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Strong collective attraction in colloidal clusters on a liquid-air interface

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It is shown that in a cluster of many colloids, trapped at a liquid-air interface, the well-known vertical-force-induced pairwise logarithmic attraction changes to a strongly enhanced power-law attraction. In large two-dimensional clusters, the attraction energy scales as the inverse square of the distance between colloids. The enhancement is given by the ratio η=(square of the capillary length)/(interface surface area per colloid) and can be as large as 10^5. This explains why a very small vertical force on colloids, which is too weak to bring two of them together, can stabilize many-body structures on a liquid-air interface. The profile of a cluster is shown to consist of a large slow collective envelope modulated by a fast low-amplitude perturbation due to individual colloids. A closed equation for the slow envelope, which incorporates an arbitrary power-law repulsion between colloids, is derived. For example, this equation is solved for a large circular cluster with the hard-core colloid repulsion. It is suggested that the predicted effect is responsible for mysterious stabilization of colloidal structures observed in experiments on a surface of isotropic liquid and nematic liquid crystal.

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I. INTRODUCTION

A vertical force f applied to each of two colloids, trapped at a liquid-air interface, induces their logarithmic attraction with the potential

$$U_2 = -\frac{f^2}{2\pi\gamma}\ln(\lambda/L), \tag{1}$$

where γ is the surface tension of the interface, $\lambda=\sqrt{\gamma/p}$ is the capillary length of the liquid with the specific weight p, and $L \ll \lambda$ is the distance between the colloids [1,2]. The vertical force f can be of different origin, e.g., the colloid's weight minus buoyancy [1,2]. This is called capillary attraction. Equation (1) is a good approximation of the interaction of a colloid pair for distances L much larger than the colloid size $2R$. Usually, however, one deals with the interface with many colloids that can form variety of two-dimensional structures, in which L can be very close to $2R$ [3–16]. Some of them, such as clusters on an isotropic liquid [4–6,8] and hexagonal lattices on a nematic liquid crystal [14–16], are stabilized by attractive forces between colloids. Analysis shows that an appreciable attractive component is also present in many structures stabilized by repulsion [11,12]. The general problem of stabilization of colloidal structures on a liquid-air interface requires knowledge of the attractive forces in many-body colloidal systems. So far this problem has been addressed in terms of the pairwise potential U_2 (1) [4–6,8,15,16,18–20] or by considering three- and four-colloid systems [17]. However, the long-range character of U_2 casts considerable doubt on its applicability to the many-body problem. First, U_2 is derived under the simplifying assumption that the interface profile with two colloids is a sum of the profiles induced by each of them individually [1,2,18,19]. It can be verified that even in a system of three colloids at not very small distances, this assumption results in nonphysical profiles (with maxima outside the colloid-liquid contact lines). Second, the contribution of a long-range potential to the energy at a given point is growing with the distance from this point, so that the many-body effect of the periphery can be more important than the pairwise contribution of the close neighbors. Therefore, many colloids on the liquid interface have to be considered as an actual many-body system without resorting to the pairwise potential U_2. Moreover, experimental data [4–6,12,15,16,20] have shown that Eq. (1) predicts a much weaker attraction than is actually required for stabilization of the structures observed.

The usual problem researchers encounter when trying to explain a stabilization of colloidal clusters at a liquid-air interface is that, given that the repulsion energy is known, the force f is highly insufficient to induce the pairwise capillary attraction U_2, Eq. (1), of the same order. When the liquid is isotropic, the force f is usually due to the gravity and is equal to the colloid weight minus buoyancy [4–6]; recent development of the field of nematic emulsions has given another example when the force f experienced by colloids on a nematic-liquid-crystal–air interface is due to the elasticity of the anisotropic nematic liquid [14–16,20]. Typically, on a liquid surface one observes a stable cluster (or hexagonal lattice) of micrometer-sized colloids where the force f is sufficient to provide the capillary attraction energy U_2 of order $\sim(10^{-3}-10^{-2})kT$, whereas the destabilizing repulsion energy is at the least of the order of kT due to the necessarily present chaotic thermal motion [4,5], or even as large as 10^2kT due to the force of electrostatic [6] or elastic [14–16,20] origin. Nevertheless, the clusters are stabilized by some attraction that should be four to five orders of magnitude stronger than the pairwise attraction given by formula (1). In addition, the diversity of shapes of different many-body structures formed by colloids on a liquid surface is both impressive and challenging: circular clusters, frothlike clusters with voids separated by thin bands, and cellular voids separated by chains of colloids. The origin of this mysteriously strong capillary attraction stabilizing all these shapes of colloidal clusters on a liquid surface remains unknown. The authors of Ref. [6] at-

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tributed the strong attraction they revealed experimentally to a very peculiar shape of the colloid-liquid contact lines. Apart from the particular problems this interpretation has to face, this approach exemplifies the current situation when either the strong colloidal attraction is explained by factors very specific to a given system or it is admitted that its origin is unknown. The data on the cluster stabilization on a liquid surface, however, point to the existence of some universal attraction source. In this paper, I show that in a cluster of many colloids the interaction is very different from U_2: the collective effect results in a universal attractive force that is much stronger than the pairwise one and no longer logarithmic. The many-body attraction potential is found to be proportional to the enhancement factor $\eta=\lambda^2/$(surface area per colloid), which scales as L^{-2}. The enhancement factor can be as large as 10^4-10^5. It is shown how this interaction can explain large two-dimensional clusters. In Sec. II, the strong attraction is derived from simple qualitative arguments. Section III presents exact equations describing the meniscus with colloids. In Sec. IV, it is shown that the meniscus height consists of a large slow envelope and low-amplitude fast modulation. In Sec. V, the coarse-graining approach is developed, the repulsive force is introduced into the theory, and the general formula for the collective attractive force and a closed equation for the slow envelope are derived. In Sec. VI, this equation is solved for a particular case of a large circular cluster, stabilized by the hard-core repulsion, and the enhancement of the attractive force, attractive energy, and the slow envelope in comparison to their single-colloid values is presented. In Sec. VII, it is shown that the obtained results can explain the mysterious attraction in large clusters on surfaces of a nematic liquid crystal and isotropic liquids observed experimentally.

II. QUALITATIVE DERIVATION OF THE MANY-BODY ATTRACTION

I will begin by presenting a key idea leading to the strong attraction. Let a large number N of colloids occupy an interface surface area of a radius R_N, i.e., an average surface area per colloid is $S_1=\pi R_N^2/N$. A vertical force f in the upward direction is applied to every colloid, which makes the interface height h increase in the cluster area. Clearly, the variation of h in this cluster has two quite different length scales. The short one is determined by the periodicity L of the colloids' arrangement and is thus related to S_1 as $\pi L^2/4\sim S_1$. The long one is determined by the cluster size $R_N \gg L$, i.e., roughly speaking, it has almost a constant value H within the cluster and smoothly vanishes over its outskirts. Thus, H is the simple average of h over the length scale of several cluster periods L and must be determined by average quantities such as S_1. This H can be easily estimated from the average of the standard pressure balance on the interface: the average upward pressure increase due to the force f is $P_f=f/S_1$ and must be balanced by the correspondent decrease of the hydrostatic pressure $P_{\text{hyd}}=-pH$. The equation $P_f+P_{\text{hyd}}=0$ gives $H\sim f/pS_1$. Let us compare this with the f-induced height h_1 of a single remote colloid. Such a colloid occupies the surface area $\sim\pi\lambda^2$ restricted by the capillary length, and the averaged pressure balance gives $h_1\sim f/p\pi\lambda^2=f/\pi\gamma$, which is indeed a correct estimate [cf. Eq. (2) below]. But this h_1 is much less than H: the above estimates can be cast in the form $H\sim h_1\eta$, where $\eta=\pi\lambda^2/S_1\sim(\lambda/L)^2\gg 1$, since the capillary length λ is of a millimeter scale whereas L is just about several micrometers. We see that the average height of the cluster is η times the height of a single remote colloid with $\eta\sim 10^4-10^5$. At the same time, the fast variation $h-H$ should not depend on the overall height of the interface and thus is expected to be of the order of h_1. Thus, the key difference between the energies and forces in a few colloid system and in a dense cluster lies in the enhancement $\eta=H/h_1$, for the attractive energy per colloid is determined by the work fh done by the force f to elevate the colloid along with the interface. Using this as a guiding idea, the many-body effect can be simply estimated as follows.

The pair attraction derives from the energy gain $\propto hf$ equal to the work done by the force f when the height of the interface is changed by h [1,2,21]. For a single colloid with the radius R of the contact line, this $h=h_1$, where

$$h_1=\frac{f}{2\pi\gamma}\ln(\lambda/R), \tag{2}$$

and the energy gain of the colloid is $h_1 f\sim f^2/2\pi\gamma$, which is of the same order as the energy U_2 of the pairwise attraction [1,2]. Now we will show that for a cluster of N colloids separated by distances $L\ll\lambda$, the variation of the interface profile $\tilde{h}\sim h_1$, while the total height h over (or under) the unperturbed meniscus far from the cluster is much larger: it is the sum $h=H+\tilde{h}$, where H varies much slower than $\tilde{h}$, but $H\gg\tilde{h}$; see Fig. 1(a). To estimate h in comparison with $\tilde{h}\sim h_1$, let us for a moment view the interface occupied by the colloids as smooth with a constant height H. As the hydrostatic pressure on the colloid's surface submerged in the liquid depends on the height H of the interface, the total force f_c acting on a colloid depends on H. Namely,

$$f_c=f-pHS_c, \tag{3}$$

where f is H independent and the second term accounts for the change of the hydrostatic pressure on the colloid; S_c is the surface area bounded by the contact line. For simplicity, the constant force f here and henceforth is assumed to be the same for all colloids. Due to the contact with colloids, the plane surface of the height H is subject to the average pressure $P_c=f_c/S_1$, where $S_1\propto L^2$ is the surface area of the cluster per colloid. The total force $(f_c/S_1)S_1=f_c$ due to this pressure must be equalized by the hydrostatic pressure $-pH$ acting on the free meniscus, which has the surface area S_1-S_c. Thus, the force balance on the flat cluster's surface has the form

$$(f-pHS_c)-pH(S_1-S_c)=0, \tag{4}$$

from which $f=pHS_1$. This equality is particularly clear: in the equilibrium, the force f on each colloid must be balanced by the hydrostatic pressure on the piece of the interface per colloid. Thus, the height H is given by the formula

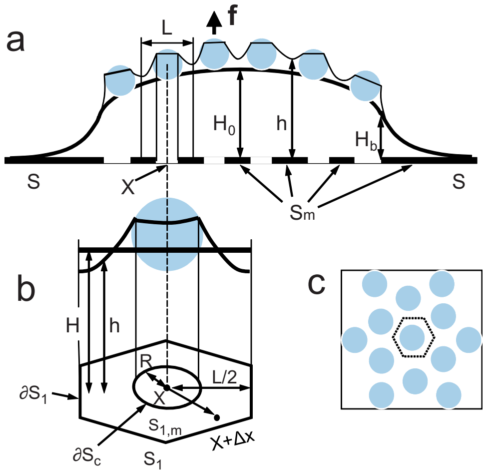

FIG. 1. (Color online) (a) Cluster of spherical colloids on a liquid-air interface, its exact height h and slow envelope H induced by the force f directed upward. The magnitudes of H, h, and $\tilde{h}=h-H$ are greatly exaggerated: while the colloid diameter and the separation L are of several micrometers, H can be as large as a micrometer, whereas the fast modulation $\tilde{h}$ is just about a nanometer. (b) Single cell of the interface around the colloid at X and its projection S_1 onto the reference plane S. (c) Top view on a hexagonal cluster of 13 colloids; the dashed line shows the boundary ∂S_1 of the single elementary cell S_1.

$$H=\frac{f}{S_1 p}=h_1\frac{2\pi\lambda^2}{S_1\ln(\lambda/R)}\sim h_1\left(\frac{\lambda}{L}\right)^2. \tag{5}$$

As usually $\lambda\sim 1$ mm whereas $L\sim$ several μm, this $H\gg h_1$. At the same time, the variation $\tilde{h}$ of the meniscus profile is expected not to depend explicitly on the overall height H of the cluster surface and hence $\tilde{h}\sim h_1$ (a detailed estimate of h_1 will be done in Sec. IV). Thus, $H\gg\tilde{h}$ in accord with the above assumption of an almost flat interface. As a result, the energy gain per colloid in the cluster $E_N/N\sim fH\sim U_2(\lambda/L)^2\gg U_2$, and the attractive force $\sim U_2(\lambda/L)^2/L$, which is at least a few orders of magnitude larger than the pair force $\sim U_2/L$.

The same conclusion can be achieved by considering conservation of the liquid's volume. The interface profile induced by a single colloid is known to be [2]

$$h(r)=\frac{h_1K_0(r/\lambda)}{K_0(R/\lambda)}, \tag{6}$$

where K_n is a modified Bessel function of the second kind of order n, and r is the distance from the colloid's center. The total volume of liquid over (or under if $f<0$) the remote flat meniscus of a single colloid is

$$V_1=2\pi\int_R^\infty hr\,dr=f\lambda^2/\gamma. \tag{7}$$

Then N colloids have the volume $Nf\lambda^2/\gamma$. If these colloids formed a cluster of the surface area NS_1 in which the surface height is H, then the volume of liquid is NHS_1. But the volume of liquid should not change during the clusterization process. Then, equating the volumes of liquid in the cluster and in the system of N well-separated colloids gives again the estimate (5).

Now it is in order to do some numerical estimates and comment on the result qualitatively obtained above. For typical value of the surface tension $\gamma\sim 10^{-2}$ J/m^2, the force f giving rise to $U_2\sim kT$ is of the order $f\lesssim 10^{-11}N$ while the height $h_1\sim 5$ nm; for $U_2\sim 10^{-3}kT$, $f\sim 10^{-12}N$ and $h_1\sim 0.5$ nm. In both cases, the derivative $|\nabla_n h(R)|=f/(2\pi\gamma R)$ of the height h in the direction normal to the colloid's surface is very small, $|\nabla_n h(R)|\lesssim 10^{-3}$. This justifies the use of the approximate expression $\gamma\nabla_n h(R)$ for the density of the surface-tension-induced vertical force on the contact line: this widely used expression is essential both for the derivation of Eq. (1) [1,2] and for our theory developed below.

Let us now estimate the smooth coarse-grained height H (5) and the many-body attraction energy E_N/N per colloid in a cluster of colloids separated by the distance L, say, $L\sim 10$ μm, and for the capillary length $\lambda=1$ mm. Equation (5) gives that if the force $f\sim 10^{-12}N$, then $H\sim 1$ μm and $E_N/N\sim 10^2kT$ as compared to the pairwise energy $U_2\sim 10^{-3}kT$; if $f\lesssim 10^{-11}N$, then $H\sim 10$ μm and $E_N/N\lesssim 10^5kT$ as compared to the pairwise energy $U_2\sim kT$. We see that our estimates show a strong colloidal attraction on a liquid surface, which is consistent with the experimental data and explained solely in terms of the standard capillary quantities as an essentially many-body effect. Now we will derive a more precise result from the equations of interface statics.

III. STATIC EQUILIBRIUM OF A LIQUID INTERFACE WITH A CLUSTER OF COLLOIDS: DETAILED DESCRIPTION

Consider a liquid-air interface with a cluster of N colloids and choose the reference plane S which coincides with the flat meniscus far from the cluster, Fig. 1(a). The height $h(\mathbf{x})$ is the vertical deviation of the liquid surface from S at $\mathbf{x}\in S$. The meniscus (part of the interface outside the colloids), its inner boundary with colloids (all the contact lines), and the remote outer boundary have the onto-S projections S_m, ∂S_m, and ∂S_{out}, respectively. The intrinsic contact line ∂S_m consists of the onto-S projections ∂S_c of the contact lines of individual colloids, $\partial S_m=\cup\,\partial S_c$ (for brevity we will call S_m just meniscus, and ∂S_m and ∂S_c just the total and individual contact line). The meniscus is subject to a pressure $P(\mathbf{x})$ of any origin except of the hydrostatic one, which is $\propto h$ and described separately. The vertical force f_c is transferred to the meniscus via the contact line. The total force Σf_c on the contact line is distributed over the total inner meniscus boundary ∂S_m with the line density $\tilde{f}_c$,

$$\int_{\partial S_m} dl\tilde{f}_c=\sum f_c, \tag{8}$$

where the summation is over all colloids in the cluster. The extrema of the energy functional must coincide with the correct equations describing the static equilibrium on the meniscus S_m and on its boundaries ∂S_m and ∂S_{out}. Under the standard assumption that the derivatives of h are very small, this energy functional has the form

$$E\{h\} = \frac{\gamma}{2}\int_{S_m} dS[(\nabla h)^2 + \lambda^{-2}h^2 - 2\gamma^{-1}Ph] - \int_{\partial S_m} dl \int_0^{h(l)} dh' \tilde{f}_c(h'), \tag{9}$$

where ∇ is the $2d$ gradient operator; h, P, and f are positive in the upward direction. The first term is the standard energy of the meniscus S_m plus its potential energy in the field of the pressure on the interface. The last term is the potential energy of the colloid calculated as the work done on it by the contact line. The work done by the element dl thereof when it is displaced by $dh(l)$ is equal to $-dl\tilde{f}_c(h)dh$; the total work to displace dl by $h(l)$ is obtained by the h integration from 0 to $h(l)$, where $h(l)$ is the interface height at point l of the contact line ∂S_m. The total work of the contact line is obtained by the l integration along the whole contact line ∂S_m. If the force f_c is homogeneously distributed along the contact line, then $\tilde{f}_c = f_c/2\pi R$, the height does not depend on the point l of the contact line, $h(l) = h =$const, and the last integral in Eq. (9) takes its simple familiar form

$$\int_{\partial S_m} dl \int_0^h dh(f_c/2\pi R) = 2\pi R(f_c/2\pi R)h = f_c h. \tag{10}$$

The Euler-Lagrange equation and boundary conditions for $E\{h\}$ read

$$\Delta h - \lambda^{-2}h + \gamma^{-1}P = 0, \quad \mathbf{x} \in S_m, \tag{11}$$

$$\gamma\nabla_n h = \tilde{f}_c(\mathbf{x}), \quad \mathbf{x} \in \partial S_m, \tag{12}$$

$$h = 0, \quad \mathbf{x} \in \partial S_{\text{out}}, \tag{13}$$

where $\nabla_n h$ is the derivative along the outer normal to the meniscus boundary (at ∂S_m it is directed inward to the colloids). Equations (11) and (12) are the correct equations of the force balance at each point of, respectively, the meniscus and the contact lines, which justifies the form of the functional $E\{h\}$ (9). The condition (13) implies that the interface is large so that far from the cluster its height remains unperturbed.

The functional (9) describes the interaction of any number of colloids of arbitrary shape. The colloids as the sources of the interface deformations enter the theory via the boundary conditions (12) on their contact lines. Under the standard assumption $|\nabla_n h| \ll 1$, implied in our consideration, the contact lines (meaning their projection onto S) do not depend on h and can be taken in their reference form obtained for $f_c = P = \lambda^{-2} = 0$, i.e., when the meniscus is flat and the only forces present are those of the surface tensions (of the three interfaces involved) [1,2]. Thus, each contact line ∂S_c has a shape that does not depend on h, remains always the same, but can change its position and orientation along with the colloid. In what follows, we assume for simplicity that all the contact lines are circumferences of the same radius R and therefore can only change positions X of their centers.

The equilibrium value E of $E\{h\}$ is obtained by multiplying Eq. (11) with h and integrating over S_m. After the by-part integration of the Δh term and use of the boundary conditions (12) and (13), one obtains

$$E = -\frac{1}{2}\int_{S_m} dSPh - \frac{1}{2}\int_{\partial S_m} dl \int_0^{h(l)} dh' \tilde{f}_c(h'). \tag{14}$$

So far we have considered the exact profile h. Now we will first show that h can be represented as the sum $h = \tilde{h} + H$, where $\tilde{h}$ is fast varying over the length scale $\sim L$ but is small, whereas H is a slow function, but much larger than $\tilde{h}$, Fig. 1; then make the correspondent simplifications, introduce potential of a repulsive force between colloids, and finally derive an equation for the slow envelope H. Note that, as shown below, Eq. (42), under condition (13) the total volume of liquid is automatically conserved if the derivative of h at the cluster boundary is continuous.

IV. FAST AND SLOW COMPONENTS OF *h*

The part S_N of the total interface area occupied by the cluster consists of the cells with the onto-S projections $S_1(X)$, one cell per colloid centered at X, Figs. 1(b) and 1(c). In general, these cells might be different, but close to equilibrium they have more or less similar dimensions $\sim L$ and the surface area $S_1 \approx S_N/N$ (we use the same notations for two-dimensional sets and their surface areas). Each cell S_1 is separated from other cells by a closed line ∂S_1 at which the normal derivative of h vanishes, $\nabla_n h = 0$. As said above, we assume that all the contact lines ∂S_c are circumferences of radius R. If, e.g., such colloids form a hexagonal lattice, Figs. 1(b) and 1(c), then each S_1 is the Wigner-Seitz cell and each line ∂S_1 is a regular hexagon, at which, due to the symmetry, $\nabla_n h = 0$.

We assume that the pressure P changes little over the cell size and the only source of the fast variation of h is the force on the contact lines with colloids. In the polar coordinates $\Delta X = (\Delta r, \phi)$ with the onset at X, Fig. 1(b), the solution of Eq. (11) for the single cell $S_1(X)$ is

$$h = aK_0(\Delta r/\lambda) + bI_0(\Delta r/\lambda) + \tilde{\tilde{h}}(\Delta r, \phi) + (\lambda^2/\gamma)P, \tag{15}$$

where K_0 and I_0 are modified Bessel functions. The function $\tilde{\tilde{h}}$ is periodic or close to periodic in ϕ. For instance, in the case of a hexagonal lattice, the symmetry dictates that

$$\tilde{\tilde{h}}_{\text{hex}} = \sum_{n=1}^{\infty} [c_n K_{6n}(\Delta r/\lambda) + d_n I_{6n}(\Delta r/\lambda)]\cos(6n\phi) \tag{16}$$

with certain coefficients c_n and d_n.

This h (15) is subject to the two boundary conditions: Eq. (12), at the contact line $\partial S_c(X)$, and $\nabla_n h = 0$, at the outer cell boundary $\partial S_1(X)$, which can be approximated by the circumference of radius $L/2$ and surface area $S_1 = \pi L^2/4$. Because of its quasiperiodicity in ϕ, $\tilde{\tilde{h}}$ does not contribute to the line integral over the contours $\partial S_c(X)$ and $\partial S_1(X)$, which can be used to find the constants a and b in Eq. (15). Using the small-x asymptotics $K_0(x)\approx -\ln x$, $I_0(x)\approx 1+x^2/4$ in the expression (15), and integrating Eq. (12) along the single contact line ∂S_c gives

$$2\pi\gamma[a-(R^2/2\lambda^2)b]=f_c. \tag{17}$$

Integrating $\nabla_n h=0$ along the outer boundary ∂S_1 gives another equation,

$$a-(L^2/8\lambda^2)b=0. \tag{18}$$

Solving the system (17) and (18) with respect to a and b, one gets $h=\tilde{h}+H$, where

$$\tilde{h}=\tilde{h}_0[\ln(\lambda/\Delta r)+8(\Delta r/L)^2+\tilde{\tilde{h}}(\Delta r,\phi)], \tag{19}$$

$$\tilde{h}_0=\frac{f_c}{\pi\gamma(1-4R^2/L^2)}, \tag{20}$$

and

$$H=\frac{f_c}{\pi\gamma}\frac{(4\lambda/L)^2}{(1-4R^2/L^2)}+P/p. \tag{21}$$

Now we see that H in Eq. (21) can be identified with H in Eqs. (5) and (3). Substituting f_c from Eqs. (3) and (21) and solving the thus obtained equation with respect to H gives

$$H=\frac{f}{\pi\gamma}(4\lambda/L)^2+\frac{P(1-4R^2/L^2)}{pg}. \tag{22}$$

In terms of the surface areas $S_1=\pi L^2/4$ and $S_c=\pi R^2$ and h_1 (2), the above formulas for the two amplitudes go over into

$$H=\frac{h_1}{\ln(\lambda/R)}\frac{2\pi\lambda^2}{S_1}+\frac{P(S_1-S_c)}{pS_1}, \tag{23}$$

$$\tilde{h}_0=H\bigg/\left(\frac{2\pi\lambda^2}{S_1}\right). \tag{24}$$

We see that H, which reproduces Eq. (5) for $P=0$, is much larger than $\tilde{h}_0$: $H\sim h_1(\lambda/L)^2$, whereas $\tilde{h}_0\sim h_1$. Note that the first term in $\tilde{h}$ (19) goes over into h_1 when $\Delta r=R$ and $S_1\to 2\pi\lambda^2$, as it should be.

The solution (19)–(21) has a clear meaning. Neglecting $\nabla_n H$ as compared to $\nabla_n\tilde{h}$ and using $\nabla_n h(\partial S_1)=0$, the fast component $\tilde{h}$ can be estimated from Eq. (12): $\tilde{h}\sim(f/\pi L)(L/2\gamma)=(f/2\pi\gamma)\sim h_1$. Via the contact line, the force f is transferred to the meniscus in the form of Laplace's pressure, which, in the cell of a small radius $L/2$, is large,

$$\gamma\Delta\tilde{h}\sim\gamma[\nabla_n\tilde{h}(R)-\nabla_n\tilde{h}(L/2)]/(L/2)\sim f/[2\pi(L/2)^2]$$

[the first term in Eq. (11)], and must be balanced by the hydrostatic pressure $-pH+P=(-\lambda^{-2}H+P/\gamma)\gamma$ with large H [second and third terms in Eq. (11)].

The amplitude of $\tilde{\tilde{h}}$, Eq. (15), which is periodic in the azimuthal variable ϕ and which disappeared from the averaged boundary conditions (17) and (18), can be estimated from the requirement that $\tilde{\tilde{h}}$ compensates deviation of the actual contour ∂S_1 from the circumference as to assure the condition $\nabla_n\tilde{h}=0$ at each point thereof. For the hexagonal lattice, $\tilde{\tilde{h}}\approx[1-(\sqrt{3}/2)^2]\simeq 0.25$, and one concludes that $\tilde{h}\sim\tilde{h}_0\ll H$. Thus, as expected, $\tilde{h}$ is fast changing but small, whereas H is slow but large, Figs. 1(a) and 1(b).

V. COARSE-GRAINED DESCRIPTION OF COLLOIDAL CLUSTERS: EQUATION FOR THE SLOW ENVELOPE $H(X)$

The equation for the slow envelope H is derived by averaging the exact Euler-Lagrange equation (11) over the meniscus $S_{1,m}=S_1\backslash S_c$ of the individual cell at X which has the surface area $S_{1,m}(X)=S_1(X)-S_c$, where $S_c=\pi R^2$. Substituting $h=\tilde{h}+H$ in Eq. (11) and integrating over $S_{1,m}$ in the context of the inequality $\tilde{h}\ll H$ gives

$$0=\int_{S_{1,m}}dS\Delta\tilde{h}(X,\Delta r,\phi)+\Delta H(X)S_{1,m}(X)+[-\lambda^{-2}H(X)+\gamma^{-1}P(X)]S_1(X). \tag{25}$$

The boundary conditions at ∂S_c, ∂S_1, and ∂S_{out} now have, respectively, the following form:

$$\gamma\nabla_n(\tilde{h}+H)=\tilde{f}_c(\mathbf{x}),\quad \mathbf{x}\in\partial S_c, \tag{26}$$

$$\nabla_n\tilde{h}=0,\quad \mathbf{x}\in\partial S_1, \tag{27}$$

$$H=0,\quad \mathbf{x}\in\partial S_{\text{out}}. \tag{28}$$

The first term in Eq. (25) can be transformed to the line integral, using Gauss's theorem, and then expressed via the force $f_c(X)$ from Eq. (26),

$$\int_{S_{1,m}}dS\Delta\tilde{h}=\int_{\partial S_c}dl\nabla_n\tilde{h}=f_c/\gamma-\int_{\partial S_c}dl\nabla_n H=f_c/\gamma+\int_{S_c}dS\Delta H=f_c/\gamma+S_c\Delta H. \tag{29}$$

Introducing the colloid surface density $\rho=1/S_1$ and combining Eq. (25) with Eqs. (29) and (3) gives the following equation for the slow envelope height $H(X)$:

$$\Delta H-\lambda^{-2}H+\gamma^{-1}(P+\rho f)=0. \tag{30}$$

Equation (30) determines $H(X)$ as a function of the coarse-grained coordinate X provided the effective pressure $P+\rho f$ is known. The force-induced effective pressure in the form $\rho f=f/S_1$ is in line with our qualitative consideration in Sec. II. To determine the density ρ, we need to introduce the repulsive force between colloids.

To specify the repulsive force f_{rep}, we introduce a repulsive potential U that describes the repulsive energy of a single colloid separated from colloids in the neighboring cells by the distance L. We will restrict our consideration to power-law forces,

$$f_{\text{rep}} = \frac{u}{L^n}, \tag{31}$$

where u and n are positive constants. It is easy to see that both f_{rep} and U can be considered as functions of density ρ since the distance L and the colloid density are related: $1/\rho = S_1 = \pi_c L^2/4$, where π_c is the geometrical constant of the single cell (for a hexagonal lattice $\pi_c = 2\sqrt{3}$). Then $L = (\pi_c \rho/4)^{-1/2}$ and the repulsive force (31) becomes

$$f_{\text{rep}}(\rho) = u(\pi_c \rho/4)^{n/2}. \tag{32}$$

The potential $U(\rho)$ should be introduced as to give the correct repulsive force. To introduce the potential U, one needs the energy functional. Equation (30) for the envelope H (i.e., the equation of the vertical balance) and the equation of the force balance in the horizontal direction along the meniscus can be derived from the energy functional

$$\bar{E}\{H,\rho\} = \frac{\gamma}{2}\int_S d^2X[(\nabla H)^2 + \lambda^{-2}H^2 - 2\gamma^{-1}(P+\rho f)H + 2\gamma^{-1}\rho U(\rho)] \tag{33}$$

and the single boundary condition that $H \to 0$ far from the cluster. Indeed, the equation $\delta \bar{E}\{H,\rho\}/\delta H = 0$ coincides with Eq. (30). The ρ equation, $\delta \bar{E}\{H,S_1\}/\delta \rho = 0$, reads

$$-fH + \frac{\partial \rho U}{\partial \rho} = 0. \tag{34}$$

The force density, by definition, is minus variation of the energy functional with respect to the interparticle distance L, i.e., $-\delta \bar{E}\{H,\rho\}/\delta L = -(\delta \bar{E}\{H,\rho\}/\delta \rho)(\partial \rho/\partial L)$, and the force per colloids is obtained by dividing this by the density ρ. Therefore, multiplying Eq. (34) by $-(\partial \rho/\partial L)/\rho = -1/L$, we get exactly the force balance $f_{\text{attr}} + f_{\text{rep}} = 0$, where

$$f_{\text{attr}}(X) = -\frac{fH}{L} \tag{35}$$

is the attractive force, and

$$f_{\text{rep}}(\rho) = 2\rho^{1/2}(\pi_c/4)^{1/2}\frac{\partial \rho U}{\partial \rho} \tag{36}$$

is the repulsion force. Equating Eqs. (32) and (36) yields the desired expression for the repulsive potential as a function of ρ,

$$U(\rho) = \frac{u}{n+1}(\pi_c \rho/4)^{(n-1)/2}. \tag{37}$$

Now Eq. (34) of force balance can be solved to find ρ as a function of another variable H. To this end, expression (37) is substituted into Eq. (34), whence

$$\rho = \frac{4}{\pi_c}\left(\frac{2f}{u}H\right)^{2/(n-1)}. \tag{38}$$

Making use of this formula in the H Eq. (30), one finally obtains a closed equation describing the slow envelope H, when the repulsive force dies out as a power law (31). This equation has the following form:

$$\Delta H - \lambda^{-2}H + c_n H^{2/(n-1)} + \gamma^{-1}P = 0, \tag{39}$$

where

$$c_n = \frac{4f}{\pi_c \gamma}\left(\frac{2f}{u}\right)^{2/(n-1)}. \tag{40}$$

On finding $H(X)$ from this equation, $\rho(X)$ is obtained from formula (38); then the equilibrium distance between colloids is $L(X) = (\pi_c \rho/4)^{-1/2}$ and the attractive force between colloids at X can be found from the general formula (35). We postpone discussion of Eq. (39) for different repulsion indices n until the next section.

The equilibrium value of $\bar{E}$ derives from Eqs. (33) and (30) the same way the exact energy (9) was derived above and has the form

$$\bar{E} = \frac{1}{2}\int_S d^2X[pH^2/2 - (\rho f + P)H + 2\rho U]. \tag{41}$$

Except for the repulsion term, this $\bar{E}$ can also be obtained directly from the exact equilibrium energy E (14).

To complete this section, we show that no additional care has to be taken to assure conservation of the total volume of liquid under the condition (28). The total volume V of liquid is conserved identically provided the normal derivative $\nabla_n H$ is continuous at the cluster boundary and H vanishes at the outer boundary ∂S_{out} of the meniscus. Indeed, calculating this volume with H expressed from the equilibrium equation (30), one has

$$\begin{aligned} V &= \int_S d^2X H = \lambda^2 \int_S d^2X[\Delta H + (P+\rho f)/\gamma] \\ &= \lambda^2 \int_{\partial S_{\text{out}}} dl \nabla_n H + \frac{1}{p}\int_S d^2X P + (f\lambda^2/\gamma)N \\ &= \frac{1}{p}\int_S d^2X P + NV_1, \end{aligned} \tag{42}$$

where V_1 is the volume (7) over (under) the meniscus of a single remote colloid and

$$N = \int_S d^2X \rho(X) \tag{43}$$

is the total number of colloids in the cluster. Thus, if the total surface S is very large (formally, unrestricted), V is the same before and after the cluster has been created.

VI. PROFILE OF THE MANY-BODY CLUSTER WITH HARD-CORE REPULSION AND COLLECTIVE COLLOIDAL ATTRACTION

Let us briefly discuss the form of the H equation (39) for some repulsion indices n. The repulsive force scales as L^{-4} in two important cases of charged colloidal clusters: on a polar liquid, when there is the dipole-dipole repulsion [3,6], and on a nonpolar liquid when there is a direct repulsion between the net charges of colloids' tops above the liquid surface [7].

The L^{-4} repulsion was also assumed in clusters on a nematic surface [14–16,24] and experimentally confirmed by measuring repulsion of two colloids [24]. In this case, the repulsion is due to the interaction of elastic dipoles via the nematic director field [22,23]. For $n=4$, $c_n H^{2/(n-1)} = c_n H^{2/3}$, the H equation is nonlinear and its solution is not easy to find if the cluster is circular. Another important case is that of $n=6$, which can be realized in a cluster of elastic quadrupoles [22,23] trapped at a nematic surface [20], and in a cluster of charged colloids on a polar interface [13]. Then the H equation contains nonlinearity $H^{1/2}$. In both cases, finding an azimuthally symmetric solution to the H equation would most likely involve a numerical approach. To illustrate the general theory here, we prefer to avoid such complication and consider an easily solved system to demonstrate the general many-body effect. There is an important and, at the same time, simple example of a hard-core repulsion. In this case, the attraction force (35) compresses the cluster until the colloids touch each other and thus a densely packed cluster is formed. The repulsive interaction in this case has the form

$$U_{\mathrm{hc}} = \begin{cases} \infty, & L \leqslant D, \\ 0, & L > D, \end{cases} \tag{44}$$

where D is a constant equal to the colloid's diameter. Consider a large cluster of N colloids with radius $R_N \gg \lambda$ and set $P=0$. Then the equilibrium density is

$$\rho = \begin{cases} 4/(\pi_c D^2), & r \leqslant R_N, \\ 0, & r > R_N, \end{cases} \tag{45}$$

where r is the distance from the cluster's center. The H equation (30) with this ρ has the solution

$$H(r) = \begin{cases} \dfrac{4f}{p\pi_c D^2} - A I_0(r/\lambda), & r \leqslant R_N, \\ H_b K_0(r/\lambda)/K_0(R_N/\lambda), & r > R_N, \end{cases} \tag{46}$$

where A is a constant to be found. The function $H(r)$ and its r derivative at the cluster boundary must be continuous. The first condition, $H_b = H(R_N)$, reads

$$H_b = \frac{4f}{p\pi_c D^2} - A I_0(R_N/\lambda). \tag{47}$$

The second condition is obtained by differentiating $H(r)$ at $r=R_N$ and equating the derivatives at both sides, which gives

$$A I_1(R_N/\lambda) = \frac{H_b K_1(R_N/\lambda)}{\lambda K_0(R_N/\lambda)}. \tag{48}$$

To find the solution of the system (47) and (48), we use the identity $I_0(x)K_1(x) + I_1(x)K_0(x) = 1/x$ and the large argument asymptotics of the modified Bessel functions ($R_N/\lambda \gg 1$): $K_0(x) \simeq K_1(x) \simeq \sqrt{\pi/2x}\exp(-x)$, $I_0 \simeq \sqrt{1/2\pi x}\exp(x)$. As a result, the entire envelope profile can be put into the following final form:

$$H(r) = \frac{4f}{p\pi_c D^2} \begin{cases} 1 - \sqrt{\dfrac{\pi R_N}{2\lambda}} e^{-R_N/\lambda} I_0(r/\lambda), & r \leqslant R_N, \\ \dfrac{1}{2}\sqrt{R_N/r}\, e^{-(r-R_N)/\lambda}, & r > R_N. \end{cases} \tag{49}$$

Thus, within the area covered with colloids, the envelope height is decreasing from $H_0 \simeq 4f/(p\pi_c D^2)$ at the cluster center to $H_b = H_0/2$ at the cluster boundary, and outside the cluster it decreases $\propto r^{-1/2}\exp[-(r-R_N)/\lambda]$, Fig. 1(a). Then formula (35) tells us that the magnitude of the attractive force on colloids in the cluster ranges from $fH_0/2D$ to fH_0/D, i.e.,

$$|f_{\mathrm{attr}}(R_N)| = \frac{2f^2}{p\pi_c D^3} \leqslant |f_{\mathrm{attr}}(X)| \leqslant \frac{4f^2}{p\pi_c D^3} = |f_{\mathrm{attr}}(0)|. \tag{50}$$

The total energy $\bar{E}$ of the interface with the cluster is obtained by calculating the integral (41) with the profile $H(r)$ (49) and employing that $R_N/\lambda \gg 1$. The result is

$$\bar{E} \simeq -\frac{4\pi f^2 R_N^2}{p(\pi_c D^2)^2}\left(1 - \frac{\lambda}{2R_N}\right). \tag{51}$$

As the total number of particles N in the cluster is

$$N = \frac{4\pi R_N^2}{\pi_c D^2}, \tag{52}$$

the total energy of the large cluster can also be expressed as

$$\bar{E} \simeq -\frac{f^2 N}{p\pi_c D^2}. \tag{53}$$

The results obtained for the large cluster with the hard-core colloid repulsion represent a general situation if our particular colloids' separation D is replaced by an arbitrary separation L. The maximum envelope height H_0, the energy per colloid, $\bar{E}/N$, and the maximum attractive force between colloids, $f_{\mathrm{attr}}(0)$, can be cast into the form

$$H_0 = \frac{\eta}{\ln(\lambda/R)} h_1, \tag{54}$$

$$\bar{E}/N = -\eta \frac{f^2}{8\pi\gamma}, \tag{55}$$

$$f_{\mathrm{attr}}(0) = -\eta \frac{f^2}{2\pi\gamma L} = -\frac{4f^2}{\pi_c p L^3}, \tag{56}$$

where $\eta(L)$ is the enhancement factor,

$$\eta(L) = \frac{2\pi\lambda^2}{S_1(L)} = \frac{2\pi\lambda^2}{\pi_c (L/2)^2}. \tag{57}$$

It shows the many-body enhancement of the pair stabilizing effect in the cluster. The factor η is of the order $[\mathrm{mm}/(\text{a few }\mu\mathrm{m})]^2$, which gives $\eta \sim 10^4 - 10^5$ or even larger. Thus, $H_0 \gg h_1$ and H_0 coincides with Eq. (5). The attraction energy per colloid $\bar{E}/N$ in the cluster, where colloids are separated by $L \ll \lambda$, is much larger in the magnitude than the energy (1) of the pair attraction $U_2(L)$. The attractive force $f_{\rm attr}$ between colloids in a cluster behaves as L^{-3} and is much stronger than the pair force $f^2/2\pi\gamma L$. Formulas (54)–(57) confirm the results of our qualitative consideration in Sec. II: according to the estimates made there, for $f \sim 10^{-12} N$, when the pair attraction energy would be just $U_2 \sim 10^{-3} kT$, the many-body effect lifts the interface by about 1 μm and induces the attraction of the order $\bar{E}/N \propto 10^2 kT$. Thus, the mystery of the strong attraction in large clusters on a liquid surface is resolved.

VII. DISCUSSION AND CONCLUSION

The result of this paper is that the many-body effect can enhance stabilization of colloidal clusters by the factor $\eta \sim 10^4 - 10^5$, and the attraction force scales as L^{-3}. This can explain the stability and the very existence of two-dimensional colloidal structures observed in experiments. The profile of a large cluster consists of a smooth and large envelope H that is modulated by a fast low-amplitude component $\tilde{h}$. The slow envelope $H \sim \eta h_1$ and can be of order of a micrometer. The fast component $\tilde{h} \sim h_1$, where h_1 is the usual meniscus height induced by a single remote colloid, which is usually less than a nanometer. The role of the fast variation $\tilde{h}$ is the same for a single remote colloid and for a cluster, i.e., to convert the force on colloids into a pressure on the interface. The slow H is the collective, many-body effect reflecting the averaged pressure balance, which cannot be obtained from a pairwise approximation, whereas the fast modulation $\tilde{h}$ is the perturbation of this curved "vacuum" profile by a single colloid. The envelope H is responsible for the strong attraction and can be found from Eq. (39), which incorporates a repulsive force scaling as arbitrary power law with the exponent n. In conclusion, I will briefly discuss the experimental data on cluster formation on a nematic liquid crystal, Refs. [14–16], and on an isotropic liquid, Refs. [4–6].

The experimental data, which most explicitly point to some mysteriously strong attraction in large clusters of colloids on a liquid surface, were obtained on a nematic-liquid-crystal–air interface by Nazarenko and co-workers [14–16]. The colloids form hexagonal and quasihexagonal lattices with different periods L that can coexist [15,16] and be transformed into each other under certain conditions [16]. The lattice shape, including anisotropy of the quasihexagonal lattice, the transition between the hexagonal, and quasihexagonal lattices, and the origin of the repulsion between the colloids can be well described under the assumption that the lattices are stabilized by the capillary attraction induced by a vertical force on the colloids [16]. This force is definitely due to the elasticity of the nematic liquid as the stabilization holds only while the liquid is in its nematic phase and disappears in the isotropic phase. Analysis of Ref. [20] shows, however, that the repulsion energy in these lattices is at least four orders of magnitude larger than the pair attraction energy (1) induced by the upthrust due to the nematic elasticity. As the lattice period $L \sim 10$ μm, the many-body enhancement (57) is about $\eta \sim 10^4$ or larger, which explains the stabilization of lattice structures on a nematic-liquid-crystal–air interface. In addition, the many-body theory predicts that, because of the different periods, the mean height H in the hexagonal and quasihexagonal lattices is also different, which, in principle, can be detected experimentally.

Onoda [4] has observed a cluster formation of 2-μm colloids on water under the condition that the repulsion energy and the chaotic thermal energy were close in their magnitudes. Under this condition, the size of a cluster was the most sensitive parameter of the clusterization process. Once clusters, which had the hexagonal dense packing intrinsic structure, contained around 14 particles, a permanent order was observed, whereas smaller clusters could lose colloids and diminish. Onoda called this clusterization reversible. He attributed the attraction to the van der Waals force as the energy of the capillary attraction estimated by Eq. (1) was three orders of magnitude smaller than kT. However, the well-pronounced dependence of the cluster stability on its size has certainly a collective nature and indicates that it is a long-range force that is responsible for the effect. Although our results were obtained for large clusters, the general trend is expected to be similar for smaller clusters, too. Then Eq. (57) clearly shows that the capillary attraction can indeed give the stabilizing energy $\sim$several kT. Small clusters with $L \ll R_N \ll \lambda$ deserve individual consideration and will be addressed elsewhere.

Spreading small charged bids on a liquid surface, Ruiz-García, Gámez-Gorrales, and Ivlev [5] and then Stamou, Duschl, and Johannsmann [6] have observed a variety of clusters and, in particular, two-dimensional circular clusters. The capillary attraction was found to lack at least five orders of magnitude to compensate for the electrostatic repulsion of the charged bids. The idea of Ref. [6] is that, because of uncontrolled surface patterns, there is variation of h along the colloid-liquid contact line, which has two very different scales: the amplitude $\sim$50 nm and the wavelength $\sim$half of the length of the contact line $\sim\mu$m. This results in the quadrupolar attractive potential $\propto L^{-4}$. The main problem of this approach is that, since the repulsion potential scales as L^{-3}, for small L the attraction is stronger than the repulsion and thus the colloids' surfaces have to be in contact with each other [the stabilizing repulsion is of the form (44)], whereas the experiment shows the stabilization for distances L considerably larger than the colloid diameter. In other words, the attractive potential should decrease slower than L^{-3}. In any case, this mechanism should be complimented by the collective capillary attraction, which can be four or five orders of magnitude higher than the estimate based on the pair potential (1). Moreover, the collective attraction with the energy scaling as L^{-2} can play the role of the slowly decreasing attractive potential, mentioned above, and eliminate the main difficulty, i.e., explaining the large equilibrium separation of colloids.

To conclude, the collective effect predicted here has a well-known manifestation: under the force of gravity, droplets of rain on a tent surface tend to coalesce into a single heavy droplet, which then inflects the tent and can cause leakage. Campers know that this effect can be quite strong.

[1] M. M. Nicolson, Proc. Cambridge Philos. Soc. **45**, 288 (1949).
[2] D. Y. C. Chan, J. D. Henry, and L. R. White, J. Colloid Interface Sci. **79**, 410 (1981).
[3] P. Pieranski, Phys. Rev. Lett. **45**, 569 (1980).
[4] G. Y. Onoda, Phys. Rev. Lett. **55**, 226 (1985).
[5] J. Ruiz-García, R. Gámez-Corrales, and B. I. Ivlev, Phys. Rev. E **58**, 660 (1998).
[6] D. Stamou, C. Duschl, and D. Johannsmann, Phys. Rev. E **62**, 5263 (2000).
[7] R. Aveyard, B. P. Binks, J. H. Clint, P. D. I. Fletcher, T. S. Horozov, B. Neumann, V. N. Paunov, J. Annesley, S. W. Botchway, D. Nees, A. W. Parker, A. D. Ward, and A. N. Burgess, Phys. Rev. Lett. **88**, 246102 (2002).
[8] M. G. Nikolaides, A. R. Bausch, M. F. Hsu, A. D. Dinsmore, M. P. Brenner, C. Gay, and D. A. Weitz, Nature **420**, 299 (2004).
[9] E. C. Mbamala and H. H. von Grünberg, Phys. Rev. E **67**, 031608 (2003).
[10] A. I. Campbell, V. J. Anderson, J. S. van Duijneveldt, and P. Bartlett, Phys. Rev. Lett. **94**, 208301 (2005).
[11] F. Ghezzi and J. C. Earnshaw, J. Phys.: Condens. Matter **9**, L517 (1997).
[12] M. Quesada-Pérez, A. Monch-Jordá, F. Martinez-López, and R. Hidalgo-Alvarez, J. Chem. Phys. **115**, 10897 (2001).
[13] L. Foret and A. Würger, Phys. Rev. Lett. **92**, 058302 (2004).
[14] V. G. Nazarenko, A. B. Nych, and B. I. Lev, Phys. Rev. Lett. **87**, 075504 (2001).
[15] I. I. Smalyukh, S. Chernyshuk, B. I. Lev, A. B. Nych, U. Ognysta, V. G. Nazarenko, and O. D. Lavrentovich, Phys. Rev. Lett. **93**, 117801 (2004).
[16] A. B. Nych, U. M. Ognysta, V. M. Pergamenshchik, B. I. Lev, V. G. Nazarenko, I. Muševic, M. Škarabot, and O. D. Lavrentovich, Phys. Rev. Lett. **98**, 057801 (2007).
[17] J.-B. Fournier and P. Galatola, Phys. Rev. E **65**, 031601 (2002).
[18] P. A. Kralchevsky and K. Nagayama, Adv. Colloid Interface Sci. **85**, 145 (2000).
[19] M. Oettel and S. Dietrich, Langmuir **24**, 1425 (2008).
[20] M. Oettel, A. Domínguez, M. Tasinkevych, and S. Dietrich, Eur. Phys. J. E **28**, 99 (2009).
[21] This shows that naming the attraction "capillary" might be misleading as the capillary force itself is repulsive.
[22] T. C. Lubensky, D. Pettey, N. Currier, and H. Stark, Phys. Rev. E **57**, 610 (1998).
[23] V. M. Pergamenshchik and V. O. Uzunova, Phys. Rev. E **76**, 011707 (2007); Eur. Phys. J. E **23**, 161 (2007).
[24] U. M. Ognista, A. B. Nych, V. G. Nazarenko and B. I. Lev, Ukr. J. Phys. **52**, 633 (2007).