilibration processes are fast on the time scale of an experiments [12,19,21], it is justified to view the total liquid in the sample as a liquid reservoir, and assume the Laplace pressure P to be the relevant control parameter. If this is the case, we need to consider local minima of the Grand interfacial free energy

$$\mathcal{G} = \mathcal{E} - P V. \quad (2)$$

The grand interfacial free energy takes into account the work received from or done at the volume reservoir, respectively. We will refer to this case as the “Laplace pressure controlled case.”

Any extremum of the free energy \mathcal{E} under the constraint of a fixed volume V necessarily satisfies two conditions. The first condition is expressed by the Young-Laplace equation:

$$P = 2H\gamma^{lv}, \quad (3)$$

that holds in every point of the interface Σ^{lv} . The mean curvature H is the sum of the two principal curvatures, or any pair of normal curvatures of the interface into orthogonal direction; see for instance Ref. [28]. In the absence of gravity, the Laplace pressure P is independent on the position which implies that Σ^{lv} is a surface of constant mean curvature.

The second necessary condition of a local free energy minimum is due to Young, Dupré, and Laplace and expresses the mechanical equilibrium at every point the three phase contact line:

$$\gamma^{lv} \cos \theta_0 = \gamma^{sv} - \gamma^{sl}. \quad (4)$$

The equilibrium contact angle θ_0 , also termed Young’s or material contact angle, is determined solely by interfacial free energies. As already mentioned, for a comparison to “real” surfaces, we need to account for the dissipation of work during and advancing or receding motion of the three phase contact line, and consider static advancing and static receding contact angles θ_a and θ_r , respectively, instead of Young’s angle θ_0 .

Owing to inherent nonlinearity of the energy functional Eq. (1), the interfacial free energy \mathcal{E} may exhibit more than one local extremum for a given liquid volume V and given positions $\bar{\mathbf{r}}$ of the beads. The equilibrium shapes can be distinguished by suitable order parameter describing the interfacial shape. The free energy \mathcal{E} of these equilibrium shapes is a function $E(\bar{\mathbf{r}}, V)$ in a certain range of bead coordinates $\bar{\mathbf{r}}$ and liquid volume V .

In the many instances one finds multiple local energy minima for given positions $\bar{\mathbf{r}}$, volume V , and material contact angle θ_0 . In this case, the function $E(\bar{\mathbf{r}}, V)$ is multivalued and forms a number of branches (or “leafs”). Analogous statements hold for the Grand free energy \mathcal{G} and the corresponding energy landscape $G(\bar{\mathbf{r}}, P)$, where the Laplace pressure P represents the accessible control parameter, instead of the liquid volume V .

Any interfacial configuration that satisfies Eqs. (3) and (4) is an extremum of the interfacial energy \mathcal{E} for the given Laplace pressure P in Eq. (3). From this observation we can conclude that an extremum of the free energy Eq. (1) for a certain volume V is also an extremum of the Grand free energy Eq. (2) for a certain Laplace pressure P and vice versa. This implies that the set of interfacial equilibria in the volume controlled case and in the Laplace pressure controlled case are identical. The mechanical stability of these extrema, however, may differ between the volume and the pressure controlled cases. Apart from a constant, the free energies \mathcal{G} and \mathcal{E} are identical for all interfacial configurations enclosing the same volume V . Hence, any local minimum of \mathcal{G} will be also a local minimum of \mathcal{E} under the constraint of a constant volume V , where the Laplace pressure P in \mathcal{G} can be regarded as a Lagrange multiplier. Therefore, mechanical stability in the Laplace pressure controlled case always implies mechanical stability in the volume controlled case. The converse statement, however, is not necessarily true: the liquid may exhibit more locally stable states in the volume controlled case as compared to the Laplace pressure controlled case.

At specific values of the relevant control parameters liquid volume V or Laplace pressure P and bead configuration $\bar{\mathbf{r}}$, termed ‘‘bifurcation points,’’ the number of local minima and saddle points of the energy functionals \mathcal{E} and \mathcal{G} changes. Bifurcation points can be classified according to universal aspects of the underlying energy landscape, i.e., the number of control parameters and order parameters as well as the symmetries of the energy functionals. More details on this subject of catastrophe theory can be found, e.g., in Refs. [29,30].

B. Capillary forces

The interfacial free energy $E(\bar{\mathbf{r}}, V)$ of a branch of liquid equilibrium states can be employed to compute the capillary force acting on the beads. If we assume that E equals the reversible work during displacement of the beads, the total force \mathbf{F}_i acting on bead i can be obtained, besides a negative sign, from the energy gradient

$$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} E(\bar{\mathbf{r}}, V), \quad (5)$$

with respect to the Cartesian coordinates \mathbf{r}_i of the particles $i \in \{1, 2, \dots, N\}$.

Capillary forces are unique for the equilibrium conformation of the liquid in contact to the beads, and do not depend on whether the liquid volume or the Laplace pressure is considered as the controlled parameter. Whenever $\partial_V \tilde{P}(\bar{\mathbf{r}}, V) \neq 0$, we can find the inverse function $V = \tilde{V}(\bar{\mathbf{r}}, P)$ for given bead positions $\bar{\mathbf{r}}$, where we use the tilde to distinguish the variable from the respective function. As shown in the Sec. 1 of the Appendix, we can derive the identity

$$\nabla_{\mathbf{r}_i} G(\bar{\mathbf{r}}, P) = \nabla_{\mathbf{r}_i} E(\bar{\mathbf{r}}, V)|_{V=\tilde{V}(\bar{\mathbf{r}}, P)}, \quad (6)$$

expressing that the capillary forces in a mechanical equilibrium are the same in the volume controlled case and the Laplace pressure controlled case, provided we consider corresponding values of the volume V and the Laplace pressure P . Higher derivatives of $E(\bar{\mathbf{r}}, V)$ and $G(\bar{\mathbf{r}}, P)$ with respect to the coordinates $\bar{\mathbf{r}}$ [evaluated at a Laplace pressure $P = \tilde{P}(\bar{\mathbf{r}}, V)$], however, differ in the general case.

Once the interfacial energies $\tilde{E}(\bar{\mathbf{r}}, V)$ or $\tilde{G}(\bar{\mathbf{r}}, P)$ are known, we can derive the capillary force \mathbf{F}_i from partial derivatives with respect to the Cartesian coordinates $r_{i\alpha}$, $\alpha \in \{x, y, z\}$ for every bead i . This approach is numerically cumbersome because one needs to scan a high dimensional function over a large range of parameters. Calculating the capillary forces directly from the configuration Σ^{lv} of the interface in a local minimum of \mathcal{E} or \mathcal{G} , respectively, involves integrations over the three phase contact line of the interface which is numerically much less costly.

To determine the total capillary force acting on each single bead, let us first imagine that every bead is enclosed by a control surface. This virtual control surface shall be infinitesimally close to the bead surface. By definition, the control surface must not intersect with any of the adjacent beads. Integration of the normal component of the stress tensor over the control surface yields the total capillary force on a bead. In a mechanical equilibrium of the interfaces, the bulk fluids, and the beads the fluid is at rest relative to the beads which implies that viscous stresses are absent. The magnitude

and direction of this force is independent on the particular choice of the control surface.

The total capillary force \mathbf{F}_i acting on bead $i = 1, 2, 3$ can be split into a contribution of the pressure in the liquid and ambient fluid (superindex p) and a contribution that stems from the interfacial tension (superindex t):

$$\mathbf{F}_i = \mathbf{F}_i^p + \mathbf{F}_i^t. \quad (7)$$

The first contribution \mathbf{F}_i^p is given by the Laplace pressure P multiplied by the local surface normal \mathbf{N}^s of the solid, and integrated over the surface Σ_i^{ls} of the bead i in contact to the liquid:

$$\mathbf{F}^p = \int_{\Sigma_i^{\text{ls}}} dA P \mathbf{N}^s. \quad (8)$$

Note that this contribution to the capillary force vanishes if the bead is completely immersed in the liquid provided that P is independent on \mathbf{r} .

The second contribution \mathbf{F}_i^t arises only in the presence of a three phase contact line Γ_i on the bead i , i.e., if bead i is partially wet. Locally, the interfacial tension γ^{lv} of the liquid-vapor interface Σ^{lv} pulls into a direction perpendicular to both the tangent vector \mathbf{t} of the contact line Γ_i , and the local normal vector \mathbf{N} of Σ^{lv} in a point \mathbf{r} on Γ_i , which is expressed as a force per unit length,

$$\mathbf{f} = \gamma^{\text{lv}} (\mathbf{N}^s \sin \theta - \mathbf{n}^s \cos \theta). \quad (9)$$

The sketch in Fig. 2(b) illustrates the definition of the two local orthonormal vector bases $\{\mathbf{t}, \mathbf{N}, \mathbf{n}\}$ of the liquid vapor interface Σ^{ls} and $\{\mathbf{t}, \mathbf{N}^s, \mathbf{n}^s\}$ on the surface Σ^s of the bead, as well as the local contact angle θ between Σ^{ls} and Σ^s in a point $\mathbf{r} \in \Gamma_i$. The surface normal of the free interface, \mathbf{N} , and the local normal of the bead surface, \mathbf{N}^s , allow us to express the local contact angle as

$$\cos \theta = \mathbf{N} \cdot \mathbf{N}^s. \quad (10)$$

The vectorial line force Eq. (9) integrated over the contact line Γ_i on bead i yields the total force that the liquid-vapor interface exerts on bead i :

$$\mathbf{F}_i^t = \int_{\Gamma_i} d\ell \mathbf{f}(\mathbf{r}). \quad (11)$$

In our numerical energy minimizations, integrals of Eq. (9) over the contact line can be performed as summations of the corresponding expressions over the edges of the mesh representing the contact line. Employing the divergence theorem, one can re-express the surface integral in Eq. (8) by line a integral over suitable functions of the local Cartesian coordinates of the point on the contact line as well as the Cartesian components of the normal and conormal vector in that point.

In the remainder of this article, we will consider the ideal case of a homogeneous bead surfaces for a vanishing contact angle hysteresis where the local contact angle is identical to Young’s angle θ_0 as given by Eq. (4). The computation of capillary forces through an integration of local interfacial and normal stresses on the beads following Eqs. (7)–(11) is not restricted to the case of vanishing contact angle hysteresis. In contrast to the computation of forces from the free energy landscape, this approach can be applied to any liquid configuration where only the free interface is in mechanical equilibrium with the bulk fluids.

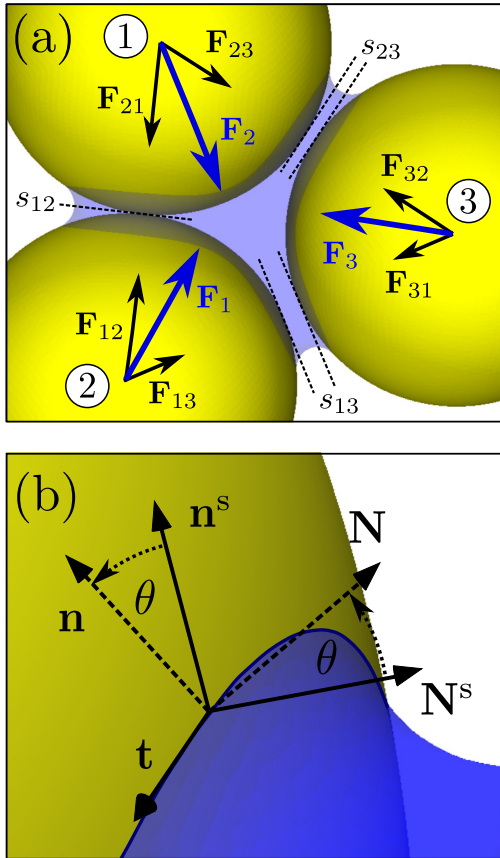


FIG. 2. (a) Geometry of three spherical beads with arbitrary gap openings s_{ij} , $i \neq j \in \{1,2,3\}$. The total capillary force \mathbf{F}_i acting on sphere i (blue arrows) is decomposed into force pairs acting along the line joining the bead centers (black arrows). (b) Local orthonormal vector bases in a point \mathbf{r} of the contact line Γ_i of a liquid-vapor interface Σ^{lv} on the surface Σ_i^s of beads i . Here, \mathbf{t} denotes the tangent to Γ_i , \mathbf{N}^s the normal of Σ_i^s , \mathbf{N} the normal of Σ^{lv} , θ the contact angle, while \mathbf{n} and \mathbf{n}^s denote the outward pointing conormal vectors on Σ^{lv} and Σ^s , respectively.

C. Numerical implementation

Due to a lack of high symmetries like, e.g., the rotational symmetry, the computation of the equilibrium shapes of a liquid volume wetting three spheres can be achieved only by means of numerical methods. In this work we employ a numerical minimization of the interfacial energy with the freely available software Surface Evolver developed by Brakke [31]. A fundamental idea behind this method is that the shape of a liquid droplet in contact with a rigid substrate is entirely fixed by the configuration of the free liquid-vapor interface.

In the numerical model of the liquid in contact with the beads, the shape of the liquid-vapor interface is approximated by a mesh of small triangles spanning a set of nodes. The interfacial energy is a function of the $3N$ coordinates of the nodes, and can be minimized using a number of built-in optimization algorithms [31]. Nodes of the mesh which represent the three phase contact line have to glide and stay on the spherical surface of one of the beads. Local geometrical constraints keep the nodes of the contact line on the surface. Contributions to the interfacial energy which stem

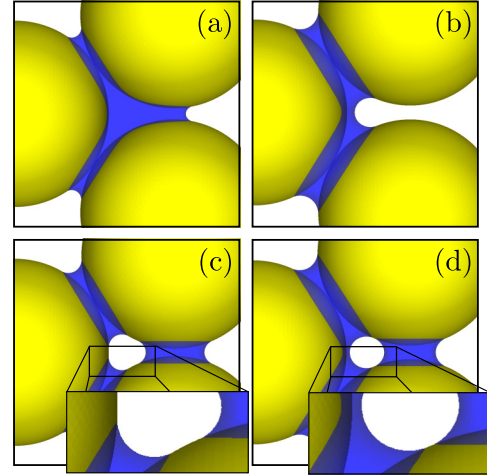


FIG. 3. Liquid morphologies in contact to three beads of equal radius with one nonzero gap opening showing (a) a trimer, (b) a dimer, (c) three pendular bridges, and (d) a dimer coexisting with a single pendular bridge; cf. also the magnifications of (c) and (d).

from the surface of the beads in contact with the liquid are completely determined by the configuration of the boundary to the liquid-vapor interface and are numerically computed from line integrals of suitably chosen functions over the closed contact line [31].

It is not restrictive to assume the centers of the three beads to lie in the plane $z = 0$, and compute only half of the liquid morphology by exploiting the reflection symmetry with respect to the plane at $z = 0$. To account for the possibility of local energy minima with a different topology of the liquid-vapor interface, but for the same values of control parameters, we employed a series of initial configurations in the numerical model, each equipped with a meaningful interfacial topology. Figure 3 shows the four configurations between three beads that were found in our numerical calculations. However, we cannot completely rule out the possibility to find even more physically meaningful local energy minima, i.e., with liquid-vapor interfaces that are not self-intersecting or penetrating into the beads.

During minimization of the interfacial energy, the condition of a constant liquid volume is imposed through a global integral constraint on the total volume, being the sum over all liquid bodies. Provided the configuration is in a local minimum of the interfacial free energy, the Lagrange multiplier corresponding to this integral constraint that has to be calculated in every minimization step is identical to the Laplace pressure P , i.e., the pressure difference across the liquid-vapor interface. Alternative to the ensemble of interfacial configurations enclosing a constant volume, one may consider an ensemble where the Laplace pressure of the liquid is fixed by a reservoir while the total liquid volume is allowed to adjust.

A variety of gradient based energy minimizations schemes including a conjugate gradient descent are implemented in the Surface Evolver [31]. Furthermore, a complete script language allows us to extract geometrical quantities from the liquid-air interface, such as the position of special points of the contact line. Long and short edges of the triangulation are refined, respectively, removed from the mesh after a number of

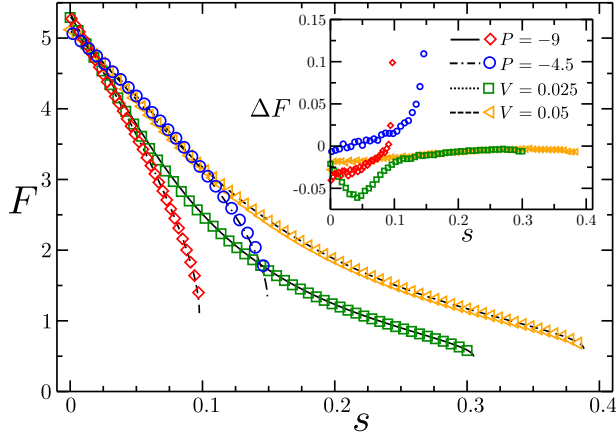


FIG. 4. Capillary forces F of a pendular bridge between two spherical beads as a function of the surface-to-surface separation s in the volume controlled case for $V = 0.025, 0.05$, and Laplace pressure controlled case for $P = -9, -4.5$. Exact solutions are shown as lines while numerical energy minimizations using the surface evolver are displayed by symbols. Inset: Force difference ΔF between energy minimizations and corresponding analytical solutions as a function of s .

minimization steps in order to keep the size distribution of the triangles in a desired range. Subsequent edge flipping allows the mesh to adapt to large changes of the liquid configuration.

To optimize the convergence we alternate coarse and fine triangulation meshes: coarse after changes of one or more control parameters are modified, to allow a fast evolution of the liquid interface, and fine when converging to an equilibrium morphology. The typical edge length of a fine triangulation is approximately 0.025 in units of the bead radius, while the typical number of nodes in a trimer morphology on the order of ~ 1000 , with fluctuations on around 20%. To account for flat parts of the energy landscape, the convergence criterion is not based on an energy difference, but rather on the maximum relative displacement among all nodes during each minimization step. Quantities of interest are averaged over the last 30 steps and written to the data file after the convergence criterion is satisfied.

To assess the accuracy of our numerical method, we validate the capillary forces of a pendular bridge for a given volume or Laplace pressure with exact solutions of the interfacial profile; cf. Fig. 4 and Section 3 of the Appendix. Besides a small region of surface-to-surface separations s close to the point of rupture s^{\max} , the difference of capillary forces F obtained by energy minimization and the “analytical” solutions remains below $\approx 1\%$ with respect to the maximum value F^{\max} attained at $s = 0$. Only close to the point of rupture, the relative difference increases to $\approx 2.5\%$. We expect to find a similar relative error for the capillary forces of the trimer morphology where the same meshing routines were applied during numerical energy minimizations.

Performing numerical computations of interfacial energies, Laplace pressures, and forces, it is useful to employ dimensionless rescaled physical quantities. For later convenience, we rescaled any length in the system by $L_0 \equiv R$ and express volumes in units of $V_0 \equiv R^3$. Energies will be rescaled by $E_0 \equiv \gamma^{\text{lv}} R^2$ and, consequently, capillary forces and the Laplace

pressure by a force scale $F_0 \equiv \gamma^{\text{lv}} R$ and pressure scale $P_0 \equiv \gamma^{\text{lv}}/R$, respectively. For the sake of brevity and to improve the readability of the text, we will from now on refer to the nondimensional rescaled quantities, if not otherwise mentioned.

III. RESULTS

Throughout this work we consider three identical spherical beads, as illustrated in the sketch of Fig. 2. Assuming a wetting liquid in our numerical energy minimizations we set the contact angle to $\theta_0 = 5^\circ$. Two of the three bead pairs in the numerical model are in contact, while the third pair exhibits a finite gap. Without losing generality, we chose gap openings $s_{12} > 0$ and $s_{13} = s_{23} = 0$, i.e., beads 1 and 2 are not in mechanical contact. Hence, the two remaining control parameters that define the relative position of the beads are s_{12} and either the liquid volume V or the Laplace pressure P .

A. Liquid morphologies

Figure 3 presents all mechanically stable interfacial morphologies encountered in our numerical energy minimizations in the volume controlled case. These are the trimer of three coalesced pendular bridges in panel (a) of Fig. 3, a dimer of two coalesced bridges at the contacts in (b), three isolated pendular bridges in (c), and a bridge dimer at the contacts coexisting with a pendular bridge across the gap in (d). Throughout this work we assume that separate liquid bodies can be exchange volume. Consequently, the relevant parameter in the volume controlled case is the total volume of all liquid bodies.

Inspection of the liquid-vapor interface of the dimer and the trimer shows that both interfaces are topologically equivalent to the surface of a sphere perforated by three holes. Despite this similarity, the overall shape of a trimer and dimer are qualitatively different. The liquid of a trimer fills the central opening, or throat, formed by the three adjacent beads. In the presence of a dimer, however, the central part of this throat is empty of liquid. Dimer morphologies can thus be described by a pair of pendular bridges that have coalesced in a small section of their contact lines.

To distinguish the trimer from the dimer morphologies, and to detect certain types of instabilities that occur during quasistatic changes of one or more control parameters, we consider two suitable shape descriptors as indicated in Fig. 5. Let us imagine a cut through the liquid body by the symmetry plane $x = 0$ orthogonal to the plane $z = 0$ passing through the centers of the spheres. The first shape descriptor is now the distance d between the intersection of liquid interface and the y axis, and the surface of bead 3; cf. Fig. 5. As a second shape descriptor, we chose the smallest distance h of two points on the concave part of the upper and lower meniscus in the throat. This minimum thickness of this “liquid lamella” may become ill-defined if the meniscus in the throat lack a concave shape, unlike the example shown in Fig. 5.

The plots in Fig. 6(a) illustrate the evolution of the meniscus distance d as a function of the liquid volume V , for a set of fixed gap opening s_{12} in the range between 0.05 and 0.25. At a large gap opening $s_{12} = 0.25$, we observe a continuous increase of d for an increasing volume V , and no discontinuous jumps. The distance d follows the same curve during a volume decrease.

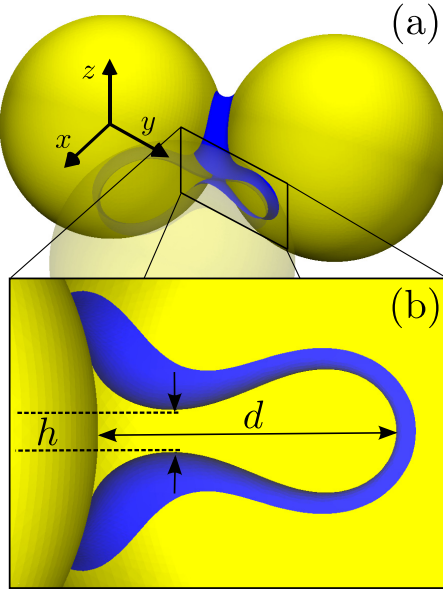


FIG. 5. (a) View of a trimer morphology with liquid volume $V = 0.2$ and material contact angle $\theta_0 = 5^\circ$ wetting a throat of three beads with one finite gap $s_{12} > 0$ and two contacts $s_{13} = s_{23} = 0$. The foremost bead and half of the liquid interface are rendered transparent to enhance the cut along the symmetry plane. (b) Magnified view of a cut through a trimer along its symmetry plane, illustrating the definition of the order parameter meniscus distance d and the distance h of the two opposing menisci in the throat.

A clear transition between trimer at large V and dimer at small V cannot be found. Only at small volumes, the dimer morphology eventually decays, caused by a decoalescence of the meniscus as $d \rightarrow 0$. This interfacial instability, indicated by square symbols in Fig. 6(a), will lead to two separated pendular bridges as a final state.

At smaller gap openings $s_{12} = 0.13, 0.17, 0.21$ the meniscus distance d shown in Fig. 6(a) displays discontinuous jumps to larger or smaller values, depending on whether the volume V is decreased or increased, respectively. Owing to these jumps, we find a range of control parameter s_{12} and V where two branches of local minima of the interfacial free energy (1) can be found in our numerical energy minimizations. This mechanical bistability between a dimer and a trimer allows a clear distinction of the morphologies. The branch of liquid conformations with the larger or smaller value of d are classified as trimers and dimers, respectively. The corresponding interfacial instabilities limiting the range of mechanically stable trimers and dimers will be termed the “snap-in” and the “pop-out” instability in the remainder of this article. The latter two instabilities are indicated by downward and upward triangles, respectively, in Fig. 6.

For a gap opening s_{12} of 0.13 and smaller, the snap-in instability occurs at a volume smaller than the smallest volume that allows a stable dimer to be formed, cf. the corresponding branches shown in Fig. 6(a). Hence, trimers can directly break up into two separated pendular bridges during a volume decrease without passing through the dimer morphology. For the examples shown in Fig. 6(a), the trimer branch terminates for a finite value $d > 0$ at gap opening s_{12} of 0.05 and 0.09.

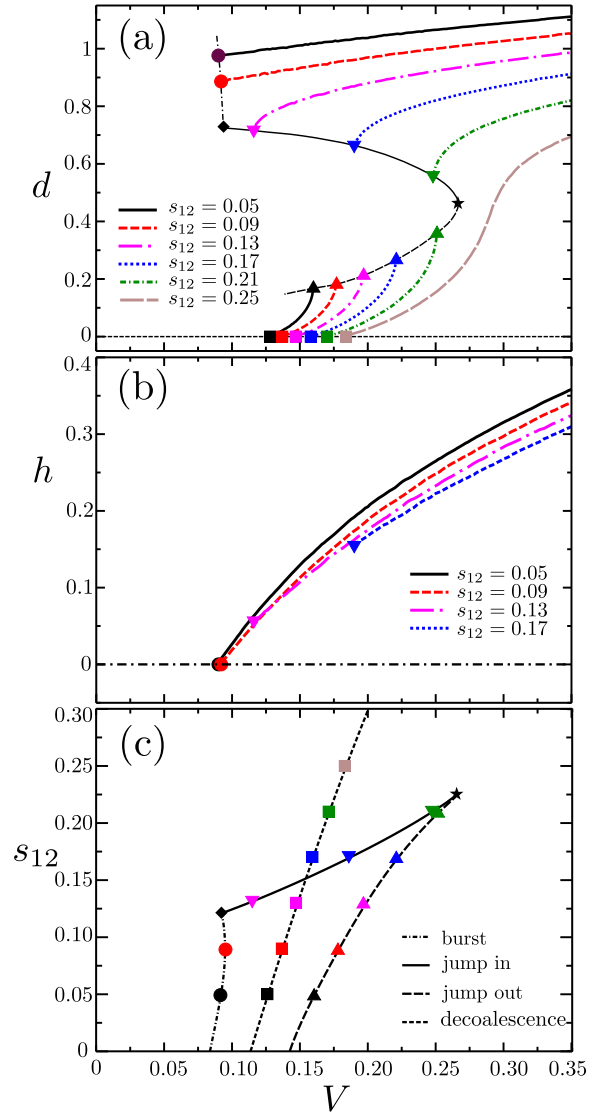


FIG. 6. (a) Distance d between the outer meniscus at the gap and the surface of sphere 3 as a function of the volume V for different gap openings s_{12} . (b) Minimal distance h of the two opposing menisci in the throat as function of V for the same values of s_{12} . (c) Morphology diagram in terms of the V and s_{12} displaying the lines of instabilities as outlined in the main text. The bifurcation point and the kink are indicated by the star (\star) and diamond (\blacklozenge) symbol, respectively. For a definition of d and h , cf. also Fig. 5.

In these cases the minimal thickness h of the liquid lamella in the throat reaches zero before a discontinuous inward jump of the outer meniscus in the gap or a decoalescence can lead to the decay of the trimer. A collision of the two opposing menisci in the throat triggers a sudden opening of the liquid interfaces. The circles in the plots shown in Figs. 6(a) and 6(b) indicate this “burst” instability during a decreasing liquid volume. The burst instability of the central liquid meniscus very likely leads to three separated pendular bridges as the final state.

Figure 6(c) illustrates the stability boundaries of the trimer and dimer morphologies that correspond to one of the four possible types of instability. With systematic scans of parameters s_{12} and V , we identified a bifurcation point at

$(V^*, s_{12}^*) = (0.26, 0.22)$ as indicated by the black star in the stability diagram Fig. 6(c). The tangents to the lines indicating the snap-in and the pop-out instability become parallel and terminate in a cusp. This type of bifurcation is generically observed for systems with two control parameters and one order parameter; see, e.g., Refs. [29,30]. The lines of the snap-in instabilities and the burst emerge from a point $(V^\diamond, s_{12}^\diamond) = (0.09, 0.125)$, where the two stability lines form a kink. The latter point is indicated by a black diamond in Fig. 6(c). Note that mechanically stable dimers can exist in the “ideal” case $s_{12} = 0$ of all three beads in contact, provided that the volume falls into the narrow range between $V \approx 0.115$ and $V \approx 0.15$.

It turns out that also a mechanically stable “chimera” morphology of a dimer and an isolated pendular bridge across the finite gap is possible. In contrast to the trimer, the latter morphology is always metastable (not the global energy minimum of the interfacial energy) and can be found only in a small region of control parameters. As for a single bridge dimer, a volume decrease will likely induce a breakup of the interface between the two coalesced bridges and the formation of three pendular bridges. Alternative to decoalescence, we observed that the pendular bridge located at the gap may transfer liquid into the dimer and break up.

An increase of the liquid volume of the dimer chimera state, however, will lead to a coalesce of the dimer and the pendular bridge at the gap. The resulting trimer will completely fill the throat opening. Similar to the decay at decreasing volume, an increase of the gap opening at fixed volume could induce a rupture of the pendular bridge spanning the gap. Here, we can speculate that the liquid will first form a transient dimer that finally decays, after a pop-out of the meniscus between the two coalesced bridges, into a trimer.

B. Experiments

Motivated by the results of our numerical energy minimizations in Sec. III A, we investigated the decay of the trimer morphology and the final states during a slow decrease of liquid volume in an experimental realization. To this end, we fix three spherical ruby beads of identical radius $R = (300 \pm 5) \mu\text{m}$ (purchased from Saphirwerk Industrieprodukte AG and Sandoz Fils Sa, both Switzerland) on a microscopy glass slide using modeling clay. Two pairs of the beads are in mechanical contact ($s_{13} = s_{23} = 0$) while a small separation is intentionally left between the surfaces of the third pair ($s_{12} > 0$). Deionized water is employed as a volatile wetting liquid with a receding contact angle of $\theta_r \lesssim 10^\circ$ on the surface of the cleaned ruby beads, similar to the material angle of $\theta_0 = 5^\circ$ in our numerical energy minimizations in Sec. III A. In the beginning of the experiment a small water droplet is placed in the throat formed by the three ruby beads. During evaporation the shape of the meniscus is recorded by optical microscopy in the top view; cf. also Fig. 7(a). Experiments are performed at similar temperatures and relative humidities to ensure comparable evaporation rates.

Examples of video frames of a trimer recorded during a typical evaporation experiment are displayed in Fig. 7(a) for two gap openings. In good agreement with the numerical results of the previous Sec. III A, we observe a burst instability

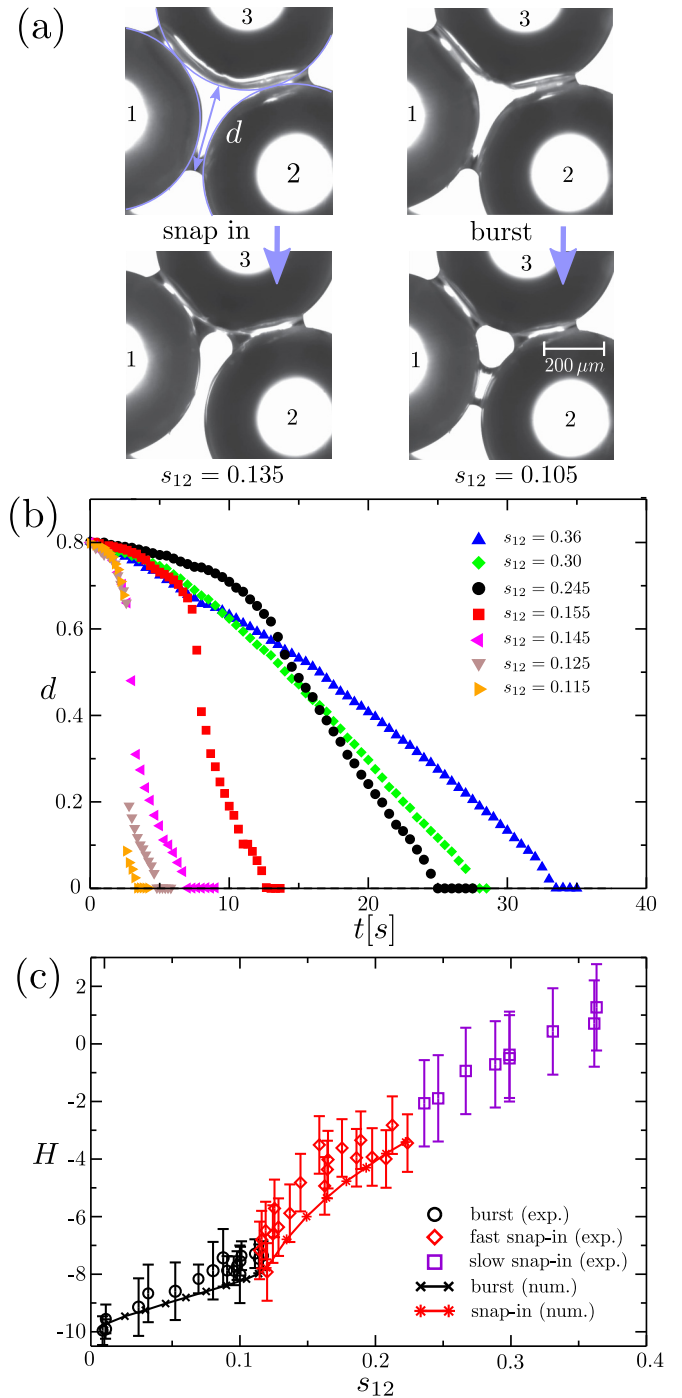


FIG. 7. Evaporation of water bridge trimers in an assembly of three ruby beads with a radius of $R = (300 \pm 5) \mu\text{m}$ with a finite gap between beads 1 and 2. (a) Optical micrographs of a pendular bridge trimer with a finite gap opening $s_{12} = 0.115$ (top left) and $s_{12} = 0.135$ (top right) and the corresponding final states of the burst instability (left bottom) and snap-in instability (bottom right). (b) Distance d of the outer meniscus in the gap from the surface of the opposing bead as a function of time t elapsed after the meniscus has passed a distance $d = 0.8$ for different gap opening s_{12} . (c) Estimated mean curvature H of an evaporating trimer at the point of instability as a function of the gap opening s_{12} in evaporation experiments and numerical energy minimizations.

for $s_{12} = 0.115$ (left column) and a discontinuous snap-in at $s_{12} = 0.145$ (right column). The distance of the meniscus in the gap to the surface of the opposing bead is denoted as d ; cf. also Fig. 7(a) and Sec. III A. According to our convention, we rescaled the distance d by the bead radius R .

Figure 7(b) shows the meniscus distance d extracted from the video frames as a function of time t for a series of gap openings s_{12} . To compare the temporal evolution of d during a snap-in for different values of the gap opening s_{12} , we chose an individual offset on the time axis for each curve in Fig. 7(b) such that the meniscus distance at time $t = 0$ attains the value $d = 0.8$.

Irrespective of the gap opening s_{12} , the meniscus distance d is monotonously decreasing as time t passes. The crossover from a sudden, discontinuous snap-in to a gradual and continuous decrease of d occurs between gap openings s_{12} of 0.155 and 0.245. At this point, we observe also a qualitative change in the form of the functions shown in Fig. 7(b), which display an increasing s-like shape of the curves as s_{12} is decreased. The transition agrees well with the predictions of our numerical energy minimizations in Sec. III A, where we expect a bifurcation point at a gap opening $s_{12}^* = 0.22$ separating the continuous from the discontinuous trimer decay. The corresponding measured meniscus distance d^* at the expected bifurcation point as well as the values of d at the onset of the snap-in instability for $s_{12} < s_{12}^*$ agree well with the numerically obtained results of Sec. III A shown in Fig. 6.

The snap-in instability was not observed in our evaporation experiments at gap openings $s_{12} \lesssim 0.115$. In the latter cases, the trimer decays upon a volume reduction because the central part of liquid-vapor undergoes a sudden burst instability. In the majority of cases the final state attained after the snap-in instability at $s_{12} > 0.12$ is a pendular bridge dimer. In contrast to the snap-in instability, burst instabilities occur for small gap openings $s_{12} < 0.12$, only, and lead to a final state of three pendular bridges.

For a quantitative comparison of the trimer instabilities observed in different experimental realizations and our numerical energy minimizations, it is useful to consider the mean curvature H of the liquid-vapor interface at the onset of the instability leading to the decay of the trimer. To this end we extracted the projected shape of the menisci of the coalesced pendular bridges spanning the pair of beads that are in contact. Because the outer parts of these interfaces are hardly affected by the liquid in the throat connecting the pendular bridges, the projected contours of these menisci are still close to the shape of an isolated pendular bridge. Adopting the toroidal approximation of pendular bridges for these menisci, we fit the in-plane contour of the outer menisci by circular arcs. The mean curvature H of the interface is the arithmetic mean $H = (\kappa_{\parallel} + \kappa_{\perp})/2$ of the in-plane (\parallel) and out-of-plane (\perp) curvatures $\kappa_{\parallel} = 1/r_{\parallel}$ and $\kappa_{\perp} = 1/r_{\perp}$, respectively. Here, r_{\parallel} is the radius of the fitted arc while r_{\perp} denotes the distance of the outer meniscus from the respective contact of the bead pair. This geometrical analysis of the liquid interface is done only on the last video frame that still shows a complete trimer, or before the outer meniscus in the gap accelerated while approaching the snap-in instability.

Figure 7(c) displays the values of the mean curvature H estimated in our experiments for various gap openings s_{12} .

In comparison to the experimental data, we plot in Fig. 7(c) the corresponding values of the mean curvature obtained in our numerical energy minimizations. A transition between the snap-in and the burst instability is clearly visible as a kink in both the experimental and the numerical data. A small systematic shift in the mean curvature between the experimental data points and the numerical results is apparent in the plot of Fig. 7(c), but the numerical data fall into the range of the experimental uncertainties. Our experimental data show a cross-over between the burst and the snap-in instability for a gap opening $s_{12} \approx 0.12$. This value coincides perfectly with the numerically determined value where we assumed a material contact angle of $\theta_0 = 5^\circ$.

C. Capillary forces

After discussing the spectrum of liquid equilibria and their instabilities in Secs. III A and III B, we will now turn to the capillary forces on the beads in contact to the liquid. It is evident that the total capillary force acting on a single bead in the presence of three axially symmetric pendular bridges is a superposition of central forces.

As long as we consider ideal spherical beads with a vanishing contact angle hysteresis, the total capillary force \mathbf{F}_i on a bead $i \in \{1, 2, 3\}$ in the presence of the trimer or dimer morphology can be decomposed into central force pairs; cf. the illustration in Fig. 2. Provided the bead centers do not lie on the same line, this decomposition is unique. This finding is derived from the observation that the interfacial free energy Eq. (1) is invariant under arbitrary simultaneous rigid translations and rotations of beads and liquid. A proof is given in Sec. 2 of the Appendix for arbitrary equilibrium liquid morphologies in contact with three spherical beads. Similar conclusions were reached by Admal and Tadmor in Ref. [32] considering forces on the molecular level for general three and four body interactions.

Due to the reflection symmetry of the particular bead configuration considered in this work, the magnitudes of the pair forces F_{ij} with $i, j \in \{1, 2, 3\}$ are invariant upon interchanging bead 1 with bead 2. Hence, the capillary forces satisfy $F_{13} = F_{23}$, and we need to consider only two independent forces: the force F_{12} acting across the gap and the force F_{13} acting at one of the two contacts.

1. Three pendular bridges

Figures 8(a) and 8(b) illustrates the capillary forces F_{12} and F_{13} , respectively, for a symmetric bead configuration with one finite gap opening $s_{12} > 0$ and two contacts $s_{13} = s_{23} = 0$ in the presence of three pendular bridges with total volume V . As mentioned in the beginning of Sec. III A, we assume a mutual exchange of liquid volume between the bridges. This transport can be due to liquid films on the surface of the beads or diffusion through the continuous fluid phase. The Laplace pressure P of the bridges as a function of gap opening s_{12} and total volume V is shown in Fig. 8(c).

The dashed lines in the color maps Figs. 8(a)–8(c) indicate the region (s_{12}, V) where configurations of three pendular bridges are mechanically stable. Whenever the boundary of the latter region is reached during an adiabatically slow change of s_{12} and V , the bridge ensemble will become unstable and decay

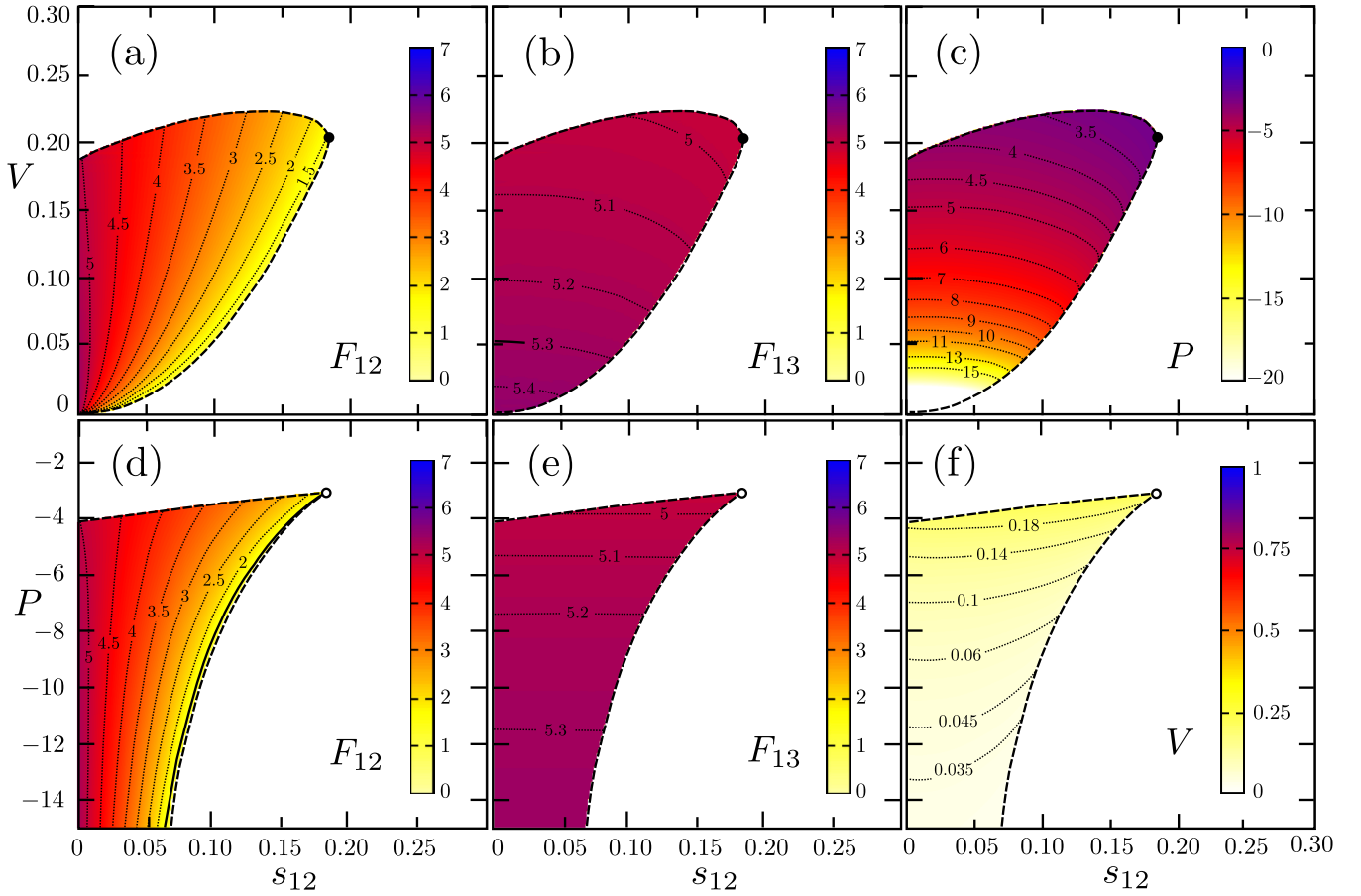


FIG. 8. Attractive capillary forces F_{12} across the gap (a) and F_{13} at the contact (b) in presence of three pendular bridges as a function of the gap opening s_{12} and liquid volume V . Capillary forces F_{12} and F_{13} and volume V of three pendular bridges in the pressure controlled case are shown in panels (c), (d), and (f), respectively, as a function of s_{12} and P .

into an interfacial morphology with a lower interfacial free energy. For small total volumes V below the full circle symbol in Fig. 8, the ensemble of three pendular bridges becomes unstable with respect to a mutual exchange of volume. In the course of this instability, the pendular bridge located at the gap will be spontaneously “sucked up” by the two bridges at the contacts. In the upper part of the stability limit left of the symbol, we observe that the contact lines of at least one pair of bridges touch, followed by coalescence.

Inspection of Fig. 8(a) shows that the attractive force F_{12} acting across the gap at a fixed total liquid volume V of the bridges varies strongly with the gap opening s_{12} , dropping from a value of $F_{12} \approx 5$ at $s_{12} = 0$ to $F_{12} \approx 0$ at the gap opening $s_{12} = s_{12}^{\max}(V)$ on the stability limit for the given volume V . The values of F_{12} at $s_{12} = 0$ and $s_{12} = s_{12}^{\max}(V)$ are rather insensitive with respect to changes in V ; cf. Fig. 8. As expected, the force F_{12} for a vanishing gap opening $s_{12} = 0$ increases slightly with decreasing V , and approaches the value $2\pi \cos \theta_0 \approx 6.23$ of a pendular bridge only in the asymptotic limit $V \rightarrow 0$ [2]. The value of maximum gap opening $s_{12} = s_{12}^{\max}(V)$, however, depends strongly on the total liquid volume V .

In contrast to F_{12} , the attractive capillary force F_{13} at the bead contacts shown in Fig. 8(b) does not display a significant variation with either the gap opening s_{12} or the total volume V . We obtain values $F_{13} \approx 5.5$ with a slight increase to

$F_{13} \approx 6.23$ in the asymptotic limit $V \rightarrow 0$, as expected from the force F_{12} at $s_{12} = 0$. The Laplace pressure P of three communicating pendular bridges in Fig. 8(c) depends on both control parameters, s_{12} and V . Apparently, the dependence of P on V is more pronounced than the dependence of P on the gap opening s_{12} .

In many instances it is appropriate to assume that the liquid clusters in the wet granular assembly exchange volume with neighboring liquid structures [12,19,21]. Here, the neighboring structures act as a liquid reservoir, and one may regard the average Laplace pressure in the granular bed to be a suitable control parameter. In the latter case, an equilibrated liquid cluster represents a local minimum of the Grand interfacial energy \mathcal{G} at a given Laplace pressure P rather than a local minimum of the interfacial energy \mathcal{E} for a fixed volume V .

Capillary forces F_{12} and F_{13} of three pendular bridges in the pressure controlled case are shown in Figs. 8(d) and 8(e) as a function of gap opening s_{12} and Laplace pressure P . We find the same crossover between the decay modes as in the volume controlled case discussed above. For high Laplace pressures P (with negative sign, but with low magnitude), the pendular bridges are unstable with respect to coalescence while for small values of P (i.e., with negative sign, and large magnitude), the bridge at the gap becomes unstable with respect to a volume exchange with the reservoir. The corresponding stability limit

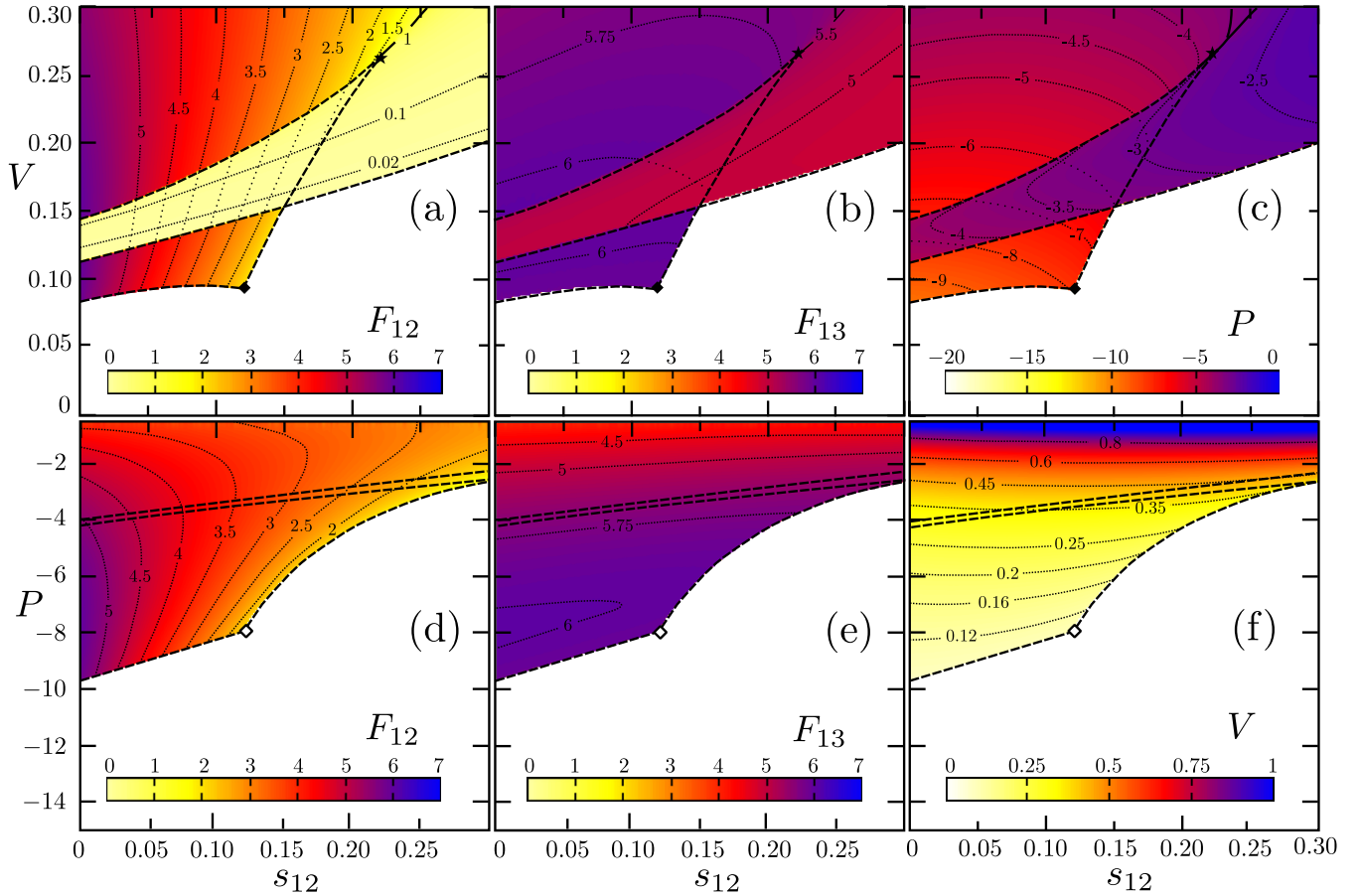


FIG. 9. Attractive capillary forces F_{12} across the gap (a), F_{13} at the contact (b), and Laplace pressure P of trimer or dimer (c) as a function of the gap opening s_{12} and liquid volume V . In regions of trimer or dimer bistability, the forces of the morphology with the smaller meniscus distance d is displayed; cf. also the diagram in Fig. 6. Capillary forces F_{12} and F_{13} , and volume V of a trimer or dimer morphology in the pressure controlled case are shown in panels (d)–(f), respectively, as a function of s_{12} and P .

in Figs. 8(a)–8(c) is shown as a dashed line where the open circle symbol indicates the crossover between the two modes of instability.

Similar to the volume controlled case, the force F_{12} acting across the gap decays with increasing gap opening s_{12} ; cf. Fig. 8(d). At a fixed gap opening s_{12} , the capillary forces become stronger with a decreasing Laplace pressure P (i.e., with negative sign and increasing magnitude), reaching the asymptotic value $2\pi \cos \theta \approx 6.23$ for $s_{12} = 0$ only in the limit $P \rightarrow -\infty$. Close to the straight segment of the stability boundary left of the symbol related to bridge coalescence, we find $F_{12} \approx 5$, similar to the magnitude in the volume controlled case at large V . Figure 8(e) displays the capillary force at the bead contacts, F_{13} , which is insensitive with respect to P , and with similar magnitude in the range $F_{13} \approx 5$ close to coalescence. For completeness, the total volume V of the three bridges is shown the last panel of Fig. 8(f).

2. Trimer or dimer morphology

In the following we will discuss the capillary forces of the trimer or dimer morphology in the volume and pressure controlled cases. Figures 9(a) and 9(b) display the magnitude of the attractive capillary forces F_{12} at the gap opening and F_{23} at the bead contacts. In regions where both the dimer

and the trimer are locally stable shapes for the given values of the control parameter gap opening s_{12} and liquid volume V , the map displays the forces corresponding to the trimer. Apparently, the attractive force F_{12} a trimer exerts across the gap depends strongly on the gap opening s_{12} , but only weakly on the liquid volume V . As expected from the liquid distribution between the beads, the attractive force F_{12} of a trimer is larger than the corresponding force of a dimer for the same values of s_{12} and V .

In contrast to F_{12} , the attractive capillary force F_{13} of a trimer acting at the two bead contacts varies only slightly with the gap opening s_{12} , and hardly depends on the volume V . The magnitude of F_{13} varies around a value of 6, i.e., differs only slightly from the asymptotic value $2\pi \cos \theta_0 \approx 6.23$ for pendular bridges between two spherical beads in contact in the limit $V \rightarrow 0$. Similar to the trimer morphology, a pendular bridge dimer exerts a rather constant attractive force F_{13} between beads in contact. The value $F_{13} \approx 5$ of a dimer is smaller as compared to the capillary force in the presence of a trimer with an identical volume.

In addition to the capillary forces, Fig. 9(c) shows the Laplace pressure P of the dimer or trimer morphology. The Laplace pressure depends mainly on the liquid volume V and only weakly on the gap opening s_{12} . Dimers display a larger Laplace pressure P (i.e., negative with a smaller magnitude)

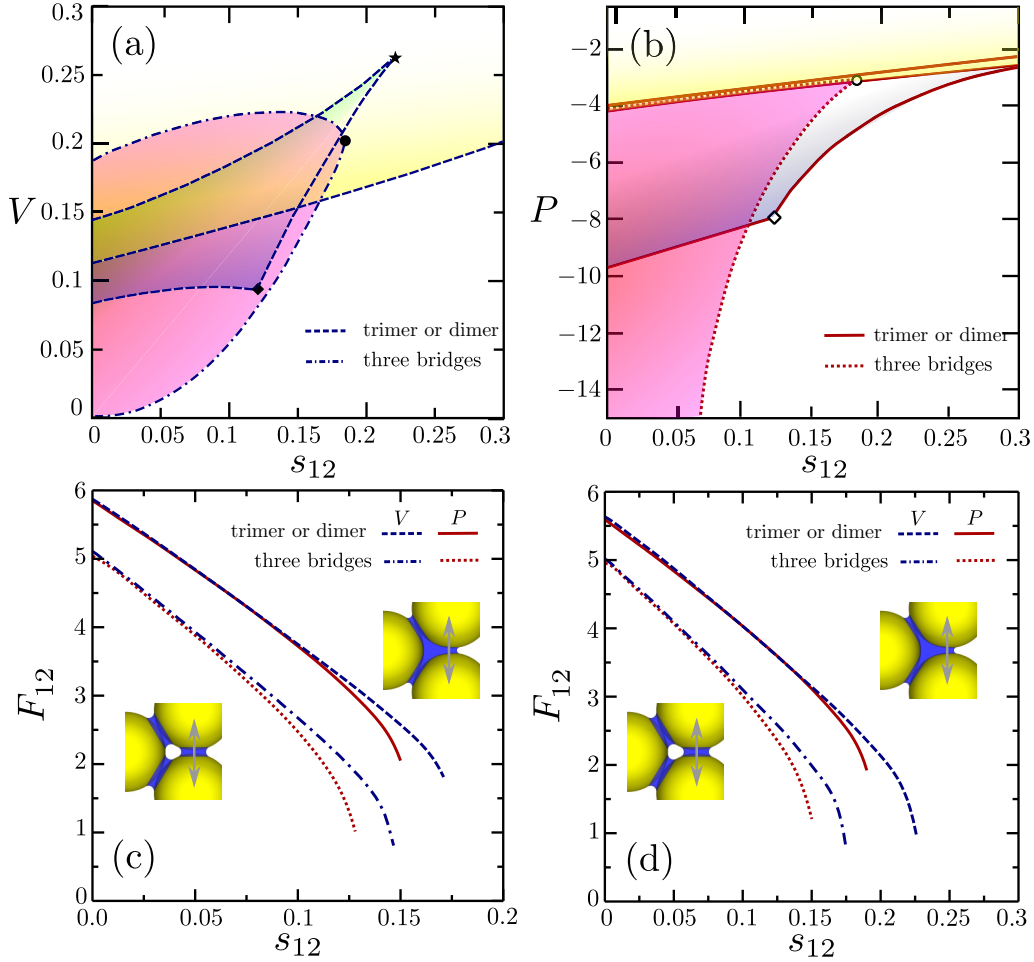


FIG. 10. Comparison of the stability boundaries of a trimer or dimer morphology and of three pendular bridges in terms of the gap opening s_{12} and (a) the total liquid volume V in the volume controlled case or (b) the Laplace pressure P in the pressure controlled case. (c) Capillary force F_{12} at the gap as a function of gap opening s_{12} . Shown are data for three pendular bridges at a fixed total volume $V = 0.116$ (dashed-dotted lines) and for a fixed Laplace pressure $P = -6$ (dotted line) in comparison to data for the trimer morphology at a fixed volume $V = 0.190$ (dashed line) and for a fixed Laplace pressure $P = -6$ (solid line). (d) Data for three pendular bridges of fixed total volume $V = 0.164$ (dashed-dotted line) and for a fixed Laplace pressure $P = -4.5$ (dotted line) in comparison to data for a trimer at fixed volume $V = 0.264$ (dashed line) and for a fixed Laplace pressure $P = -4.5$ (solid line).

as compared to a trimer at the same volume. Filling the throat with the available volume of the dimer requires a transfer of liquid from the region of the coalesced pendular bridges. This redistribution of liquid is accompanied by a decrease of the Laplace pressure. Note that the Laplace pressure of a trimer is typically negative but may become positive for large volumes.

In analogy to the volume controlled case, we display in Figs. 9(d) and 9(e) the capillary force F_{12} at the gap and F_{13} at the contacts, respectively, for liquid morphologies in the Laplace pressure controlled case. It is apparent that the region in the (s_{12}, P) plane where the dimer or trimer morphology exists as a local minimum of the Grand interfacial free energy displays a shape similar to the region in the volume controlled case. In the pressure controlled case, a trimer decays during changes of s_{12} and P either by a snap-in of the liquid menisci in the gap or by a burst instability leading to an opening of the throat.

The Laplace pressure at the burst instability increases approximately linearly with the gap opening s_{12} , and the

corresponding curve $P(s_{12})$ terminates together with the line of the snap-in instability in a point $(s_{12}^{\diamond}, P^{\diamond}) = (0.12, -8.5)$. At this point, the stability boundary of the trimer in the (s_{12}, P) plane exhibits a kink. The stability boundaries corresponding to the snap-in and pop-out instabilities join smoothly in a cusp bifurcation point at $(s_{12}^*, P^*) = (0.4, -2.3)$ which lies outside the range shown in Figs. 9(d)–9(f). The two almost parallel dashed lines in the upper region of the color plots Figs. 9(d)–9(f) indicate the narrow region where dimers can exist as metastable configurations in the Laplace pressure controlled case.

In full analogy to the volume controlled case, the capillary force F_{12} of a trimer acting across the gap in the Laplace pressure controlled case displays a strong dependence on the gap opening s_{12} , but varies only weakly with the Laplace pressure P . A stronger dependence is observed only above a value of $P \approx -4.5$, at a point where the trimer itself would have already coalesced with other neighboring liquid structures (bridges or trimers) inside the random assembly of

spherical beads [12,21]. The capillary force F_{12} at the gap created by the trimer is approximately by a factor ~ 1.1 larger than the capillary force of a single bridge at a prescribed Laplace pressure of $P = -4.5$ at the same distance s_{12} .

Figure 9(e) reveals that the capillary force F_{13} at the contacts depends on the magnitude of the Laplace pressure P , while F_{13} is virtually constant with respect to the gap opening s_{12} . Also in this case, the capillary force is approximately by a factor ≈ 1.1 larger than the force for a single pendular bridge at the contact held at the same value of $P = -4.5$. The liquid volume V of a trimer in the Laplace pressure controlled case depends to a larger degree on the magnitude of P and only weakly on the gap opening s_{12} ; cf. the color plot in Fig. 9(f). An analogous statement applies to an ensemble of three isolated pendular bridges that are allowed to exchange liquid.

Simulations of the mechanics and dynamics of large wet granular assemblies require efficient models for capillary cohesion. At low liquid saturations, in the regime of pendular bridges, the cohesive force can be treated as a superposition of two-body forces. For saturations in the funicular regime, a simple mapping of the capillary cohesion forces onto an equivalent ensemble of pendular bridges would be desirable. In the simplest approach, one would assume that the magnitude of capillary forces caused by the trimer are similar to those in the presence of three pendular bridges for the same volume or Laplace pressure.

Figures 10(a) and 10(b) provide a quantitative comparison of the stability boundaries of three pendular bridges to the ones of the trimer or dimer morphology in the volume controlled and the pressure controlled cases, respectively. The plots in Figs. 10(c) and 10(d) display the capillary force at the gap for three pendular bridges and the trimer or dimer morphology as a function of the gap opening. As we are plotting the capillary force F_{12} and F_{13} in the volume controlled and the Laplace pressure controlled cases in the same plot, we chose specific values of volume V and Laplace pressure P . For these particular values of the control parameters, the morphologies in the pressure and volume controlled cases are identical at zero gap opening $s_{12} = 0$. From the discussion in Sec. III C we can conclude that also the capillary forces between the beads must be the same.

Figures 10(c) and 10(d) clearly demonstrate that a trimer or dimer morphology induces a higher attractive force across the gap than three pendular bridges held at the same Laplace pressure. An analogous statement applies for a trimer and three communicating pendular bridges in the volume controlled case. If we now assume the contribution of the Laplace pressure to be the only contribution to the capillary force, we could expect to find an increased cohesion in the presence of a trimer due to the central region between the beads that, in contrast to three pendular bridges, is filled by liquid. But at the same time, the contact line of a trimer morphology is shorter than the length of the contact lines of all three pendular bridges. Due to this reduced length, the surface tension of the liquid-vapor interface in a trimer contributes less to the cohesive capillary force as compared to three pendular bridges. While the relative magnitude of these two effects is not evident from simple geometrical arguments, the direct comparison of

numerical data in Fig. 10 for Laplace pressure $P = -4.5$ (c) and -6 (d) indicate that the increase due to the enhanced suction dominates over the decrease of the direct contribution of interfacial tension. In addition to the increased cohesion in the trimer, the snap-in transition from trimer to dimer occurs at a larger gap opening as compared to the point where the pendular bridge at the gap decays. Hence, the total work to break up a trimer by increasing the gap opening s_{12} exceeds the work required to rupture a capillary bridge at the gap.

IV. CONCLUSION AND OUTLOOK

In this article we have explored the morphology and capillary forces of a pendular bridge trimer representing the most fundamental liquid cluster in disordered assemblies of wet spherical beads. We have focused our study on local triangular bead configurations with two contacts and one finite gap. Numerical minimizations of the interfacial energy reveal a shape bistability between a dimer and a trimer of pendular bridges. The capillary hysteresis between trimer and dimer shapes is present both in the volume and in the Laplace pressure controlled cases. As the gap opening is changed, we find a cross-over between two different interfacial instabilities that can occur during a quasistatic volume reduction. At small gap openings the two opposing menisci in the triangular throat touch and break up in a sudden burst. For intermediate gap openings, however, the trimer decays by a discontinuous snap-in of the meniscus located at the gap once the meniscus is close to the narrowest point between the bead surfaces. A continuous motion of the meniscus is observed in wide gaps. Systematic evaporation experiments in the geometry of three beads with a single finite gap opening quantitatively reproduce the transition from a snap-in to a burst instability of a trimer as the gap opening is decreased.

In respect to the modeling of the attractive capillary forces in an assembly of spherical beads, it is well justified to replace the bridge dimer by two separate pendular bridges which are held at the same Laplace pressure as the dimer. Bridge trimers, however, induce attractive capillary forces across the gap that are slightly larger than the force of a pendular bridge at the gap for the same Laplace pressure. The rupture distance of the pendular bridge at the gap is systematically larger than the gap opening where the snap-in transition from trimer to dimer occurs. Hence, trimers of pendular bridges not only yields to an increased cohesion between the beads but also the range over which the increased capillary force act is enlarged. Both effects lead to an enhanced dissipation of work during a slow deformation of a granular assembly. These two observations may already be sufficient to explain the shallow maximum of the strength of wet granulates in the funicular regime reported in experiments [12,21].

ACKNOWLEDGMENTS

The authors would like to thank R. Mani, D. Kadau, and H.-J. Herrmann for fruitful discussions. This work has been funded by the German Research Foundation (DFG) within the SPP 1486 ‘‘PiKo’’ under Grant No. HE 2016/14-2.

APPENDIX

1. Equivalence of capillary forces

Respecting the sign convention of the Laplace pressure, we find the identity

$$P = \tilde{P}(\bar{\mathbf{r}}, V) = \partial_V E(\bar{\mathbf{r}}, V). \quad (\text{A1})$$

Starting from the definition (2) of the Grand interfacial free energy \mathcal{G} , differentiation with respect to the coordinates $\bar{\mathbf{r}}$ and using Eq. (A1) we obtain the following identity:

$$\nabla_{\mathbf{r}_i} G(\bar{\mathbf{r}}, P) = \nabla_{\mathbf{r}_i} E(\bar{\mathbf{r}}, \tilde{V}(\bar{\mathbf{r}}, P)) - P \nabla_{\mathbf{r}_i} \tilde{V}(\bar{\mathbf{r}}, P). \quad (\text{A2})$$

By the chain rule of differentiation, we can write the first term in Eq. (A2) as

$$\begin{aligned} \nabla_{\mathbf{r}_i} E(\bar{\mathbf{r}}, \tilde{V}(\bar{\mathbf{r}}, P)) &= \nabla_{\mathbf{r}_i} E(\bar{\mathbf{r}}, V)|_{V=\tilde{V}(\bar{\mathbf{r}}, P)} \\ &+ \partial_V E(\bar{\mathbf{r}}, V)|_{V=\tilde{V}(\bar{\mathbf{r}}, P)} \nabla_{\mathbf{r}_i} \tilde{V}(\bar{\mathbf{r}}, P), \end{aligned} \quad (\text{A3})$$

and using the expression Eq. (A1) for the Laplace pressure, we finally obtain

$$\nabla_{\mathbf{r}_i} G(\bar{\mathbf{r}}, P) = \nabla_{\mathbf{r}_i} E(\bar{\mathbf{r}}, V)|_{V=\tilde{V}(\bar{\mathbf{r}}, P)}, \quad (\text{A4})$$

which proves the equivalence of capillary forces in the volume and pressure ensembles.

2. Decomposition of forces

First, we will consider the case of three identical beads whose centers are not colinear, i.e., $\mathbf{r}_{12} \times \mathbf{r}_{13} \neq \mathbf{0}$ where $\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j$ are the relative positions of the bead centers \mathbf{r}_i , $i \in \{1, 2, 3\}$. The co-linear case will be discussed separately.

Employing the unit vector \mathbf{n}_{ij} pointing from the center of bead i to the center of bead j , and the unit vector \mathbf{n}^\perp given by

$$\mathbf{n}^\perp = \frac{\mathbf{r}_{12} \times \mathbf{r}_{13}}{|\mathbf{r}_{12} \times \mathbf{r}_{13}|}, \quad (\text{A5})$$

we can decompose the forces \mathbf{F}_i onto bead i into a sum of forces

$$\sum_{\substack{j=1 \\ j \neq i}}^3 F_{ij} \mathbf{n}_{ij} + F_i^\perp \mathbf{n}^\perp = \mathbf{F}_i \quad (\text{A6})$$

with $i \in \{1, 2, 3\}$. Since the three vectors $\mathbf{n}_{12}, \mathbf{n}_{13}, \mathbf{n}^\perp$ are not collinear and thus form a basis of the three dimensional Euclidean space, the decomposition according to Eq. (A6) of \mathbf{F}_1 is unique. An analogous statement hold for the forces \mathbf{F}_2 and \mathbf{F}_3 , respectively. To prove the conjecture that the three body force can be uniquely decomposed into a sum over central force pairs, we have to show that $F_{ij} = -F_{ji}$ as well as $F_i^\perp = 0$ holds for all $i, j \in \{1, 2, 3\}$ and $j \neq i$.

We start our proof with the observation that the interfacial free energy is invariant under continuous rigid rotations of the three bead centers around an arbitrary axis. Hence, in the absence of contact angle hysteresis the total torque on the spherical beads vanishes:

$$\sum_{i=1}^3 (\mathbf{r}_i \times \mathbf{F}_i + \mathbf{T}_i) = \mathbf{0}, \quad (\text{A7})$$

where \mathbf{T}_i is torque acting on bead i about its center \mathbf{r}_i . Additionally, the invariance of the interfacial energy with

respect to rotations of the beads around an arbitrary axis passing through its center yields $\mathbf{T}_i = \mathbf{0}$ for $i \in \{1, 2, 3\}$. Together with Eq. (A7) we arrive at the identity

$$\sum_{i=1}^3 \mathbf{M} \cdot [\mathbf{F}_i \times (\mathbf{r}_i - \mathbf{r}_0)] = 0, \quad (\text{A8})$$

which holds for an arbitrary rotation axis $|\mathbf{M}| = 1$ and center of rotation, \mathbf{r}_0 , because all forces \mathbf{F}_i with respect to the centers of the beads must sum to zero. The latter statement is a direct consequence of the invariance of the free energy with respect to continuous rigid translations. Without restricting generality, we chose the center $\mathbf{r}_0 \equiv \mathbf{r}_1$ and a direction $\mathbf{M} \equiv \mathbf{n}^\perp$ of the axis. Equation (A8) can be now rewritten as

$$\mathbf{n}^\perp \cdot [(F_{23} \mathbf{n}_{23} + F_2^\perp \mathbf{n}^\perp) \times \mathbf{r}_{13} + (F_{32} \mathbf{n}_{32} + F_3^\perp \mathbf{n}^\perp) \times \mathbf{r}_{12}] = 0. \quad (\text{A9})$$

By the definition of the unit vectors \mathbf{n}^\perp and $\mathbf{n}_{23} = -\mathbf{n}_{32}$, we have $\mathbf{n}^\perp \cdot \mathbf{n}_{ij} = 0$ and

$$\mathbf{n}_{23} \times \mathbf{r}_{13} = -\mathbf{n}_{32} \times \mathbf{r}_{12} = \frac{2 A_\Delta}{|\mathbf{r}_{23}|} \mathbf{n}^\perp, \quad (\text{A10})$$

where A_Δ is the area of the triangle defined by the three bead centers. With Eqs. (A10) and (A9), we arrive at $F_{23} = -F_{32}$. The choice of bead indices was arbitrary which implies that also $F_{12} = -F_{21}$ and $F_{13} = -F_{31}$ must hold.

In order to show $F_1^\perp = F_2^\perp = F_3^\perp = 0$, we chose a rotation axis in the plane of the three bead centers, passing through the center of bead 1. The direction of the rotation axis is given by

$$\mathbf{M} \equiv \frac{\mathbf{r}_{21} + \mathbf{r}_{31}}{|\mathbf{r}_{21} + \mathbf{r}_{31}|} \quad (\text{A11})$$

where $\mathbf{r}_0 \equiv \mathbf{r}_1$. With this choice, the torque acting on the beads has to satisfy

$$\frac{(\mathbf{r}_{21} + \mathbf{r}_{31}) \times \mathbf{n}^\perp (F_2^\perp - F_3^\perp)}{|\mathbf{r}_{21} + \mathbf{r}_{31}|} = 0, \quad (\text{A12})$$

which gives $F_2^\perp = F_3^\perp$.

Following the same line of arguments for a rotation axis passing through the center of bead 2 and the point $\mathbf{r}_2 + (\mathbf{r}_{12} + \mathbf{r}_{32})/2$, we obtain $F_1^\perp = F_2^\perp$. Since the sum of overall forces \mathbf{F}_{ij} in the plane of the three bead centers vanishes, also all normal forces must sum to zero, leaving as the only possibility $F_1^\perp = F_2^\perp = F_3^\perp = 0$.

In the case of three colinear bead centers, a unique decomposition into three central force pairs must not necessarily be possible. A simple counterexample is forces $\mathbf{F}_1 = \mathbf{F}_3$ and $\mathbf{F}_2 = -2\mathbf{F}_1$, all orthogonal to the line, distances $\mathbf{r}_{12} = \mathbf{r}_{32}$ where bead 2 is located halfway in between beads 1 and 3. The singular nature of this case can be easily seen when approaching the co-linear configuration from a non-linear configuration. If there is no spontaneous symmetry breaking of the liquid shape, all capillary forces must act parallel to the line passing through the bead centers which, again, allows a unique decomposition into central force pairs.

3. Delaunay shapes

The free interface of a cylindrically symmetric pendular bridge is a surface of constant mean curvature. A general parameterization of these shapes was constructed by Delaunay [5,33] and can be expressed in cylindrical coordinates (r, ϕ, z) as $z = \mathcal{Z}(r)$ with a function

$$\mathcal{Z}(r) = r_o E(\phi, k) \pm r_i F(\phi, k) + \mathcal{R}, \quad (\text{A13})$$

where $\mathcal{R} = \sqrt{(r_o^2 - r^2)(r^2 - r_i^2)}/r$. Definitions of the incomplete elliptic integrals $E(\phi, k)$ and $F(\phi, k)$ are found, e.g., in Ref. [34]. The two parameters r_o and r_i denote the minimal and maximal distance, respectively, of a point on the surface from the z axis. A plus sign in Eq. (A13) describes an unduloid surface while the negative sign corresponds to a self-intersecting nodoid surface. For both types of surfaces, the modulus k and phase angle ϕ read

$$k = \sqrt{\frac{r_o^2 - r_i^2}{r_o^2}} \quad \text{and} \quad \phi = \arcsin\left(\frac{r_o \sqrt{r^2 - r_i^2}}{r \sqrt{r_o^2 - r_i^2}}\right). \quad (\text{A14})$$

The mean curvature of a Delaunay surface is simply given by

$$H = \frac{1}{r_o \pm r_i} > 0, \quad (\text{A15})$$

where the plus sign corresponds to the unduloid surface and the negative sign to a nodoid surface. Spheres and catenoids are obtained as limiting shapes for $0 < r_o < \infty$, $r_i \rightarrow 0$ and $r_o \rightarrow \infty$, $0 < r_i < \infty$, respectively.

To construct the shapes of capillary bridges in the pressure controlled case, we consider unduloid solutions for $P > 0$ and the inner, inverted part of a nodoid solution for $P < 0$. In the latter case, we need to multiply the right-hand side of Eqs. (A13) and (A15) by -1 to account for the inverted orientation of the interface. Regular nodoid segments for $P > 0$ can be excluded as they correspond to unstable repulsive pendular bridges. In the following the positive and negative signs refer to regular unduloid and inverted nodoid shapes, respectively.

In the Laplace pressure controlled case, we use relation Eq. (A15) to express the outer radius r_o by the inner radius

r_i and H . To match the contact angle θ_0 on the surface of the beads with radius R , we determine the contact line radius r_c for given minimal radius r_i as a solution of the implicit equation

$$R \cos(\alpha(r_c) + \theta_0) = r_c \quad (\text{A16})$$

with the slope angle

$$\alpha(r) = \pm \arctan\left(\frac{\sqrt{(r_o^2 - r^2)(r^2 - r_i^2)}}{r^2 \pm r_o r_i}\right) \quad (\text{A17})$$

of the unduloid for $H > 0$ (positive sign) or the inverted nodoid for $H < 0$ (negative sign). The solution r_c of Eq. (A16) is then used to compute the surface-to-surface separation

$$s = 2[\pm \mathcal{Z}(r_c) - R + \sqrt{R^2 - r_c^2}] \quad (\text{A18})$$

of the spherical beads. The volume enclosed by the Delaunay surface between plane cuts at $z = 0$ and $z = \pm \mathcal{Z}(r)$ is given by [35]

$$\mathcal{V}(r) = \pm \frac{\pi}{3} [(2r_o^3 + 2r_i^2 r_o \pm 3r_o^2 r_i) E(\phi, k) - r_o r_i^2 F(\phi, k) + (r^2 + 2r_o^2 + 2r_i^2 \pm 3r_o r_i) \mathcal{R}] \quad (\text{A19})$$

and, corrected by the volume of a spherical cap,

$$V_c(r) = \frac{\pi}{3} [(R - \sqrt{R^2 - r^2})^2 (2R + \sqrt{R^2 - r^2})], \quad (\text{A20})$$

with radius R and base radius r , yields the liquid volume of the pendular bridge

$$V = 2[\mathcal{V}(r_c) - V_c(r_c)]. \quad (\text{A21})$$

The corresponding capillary force is derived from a stress balance at a plane cut through the liquid neck at $z = 0$ as

$$F = 2\pi r_i (1 - H r_i). \quad (\text{A22})$$

To compute the capillary force of a pendular bridge for a given volume, we follow the same procedure as for the pressure controlled case, but compute a series of solutions for various mean curvatures H . The mean curvature that yields the desired liquid volume is obtained from an interpolation of $V(H)$, and is further employed to calculate the surface-to-surface separation s from Eq. (A18) and capillary force F according to Eq. (A22).

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