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Young–Laplace equation for liquid crystal interfaces
The equilibrium shape of fluid-fluid interfaces: Derivation and a new numerical method for Young’s and Young-Laplace equations

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Many physical problems require explicit knowledge of the equilibrium shape of the interface between two fluid phases. Here, we present a new numerical method which is simply implementable and easily adaptable for a wide range of problems involving capillary deformations of fluid-fluid interfaces. We apply a simulated annealing algorithm to find the interface shape that minimizes the thermodynamic potential of the system. First, for completeness, we provide an analytical proof that minimizing this potential is equivalent to solving the Young-Laplace equation and the Young law. Then, we illustrate our numerical method showing two-dimensional results for fluid-fluid menisci between vertical or inclined walls and curved surfaces, capillary interactions between vertical walls, equilibrium shapes of sessile heavy droplets on a flat horizontal solid surface, and of droplets pending from flat or curved solid surfaces. Finally, we show illustrative three-dimensional results to point out the applicability of the method to micro- or nano-particles adsorbed at a fluid-fluid interface. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4904391]

I. INTRODUCTION

Fluid-fluid interfaces are of fundamental importance for a great number of applications in soft matter. For example, the adsorption of colloids, nanoparticles, polymers, or proteins at fluid-fluid interfaces are highly relevant for industrial products (food,1 Pickering Emulsion,2–4 particle synthesis,5 cosmetics, paints, etc.) and vital for engineering processes (washing, coating, water purification, etc.). Such phenomena have also an interest from a scientific point of view due to the specific particle-particle interactions that arise at such interfaces.6–12 A fundamental role in the underlying physics is played by the capillary deformations of a fluid-fluid interface when it comes into contact with a solid surface. The capillary interactions induced by these deformations can be exploited, for example, in the self-assembly of interface adsorbed colloidal particles,13–16 which can be directed by manipulating, e.g., the interface shape,17–19 the particle shape,20–23 or the particle concentration.24,25 The capillary deformations may also play an important role in the adsorption of a single non-spherical colloidal particle at a fluid-fluid interface, which is a recurrent issue in soft matter (e.g., Refs. 26–30). In recent works,31–36 the equilibrium configuration of such a colloidal particle has been studied theoretically, neglecting however the capillary deformations. This study is a step towards understanding the role of capillary deformations for such non-trivial geometries.

In this work, we investigate the shape of an interface between two homogeneous fluid phases in the presence of external solid surfaces and possibly gravity. We focus on the equilibrium configuration only, without taking into account the dynamics of these systems. We study the problem from a macroscopic point of view, so we treat the interface as a two-dimensional surface with zero thickness and without capillary waves. A free energy $\gamma S$ is assigned to an interface with surface area $S$ between two demixed fluids, where $\gamma$ is the associated surface tension. The preferred shape of the interface is the one with minimum free energy, i.e., minimum $S$, which is a flat surface for a free meniscus and a spherical shape for a finite droplet without gravity. However factors like gravity, the wettability of the solids in contact with the interface, electrostatic fields, etc., influence the free energy of the interface and so deform it in a non-trivial way.

In absence of electric fields, the fluid-fluid interface shape is described by the Young-Laplace equation and Young’s law (see Eqs. (18) and (24) in Sec. II). These equations, usually proved through mechanical force-balance arguments (e.g., Refs. 37–39), can be obtained using a variational principle (e.g., Refs. 40 and 41). For completeness in Sec. II, we prove this showing a short derivation (partially new, to the best of the author’s knowledge) in which we minimize the total thermodynamic potential of a fluid-fluid-solid system with respect to the fluid-fluid interface shape.

As the Young and Young-Laplace equations have an analytic solution only in the simplest cases, the interface shape is usually calculated numerically. A widely used approach to calculate a minimum energy surface is by means of the Surface Evolver program.42 But several other approaches, both theoretical and numerical, have been used for studying the fluid-fluid interface shape in different physical problems, e.g., meniscus shapes and capillary interactions,43–52 droplet shapes,53–57 diffuse interfaces,58–60 or fluid-fluid interfaces in contact with deformable solids.61–63

In this article, we introduce a new numerical method to obtain the minimum-energy shape of a fluid-fluid interface. It
is simply implementable and easily adaptable to study a wide range of problems. Thanks to these advantages, we believe our method can be useful in future research in the soft-matter field, in particular for studying non-spherical micro- or nanoparticles at interfaces.

II. THEORY

In this section, we prove that solving the Young-Laplace equation and imposing Young’s law is equivalent to minimizing the thermodynamic potential of a fluid-fluid system in contact with a solid at a fixed position. Although such a proof is widely known and accepted (a first version is due to Gauss), here we present a concise version for completeness. We consider (see Fig. 1) a fixed volume \( V \) that contains two demixed fluids and that is surrounded by a solid surface with fixed position. We assume the solid to be non-deformable. Henceforth, we denote the two fluids by fluid 1 and fluid 2, where fluid 1 is the lighter one. The volume and bulk mass density are, respectively, \( V_1 \) and \( \rho_1 \) for fluid 1, \( V_2 \) and \( \rho_2 \) for fluid 2, with \( V_1 + V_2 = V \). The fluids are in contact with a reservoir that keeps constant the temperature \( T \) and the chemical potentials \( \{ \mu_i \}_{i=1}^N \), where \( s \) is the total number of chemical species present in fluid 1 and fluid 2, and \( \mu_i \) is the chemical potential of the \( i \)th species. From now on, we ignore the \( T \) and \( \{ \mu_i \}_{i=1}^N \) dependence as they are not relevant in our derivation. We introduce a Cartesian coordinate system with the \( z \) axis anti-parallel to the gravity direction. For simplicity, we assume that the fluid-fluid interface can be written as a function \( h = h(x,y) \), although our derivation can be easily extended for more general surfaces (e.g., with overhangs). The surface area of the solid wall in contact with fluid 1 is \( W_1[h] \), and that with fluid 2 is \( W_2[h] \), where \( [h] \) means a functional dependence with respect to \( h \). The surface tensions associated to the three interfaces fluid 1-fluid 2 and solid-fluid 2, which play an important role in the derivation below, are highlighted the fluid 1-fluid 2 and solid-fluid 2 interfaces, which play an important role in the derivation below.

![Fig. 1. Sketch of a fluid-fluid interface. The fluids are bounded by a fixed solid surface and they are in contact with a reservoir that keeps constant the temperature and the chemical potentials of all species. In blue and red are highlighted the fluid 1-fluid 2 and solid-fluid 2 interfaces, which play an important role in the derivation below.](image)

The total thermodynamic potential of this system is

\[
\Omega[h] = \gamma S[h] + \gamma_1 W_1[h] + \gamma_2 W_2[h] + E_g[h] + \Omega_1(V_1[h]) + \Omega_2(V_2[h]),
\]

where \( S[h] \) is the surface area of the fluid-fluid interface, \( \Omega_1(V_1[h]) \) and \( \Omega_2(V_2[h]) \) are the bulk grand canonical potentials of fluid 1 and 2, respectively, and \( E_g[h] \) is the gravitational energy of the system, given by

\[
E_g[h] = g \rho_1 \int_{V_1[h]} z \, d\mathbf{r} + g \rho_2 \int_{V_2[h]} z \, d\mathbf{r}
\]

with \( \mathbf{r} = (x,y,z) \) and \( g \) the gravity acceleration. Here, we assume that the two fluids have a constant mass density on a length scale at least of the order of the capillary deformations. Note that the integration domains over \( V_1[h] \) and \( V_2[h] \) are functionals of \( h \).

The total area of the fluid 1-fluid 2 interface is

\[
S[h] = \int_D dxdy \sqrt{1 + h_x^2 + h_y^2},
\]

where \( D \) is the domain of \( h \) and \( h_\alpha = \frac{\partial h(x,y)}{\partial \alpha} \), with \( \alpha = x,y \). The functional derivative of \( S \) with respect to \( h \) is

\[
\frac{\delta S}{\delta h(x,y)} = h_x \left( 1 + h_y^2 \right) + h_y \left( 1 + h_x^2 \right) - 2 h_x h_y h_{xy},
\]

where \( h_{\alpha\beta} = \frac{\partial^2 h(x,y)}{\partial \alpha \partial \beta} \), with \( \alpha, \beta = x, y \). Equation (4) can be written as

\[
\frac{\delta S}{\delta h(x,y)} = \nabla \cdot \mathbf{n}(x,y),
\]

where \( \mathbf{n}(x,y) = \frac{\nabla (z - h(x,y))}{|\nabla (z - h(x,y))|} \) is the unit normal to the \( h \) surface in the point \((x,y,h(x,y))\), pointing from fluid 2 toward fluid 1. We assume now that the solid-fluid 2 interface can be written as a function \( f = f(x,y) \). As before we do this for simplicity, although it is easy to extend the derivation to more general surfaces. Note that \( f \) is a functional of \( h \), since \( f \) and \( h \) are connected at the three-phase contact line. The areas of the solid walls in contact with the fluids can be written as

\[
W_2[h] = \int_D dxdy \sqrt{1 + f_x^2 + f_y^2},
\]

\[
W_1[h] = W - W_2[h],
\]

where \( W \) is the total surface area of the solid in contact with the fluid-fluid system that does not depend on \( h \). Note that the domain of \( f \) coincides here with that of \( h \). The functional derivative of the solid-fluid surface energy with respect to \( h \) is

\[
\frac{\delta (\gamma_1 W_1 + \gamma_2 W_2)}{\delta h(x,y)} = \Delta \gamma \int_D du dv \frac{\delta W_2}{\delta f(u,v)} \frac{\delta f(u,v)}{\delta h(x,y)} + \Delta \gamma \int_D du dv \nabla \cdot \mathbf{N}(u,v) \frac{\delta f(u,v)}{\delta h(x,y)} = \Delta \gamma \Phi(x,y),
\]

where \( \Delta \gamma = \gamma_1 - \gamma_2 \) is the difference in surface tension between the two fluids.
where $\Delta \gamma = \gamma_2 - \gamma_1$, where we defined the integral as $\Phi(x,y)$ for later convenience, and where

$$\hat{N}(x,y) = \frac{\nabla(z-f(x,y))}{|\nabla(z-f(x,y))|}$$  (10)

is the unit normal to the $f$ surface in $(x,y,f(x,y))$, pointing from the solid toward fluid 2. The functional derivative $\delta f/\delta h$ is explicitly written as

$$\frac{\delta f(u,v)}{\delta h(x,y)} = \begin{cases} \delta(x-u)\delta(y-v), & \text{if } (x,y) \in \{t\}, \\ 0, & \text{otherwise}, \end{cases}$$

where $\delta(x)$ is the Dirac delta function and $\{t\}$ is the set of all the points $(x,y)$ where $f(x,y) = h(x,y)$, i.e., such that $(x,y,h(x,y))$ is a point of the solid-fluid 1-fluid 2 three-phase contact line.

Equation (2) can be written as

$$E_x[h] = g \rho_1 \int_V z \, d\mathbf{r} + \frac{g \Delta \rho}{2} \iint_D (\hat{n}^2 - f^2) \, dx \, dy$$  (11)

with $\Delta \rho = \rho_2 - \rho_1$. The functional derivative of $E_x$ with respect to $h$ is

$$\frac{\delta E_x}{\delta h(x,y)} = g \Delta \rho h(x,y).$$  (12)

Here, the $\delta f/\delta h$ term does not appear because its contribution is canceled by the $h^2$ term.

The grand canonical potentials can, by extensiveness, be written as

$$\Omega(V_1) + \Omega(V_2) = -P_1 V_1[h] - P_2 V_2[h],$$  (13)

where $P_1$ and $P_2$ are the bulk pressures of fluids 1 and 2, i.e., their pressures at the reference level $z = 0$. Using that

$$V_1[h] = V - V_2[h], \quad V_2[h] = \int_D dxdy(h-f),$$

we find that

$$\frac{\delta[\Omega_1(V_1) + \Omega_2(V_2)]}{\delta h(x,y)} = -\Delta P,$$  (15)

with $\Delta P = P_2 - P_1$. Again, $\delta f/\delta h$ does not appear here because its contribution is canceled by the $h$ term.

Finally, we use the minimum energy principle to state that the functional derivative with respect to $h$ of the total thermodynamic potential $\Omega_t$ (Eq. (1)) is zero at equilibrium, that is,

$$\frac{\delta \Omega_t[h]}{\delta h(x,y)} = 0.$$  (16)

Using Eqs. (5), (9), (12), and (15), we obtain from Eq. (16) that

$$\gamma \nabla \cdot \hat{n}(x,y) + \Delta \gamma \Phi(x,y) + g \Delta \rho h(x,y) - \Delta P = 0,$$  (17)

with $\Phi(x,y)$ defined in Eq. (9). First, we consider this equation for all the $(x,y) \notin \{t\}$, i.e., where the interface is not in contact with the solid surface. Here, $\Phi(x,y) = 0$, so it follows:

$$\gamma \nabla \cdot \hat{n}(x,y) = \Delta P - g \Delta \rho h(x,y),$$  (18)

which is the celebrated Young-Laplace equation. It is an equation for $h(x,y)$ at fixed $\Delta P$, which acts as a Lagrange multiplier to set $V_2$ and $V_1 = V - V_2$ to the imposed volumes of fluid 2 and fluid 1, respectively. Usually in this equation, the mean curvature of $h(x,y)$ is introduced, defined as $\nabla \cdot \hat{n}(x,y)/2$.

To derive the Young Law, we take Eq. (17) for any $(x,y) \in \{t\}$, i.e., in a three-phase contact point, obtaining

$$\gamma \nabla \cdot \hat{n}(x,y) + \Delta \gamma \nabla \cdot \hat{N}(x,y) = \Delta P - g \Delta \rho h(x,y).$$  (19)

We now consider an infinitesimal volume $dV$ located inside fluid 2 and in contact with the three-phase contact line. The volume $dV$ is delimited at one face by the fluid 1-fluid 2 interface, at another face by the fluid 2-solid interface, and at the remaining three faces by planes orthogonal to the fluid 2-solid interface (see Fig. 2). We take $dV$ small enough to assume $h(x,y)$ and $f(x,y)$ to be linear and integrate Eq. (19) over $dV$. The right-hand side of Eq. (19) is constant over $dV$ in the limit $dV \rightarrow 0$ so its integration gives zero contribution in this limit. Hence, we find

$$\int_{dV} \nabla \cdot \left[ \hat{n}(x,y) + \frac{\Delta \gamma}{\gamma} \hat{N}(x,y) \right] d\mathbf{r} = 0,$$  (20)

which, upon applying the divergence theorem, yields

$$w(x,y) \cdot \left[ \hat{n}(x,y) + \frac{\Delta \gamma}{\gamma} \hat{N}(x,y) \right] = 0,$$  (21)

where

$$w(x,y) = \hat{n}(x,y)dS - \hat{N}(x,y)dW + \hat{a}dH + \hat{b}dA + \hat{c}dA,$$  (22)

with $\hat{n}$, $-\hat{N}$, $\hat{a}$, $\hat{b}$, and $\hat{c}$ the normals toward outside of the various faces of $dV$ (see Fig. 2). The areas of these faces are, respectively, $dS$, $dW$, $dH$, $dA$, and $dA$. By definition of $dV$, we have $\hat{n} \cdot \hat{b} = \hat{n} \cdot \hat{c} = \hat{N} \cdot \hat{a} = \hat{N} \cdot \hat{b} = \hat{N} \cdot \hat{c} = 0$. We call $\theta$ the angle formed by the fluid 1-fluid 2 interface with the solid-fluids interface and measured inside fluid 2 (so inside $dV$). Therefore, $\hat{n} \cdot \hat{a} = -\sin \theta$ and $\hat{n} \cdot \hat{N} = \cos \theta$. Then by definition of the normal $\hat{n} \cdot \hat{n} = \hat{N} \cdot \hat{N} = 1$, and hence from Eq. (21), it follows that:

$$\frac{\Delta \gamma}{\gamma} = \frac{\cos \theta dW + \sin \theta dH - dS}{\cos \theta dS - dW}.$$  (23)

If we use now that $dH = \sin \theta dS$, we obtain

$$\frac{\gamma \gamma_1 - \gamma \gamma_2}{\gamma} = \cos \theta,$$  (24)

FIG. 2. Profile and 3D view of the infinitesimal volume $dV$ on which we integrate Eq. (19). We chose $dV$ small enough to consider $h(x,y)$ and $f(x,y)$ linear within it. One face of $dV$ is the fluid 1-fluid 2 interface (colored in blue in the picture on the right), and it has normal $\hat{n}$ and area $dS$. Another face of $dV$ is the solid-fluid 2 interface, with normal $-\hat{N}$ and area $dW$. The remaining three faces of $dV$ are orthogonal to the solid-fluid 2 interface and have, respectively, normal $\hat{a}$, $\hat{b}$, and $\hat{c}$ and area $dH$, $dA$, and $dA$. 

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which is Young’s law. It tells that the contact angle of the fluid 1−fluid 2 interface with the solid surface is univocally fixed by the three surface tensions.

We have thus proven that minimizing the potential $\Omega$, of a fluid-fluid-solid system (Eq. (1)) with respect to the fluid-fluid interface shape is equivalent to solving the Young-Laplace equation and the Young law.

III. NUMERICAL METHOD

In our method, we find the equilibrium shape of a fluid−fluid interface for a given volume of each fluid. This is done by calculating numerically the interface shape that minimizes the following thermodynamic-potential functional:

$$E = \gamma S + (\gamma_2 - \gamma_1)W_2 + g\Delta\rho \int_{V_2} z \, d\mathbf{r}, \quad \text{(25)}$$

with the constraint that the volumes $V_1$ and $V_2$ of fluid 1 and fluid 2 have a preset value. Here, $S$ is the area of the fluid 1−fluid 2 interface, $W_2$ is the area of the solid surface in contact with fluid 2. We recall that $S$, $W_2$, $V_1$, $V_2$, and $E$ are functional of the fluid-fluid interface shape. From the Lagrange multipliers theorem, it follows that we are minimizing the potential:

$$\Omega = E - P_1V_1 - P_2V_2, \quad \text{(26)}$$

where the Lagrange multipliers $P_1$ and $P_2$ depend on the choice of $V_1$ and $V_2$. This expression for $\Omega$ is identical to Eq. (1), except for a shift in the energy reference level not depending on the fluid-fluid interface shape. Therefore, the interface shape that we calculate minimizing $\Omega$ (Eq. (26)) is the one that solves the Young-Laplace equation and the Young Law, as proved in Sec. II. For convenience, we rewrite $E$ (Eq. (25)) as

$$E = \gamma S - W_2 \cos \theta + \ell^2 \int_{V_2} z \, d\mathbf{r}, \quad \text{(27)}$$

where

$$\ell = \sqrt{\frac{\gamma}{g \Delta \rho}}, \quad \text{(28)}$$

is the capillary length and $\cos \theta$ is defined by Eq. (24). Thus, given the fluid volumes and the configuration of the external solid surfaces, the input parameters that determine the shape of the fluid−fluid interface are $\cos \theta$ and $\ell$.

For simplicity and illustration purpose, we consider here systems with translational invariance along the Cartesian coordinate $y$, so that the fluid-fluid interface can be represented by a 2D profile (but a generalization of our method to 3D systems without symmetries is straightforward and will be presented elsewhere). We represent the interface profile using a set of points forming a 1D grid, as shown in Fig. 3. We indicate the two extreme points of the grid with $C_1$ and $C_2$, which are constrained to stay on the imposed solid boundaries of the fluid-fluid system. We call the remaining points $P_i$ ($i = 1, \ldots, N$) “free points,” and these are allowed to be wherever outside the solids in the $(x,z)$-plane. The interface is given by the set of segments linking any two consecutive points (by definition, $P_{i+1}$ is consecutive to $P_i$, $P_i$ to $C_1$ and $C_2$ to $P_N$). The fluid volume is set by the initial positions of the grid points.

The interface equilibrium shape follows from the positions of the points that minimize $E$ (Eq. (27)) fulfilling the constraint of a fixed volume for the fluids. To find these positions, we apply a simulated annealing algorithm,\textsuperscript{65} that is an adaptation of a Monte Carlo method, where a temperature is artificially introduced and gradually lowered during the simulation. This drives the system toward its minimum energy configuration in a way that resembles an annealing process, from which the name of the method is derived. In our model, we change randomly the point positions, keeping the fluid volumes $V_1$ and $V_2$ constant and not allowing unphysical configurations (e.g., self-intersecting, see Appendix). Every configuration change is then accepted with probability

$$\mathcal{P} = \begin{cases} 1, & \text{if } \Delta E < 0 \\ \exp \left( -\frac{\Delta E}{k_BT} \right), & \text{if } \Delta E \geq 0 \end{cases} \quad \text{(29)}$$

where $\Delta E$ is the variation of $E$ (Eq. (27)) between the old and the new configuration of the points, and $T$ is the temperature-like control parameter ($k_B$ is the Boltzmann constant). In the simulation, these configuration changes are performed continuously while $T$ is gradually lowered starting from an initial $T_0$. When $T$ becomes zero, the simulation ends. Thanks to the randomness involved, the simulated annealing has the advantage of providing escape routes out of metastable states, unlike energy-gradient methods. However, the speed of the $T$ decrement and the initial value $T_0$ must be chosen slow and high enough, respectively. To avoid metastable states, $k_BT_0$ needs to be much bigger than the energy barrier of these states. An adequate choice of $T_0$ and its decrement speed depends on the discrepancy between the initial configuration of the points and the final solution. As a general rule: The slower is the decrement of $T$, the better is the approximation of the final solution. If different equivalent global minima of the energy are present, then the method finds randomly only one of these. A detailed description on the implementation of our method is provided in the Appendix.

It is worth to mention that our method can be adapted to work at constant pressure instead of constant volume by removing the constraint of a fixed volume and by minimizing the potential $\Omega$ (Eq. (26)), instead of $E$ (Eq. (27)). This can be useful, for example, for studying curved fluid-fluid interfaces.
IV. RESULTS

We present some results as obtained from our method. The main aim of this section is to show that this method is applicable to a wide range of physical problems involving the equilibrium shape of fluid-fluid interfaces. All the systems shown here have translational invariance along the $y$ direction, pointing out of the paper. The simulation parameters ($N$, $T_0$, etc.) used for the various results are reported in Table II of the Appendix.

A. Meniscus close to a vertical wall

First, to prove the accuracy of the method, we consider the case of a fluid-fluid interface in the half-space $x > 0$ close to a vertical wall located in the plane $x = 0$. In this case, it is known analytically that the height profile $z(x)$ of the meniscus is expressed\textsuperscript{66,67} by the inverse relation

$$
x(z) = \frac{\ell}{2} \cosh \left(\frac{2z}{\ell}\right) - \cosh \left(\frac{2z_0}{\ell}\right)
- \sqrt{4 - \frac{z^2}{\ell^2}} + \sqrt{4 - \frac{z_0^2}{\ell^2}},
$$

(30)

where $z$ is negative if $\cos \theta \leq 0$ and positive otherwise, and the contact height $z_0 = z(0)$ is given by

$$
z_0^2 = 2\ell^2(1 - \sin \theta).
$$

(31)

In Fig. 4, we show the interface profiles obtained from our numerical method with $N = 28$ free points of the grid for different values of $\cos \theta$. For comparison, we also plot the corresponding analytical solutions of Eq. (30), which are indistinguishable from our numerical curves. To reproduce the flatness of the meniscus for $x \to \infty$, we placed another vertical wall with contact angle $\pi/2$ far beyond the scale of Fig. 4. All the numerical and analytical solutions shown are slightly shifted in $z$ such that $z(20\ell) = 0$. The inset of Fig. 4 also shows excellent agreement between our numerical results and the analytic expression Eq. (31) of the contact height.

In Fig. 5, we study the influence of the number of points on the solution. We consider the system of Fig. 4 for the case $\cos \theta = 0.9$, and we show the numerical solutions we obtain using a grid with a different number of free points, i.e., $N = 3$ (a), $N = 8$ (b), $N = 38$ (c) and $N = 38$ (d). We show the numerical solutions shifted in $z$ to match our solutions at $x = 20\ell$. The initial configuration is limited by a vertical wall with contact angle $\pi/2$. For convenience, we show the solutions only in the region $x \in [0, 10\ell]$. The dotted lines are the analytical solutions from Eq. (30) shifted in $z$ to match our solutions at $x = 20\ell$. The initial configuration of the points is a equally spaced grid on the $x-$axis. The final profiles indicate migration of the points during the simulation to pack more on the curved part of the interface. The insets show the behavior of the energy $E$ (Eq. (27), $\gamma_y$ is the length of the system in $y$) with respect to the number of cycles performed in the simulation. These graphs prove that during the simulation, the system evolves toward configurations with lower energy, the more so for a larger number of grid points $N$.

![FIG. 4. Height profiles $z(x)$ of fluid-fluid menisci with capillary length $\ell$ close to a vertical wall in the plane $x = 0$ for different contact angles $\theta$. The full lines are obtained numerically from our algorithm and shifted in $z$ to have the same asymptotic height for $x \to \infty$. The dotted lines are the analytical solutions from Eq. (30), indistinguishable from the numerical curves. In the inset, the numerical values of the capillary rise $z_0$ (black crosses) are compared with the analytic result of Eq. (31) (full line).](image-url)

![FIG. 5. Height profile $z(x)$ of a fluid-fluid meniscus close to a vertical wall in $x = 0$ with contact angle $\theta$ and $\cos \theta = 0.9$. We show the numerical solutions obtained using a grid with a different number of free points (a): $N = 3$; (b): $N = 8$; (c): $N = 38$; (d): $N = 38$ and the points are plotted in the graph. The right in the half-space $x > 20\ell$, the fluid-fluid system is limited by a vertical wall with contact angle $\pi/2$. For convenience, we show the solution only in the region $x \in [0, 10\ell]$. The dotted lines are the analytical solutions from Eq. (30) shifted in $z$ to match our solutions at $x = 20\ell$. The initial configuration of the points is a equally spaced grid on the $x-$axis. The final profiles indicate migration of the points during the simulation to pack more on the curved part of the interface. The insets show the behavior of the energy $E$ (Eq. (27), $\gamma_y$ is the length of the system in $y$) with respect to the number of cycles performed in the simulation. These graphs prove that during the simulation, the system evolves toward configurations with lower energy, the more so for a larger number of grid points $N$.](image-url)
all the simulations, with a lower energy at higher number of grid points $N$, i.e., the approximation of the numerical solution improves by increasing $N$. Therefore, a good way to choose a proper value for $N$ is to repeat the simulation using higher values of $N$, until the energy of the final solution does not vary anymore (within the desired precision).

The relatively small number of points needed to describe the interface is important to generalize to two-dimensional interfaces (i.e., three-dimensional systems).

**B. Meniscus between flat and/or curved surfaces**

Our numerical method is very general and allows to consider solid boundaries of any shape, which is important for future studies of odd-shaped nano-particles for instance. In this subsection, we provide some examples presenting results for fluid-fluid menisci located between inclined walls and/or curved surfaces.

In Fig. 6, we show some numerical solutions for the shape of a meniscus between two inclined walls. The two walls are symmetric with respect to a central vertical axis and as expected also the solutions fulfill this symmetry. Another indication of the correctness of our method is given by the contact angle that each numerical solution forms with the two external surfaces. The numerical value $\theta^*$ of the contact angle of the meniscus with each solid surface is calculated from the positions of the point of the interface grid constrained on that surface and its first neighbor ($P_i$ for $C_1$ and $P_N$ for $C_2$). The obtained values of $\cos \theta^*$ for each solution match very well with the input parameter $\cos \theta$; in particular, we find that $|\cos \theta^* - \cos \theta| < 0.05$ in all cases. A higher precision can be achieved by increasing the number of points $N$ of the interface.

In Fig. 7, we present analogous results for fluid-fluid menisci located between a curved surface and an inclined wall (a), and inside a cylindrical cavity with symmetry axis pointing out of the paper (b). In both these systems, the numerical solutions are obtained using different values of $\cos \theta$ and different volumes for fluid 2 (the fluid below). We see that, as expected, the meniscus adapts its shape upon changing the fluid volume to keep its contact angles with the external surfaces constant. We point out once more that we are not imposing a priori this constraint for the contact angles of the meniscus, but this is automatically obtained upon minimizing the thermodynamic potential $E$ (Eq. (27)) of the system.

**C. Capillary interaction**

In this section, we present results on the capillary interaction between two vertical flat walls, although solid surfaces with any other shape can be taken into account as well.

In Fig. 8, we consider a system of two vertical walls, each of width $\ell$, immersed in the fluid-fluid interface and at a surface-to-surface distance $D$ from each other. The origin of the $x$ axis is in the middle between the two walls. The whole fluid-fluid system is enclosed between two external vertical walls in the half-planes $x < -15\ell$ and $x > 15\ell$, respectively, far beyond the scale of the graphs in Fig. 8. Three one-dimensional grids of points are necessary to represent the interface: One set between the two inner central walls and the other two between the external walls and the central walls. During the simulation, fluid 2 can exchange volume between these three regions, but the sum of the volumes below the three interfaces is kept constant. The central wall on the left has contact angle $\theta_l$, the one on the right $\theta_r$. We assign a contact angle $\theta = \pi/2$ to the two external walls, to induce a flat meniscus far from the two central walls in order to mimic an infinite system.

To consider in our model the presence of solid surfaces with different contact angles, we generalize Eq. (27) to

$$E = \gamma \left[ S - \sum_k W_2(k) \cos \theta_k + \epsilon^2 \int_{V_2} z \, dz \right],$$

where the $k$-sum is over all the solid walls, $\theta_k$ is the contact angle of the $k$th solid surface, and $W_2(k)$ is its surface area in contact with fluid 2. In the system of Fig. 8, we have $k = 2$, with the two solid walls referred to as left ($l$) and right ($r$).
For the system considered in Fig. 8, we have calculated the shape of the fluid-fluid interface for several surface-to-surface distances between the left and right wall, using as contact angles: (a) \( \cos \theta_l = \cos \theta_r = 0.8 \); (b) \( \cos \theta_l = \cos \theta_r = -0.5 \); (c) \( \cos \theta_l = 0.8 \) and \( \cos \theta_r = -0.5 \). In Fig. 8(a), we see the capillary rise of the interface obtained by decreasing \( D \), and in Fig. 8(b), we see the capillary drop. The height of the capillary rise is greater than the depth of the capillary drop—at the same \( D \)—because in the former case the contact angle has a larger absolute value. In case (c), we see the interface shape due to the interplay between a capillary rise and drop.

For each of the cases (a), (b), and (c) of Fig. 8, we report on the very right the effective potential \( E(D) \) and the force \( F(D) \) of the capillary interaction between the two central walls, defined as \( F \equiv dE/dD \). Here, \( E(D) \) is the minimum of the functional of Eq. (32) and it is computed as described in the appendix. In the insets, we show \( E(D) \) shifted to be zero at \( D = 5\ell \). We consider \( F \) only for \( D \leq 5\ell \), such that the minimum distance between the central walls and the external walls always exceeds \( 10\ell \). So we can reasonably assume that the effects of the external walls on \( F \) are negligible. For both the cases (a) and (b), we see an attractive force. In (a), the force is stronger than in (b) because the absolute value of the contact angle is greater. In (c), we observe a repulsive force at large separations due to the fact that \( \cos \theta_l \) and \( \cos \theta_r \) have different signs. However, there is a maximum in \( E(D) \) for \( D \geq 0.5\ell \) and so an attractive force between the walls exists when they are closer than about \( 0.5\ell \).

This is caused by the different absolute values of \( \cos \theta_l \) and \( \cos \theta_r \), which generate a slight capillary rise for small \( D \), as we can see in Fig. 8(c).

In Fig. 9, we report the \( D \) dependence of the capillary rise \( z_c \) between the two walls at \( x = 0 \) for the cases (a) and (b) of Fig. 8. The reference level \( z = 0 \) is the height of the interface at \( x = \pm 15\ell \). Our numerical values (symbols) are compared with an approximate analytical result (line) given by

\[
z_c = \frac{2\ell^2}{D} \cos \theta.
\]

Equation (33) follows from the approximation, valid for two narrow vertical walls, that the meniscus between them has a cylindrical shape. To check this, use that the mean curvature \( \nabla \cdot \hat{n}/2 \) of a surface can be written as \(-\left(\kappa_1^{-1} + \kappa_2^{-1}\right)\), where \( \kappa_1 \) and \( \kappa_2 \) are the two radi of curvature. For the central point of a meniscus with cylindrical shape, we have \( \kappa_1 = R \), with \( R \) the radius of the circular section of the cylinder, and \( \kappa_2 = \infty \). Then applying Eq. (18) for \( x \to \pm 15\ell \), we have that \( \Delta P = 0 \), because here \( \nabla \cdot \hat{n} = 0 \), as the interface is flat, and \( h = 0 \) for the choice of the reference level. So the Young-Laplace Eq. (18) for the central point of the meniscus becomes \( 2\gamma = g\Delta_P z_c \). Equation (33) follows using that \( D = 2R \cos \theta \) (see Fig. 8(c), right panel). The agreement of our numerical values with Eq. (33) is quite good for \( D < \ell \), confirming that the approximation of a cylindrical shape for the meniscus is good for small \( D \).
D. Two-dimensional sessile and pendant droplets

In this subsection, we show that our numerical method is also usable for studying equilibrium shapes of droplets. Recall that here, we only consider two-dimensional droplets.

In Fig. 10, we report the equilibrium shape of a two-dimensional sessile droplet on a flat solid surface. The droplet is formed by fluid 2, which is the heavier of the two fluids. The numerical solutions are computed using different values of $\ell$ and $\cos \theta$. Considering $\gamma$ and the volume of the droplet as fixed constants, it follows that a lower $\ell$ corresponds to a higher $\Delta \rho$, i.e., to a heavier droplet. As a matter of fact in each graph of Fig. 10, we see that, for droplets with the same volume and contact angle, the effect of the gravity on the droplet shape increases by lowering $\ell$. As shown, our method is able to treat also the extreme case of low wettability (we see the case $\cos \theta = -0.9$ in the third graph of Fig. 10). As another indication of the correctness of the method, the equilibrium shapes are symmetric with respect to a central symmetry axis (in the figure, the solutions are shifted in $x$ to align their axes).

In Fig. 11, we show analogous results for two-dimensional droplets pending from a flat horizontal surface (a) and a highly curved surface (b). Here, fluid 2 forms a droplet that is located above the lighter fluid 1. This droplet does not fall down because it is wetting an upper solid surface that keeps it in mechanical and thermodynamical equilibrium. Such a situation is obtained in our model by changing the sign of the gravity vector, i.e., using for the functional $E$ the expression

$$ E = \gamma \left[ S - W_2 \cos \theta - \ell^2 \int z \, d\mathbf{r} \right], $$

instead of Eq. (27). We point out that a sessile droplet formed by a fluid lighter than the surrounding fluid also has an energy given by Eq. (34), and in this case, the minus sign multiplying $\ell^2$ is needed because $\Delta \rho$ is negative (see Eq. (25)). Therefore, the results we present for pendant droplets are likewise valid for sessile droplets lighter than the fluid outside.

If the gravitational force is too strong, i.e., $\ell$ too low, then our method does not find an equilibrium configuration (all the free points of the interface keep going in the direction of $\mathbf{g}$ until the simulation stops). This corresponds to the physical situation in which the pendant droplet detaches itself or partially falls down.

In Fig. 11(a), we see equilibrium shapes of pendant droplets from a flat solid surface, obtained numerically using different values of $\ell$ and $\cos \theta$. As an indication of the correctness of our method, the equilibrium shapes are symmetric with respect to a central symmetry axis (in the figure, the solutions are shifted in $x$ to align their axes). Moreover, as expected, our solutions show that by decreasing $\ell$, the effect of the gravity on the droplet shape is increased. As said before, under a certain value of $\ell$, our method does not find an equilibrium configuration for the pendant droplet, that is, the grid points keep going in the direction of $\mathbf{g}$ until the simulation ends. For a fixed volume of the droplet, we found that this limit value $\ell^*$ increases by lowering $\cos \theta$. The value of $\ell^*$ we obtained for the three contact angles considered in Fig. 11(a) is reported in Table I. However, we point out that there could be a certain inaccuracy in this value. Indeed, a simulation with $\ell$ below $\ell^*$ can still produce a stable equilibrium shape for the pendant droplet if the annealing is too fast or the initial temperature $T_0$ is too low. This happens because the grid points, that during the simulation would keep going in the direction of $z$ (as $\ell < \ell^*$), get trapped in a metastable state, and so they form a metastable equilibrium shape instead of falling down. The closer is $\ell$ to $\ell^*$ (with $\ell < \ell^*$), the slower the annealing and the higher $T_0$ need...
Equilibrium profiles of a 2D droplet pending from (a) a flat solid surface; (b) a highly curved solid surface. The fluid forming the droplet is heavier than the fluid outside. The solutions are obtained numerically by our method using different values of $\cos \theta$ and $\ell$ in the potential $E$ (Eq. (34)). The vertical axis is $z/\sqrt{A}$ and the horizontal axis $x/\sqrt{A}$, with $A$ the area of the droplet. As expected our solutions show that, for a fixed $\cos \theta$, decreasing the value of $\ell$ means to increase the gravity effect on the droplet shape. Moreover, the results in (b) show that, by changing the wettability of the system, the droplet prefers to wet a solid surface with a different curvature. Therefore, its minimum energy position on the solid surface changes with respect to $\cos \theta$.

![Equilibrium profiles of a 2D droplet](image)

FIG. 11. Equilibrium profiles of a 2D droplet pending from (a) a flat solid surface; (b) a highly curved solid surface. The fluid forming the droplet is heavier than the fluid outside. The solutions are obtained numerically by our method using different values of $\cos \theta$ and $\ell$ in the potential $E$ (Eq. (34)). The vertical axis is $z/\sqrt{A}$ and the horizontal axis $x/\sqrt{A}$, with $A$ the area of the droplet. As expected our solutions show that, for a fixed $\cos \theta$, decreasing the value of $\ell$ means to increase the gravity effect on the droplet shape. Moreover, the results in (b) show that, by changing the wettability of the system, the droplet prefers to wet a solid surface with a different curvature. Therefore, its minimum energy position on the solid surface changes with respect to $\cos \theta$.

TABLE I. The limit value $\ell^*$ of $\ell$, below which the two-dimensional pendant droplet shapes calculated by our numerical method are not stable. With $A$, we refer to the area of the droplet. As shown, $\ell^*$ depends on the contact angle $\theta$ of the droplet. For $\ell$ above $\ell^*$, some equilibrium pendant droplet shapes are plotted in Fig. 11(a).

<table>
<thead>
<tr>
<th>$\cos \theta$</th>
<th>$-0.9$</th>
<th>$0.0$</th>
<th>$0.9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ell/\sqrt{A}$</td>
<td>$3.1$</td>
<td>$2.7$</td>
<td>$2.0$</td>
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</table>

V. SUMMARY AND CONCLUSIONS

We have introduced a new numerical method able to calculate the equilibrium shape of a fluid-fluid interface in the presence of external solid surfaces and possibly gravity. First in Sec. II, we have presented a short proof that the Young-Laplace Eq. (18) and Young’s Law (24) derive from the minimization of the thermodynamic potential (Eq. (1)) of the fluid-fluid system. Then in Sec. III, we have illustrated our method, providing in the Appendix a detailed description of the algorithm implementation for 1D fluid-fluid interfaces. Finally in Sec. IV, we have presented some results to show the applicability of this method to a wide range of problems. In Sec. IV A, we have proved the correctness of our numerical method showing an excellent agreement between numerical and analytical solutions. In Sec. IV B, we have reported the shape of menisci in contact with vertical or inclined walls and curved surfaces to show the possibility of considering any kind of shape for the solid surfaces in contact with the interface. This is relevant for future applications to colloidal particles of various shapes. In Sec. IV C, we have exploited our method to study the capillary rise and capillary interactions. In this paper, we have considered the capillary interaction between vertical flat solid surfaces, although the same analysis can be done for solid surfaces with any shape. We have shown how the magnitude and the sign of the capillary interaction between the two solids change by tuning the solids contact angle and distance. In Sec. IV D, we have applied our numerical method to study the equilibrium shape of two-dimensional droplets. In principle, three-dimensional droplets can be studied with the same method, and results about this will be presented elsewhere. We have considered both sessile droplets on a horizontal flat solid surface and pending droplets from flat horizontal and curved solid surfaces. We have shown how their shape varies by tuning the wettability and the weight of the droplet. We have also pointed out that by our method, we can study the preferred position of the droplet on the solid with respect to the solid surface curvature.

To focus on the basic ingredients of the method and on the fundamental underlying physics, in this work, we have considered only systems with translational invariance along a direction orthogonal to the gravity vector, i.e., represented by a 1D fluid-fluid interface. However, the method can be applied to generic 3D systems, i.e., requiring 2D fluid-fluid interfaces. In particular, we believe that our numerical method is very valuable for the study of adsorbed micro- or nanoparticles at fluid-fluid interfaces. To show that the method can indeed be applied to this kind of 3D problems, we report in Fig. 12(a), the equilibrium shape of a fluid-fluid interface with a different contact angle prefers a different curvature of the solid surface that it is wetting; for high contact angles, the droplet prefers a lowly curved convex surface rather than a highly curved one, and for low contact angle, it prefers a highly curved convex surface. Therefore, the final position of the droplet on the heterogeneously curved solid surface is given by an interplay between gravitational force, fluid-fluid, and fluid-solid interactions.
close to a solid parallelepiped with a fixed position, horizontal with respect to the unperturbed fluid-fluid interface plane. The horizontal sides of this particle are ten times the capillary length $\ell$. Therefore, each vertical face of the particle is large enough with respect to $\ell$ to behave as a vertical wall for the fluid-fluid interface if we stay far enough from the particle corners. Indeed, see the right panel in Fig. 12(a), the fluid-fluid interface height profile, as obtained numerically by our method, matches with the analytical prediction of Eq. (30).

In (b), there is a solid ellipsoid with the long axis equal to $6\ell$ and the short axis equal to $2\ell$, inclined with angle $\pi/5$ with respect to its vertical position, and with center of mass at $z = 0$ and with its four $10\ell \times 4\ell$ faces parallel to the $z$ direction. In (a), right panel, the height profile of the fluid-fluid interface is shown along the red line marked in the 3D view in the left panel, with $d$ the distance from the particle surface. The red dots are the positions of the fluid-fluid interface grid points obtained numerically by our method. The dotted line is the analytic solution of Eq. (30).

In (c), there are two solid vertical cylinders with height $2\ell$, radius $\ell$, center of mass in $z = 0$, and with a surface-to-surface distance equal to $\ell$. In (a), right panel, the height profile of the fluid-fluid interface is shown along the red line marked in the 3D view in the left panel, with $d$ the distance from the particle surface.
crosses a solid surface or the interface, then the move is rejected and the program goes to step “(l).”

If the selected point is C_k (k = 1, 2), it is moved along s_k (in one of the two possible directions, randomly chosen) until it covers a path of length δ, where δ is randomly chosen within [0, δ_{max}/2]. Given its new position C_k', if the segment C_k'P_j or P_N C_k' crosses the interface, the move is rejected and the program goes to step “(l).”

(e) The variation δε_ε of the gravitational term of ε due to the point move in step “(d)” is calculated.

If the point moved is a free point, say P_i, then: δε_ε = a â(ÅP_iB) + b â(ÅP_i'B), where A and B are the two closest neighbors of P_i on the interface, and â(ÅABC) is the gravitational energy of the triangle ABC, scaled with ξ_y and γ, and it is computed as

\[ \hat{G}(ABC) = \frac{\hat{A}(ABC) (A + B + C) \cdot z}{l^2}, \]

where \( \hat{A}(ABC) \) is the area of the triangle ABC. Then, \( a, b = \pm 1 \), where (see Fig. 13(a)) b is equal to the sign of \([\hat{A}(A-P') \times (A-P')'] \cdot \hat{y} \), with \( \hat{y} \) the normal in the y direction (i.e., pointing out of the paper). Then, \( a = b \) if the segment P_iP_j intersects the line passing through the segment AB, otherwise \( a = -b \).

If the point moved is C_k (k = 1, 2), then the area between s_k, C_i'P_j and C_i'P_i (or s_k, C_j'P_i and C_j'P_j) is decomposed into a certain number of triangles T_j (see Fig. 13(b)), and δε_ε = ± \( \sum_j \hat{G}(T_j) \), with the sign “±” positive if fluid 2 is gaining volume (moving C_k in C_k'), otherwise negative.

(f) The interface surface variation δS due to the point move in step “(d)” is calculated as the length variation of the segments forming the interface (and it is negative if the total length of the segments was decreased, positive otherwise).

(g) If the point moved in “(d)” is C_k (k = 1, 2), then the variation in the kth solid surface wet by fluid 2 is computed as δW_k(δ) = ± \( \int_{C_k'} s_k(u) du \), with “±” positive if fluid 2 is gaining volume (moving C_k in C_k'), otherwise negative. If the point moved in “(d)” is a free point, then δW_k(δ) = 0.

(h) The volume variation δV of the fluid 2 is calculated. If the point moved in “(d)” was a free point, say P_i, then, \( \delta V = a \hat{A}(AP_iB) + b \hat{A}(AP_i'B) \), where A and B are the two closest neighbors of P_i on the grid. \( \hat{A}(ABC) \) is the area of the triangle ABC, and \( a, b = \pm 1 \). The signs of \( a \) and \( b \) are computed as described in step “(e).” If the point moved in “(d)” was C_k (k = 1, 2), then the area between s_k, C_i'P_j and C_i'P_i (or s_k, C_j'P_i and C_j'P_j) is decomposed into a certain number of triangles T_j (see Fig. 13(b)) and \( \delta V = \pm \sum_j \hat{A}(T_j) \), with “±” positive if fluid 2 is gaining volume (moving C_k in C_k'), otherwise negative.

(i) Another point is randomly selected and it is moved to compensate the volume variation calculated in step “(b).” Just for simplicity, in this step, we choose only free points. Say P_j is the selected point. First, the point O at a distance \( l = \sqrt{\|\hat{A}(AB)\|/\|AB\|} \) from the segment AB is calculated (see Fig. 13(c)), where A and B are the two closest neighbors of P_j, \( \delta V = \hat{A}(AP_j \times AB)/2 \). The side of O with respect to the segment AB is such that AO \( \times \) AB has the same sign as \( \delta V \).

Then, the new position P_j’ is found moving O by a random amount \( \delta \in [0, \delta_{max}/2] \) in one of the two directions parallel to AB (which direction is randomly chosen). In this way, the total volume variation due to the moves in this step and in step “(d)” is zero. If the segment P_iP_j crosses a solid surface or the interface, then the move is forbidden and the program goes to the step “(l).”

(j) The variations due to the move in step “(i)” in the gravitational part of ε and in the fluid-fluid surface (respectively, \( \delta \epsilon_\epsilon \) and \( \delta S' \)) are computed as described in the steps “(e)” and “(f).” Then, the total variation in the functional ε due to the moves in the steps “(d)” and “(i)” is calculated as \( \delta \epsilon_\epsilon = \delta \epsilon_\epsilon + \delta \epsilon_\epsilon' + \delta S' + \delta S'' - \cos \theta_k \delta W_k(\delta) \), where \( \theta_k \) is the contact angle of the kth solid surface.

(k) With a probability \( P \) (see Eq. (29)) the new configuration of the system is accepted, where \( \Delta E = \gamma \xi_y \delta \epsilon_\epsilon \), otherwise the two points moved, respectively, in step “(d)” and “(i)” return to their previous positions.

(l) The program returns to step “(d).” Every M times this step is performed, T is decreased by an amount \( \delta T \). If \( T \leq 0 \), then the simulation ends.

To efficiently run this algorithm and obtain the correct solution, it is necessary to choose properly all the simulation parameters involved (\( T, T_0, N, \delta_{max}, M, \) and \( \delta_T \)). In principle, a good choice of this set can be found only heuristically. However, this problem, which is intrinsic to the method, needs to be faced only in a first stage. Then, the method can be applied systematically to a certain class of problems by keeping the same structure of parameters, with at most some minor adjustments. In Table II, we report all the simulation parameter values that we used for the results of Sec. IV.

This algorithm can be adapted to simulate a system where two or more one-dimensional grids of points are necessary to represent the interface (like in Sec. IV C). The necessary modifications are in step “(b),” defining all the solid surfaces, grids of points, and two constrained points for each grid, and in the step “(i),” choosing the free point randomly from every grid, to allow the exchange of volume between the regions below the different grids.

For the results of Sec. IV C (Fig. 8), we need the total energy \( E = \gamma \xi_y \delta \epsilon_\epsilon \) (Eqs. (27)-(32)) of the final solution. We
TABLE II. Simulation parameters used in the various results shown in Sec. IV. $\delta_{max}$ is set to 0.5 $\ell$ in all the simulations. About Fig. 8, $N$ is referred to each one of the three grids of points. Each simulation was performed on an ordinary office PC and required few minutes to be completed.

<table>
<thead>
<tr>
<th>Fig.</th>
<th>$N$</th>
<th>$k_B T_{0}$</th>
<th>$k_B \delta T$</th>
<th>$M$</th>
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<td>4,6,7(b)</td>
<td>28</td>
<td>$10^{-5}$</td>
<td>$10^{-7}$</td>
<td>$10^{5}$</td>
</tr>
<tr>
<td>5</td>
<td>several</td>
<td>$10^{-5}$</td>
<td>$10^{-7}$</td>
<td>$10^{5}$</td>
</tr>
<tr>
<td>7(a)</td>
<td>28</td>
<td>0.01</td>
<td>$10^{-4}$ if $T &gt; 10^{-4}$, otherwise $5 \cdot 10^{-7}$</td>
<td>$2 \cdot 10^{2}$</td>
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<td>8</td>
<td>13</td>
<td>0.11</td>
<td>$10^{-4}$ if $T &gt; 10^{-4}$, otherwise $5 \cdot 10^{-7}$</td>
<td>$3 \cdot 10^{5}$</td>
</tr>
<tr>
<td>10,11(a)</td>
<td>48</td>
<td>0.01</td>
<td>$10^{-4}$ if $T &gt; 10^{-4}$, otherwise $5 \cdot 10^{-7}$</td>
<td>$2 \cdot 10^{2}$</td>
</tr>
<tr>
<td>11(b)</td>
<td>38</td>
<td>0.01</td>
<td>$10^{-4}$ if $T &gt; 10^{-4}$, otherwise $5 \cdot 10^{-7}$</td>
<td>$2 \cdot 10^{2}$</td>
</tr>
</tbody>
</table>

calculate this using

$$e = \varepsilon_{\ell} + S - \sum_{k} W_{2}(k) \cos \theta_{k},$$

(A2)

where $S$, $W_{2}(k)$, and $\varepsilon_{\ell}$, respectively, are the fluid-fluid surface, the $k$th solid-fluid 2 surface, and the gravitational part of $e$ (all referred to the final solution). They are computed updating their initial values as $S + \delta S + \delta S'$, $W_{2}(k) + \delta W_{2}(k)$, and $\varepsilon_{\ell} + \delta \varepsilon_{\ell} + \delta \varepsilon'_{\ell}$ in step "(k)" every time a new configuration is accepted.

To get the results of Sec. IV D about the pendant droplets (Fig. 11), the algorithm is modified to minimize Eq. (34) instead of Eq. (27). This is done simply by changing the signs of $\delta \varepsilon_{\ell}$ and $\delta \varepsilon'_{\ell}$ in step "(j)."
64 J. C. F. Gauss, Principia Generalia Theoriae Figurarum Fluidorum (Dieterichs, 1830).