The Importance of Boundary Conditions for Fluctuation Induced Forces between Colloids at Interfaces

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(Dated: September 26, 2018)

We calculate the effective fluctuation induced force between spherical or disk-like colloids trapped at a flat, fluid interface mediated by thermally excited capillary waves. This Casimir type force is determined by the partition function of the system which in turn is calculated in a functional integral approach, where the restrictions on the capillary waves imposed by the colloids are incorporated by auxiliary fields. In the long-range regime the fluctuation induced force is shown to depend sensitively on the boundary conditions imposed at the three-phase contact line between the colloids and the two fluid phases. The splitting of the fluctuating capillary wave field into a mean-field and a fluctuation part leads to competing repulsive and attractive contributions, respectively, which give rise to cancellations of the leading terms. In a second approach based on multipole expansion of the Casimir interaction, these cancellations can be understood from the vanishing of certain multipole moments enforced by the boundary conditions. We also discuss the connection of the different types of boundary conditions to certain external fields acting on the colloids which appear to be realizable by experimental techniques such as the laser tweezer method.

PACS numbers: 82.70.Dd, 68.03.Kn

I. INTRODUCTION

The structure formation of nanoscopic colloidal particles adsorbed at fluid interfaces has attracted an increasing interest in recent years because of the various applications such systems exhibit, as in the design of nanoscale devices\textsuperscript{1} (e.g. for optical applications), and also because of the physical insights offered, e.g. for the understanding of protein aggregation on cell membranes. The practical importance arises from the fact that nano- and microcolloids are very effectively trapped by fluid interfaces\textsuperscript{2}. The high stability of partially wetting colloids (with their size ranging from nm to \(\mu \text{m}\)) at interfaces enables the formation of two-dimensional ordered structures and also of rather complex mesoscale patterns (cf. Refs.\textsuperscript{3,4,5,6,7,8,9,10,11}). In spite of the numerous experimental and theoretical efforts in the last decade, the nature of the effective forces between the colloids governing the arrangement of the colloids trapped at the interface is not fully understood yet. This holds in particular for the mesoscale pattern formation which points to sizeable and quite long-ranged attractions between the colloids. For the colloidal interactions at interfaces three different regimes may be distinguished. For colloid sizes of about 0.5 – 5 \(\mu \text{m}\), capillary forces are important. Though gravity is known to be unimportant in this regime, electrostatic forces (either caused only by the charge distributions on the colloid surface and the fluid phases, or additionally imposed by an external field) may lead to interfacial deformations and, hence, to considerable capillary interactions\textsuperscript{12,13,14}. In this regime, also strong effects of colloid surface inhomogeneities leading to an undulated three-phase contact line appear to be relevant\textsuperscript{15}. In the opposite limit of colloid sizes of a few nanometers, effects of interparticle correlations within the interface become important and determine the structural properties of the system. In this regime the colloidal interactions should be treated by truly microscopic fluid theories like density functional or inhomogeneous integral equation approaches (for a general scheme, see Ref.\textsuperscript{15}, and for results on correlations within a free interface, see Refs.\textsuperscript{16,17}). In between these two regimes, the microscopic one which must be tackled with the full power of classical statistical mechanics and the macroscopic one where thermal fluctuations appear to be unimportant, a coarse-grained picture of the fluctuating fluid interface should be applied. Within such a picture, the properties of fluid interfaces are very well described by an effective capillary wave Hamiltonian which governs both the equilibrium interface configuration and the thermal fluctuations (capillary waves) around this equilibrium (or mean-field) position. As postulated by the Goldstone theorem the capillary waves are long-range correlated. The interface breaks the continuous translational symmetry of the system, and in the limit of vanishing external fields – like gravity – it has to be accompanied by easily excitable long wavelength (Goldstone) modes – precisely the capillary waves\textsuperscript{18}. The fluctuation spectrum of the capillary waves will be modified by colloids trapped at the interface and therefore leads to fluctuation-induced forces between them. In the case of anisotropic colloids (rods) these forces have been evaluated in Ref.\textsuperscript{19} and shown to lead to an orientational dependence. Furthermore we note that
there is numerous work on the force between inclusions on membranes where the membrane shape fluctuations take the role of capillary waves, see e.g. Refs. 19, 20. In this paper, we shall address the fluctuation–induced effects of capillary waves on rotationally symmetric colloids, i.e., spherical or disk-like ones, and pay special attention to the effects of the boundary conditions at the three–phase contact line (where the fluid interface meets the colloid surface) on the large–distance behavior of the fluctuation–induced force. In previous work 21 we have established the independence of the short–distance behavior on the boundary conditions. For colloids at contact, the fluctuation–induced force is attractive and diverging, albeit the divergence is somewhat slower than for the ubiquitous van der Waals (vdW) forces. However, as discussed in Ref. 21, the fluctuation–induced force dominates for specially prepared system (such as index–matched ones) and hence it leads to colloidal aggregation at the interface.

Put in broader context, the prototype of such a fluctuation induced force as considered here is the original Casimir effect of the zero-temperature, long-ranged quantum fluctuations of the electromagnetic field confined between two conducting plates 22 that was predicted by Hendrik Casimir in 1948. In 1978 this was extended by Fisher and de Gennes 25 to critical systems like bulk fluids near the critical point or in binary mixtures near their critical demixing point where instead of long-ranged quantum fluctuations one has long-ranged critical fluctuations 24. An even more common example for long-range correlated fluctuations in thermal systems are the already mentioned Goldstone modes accompanying broken continuous symmetries. These modes are ubiquitous in condensed matter physics with famous examples being director fluctuations in liquid crystals 25, phase fluctuations in superfluids 26 or capillary waves at fluid interfaces mentioned above 27.

Both, the great experimental progress (see e.g. Ref. 28) and the fundamental interest in the Casimir effect have triggered numerous studies in this field in the last twenty years. In spite of this effort, still the only exactly solvable case is Casimir’s original one of two parallel infinite planes. An almost closed solution has been obtained for the plate-cylinder case very recently 29. In more complex geometries, analytical results usually are only available in asymptotic ranges, and the strong dependence of the Casimir force on the geometrical arrangement of the system has been shown in the case of the fluctuating medium being a free scalar field for various configurations like, e.g., immersed metallic spheres 30 or cylinders 29 and plates. A standard, though uncontrolled, approximation for the Casimir interaction between one curved body and a plate or two curved bodies at short distances is the well-known proximity force approximation which presumes pairwise additivity and which is in the same spirit as the Derjaguin approximation 31 well known from calculations of the van der Waals force between macroscopic bodies. The limitations of this approach are, e.g., investigated perturbatively and numerically in Refs. 32, 33.

In a study on the pairwise additivity of the Casimir force 34 Golestanian investigated the force between spheres in a fluctuating medium described by a free scalar field in arbitrary dimension $D$. Using a terminology borrowed from electrostatics, the scalar “field” corresponds to the potential and if the spheres are presumed to be metallic, one can distinguish two types of boundary condition: (i) the spheres are grounded, corresponding to zero potential at their surface (Dirichlet boundary conditions) and (ii) the spheres are isolated with constant charge, in which case one averages over the surface potential. The asymptotic Casimir force between two spheres at distance $d$ strongly depends on the type of boundary condition: in case (i) the author finds $F_{\text{ground}} \sim 1/d^{(D-2)+1}$ and for case (ii) $F_{\text{iso}} \sim 1/d^{D+1}$. In relation to this study, our present work is only concerned with the case $D = 2$. The boundary conditions introduced above correspond to the physically realizable conditions of a fixed colloid with pinned three–phase contact line (grounded case) and a vertically fluctuating colloid with pinned contact line (isolated case). Furthermore we will identify two more physically realizable boundary conditions (arbitrarily fluctuating colloid with pinned contact line and colloid with freely fluctuating contact line) which lead to different results for the Casimir force again. Also we will find that in $D = 2$ the general result for $F_{\text{ground}}$ is modified since care is needed to perform the limit to a massless fluctuating field. We will elucidate the appearance of the leading terms in an asymptotic expansion of the Casimir force from two different computational schemes. In the first one, the force is calculated by splitting the fluctuating field into a mean field and a fluctuation part as, e.g., it is well known from the functional integrals in quantum mechanics. Then the partition function consists of two parts which can be computed separately and lead to a repulsive and an attractive contribution to the Casimir interaction, respectively. The leading non-vanishing term in the asymptotic behaviour for large colloid separations then strongly depends on the type of boundary conditions under consideration. In an alternative approach this can be understood from an auxiliary multipole expansion of the interaction between the colloids similar as in Ref. 35. One can relate each type of boundary conditions to a suppression of certain auxiliary multipoles on the colloids and the leading term of the Casimir force is obtained from the first non-vanishing multipole-multipole interaction.

The paper is organized as follows. In Sec. III we will introduce the model system by an effective Hamiltonian. We will show how the partition function can be calculated via functional integrals in two distinct ways mentioned above and how the various boundary conditions can be implemented. Then we will compute the corresponding
functional integrals in Secs. III IV and V in the asymptotic regimes of long and short colloid separations \( d \) and numerically in the full range of \( \bar{d} \), respectively, and compare analytical with numerical results in the discussion part, Sec. VI. In Sec. VI we will also discuss possible experimental tests for this type of Casimir force through the implications of an additional external potential for the colloids, which may, e.g., be realized by optical tweezers.

II. MODEL

In this section we derive an effective Hamiltonian for the free energy changes associated with thermally excited height fluctuations of the interface between two fluid phases I and II at which two nano– or microscopic colloids are trapped. As described above, this configuration is very stable against thermal fluctuations for colloids with a partially wetting surface. The colloids are assumed to be either spherical with radius \( R \) or disclike with radius \( R \) and thickness \( H \). In the absence of charges and for colloid sizes \( R \lesssim 1 \mu m \) the weight of the particles can be neglected. Thus the equilibrium configuration of minimal free energy is the flat interface and spherical colloids are positioned such that Young’s law holds at the horizontal three-phase contact line which is a circle with radius \( r_0 = R \sin \theta \). Young’s angle, measured through phase II (assumed to be of higher density than phase I), is determined by \( \cos \theta = (\gamma_I - \gamma_{II})/\gamma \) where \( \gamma \) is the surface tension of the interface between I/II, and \( \gamma_{II} \) is the surface tension between the colloid and phase I [II], respectively (c.f. fig. 1). For disclike colloids, the contact line is either the upper \((\theta < \pi/2)\) or lower \((\theta > \pi/2)\) circular edge, so that its radius is given by \( r_0 = R \). For both spheres and disks the cross-section of the colloids with the flat interface is given by the interior of a circle which we refer to as \( S_{i,ref} \) below, and, therefore both cases can be treated within the same model in the following. We take the flat interface \( S_{men,ref} \) as the reference configuration with respect to which free energy changes are measured, and choose it to be the plane \( z = 0 \) with the two circular holes \( S_{i,ref} \) of radius \( r_0 \) in it: \( S_{men,ref} = \mathbb{R}^2 \setminus \cup_i S_{i,ref} \) (see fig. 2). Deviations from the planar reference interface \( z = 0 \) are assumed to be small and without overhangs or bubbles. That allows using the Monge representation \((x, y, z = u(x, y)) = (x, z = u(x))\) as a parametrization of the actual interface positions. The free energy costs for thermal fluctuations around the flat reference interface is determined by the change in interfacial energy of all interfaces (I/II, colloid/I and colloid/II):

\[
\mathcal{H}_{tot} = \gamma \Delta A_{men} + \gamma_I \Delta A_I + \gamma_{II} \Delta A_{II} .
\] (1)

The first term in Eq. (1) expresses the energy needed for creating the additional meniscus area associated with the height fluctuations and is given by

\[
\gamma \Delta A_{men} = \gamma \int_{S_{men}} d^2x \sqrt{1 + |\nabla u|^2} - \gamma \int_{S_{men,ref}} d^2x \approx \frac{\gamma}{2} \int_{S_{men,ref}} d^2x (|\nabla u|^2 + \gamma \Delta A_{proj}) .
\] (2)

In Eq. (2), \( S_{men} \) is the meniscus area projected onto the plane \( z = 0 \) (where the reference interface is located) and \( S_{men,ref} \) is the meniscus in the reference configuration mentioned above. \( \Delta A_{proj} = \int_{S_{men} \setminus S_{men,ref}} d^2x \) is the change in projected meniscus area with respect to the reference configuration. In the second line we have applied a small gradient expansion which is valid for slopes \( |\nabla u| \ll 1 \) and which provides the long wavelength description of the interface fluctuations we are interested in. Note that the first line of Eq. (2) constitutes the drumhead model which is well-known in the renormalization group analysis of interface problems, but is also used for the description of elastic surfaces (c.f. Ref. [15]).

As discussed in the Introduction, the center of colloid \( i \) may fluctuate vertically (measured by \( h_i \)) around the reference position as well as the contact line itself may do. This leads to changes in the interfacial areas colloid/I[II] (\( \Delta A_{I[II]} \neq 0 \) in Eq. (1)). In order to determine the corresponding energy costs we introduce the vertical position of the contact line at colloid \( i \) as a function of the polar angle \( \varphi_i \), defined on the reference contact line circles \( \partial S_{i,ref} \), by its Fourier expansion

\[
f_i = u(\partial S_{i,ref}) = \sum_{m=-\infty}^{\infty} P_{im} e^{im\varphi_i} .
\] (3)

and refer to the Fourier coefficients \( P_{im} \) as boundary multipole moments below. Since \( f_i \) is real, we have \( P_{im} = P_{i,-m}^{*} \). Following Ref. [15], the free energy changes associated with \( \Delta A_{proj} \) and \( \Delta A_{I[II]} \) can be expanded
are included by $\delta$ obtained by a functional integral over all possible interface configurations $F$ centers and gives rise to an effective force the colloid centers which is determined by the free energy $F$ the interface height fluctuations, therefore, introduces a long wavelength cutoff and leads to an additional term a natural damping for capillary waves. Accounting also for the costs in gravitational energy associated with the capillary wave model ceases to remain valid. The long wavelength divergence is reminiscent to the interfacial area created by the height fluctuations, and the boundary Hamiltonians $H_{b,i}$, $i = 1, 2$, have a crucial influence on the resulting effective interaction between the colloids and may therefore be collected in a boundary Hamiltonian $H_{i,b}$ (see App. A):

$$ H_{b,i}[f_i, h_i] = \gamma \Delta A_{\text{proj}} + \gamma_i \Delta A_I + \gamma_H \Delta A_H $$

$$ = \frac{\pi \gamma}{2} \left[ 2(P_{i0} - h_i)^2 + 4 \sum_{m \geq 1} |P_{im}|^2 \right]. \quad (4) $$

Putting Eqs. (1), (2) and (4) together, the total free energy change is the sum

$$ \mathcal{H}_{\text{tot}} = \mathcal{H}_{\text{cw}} + H_{b,1} + H_{b,2} = \frac{\gamma}{2} \int_{S_{\text{men,ref}}} d^2x (\nabla u)^2 + H_{b,1} + H_{b,2} \quad (5) $$

of the capillary wave Hamiltonian $\mathcal{H}_{\text{cw}}$ which describes the free energy differences associated with the additional interfacial area created by the height fluctuations, and the boundary Hamiltonians $H_{b,i}$, combining all effects related to fluctuations of the three-phase contact line on the colloid surfaces. As is well-known, the Hamiltonian $\mathcal{H}_{\text{cw}}$ is plagued with both a short-wavelength and a long-wavelength divergence which, however, can be treated by physical cutoffs. The natural short-wavelength cut-off is set by the molecular length-scale $\sigma$ of the fluid at which the capillary wave model ceases to remain valid. The long wavelength divergence is reminiscent to the fact that the capillary waves are Goldstone modes. Of course, in real systems the gravitational field provides a natural damping for capillary waves. Accounting also for the costs in gravitational energy associated with the interface height fluctuations, therefore, introduces a long wavelength cutoff and leads to an additional term ("mass term") in the capillary wave Hamiltonian,

$$ \mathcal{H}_{\text{cw}} = \frac{\gamma}{2} \int_{S_{\text{men,ref}}} d^2x \left[ (\nabla u)^2 + \frac{u^2}{\lambda_c^2} \right] \quad (6) $$

Here the capillary length is given by $\lambda_c = [\gamma/|\rho_{i1} - \rho_i| g]^{1/2}$, where $\rho_i$ is the mass density in phase $i$ and $g$ is the gravitational constant. Usually, in simple liquids, $\lambda_c$ is in the range of millimeters and, therefore, is by far the longest length scale in the system. In fact, here it plays the role of a long wavelength cutoff of the capillary wave Hamiltonian $\mathcal{H}_{\text{cw}}$, and we will discuss our results in the limit $\lambda_c \gg R$ and $\lambda_c \gg d$. However, as we will see below, care is required when taking the limit $\lambda_c \to \infty$ (corresponding to $g \to 0$), since logarithmic divergencies appear \[35\]. Another common way to introduce a long-wavelength cut-off is the finite size $L$ of any real system. As discussed in Ref. [13], the precise way of incorporating the long-wavelength cut-off is unimportant for the effects on the colloidal length scale. As an example, in both approaches the width of the interface related to the capillary wave is logarithmically divergent, $\langle u(0)^2 \rangle \sim \ln \lambda_c/L/\sigma$.

Via the integration domain of $\mathcal{H}_{\text{cw}}$, the total Hamiltonian of the system, Eq. (6), implicitly depends on the geometric configuration. This leads to a free energy which depends on the mean distance $d$ between the colloids and gives rise to an effective force $F(d) = -(\partial F)/\partial d$, as function of the mean local distance between the colloid centers which is determined by the free energy $F(d) = -k_B T \ln Z(d)$. The partition function $Z(d)$ is obtained by a functional integral over all possible interface configurations $u$ and $f_i$; the boundary configurations are included by $\delta$-function constraints,

$$ Z = Z_0^{-1} \int \mathcal{D}u \exp \left\{ -\frac{\mathcal{H}_{\text{cw}}[u]}{k_B T} \right\} \prod_i \int \mathcal{D}f_i \prod_{\mathbf{x}_i \in \partial S_{i,\text{ref}}} \delta[u(\mathbf{x}_i) - f_i(\mathbf{x}_i)] \exp \left\{ -\frac{\mathcal{H}_{b,i}[f_i, h_i]}{k_B T} \right\}. \quad (7) $$

Here $Z_0$ is a normalization factor such that $Z(d \to \infty) = 1$ and ensures a proper regularization of the functional integral. Via the $\delta$-functions the interface field $u$ is coupled to the contact line height $f_i$ and therefore, the boundary Hamiltonians $H_{i,b}$ have a crucial influence on the resulting effective interaction between the colloids as we will see below. In the next subsection we discuss possible situations for the boundary conditions at the three phase contact line and specify the corresponding integration measure $\mathcal{D}f_i$. 

FIG. 1: Side view on the reference configuration (here the colloids are assumed to be spheres).
A. Boundary conditions at the three-phase contact line

We shall discuss two different realizations of the boundary conditions for the contact line, namely

- Case (A): The contact lines and the vertical colloid positions fluctuate freely; this corresponds to the physical situation of smooth, spherical colloids. In this case, the integration measure is given by $\mathcal{D}f_i = \int dh_i \prod_m dP_{im}$ and encompasses integration over all boundary multipole moments.

- Case (B): The contact lines (the circles $\partial S_i,_{\text{ref}}$ in the reference configuration) are pinned to the colloid surface. This corresponds to disklike colloids or Janus spheres consisting of two different materials, or to colloids with a very rough surface. Within the pinning case, we furthermore distinguish the following three situations:

  (B1) The colloid positions are frozen, thus there are no integrations over the boundary terms.

  (B2) The vertical positions of the colloids fluctuate freely, thus boundary monopoles must be included in the integration measure so that $\mathcal{D}f_i = dh_i dP_{i0} \delta(P_{i0} - h_i)$.

  (B3) The vertical position and the orientation of the colloids (tilts) fluctuate freely. Up to second order in the tilts this corresponds to the inclusion of boundary dipoles in the integration measure, thus $\mathcal{D}f_i = dh_i dP_{i0} dP_{i1} dP_{i-1} \delta(P_{i0} - h_i)$. \[46\]

The $\delta$-function expresses the pinning condition.

In the following subsections we introduce two distinct schemes to compute the partition function $Z(d)$ in Eq. (7) which allows us to discuss the results from different perspectives. The first one is based on a splitting of $Z$ in a mean-field and a fluctuation part, whereas for the second one we extend the fluid interface – artificially – to the interior of the reference circles $S_i,_{\text{ref}}$. As we will see, in the first approach, the mean-field part leads to a repulsive and the fluctuation part to an attractive Casimir force. The interplay of these two contributions gives rise to an cancellation of the leading terms in the asymptotic range $r_0 \ll d$ which sensitively depends on the chosen boundary conditions. In the second approach, the asymptotic Casimir force can be expanded in multipole interactions of auxiliary fields defined on $S_i,_{\text{ref}}$ and the appearance of a different behaviour in the long-range regime for different boundary conditions can be understood straightforwardly as the result of vanishing multipole moments of the auxiliary fields, enforced by the boundary conditions.

FIG. 2: Reference configuration with two circles $S_i,_{\text{ref}}$ representing the reference contact line on the colloid surfaces (here the colloids may be disks or spheres).
B. Mean-field and fluctuation part

As the capillary wave Hamiltonian is Gaussian in the field $u$ of the local interface position, a standard procedure for the evaluation of the functional integral is the decomposition into a mean-field and a fluctuation part,

$$ u = u_{\text{mf}} + v. $$

(8)

The mean-field part solves the Euler–Lagrange equation of the capillary wave Hamiltonian $H_{cw}$,

$$ (-\Delta + \lambda_c^{-2}) u_{\text{mf}} = 0 $$

(9)

with the boundary condition $u_{\text{mf}}|_{\partial S_{i,\text{ref}}} = f_i$. Consequently the fluctuation part is pinned to zero at the contact line, $v|_{\partial S_{i,\text{ref}}} = 0$. Then the partition sum $Z = Z_{\text{fluc}}Z_{\text{mf}}$ separates into a product of a fluctuation part independent of the boundary conditions, and a mean field part depending on the boundary conditions (which may fluctuate theirselves, see the cases (A), (B2), and (B3)):

$$ Z_{\text{fluc}} = Z_0^{-1} \int_d Du \prod_{i=1}^2 \prod_{x \in \partial S_{i,\text{ref}}} \delta(v(x)) \exp \left\{ -\frac{H_{cw}[v]}{k_B T} \right\}, $$

$$ Z_{\text{mf}} = \prod_{i=1}^2 \int_{\mathcal{D}f_i} \exp \left\{ -\frac{\gamma}{2k_B T} \sum_i \int_{\partial S_{i,\text{ref}}} d\ell_i f_i(x_i) (\partial_n u_{\text{mf}}(x_i)) \right\} \exp \left\{ -\frac{\mathcal{H}_{b,i}[f_i, h_i]}{k_B T} \right\}. $$

(10)

The first exponential in $Z_{\text{mf}}$ stems from applying Gauss’ theorem to the energy associated with $u_{\text{mf}}$. In this term $\partial_n u_{\text{mf}}$ denotes the normal derivative of the mean–field solution towards the interior of the circle $\partial S_{i,\text{ref}}$.

For intermediate asymptotic distances between the colloids ($r_0 \ll d \ll \lambda_c$), $Z_{\text{fluc}}$ and $Z_{\text{mf}}$ are analyzed separately in Secs. II A and II B respectively.

This procedure to split the functional integral into a mean field part and a fluctuation part with a zero boundary condition is equivalent to the standard calculation of the quantum mechanical path integral for a single particle in a harmonic potential. The mean field part corresponds to the classical action and the fluctuation part evaluated becomes the fluctuation determinant (see, e.g., Ref. [57]).

C. Alternative approach (Kardar’s method)

An alternative scheme to calculate the partition function of the two colloids and the fluctuating interface without splitting it into a mean-field and fluctuation part can be devised if the interface height field $u(x, y)$ which enters the functional integral for $Z$ is extended to the interior of the circles $S_{i,\text{ref}}$. Thus the measure of the functional integral for $Z$ is extended by $Du(x)|_{x \in S_{i,\text{ref}}}$ and the integration domain in the capillary wave Hamiltonian is enlarged to encompass the whole $\mathbb{R}^2$. We note that physically the free energy of the system must not change since in the interior of $S_{i,\text{ref}}$ the interface is pinned to the colloid surface. A method similar to this ansatz was introduced in Ref. [19] by Kardar et al., which investigates effective forces between rods on fluctuating membranes and films, and therefore we refer to it as Kardar’s method in the following.

On the colloid surfaces, the interface height field is given by the three phase contact line, $u(\partial S_{i,\text{ref}}) \equiv f_i$. We extend $u$ continuously to the interior of the circles $S_{i,\text{ref}}$ via

$$ u(S_{i,\text{ref}}) \equiv f_{i,\text{ext}}(r_i, \varphi_i) = \sum_{m} \left( \frac{r_i}{r_0} \right)^{|m|} P_{im} e^{im\varphi_i}, $$

(11)

where $r_i$ and $\varphi_i$ are the polar coordinates with respect to circle $S_{i,\text{ref}}$ and where the boundary multipoles satisfies $P_{im} = P_{i,-m}^*$. Note that the choice of $u(S_{i,\text{ref}})$ is not unique since the continuity at the boundaries $\partial S_{i,\text{ref}}$ is the only requirement. The specific choice in Eq. (11) is convenient for the further calculations since $\Delta f_{i,\text{ext}} = 0$ in $S_{i,\text{ref}} \setminus \partial S_{i,\text{ref}}$. Extending the integration domain of the capillary wave Hamiltonian in Eq. (6), $\Omega = \mathbb{R}^2 \setminus \cup_i S_{i,\text{ref}} \rightarrow \mathbb{R}^2$ generates an additional energy contribution

$$ -\mathcal{H}_{i,\text{corr}} = \frac{\gamma}{2} \int_{S_{i,\text{ref}}} d^2x \left[ (\nabla u)^2 + \frac{u^2}{\lambda^2} \right] $$

$$ \simeq 2\pi \gamma \sum_{m \geq 1} m |P_{im}|^2. $$

(12)
In Eq. (12) we have already omitted the contributions from the gravitational term in $\mathcal{H}_{cw}$ which are of order $(r_0/\lambda)^2 \ll 1$. From Eq. (12) we see that the additional terms created by the extension of the integration domain of the capillary wave Hamiltonian $\mathcal{H}_{cw}$ are not constant in the – possibly fluctuating – boundary multipole moments $P_{\text{sm}}$ and therefore lead to artificial contributions to the partition function $Z$. These unphysical contributions have to be corrected by adding $\mathcal{H}_{i,\text{corr}}$ to the extended capillary wave Hamiltonian $\mathcal{H}_{\text{cw}}[\Omega \equiv \mathbb{R}^2]$. The total Hamiltonian then reads

$$\mathcal{H}_{\text{tot}} = \mathcal{H}_{\text{cw}} + \sum_{i=1}^{2} [\mathcal{H}_{i,b} + \mathcal{H}_{i,\text{corr}}].$$

As in the previous sections the partition function is written as a functional integral over all possible configurations of the interface position $u$ and the boundary lines, expressed by $f_i$,

$$Z = Z_0^{-1} \int \mathcal{D} u \prod_{i=1}^{2} \mathcal{D} f_i \prod_{x_i \in S_{i,\text{ref}}} \delta[u(x_i) - f_{i,\text{ext}}(x_i)] \exp \left\{ -\frac{\mathcal{H}_{\text{tot}}[f_i, u]}{k_B T} \right\},$$

where the product over the $\delta$-functions enforces the pinning of the interface at the positions of the colloids. In contrast to Eq. (7), these product extends over all $x \in S_{i,\text{ref}}$ instead of $\partial S_{i,\text{ref}}$, only. The analysis of $Z$ in this form for intermediate asymptotic distances $d$ is presented below in Sec. III D.

### III. LONG-RANGE BEHAVIOR

In this section analytical expressions for the fluctuation induced force in the intermediate asymptotic regime $r_0 \ll d \ll \lambda_c$ are calculated. In Secs. III A and III B we will evaluate the partition functions of fluctuation and the mean-field part, respectively. From these two contributions we obtain the asymptotic form of the total Casimir force, which in turn will be calculated directly in Sec. III D applying the approach introduced in Sec. II C.

#### A. Fluctuation part

The fluctuation part appears in all cases (A) and (B1)–(B3) for the boundary conditions introduced in Sec. II A. In the case (B1) (pinned contact line with frozen colloid) it constitutes the full result for the partition function because $u_{\text{mf}} = 0$ and $Z_{\text{mf}} = 1$. We express the $\delta$-functions in the fluctuation part of the partition function (10) by their integral representation via auxiliary fields $\psi_i(x_i)$ defined on the interface boundaries $\partial S_{i,\text{ref}}$. This enables us to integrate out the field $u$ leading to

$$Z_{\text{fluc}} = \int \mathcal{D} \psi_i \exp \left\{ -\frac{k_B T}{2\gamma} \sum_{i,j=1}^{2} \int_{\partial S_{i,\text{ref}}} d\ell_i \int_{\partial S_{j,\text{ref}}} d\ell_j \psi_i(x_i) G(|x_i - x_j|) \psi_j(x_j) \right\},$$

where $d\ell_i$ is the infinitesimal line segment on the circles $\partial S_{i,\text{ref}}$. In Eq. (15) we introduced the Greens function of the operator $(-\Delta + \lambda_c^{-2})$ which is given by $G(x) = K_0(|x|/\lambda_c)/(2\pi)$ where $K_0$ is the modified Bessel function of the second kind. In the range $d/\lambda_c \ll 1$ and $r_0/\lambda_c \ll 1$, we can use the asymptotic form of the $K_0$ for small arguments, such that $2\pi G(|x|) \approx -\ln(\gamma_c|x|/2\lambda_c)$. Here, $\gamma_c \approx 1.781972$ is the Euler-Mascheroni constant exponentiated.

We introduce auxiliary multipole moments as the Fourier-transforms of the auxiliary fields $\psi_i$ on the contact line circles $\partial S_{i,\text{ref}}$,

$$\hat{\psi}_{im} = \frac{r_0}{2\pi} \int_0^{2\pi} d\phi_i e^{im\phi_i} \psi_i(x_i(\phi_i))$$

The analogous multipole decomposition for the Greens function $G(|x_i - x_j|)$ is calculated in App. B. Using it, the double integral in the exponent of Eq. (15) can be written as a double sum over the Fourier components, consisting of a self-energy part

$$G_{\text{self}} = \sum_i \int_{\partial S_{i,\text{ref}}} d\ell_i \int_{\partial S_{j,\text{ref}}} d\ell_j \psi_i(x_i) G(|x_i - x_j|) \psi_j(x_j)$$
\[ F_{\text{fluc}} = \frac{k_B T}{2} \sum_n f_{\text{fluc}}^n \left( \frac{r_0}{d} \right)^{2n} , \]

where the coefficients \( f_{\text{fluc}}^n \) depend on the logarithms \( -\ln(\gamma_c d/2\lambda_c) \) and \( -\ln(\gamma_c r_0/2\lambda_c) \). We show the first few coefficients in Tab. 1. The number of auxiliary multipoles included in the calculation of the asymptotic form of \( F_{\text{fluc}} \) in Eq. (21) is determined by the desired order in \( r_0/d \). The individual contributions in this expansion can be understood as (possibly higher order) auxiliary multipole-multipole interactions, related to specific products of the matrix elements of \( \hat{G} \). So, e.g., all the logarithmic contributions to the coefficients in Eq. (21) are related to interactions of the auxiliary monopoles. Note that we cannot perform \( \lim_{\lambda_c \to \infty} f_{\text{fluc}}^n \) because of the logarithmic divergencies mentioned above. These logarithmic divergencies are reminiscent of the long-range correlations of the capillary waves which lead to a width of the free interface which diverges logarithmically with \( \lambda_c \) or with the system size if gravity is absent. For the Casimir force itself, however, we find a finite value in the limit \( \lambda_c \to \infty \). In the asymptotic range \( r_0/d \ll 1 \) and in the limit \( \lambda_c/d \to \infty \) the leading term of the fluctuation force is governed by the first term in the series Eq. (21), \( f_{\text{fluc}}^0 \), and reads

\[ F_{\text{fluc}} = k_B T \frac{\partial}{\partial d} \ln Z_{\text{fluc}} \to -\frac{k_B T}{2} \frac{1}{d \ln(d/r_0)} + O(d^{-3}) , \quad \frac{d}{r_0} \gg 1, \quad d \to 0 . \]
TABLE I: Leading coefficients of Eq. (21)

| 2n | \(2f_{2n}^{\text{fluc}}/k_B T\) |
|-----|----------------------------------|
| 0   | \[\ln \left( \frac{2\eta r_0}{2\lambda_c} \right) - \ln \left( \frac{2\eta d}{2\lambda_c} \right) \equiv \ln g_0^{\text{fluc}}\] |
| 2   | \(\frac{2 \ln \left( \frac{2\eta d}{2\lambda_c} \right)}{g_0^{\text{fluc}}}\) |
| 4   | \[-2 + \frac{1 + \frac{3}{2} \ln \left( \frac{2\eta r_0}{2\lambda_c} \right) + \frac{3}{2} \ln \left( \frac{2\eta d}{2\lambda_c} \right)}{g_0^{\text{fluc}} - f_2^{\text{fluc}} f_4^{\text{fluc}}} + \frac{1}{2} (f_2^{\text{fluc}})^2\] |
| 6   | \[-8 + \frac{1 + \frac{3}{2} \ln \left( \frac{2\eta r_0}{2\lambda_c} \right) + \frac{3}{2} \ln \left( \frac{2\eta d}{2\lambda_c} \right)}{g_0^{\text{fluc}} - f_2^{\text{fluc}} f_4^{\text{fluc}}} - f_2^{\text{fluc}} f_6^{\text{fluc}} + \frac{1}{2} (f_2^{\text{fluc}})^3\] |
| 8   | \[-30 + \frac{1 + \frac{3}{2} \ln \left( \frac{2\eta r_0}{2\lambda_c} \right) + \frac{3}{2} \ln \left( \frac{2\eta d}{2\lambda_c} \right)}{g_0^{\text{fluc}} - f_2^{\text{fluc}} f_4^{\text{fluc}}} - \frac{1}{2} (f_2^{\text{fluc}})^2 - f_2^{\text{fluc}} f_6^{\text{fluc}} + (f_2^{\text{fluc}})^2 f_4^{\text{fluc}} - \frac{1}{2} (f_2^{\text{fluc}})^4\] |

and that the free energy difference corresponding to Eq. (22), \(\mathcal{F}(d) \sim \ln \ln(\eta_0/d)\), is actually ill-defined, because the effective colloidal interaction in case (B1) – fixed colloids and pinned interface – is only meaningful for a finite capillary length \(\lambda_c\).

**B. Mean-field part**

The calculation of \(Z_{\text{mf}}\) (Eq. (10)) requires the solution of the Euler-Lagrange equation (9), \((-\Delta + \lambda_c^{-2}) u_{\text{mf}}(x) = 0\) for \(x \in \mathbb{R}^2 \setminus \cup_i S_i,\text{ref}\) and the (fluctuating) boundary conditions

\[u_{\text{mf}}(x_i) = f_i(x_i)\]  
(24)

with \(x_i \in \partial S_i,\text{ref}\) and \(u_{\text{mf}}(x) \to 0\) for \(|x| \to \infty\). In fact a solution to a similar problem (with Neumann boundary conditions) was given in Ref. [38] in terms of bipolar coordinates which, however, is involved if applied to the general Dirichlet boundary conditions in our case. For our purpose it is more convenient to write the solution as a superposition

\[u_{\text{mf}}(x) = u_1(x - r_1) + u_2(x - r_2) \equiv u_1(r_1, \varphi_1) + u_2(r_2, \varphi_2),\]  
(25)

where \(r_i\) is the center position of circle \(S_i,\text{ref}\). The general solutions \(u_i\) of the mean-field equation (9) in polar coordinates \((r_i, \varphi_i)\) with respect to the centers of the reference contact line circles \(S_i,\text{ref}\) (see Fig. 2) can be written as linear combinations

\[u_i(r_i, \varphi_i) = \sum_m A_{im} a_{im}(r_i, \varphi_i)\]  
(26)
The functions $a_{im}$ are defined by

$$
\begin{align*}
a_{i0}(r_i, \varphi_i) &= \frac{K_0(r_i/\lambda_c)}{K_0(r_0/\lambda_c)} \approx \frac{\ln(\gamma_c r_i/2\lambda_c)}{\ln(\gamma_c r_0/2\lambda_c)} \\
a_{im}(r_i, \varphi_i) &= \frac{K_m(r_i/\lambda_c)}{K_0(r_0/\lambda_c)} e^{im\varphi_i} \approx \left(\frac{r_0}{r_i}\right)^{|m|} e^{im\varphi_i},
\end{align*}
$$

(27)

which are normalized for convenience and where we have used the asymptotic form of the modified Bessel functions $K_m$ for small arguments $r_i/\lambda_c \ll 1$. As the solution has to match the boundary conditions at both circles $\partial S_{1,\text{ref}}$ and $\partial S_{2,\text{ref}}$, we project $u_{\text{mf}}$ onto the complete set of functions on $\partial S_{1,\text{ref}}$, $e^{im\varphi_1}$, and on $\partial S_{2,\text{ref}}$, $e^{im\varphi_2}$, respectively. The expansion coefficients of these projections of $u_{\text{mf}}$ must equal the boundary multipole moments at the corresponding circle which leads to a system of linear equations for the expansion coefficients \{A_{im}, B_{im}\} of the $u_i$,

$$
A_{1m} + \sum_{n=-n_{\text{max}}}^{n_{\text{max}}} a_{1,mn} A_{2n} = P_{1m} \\
A_{2m} + \sum_{n=-n_{\text{max}}}^{n_{\text{max}}} a_{2,mn} A_{1n} = P_{2m}.
$$

(28)

In Eq. (28), the matrix coefficients $a_{1,mn}$ are given by the projection coefficients

$$
a_{1,mn} = \frac{1}{2\pi} \int_0^{2\pi} d\varphi_1 e^{im\varphi_1} a_{2n}(r_2, \varphi_2),
$$

(29)

and analogously $a_{2,mn}$ is given in terms of the projection of $a_{im}(r_1, \varphi_1)$ onto $e^{im\varphi_2}$. In Eq. (28), we have truncated the Fourier expansions at a maximum order $n_{\text{max}}$. Indeed, the numerical solution shows rapid convergence of the expansions in Eq. (28) in the whole range of colloid-colloid separations $d$, such that they can be truncated at $n_{\text{max}} \approx 20$. Through the inversion of the linear system (28) the coefficients $A_{im}$ and $B_{im}$ can be expressed as linear combinations of the boundary multipoles,

$$
A_{im} = \sum_{j=0}^{2} \sum_{n=-n_{\text{max}}}^{n_{\text{max}}} p_{imjn} P_{jn}.
$$

(30)

Using the asymptotic forms of the functions $a_{im}$ given in Eq. (27), expressing $r_2 = r_2(d, r_1, \varphi_1)$ and $\varphi_2 = \varphi_2(d, r_1, \varphi_1)$ by the polar coordinates with respect to circle $S_{1,\text{ref}}$ and vice versa for circle $S_{2,\text{ref}}$, and expanding the projection coefficients $a_{i,mn}$ in Eq. (28) in $r_0/d$, the coefficients $p_{imjn}$ in Eq. (30) can be written as a power series in $r_0/d$. Inserting the solution (25) with the expression (30) for the $A_{im}$ into the line integrals for the mean field energy $H[u_{\text{mf}}]$ in the exponent of Eq. (10), we can write $H[u_{\text{mf}}]$ as a quadratic form of the boundary multipole moments $P_{im}$, described by a matrix $E$ with block structure,

$$
H_{\text{mf}} = -\frac{\gamma r_0}{2} \sum_i \int_0^{2\pi} d\varphi_i f_i(\varphi_i) \frac{\partial H_{\text{mf}}(x(\varphi_i))}{\partial r_i} + \sum_i H_{b,i} f_i + h_i
$$

$$
= \frac{\gamma}{2} \left(\tilde{f}_1 \tilde{f}_2\right)^T \begin{pmatrix} E_{\text{self}} & E_{\text{int}} \\ E_{\text{int}} & E_{\text{self}} \end{pmatrix} \left(\tilde{f}_1 \tilde{f}_2\right) + \pi \gamma \sum_i (P_{i0} - h_i)^2,
$$

(31)

Here, the submatrices $E_{i,\text{self}}$ and $E_{i,\text{int}}$ describe the coupling energy of the multipole moments of the same contact line $f_i$ and from different contact lines, respectively, and their elements are given by

$$
E_{i,\text{self}}^{mn} = 2\pi \delta_{mn} (1 - \delta_{m0}) - \int_0^{2\pi} r_0 d\varphi_i e^{im\varphi_i} \sum_k p_{ik} \frac{\partial}{\partial r_i} a_{ik}(r_i, \varphi_i),
$$

(32)

$$
E_{12,\text{int}}^{mn} = -\int_0^{2\pi} r_0 d\varphi_1 e^{im\varphi_1} \sum_k p_{2k} \frac{\partial}{\partial r_1} a_{2k}(r_2(\varphi_1), \varphi_2(\varphi_1)),
$$

(33)

and analogously for $E_{21,\text{int}}^{mn}$. Applying again the expansions of the functions $a_{ik}$ in powers of $r_0/d$ in the expression for $E_{12,\text{int}}^{mn}$ and using the series expressions for the coefficients $p_{imjn}$, the matrix elements can be written as a
TABLE II: Leading coefficients \( 2 f_{2n}^\text{fluc} / k_B T \) of Eq. (35) for various boundary conditions. The coefficients \( f_{n}^\text{fluc} \) are given in Tab. II.

| \( 2n \) | case (B2): only monopoles | case (B3): mono- and dipoles | case (A): all multipoles |
|-------|-----------------|-----------------|-----------------|
| 0     | \(-f_{0}^\text{fluc}\) | \(-f_{0}^\text{fluc}\) | \(-f_{0}^\text{fluc}\) |
| 2     | \(-f_{2}^\text{fluc}\) | \(-f_{2}^\text{fluc}\) | \(-f_{2}^\text{fluc}\) |
| 4     | \(-f_{4}^\text{fluc} - 2\) | \(-f_{4}^\text{fluc} - 2\) | \(-f_{4}^\text{fluc} - 2\) |
| 6     | \(-f_{6}^\text{fluc} - 8\) | \(-f_{6}^\text{fluc} - 8\) | \(-f_{6}^\text{fluc} - 8\) |
| 8     | \(-f_{8}^\text{fluc} - 31\) | \(-f_{8}^\text{fluc} - 31\) | \(-f_{8}^\text{fluc} - 31\) |

Power series in \( r_0 / d \) in the asymptotic range \( r_0 \ll d \ll \lambda_c \). The mean field part of the partition sum Eq. (10) can then be written as

\[
Z_{\text{mf}} = \int \prod_i D f_i \exp \left\{ -\frac{\mathcal{H}_{\text{mf}}}{k_B T} \right\}
\]

(34)
such that the \( d \)-dependent part of \( Z_{\text{mf}} \) is proportional to \( \det \mathbf{E} \). As discussed in Sec. II A, the functional measure is given by a product \( D f_i = dh_i \prod_{m=-M}^{M} dP_{mn} \), where \( M \) depends on the chosen model for the boundary condition at the contact line. Inserting the power series of the matrix elements \( E_{mn}^{\text{int}} \) and \( E_{mn}^{\text{self}} \), and expanding the free energy \( F_{\text{mf}}(d) \propto k_B T \ln \det \mathbf{E} \), we arrive at a series similar in form to the fluctuation part, Eq. (21),

\[
F_{\text{mf}}(d) = \frac{k_B T}{2} \sum_n f_{2n}^\text{mf} \left( \frac{r_0}{d} \right)^{2n},
\]

(35)
where again the coefficients \( f_{2n}^\text{mf} \) are functions of the monopole self-energy and interaction coupling elements, \( -\ln(\gamma e r_0 / 2 \lambda_c) \) and \( -\ln(\gamma e d / 2 \lambda_c) \), respectively. The exact form of the \( f_{2n}^\text{mf} \) can be recovered from Tab. II Before discussing the analytic structure of the dependence on \( d \), we remind the reader that the integration measure \( D f_i \) differs between the cases (A) – no pinning, (B2) – pinning and height fluctuation of the colloids, and (B3) – pinning with collective height and tilt fluctuations of the contact line.

In all these cases for the boundary conditions we have a mean-field contribution, and the leading term of the free energy in the long-range regime \( d \gg r_0 \) (with \( \lambda_c \to \infty \)) is determined by the boundary monopole-monopole interaction and leads to a repulsive effective force between the colloids:

\[
F_{\text{mf}} = k_B T \frac{\partial}{\partial d} \ln Z_{\text{mf}} \to \frac{k_B T}{2} \frac{1}{d \ln(d/r_0)} + \mathcal{O}(d^{-3}), \quad \frac{d}{r_0} \gg 1, \frac{d}{\lambda_c} \to 0.
\]

(36)
So the leading term of the mean-field contribution is equal in size but opposite in sign to the fluctuation contributions, and thus these terms cancel. We will discuss the leading terms of the total Casimir and their connection to the type of boundary conditions which is considered in the next subsection in more detail.

C. Total Casimir force for \( d \gg r_0 \)

The \( 1/d \) asymptotics for both the mean-field and the fluctuation part at hand, we will discuss the total effective force \( F \), which due to \( Z = Z_{\text{fluc}} Z_{\text{mf}} \) is obtained as \( F = F_{\text{fluc}} + F_{\text{mf}} \). As discussed before, the mean-field result depends on the type of boundary conditions under consideration. In all cases the large \( d \) expansion of the mean-field part of the partition sum (with \( \lambda_c \to \infty \)) leads to a repulsive effective force between the colloids, whereas the fluctuation contribution is attractive. So the total Casimir force between the colloids is determined by an interesting interplay between the two–dimensional “bulk” fluctuations and one–dimensional boundary fluctuations influencing the two–dimensional “bulk” by a change of the mean-field.

Combining the expansions of the mean-field and the fluctuation free energies, Eqs. (35) and (21), the asymptotic form of the total Casimir can be written as a power series in \( r_0 / d \),

\[
F(d) = -\frac{k_B T}{2} \frac{\partial}{\partial d} \sum_n [ f_{2n}^{\text{mf}} + f_{2n}^{\text{fluc}} ] \left( \frac{r_0}{d} \right)^{2n}.
\]

(37)
For a pinned contact line and fixed colloids, \( f_{2n}^{mf} = 0 \) for all \( n \), and the full Casimir force is given by the fluctuation part result Eq. (22). As we have seen above, for fluctuating boundary conditions, the leading terms of \( F_{\text{fluc}} \) and \( F_{\text{fluc}} \) (Eqs. 38 and 22) cancel. The same holds for the first subleading terms, for which we find \( f_2^{\text{fluc}} = -f_2^{\text{fluc}} \) for all types of boundary conditions with a mean-field contribution. The form of \( f_4^{mf} \), however, is different for the cases (B2), and (B3) and (A), respectively. In the simplest case of a pinned contact line with height (or monopole) fluctuations of the colloid, we find \( f_8^{mf} = -f_8^{mf} \), that is, \( f_8^{mf} + f_8^{\text{fluc}} = -1 \), such that in case (B1) the leading term of the fluctuation-induced force in the limit \( \frac{d}{r_0} \gg 1 \), \( \frac{d^2}{r_0^2} \rightarrow 0 \) is attractive and stemming from the fluctuation part, and can written as

\[
F \rightarrow -\frac{4 k_B T}{r_0} \left( \frac{r_0}{d} \right)^5.
\]

For a pinned contact line with tilt and height fluctuations (boundary mono- and dipoles, case (B3)) and for the generic case of an unpinned and fluctuating contact line (described by all boundary multipoles, case (A)), we find that this term also cancels: \( f_8^{mf} = -f_8^{mf} \) and \( f_6^{mf} = -f_6^{mf} \). In these cases, the first non-vanishing coefficient in the expansion Eq. 37 is stemming from the fluctuation part as well. In case (B3) it is given by \( f_8^{mf} + f_8^{\text{fluc}} = -9 \) which leads to

\[
F \rightarrow -\frac{72 k_B T}{r_0} \left( \frac{r_0}{d} \right)^9.
\]

For case (A) we find \( f_6^{mf} + f_6^{\text{fluc}} = -1 \) leading to an attractive Casimir force which (in the limit \( \frac{d}{r_0} \gg 1 \), \( \frac{d^2}{r_0^2} \rightarrow 0 \)) reads

\[
F \rightarrow -\frac{8 k_B T}{r_0} \left( \frac{r_0}{d} \right)^9.
\]

D. Karadar’s method

Here we calculate the partition function directly without splitting the fluctuating field \( u \) into a mean-field and a fluctuation part. The starting point is Eq. (13) from Sec. IIIA. The \( \delta \)-functions can again be expressed by auxiliary fields \( \psi_i \), now defined on the two-dimensional circular domains \( S_{i,\text{ref}} \) as opposed to the auxiliary fields of Sec. IIIA which are defined on the one-dimensional circles \( \partial S_{i,\text{ref}} \):

\[
Z = \int D\psi \prod_{i=1}^{2} D\psi_i \int Df_i \exp \left\{ \frac{-\mathcal{H}_{\text{tot}}[f_i, u]}{k_B T} + i \int_{S_{i,\text{ref}}} d^2 x \psi_i(x) [u(x) - f_i,\text{ext}(x)] \right\}.
\]

The function \( f_i,\text{ext} \) which describe the interface extension to \( S_{i,\text{ref}} \) have been defined in Eq. (11) in terms of a multipole expansion in the \( P_{im} \). The total Hamiltonian contains the capillary wave Hamiltonian, the boundary and correction terms (see Sec. IIIA) and reads

\[
\mathcal{H}_{\text{tot}} = \frac{\gamma}{2} \int_{\mathbb{R}^2} d^2 x \left[ (\nabla u)^2 + \frac{u^2}{\lambda_x^2} \right] + \frac{\pi \gamma}{2} \sum_i \left[ 2(P_{i0} - h_i)^2 + 4 \sum_{|m| \geq 1} (1 - |m|) |P_{im}|^2 \right].
\]

Similarly to the evaluation of the fluctuation part, Sec. IIIA we introduce multipole moments \( \Psi_{im} \) of the auxiliary fields by inserting unity into \( Z \), Eq. (41):

\[
1 = \int \prod_{i=1}^{2} \prod_m d\Psi_{im} \delta \left( \Psi_{im} - \int_{S_{i}} d^2 x \frac{r}{r_0} |m| e^{-imr} \psi(x) \right).
\]

In contrast to the evaluation of the fluctuation term in Sec. IIIA, there will be constraints on the lowest multipoles which contribute to \( Z \). To see this we note that, after shifting \( h_i \rightarrow h_i - P_{i0} \), the Hamiltonian \( \mathcal{H}_{\text{tot}} \) does not depend anymore on the boundary monopole moments \( P_{i0} \) and the dipole moments \( P_{i1} \) and the only dependence of \( Z \) on these moments is through the constraint function \( f_{i,\text{ext}} \). Recalling the definition of the integration measure \( Df_i \) for the various boundary conditions, Sec. IIIA and performing the integration over \( P_{i0} \)
and $P_{i1}$ where applicable, we immediately find

$$Z \sim \begin{cases} \int \prod_{i=1}^{2} d\Psi_{im} \ldots \delta(\Psi_{i0}) \ldots & \text{case (B2)} \\ \int \prod_{i=1}^{2} d\Psi_{im} \ldots \delta(\Psi_{i0}) \delta(\Psi_{i-1}) \delta(\Psi_{i1}) \ldots & \text{cases (A) and (B3)} \end{cases}$$ (44)

Having noticed these constraints on the auxiliary fields, we proceed by integrating over the field $u$ in Eq. (41):

$$Z = \int \prod_{i=1}^{2} D\psi_{i} \int Df_{i} \exp \left\{ -\frac{k_{B}T}{2\gamma} \sum_{i,j=1}^{2} \int_{S_{i,\text{ref}}} d^{2}x_{i} \int_{S_{j,\text{ref}}} d^{2}x_{j} \psi_{i}(x_{i}) G(|x_{i} - x_{j}|) \psi_{j}(x_{j}) \right. - \frac{\pi\gamma}{2k_{B}T} \left[ 2(P_{i0} - h_{i})^{2} + 4 \sum_{|m| \geq 1} (1 - |m|) |P_{im}|^{2} \right] - i \sum_{m} \psi_{im} P_{im} \right\} \times \exp \left( \frac{\pi\gamma}{2k_{B}T} \left[ 2(P_{i0} - h_{i})^{2} + \sum_{|m| \geq 1} (1 - |m|) |P_{im}|^{2} \right] - i \sum_{m} \psi_{im} P_{im} \right)$$ (45)

where – as in Eq (15) – $G$ is the Greens function of the capillary wave Hamiltonian. A somewhat longer calculation shows that $Z$ can be split into an interaction part (coupling the auxiliary multipole moments $\Psi_{im}$ for different colloid labels $i$), a self-energy part (depending on $\Psi_{im}$ for each value of $i$ separately) and a remainder (the sum of boundary and correction Hamiltonian):

$$Z = \int \prod_{i=1}^{2} d\Psi_{im} \int Df_{i} \exp \left\{ -\frac{k_{B}T}{2\gamma} \left( \mathcal{H}_{\text{int}}[\Psi_{1m}, \Psi_{2m}] + \mathcal{H}_{i,\text{self}}[\Psi_{im}] \right) \right\} \times$$

$$\quad \exp \left( \frac{\pi\gamma}{2k_{B}T} \left[ 2(P_{i0} - h_{i})^{2} + \sum_{|m| \geq 1} (1 - |m|) |P_{im}|^{2} \right] - i \sum_{m} \psi_{im} P_{im} \right)$$ (46)

The interaction part

$$\mathcal{H}_{\text{int}} = 2 \int_{S_{1,\text{ref}}} d^{2}x_{1} \int_{S_{2,\text{ref}}} d^{2}x_{2} \psi_{1}(x_{1}) G(|x_{1} - x_{2}|) \psi_{2}(x_{2})$$

$$= \frac{1}{2\pi} \left[ -2 \ln \left( \frac{\gamma_{\text{d}} d}{2\lambda_{c}} \right) \Psi_{10}\Psi_{20} + \sum_{l_{1},l_{2} \geq 0} \frac{(-1)^{l_{1}+l_{2}}}{l_{1}+l_{2}} \left( \frac{r_{0}}{d} \right)^{l_{1}+l_{2}} \left( \Psi_{l_{1}l_{1}} \Psi_{2l_{2}} + \Psi_{1-l_{1}} \Psi_{2-l_{2}} \right) \right]$$ (47)

is a bilinear form in the auxiliary multipole moments; it was derived using the multipole expansion of the Greens function $G(|x_{1} - x_{2}|) \simeq -\ln(\gamma_{d} |x_{1} - x_{2}| / 2\lambda_{c})$ (valid for $d \gg r_{0}$) which is presented in App. B in more detail. The self-energy part

$$\exp \left( -\frac{k_{B}T}{2\gamma} \mathcal{H}_{i,\text{self}} \right) = \int \prod_{i=1}^{2} D\psi_{i} \delta \left( \Psi_{im} - \int_{S_{i}} d^{2}x (r/r_{0})^{m} e^{-im\varphi} \psi(x) \right) \exp \left( i \sum_{m} \psi_{im} P_{im} \right) \times$$

$$\exp \left( -\frac{k_{B}T}{2\gamma} \int_{S_{i}} d^{2}x \int_{S_{i}} d^{2}x' \psi_{i}(x) G(|x - x'|) \psi_{i}(x) - i \int_{S_{i,\text{ref}}} d^{2}x \psi_{i}(x) f_{i,\text{ext}}(x) \right)$$ (48)

is evaluated in App. C with the result

$$\mathcal{H}_{i,\text{self}} = -|\Psi_{00}|^{2} \frac{\ln(\gamma_{d} r_{0} / 2\lambda_{c})}{2\pi} + \sum_{m > 0} |\Psi_{im}|^{2} \frac{2\pi |m|}{2\pi|m|}$$ (49)

Combining Eqs. (46), (47), and (49), the partition function can be written as

$$Z = \int \prod_{i=1}^{2} d\Psi_{im} \int Df_{i} \exp \left\{ -\frac{k_{B}T}{2\gamma} \left( \mathbf{\Psi}_{1} \mathbf{\hat{H}}_{\text{self}} \mathbf{\hat{H}}_{\text{int}} + \mathbf{\hat{H}}_{\text{int}} \mathbf{\hat{H}}_{\text{self}} \right) \right\}$$ (50)
where the vectors $\Psi_i = (\Psi_{i0}, P_{i0}, \Psi_{i1}, P_{i1}, \Psi_{i-1}, P_{i-1}, \ldots)$ – in contrast to $\hat{\Psi}_i$ in Sec. [11A] – contain all involved auxiliary and boundary multipole moments. The elements of the matrix $H$ describe the coupling of these multipole moments, where the self-energy block couples multipoles defined on the same circles $S_{i,\text{ref}}$. The self energy matrix $\hat{H}_{\text{self}}$ can be read off Eqs. [46] and [49]. The elements of the interaction matrix $\hat{H}_{\text{int}}$ are determined by the interaction energy $H_{\text{int}}$ in Eq. [47] and couple the auxiliary multipole moments of different colloids. All matrix elements representing couplings of other multipoles are zero.

Similar as in Eqs. [19] and [54], the exponent in Eq. [50] is a bilinear form, however, here combined for all types, boundary multipole moments $P_{im}$ and auxiliary multipoles $\Psi_{im}$. The computation of the partition function amounts to the calculation of $\det \hat{H}$. Expanding the logarithm of this determinant for $r_0/d \ll 1$, and taking the derivative with respect to $d$, we directly obtain the asymptotic form Eq. [37] for the total Casimir force,

$$F(d) = -\frac{k_B T}{2} \frac{\partial}{\partial d} \sum_n f^{\text{kardar}}_n \left( \frac{r_0}{d} \right)^{2n}.$$  

with $f^{\text{kardar}}_n = f^{\text{bac}}_n + f^{\text{mf}}_n$ as it should be. In contrast to the calculation before, the different leading power laws for the different cases (A) and (B1)–(B3) can be understood easily. We note that the interaction between the auxiliary multipoles $\Psi_{im}$ and $\Psi_{jn}$ in $H_{\text{int}}$, Eq. [47], scales like $(r_0/d)^{m' + n'}$. Thus, the leading order of the total fluctuation induced force between the two colloids is determined by the first non-vanishing auxiliary multipole moment $\Psi_{im}$ and (as follows from $\det \hat{H}$) gives rise to a force $F(d) \propto 1/d^{2m' + 1}$ (for $m' > 0$) or $F(d) \propto 1/(d \ln d)$ (for $m' = 0$). As explained in the beginning of this subsection, the different boundary conditions lead to certain constraints on the auxiliary multipoles: According to Eq. [44], the leading term in $F(d)$ arises from a monopole–monopole interaction of the auxiliary field in case (B1), from a dipole–dipole interaction in case (B2), and from a quadrupole–quadrupole interaction in cases (B3) and (A). We remind the reader that the constraints of vanishing auxiliary monopole and dipole moments result from the independence of $H_{\text{tot}}$ of the boundary monopole and dipole moments and that this is only captured correctly by the inclusion of the correction Hamiltonian $H_{\text{corr}}$ (see Sec. [11D]).

At this point we insert the following observation: If the sum of boundary and correction Hamiltonian were zero, all multipole moments $\Psi_{im}$ would be zero and consequently all coefficients in the expansion of the Casimir force in terms of $r_0/d$ would vanish – i.e. the total Casimir force would be zero. This happens for the boundary Hamiltonian [52]

$$H_{b,i} = 2\pi \gamma \sum_{m \geq 1} m |P_{im}|^2$$  

$$= \frac{\gamma}{16\pi} \int_{\partial S_{i,\text{ref}}} d\phi \int_{\partial S_{i,\text{ref}}} d\phi' \frac{|f_i(\phi) - f_i(\phi')|^2}{\sin^2 \frac{1}{2} (\phi - \phi')}.$$  

Thus we see that the boundary Hamiltonian needs to be of nonlocal nature in the contact line height $f_i$ to make the Casimir force vanish.

**IV. SHORT–RANGE BEHAVIOR**

A. Fluctuation part

In the opposite limit of small surface–to–surface distance $h = d - 2r_0 \ll r_0$ the fluctuation force can be calculated by using the Derjaguin (or proximity) approximation [31]. It consists in replacing the local force density on the contact lines by the result for the fluctuation force per length $f_{2d}(h)$ between two parallel lines with a separation distance $h$ and integrating over the two opposite contact line half–circles to obtain the total effective force between the colloids.

The Casimir force between two parallel surfaces was calculated in Ref. [36] in a general approach and explicitly for three-dimensional problems. Applied to two dimensions we obtain $f_{2d}(h) = -k_B T \pi/(24h^2)$. Integrating over the opposing contact line half–circles yields

$$F_{\text{bac}} \approx -\frac{\pi k_B T}{24} \int_0^{r_0} dy \frac{1}{(h + 2r_0 - 2\sqrt{r_0^2 - y^2})^2} \left( \frac{r_0}{h} \rightarrow \infty \right) \rightarrow -\frac{k_B T \pi^2}{48} \frac{r_0^{1/2}}{h^{3/2}} + O(h^{-1/2}).$$  

(54)
for the dominant contribution to the Casimir force from the fluctuation part in the limit $h/r_0 \ll 1$. Note, that this strong increase as $h \to 0$ is a consequence of the finite (mesoscopic) size of the colloids and is missed if the colloids are approximated by pointlike objects. 

**B. Mean-field part**

Here, we exemplify the asymptotic behaviour of the mean–field force for close colloid separations $h \to 0$ by case (B2) for the boundary conditions where only fluctuations of the boundary monopoles occur. From the numerical results (see next section) we observe that the type of divergence of the mean–field force as $h \to 0$ is obtained correctly by considering only monopole fluctuations; including higher multipole moments affects the force only by a multiplicative constant. (This is in marked contrast to the long-range regime.)

In order to apply the Derjaguin approximation, we calculate the mean-field between two parallel lines $\partial S_{1/2}$ on which the field is pinned to a fluctuating value $u_{mf}(\partial S_i) = P_0$ (corresponding to monopole boundary conditions). The mean-field energy $\mathcal{H}_{mf}$ in Eq. (31) is represented by a $2 \times 2$-matrix $\mathbf{E}$. By diagonalizing $\mathbf{E}$ we can write $\mathcal{H}_{mf} = \frac{2\mathcal{L}}{h} (e_s Z^2 + e_a (\Delta z^2))$, where $e_s$ and $e_a$ are the eigenvalues of $\mathbf{E}$, and $Z = P_{10} + P_{20}$ and $\Delta z = P_{10} - P_{20}$ are the symmetric and the antisymmetric superposition of $u_{mf}$ at the boundaries $\partial S_i$, respectively. $L_y$ is the length of the boundary lines. In fact, the line densities $e_s$ and $e_a$ correspond up to a factor to the mean field energies of the solutions of the mean-field equation (24) with symmetric $(u_{s|\partial S_{1/2}} = Z)$ and antisymmetric $(u_{a|\partial S_{1/2}} = \pm \Delta z)$ boundary conditions, respectively, and the general mean field solution is given by $u_{mf} = (u_s + u_a)/2$. For $\lambda_c \to \infty$ the mean–field equation reduces to the Laplace equation $\Delta u_{mf} = 0$ between parallel lines which are in $x$-direction a distance $h$ apart. The antisymmetric and symmetric solutions read $u_s = (2\Delta z/h) x$ and $u_a = \text{const.}$, respectively, with the corresponding line densities $e_s = 0$ and $e_a = 4/h$. A vanishing $e_a$ signifies that a collective vertical shift of the interface does not cost any energy. This leads to the divergence of the integral over $Z$ in the partition function $Z_{mf}$, which physically is not interesting and can be neglected. Applying the Derjaguin approximation (similar to Eq. (24)) to only the antisymmetric mode yields the corresponding energy $E_a$ for the two circles a distance $h$ apart:

$$E_a \approx -2\gamma \int_0^{r_0} dy \frac{2(\Delta z)^2}{h + 2r_0 - 2\sqrt{r_0^2 - y^2}} \approx 2\pi \gamma (\Delta z)^2 \sqrt{\frac{r_0}{h}} + \mathcal{O}(1). \quad (55)$$

Thus the $h$ dependent mean-field part of the free energy reads $F_{mf} \approx -k_B T \ln \int d(\Delta z) \exp(-E_a/k_B T) = (k_B T/4) \ln(h/r_0) + \text{const}$. So, in the limit $h = d - 2R \to 0$ the leading (divergent) part of the effective mean-field force $F_{mf}$ is repulsive and reads

$$F_{mf}(h \to 0) \approx \frac{k_B T}{4h}. \quad (56)$$

It appears physically less obvious why the Derjaguin approximation could also be applied to higher boundary multipole moments $n$, especially if $h \lesssim R/n$. If one nevertheless does so one finds that in this regime $h \lesssim R/n$ the mean–field force diverges slower than $1/h$ whereas for $h \ll R/n$ the monopole behavior is recovered. This is in accordance with our numerical results.

**V. INTERMEDIATE DISTANCES: NUMERICAL CALCULATION**

For intermediate distances $d \approx r_0$ the fluctuation induced force has to be calculated numerically. We will do this as in the previous sections for the fluctuation and the mean-field part separately. For the fluctuation part, we shall apply a method which was introduced in Ref. 33. The starting point is Eq. (15) for the partition function $Z_{\text{fluc}}$. Introducing an equidistant mesh with $N$ points $\varphi_{ij} = (2\pi/N) j$, $0 \leq j < N$, on the contact line circles $\partial S_{1/2\text{rel}}$ converts the double integral in the exponent to a double sum. Then the functional integrals over the $\psi_i$ are replaced by ordinary Gaussian integrals over the $\psi_i(x_i(\varphi_{ij}))$, $\mathcal{D}\psi_i \approx \prod_{j=1}^N dx_i(\varphi_{ij})$. In the exponent, the $\psi_i(x_i(\varphi_{ij}))$ are coupled by a matrix $\mathbf{G}$ with elements $G_{ij}^{jk} = G((x_i(\varphi_{ij}) - x_j(\varphi_{ij'}))).$ Performing the Gaussian integrals and disregarding divergent and $d$-independent terms immediately leads to $F_{\text{fluc}} = (k_B T/2) \ln \det(\mathbf{G}_{\infty}^{-1}\mathbf{G}(d)))$ for the fluctuation free energy. Here, $\mathbf{G}_{\infty} \equiv \lim_{d \to +\infty} \mathbf{G}(d)$. It contains the self energy contributions and is needed for the regularization of the free energy. Deriving with respect to $d$, the Casimir force can be written as

$$F_{\text{fluc}}(d) = -\frac{k_B T}{2} \text{tr}[\mathbf{G}(d)^{-1} \partial_d \mathbf{G}(d)] . \quad (57)$$
The advantage of the direct calculation of the force is that Eq. (57) does not contain any divergent parts which would require regularization, thus easing the numerical treatment considerably. The determinant is computed by using a standard LU decomposition. We find good convergence of the numerical routine also for small $d$ if $N \approx 5000$, which, however, demands a computation time of about 30 hours for each distance point on a standard PC. As discussed in Sec. VI and shown in Figs. 3, we find very good agreement between analytical and numerical results.

The numerical calculation of the mean-field Casimir force can be done very conveniently with the method described in Sec. III B. In order to avoid complex numbers, we used sin- and cos-modes instead of Fourier-modes for the numerical computations. It is straightforward to rewrite the corresponding equations in Sec. III B by using their real and imaginary parts. Via a numerical evaluation of the integrals for the projection coefficients $a_{i,mn}$ in Eq. (29) and inversion of the linear system Eq. (28) the elements $E_{i,\text{self}}^{\text{mn}}$ and $E_{12,\text{int}}^{\text{mn}}$ of the matrix $E$ are computed, see Eqs. (38) and (39). Calculating $\ln \det E$ then provides the free energy $F_{\text{mf}}$, and the numerical derivative finally the mean-field Casimir force $F_{\text{mf}}$. This scheme turns out to be very efficient and provides results for $F_{\text{mf}}$ within seconds. Indeed, the numerical calculations show that it is sufficient to consider $n_{\text{max}} \approx 20$ modes in the expansions of the $u_i$ in Eq. (26) in order to achieve convergence of the results.

VI. DISCUSSION OF RESULTS AND OF POSSIBLE REALIZATIONS

In Fig. 2 we compare numerical results with the analytical expressions for the Casimir force for the long-range asymptotics (Sec. III C) and for very small colloid-colloid separations (Sec. IV), respectively.

For all cases considered for the boundary conditions, (B1)–(B3) and (A), we find a very good agreement with the analytical predictions, Eqs. (29) and (38–41) in the long range regime for colloid separations $d \gtrsim 5r_0$. In the short-range regime, the fluctuation induced force depends much less on the specific type of boundary conditions at the contact line. In fact, in this regime, the divergence of fluctuation part force (which applies to all cases), $\sim -h^{-3/2}$, is dominating the total force in this regime and leads to a strong net attraction. This may have an important influence on the effect of colloid aggregation at interfaces and is discussed in more detail in Ref. [21], especially with regard to the van der Waals force. As can be seen from the plots in Fig. 3 in case (B1) (fixed colloids, no mean-field force) the Derjaguin approximation describes well the numerical data also for intermediate colloid separations $r_0/h = r_0/(d - 2r_0) \lesssim 5$. In the plots for cases (B2), (B3) and (A), however, we see that the repulsive contribution from the mean-field part showing a weaker divergence $\sim 1/h$ leads to a strong decrease of the total force for $r_0/h = r_0/(d - 2r_0) \geq 1$, which, by increasing $d$, converges to the power laws governing the long-range asymptotics. The rapid decrease of the total force actually renders the Casimir force effectively short-ranged for the cases (B3) and (A). Note that because of this rapid decay $\sim -1/d^9$, the competing attractive and repulsive contributions from the fluctuation and mean-field part are of almost equal size and our numerical methods which are based on the addition of these quantities are afflicted with numerical uncertainties and are not able to provide reliable results for $d \gtrsim 15r_0$.

In experimental realizations, fixing the colloids as required in case (B1) might, e.g., be realized by a laser tweezer. In such a setup, the fixing is usually, of course, not exact, but means that the vertical movement of the colloid centers is restricted by an external potential. Including such an external potential for the colloids in our model in fact lowers the repulsive contribution from the mean-field part (as compared to the unfixed case), and therefore leads to an increased long-ranged attractive total Casimir force dominated by the leading term of the fluctuation part, Eq. (22). The extent of this increase is controlled by the strength of the external potential for the colloids, as we will show in the next subsection.

A. External potential on the colloids

In the effective Hamiltonian introduced in Sec. II we considered only free energy differences resulting from the changes of interfacial areas which are associated with fluctuations around the flat reference configuration. In this subsection we will extend this model to external potentials $V_i(h_i)$ acting on the vertical position $h_i$ of the center of colloid $i$. We will concentrate on the cases of a constant external force $F_0e_z$ and a harmonic potential for colloid $i$, corresponding to $V_i(h_i) = -F_0h_i$ and $V_i(h_i) = \frac{1}{2}D_i(h_i - h_{0,i})^2$, respectively. The vertical forces $F_0$ include, e.g., gravity, whereas the harmonic potential can be realized by a laser tweezer. So this is of particular interest for case (B1) where the colloid positions are fixed.
Then, the total effective Hamiltonian of the two colloids adsorbed at the fluid interface reads

$$\mathcal{H} = \mathcal{H}_{cw} + \sum_i \{ \mathcal{H}_{b,i} + V_i(h_i) \}. \quad (58)$$

Note, that the approximations performed in Sec. II in deriving the capillary wave and boundary Hamiltonian remain valid here if the external force or the displacement of the harmonic potential are small on the scale set by the surface tension, i.e., $F_i \ll 2\pi\gamma r_0$ and $D_i h_0 \ll 2\pi\gamma r_0$, respectively.

The additional external potential has two implications which we will discuss in the following. First, it leads to a deformed equilibrium meniscus as compared to the flat reference interface, which gives rise to a "classical" capillary interaction between the colloids [13]. Secondly, through the coupling of the colloid position $h_i$ to the interface field $u$ in the boundary Hamiltonian $\mathcal{H}_{b,i}$, the thermal movement of the colloids in the potential $V_i$ can also influence the fluctuation induced ("non classical") force between the colloids.

As described in detail in Ref. [13], the equilibrium meniscus $u_{eq}$ can be found by minimizing the effective Hamiltonian $\mathcal{H}$ with respect to the colloid position $h_i$ and the interface height $u(x,y)$. The equilibrium colloid height $h_{i,eq}$ is determined from the condition $\partial\mathcal{H}/\partial h_i = 0$ and depends on both the external potential and the mean height of the three phase contact line on the colloid surfaces. The interface field $u_{eq}$ fulfills the Euler-Lagrange equation (24) of $\mathcal{H}_{cw}$ with the boundary condition [13]

$$\frac{\partial u_{eq}(x)}{\partial n_i} = \frac{u_{eq}(x) - h_{i,eq}}{r_0}, \quad (59)$$
where \( \partial/\partial n_i \) is the derivative in the outward normal direction of \( \partial S_{i,\text{ref}} \). Using the general form of Eqs. (25) and (26) for \( u_{\text{eq}} \) and projecting the boundary conditions (59) on \( \partial S_{i,\text{ref}} \) onto \( e^{im\phi_i} \), as in Sec. 11.13 leads again to a linear system for the expansion coefficients \( A_i \sim m \). For a constant external force, we obtain in the asymptotic range \( r_0 \ll d \ll \lambda_c \):

\[
u_{\text{eq}} \simeq -\frac{F_1}{2\pi\gamma} \ln \left( \frac{\gamma_c r_1}{2\lambda_c} \right) - \frac{F_2 r_0}{2\pi\gamma d} \frac{r_0}{r_1} \cos(\varphi_1) - \frac{F_2}{2\pi\gamma} \ln \left( \frac{\gamma_c r_2}{2\lambda_c} \right) - \frac{F_2 r_0}{2\pi\gamma d} \frac{r_0}{r_2} \cos(\varphi_2)
\]

(60)

for the leading terms in \( r_0/d \) of the equilibrium meniscus \( u_{\text{eq}} \) (see Fig. 2 for the definitions of \( r_i \) and \( \varphi_i \)). The capillary interaction arising from the meniscus deformation is given by [13].

\[
V_{\text{men}}(d) = \mathcal{H}(d) - \sum_i \mathcal{H}_{i,\infty}
\]

\[
\approx \frac{F_1 F_2}{2\pi\gamma} \ln \left( \frac{\gamma c d}{2\lambda_c} \right) + \frac{F_1^2 + F_2^2}{4\pi\gamma} \left( \frac{r_0}{d} \right)^2.
\]

(61)

Here, \( \mathcal{H}_{i,\infty} \) is the effective energy associated with a single colloid system. The first term in the second line of Eq. (61) is the well known logarithmic flotation force. Note, that in the absence of electrostatic forces the main contribution to the external force usually is gravity which can be neglected for colloid radii \( \leq 1 \mu m \) as it is much smaller than the thermal energy \( k_B T \). The second term describes the leading behaviour of the capillary interaction if there is an external force only applied to one of the colloids – and it leads to a repulsive force between the colloids.

For harmonic external potentials the equilibrium meniscus and the capillary interaction potential is calculated in the same way but results in a somewhat lengthy expression for \( V_{\text{men}} \). Focusing onto the symmetric case of identical potentials for both colloids, we find that \( V_{\text{men}} \) vanishes in the limit \( \lambda_c \to \infty \): In the absence of gravity a parallel shift of the whole interface does not cost any energy, and, therefore, the response of the system on the presence of the harmonic potentials on the colloids is a shift of the planar interface to a new equilibrium position \( u_{\text{eq}} = -h_0 = h_{0i} \) – without a meniscus deformation and, hence, without causing a capillary interaction. The leading term for \( 1/\lambda_c \) small is given by

\[
V_{\text{men}} \simeq \frac{4\pi\gamma h_0^2 \ln(\gamma c d/2\lambda c)}{(2\pi\gamma/D - \ln(\gamma c r_0/2\lambda c))(2\pi\gamma/D - \ln(\gamma c r_0 d/4\lambda^2))}.
\]

(62)

If the minimum of the harmonic potentials on the colloids are not identical, we find an additional term

\[
V_{\text{men}} \xrightarrow{\lambda_c \to \infty} \frac{\pi\gamma(h_{0i} - h_{0j})^2}{1 + \pi\gamma(1/D_1 + 1/D_2) + \ln d/r_0}
\]

(63)

which is not vanishing in the limit \( \lambda_c \to \infty \).

The influence of the external potential on the fluctuation induced force is most conveniently discussed by splitting the interfacial field into an equilibrium and a fluctuation part, \( u = u_{\text{eq}} + \Delta u \), similar to the splitting into a mean-field part \( u_{\text{mf}} \) and a fluctuation part \( v \) described in Sec. 11.13 and analogously \( h_i = h_{i,\text{eq}} + \Delta h_i \) for the vertical position of the colloids center. Note, however, that \( u_{\text{eq}} \) fulfills the boundary conditions (59), whereas \( u_{\text{mf}} \) is the mean-field part of \( \Delta u \), i.e. \( \Delta u = u_{\text{mf}} + v \), which fulfills the boundary conditions Eq. (53) corresponding to thermal fluctuations of the contact line around its equilibrium position. Inserting this decomposition of the interfacial field \( u \) into the extended Hamiltonian Eq. (58) and performing some conversions of the integrals by exploiting Eqs. (21) and (22) together with Gauss’ theorem, we find a quite distinct behaviour for the cases of a constant external force and of a harmonic potential. In the first case we can rewrite the effective Hamiltonian in the form \( \mathcal{H}[u_{\text{eq}} + \Delta u] = \mathcal{H}[u_{\text{eq}}] + \mathcal{H}_{\text{ext}}[\Delta u] + \mathcal{H}_b[\Delta u, \Delta h_i] \). That means that the effective Hamiltonian relevant for the fluctuation induced force is independent of the external force in this case. The only effect of a constant external force, hence, is the deformation of the equilibrium meniscus which leads to the classical interaction described by Eq. (61). In the case of a harmonic external potential, however, we find \( \mathcal{H}[u_{\text{eq}} + \Delta u] = \mathcal{H}[u_{\text{eq}}] + \mathcal{H}_{\text{ext}}[\Delta u] + \mathcal{H}_b[\Delta u, \Delta h_i] + \mathcal{H}_h[\Delta h_i] \), i.e. compared to the functional integral Eq. (7) we have to introduce an additional harmonic potential term \( \Delta h_i \) of the deviation \( \Delta h_i \) of the colloid position from its equilibrium value \( h_{i,\text{eq}} \) in the expression for the partition function describing the thermal fluctuations of the interface and the colloids. The additional potential term \( V_i = (D_i/2)(\Delta h_i)^2 \), which is centered at \( \Delta h_i = 0 \), can be included in the boundary Hamiltonians \( \mathcal{H}_{i,b} \) and leads to additional terms in the self-energy parts of Eq. (52) for the mean-field part of the partition function. The integrals over the \( \Delta h_i \) and the boundary multipole can be performed as before. The additional potentials \( V_i \) leads to modifications of the
determinant of the matrix $E$. Because of the different form of integration measure for the cases of a pinned and an unpinned contact line (c.f. Sec. IIIA), these modifications differ for the two types of boundary conditions. For the leading term of the mean-field Casimir force we can write

$$F_{mf} \propto k_B T \frac{1}{2} \frac{1}{d \ln d/r_0} \frac{1}{1 + \frac{c_1}{c_2} \ln(d/r_0)},$$

(64)

where $c_i = D_i/(\pi \gamma)$ for a pinned contact line and $c_i = 2/(1 + 2\pi \gamma/D_i)$ for an unpinned contact line. So the inclusion of the harmonic potential leads to a decreased mean-field contribution to the fluctuation induced force as compared to Eq. (30) which decreases with increasing strength $D_i$ of the potentials. For a pinned contact line, in this way the leading term of mean-field contribution to the Casimir force can be switched on in a controlled way by an external laser tweezer potential. In the limit $D_i \to 0$ we recover for both cases the result from Sec. IIIA, Eq. (30), which gives rise to the cancellation of the leading terms with that of the fluctuation part. This is expected because $D_i = 0$ corresponds to the cases (A), (B2) or (B3) where height fluctuations of the colloids are not suppressed by external potentials. In the opposite limit $D_i \to \infty$, however, we find $F_{mf} \to 0$ from Eq. (34) for a pinned contact line. This corresponds to case (B1) of frozen colloid positions and a pinned contact line and where the full Casimir force is given by the fluctuation part Eq. (28). In the case of an unpinned contact line, this effect is less pronounced. Then the original form of the mean-field Casimir force, Eq. (30), is diminished by an additional factor $1/(1 + \ln d/r_0)$ in the limit $D_i \to \infty$.

For the linear external potential (constant force on the colloids) – also relevant for a laser tweezer with relatively large displacement – the only effect is an additional capillary interaction to the fluctuation induced force. The relative importance of these two contributions to the colloid interaction is determined by their amplitudes $F_{\gamma}^2/\gamma$ and $k_B T$, respectively. For a harmonic external potential, the relevance of the external potential on both the classical capillary interaction (cf. Eqs. (21) – (22)) and on the fluctuation induced force Eq. (34), is governed by the ratio $\gamma/D_i$ of the surface tension and the stiffness, $D_i$, of the harmonic potential. For typical values for the surface tension in the range of $\gamma \approx 10 \text{ mN/m}$ and a stiffness $D_i \approx 10^{-3} \text{ mN/m}$ of the harmonic tweezer potential, we find that the classical interaction can be neglected compared to the fluctuation force (whose strength is governed by $k_B T$), but, also, the effect of the external potential on the Casimir force is marginal. For steeper tweezer potentials or lower surface tensions (c.f., e.g., Ref. [43]), such that $\gamma/D_i \leq 1$, we find an increasing influence of the the external potential. Then the mean-field part $F_{mf}$ of the fluctuation induced force is considerably decreased which leads to a more attractive total Casimir force because the fluctuation part then will dominate $F_{mf}$ (c.f. Sec. IIIA). On the other hand, in this regime also the classical capillary interaction reaches the magnitude of the fluctuation induced force.

VII. SUMMARY

The restrictions that two rotational symmetric colloids trapped at a fluid interface impose on the thermally excited interfacial fluctuations (capillary waves) by their sheer presence lead to a thermal Casimir force. This effective fluctuation force can be calculated by a decomposition of the interfacial partition function into a mean-field and a fluctuation part both numerically in the whole range of colloid separations $d$ and analytically for the asymptotic ranges of either small or large separations. In the long-range limit, $d \gg r_0$, the resulting force depends crucially on the boundary conditions at the three-phase contact line on the colloids’ surfaces. There one observes an interesting interplay between the attractive interaction from the interface fluctuations and a repulsive interaction caused by the fluctuating boundary conditions (mean-field part). This results in a cancellation of the leading terms up to a certain order in $1/d$, which is determined by the specific model considered for the boundary conditions. For freely fluctuating colloids – either with a pinned (B3) or unpinned (A) contact line – the Casimir force is characterized by a fast decay $\propto -d^{-9}$. For a pinned contact line, fixing colloidal degrees of freedom leads to longer-ranged forces which are $\propto -d^{-5}$ if the orientation of the colloids is fixed and $\propto -1/d \ln d$ if both orientation and vertical position are fixed. This cancellation of the leading terms from the mean-field and the fluctuation part can be understood in an alternative approach to compute the partition function of the system in which the analogy of the effective Hamiltonian to electrostatics is exploited. In this approach the fluctuation induced force can be interpreted in terms of an interaction between auxiliary multipole moments defined on the area enclosed by the contact line of the colloids. The various boundary conditions at the three phase contact line translate into conditions for the auxiliary multipoles. The asymptotics of the fluctuation induced force for intermediate colloid separations then is determined by the interaction of the leading non-vanishing auxiliary multipoles.
In the opposite limit of a close colloid-colloid separation $h = d - 2r_0 \ll r_0$, the effect of the boundary conditions is much less pronounced. Both the mean-field and the fluctuation part diverge for $h \to 0$, but the resulting force is dominated by $F_{\text{fluc}} \sim h^{-3/2}$ (compared to $F_{\text{mf}} \sim h^{-1}$), leading to a strong Casimir interaction in this regime (c.f. Fig. 3).

For typical values in experimental situations, the fluctuation force will dominate "classical" capillary forces arising from meniscus deformations by an external potential. Nevertheless, such external potentials provide the possibility to tune the fluctuation force directly or to superimpose "classical" and fluctuation forces by a sophisticated choice of the experimental setting.

APPENDIX A: THE BOUNDARY HAMILTONIAN $H_{i,b}$

From Eq. (4) we find that the boundary Hamiltonians $H_{i,b}$ consists of three parts. In this appendix we show how $H_{i,b}$ can be expressed in terms of the boundary multipole moments $P_{im}$, leading to the second order expansion given in Eq. (4). For the case (A) of spherical colloids and a fluctuating contact line all areas $\Delta A_{I/II}$ and $\Delta A_{\text{proj}}$ are nonzero. For the case (B3) of a pinned contact line (disks or Janus spheres), $\Delta A_{I/II} = 0$ and the boundary Hamiltonians are fully determined by the change in the projected meniscus area $\Delta A_{\text{proj}}$. (For the remaining cases (B1) and (B2) all area changes vanish and thus the boundary Hamiltonian is zero.) It is sufficient to determine the area changes $\Delta A'_{I/II} = 0$ and $\Delta A'_{\text{proj}}$ for a single colloid; the total area changes are just given by a sum of these.

If the three phase contact is slowly varying without overhangs it can be written as a function of polar angle $\varphi$, and for spherical colloids its distance to the z-axis is given by

$$r_0(\varphi) = \sqrt{R^2 - (h_0 + u(r_0(\varphi)))^2} = \sqrt{r_0^2 - 2R \cos \theta u(r_0(\varphi)) - u(r_0(\varphi))^2},$$

where $u(r_0(\varphi))$ is the height of the three phase contact line, and $h_0 = -R \cos \theta$ is the height of the colloid center in the reference configuration (c.f. Sec. II). For the second equality we have have used $r_0 = R \sin \theta$.

Following App. A in Ref. 13, we parametrize the projection of the actual three phase contact line onto the reference plane in terms of the polar angle $\varphi$ and write ($h$ is the change in vertical position of the colloid center with respect to the reference configuration)

$$\gamma_1 \Delta A'_I + \gamma_1 \Delta A'_{II} = \frac{\gamma_1}{2} \int_0^{2\pi} d\varphi \left[ u(r_0(\varphi)) - h \right]^2 + \frac{\gamma_1}{2} \int_0^{2\pi} d\varphi \left[ r_0^2(\varphi) - r_0^2(\varphi) \right].$$

FIG. 4: Numerical calculation of mean-field part $F_{\text{mf}}$ of the Casimir force with harmonic external potential for the colloids for $D_i/\gamma = 1$ (triangles, compared to the analytical result Eq. (54) solid line) and $D_i/\gamma = 0.1$ (pluses) in the case of pinned contact line. The circles show the fluctuation part $-F_{\text{fluc}}$ of the Casimir force, which has to be added to $F_{\text{mf}}$ to obtain the total force. As can be seen from the plot, for increasing $D_i/\gamma$ the fluctuation part becomes dominant.
\[ \gamma \Delta A'_{\text{proj}} = \gamma \int_0^{2\pi} d\varphi \int_{r_0}^{r_*} dr \frac{r^2}{2} \left[ r^2(\varphi) - r_0^2 \right] , \]  
\text{(A2)}

where in the first term in second line we have replaced \( u(r_0(\varphi)) \approx u(r_0, \phi) \equiv f \), i.e. we have replaced the contact line height by the meniscus height at the reference contact circle, since this approximation produces only terms which are at most of third order in the boundary multipoles. The second contribution to \( \mathcal{H}_b \) stems from the changes in the projected meniscus area and can be written as

\[ \gamma \Delta A'_{\text{proj}} = \gamma \int_0^{2\pi} d\varphi \int_{r_0}^{r_*} dr \frac{r^2}{2} \left[ r^2(\varphi) - r_0^2 \right] \]  
\text{(A3)}

In case (A), \( \Delta A'_{\text{proj}} \neq 0 \), and both, Eq. \ref{A2} and \ref{A3}, are contributing to \( \mathcal{H}_{i,b} \), leading to a cancellation of the contribution from the change in the projected meniscus area of Eq. \ref{A3} by the second term in Eq. \ref{A3}. Inserting the decomposition of \( f(\varphi) \) from Eq. \ref{A3} (omitting the colloid label \( i \)) we find

\[ \mathcal{H}_b \approx \frac{\pi \gamma}{2} \left[ 2(P_0 - h)^2 + 4 \sum_{m \geq 1} |P_m|^2 \right] . \]  
\text{(A4)}

For the case (B3) there are also tilt fluctuations of the vertical axis of the three phase contact line circle which can be parametrized by a boundary height according to \( f = P_1 e^{i\varphi} + P_{-1} e^{-i\varphi} \), the projection of the tilted circle onto the reference plane \( z = 0 \) is an ellipse, and we find for the boundary Hamiltonian according to Eq. \ref{A3}

\[ \mathcal{H}_b \approx \pi \gamma (|P_1|^2 + |P_{-1}|^2) \]  
\text{(A5)}

Note, however, that we can write \( \mathcal{H}_{b,i} \) as in Eq. \ref{A} for all cases for the boundary conditions, (A) and (B1)–(B3), since the integration measure \( Df_i \) for the contact line is constructed such that only the actual terms for the respective cases contribute, see Sec. II A.

**APPENDIX B: EXPANSION OF THE GREENS FUNCTION**

In this appendix we derive the multipole expansion of the Greens function \( G(|x|) \approx -1/(2\pi) \ln(\gamma e |x|/2\lambda_c) \) between two “charged” (charges generating the auxiliary field \( \psi_i \)) and isolated regions (\( \partial S_{i,\text{ref}} \) in Sec. III A and \( S_{i,\text{ref}} \) in Sec. III D). The method we apply is known from electrostatics and goes back to Schwinger (c.f. \cite{44}) and is referred to as the Schwinger technique in the literature. In doing so, we use the analogy of our problem to two-dimensional electrostatics. As starting point we use the fact that the logarithm is the generating function of the Gegenbauer polynomials. Using \( |x - x'| = \sqrt{r^2 + r'^2 - 2rr' \cos(\varphi - \varphi')} \) and exploiting some properties of the Gegenbauer polynomials \cite{45}, we find

\[ \ln |x - x'| = \ln r + \sum_{l \geq 1} \frac{1}{l} \left( \frac{x'}{r} \right)^l \cos(l\varphi - l\varphi') , \]  
\text{(B1)}

where we assumed \( r' < r = |x| \). Comparing Eq. \ref{B1} to the Taylor expansion of the logarithm, we find

\[ \frac{(-x' \cdot \nabla)^l}{l!} \ln r = \begin{cases} \frac{\ln r}{l} & \text{for } l = 0 \\ \frac{(-1)^l}{l!} \left( \frac{x'}{r} \right)^l \left( e^{i(l\varphi - l\varphi')} + e^{-i(l\varphi - l\varphi')} \right) & \text{for } l > 0 \end{cases} . \]  
\text{(B2)}

On the other hand, introducing \( \xi_{\pm} = \partial_\varphi \pm i\partial_\theta \) and using \( \xi_+ \xi_- \ln r = \xi_- \xi_+ \ln r = 0 \), we can write

\[ \frac{(-x' \cdot \nabla)^l}{l!} \ln r = \frac{(-1)^l}{l!} \left( \frac{x'}{r} \right)^l \left( e^{-il\varphi'} \xi_+ + e^{il\varphi'} \xi_- \right) \ln r \]  
\text{(B3)}

Identifying Eqs. \ref{B1} and \ref{B3} we obtain

\[ \xi_{\pm} \ln r = -(-2)^{l-1}(l-1)! \frac{e^{\pm il\varphi}}{r^l} \]  
\text{(B4)}
With Eq. (B4) at hand and for \( \mathbf{x}_1 = \mathbf{r}_1 \) and \( \mathbf{x}_2 = \mathbf{d} + \mathbf{r}_2 \) residing on different circles we obtain for the Greens function \( G(|\mathbf{x}_2 - \mathbf{x}_1|) \)

\[
- \frac{1}{2\pi} \ln \left( \frac{\gamma c|\mathbf{d} + \mathbf{r}_2 - \mathbf{r}_1|}{2\lambda_c} \right) = - \frac{1}{2\pi} \ln \left( \frac{\gamma c d}{2\lambda_c} \right) + \frac{1}{2\pi} \sum_{l_1, l_2 \geq 0} \frac{(\mathbf{r}_1 \cdot \nabla)^{l_1} (\mathbf{r}_2 \cdot \nabla)^{l_2}}{l_1! l_2!} \ln r
\]

\[
= - \frac{1}{2\pi} \ln \left( \frac{\gamma c d}{2\lambda_c} \right)
\]

\[
+ \frac{1}{2\pi} \sum_{l_1, l_2 \geq 0} \frac{(\mathbf{r}_1 \cdot \nabla)^{l_1} (\mathbf{r}_2 \cdot \nabla)^{l_2}}{l_1! l_2!} \left[ e^{-i(l_1 \phi_1 + l_2 \phi_2)} \xi_{l_1 + l_2} + e^{i(l_1 \phi_1 + l_2 \phi_2)} \xi_{-l_1 - l_2} \right] \ln r
\]

\[
= - \frac{1}{2\pi} \ln \left( \frac{\gamma c d}{2\lambda_c} \right)
\]

\[
+ \frac{1}{2\pi} \sum_{l_1, l_2 \geq 0} \left[ (\mathbf{r}_1 \cdot \nabla)^{l_1} (\mathbf{r}_2 \cdot \nabla)^{l_2} \right] \left[ e^{-i(l_1 \phi_1 + l_2 \phi_2)} + e^{i(l_1 \phi_1 + l_2 \phi_2)} \right]. \tag{B5}
\]

In Sec. IIIA we also need the multipole expansion of \( G(|\mathbf{x}_2 - \mathbf{x}_1|) \) for \( \mathbf{x}_i \) residing on the circumference \( \partial S_{i,\text{ref}} \) of the same circle in order to calculate the elements of the self-energy matrix, Eq. (17). Using Eq. (B1), we obtain with \( |\mathbf{x}_1 - \mathbf{x}_2| = r_0 \sqrt{2 - 2 \cos(\phi_1 - \phi_2)} \)

\[
G(|\mathbf{x}_1 - \mathbf{x}_2|) \simeq - \frac{1}{2\pi} \ln \left( \frac{\gamma c r_0}{2\lambda_c} \right) - \frac{1}{2\pi} \ln[1 - \cos(\phi_2 - \phi_1)]
\]

\[
= - \frac{1}{2\pi} \ln \left( \frac{\gamma c r_0}{2\lambda_c} \right) + \frac{1}{2\pi} \sum_{l \geq 1} \frac{1}{2l} \left[ e^{i\phi_1 - i\phi_2} + e^{-i\phi_1 + i\phi_2} \right]. \tag{B6}
\]

Here the prerequisite \( r' < r \) of Eq. (B1) is not fulfilled, and the series in Eq. (B6) is not convergent. It has to be understood in a formal sense, since it only provides the Fourier coefficients for a finite number of modes which actually contribute to the effective interaction in the long-range regime (see Sec. IIIA for details).

**APPENDIX C: KARDAR’S METHOD: CALCULATION OF THE SELF-ENERGY**

The self–energy part, Eq. (49), is evaluated quite similarly as in Ref. [19]. We eliminate the \( \delta \) functions by introducing conjugate multipole moments \( \Psi_{im} \) of the auxiliary fields:

\[
\delta \left( \Psi_{im} - \int_{S_{i,\text{ref}}} d^2x (r/r_0)^{|m|} e^{-i m \phi} \psi(x) \right) = \int d\tilde{\Psi}_{im} \exp \left( i \tilde{\Psi}_{im} \left[ \Psi_{im} - \int_{S_{i,\text{ref}}} d^2x (r/r_0)^{|m|} e^{-i m \phi} \psi(x) \right] \right). \tag{C1}
\]

This brings \( Z_{i,\text{self}} = \exp\{- k_B T/(2\gamma) \mathcal{H}_{i,\text{self}}\} \) into the form

\[
Z_{i,\text{self}} = \prod_m d\tilde{\Psi}_{im} \int D\psi_i \exp \left\{ - \frac{k_B T}{2\gamma} \int_{S_{i,\text{ref}}} d^2x \int_{S_{i,\text{ref}}} d^2x' \psi_i(x) G(|x - x'|) \psi_i(x) \right. 
\]

\[
- i \int_{S_{i,\text{ref}}} d^2x \psi_i(x) \sum_m \left( \frac{r_i}{r_0} \right)^{|m|} (P_{im} + \tilde{\Psi}_{im}) e^{i m \phi} + i \sum_{m = -\infty}^{\infty} (P_{im} + \tilde{\Psi}_{im}) \Psi_{im} \right\}. \tag{C2}
\]

The functional integral \( \int D\psi_i \) in Eq. (C2) can be converted into a functional integral over a constrained height field \( h(x) \); this corresponds to a reversal of the step from Eq. (14) to Eq. (15).

\[
Z_{i,\text{self}} = \prod_m d\tilde{\Psi}_{im} \exp \left\{ \sum_{m = -\infty}^{\infty} (P_{im} + \tilde{\Psi}_{im}) \Psi_{im} \right\} \int D h \prod_{x_i \in S_{i,\text{ref}}} \delta \left( h(x_i) - \sum_m \left( \frac{r_i}{r_0} \right)^{|m|} (P_{im} + \tilde{\Psi}_{im}) e^{i m \phi} \right)
\]

\[
\times \exp \left\{ - \frac{\gamma}{2k_B T} \int d^2x \left[ (\nabla h)^2 + \frac{h^2}{\lambda_c^2} \right] \right\}. \tag{C3}
\]
In Eq. (C3), the $\delta$-functions describe the pinning of the field $h$ in the region $S_{i,\text{ref}}$. This contribution can be evaluated directly, such that the remaining functional integral reads

$$Z_{i,\text{self}} \approx \int \prod_m d\tilde{\Psi}_{im} \exp \left\{ -\frac{2\pi \gamma}{k_B T} \sum_{m \geq 1} m |P_{im} + \tilde{\Psi}_{im}|^2 + i \sum_{m = \infty} m (P_{im} + \tilde{\Psi}_{im}) \Psi_{im} \right\} \times \int D\tilde{h} \prod_{x_i \in \partial S_{i,\text{ref}}} \delta \left( h(x) - \sum_{m} (P_{im} + \tilde{\Psi}_{im}) e^{im\varphi} \right) \times \exp \left\{ -\frac{\gamma}{2k_B T} \int_{\partial S_{i,\text{ref}}} d^2x \left[ (\nabla h)^2 + \frac{h^2}{\lambda_c^2} \right] \right\}, \quad (C4)$$

where the $\delta$-functions fix $h(x)$ at the boundaries $\partial S_{i,\text{ref}}$ of the integration domain. Splitting the auxiliary field into two parts as in Eq. (8), $h = h_0 + h_1$, where $(-\Delta + \lambda_c^{-2}) h_0 = 0$ with the boundary conditions $h_0(x)|_{\partial S_{i,\text{ref}}} = \sum_{m=\infty}^\infty (P_{im} + \tilde{\Psi}_{im}) e^{im\varphi}$, and $h_1(x)|_{\partial S_{i,\text{ref}}} = 0$, and applying Gauss’ theorem to the integral in the exponent of Eq. (C4) leads to

$$Z_{i,\text{self}} = \int \prod_m d\tilde{\Psi}_{im} \exp \left\{ -\frac{2\pi \gamma}{k_B T} \sum_{m \geq 1} m |P_{im} + \tilde{\Psi}_{im}|^2 + i \sum_{m = \infty}^\infty (P_{im} + \tilde{\Psi}_{im}) \Psi_{im} \right\} \times \exp \left\{ -\frac{\gamma}{2k_B T} \int_{\partial S_{i,\text{ref}}} d^2x \left[ (\nabla h_0)^2 + \frac{h_0^2}{\lambda_c^2} \right] \right\} \times \int D\tilde{h_1} \prod_{x \in \partial S_{i,\text{ref}}} \delta (h_1(x)) \exp \left\{ -\frac{k_B T}{2\gamma} \int_{\partial S_{i,\text{ref}}} d^2x \left[ (\nabla h_1)^2 + \frac{h_1^2}{\lambda_c^2} \right] \right\}. \quad (C5)$$

The functional integral over $h_1$ only yields a constant factor independent of any multipole moment, which will be disregarded below. To compute the line integral in Eq. (C5), we write the general solution of the differential equation for $h_0$ in $\mathbb{R}^2 \setminus S_{i,\text{ref}}$ (c.f. Sec. III.B) $h_0(x) = \sum_m (K_m(r/\lambda_c)/K_m(r_0/\lambda_c))C_m e^{im\varphi}$. By comparison to the boundary conditions the coefficients are determined straightforwardly as $C_m = P_{im} + \tilde{\Psi}_{im}$. Then, the line integral evaluates to $2\pi |P_{im} + \tilde{\Psi}_{im}|^2 f(m)$ with $f(m) = |m| (|m| \geq 1)$ and $f(0) = -1/(\ln(\gamma_0 r_0/2\lambda_c))$, such that the self energy part reads

$$Z_{i,\text{self}} = \int \prod_m d\tilde{\Psi}_{im} \exp \left\{ -\frac{4\pi \gamma}{k_B T} \sum_{m \geq 0} f(m) (1 + \delta_{m0}) |P_{im} + \tilde{\Psi}_{im}|^2 + i \sum_{m = \infty}^\infty (P_{im} + \tilde{\Psi}_{im}) \Psi_{im} \right\}. \quad (C6)$$

and thus $\mathcal{H}_{i,\text{self}}$ is given by (up to unimportant additive constants)

$$\mathcal{H}_{i,\text{self}} = \sum_{m \geq 1} \frac{|\Psi_{im}|^2}{2\pi f(m)}. \quad (C7)$$

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