

This is the accepted manuscript made available via CHORUS, the article has been published as:

Three-body fluctuation-induced interaction at fluid interfaces: A strong deviation from the pairwise summation

Ehsan Noruzifar, Jef Wagner, and Roya Zandi

Phys. Rev. E **87**, 020301 — Published 13 February 2013

DOI: [10.1103/PhysRevE.87.020301](https://doi.org/10.1103/PhysRevE.87.020301)

Three Body Fluctuation-Induced Interaction at Fluid Interfaces: A Strong Deviation from the Pairwise Summation

Ehsan Noruzifar, Jef Wagner, and Roya Zandi

Department of Physics and Astronomy, University of California, Riverside, California 92521, USA

We present a new method based on the scattering technique to investigate fluctuation-induced forces at a fluid interface. The scattering approach, well suited to the study of many body systems of arbitrary geometries, is augmented to include boundary fluctuations. Using this method, we study the deviation of the total fluctuation-induced interaction from the sum of pairwise energies for three colloidal particles. We consider both frozen and fluctuating colloids and obtain a very good agreement between analytical and numerical results. We find a marked difference in the three body fluctuation-induced free energy between the frozen and fluctuating colloids, both in sign and relative size.

With the construction of micro- and nano-electro-mechanical devices (MEMS and NEMS) [1–3] and the desire to understand biological processes in greater details, it has become necessary to have a complete understanding of fluctuation-induced forces. These forces were first predicted by Casimir in 1948 who showed that confinement of zero point energy fluctuations of the electromagnetic field between two conducting plates in vacuum gives rise to long ranged attractive interactions [4, 5]. Thirty years later, Fisher and de Gennes noted that imposing constraints on the thermal, rather than quantum, fluctuations in fluids in the vicinity of their critical points also results in similar long-ranged forces [6]. Since then, the thermal versions of Casimir forces have been investigated in various theoretical and experimental studies [7–19].

In particular, due to the industrial applications and importance in biological systems, the thermal fluctuation-induced forces between colloidal particles have been studied within the last few years. For example, the experiments of Hertlein *et. al.* reveal the presence of repulsive and attractive fluctuation-induced forces on colloidal particles immersed in a near-critical binary mixture in the vicinity of a wall [11]. The thermal fluctuation-induced force also plays an important role in the effective interaction between colloidal particles trapped between two fluid phases [20, 21].

There have been previous works using various techniques to study fluctuation-induced forces at interfaces with interesting results [12–19]. There are, however, a number of complications associated with each of these methods. The most common is the difficulty of calculating the interaction between colloids at very small separations and matching it with the Derjaguin approximation [22]. Moreover, extending the previous methods to various geometries and many particle systems can be tedious.

In this work we study the interaction between colloids trapped at a fluid interface using the scattering formalism [23–25], which is widely used to obtain quantum fluctuation-induced forces. The scattering formalism presents a straightforward approach for treating various

geometries and many body systems and is numerically faster compared to previous methods.

Furthermore, the scattering method simplifies the fluctuation-induced calculations by writing the energy into the translation matrices (\mathbb{U}) and scattering matrices or T -matrices (\mathbb{T}). The translation and T -matrices describe how a fluctuation propagates through the field between the objects and how fluctuations interacts with the objects, respectively.

The important difference between the QED Casimir effect and the fluctuation-induced forces between colloids at an interface is that the colloids and their boundaries can fluctuate. This work extends the scattering method to include these effects, by separating out the interface and colloid Hamiltonians. This new extension can simplify the problem by separating the properties of the colloid, as well as the type of fluctuations, from the calculation of the T -matrix. Note, in contrast to previous works [12–16, 19], the calculation of the T - and the translation matrices are completely decoupled.

In order to demonstrate the effectiveness of this new technique, we calculate the fluctuation-induced forces between three spherical Janus colloids at an interface. We study three different fluctuation scenarios: (i) colloids frozen at the interface; (ii) bobbing colloids that fluctuate only vertically; and (iii) bobbing and tilting colloids that both fluctuate vertically and tilt side to side. Surprisingly we find different three body behaviors for fixed and fluctuating colloids. The three body effect for the fixed colloids is repulsive and comparable to the two body interaction, while for fluctuating colloids is attractive and comparable only at short separations.

In the following, we briefly explain the derivation of the scattering formalism for colloids at fluid interfaces. Moreover, we show some numerical and analytical results obtained with this technique. Note that due to the rapid communications format, we only outline the important steps. The details of the derivations and calculations are left for a more complete exposition [26].

We consider an infinite interface between two fluid phases characterized by the surface tension σ . At equi-

librium, the interface is flat and placed at $z = 0$. We suppose that the thermal height fluctuations of the interface are small without overhangs and bubbles. Therefore, we express the interface height profile in the Monge representation, *i.e.* $z = u(\mathbf{x})$. The capillary wave Hamiltonian [15, 16] then becomes

$$\mathcal{H}_{\text{int}}[u] \approx \frac{\sigma}{2} \int_{\mathbb{R}^2} d^2x \left[(\nabla u)^2 + \frac{u^2}{\lambda_c^2} \right], \quad (1)$$

where $\lambda_c = \sqrt{\sigma/(\Delta\rho g)}$ is the capillary length with $\Delta\rho = \rho_1 - \rho_2$, the difference in the mass density of the two fluid phases.

We now introduce N colloidal particles at the interface between two fluid phases. The colloid Hamiltonian will be defined as the energy costs associated with the insertion of a colloid,

$$\begin{aligned} \mathcal{H}_{\text{col}}^i[f_i, h_i] = & -\frac{\sigma}{2} \int_{\Omega_i} d^2x \left[(\nabla f_i)^2 + \frac{f_i^2}{\lambda_c^2} \right] \\ & + \sigma \Delta\Omega_i[f_i] + (\sigma_{i,\text{I}} - \sigma_{i,\text{II}}) \Delta A_{i,\text{I}}[f_i, h_i], \end{aligned} \quad (2)$$

where h_i is the height of the center of mass of the colloid i with respect to the equilibrium interface, and $\sigma_{i,\text{I(II)}}$ is the surface tension between the colloid i and the fluid phase I(II). The contact line field $f_i(\mathbf{x})$ is the height at which the fluid interface intersects the colloid, and is extended into the interior of the colloid. The cross sections of the colloid i with the equilibrium and fluctuating interfaces are denoted by Ω_i^{ref} and Ω_i , respectively, and $\Delta\Omega = \Omega_{\text{ref}} - \Omega$ is the change in the projected area. The surface area of the colloid in contact with the fluid phase I(II) is represented by $A_{i,\text{I(II)}}$ where $\Delta A_{i,\text{I}}$ is the change in the area of the colloid i in the fluid phase I. Note that for Janus particles the total area of the colloid does not change $\Delta A_{\text{I}} = -\Delta A_{\text{II}}$. In addition, the gravitational energy due to the colloid height h_i is negligible and can be ignored in Eq. (2) because $h_i/\lambda_c \ll 1$.

The first term in Eq. (2) is associated with excluding the projected areas Ω_i from the interface since the integration domain in Eq. (1) covers the whole \mathbb{R}^2 space. The second term represents the energy costs related to the change of the projected area for a colloid in the fluctuating vs reference interface, and the third term is the energy costs due to the change in the area of the colloids in the phase I and II.

The total Hamiltonian of the system is the sum of the interface and N colloid Hamiltonians, $\mathcal{H}_{\text{tot}} = \mathcal{H}_{\text{int}}[u] + \sum_{i=1}^N \mathcal{H}_{\text{col}}^i[f_i, h_i]$, and the partition function \mathcal{Z} is the sum over all interface and colloid configurations

$$\mathcal{Z} = \int_{\mathcal{C}} \mathcal{D}u \prod_{i=1}^N \mathcal{D}f_i \exp \left[-\frac{\mathcal{H}_{\text{tot}}}{k_B T} \right], \quad (3)$$

with \mathcal{C} representing the constraints imposed by the colloidal particles on the interface height fluctuations. At

the surface of the colloid i the interface height field u is constrained by the contact line field f_i . A Dirac delta functional is used to implement the constraints, $\delta[u - f_i] = \int \prod_{i=1}^N \mathcal{D}\psi_i \exp[i \int_{\Omega_i} d^2x \psi(u - f_i)]$, where we have introduced the auxiliary field $\psi_i(\mathbf{x})$. Equation (3) can be separated as

$$\mathcal{Z} = \int \prod_{i=1}^N \mathcal{D}\psi_i \mathcal{Z}_{\text{int}} \mathcal{Z}_{\text{col}}, \quad (4)$$

where \mathcal{Z}_{int} and \mathcal{Z}_{col} correspond to the partition functions related to the interface and colloid fluctuations respectively.

The integration over the scalar field u in the interface partition function can be performed and results in

$$\mathcal{Z}_{\text{int}} = C_0 \exp \left(-\frac{k_B T}{2\sigma} \sum_{i,j=1}^N G_{ij} \right), \quad (5)$$

where C_0 is a constant and

$$G_{ij} = \int_{\Omega_i} d^2x \int_{\Omega_j} d^2x' \psi_i(\mathbf{x}) G(\mathbf{x}, \mathbf{x}') \psi_j(\mathbf{x}'). \quad (6)$$

In Eq. (6), $G(\mathbf{x}, \mathbf{x}')$ is the Green's function of the capillary wave equation for the free interface and can be expanded in terms of the solutions to the capillary wave equation, *i.e.* $(-\nabla^2 + \lambda_c^2)u(\mathbf{r}) = 0$. Using separation of variables in a coordinate system centered on a colloid, the capillary wave equation has two solutions: the solution regular at origin, which corresponds to the incident field in the scattering method $\phi_{\alpha}^{\text{inc}}(\mathbf{r})$; and a solution that dies off at infinity, which corresponds to the scattered field $\phi_{\alpha}^{\text{sct}}(\mathbf{r})$. The expansion of the Green's function $G(\mathbf{x}, \mathbf{x}')$ and the auxiliary field ψ_i in terms of these solutions are $G(\mathbf{x}, \mathbf{x}') = \sum_{\alpha} c_{\alpha} \phi_{\alpha}^{\text{inc}}(\mathbf{x}) \phi_{\alpha}^{\text{sct}}(\mathbf{x}')$ and $\psi_i(\mathbf{x}) = \sum_{\alpha} \Psi_{\alpha} \phi_{\alpha}^{\text{inc}}(\mathbf{x})$, respectively, with c_{α} the expansion coefficient and Ψ_{α} the multipole coefficient. Plugging these equations into Eq. (6), we find $G_{ij} = \sum_{\alpha\beta} c_{\alpha} \Psi_{i\alpha} \mathbb{U}_{\alpha\beta}^{ij} \Psi_{j\beta}$ for $i \neq j$ and $G_{ii} = -\sum_{\alpha\beta} c_{\beta} \Psi_{i\alpha} [\mathbb{T}_{\alpha\beta}^i]^{-1} \Psi_{i\beta}$ for $i = j$. The translation matrix \mathbb{U}^{ij} describes the couplings between the partial waves on distinct colloids. The scattering amplitude matrix \mathbb{T}^i relates the incident and scattered fields, and depends only on the shape of the colloid. Inserting the expressions for G_{ij} in Eq. (4), we find

$$\begin{aligned} \mathcal{Z}_{\text{int}} = C_0 \exp \left[\frac{k_B T}{2\sigma} \sum_{i=1}^N \Psi_i^{\dagger} \mathbf{C} [\mathbb{T}^i]^{-1} \Psi_i \right. \\ \left. - \frac{k_B T}{2\sigma} \sum_{i \neq j=1}^N \Psi_i^{\dagger} \mathbf{C} \mathbb{U}^{ij} \Psi_j \right]. \end{aligned} \quad (7)$$

The matrix (\mathbf{C}) in Eq. (7) is a diagonal matrix with the elements that are the coefficient of the Green's function expansion, and Ψ_i is a vector with elements that are the multipole moments associated with the particle i .

We evaluate the colloid partition function following the same steps as the ones we took to calculate the interface partition function. The colloid Hamiltonian in Eq. (2) is expanded to be quadratic in the contact line field f_i , and then the field is expanded in terms of the incident solutions,

$$f_i(\mathbf{x}) = \sum_{\alpha} P_{\alpha} \phi_{\alpha}^{\text{inc}}(\mathbf{x}). \quad (8)$$

After expansion the colloid partition function is

$$\mathcal{Z}_{\text{col}} = \int \prod_{i=1}^N \mathcal{D}P_i \exp \left\{ -\frac{1}{k_B T} \sum_{i=1}^N \mathbf{P}_i^T \mathbf{H}_{\text{col}}^i \mathbf{P}_i - \frac{i}{2} (\mathbf{P}_i^{\dagger} \boldsymbol{\Psi}_i + \mathbf{P}_i \boldsymbol{\Psi}_i^{\dagger}) \right\}, \quad (9)$$

where the exact form of $\mathbf{H}_{\text{col}}^i$ depends on the type of colloid fluctuations and will be presented below. We now insert Eqs. (9) and (7) into Eq. (4) to obtain the total partition function \mathcal{Z} . The resulting partition function is a Gaussian integral over the multipoles $\boldsymbol{\Psi}$ and \mathbf{P} . The fluctuation-induced free energy at temperature T can be then obtained through $\mathcal{E}/k_B T = -\ln(\mathcal{Z}/\mathcal{Z}_{\infty})$, with \mathcal{Z}_{∞} corresponding to the partition function with all the colloids placed at infinite distance from each other. The fluctuation-induced energy as a function of the T -matrix and the translation matrix \mathbf{U} then reads as

$$\frac{\mathcal{E}}{k_B T} = \frac{1}{2} \ln \det(\mathbf{1} - \tilde{\mathbf{T}}\mathbf{U}), \quad (10)$$

where $\mathbf{U}_{ij} = \mathbb{U}^{ij}(1 - \delta_{ij})$ and $\tilde{\mathbf{T}}_{ij} = \tilde{\mathbf{T}}^i \delta_{ij}$ with $\tilde{\mathbf{T}}^i$ the modified T -matrix of the colloid i given by

$$\tilde{\mathbf{T}}^i = \mathbf{T}^i - \mathbf{T}^i [\mathbf{C} \mathbf{T}^i \mathbf{C}^{-1} + \frac{2}{\sigma} \mathbf{C} \mathbf{H}_{\text{col}}^i]^{-1} \mathbf{T}^i. \quad (11)$$

Note while \mathbf{T} depends only on the shape of the colloid, $\tilde{\mathbf{T}}$ also depends on \mathbf{H}_{col} which in turn depends on the specific fluctuations that the colloid undergoes. Equations (10) and (11) can be used to obtain the fluctuation-induced interaction between N colloidal particles at a fluid interface.

We now employ Eq. (10) to calculate the fluctuation-induced free energy between three identical spherical colloids with radius R trapped at an interface. For simplicity we assume that the colloids are Janus particles, *i.e.* the contact line is pinned to the colloid surface such that the area of the colloidal particles in two fluid phases does not change, *i.e.* $\Delta A_{i,I} = 0$. In addition, we set the equilibrium contact angle to $\pi/2$. Using the solutions to the Helmholtz equation in polar coordinates, the T -matrix for colloidal particles with circular cross section at the flat interface reads

$$\mathbb{T}_m = -\frac{I_m(R/\lambda_c)}{K_m(R/\lambda_c)}, \quad (12)$$

where I_m and K_m are the modified Bessel functions of the first kind and second kind, respectively. In order to obtain the fluctuation-induced energy given by Eq. (10), it is necessary to calculate \mathbf{H}_{col} or more specifically the modified $\tilde{\mathbf{T}}$ given in Eq. 11. To find \mathbf{H}_{col} we assume that the colloids are: (i) frozen, allowing no fluctuation; (ii) bobbing, allowing the colloids to fluctuate up and down; and (iii) bobbing and tilting, allowing the colloids to fluctuate both up and down as well as tilt side to side.

The modified T -matrix, $\tilde{\mathbf{T}}$, of a frozen colloid at the interface simplifies to the regular T -matrix \mathbf{T} . This is due to the fact that the frozen particles are exposed to an infinite potential barrier to fluctuate, *i.e.*, the elements of the matrix $\mathbf{H}_{\text{col}}^i$ tend to infinity. From Eq. (11), we find $\tilde{\mathbf{T}} = \mathbf{T}$.

For bobbing colloidal particles, the elements of the modified T -matrix $\tilde{\mathbf{T}}_m$ are the same as those of the regular T -matrix \mathbf{T}_m except for the elements with the partial wave number $m = 0$. To obtain the elements of the matrix $\mathbf{H}_{\text{col}}^i$, one should note that the projection of the bobbing colloids at the interface does not change, therefore $\Delta\Omega = 0$ in Eq. (2). Substituting Eq. (8) into Eq. (2), we find the elements of the matrix $\mathbf{H}_{\text{col}}^i$ in the basis of multipoles \mathbf{P}_i . In the limit $R/\lambda_c \ll 1$, we have $\mathbf{H}_{\text{col}} \approx -\pi\sigma R^2/\lambda_c$ for $m = 0$ and $\mathbf{H}_{\text{col}} \approx \infty$ for $m \neq 0$. From Eq. (11) we immediately find that for $m = 0$, $\tilde{\mathbf{T}}_0 \approx 0$ and for $m \neq 0$, $\tilde{\mathbf{T}}_m \approx \mathbf{T}_m$.

For colloids that both bob and tilt, the elements of the modified T -matrix $\tilde{\mathbf{T}}_m$ for $|m| = 0, 1$ are zero but are the same as the regular T -matrix elements for $|m| > 1$. Note that in contrast to the bobbing colloids case, the projected area for the bobbing and tilting colloids changes with the fluctuations, *i.e.* $\Delta\Omega \neq 0$. After calculating the change in the projected area for small tilt angles, at $R/\lambda_c \ll 1$ limit, we find $\mathbf{H}_{\text{col}} \approx -\pi\sigma R^2/\lambda_c^2, 0, \infty$ for $m = 0, |m| = 1$ and $|m| > 1$ respectively. Therefore, we have $\tilde{\mathbf{T}}_0, \tilde{\mathbf{T}}_{\pm 1} \approx 0$, for $|m| = 0, 1$ and $\tilde{\mathbf{T}}_m \approx \mathbf{T}_m$ otherwise.

We emphasize that the matrix \mathbf{H}_{col} can be thought of as the energy penalty paid for the fluctuations in the \mathbf{P} basis. For the frozen colloids, there is an effectively infinite potential barrier for any fluctuations which move the contact line from its equilibrium position, while for bobbing colloids the $m = 0$ fluctuations can be accommodated by the colloids freedom of movement in the up and down directions. Therefore, $\mathbf{H}_{\text{col}} = \infty$ for all m for frozen colloids, while $\mathbf{H}_{\text{col}} \approx 0$ for $m = 0$ for bobbing colloids. A similar argument applies to the bobbing and tilting colloids, where there will also be no penalty for the $m = \pm 1$ fluctuations.

To calculate the fluctuation-induced energy given in Eq. (10), we also need to calculate the translation matrix in polar coordinate, which can be obtained by using the Graff's addition theorem for Bessel functions [27]. We find $\mathbb{U}_{mm'}^{ij} = (-1)^{m'} e^{i(m-m')\phi_{ij}} K_{m-m'}(d/\lambda_c)$ with ϕ_{ij} the angle between the coordinate systems fixed to the

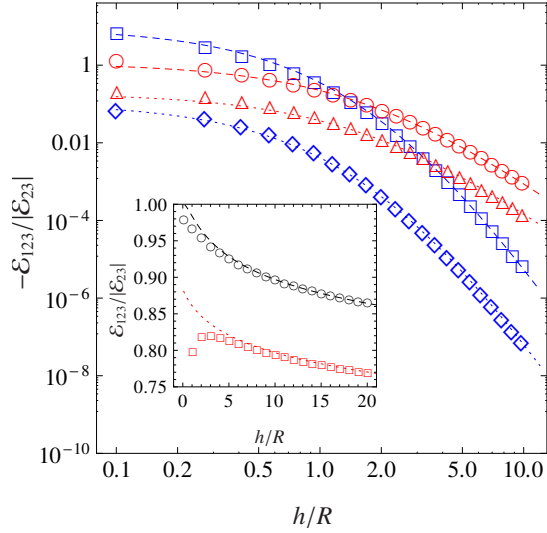


FIG. 1. (Color online) Three body effect for colloids on a line with $d_{12} = d_{13} = d_{23}/2$ and on an equilateral triangle with $d_{12} = d_{13} = d_{23}$: The ratio of the three body energy \mathcal{E}_{123} to the absolute value of the two body energy \mathcal{E}_{23} vs. the surface-to-surface separation of the colloids 1 and 2, h/R . The dashed and dotted lines represent the asymptotic results of Eqs. (15) and (16) for the colloids in the linear and triangular configurations, respectively. Blue squares (linear configuration) and diamonds (triangular configuration) denote the numerical results for the bobbing and tilting colloids. Red circles (linear configuration) and triangles (triangular configuration) show the numerical results for the bobbing only colloids. Inset: Three body effect for *fixed* colloids in the linear and triangular configurations. The dashed and dotted lines show the asymptotic result in Eq. (14). The black circles (linear configuration) and red squares (triangular configuration) represent the numerical results for the fixed colloids.

colloids i and j .

Employing the translation and T -matrices described above, we write

$$\mathcal{E} = \sum_{i < j=1}^3 \mathcal{E}_{ij} + \mathcal{E}_{123}, \quad (13)$$

where the first term is sum over the two-body interactions and the second term \mathcal{E}_{123} is the free energy due to the three body effect. For three fixed colloids at the interface, the asymptotic three body effect $d_{ij}/R_i \gg 1$ in the limit $\lambda_c \gg R_i, d_{ij}$ reads

$$\frac{\mathcal{E}_{123}}{k_B T} \approx \frac{1}{2} \ln \left[\frac{1 - (g_{12}^2 + g_{13}^2 + g_{23}^2 + 2g_{12}g_{13}g_{23})}{(1 - g_{12}^2)(1 - g_{13}^2)(1 - g_{23}^2)} \right], \quad (14)$$

with $g_{ij} = \frac{\ln(2\lambda_c/d_{ij})}{\sqrt{\ln(2\lambda_c/R_i) \ln(2\lambda_c/R_j)}}$, R_i the radius of the colloid i and d_{ij} the center-to-center distance between the colloids i and j . Note that the energy in Eq. (14) depends only on the distance between the colloids.

For three bobbing colloids at the interface, the asymptotic energy in the limit $\lambda_c \gg R_i, d_{ij}$ reads

$$-\frac{\mathcal{E}_{123}}{k_B T} \approx \frac{R_1^4 R_2^2 R_3^2}{d_{12}^4 d_{13}^4} + \frac{R_1^2 R_2^4 R_3^2}{d_{12}^4 d_{23}^4} + \frac{R_1^2 R_2^2 R_3^4}{d_{13}^4 d_{23}^4}. \quad (15)$$

Equation (15) is in agreement with the result in Refs. [17, 18] and shows that the three body asymptotic energy is much smaller than the two body interaction d^{-4} . Therefore, at large separations, for bobbing colloids the sum of pairwise energies gives a very good approximation to the fluctuation-induced energy.

For three bobbing and tilting colloids, the three body energy in the limit $\lambda_c \gg R_i, d_{ij}$ reads

$$-\frac{\mathcal{E}_{123}}{k_B T} \approx 81 \left(\frac{R_1^8 R_2^4 R_3^4}{d_{12}^8 d_{13}^8} + \frac{R_1^4 R_2^8 R_3^4}{d_{12}^8 d_{23}^8} + \frac{R_1^4 R_2^4 R_3^8}{d_{13}^8 d_{23}^8} \right). \quad (16)$$

In this case the two body interaction scales with d^{-8} , and as such the pairwise energy summation again provides a good approximation for the total fluctuation-induced energy.

Figure 1 depicts the ratio of the three body effects to the absolute value of the two body energies vs. the surface-to-surface separation, $h/R = d_{12}/R - 2$, for two different configurations: colloids sitting on a line ($d_{12} = d_{13} = d_{23}/2$) or at the vertices of an equilateral triangle ($d_{12} = d_{13} = d_{23}$). As shown in the figure, there is a very good agreement between the asymptotic energies (dashed and dotted lines) given by Eqs. (14)-(16) and the numerical results (symbols) calculated by Eq. (10).

As illustrated in the figure, the three body effect \mathcal{E}_{123} is very small at large separations for bobbing only (red circles and triangles) and bobbing and tilting colloids (blue squares and diamonds) in both configurations. In contrast, the inset in Fig. 1 shows that the three body effect energy \mathcal{E}_{123} for *fixed* colloids is comparable to their two body interaction with the opposite sign, *i.e.*, there is a strong deviation from the pairwise summation for the case of fixed colloids in both linear and triangular configurations, see the circles and squares in the inset. Quite interestingly, since the three body effect for fixed colloids is positive (repulsive), the total energy is smaller than the sum of pairwise added interaction energies, *i.e.* $\mathcal{E}_{\text{tot}} < \mathcal{E}_{12} + \mathcal{E}_{13} + \mathcal{E}_{23}$.

In summary, we have presented an effective method to study the fluctuation-induced forces at fluid interfaces using a modified scattering method, in which the separation of the interface and colloid free energies enables us to treat various interface and colloid fluctuations. The new approach has many advantages, such as the treatment of many colloid systems, quick numerical calculations, and the treatment of different colloid fluctuations.

As an example, we studied the three body interaction between frozen and fluctuating spherical Janus colloids and found a very interesting difference between them. For both frozen and fluctuating colloids the two body

interactions are attractive. However, for frozen colloids the three body interactions are repulsive weakening the interaction compared to the pairwise summation, while for fluctuating colloids the three body interactions are attractive strengthening the interaction. In addition, we found that the three body interaction for the frozen colloids is non-negligible for the complete range of interactions, while the three body interactions for the fluctuating colloids are negligible for larger separations.

Due to the non-trivial behavior of these forces, a better knowledge of them will shed light on structure formation and crystallization phenomena at the fluid interfaces.

Authors would like to thank Mehran Kardar for useful discussions. This work was supported by the NSF through grants DMR-06-45668 (RZ).

-
- [1] F. M. Serry, D. Walliser, and G. J. Maclay, *Journal of Applied Physics* **84**, 2501 (1998).
 - [2] E. Buks and M. L. Roukes, *Phys. Rev. B* **63**, 033402 (Jan 2001).
 - [3] H. B. Chan, V. A. Aksyuk, R. N. Kleiman, D. J. Bishop, and F. Capasso, *Science* **291**, 1941 (2001).
 - [4] H. B. G. Casimir and D. Polder, *Phys. Rev.* **73**, 360 (Feb 1948).
 - [5] H. B. G. Casimir, *Proc. Koninklijke Nederlandse Akad. Wetenschappen* **B51**, 793 (1948).
 - [6] M. E. Fisher and P. G. de Gennes, *C. R. Acad. Sci. Paris B* **287**, 207 (1978).
 - [7] R. Zandi, J. Rudnick, and M. Kardar, *Phys. Rev. Lett.* **93**, 155302 (Oct 2004).
 - [8] R. Garcia and M. H. W. Chan, *Phys. Rev. Lett.* **83**, 1187 (Aug 1999).
 - [9] M. Goulian, R. Bruinsma, and P. Pincus, *EPL (Europhysics Letters)* **22**, 145 (1993).
 - [10] M. Krech and S. Dietrich, *Phys. Rev. A* **46**, 1886 (Aug 1992).
 - [11] C. Hertlein, L. Helden, A. Gambassi, S. Dietrich, and C. Bechinger, *Nature* **451**, 172 (2008).
 - [12] R. Golestanian, M. Goulian, and M. Kardar, *Phys. Rev. E* **54**, 6725 (Dec 1996).
 - [13] H. Lehle, E. Noruzifar, and M. Oettel, *Eur. Phys. J. E* **26**, 151 (2008).
 - [14] E. Noruzifar and M. Oettel, *Phys. Rev. E* **79**, 051401 (May 2009).
 - [15] H. Lehle, M. Oettel, and S. Dietrich, *Europhys. Lett.* **75**, 174 (2006).
 - [16] H. Lehle and M. Oettel, *Phys. Rev. E* **75**, 011602 (Jan 2007).
 - [17] C. Yolcu, I. Z. Rothstein, and M. Deserno, *EPL (Europhysics Letters)* **96**, 20003 (2011).
 - [18] C. Yolcu, I. Z. Rothstein, and M. Deserno, *Phys. Rev. E* **85**, 011140 (Jan 2012).
 - [19] H.-K. Lin, R. Zandi, U. Mohideen, and L. P. Pryadko, *Phys. Rev. Lett.* **107**, 228104 (Nov 2011).
 - [20] F. Bresme and M. Oettel, *Journal of Physics: Condensed Matter* **19**, 413101 (2007).
 - [21] M. Oettel and S. Dietrich, *Langmuir* **24**, 1425 (2008).
 - [22] B. V. Derjaguin, *Kolloid Z.* **69**, 155 (1934).
 - [23] T. Emig, N. Graham, R. L. Jaffe, and M. Kardar, *Phys. Rev. Lett.* **99**, 170403 (Oct 2007).
 - [24] T. Emig, N. Graham, R. L. Jaffe, and M. Kardar, *Phys. Rev. D* **77**, 025005 (Jan 2008).
 - [25] S. J. Rahi, T. Emig, N. Graham, R. L. Jaffe, and M. Kardar, *Phys. Rev. D* **80**, 085021 (Oct 2009).
 - [26] E. Noruzifar, J. Wagner, and R. Zandi, in preparation.
 - [27] “NIST Digital Library of Mathematical Functions,” <http://dlmf.nist.gov/>, Release 1.0.5 of 2012-10-01, online companion to [?].