we present the interface fluctuation approach to calculate the interaction between colloidal particles trapped at a fluid interface. Since, in addition to the interaction between the colloids may also fluctuate in this system, we implement the fluctuation of the boundaries into the scattering formalism and investigate how the interaction between colloids is modified by their fluctuations. This general method can be applied to any number of colloids with various geometries at an interface. We apply the formalism derived in this work to a system of spherical colloids at the interface between two fluid phases. For two spherical colloids, this method very effectively reproduces the previous known results. For three particles we find analytical expressions for the large separation asymptotic energies and numerically calculate the Casimir interaction at all separations. Our results show an interesting three body effect for fixed and fluctuating colloids. While the three body effect strengthens the attractive interaction between fluctuating colloids, it diminishes the attractive force between colloids fixed at an interface.

I. INTRODUCTION

Colloidal particles at a fluid interface can form complex two dimensional (2D) patterns [12]. A deep understanding of different interactions between the colloids trapped at the interface is necessary to explain the observed patterns. Among the forces present at the interface, the importance of fluctuation-induced forces has become more apparent recently, due to the advancement of technology for the detection of these forces at nano scale [3, 5].

Fluctuation-induced forces were first predicted by Casimir in 1948 [6] who showed that in vacuum, confinement of quantum fluctuations of the electromagnetic fields by two parallel uncharged conductors gives rise to an attractive force between them. Since then, several experiments have measured these forces with high precision [7-11]. Quite interestingly, this effect is not restricted to electromagnetic systems and can be generalized to any fluctuating field in which the fluctuations are modified by the presence of external objects. For example, Casimir-like forces exist between particles embedded in a membrane or trapped at a fluid interface, which restrict thermal height fluctuations of the membrane or fluid interface. Indeed, the fluctuation-induced forces in soft matter systems have been subject of intense research for several decades now [12-15].

About 20 years ago, fluctuation-induced forces were investigated between thin rods on a film [13] through a path integral formalism for manifolds [16]. Later the formalism was used to study the fluctuation-induced forces between disks and spherical colloids [17, 18] as well as ellipsoidal colloids trapped at a fluid interface between two fluid phases [19, 20]. In a recent work, an effective field theory method has been employed to find the asymptotic expansion of the fluctuation-induced interaction [21, 22]. Around the same time, Lin et al. presented a Green’s function method to calculate the fluctuation-induced forces between soft and hard particles embedded in a membrane [23].

In this work, we study the interaction between colloidal particles due to the confinement of thermal height fluctuations of the interface. Since the shape and degrees of freedom of the fluctuations contribute significantly to the interactions between the colloids at the interface, we use the scattering formalism [24, 25], which has proven to be very effective for the calculation of the Casimir forces between many objects with different geometries and material properties. The method is also extremely efficient for numerical calculations, especially at short separation.

The scattering method has been widely and successfully used for the calculation of the QED Casimir forces [26-33]. While in all the QED cases the position of the external objects are assumed to be fixed in space, for the colloids trapped at an interface both the object and interface fluctuate. To this end, the most significant aspect of this work is to include the colloid fluctuations into the scattering formalism.

The scattering method simplifies the fluctuation-induced problems by separating the calculation into finding the translation matrices (U) and scattering matrices or T-matrices (T). The U matrix corresponds to the way the fluctuations propagate through the field between the objects and the T-matrix represents the interaction of the object with the fluctuations. This work further simplifies the problem by separating the way a particle interacts with fluctuations from the type of fluctuations the particle undergoes.

We apply this modified scattering method to calculate the interaction between spherical Janus particles. In particular, we study three different types of particle fluctuations: colloids frozen at a vertical position, bobbing colloids that fluctuate only vertically with the interface, and bobbing and tilting colloids that both fluctuate vertically and tilt side to side. We are able to easily reproduce the previously known results between two spherical Janus particles. We also calculate the fluctuation-induced interaction between three particles and find that both bobbing only and bobbing and tilting particle fluctuations weaken the attractive interaction between particles. In contrast, the three body effect makes the attractive Casimir force stronger between frozen particles.

The structure of the paper is as follows: We present
the general form of the Hamiltonian for colloids trapped at a fluid interface in Sec. II and introduce the partition function of the colloids trapped at the interface in Sec. III. The corresponding partition function in terms of the scattering parameters is evaluated in Sec. IV. Using the derived partition function, the general form of the Casimir energy for colloids with arbitrary geometry is obtained in Sec. V and the application of this method to a system of spherical janus colloids is presented in Section VII. A summary of this work and our main conclusions are presented in Sec. VIII. Note that a brief introduction to this method was published by the authors in Ref. [34].

II. HAMILTONIAN

We consider an infinite interface between two fluid phases, characterized by the surface tension $\sigma$. Due to the thermal fluctuations in the system, the interface deviates from its equilibrium flat position placed at $z = 0$. We assume that the thermal height fluctuations are small, without overhangs and bubbles. To this end, we parameterize the interface height profile with the Monge representation, i.e. $z = u(\mathbf{x})$. The free energy costs associated with the interface fluctuation is then

$$\mathcal{H}_{\text{int}}[u] = \sigma \int_{\mathbb{R}^2} d^2 x \left[ \sqrt{1 + (\nabla u)^2} - 1 + \frac{\Delta \rho g}{2 \sigma} u^2 \right], \quad (\text{II.1})$$

where the first two terms represent the energy costs associated with the height fluctuations and the third term represents the change in the gravitational energy. Since the thermal fluctuation does not create a huge change in the interface profile, we perform a small gradient expansion ($|\nabla u| \ll 1$) in Eq. (II.1) and obtain the capillary wave Hamiltonian

$$\mathcal{H}_{\text{int}}[u] \approx \mathcal{H}_{\text{cw}}[u] = \frac{\sigma}{2} \int_{\mathbb{R}^2} d^2 x \left[ (\nabla u)^2 + \frac{u^2}{\lambda_c^2} \right], \quad (\text{II.2})$$

with $\lambda_c = \sqrt{\sigma/(\Delta \rho g)}$ the capillary length. Minimizing the interface Hamiltonian with respect to the height $u$, subject to the boundary condition $u = 0$ as $x$ goes to $\infty$, we find the capillary wave Helmholtz equation,

$$(-\nabla^2 + \lambda_c^2) u(\mathbf{r}) = 0. \quad (\text{II.3})$$

We will discuss the solutions of the above equation in the next section.

For each colloid we must then add the following term to the total Hamiltonian

$$\mathcal{H}_{\text{col}}[^i u, f_i] =$$

$$-\sigma \left( \int_{\Omega_i} d^2 x \sqrt{1 + (\nabla u)^2} - \int_{\Omega_i^{\text{ref}}} d^2 x \right)$$

$$- \frac{\Delta \rho g}{2} \left( \int_{\Omega_i} d^2 x \ u^2 - h_i^2 \Omega_i \right)$$

$$+ (\sigma_{i,1} - \sigma_{i,11}) \Delta A_{i,1}, \quad (\text{II.4})$$

with $\Omega_i$ the projected area of the interior of the colloid, $h_i$ height of the center of mass of the colloid with respect to its equilibrium position, $\sigma_{i,1}(\Pi)$ the surface tension between the colloid and the fluid in phase I(II), and $\Delta A_{i,1}$ the change in the contact area between the colloid and fluid phase I. Note that all these parameters are functions of the contact line between the interface and the colloid, represented by the field $f_i$. The second line in Eq. (II.4) is from the exclusion of energy associated with the interior regions of the colloid $i$ from the fluid-fluid interface, the third line is the change in the gravitational potential energy, and the fourth line is the added fluid-colloid surface energy. Performing a small gradient expansion ($|\nabla u| \ll 1$) in Eq. (II.4), we find

$$\mathcal{H}_{\text{col}}[^i u, f_i] = -\frac{\sigma}{2} \int_{\Omega_i} d^2 x \left[ (\nabla u)^2 + \frac{u^2}{\lambda_c^2} \right]$$

$$+ \frac{\sigma}{2} \Omega_i \left[ \frac{h_i^2}{\lambda_c^2} \right]$$

$$+ \sigma \Delta \Omega_i + (\sigma_{i,1} - \sigma_{i,11}) \Delta A_{i,1}, \quad (\text{II.5})$$

with $\Delta \Omega_i = \Omega_{i,\text{ref}} - \Omega_i$ the change in the projected area of the colloid from its equilibrium position. Note that the second line has a negligible contribution in the colloids free energy and will be dropped as the fluctuations are small and as such $h_i/\lambda_c \ll 1$. The first term can be integrated by parts to give a correction Hamiltonian to the interface term

$$H_{\text{cor}}[^i u] = -\frac{\sigma}{2} \int_{\Omega_i} d^2 x \ u \left(-\nabla^2 + \lambda_c^{-2} \right) u, \quad (\text{II.6})$$

and the boundary term from the integration by parts can be combined with the remaining terms to give a boundary Hamiltonian

$$H_{b}[^i u] = -\frac{\sigma}{2} \int_{\partial \Omega_i} d x (\hat{n} \cdot \nabla u) u + \sigma \Delta \Omega_i + (\sigma_{i,1} - \sigma_{i,11}) \Delta A_{i,1} \quad (\text{II.7})$$

The total Hamiltonian of the interface and colloids system is then given by,

$$\mathcal{H}_{\text{tot}}[u, f_1, \ldots, f_N] = \mathcal{H}_{\text{int}}[u]$$

$$+ \sum_{i=1}^{N} \left( \mathcal{H}_{\text{cor}}[^i u] + \mathcal{H}_{b}[^i u] \right). \quad (\text{II.8})$$

We use Eq. (II.8) to find the partition function and the Casimir energy in the colloidal system at the fluid interface.

III. PARTICITION FUNCTION

In this section we find the partition function of the canonical ensemble of colloidal particles trapped at the interface between two fluid phases. Using Eq. (II.8), the
partition function at temperature \( T \) is

\[
Z = \int_{\mathcal{C}} \mathcal{D}u \prod_{i=1}^{N} \mathcal{D}f_i \exp \left[ \frac{-\mathcal{H}_{\text{tot}}}{k_B T} \right], \tag{III.1}
\]

where \( \mathcal{C} \) denotes the constraint imposed by the fact that the interface height field \( u \) matches the contact line fields \( f_i \). By defining the auxiliary fields \( \psi_i(x) \) on the boundary of the projected areas \( \delta \Omega_i \), the constraint can be replaced with a Dirac delta functional

\[
\delta[u - f_i] = \frac{k_B T}{\sigma} \int \mathcal{D} \psi_i \exp \left[ i \frac{\sigma}{k_B T} \int_{\delta \Omega_i} dx \psi_i(u - f_i) \right]. \tag{III.2}
\]

Inserting Eq. (III.2) into Eq. (III.1), we have

\[
Z = \int \prod_{i=1}^{N} \mathcal{D} \psi_i \ Z_{\text{int}} \ Z_{\text{col}}, \tag{III.3}
\]

where

\[
Z_{\text{int}} = \int \mathcal{D}u \exp \left[ -\mathcal{H}_{\text{int}}[u] + \sum_{i=1}^{N} \mathcal{H}_{\text{cor}}[u] \right] \frac{k_B T}{\sigma} \sum_{i=1}^{N} \int_{\delta \Omega_i} dx \ b \psi_i \right] \exp \left[ +i \frac{\sigma}{k_B T} \sum_{i=1}^{N} \int_{\delta \Omega_i} dx \ u \psi_i \right], \tag{III.4}
\]

and

\[
Z_{\text{col}} = \int \prod_{i=1}^{N} \mathcal{D} f_i \exp \left[ -\sum_{i=1}^{N} \mathcal{H}_{i}[f_i] \right] \frac{k_B T}{\sigma} \sum_{i=1}^{N} \int_{\delta \Omega_i} dx \ b \psi_i \right] \exp \left[ -i \frac{\sigma}{k_B T} \sum_{i=1}^{N} \int_{\delta \Omega_i} dx \ f_i \psi_i \right]. \tag{III.5}
\]

Equations (III.3), (III.4), and (III.5) reveal that we can separate the partition function into the interface and colloid parts, \( Z_{\text{int}} \) and \( Z_{\text{col}} \).

The integration over the field \( u \) in the interface partition function \( Z_{\text{int}} \) can be done easily, and we find

\[
Z_{\text{int}} = C_0 \exp \left[ -\frac{\sigma}{2k_B T} \sum_{i,j=1}^{N} G_{ij} \right], \tag{III.6}
\]

with \( C_0 \) a constant and

\[
G_{ij} = \int_{\delta \Omega_i} \mathcal{D}x \int_{\delta \Omega_j} \mathcal{D}x' \psi_i(x) G(x,x') \psi_j(x'), \tag{III.7}
\]

where \( G(x,x') \) is the Green’s function of the capillary wave Hamiltonian for the free interface. The Green’s function is unique up to an homogeneous solution, which we can specify by demanding that the Green’s function be regular on the interior of the colloids \( \Omega_i \).

**IV. Evaluating the Partition Function**

In this section, we use the scattering approach to evaluate the partition function, (III.6). The scattering approach relies on expanding the fluctuating fields in a complete set of solutions to the corresponding wave equation in order to evaluate the partition function. This section proceeds in the following manner: the integrals of the Green’s function in Eq. (III.7) are evaluated for \( i \neq j \) when the integration takes place on different colloids, and for \( i = j \) when the integration is over a single colloid. The boundary matrix \( H^j_i \) is then defined by expanding the boundary Hamiltonian to lowest order.

Before proceeding it is necessary to define some properties of the solutions of the capillary wave equation. For each colloid, space can be divided into interior \( x \in \Omega_i \) and exterior \( x \notin \Omega_i \) regions. The capillary wave equation will have two sets of independent solutions: \( \phi_{inc}^{i\alpha}(x) \) regular over the interior and \( \phi_{cor}^{i\alpha}(x) \) regular over the exterior. The index \( \alpha \) is a separation constant if the solutions are found through separation of variables, and is the same for both incident and scattered solutions.

Both sets of solutions are complete and orthonormal over the space \( \delta \Omega_i \), so any function defined on \( \delta \Omega_i \) can be written as an expansion in terms of the incident solutions. To this end, we will expand both \( \psi_i(x) \) and \( f_i(x) \) as

\[
\psi_i(x) = \sum_{\alpha} \Psi_{i\alpha} \phi_{inc}^{i\alpha}(x), \tag{IV.1}
\]

\[
f_i(x) = \sum_{\alpha} P_{i\alpha} \phi_{inc}^{i\alpha}(x), \tag{IV.2}
\]

where \( \Psi_{i\alpha} \) and \( P_{i\alpha} \) are the expansion coefficients. We employ the expansions of \( \psi_i(x) \) and \( f_i(x) \) in Eqs. (IV.1) and (IV.2) to find the Green’s function, Eq. (III.7), used in the calculation of the interface partition function \( Z_{\text{int}} \), Eq. (III.6).

**A. Interface Part**

The \( G_{ij} \) term given in Eq. (III.6) for the interface partition function \( Z_{\text{int}} \) can be simplified using Eqs. (III.7) and (IV.1)

\[
G_{ij} = \sum_{\alpha} \Psi_{i\alpha} M_{i\alpha}^{ij} \Psi_{j\beta}. \tag{IV.3}
\]

where \( M_{i\alpha}^{ij} \) is given by the integral

\[
M_{i\alpha}^{ij} = \int_{\delta \Omega_i} \mathcal{D}x \int_{\delta \Omega_j} \mathcal{D}x' \phi_{inc}^{i\alpha}(x) G(x,x') \phi_{inc}^{j\beta}(x'). \tag{IV.4}
\]

Note that the indices \( i \) and \( j \) refer to the auxiliary field defined on the objects \( i \) and \( j \). Two different cases need to be considered: \( i \neq j \) and \( i = j \).
1. Interaction terms: \( i \neq j \)

For the interaction terms if \( i \neq j \), then \( x \) and \( x' \) are on different colloids. In that special case the free Green’s function can be explicitly written as a product of incident and scattered solutions

\[
G(x, x') = \sum_{\alpha} c_{\alpha} \phi_{i\alpha}^{\text{inc}}(x) \phi_{i\alpha}^{\text{sct}}(x'),
\]

with \( x \in \Omega_i \) and \( x' \notin \Omega_i \). The quantity \( c_{\alpha} \) is the expansion coefficient. The integral in Eq. (IV.4) is then given by the product of two integrals

\[
M_{ij}^{\alpha\beta} = \sum_{\gamma} c_{\alpha} \int_{\delta\Omega_i} dx \phi_{i\alpha}^{\text{inc}}(x) \phi_{j\gamma}^{\text{sct}}(x) \frac{\delta}{\delta x_j} \phi_{i\gamma}^{\text{inc}}(x')
\]

with \( c_{\alpha} \) the expansion coefficient. In order to evaluate the second integral, we use the property that the incident solutions \( \phi_{i\alpha}^{\text{inc}}(x) \) are complete on the contact line of particle \( j \) and write the scattered solution from particle \( i \), \( \phi_{i\alpha}^{\text{sct}}(x') \), as

\[
\phi_{i\alpha}^{\text{sct}}(x') = \sum_{\lambda} U_{ij}^{\alpha\lambda} \phi_{j\lambda}^{\text{inc}}(x').
\]

The elements of the translation matrix, \( U_{ij}^{\alpha\lambda} \), are the expansion coefficients of the scattered solution from particle \( i \) in terms of the incident solution for particle \( j \). Inserting Eq. (IV.7) into Eq. (IV.6) and using the orthonormality of the solutions, one immediately finds the \( M \)-matrix elements in terms of the elements of translation matrix, \( U_{ij}^{\alpha\lambda} \)

\[
M_{ij}^{\alpha\beta} = c_{\alpha} U_{ij}^{\alpha\beta}.
\]

The calculation of the elements of \( M \)-matrix is more complex in case of self-interaction, \( i = j \).

2. Self-interaction terms: \( i = j \)

We proceed with the evaluation of self-interaction terms by defining the function,

\[
g_{i\alpha}(x) = \int_{\delta\Omega_i} dx \phi_{i\alpha}^{\text{inc}}(x) G(x, x'),
\]

over the two different regions,

\[
g_{i\alpha}(x') = \begin{cases} 
    g_{i\alpha}^{\text{in}}(x') & \text{for } x' \in \delta\Omega_i, \\
    g_{i\alpha}^{\text{out}}(x') & \text{for } x' \notin \Omega_i.
\end{cases}
\]

Note that on the contact line, \( x' \in \delta\Omega_i \), and outside the colloid, \( x' \notin \Omega_i \). We can now calculate the matrix elements, \( M_{ij}^{ii} \), given in Eq. (IV.4) as an integral over the contact line

\[
M_{ii}^{ij} = \int_{\Omega_i} dx g_{i\alpha}^{\text{in}}(x) \phi_{i\alpha}^{\text{inc}}(x).
\]

Using Eq. (IV.11) and the orthonormality property of the \( \phi_{i\alpha}^{\text{inc}} \) functions, the \( g_{i\alpha}^{\text{in}} \) function can be expanded on the contact line as

\[
g_{i\alpha}^{\text{in}}(x) = \sum_{\beta} M_{ii}^{\alpha\beta} \phi_{i\beta}^{\text{inc}}(x).
\]

Further, the \( g_{i\alpha}^{\text{out}} \) function defined outside the colloid can be written as

\[
g_{i\alpha}^{\text{out}}(x) = g_{i\alpha}^{\text{in}} + \Delta g_{i\alpha}(x).
\]

The expansion is allowed because the correction term \( \Delta g_{i\alpha} \) can be defined as the difference of the \( g_{i\alpha}^{\text{out}}(x) \) defined on the exterior and the \( g_{i\alpha}^{\text{in}} \) function defined on the boundary. The \( g_{i\alpha}^{\text{out}} \) function is a solution to the homogeneous capillary wave equation and can be expressed in terms of \( \phi_{i\alpha}^{\text{inc}} \) and \( \phi_{i\alpha}^{\text{out}} \). The \( g_{i\alpha}^{\text{in}} \) function is defined on the boundary \( \delta\Omega_i \), and the incident field \( \phi_{i\alpha}^{\text{inc}} \) are complete on the boundary. Note that the correction term must go to zero on the boundary, and therefore, we have

\[
\phi_{i\beta}^{\text{inc}}(x') + \sum_{\gamma} T_{\beta\gamma} \phi_{i\gamma}^{\text{sct}}(x') = 0,
\]

which defines regular \( T \)-matrix as the Dirichlet scattering matrix.

We now insert Eqs. (IV.14) and (IV.12) into Eq. (IV.13) and consider the fact that the \( g_{i\alpha}^{\text{in}} \) function must remain regular in the exterior of the particle. This lets us relate \( \chi_{i\alpha} \) term in Eq. (IV.14) to the \( M_{ii}^{\alpha\beta} \) matrix coefficients

\[
\chi_{i\alpha} = -M_{ii}^{\alpha\beta}.
\]

Thus the function \( g_{i\alpha}^{\text{out}}(x) \) given in Eq. (IV.13) can be written as

\[
g_{i\alpha}^{\text{out}}(x) = -\sum_{\beta} M_{ii}^{\alpha\beta} \phi_{i\beta}^{\text{inc}}(x).
\]

A second definition for the \( g_{i\alpha}^{\text{out}} \) function can be obtained inserting Eq. (IV.5) into Eq. (IV.9)

\[
g_{i\alpha}^{\text{out}}(x') = \sum_{\beta} c_{\beta} \int_{\delta\Omega_i} dx \phi_{i\beta}^{\text{inc}}(x) \phi_{i\beta}^{\text{inc}}(x) \phi_{i\gamma}^{\text{sct}}(x').
\]

Using the orthonormality properties of the \( \phi_{i\alpha}^{\text{inc}} \) solutions, the function \( g_{i\alpha}^{\text{out}}(x') \) given in Eq. (IV.18) becomes

\[
g_{i\alpha}^{\text{out}}(x') = c_{\alpha} \phi_{i\alpha}^{\text{sct}}(x').
\]
Comparing Eqs. (IV.17) and (IV.19), we find

\[ M^{ii}_{\alpha\beta} = -c_\alpha \left( T^i \right)^{-1}_{\alpha\beta}. \]  

(IV.20)

We will use \( M^{ii} \) and \( M^{ij} \) given in Eqs. (IV.20) and (IV.21), respectively, to calculate the interface partition function \( Z_{\text{int}} \) given in Eq. (III.6). In order to calculate the total partition function, we need to calculate the colloid partition function, which we will present in the next section.

B. Colloid Part

In order to find the colloid partition function given in Eq. (III.5), we have to calculate the boundary Hamiltonian presented in Eq. (II.8). Without explicitly defining the boundary Hamiltonian, it is not possible to evaluate and obtain a closed form expression. However, at equilibrium, the boundary Hamiltonian is stable with respect to small fluctuations for the field \( f_i \), and thus we expand it in even powers of the field \( f_i \). Using Eq. (IV.21), we are able to calculate the colloid partition function, which we will present in the next section.

C. Total Partition Function

After expanding the \( \psi \) and \( f \) fields based on Eqs. (IV.2) and (IV.1), and using the \( M \)-matrix elements given in Eqs. (IV.8) and (IV.20) and the boundary Hamiltonian elements presented in Eq. (IV.21), the total partition function becomes a Gaussian integral over the expansion coefficients \( \Psi_{i\alpha} \) and \( P_{i\alpha} \)

\[ Z = \int \prod_{i\alpha} d\Psi_{i\alpha} dP_{i\alpha} \exp \left\{ -\frac{\sigma}{2k_BT} \left( \Psi_{i\alpha} P_{i\alpha} \right) M^{ij}_{\alpha\beta} \left( \Psi_{j\beta} P_{j\beta} \right) \right\}, \]  

(IV.22)

with repeated index implying summation, and the \( M \)-matrix given by

\[ M^{ij}_{\alpha\beta} = \begin{pmatrix} c_{\alpha\gamma} U^{ij}_{\alpha\beta} & 0 \\ 0 & 0 \end{pmatrix}, \]  

(IV.23)

for \( i \neq j \) and

\[ M^{ii}_{\alpha\beta} = \begin{pmatrix} -c_\alpha \left( T^i \right)^{-1}_{\alpha\beta} \delta_{\alpha\beta} \delta_{\beta\gamma} & 0 \\ 0 & H_{\alpha\beta} \end{pmatrix}, \]  

(IV.24)

for \( i = j \). The partition function can then be calculated by performing the Gaussian integral in Eq. (IV.22) and is given in terms of the determinant of the \( M \)-matrix

\[ Z = Z_0^{''-1} \det(M)^{-\frac{1}{2}}, \]  

(IV.25)

where \( Z_0^{''} \) contains the normalization factor with the constant parameters obtained from the Gaussian integral in Eq. (IV.22). In the next section, we will use the partition function, Eq. (IV.25) to calculate the Casimir energy.

V. THE CASIMIR ENERGY

The Casimir energy at temperature \( T \) is obtained by using the Helmholtz relation,

\[ \frac{\mathcal{E}}{k_BT} = -\ln \left( \frac{Z}{Z_\infty} \right), \]  

(V.1)

with \( Z_\infty \) the partition function with all colloids taken to infinite separation. Inserting Eq. (IV.25) in Eq. (V.1), we find

\[ \frac{\mathcal{E}}{k_BT} = \frac{1}{2} \ln \det(M_\infty^{-1}M), \]  

(V.2)

with \( (M_\infty)^{ij} = \delta_{ij}M^{ii} \) containing only the self-interacting terms. The elements of the matrix \( M_\infty^{-1}M \) can be explicitly written as

\[ (M_\infty^{-1}M)^{ij}_{\alpha\beta} = 1 \delta_{ij} \delta_{\alpha\beta} + (1 - \delta_{ij}) \delta_{\alpha\gamma} \left( \begin{pmatrix} -c_{\alpha\gamma} \left( T^i \right)^{-1}_{\alpha\gamma} & \delta_{\alpha\gamma} \\ \delta_{\alpha\gamma} & H_{\alpha\gamma} \end{pmatrix} \right)^{-1} \begin{pmatrix} c_{\gamma\beta} U^{ij}_{\gamma\beta} & 0 \\ 0 & 0 \end{pmatrix}, \]  

(V.3)

with the explicit \( 2 \times 2 \) matrix indicating the \( \Psi \) or \( P \) components and the other matrix components indicated by the \( i,j \) and \( \alpha, \beta \) indexes. The block-wise inverse of the \( 2 \times 2 \) matrix can be taken and combined with the \( 2 \times 2 \) identity to give a matrix that is lower block triangular

\[ (M_\infty^{-1}M)^{ij}_{\alpha\beta} = \begin{pmatrix} \delta_{ij} \delta_{\alpha\beta} - (1 - \delta_{ij}) T_{\alpha\gamma} U^{ij}_{\gamma\beta} & 0 \\ X & \delta_{ij} \delta_{\alpha\beta} \end{pmatrix}. \]  

(V.4)

Note that the \( X \) term is non-zero, but not important because the determinant of a block triangular matrix is given by the product of the determinants of the blocks along the diagonal.

Inserting Eq. (V.4) into Eq (V.2) gives

\[ \frac{\mathcal{E}}{k_BT} = \frac{1}{2} \ln \det(1 - T U), \]  

(V.5)

with \( U_{ij} = U^{ij}(1 - \delta_{ij}) \), and \( T_{ij} = T^i \delta_{ij} \). The modified \( T \)-matrix, \( \tilde{T} \), comes from the upper left corner of
the block-wise inversion of the $M_{n,p}^m$ matrix presented in Eq. (IV.24), and is given by
\[ \mathbf{T}^i = \mathbf{T}^i - \mathbf{T}^i [C \mathbf{T}^i C^{-1} + C H^i]^{-1} \mathbf{T}^i, \]  
(V.6)
where $\mathbf{T}$ is the Dirichlet $T$-matrix matrix, $H^i$ is the boundary Hamiltonian matrix elements defined in Eq. (IV.21), and $C$ is a diagonal matrix made of the $c_\alpha$ coefficients from the Green’s function expansion in Eq. (IV.5).

The general energy expression in Eq. (V.5) gives the fluctuation-induced interaction energy between $N$ colloidal particles at a fluid interface. We use the general energy expression to find the interaction energy between two and three colloids.

A. Interaction between Two Particles

For two colloids, the Casimir energy given by Eq. (V.5) reduces to
\[ \mathcal{E}_{12} = \frac{k_B T}{2} \ln \det \left( \frac{1}{\mathbf{T}^{21}} \mathbf{T}^{12} \right). \]  
(V.7)
Using the formula for the determinant of a block matrix the two particle energy takes on the familiar form
\[ \mathcal{E}_{12} = \frac{k_B T}{2} \ln \det (1 - \mathbf{T}^{12} \mathbf{T}^{21}). \]  
(V.8)
Note that Eq. (V.5) is similar to the QED Casimir energy [24] with the $T$-matrix $\mathbf{T}$ replaced with the modified $T$-matrix $\mathbf{T}$.

B. Interaction between Three Particles

The full interaction energy given by Eq. (V.5) for three colloids can be written explicitly as
\[ \mathcal{E} = \frac{k_B T}{2} \ln \det \left( \begin{array}{ccc} 1 & \mathbf{T}^{12} & \mathbf{T}^{13} \\ \mathbf{T}^{21} & 1 & \mathbf{T}^{23} \\ \mathbf{T}^{31} & \mathbf{T}^{32} & 1 \end{array} \right) \]  
(V.9)
Applying the properties of determinants for block matrices, this expression can be further simplified as
\[ \frac{\mathcal{E}}{k_B T} = \frac{1}{2} \ln \det (1 - \mathbf{N}^{12}) + \frac{1}{2} \ln \det (1 - \mathbf{N}^{13}) \]
\[ + \frac{1}{2} \ln \det \left[ (1 - \mathbf{N}^{31})^{-1} (\mathbf{T}^{32} \mathbf{U}^{23} + \mathbf{N}^{32}) \right] \]  
(V.10)
with the $N$-matrix defined as
\[ \mathbf{N}^{ijk} = \mathbf{T}^{ij} \mathbf{U}^{jk} \mathbf{T}^{jk}. \]  
(V.11)

The first two terms of Eq. (V.10) can be identified as the two body energies between colloids 1-2 and 1-3 respectively. The third term particularly demonstrates that fluctuation-induced interactions are not pairwise additive [24]. More specifically, Eq. (V.10) shows that the interaction between colloids 2 and 3 has a more complicated form and contains the indirect scattering of colloids 2 and 3 through the colloid 1.

The full three particle interaction energy can be considered as the sum of the two body interactions plus a three-body interaction term
\[ \mathcal{E} = \sum_{i<j=1}^3 \mathcal{E}_{ij} + \mathcal{E}_{123}, \]  
(V.12)
with $\mathcal{E}_{123}$ the three body interaction, which can be evaluated by the last term in Eq. (V.10) and subtracting the two-body interaction between colloids 2 and 3
\[ \frac{\mathcal{E}_{123}}{k_B T} = \frac{1}{2} \ln \det \left[ (1 - (1 - \mathbf{N}^{31})^{-1} (\mathbf{T}^{32} \mathbf{U}^{23} + \mathbf{N}^{32}) \right] \]  
(V.13)
In the next section, we will employ Eqs. (V.8) and (V.10) to calculate fluctuation-induced interactions between two and three spherical janus particles, respectively.

VI. APPLICATIONS: CIRCULAR JANUS COLLOIDS

We now apply the scattering formalism to calculate the fluctuation-induced interactions between spherical Janus colloids. We obtain the solutions to the helmholtz equation, Eq. (II.3), for spherical particles in Subsec. VI A which we use to find the matrices $\mathbf{T}$ and $\mathbf{U}$ for janus spherical particles. In Subsec. VI B we calculate the Casimir interaction between two spherical janus particles, and in Subsec. VI C we obtain the fluctuation-induced interaction between three janus particles.

A. Capillary wave solutions

We consider spherical particles with the radius $R$, trapped at a fluid interface with surface tension $\sigma$. We assume that the colloids are of Janus type and the contact line is pinned to them with the contact angle $90^\circ$. The solutions to the Helmholtz equation, Eq. (II.3), associated with the capillary wave Hamiltonian in polar coordinates read
\[ \phi_{im}^{inc} = I_m(r/\lambda_e) e^{im\theta}, \]
\[ \phi_{im}^{pec} = K_m(r/\lambda_e) e^{im\theta}, \]  
(VI.1)
with $I_m(x)$ and $K_m(x)$ modified Bessel functions of the first and second kinds, respectively. Note that $I_m(x)$ is
regular as \( x \to 0 \) and \( K_m(x) \) as \( x \to \infty \). The free Green’s function can then be written as

\[
G(r, \theta, r', \theta') = \sum_m I_m(r_< / \lambda_c) e^{im\theta} K_m(r_> / \lambda_c) e^{-im\theta'},
\]

where \( r_< (r_> ) \) is the lesser (greater) of \( r \) and \( r' \). This form of the Green’s function implies that all \( e_m \)'s are exactly 1. In the following three subsections, we use these solutions to find closed form expressions for the translation matrix \( U \), the \( T \)-matrix \( T \), and the boundary Hamiltonian \( H \).

### 1. Translation Matrix

To derive the translation matrix in polar coordinates, we will expand the scattered solutions of the Helmholtz equation in terms of the incident solutions. In particular, we use Graf’s addition theorem for Bessel functions [35],

\[
K_m(r_i / \lambda_c) e^{im\theta_i} = \sum_{m'=\infty} \left( -1 \right)^{m'} e^{i(m-m')\theta_i} K_m-m'(d/\lambda_c) \times I_{m'}(r_j / \lambda_c) e^{im\theta_j},
\]

where \( (d, \theta_j) \) are the polar coordinates of the vector that connects the center of colloid \( i \) to colloid \( j \). Combining Eqs. (VI.7) and (VI.1) and comparing it with Eq. (VI.3), we find the translation matrix in polar coordinates

\[
U_{mm'}^{ij} = \left( -1 \right)^{m'} e^{i(m-m')\theta_i} K_{m-m'}(d/\lambda_c).
\]

We note that in most physical situations, \( \lambda_c = \sqrt{\sigma / (\Delta \rho)} \) is much larger than any other length scale in the problem. In the limit \( d/\lambda_c \ll 1 \), the translation matrix given in Eq. (VI.4) for \( m = m' \) becomes

\[
U_{mm}^{ij} = \left( -1 \right)^{m} \ln(2\lambda_c / d).
\]

and for \( m \neq m' \) is

\[
U_{mm}^{ij} \approx \frac{\left( -1 \right)^{m'}}{2} \frac{|m - m'|!}{|m - m'|} e^{i(m-m')\theta_i} \left( \frac{2\lambda_c}{d} \right)^{|m-m'|}.
\]

We will use Eqs. (VI.5) and (VI.6) along with the asymptotic forms of the \( T \)-matrix calculated in the next section, to obtain the asymptotic form of the Casimir energy, later in the paper.

### 2. Dirichlet Scattering Matrix

We now plug the solutions of Helmholtz equation given in Eq. (VI.1) into Eq. (IV.13) at the radius \( R_i \) of the circular intersection of the object with the fluid interface and find

\[
I_m(R_i / \lambda_c)e^{im\theta} + \sum_{m'} T_{mm'}^i K_m(R_i / \lambda_c)e^{im\theta} = 0,
\]

which can be further simplified using the orthogonality of the exponentials over \( \theta \) and it becomes

\[
T_{mm}^i = - \frac{I_m(R_i / \lambda_c)}{K_m(R_i / \lambda_c)}.
\]

Note that the \( T \)-matrix, \( T \), is diagonal in \( m \) (\( T_{mm'}^i = \delta_{mm'} T_{mm}^i \)). In the limit \( R/\lambda_c \ll 1 \), the \( T \)-matrix for \( m = 0 \) reads

\[
T_{00}^i \approx - \ln^{-1}(2\lambda_c / R_i),
\]

and for \( m \neq 0 \) is

\[
T_{mm}^i \approx - 2|m| \left( \frac{R_i}{2\lambda_c} \right)^{|m|}.
\]

We emphasize that the \( T \)-matrix of spherical particles is the same for any particle with circular cross-section at the fluid interface, such as disks and oblate spheroids.

### 3. Boundary Hamiltonian

The boundary Hamiltonian in Eq. (II.7) contains three terms: a surface term from the integration by parts from Eq. (II.5), a term for the change in the projected surface area, and a term for the change in the surface area of the colloid in contact with each phase.

In the small gradient expansion the first two terms cancel exactly. For a stiff Janus particle the area of the particle surrounded by the contact line \( f_i \) is fixed. If we extend the contact line field into the interior of the colloid such that it satisfies Laplace’s equation, then the equal area expression can be written

\[
\int_{\Omega_i} d^2x \sqrt{1 + (\nabla f_i)^2} = \int_{\Omega_i} d^2x.
\]

Performing a small gradient expansion on the first term and reordering the terms we get the expression

\[
\Delta \Omega_i [f_i] = - \frac{1}{2} \int_{\Omega_i} d^2x f_i \nabla f_i - \frac{1}{2} \int_{\Omega_i} d^2x f_i \Delta f_i.
\]

The first term given as an integral over the edge of the colloid will exactly cancel the surface term from the boundary Hamiltonian in Eq. (II.7). The second term is exactly zero because we defined the \( f_i \) field in the interior such that it satisfies Laplace’s equation.

Because of the cancellation of the first two terms in the boundary Hamiltonian for stiff Janus particles, the boundary Hamiltonian is given completely by the term with the interaction energies between the colloid surface
and the fluid phases. Janus particles are particles whose surface has two distinct regions with different physical properties, such as having a hydrophobic and hydrophilic regions. These regions act to pin the contact line to a given position on the particle. Mathematically this means that the boundary Hamiltonian is zero if the contact line matches the interface between the two regions of the Janus particle, and it is very large (essentially infinite) otherwise. The choice of whether to use zero or infinity depends on which types of fluctuations the colloid is allowed to undergo. If the colloid is fixed, then all fluctuations are forbidden. If the colloid is allowed to bob up and down then the \( m = 0 \) fluctuations are allowed, but all other fluctuations are still forbidden. Finally if the colloid is allowed to both bob up and down and tilt in any direction, then the \( m = 0 \) and \( m = \pm 1 \) fluctuations are allowed. The values of the boundary Hamiltonian for the various types of colloids is listed in Table I.

Using the two possible values for the boundary Hamiltonian, the modified \( T \)-matrix for spherical particles can be found using Eq. (VI.6)

\[
\tilde{T}_m = \begin{cases} 
0 & \text{if } H_m^i = 0, \\
T_m^i & \text{if } H_m^i = \infty,
\end{cases}
\]  

(VI.13)

where \( T \) is the unmodified \( T \)-matrix given in Eq. (VI.8). The Casimir interaction for fluctuating particles can be calculated using Eqs. (VI.4), (VI.8), and (VI.13).

### B. Two Spherical Particles

As shown in Section VI.A, the Casimir energy between two particles can be calculated using Eq. (VI.8). Employing the Sylvester’s determinant theorem \( \det(1 - AB) = \det(1 - BA) \) and the fact that the \( T \)-matrix is diagonal, we can write the Casimir energy between two particles as

\[
\mathcal{E} = \frac{1}{2} \ln \det(1 - N^{12}),
\]  

(VI.14)

with the \( N \)-matrix given by

\[
N_{m'm'}^{12} = \sum_{m''} D_{m'm''}^{12} D_{m''m'}^{21}.
\]  

(VI.15)

The \( D \)-matrix is the translation matrix sandwiched between the square root of two modified \( T \)-matrices

\[
D_{m'm'}^{ij} = \sqrt{T_{m}^{ij} N_{m'm'}^{ij} T_{m'}^{ij}}.
\]  

(VI.16)

The form of \( N \)-matrix given in Eq. (VI.15) is more convenient for both asymptotic analysis and numerical calculations. Considering that the capillary length is the largest length scale in the system and plugging Eqs. (VI.10) and (VI.16) into Eq. (VI.16), we find the \( D \)-matrix in the limit of \( \lambda_c \gg R, d \)

\[
D_{m'm'}^{ij} \propto \left( \frac{R_i}{2\lambda_c} \right)^{|m|} \left( \frac{R_j}{2\lambda_c} \right)^{|m'|} \left( \frac{2\lambda_c}{d} \right)^{|m-m'|}.
\]  

(VI.17)

Careful consideration of the exponents shows, that in the limit of large capillary length (\( \lambda_c \to \infty \)) only the terms in which \( m \) and \( m' \) have different signs remain non-zero. If we plug Eq. (VI.17) into Eq. (VI.15) and assume that \( R_i = R_j = R \), the \( N \)-matrix elements can be written as a power series in \( R/d \)

\[
N_{m'm'} = \sum_{m''=0}^{\infty} A_{m'm''}^{m''} \left( \frac{R}{d} \right)^{2|m''|+|m+m'|},
\]  

(VI.18)

where the \( A_{m'm''}^{m''} \) coefficients can contain logarithmic functions in terms of \( R, d, \) and \( \lambda_c \).

In the following we use the \( N \)-matrix given in Eq. (VI.15) to obtain the large separation asymptotic energies between the spherical Janus colloids for three different cases: colloids frozen at a vertical position; bobbing colloids that fluctuate only vertically with the interface; and bobbing and tilting colloids that both fluctuate vertically and tilt side to side.

#### 1. Fixed Janus colloids

To calculate the Casimir interaction between two frozen janus particles at large separations, we need to find the asymptotic form of \( \ln \det(1 - N) \). Since the determinant is invariant upon even interchanging of the rows and columns, the \( N \)-matrix can be written as

\[
N = \begin{pmatrix} 
N_{00} & N_{01} & N_{0-1} & \ldots \\
N_{10} & N_{11} & N_{1-1} & \ldots \\
N_{-10} & N_{-11} & N_{-1-1} & \ldots \\
\vdots & \vdots & \vdots & \ddots 
\end{pmatrix}.
\]  

(VI.19)

The lines in Eq. (VI.19) divide the \( N \)-matrix into four blocks. Simplifying the determinant for block matrices
gives
\[
\ln \det(1 - N) = \ln(1 - N_{00}) + \ln \det(1 - A) \\
+ \ln \det(1 - \frac{(1 - A)^{-1}B}{1 - N_{00}}),
\]  
where \( A \) is the lower right block and \( B \) is the matrix product of the lower left column and upper right row in Eq. (VI.19). Due to the scaling behavior of \( N_{m'm'} \) given in Eq. (VI.18), the asymptotic behavior of the Casimir energy for fixed particles is dominated by the first term in Eq. (VI.20). Furthermore, as discussed above, for fixed colloids trapped at the fluid interface, 

By Eq. (VI.20). Furthermore, as discussed above, for fixed colloids trapped at the fluid interface. Using the \( T \)-matrix and translation matrix \( U \) given in Eqs. (VI.19) and (VI.5) respectively, in the limit \( \lambda_c/R \gg 1 \) the asymptotic energy reads
\[
\frac{\mathcal{E}}{k_B T} \approx \frac{1}{2} \ln \left( 1 - \frac{\ln^2(2\lambda_c/d)}{\ln(2\lambda_c/R_1)\ln(2\lambda_c/R_2)} \right).
\]  
Note that Eq. (VI.21) is in complete agreement with the results presented Refs. [17, 18].

2. Bobbing Janus colloids

For bobbing colloids we have \( \bar{\mathbf{n}}_0 = 0 \) as discussed in Section VI.A.3. This implies that \( N_{mm'} = 0 \) if either \( m \) or \( m' \) is equal zero, see Eqs. (VI.15) and (VI.16). Furthermore, using the identity \( \ln(1 - N) = \sum_{n=1}^{\infty} \frac{1}{n} \text{tr}(N^n) \) and the power series relation for the \( N \)-matrix given in Eq. (VI.18) we find that only the \( s = 1 \) term and the \( m = \pm 1 \) in Eq. (VI.18) contribute to the asymptotic Casimir energy in the leading order terms in \( R/d \). The Casimir energy can then be written as
\[
\frac{\mathcal{E}}{k_B T} \approx -\frac{1}{2} \left( N_{11}^{12} + N_{-1-1}^{12} \right) .
\]  
Note that as explained in the paragraph above Eq. (VI.18), only the terms in which the signs of \( m \) and \( m' \) are the same are different from zero. Keeping only the \( m'' = 1 \) term in Eq. (VI.18) results to
\[
\frac{\mathcal{E}}{k_B T} \approx -\frac{R_1^2 R_2^2}{d^4} .
\]  
Equation (VI.23) is in agreement with the results given in Refs. [17, 18, 21]. The power law in Eq. (VI.23) will be modified if the particles can bob and tilt as presented in the next section.

3. Bobbing and tilting Janus colloids

As was discussed in Section VI.A.3 for spherical Janus colloids that can both bob and tilt the modified \( \bar{T}_m = 0 \) for \( m = 0 \) and \( m = \pm 1 \). Therefore, the \( m = \pm 2 \) terms will be the leading order terms in \( R/d \) expansion of the Casimir energy and is given by
\[
\frac{\mathcal{E}}{k_B T} \approx \frac{1}{2} \left( N_{22}^{12} + N_{-2-2}^{12} \right) .
\]  
Note that the leading contribution in the power series expansion of the \( N \)-matrix given in Eq. (VI.18) comes from the \( m'' = 2 \) term. To this end, the asymptotic energy at large separation can be written as
\[
\frac{\mathcal{E}}{k_B T} \approx -\frac{9 R_1^4 R_2^4}{d^8} .
\]  
Equation (VI.25) is in agreement with the results obtained in Refs. [17, 18] for two spherical particles. In the next section, we will investigate the interaction between three spherical particles.

C. Three Spherical Particles

Similar to the case of two particle system, it is convenient to write the Casimir energy in terms of \( D \)-matrices given in Eq. (VI.10) such that each translation matrix \( U \) is sandwiched between the square root of two \( D \)-matrices. Then, the three particle energy given in Eq. (V.13) can be written completely in terms of \( D \)-matrices as
\[
\frac{\mathcal{E}_{123}}{k_B T} = \frac{1}{2} \ln \det \left( (1 - D^{32}D^{23})^{-1} (1 - M) \right) ,
\]  
with the \( M \)-matrix
\[
M = (1 - D^{31}D^{13})^{-1} (D^{32} + D^{31}D^{12})
\]
\[
\times (1 - D^{21}D^{12})^{-1} (D^{21} + D^{21}D^{13}) .
\]  
Using the expression for the \( D \)-matrix given in Eq. (VI.17), we will calculate the large separation asymptotic interactions for the three particle system in the next section. Once again, we will consider three cases of frozen, bobbing only and bobbing and tilting colloids trapped at the fluid interface.

1. Frozen particles

For fixed colloids at the fluid interface, the \( M \)-matrix can be reordered similar to the \( N \)-matrix in Eq. (VI.19). The leading order contribution to the three body interaction, defined in Eqs. (VI.12) and (VI.13), comes from the \( m = m' = 0 \) component and is
\[
\frac{\mathcal{E}_{123}}{k_B T} \approx \frac{1}{2} \ln \left( 1 - \frac{M_{00}}{1 - D^{00}D^{00}} \right) .
\]  
Using the asymptotic expressions for the matrices \( U \) and \( T \) given in Eqs. (VI.5) and (VI.9) respectively, the three
body interaction can be written as
\[
\frac{\mathcal{E}_{123}}{k_B T} \approx \frac{1}{2} \ln \left[ \frac{1 - (g_{12}^2 + g_{13}^2 + g_{23}^2 + 2g_{12}g_{13}g_{23})}{(1 - g_{12})(1 - g_{13})(1 - g_{23})} \right],
\]  
with
\[
g_{ij} = \frac{\ln(2\lambda_c/d_{ij})}{\sqrt{\ln(2\lambda_c/R_i) \ln(2\lambda_c/R_j)}}.
\] (VI.30)

2. Bobbing only

As noted previously, for bobbing only colloids the modified \( T_0 = 0 \). Once again, the logarithmic determinant in Eq. (VI.20) can be simplified using the identity \( \ln \det(1 - N) = -\sum_{s=1}^{\infty} \frac{1}{s} \text{tr}(N^s) \). The argument of the determinant itself can be expanded in powers of the \( D \)-matrix, see Eqs. (VI.20) and (VI.27), and it can be written up to \( 4^\text{th} \) order as
\[
1 - (1 - D^{32}D^{23})^{-1} = D^{32}D^{21}D^{13} + D^{31}D^{12}D^{23}
+ D^{31}D^{13}D^{23} + D^{32}D^{21}D^{12}D^{23}
+ D^{31}D^{12}D^{23}D^{13} + \cdots. \] (VI.31)

Note that a matrix product of an odd number of \( D \)-matrices will always evaluate to zero in the limit of large capillary length. The three remaining \( 4^\text{th} \) order terms can be rewritten in terms of the \( N \)-matrices defined in Eq. (VI.15)
\[
\frac{\mathcal{E}_{123}}{k_B T} \approx -\frac{1}{2} \text{tr} \left[ N^{13}N^{32} + N^{21}N^{32} + N^{12}N^{13} \right]. \] (VI.32)

We showed in Sect. [VI.B.2] that for the two particle system, the leading order term in the interacting energy at large separation is obtained from the \( |m| = 1 \) terms given in Eq. (VI.18). The three particle asymptotics for bobbing Janus particles can now simply be read off from the two particle asymptotics in Eq. (VI.23)
\[
\frac{\mathcal{E}_{123}}{k_B T} \approx -\left( \frac{R_1^2 R_2^2 R_3^2}{d_{12}^4 d_{13}^4} + \frac{R_1^2 R_3^2 R_2^2}{d_{12}^4 d_{23}^4} + \frac{R_2^2 R_3^2 R_1^2}{d_{13}^4 d_{23}^4} \right). \] (VI.33)

3. Bobbing and tilting particles

As explained in Subsec. [VA] for the colloids that can undergo both bobbing and tilting fluctuations, \( T_0 = T_{+1} = 0 \); and thus for calculating the asymptotics, the \( |m| = 2 \) terms are the dominant ones in the sum given in Eq. (VI.18) for calculating \( N \)-matrix. Analogous to bobbing colloids, the asymptotic energy for three bobbing and tilting Janus particles can be calculated using Eq. (VI.32) and is equal to
\[
\frac{\mathcal{E}_{123}}{k_B T} \approx -81 \left( \frac{R_1^4 R_2^4 R_3^4}{d_{12}^8 d_{13}^8} + \frac{R_1^4 R_3^4 R_2^4}{d_{12}^8 d_{23}^8} + \frac{R_2^4 R_3^4 R_1^4}{d_{13}^8 d_{23}^8} \right). \] (VI.34)

FIG. 1. Comparison of the numerical and asymptotic results. The plots show the fluctuation-induced interaction between two identical spherical Janus particles of radius \( R \) as a function of surface-to-surface separation \( h/R \). The circles, squares, and triangles illustrate the numerical results for the frozen, bobbing only, and bobbing and tilting colloids, respectively. The dotted, dashed, and dotted-dashed lines show the asymptotic interactions for the frozen, bobbing only, and bobbing and tilting colloids, respectively. The solid curve at short separations shows the Casimir interaction obtained by Derjaguin approximation (VI.1).

VII. NUMERICAL RESULTS

To calculate the Casimir energy numerically, we use the general energy expression given in Eq. (V.5). The \( m \) index for the translation \( T \)-matrices given in Eqs. (VI.8) and (VI.4), respectively, is truncated at some \( m_{\text{max}} \). The Casimir energy then becomes the logarithm of a large determinant that depends on the cutoff \( m_{\text{max}} \). It can be shown numerically that Casimir energy converges exponentially in \( m_{\text{max}} \). In our numerical calculations, convergence is assumed when \( m_{\text{max}} \) is increased by 5 but the relative change in the Casimir energy is less than \( 10^{-4} \).

Figure 1 shows the fluctuation-induced interactions calculated numerically between frozen, bobbing only, and bobbing and tilting spherical Janus particles. The dotted, dashed, and dotted-dashed lines correspond to the asymptotic Casimir energies derived in Eqs. (VI.21), (VI.23) and (VI.25), respectively. As shown in the figure, there is a very good agreement at larger separations \((h/R > 2)\) between the exact numerics and asymptotic results.

Quite interestingly, at short separations \((h/R < 0.1)\), we find an excellent agreement between our results and the Derjaguin or proximity approximation [30]. The Derjaguin approximation replaces the energy at close separations with the sum over the Casimir interaction per length between parallel lines (along the contact lines of
the colloids). The energy between two parallel lines is calculated in Ref. 37 and the Derjaguin approximation for the interaction between the two spherical colloids at an interface is given by 17 18

\[ F \approx -k_B T \frac{\pi^2 R^{1/2}}{48 h^{5/2}}, \]  

(VII.1)

with \( h = d - 2R \).

Note that the scattering method is extremely fast for the calculation of fluctuation-induced interactions between two particles. A single data point is produced in less than 0.01 seconds at intermediate separations \( h/R \approx 1 \) between two particles. For shorter separations one needs to truncate all the matrices involved at larger \( n_{\text{max}} \) resulting in longer computation time. However, the longest computation time needed for a single data point was less than two minutes, for a separation of \( h/R = 0.001 \) with \( n_{\text{max}} \approx 200 \). This is a significant speedup compared to previous methods. More than 5000 points are needed to calculate the interaction energy at the separation around 0.01R using the path integral formalism, see for example Refs. 17 18.

Figure 2(a), (b) and (c) illustrate the three body effect \( \mathcal{E}_{123} \) normalized by the two body interaction \( \mathcal{E}_{23} \) between frozen, bobbing only and tilting and bobbing colloids, respectively. There is a very good agreement between the asymptotics and exact numeric results for large separation, as shown in the figure. The dashed lines and empty circles show the asymptotic results and the numerics for the three particles sitting on a line at equal distance \( (d_{12} = d_{23} = d_{13}/2) \). The dotted line and empty triangles illustrate three colloids sitting at the vertices of an equilateral triangle \( (d_{12} = d_{23} = d_{13}/2) \). The asymptotic results for the three body effect for frozen, bobbing only and bobbing and tilting spherical colloids are obtained based on Eqs. (VI.29), (VI.33) and (VI.34), respectively. The asymptotic energies for two colloids are presented in Eq. (VI.21) for frozen, Eq. (VI.23) for bobbing only, and Eq. (VI.25) for bobbing and tilting particles.

Quite interestingly we find that for the three body Casimir interaction, the three body effect for fixed colloids is repulsive and comparable to the two body interaction energy. Figure 2(a) shows that this is indeed true for all separations. On the other hand, Figs. 2(b) and 2(c) show that the three body effect for bobbing only and bobbing and tilting colloidal particles is attractive such that the total fluctuation-induced energy for three particles is larger than the sum of three pairwise interactions. Note that this strengthening effect is negligible at large separations but quite significant at short separations.

VIII. SUMMARY AND CONCLUSIONS

In this work, we extended the scattering formalism previously employed for the calculation of the Casimir interaction, the three body effect for fixed colloids is larger than the sum of three pairwise interactions. Note that this strengthening effect is negligible at large separations but quite significant at short separations.

FIG. 2. (Color online) Comparison of the numerical and asymptotic results for three spherical Janus colloids. The plots show the ratio of the three body effect \( E_{123} \) to the two body Casimir energy \( E_{23} \) versus the distance between two colloids. The empty circles and black lines represent the numerical and asymptotic energies, respectively, for the three particles sitting on a line \( (d_{12} = d_{23} = d_{13}/2) \). The empty triangles and dotted curve show the numerical and asymptotic energies, respectively, for three colloids sitting at the vertices of an equilateral triangle \( (d_{12} = d_{23} = d_{13}/2) \).
forces in QED [26,33], to obtain the Casimir interaction between colloidal particles trapped at a fluid interface. Since in soft matter systems, the colloids may also fluctuate, we implemented the effect of boundary fluctuations in the scattering method. We found that the scattering matrix of a fluctuating colloid can be written as a mixture of the scattering matrix of frozen colloids and a boundary matrix determined by the colloids fluctuations energy costs.

The augmented scattering method has several advantages: (i) It can be easily applied to colloids with different geometries compared to other techniques, as in the scattering formalism one does not need to calculate the specific Green’s function for each system separately. (ii) Inclusion of colloid fluctuations to the scattering method is developed quite generally for all geometries. (iii) The numerical calculation of the fluctuation-induced forces is much faster using the present method. (iv) Finally, the method developed in this work is also applicable to many particle systems.

To show the effectiveness of the developed method, we applied it to a system of Janus spherical colloids trapped at the interface between two fluid phases. For two particles, we reproduced the well-known asymptotic results [17,18]. For three particles, we found the asymptotic results and numerically obtained the three body effect. Besides the excellent agreement between the numerics and asymptotics, we found that the three body effect for frozen particles at the interface is repulsive and decreases the total free energy between three particles. For fluctuating colloids, we showed that the three body effect is attractive such that it strengthens the total fluctuation-induced interaction. This increase is much larger at short separations.

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