Fluctuation interactions of colloidal particles

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For like charged colloidal particles two mechanisms of attraction between them survive when the interparticle distance is larger than the Debye screening length. One of them is the conventional van der Waals attraction and the second one is the attraction mechanism mediated by thermal fluctuations of particle position. The latter is related to an effective variable mass (Euler mass) of the particles produced by a fluid motion involved. The most stronger attraction potential (up to the value of temperature $T$) corresponds to a situation of uncharged particles and a relatively large Debye screening length. In this case the third mechanism of attraction enters the game. It is mediated by thermal fluctuations of fluid density.

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I. THE SHORT STORY

Systems of charged colloidal particles exhibit a variety of unusual physical properties\cite{1,2,3}. Colloidal particles can be arranged into crystal\cite{4} and into structures with clusters and voids\cite{5,6,7}. Colloidal systems may undergo different types of phases transition\cite{8,9,10,11,12,13}. Topological phase transitions in two-dimensional system of colloidal particles have been discussed in\cite{14,15}. Unusual ensembles of colloidal particles were observed in Refs.\cite{16,17,18}. In\cite{19} buckling instabilities in confined colloidal crystal were analyzed. Interesting behaviors of colloidal in external fields were reported in\cite{20}. Colloidal particles accept in an electrolyte some surface charge, screened by counterions at Debye’s length $\lambda_D$, which results in the repulsion potential of Derjaguin, Landau, Verwey, and Overbeek (DLVO)\cite{1,2}. The DLVO theory, as a result of solution of linearized Poisson-Boltzmann equation, has been questioned in\cite{21,22}. The generalization of DLVO interaction via a modification of counterion screening was reported in\cite{23}.

The long range attraction of like charged particles is a matter of challenge and controversy in colloidal science. Very schematically, the story of the long range attraction is the following.

Initially, the long range attraction of colloidal particles on the micron scale has been reported in Ref.\cite{23}. The authors reconstructed a pair potential from measured correlation functions of a large ensemble of colloidal particles.

The authors of Refs.\cite{25,26,27} published even more surprising results when the attraction was extended over a distance of almost 4 $\mu$m. They used a laser technique releasing two particles and observing their behavior. It happened that their measurements were misinterpreted. It was observed just a macroscopic hydromechanical effect associated with specificity of measurements but not a microscopic mechanism of attraction\cite{28}.

Bechinger and his group shown for a high concentrated particle ensemble that different types of interparticle potential result in almost identical correlation functions\cite{29,30}. The conclusion was that an interaction potential should be drawn from experiments with a pair of colloidal particles but not from a large ensemble of them. Another difficulty is connected to an uncertainty in observed particle position caused by diffraction which can result in errors in calculated pair potential. See Ref.\cite{31} and references therein. To reduce the diffraction uncertainty one should use ultraviolet observations. So reliability of calculation of pair potential on the basis of statistical properties of large ensembles of particles is questionable.

Despite a lack of reliability of various experiments on determination of a microscopic mechanism of attraction of like charges it is always intriguing whether they attract or not in reality. We consider the following microscopic mechanism of attraction of two colloidal particles or a particle and a wall.

1. The conventional van der Waals attraction $u_{vdW}^{com}$ mediated by electromagnetic fluctuations.

2. The attraction $U_{com}$, mediated by thermal compression fluctuations of a fluid.

3. The attraction $J$ associated with thermal fluctuations of particle positions in a fluid. It results from variable particle masses (Euler masses) depending on a distance between them. This mechanism and the term “Euler mass” was proposed in Ref.\cite{32}.

In the first mechanism an energy of fluctuating electromagnetic waves depends on a distance between particles and, therefore, it leads to a force.

The second mechanism is generic with the first one since electromagnetic waves are just substituted by hydrodynamic ones.

In the third mechanism moving particles drag a part of a fluid. A mass of the involved fluid depends on a distance between the particles. There is a thermal drift of
the particles into the region with a larger effective mass which is analogous to classical mechanics. This can be interpreted as an effective interaction mediated by thermal fluctuations of particle positions in a fluid. In formation of the variable mass high frequency fluctuations of the particles are involved when dissipative hydrodynamic effects are not important [34]. This corresponds to Euler hydrodynamics and gives rise to the term “Euler mass”. The formation of Euler mass reminds the equipartition of the particles material \( \omega \) frequency of the fluctuating electromagnetic field since it should be much larger than the interparticle distance. A relaxation mechanisms. The first and the third ones survive when an interparticle distance becomes larger than the Debye screening length. On this distance the DL VO repulsion is very small and the above two mechanisms are the only interaction. The second mechanism works when Coulomb effects in the fluid are not pronounced. Namely, the particles are not charged and the Debye screening length is larger than the interparticle distance. A relative role of attraction \( I \) and \( u_{vdW} \) was also analyzed in Ref. [35].

A goal of this paper is to study the three above attraction potentials for two particles and for one near a wall (walls).

II. VAN DER WAALS INTERACTION

The energy of fluctuating electromagnetic field around two particles depends on a distance \( R \) between them and, therefore, results in an interaction force. It is called van der Waals force [32]. This force is mainly determined by a typical wave length \( \lambda \) of the fluctuating electromagnetic field since it should be \( \lambda \sim R \). The permittivity of the particles material \( \varepsilon(\omega) \) depends on the typically frequency \( \omega \sim c/R \). We consider relatively large interparticle distance

\[
\frac{\varepsilon}{\omega_0} < R, \quad (1)
\]

where \( \omega_0 \) corresponds to an absorption peak of \( \varepsilon(\omega) \). For example, for water \( \omega_0 \sim 10^{16} \text{ sec}^{-1} \). The estimate reads 100 \( \AA \) \( < R \).

At a finite temperature the typical wave length of the fluctuating electromagnetic field is \( hc/T \). Below the interparticle distance is not too large

\[
R < \frac{hc}{T}, \quad (2)
\]

which is equivalent to \( R < 7.4 \mu m \) at room temperature.

We consider a typical interparticle distance \( R \) of the order of one or two microns which relates to the conditions (1) and (2). In the optical interval of \( \omega \) the permittivity is determined by a refractive index and can be substituted by a dielectric constant \( \varepsilon \) for particles and a dielectric constant \( \varepsilon_0 \) for a surrounded medium. When the two dielectric constants are close to each other

\[
\frac{\varepsilon - \varepsilon_0}{\varepsilon_0} << 1 \quad (3)
\]

one can use the approach of pairwise summation to calculate the energy of electromagnetic fluctuations (the van der Waals interaction energy) [32, 36]

\[
u_{vdW}(R) = -\frac{23hc(\varepsilon - \varepsilon_0)^2}{1920\pi \varepsilon_0^{5/2} R} \left[ \frac{2a^2(20a^2 - 3R^2)}{(R^2 - 4a^2)^2} \right] + \frac{2a^2}{R^2} + \frac{\ln\left(\frac{R^2}{R^2 - 4a^2}\right)}{R^2 - 4a^2} \quad (4)
\]

In Eq. (4) the integrations occur inside the volumes of two bodies. For two identical spherical particles of the radius \( a \) and center-to-center distance \( R \) the integration in Eq. (4) results in [32, 36]

\[
u_{vdW}(h) = -\frac{23h}{6400 \varepsilon_0^{5/2} a} \left[ \frac{(\varepsilon - \varepsilon_0)^2}{\varepsilon_0^{5/2}} \right] \int_{-1}^{1} \left( 1 - z^2 \right) dz \quad (5)
\]

For a spherical particle near a flat infinite wall (the both with the dielectric constant \( \varepsilon \) ) Eq. (5) yields

\[
u_{vdW}(h) = -\frac{23}{640(\varepsilon - \varepsilon_0)^2} \frac{hc}{a} \int_{-1}^{1} \left( z + \frac{h}{a} \right)^2 dz \quad (6)
\]

In Eq. (6) \( h \) is the center-to-wall distance.

In the region of visible light for water \( \varepsilon_0 \sim 1.77 \) and for usually used polystyrene colloidal particles \( \varepsilon \sim 2.40 \). So the parameter \( (\varepsilon - \varepsilon_0)/\varepsilon_0 \simeq 0.35 \) can be considered as relatively small and, therefore, the equations (4) and (6) are reasonable approximations for van der Waals interaction.

III. INTERACTION MEDIATED BY COMPRESSION FLUCTUATIONS OF THE FLUID

Suppose two particles to be totally fixed inside a hydrodynamic medium and they serve only as obstacles for a fluid motion. There is no macroscopic motion in the system and the only motion is caused by thermal fluctuations of the fluid velocity \( \mathbf{\bar{v}}(r,t) \). In this case the free energy of thermal fluctuations of the fluid \( F(R) \) depends on the distance \( R \) between the particles. The function

\[
U_{com}(R) = F(R) - F(\infty) \quad (7)
\]

is an interaction mediated by compression fluctuations of the fluid analogously to the conventional van der Waals interaction mediated by electromagnetic fluctuations. To find the free energy of thermal fluctuations of the fluid one can start with the linearized Navier-Stokes equation

\[
\rho \frac{\partial \mathbf{\bar{v}}}{\partial t} = -\nabla p + \eta \nabla^2 \mathbf{\bar{v}} + \left( \zeta + \frac{\eta}{3} \right) \nabla \text{div} \mathbf{\bar{v}}. \quad (8)
\]
There are two types of fluid motion, one of them is a transverse sound diffusion and the second one is longitudinal sound waves associated with the density variation. The equilibrium free energy of transverse motions is determined by the Boltzmann distribution of their kinetic energies and does not depend on the friction coefficient in the thermal limit. The free energy of transverse motions in the thermal limit depends on the total volume, but not on relative positions of bodies. Therefore, transverse fluctuations do not result in an interaction.

Quite opposite situation occurs for longitudinal motions, when the total free energy is a sum of energies of different sound waves. The spectrum of sound waves depends on the distance between bodies $R$ due to hydrodynamic boundary conditions on body surfaces and this results in $R$-dependence of the free energy. Hence, the fluctuation interaction between bodies is mediated by hydrodynamic sound waves like the conventional van der Waals interaction is mediated by fluctuations of electromagnetic ones. Putting $\vec{v} = \nabla \phi / \partial t$, one can obtain from Eq. (8)

$$\rho \frac{\partial^2 \phi}{\partial t^2} = -\delta p + \left( \zeta + \frac{4n}{3} \right) \frac{\partial}{\partial t} \nabla^2 \phi. \tag{9}$$

Through thermodynamic relations and the continuity equation one can obtain $\delta p = -s^2 \nabla^2 \phi$, where $s$ is the adiabatic sound velocity \[34\]. At the typical frequency $\omega \sim s/\lambda \sim 10^{11} \text{ s}^{-1}$ ($a \sim 1 \text{ \mu m}$ is a particle radius), involved into the problem, the dissipative term in Eq. (9) is small and one can write

$$\frac{\partial^2 \phi}{\partial t^2} = \frac{s^2}{\lambda_D} \nabla^2 \phi = 0. \tag{10}$$

According to the limit of a small friction, the boundary condition for the normal derivative $\nabla_n \phi = 0$ to Eq. (10) corresponds to the Euler fluid \[34\]. From general point of view, the free energy of a system of harmonic oscillators does not depend on friction in the thermal limit.

In an electrolyte the dispersion law of sound waves can be approximated as

$$\omega^2(q) = s^2(q^2 + \frac{s^2}{\lambda_D^2}), \tag{11}$$

where $\lambda_D$ is the Debye screening length. Let us consider first the case of two infinite parallel walls separated by the distance $R$. The free energy per unit area of the system is expressed as a sum of energies of independent oscillators according to general rules of statistical physics

$$F = T \int \frac{d^3k}{(2\pi)^3} \sum_{n=1}^{\infty} \ln \left[ \omega \left( \frac{\pi n}{R} \right) \right]. \tag{12}$$

Performing the same steps as in Ref. \[33\], we obtain the interaction mediated by compression fluctuations in the form

$$U_{com} = \frac{T}{32\pi R^2} \int_0^\infty dz \ln \left[ 1 - \exp \left( -\sqrt{z + 4R^2/\lambda_D^2} \right) \right]. \tag{13}$$

In the limiting cases Eq. (13) reads

$$U_{com} = \begin{cases} -\zeta(3)/16\pi R^2, & R \ll \lambda_D \\ -\exp(-2R/\lambda_D)/8\pi R \lambda_D, & \lambda_D \ll R, \end{cases} \tag{14}$$

where $\zeta(3) \approx 1.202$ is the Riemann zeta function. At a large $R$ the interaction (14) is screened on the length $\lambda_D/2$. A possibility of interaction, mediated by non-electromagnetic fluctuations, has been proposed by Dzyaloshinskii, Lifshitz, and Pitaevskii \[32\]. The first formula (14) was obtained in Ref. \[32\]. It is similar to the result of Ref. \[33\] for electromagnetic fluctuations and perfectly conducting planes.

The fluctuation interaction (14) depends on the Debye screening length. This happens due to summation over all wave vectors in the free energy. This results in its dependence on density of states which, in turn, depends on a form of the spectrum. In our case the spectrum $\omega = s(k^2 + \lambda_D^2)^{1/2}$ brings the $\lambda_D$-dependence into the free energy.

When two objects are not flat but they are close enough interacting by small parts of their surfaces which are almost flat, one can derive an interaction potential from the flat approximation (14) integrating over the surfaces. For example, for a particle close to a flat wall when the center-to-wall distance $h$ is smaller than the particle radius $a$, the interaction can be calculated as in Ref. \[33\] and has the form

$$U_{com} = \frac{-\zeta(3)}{8} T \frac{a}{h - a}, \quad (h - a) \ll a, \lambda_D. \tag{15}$$

The analogous result for two spheres with the center-to-center distance $R$ is

$$U_{com} = -\frac{-\zeta(3)}{16} T \frac{a}{R - 2a}, \quad (R - 2a) \ll a, \lambda_D. \tag{16}$$

Equations (15) and (16) hold in a non-electrolytic fluid or in an electrolyte with a sufficiently large screening length.

IV. WHICH MECHANISM SURVIVES IN AN ELECTROLYTE

In an electrolyte the interaction $U_{com}$, mediated by plasmons, is strongly screened (14). The van der Waals interaction $u_{vdW}$, mediated by photons of a frequency in the visible range, is not sensitive to the plasmon effects. The mechanism of variable mass is connected solely with incompressible fluid fluctuations. Therefore, only the conventional van der Waals interaction $u_{vdW}$ and variable mass mechanisms $I$ can survive in an electrolyte. The interaction due to variable mass is considered in the following sections.

V. VARIABLE MASS MECHANISM

For the purpose of illustration of the variable mass mechanism one can consider a simple mechanical analogy.
Suppose a classical non-dissipative particle of the total energy $E$ moves in the harmonic potential $\alpha x^2$. When the particle mass is a constant the mean displacement $\langle x \rangle = 0$ in the harmonic potential. But in the case of a variable mass $m(x)$ the mean displacement $\langle x \rangle \neq 0$. This is due to that a particle velocity is smaller at a region of a larger mass just to keep the total energy to be constant. According to that, the particle spends more time at the region of a larger mass. This is equivalent to the certain effective attraction $I(x)$ to a region of a larger mass. As shown in Ref. [33], for a slow varying $m(x)$ the total effective potential becomes $\alpha x^2 - (E/2) \ln m(x)$.

A real particle with friction participates the Brownian motion characterized by the certain temperature $T$. We briefly repeat here the main arguments leading to an effective potential $I$ [33]. The Langevin equation, describing such processes, has the form

$$m(x) \ddot{x} + \frac{1}{2} \frac{\partial m}{\partial x} \dot{x}^2 + \frac{\partial V(x)}{\partial x} + \eta \dot{x} = \text{stochastic force.} \quad (17)$$

Short time fluctuations of the velocity $\dot{x}$ are well separated from the slow drift in an effective potential. Indeed, according to fluctuation dissipation theorem, the mean value of the kinetic energy $(m \dot{x}^2/2) = T/2$ corresponds to the equipartition law and is contributed by short time fluctuations related to the infinitely large circle in the plane of complex frequency. Substitution of that mean value to Eq. (17) leads to the effective potential $V(x) + I(x)$ [33], where

$$I(x) = -\frac{T}{2} \ln m(x). \quad (18)$$

The expression (18) is an exact result in the thermal limit (no quantum fluctuations) as the equipartition law.

We remind what happens in the conventional case of position-independent masses. In that situation in the thermal limit one can put all frequencies to be zero since they provide only quantum corrections to the partition function. The remaining part of the partition function is determined solely by a potential energy and does not depend on velocities. The scenario becomes different for a position-dependent mass. In this case one can use the following general arguments. The partition function $Z$, which is proportional to the phase volume $\Delta p \Delta x$, acquires an additional positional dependence $\Delta p \sim \sqrt{T m(x)}$ following from the momentum channel even in the thermal limit [33]. The free energy $-T \ln Z$ results in the interaction potential [33] obtained by the rigorous derivation procedure.

In a multidimensional case the kinetic energy is expressed through the mass tensor $m_{ij}(\vec{R})$ as

$$K = \frac{1}{2} m_{ij}(\vec{R}) \dot{R}_i \dot{R}_j \quad (\omega \to \infty). \quad (19)$$

As shown in Ref. [33], in the multidimensional case the interaction due to variable mass has the form

$$I(\vec{R}) = -\frac{T}{2} \ln \left[ \det m(\vec{R}) \right]. \quad (20)$$

The potential (20) has a fluctuation origin and is mediated by fast fluctuations of velocity. In terms of coordinates, when the form (19) is diagonalized, det $m$ becomes a product of principal values and the interaction (20) is reduced to a sum of terms related to principal coordinates.

VI. INTERACTION MEDIATED BY THERMAL FLUCTUATIONS OF PARTICLE VELOCITIES

To calculate the effective fluctuation potential even for a system with a complicated dynamics, one has to find in the high frequency limit the mass tensor and to insert it into Eq. (20). When particles in a fluid perform an oscillatory motion with a high frequency, the fluid velocity obeys the Euler equation everywhere in the fluid excepting a thin layer close to the particle surfaces [34]. Hence for finding the mass tensor in Eqs. (19) - (20) one has to solve the Euler equation with the zero boundary condition for a normal component of the fluid velocity. For this reason, the mass, corresponding to the high frequency limit of particle dynamics, can be called Euler mass. The effective particle mass depends on a fluid mass involved into the motion. The fluid mass depends on an interparticle distance and therefore the effective particle masses also depend on that distance.

In the case of one particle of a radius $a$ in a bulk fluid the Euler mass tensor has the form [33]

$$m_{ij} = \frac{4 \pi a^3}{3} \left( \rho_0 + \frac{\rho}{2} \right) \delta_{ij}, \quad (21)$$

where $\rho_0$ is a mass density of the particle and $\rho$ is a fluid density. The first term in Eq. (21) is related to the self mass of the particles and the second one is associated with a fluid motion.

A. Two particles in an infinite fluid

Now we calculate the Euler mass tensor for two identical particle in a fluid. The fluid velocity, normal to a particle surface, should equal a normal particle velocity on its surface. If the particle velocities are $\vec{u}_1$ and $\vec{u}_2$ there
are four independent quadratic combinations \((\vec{u}^2 + \vec{u}_2^2), \vec{u}_1 \vec{u}_2, (\vec{R} \vec{u}_1) (\vec{R} \vec{u}_2), \) and \(((\vec{R} \vec{u}_1)^2 + (\vec{R} \vec{u}_2)^2)\). Let us make the velocity transformation

\[
\vec{V} = \frac{\vec{u}_1 + \vec{u}_2}{\sqrt{2}}, \quad \vec{v} = \frac{\vec{u}_1 - \vec{u}_2}{\sqrt{2}}. \tag{22}
\]

In terms of new velocities the kinetic energy can be written in the form

\[
K = \frac{1}{2} \sum_{i=1}^{3} \left[ M_i (\vec{R}) V_i^2 + m_i (\vec{R}) v_i^2 \right], \tag{23}
\]

where \(i = 1, 2, 3\) correspond to \(x, y, z\) respectively. In the expression \((23)\) there are four independent masses only since \(M_x = M_y\) and \(m_x = m_y\). One can separate self masses of the particles \(4\pi a^3 \rho_0 / 3\) from fluid ones using the form

\[
M_i = \frac{4\pi a^3}{3} \left[ \rho_0 + \frac{\rho}{2} G_i \left( \frac{R_i}{a} \right) \right], \tag{24}
\]

\[
m_i = \frac{4\pi a^3}{3} \left[ \rho_0 + \frac{\rho}{2} g_i \left( \frac{h_i}{a} \right) \right].
\]

According to Eq. \((21)\), \(G(\infty) = g(\infty) = 1\). The easiest way to calculate the masses is to use the method illustrated in Figs. \((\text{II})\) and \((\text{III})\) where the particle velocities are shown by the arrows. The kinetic energy of the fluid in Figs. \((\text{II})\) and \((\text{III})\) are \((2\pi a^3/3) G_{x,z} (R/a) u^2\) respectively. Analogously, the fluid kinetic energies in Figs. \((\text{IV})\) and \((\text{V})\) are \((2\pi a^3/3) g_{x,z} (R/a) u^2\). The interaction potential \((20)\) takes the form

\[
I(R) = -T \left[ \ln \frac{[2\rho_0 + \rho G_z (R/a)][2\rho_0 + \rho g_z (R/a)]}{(2\rho_0 + \rho)^2} \right] \tag{25}
\]

\[+ \frac{1}{2} \ln \frac{[2\rho_0 + \rho g_z (R/a)][2\rho_0 + \rho G_z (R/a)]}{(2\rho_0 + \rho)^2}.\]

The function \(I(R)\) tends to zero at \(R \to \infty\).

**B. One particle near an infinite wall**

We consider here one particle of the radius \(a\) placed in a half-space of fluid filled out the volume \(z > 0\). The center-to-plane (the plane is at \(z = 0\)) distance is \(h\). The boundary condition at the particle surface is an equality of normal components of the fluid and the particle velocities. The normal velocity component of the fluid at the flat surface is zero. Obviously, the total kinetic energy is one half of that calculated in the previous subsection corresponding to Fig. \((\text{II})\) \((x)\) \((y)\) components and Fig. \((\text{IV})\) \((b)\) which are related to the zero normal velocity of the fluid at \(z = 0\).

It is easy now to write down the interaction potential using the results of the previous subsection. It reads

\[
I(h) = -T \left[ \ln \frac{2\rho_0 + \rho G_z (2h/a)}{2\rho_0 + \rho} + \frac{1}{2} \ln \frac{2\rho_0 + \rho g_z (2h/a)}{2\rho_0 + \rho} \right] \tag{26}
\]

where the functions \(G_z\) and \(g_z\) are the same as calculated in the previous subsection.

**C. One particle near two infinite perpendicular walls**

This situation is shown in Figs. \((\text{VI})\) \((\text{VII})\). The fluid is restricted by the conditions \(y < 0\) and \(z > 0\) where the particle is placed. The other image particles, figured out by dashed curves, serve to obey the boundary conditions in the planes \(z = 0\) and \(y = 0\) of zero normal velocities of the fluid. If to consider the whole space with incorporated image particles the total kinetic energies are

\[
K_i = 4\pi a^3 \left[ \rho_0 + \rho f_i (h/a, D/a) \right] u^2 \tag{27}
\]

with \(i = 1, 2, 3\) for Figs. \((\text{VI})\) \((\text{VII})\) respectively where the velocities of all particles are \(u\). Analogously to the previous cases, the interaction potential is

\[
I(h, D) = -T \sum_{i=1}^{3} \ln \frac{2\rho_0 + \rho f_i (h/a, D/a)}{2\rho_0 + \rho}. \tag{28}
\]

The boundary conditions are of the same type as in Sec. \((\text{VI})\) \((\text{A})\).
The kinetic energy of the fluid is given by

\[ \frac{1}{2} \rho \vec{v} \cdot \vec{v} = \frac{1}{2} \rho \vec{u} \cdot \vec{u} + \sum_i \left( \frac{\rho_i}{2} \vec{u}_i^2 - \frac{\rho_i}{2} \int_{S_i} dS \phi(n_i \vec{u}_i) \right), \]  

where \( \rho \) is the density of the fluid, \( \vec{v} \) is the fluid velocity, \( \vec{u} \) is the particle velocity, \( \rho_i \) and \( \vec{u}_i \) are the density and velocity of the \( i \)-th particle, \( S_i \) is the area of the \( i \)-th particle, \( \phi(n_i \vec{u}_i) \) is the potential energy due to the interaction between the \( i \)-th particle and the fluid, and \( n_i \) is the unit normal vector at the \( i \)-th particle.

In this chapter, we discuss the three different contributions to interaction of colloidal particles, listed in Sec. 1 in various geometries: (i) two particles in a bulk fluid, (ii) one particle over a flat surface, and (iii) one particle near two perpendicular walls.

The interaction \( U_{\text{com}} \), which is mediated by compression fluctuations of the fluid, plays an outstanding role since it is relatively large, \( U_{\text{com}}/T \sim (0.3 - 1.0) \), as follows from Figs. 6 and 8. On the other hand, the interaction \( U_{\text{com}} \) is strongly reduced by a finite Debye screening length \( \lambda_D \). Therefore, this interaction can be observed in applications.
FIG. 6: The numerically calculated attraction potentials for two particles in an infinite fluid. $\rho/\rho_0 = 1$.

FIG. 7: The numerically calculated attraction potentials for one particle and the infinite flat wall. $\rho/\rho_0 = 1$.

electrolytes with a large $\lambda_D$. In addition to that, surfaces of interacting objects should not be strongly charged to prevent domination of the Coulomb repulsion over $U_{com}$.

In a conventional electrolyte, normally used in experiments, only $u_{vdW}$ (frequencies larger than plasma one) and $I$ (non-compressive fluctuations) survive on distances larger than $\lambda_D$ where the Coulomb repulsion of charged particles is screened.

Fig. 6 relates to the case of two particles in a bulk fluid, Sec. VI A. The interaction potential $I$ (in the units of temperature $T$) is plotted by the thin solid curve. The conventional van der Waals interaction (5) is indicated by the dashed curve. The resulting potential is shown by the thick curve. It can be seen that $U_{com}$ substantially exceeds the above interaction potentials.

Figs. 7 and 8 correspond to the case of one particle near the wall, Sec. VI B. As clear from Fig. 8 $U_{com}$ is not small and is of the order of $T$.

In Fig. 9 the potential $I$ relates to one particle near two perpendicular walls.

When the intersurface distance is small the potential $I$ tends to a constant whereas the van der Waals interaction diverges as known. The results shown in Figs. 6 - 9 correspond to $\rho/\rho_0 = 1$. Under increase of this parameter the attraction becomes more pronounced. For example, for $\rho/\rho_0 = 13.6$, related to colloidal particles in mercury, the attraction potential becomes roughly more than two times larger in amplitude.

IX. DISCUSSIONS

Is it possible to experimentally observe an attraction of like-charged colloidal particles separated by micron distance? Let us analyze different physical situations.

A. No Coulomb effects

A lack of Coulomb effects means use of an electrolyte with a large Debye length $\lambda_D$ and zero charges on all surfaces. In this case DLVO repulsion is absent and the interaction mediated by compression fluctuation, $U_{com}$, substantially dominates the conventional van der Waals part $u_{vdW}$ and one mediated by particle velocities, $I$. As follows from Fig. 8 the interaction energy $U_{com}$ of a
particle of the radius $1 \mu$ and a flat plane, when surface-to-surface distance is $0.15 \mu$, is $1T$. This attraction can be experimentally observed since it is relatively large.

**B. Conventional particles in an electrolyte**

For typical electrolytes and polystyrene particles DLVO repulsion is of a short length and the interaction $U_{com}$ is well suppressed. In this situation only $u_{vdW}$ and $I$ survive. But the van der Waals interaction $u_{vdW}$ is weak and only $I$ has chances to result in an observable attraction.

The peculiarity of the interaction $I$ is that a particle is attracted stronger to a surface which better geometrically adjusts its shape. The flat surface in Fig. 7 adjusts the particle better than the counter-curved neighborèd particle in Fig. 6. Also the geometry of two walls in Fig. 9 adjust the particle shape better than one wall in Fig. 7. An attraction of a particle to a surface of the same type of curvature is most stronger.

The feature of the interaction $I$ is that it is of the order of $0.05T$ (a particle near a flat wall) and of the order of $0.1T$ (a particle near two perpendicular walls) when the intersurface distance is of the order of $0.2a \sim 2000\AA$. At a larger intersurface distances the attraction $I$ exceeds the van der Waals part.

It is promising to take a surface which adjusts the spherical particle better than two perpendicular planes. For example, it can be a cylinder with the particle inside. In this case an interaction is a few or even ten times larger than $0.1T$ (two perpendicular planes). The minimum value of an interaction potential $0.1T$, when $T$ is room temperature, is approximately a border of experimental resolution. So in a conventional electrolyte the attraction a micron sized particle to two perpendicular planes or to an interior surface of a cylinder can be experimentally observed.

**X. CONCLUSIONS**

For like charged colloidal particles two mechanisms of attraction between them survive when the interparticle distance is larger than the Debye screening length. One of them is the conventional van der Waals attraction and the second one is the attraction mechanism mediated by thermal fluctuations of particle position. The latter is related to an effective variable mass (Euler mass) of the particles produced by a fluid motion involved. The most stronger attraction potential (up to the value of temperature $T$) corresponds to a situation of uncharged particles and a relatively large Debye screening length. In this case the third mechanism of attraction enters the game. It is mediated by thermal fluctuations of fluid density.

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