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Hydrodynamic fluctuation forces

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Abstract

Two mechanisms of interaction of particles in a fluid are proposed on the basis of forces mediated by hydrodynamic thermal fluctuations. The first one is similar to the conventional van der Waals interaction, but instead of being mediated by electromagnetic fluctuations, it is mediated by fluctuations of hydrodynamic sound waves. The second one is due to a thermal drift of particles to a region with a bigger effective mass, which is formed by the surrounding fluid involved and depends on the inter-particle distance. Both mechanisms are likely to be relevant in the interpretation of the observed long-range attraction of colloidal particles, since a set of different experiments show an attraction energy of the order of $k_B T$ and, perhaps, only a fluctuation mechanism of attraction can provide this universality.

1. Introduction

Charge-stabilized colloidal suspensions exhibit a variety of unusual physical properties [1–3]. Colloidal particles can be organized into crystal [4] and into structures with clusters and voids [5–10]. A system of colloidal particles may undergo different types of phase transition [11–17]. Topological phase transitions in two-dimensional systems of colloidal particles have been reported in [18, 19]. In [20] buckling instabilities in confined colloidal crystals were analysed. Interesting behaviours of colloids in external fields were reported in [21]. Colloidal particles accept, in an electrolyte, some effective charge screened by counterions at Debye's length λ_D , which is described by the repulsion potential of Derjaguin, Landau, Verwey, and Overbeek (DLVO) [1, 2]. The DLVO theory, as a result of solution of the linearized Poisson–Boltzmann equation, has been questioned in [12, 22]. The generalization of DLVO interaction via a modification of counterion screening was reported in [23].

Despite the long history of the problem, the interaction of colloidal particles remains an area of challenge and controversy. The authors of [12], studying phase transitions in charged colloidal systems, found a substantial deviation from predictions resulting from a screened Coulomb interaction. Experimental data [24] suggest a net attraction of particles

for explanation of the measurements (see also the comment on that work [25]). Later, an attraction of micron-sized particles separated by a micron-sized distance was established experimentally. The interaction potential has been found to have a minimum $-U_0$ at a centre-to-centre particle distance R_0 of micron size. In the work [26], colloidal particles, confined between two glass planes, exhibit $U_0 \simeq 0.2k_B T$ for different ionic strengths. This type of experimental arrangement, studied in another laboratory [27], gives $U_0 \simeq (0.3-0.4)k_B T$ for different particle diameters and distances between planes. Another study of colloidal particles, confined between two glass planes, gives $U_0 \simeq 1.3k_B T$ or less for different particle diameters and distances between planes [28,29] (see also [30,31]). An attraction of $0.5k_B T$ per neighbour particle (separated by the micron-sized distance) has been deduced for the colloidal crystal in [30]. Polystyrene colloidal particles of diameter $0.5 \mu\text{m}$ at the water–air interface exhibit $U_0 \simeq 0.5k_B T$ at $R_0 \simeq 0.9 \mu\text{m}$ [32]. For micron-sized colloidal ‘molecules’ at the air–water interface [7–9], the binding energy can be estimated as a few kT . For bound particles at the fluid–fluid interface an estimate is $U_0 \sim 4kT$ [33]. As one can see, despite the different conditions (even particles at interfaces), there is a very stable common feature in all of the various experiments: the attraction minimum is always of the order of $k_B T$. This leads to the hypothesis of some common mechanism of micron-sized attraction, which is responsible for the universality of $U_0 \sim k_B T$. Note that the mean-field energies in colloidal physics (electrostatic and hydrodynamic) are a few orders of magnitude bigger than kT at room temperature.

Let us analyse some mechanisms of attraction proposed in the literature.

A principal question is that of whether like-charged particles separated by a micron distance can attract each other due to a solely electrostatic mean-field interaction (for example, by some charge redistribution) which is not accounted for by DLVO theory. This type of attraction was predicted in [34]. The results of [34] are not applicable to dielectric particles, only to those with the electrolyte inside identical to the one outside. The correct calculation of an interaction of that kind shows only repulsion, in contrast to [34]. An electrostatic attraction between like-charged particles, based on the mean-field approach, was also predicted in [35], but that conclusion was incorrect, as shown in the works [36,37]. An attractive potential force between like-charged particles at a micron distance due to a mean-field mechanism seems to be extremely unlikely, and the works [36,37] provide strong arguments in support of this statement.

The conventional van der Waals attraction, mediated by high-frequency (visible light) electromagnetic fluctuations, is very small in the micron range: less than $10^{-2} T$ at room temperature [38–41], and cannot provide the observed attraction. Measurements of this type of attraction in colloidal systems at short distances, of the order of a few hundred ångströms, have been performed in [42,43]. An analysis of the attraction at such short distances, including the influence of the surface roughness, is given in [44–47].

The van der Waals interaction mediated by the low-frequency (of the order of the plasma frequency) electromagnetic fluctuations decays fast with the distance R between two particles, as $-V_0 \exp(-2R/\lambda_D)$ [40, 48]. V_0 has in our case a thermal fluctuation origin and is less strong than the electrostatic repulsion energy even at $R \simeq \lambda_D$. The exponential dependence $\exp(-R/\lambda_D)$ of the attraction potential in [49], dealing with the same effect, differs from the above correct exponent [40,48]. The results of [49] cannot explain the attraction at $R \sim 10\lambda_D$ in [28], because the attraction, reported in [49], is too small at that distance.

The effect of correlation of counterions [50–54] (see also [55–57]) results in their rearrangement in the vicinity of a colloidal particle—of the order of the mean distance between counterions, which is less than λ_D . At that short distance, an attraction is possible as shown in [50–54]. For positions at long micron-sized distances, the correlation of counterions forms an effective charge Ze on the particle, which is screened at λ_D and determines the repulsive part of the interaction.

Depletion forces between colloidal particles originate from the influence of the thermodynamic energy caused by the finite size of the small particles which constitute the surrounding medium [58–62]. The range of the depletion interaction is determined by the size of the small particles, which are not necessary ‘small’ as in [61], where the surrounding polymer coils have macroparticle size. When the surrounding electrolyte contains only microions, the depletion force is of very short range compared to the micron scale.

In [63] a mechanical effect is proposed for explanation of the observed motion of particles towards each other, when they move away from a single wall due to the Coulomb repulsion [30, 31]. This mechanical effect is irrelevant in analysis of the interaction of free particles in a fluid or ones confined between walls or on interfaces (see also [64]).

As one can conclude, none of the above mechanisms is responsible for the set of observations of long-distance attraction of colloidal particles (perhaps excepting the mechanical effect [63], which can be relevant for the particle motion in the one-wall geometry [30]). An important clue in the search for and selection of possible mechanisms of attraction is the universality of the depth of the attraction minimum $U_0 \sim k_B T$. The most probable mechanism, satisfying this criterion, is an interaction mediated by thermal fluctuations of some physical values. This is a microscopic type of interaction, which can be formulated in terms of a potential energy. Regardless of the specifics of the fluctuating matter, the free energy of thermal fluctuations is always proportional to $k_B T$. For example, the attraction potential of two dielectric particles (refractive index n) in water (refractive index n_0) due to thermal fluctuations of the electromagnetic field is proportional to $c(n, n_0)k_B T$. If n is close to n_0 , then $c \sim (n - n_0)^2$, according to the perturbation theory. With real values of n and n_0 for polystyrene and water, the coefficient c is very small, which makes the conventional van der Waals attraction in the micron range negligible. Nevertheless, if we put formally $n \rightarrow \infty$ (zero field gradient at the surface of the particles), the attraction in the micron range is not small compared to $k_B T$ [38]. This is similar to the situation in hydrodynamics, where fluctuating electromagnetic waves are replaced by hydrodynamic ones and the fluid velocity is zero on the particle surface. Hence, one can expect the interaction, mediated by fluctuating hydrodynamic waves, to not be small like in the electromagnetic case with $n \rightarrow \infty$.

The nature of forces mediated by fluctuations of sound waves in a fluid can be clarified in the following way: the energy of the thermal fluctuations of the fluid depends on the distance between two particles, which play the role of obstacles to fluid motion, and hence this results in a force. The non-electromagnetic type of fluctuation force, discussed by Dzyaloshinskii *et al* [65], can be considered as some sort of van der Waals [38] or Casimir force [66]. We do not concern ourselves here with the history of the origin of the two names for fluctuation interactions.

In addition to the attraction mediated by fluid fluctuations, there is another mechanism of fluctuation interaction related to hydrodynamics: this is the interaction mediated by thermal fluctuations of particle positions in a fluid. The effective particle masses depend on the fluid mass involved in the motion. The fluid mass depends on the inter-particle distance and therefore the effective particle masses also depend on that distance. If the mass of a classical non-dissipative harmonic oscillator depends on the coordinate, the mean coordinate shifts to the region with bigger mass (smaller velocity), since the particle spends more time there. Analogously, for a Brownian motion of particles in a fluid, a thermal drift occurs in the direction of the bigger effective mass. As shown in this paper, the effective particle mass, which determines the effect, should be calculated on the basis of Euler (non-dissipative) hydrodynamics and it can be called the Euler mass.

The above fluctuation interactions relate to hard spheres (no mean-field interaction except an infinite repulsion on contact). If the particles are charged, the total interaction is a sum of the fluctuation ones and the Coulomb repulsion. This is discussed in section 7.

The following results are presented in the paper:

- (i) the forces of attraction between two parallel plates and spherical particles with short inter-surface distance, mediated by hydrodynamic fluctuations of sound waves, are shown to exist and they are calculated analytically;
- (ii) a novel interaction of particles in a fluid is proposed, which is based on the dependence of their effective masses on the distance between them;
- (iii) the Fokker–Planck equation for two particles in a fluid is derived;
- (iv) the difference between the measurements of a particle interaction by means of optical tweezers and a long-time statistics is pointed out and calculated.

2. The hydrodynamic van der Waals interaction

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

$$U_{\text{vdW}}(R) = F(R) - F(\infty) \quad (1)$$

is an interaction mediated by fluid fluctuations. Analogously to the conventional van der Waals interaction mediated by electromagnetic fluctuations, the potential (1) can be called *the hydrodynamic van der Waals interaction*. To find the free energy of thermal fluctuations of the fluid, one can start with the linearized Navier–Stokes equation [67]

$$\rho \frac{\partial \vec{v}}{\partial t} = -\vec{\nabla} p + \eta \nabla^2 \vec{v} + \left(\zeta + \frac{\eta}{3} \right) \vec{\nabla} \text{div } \vec{v}. \quad (2)$$

There are two types of fluid motion: one of them is a transverse 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. Since there is no static interaction for transverse motions, their equilibrium free energy 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. A quite opposite situation occurs for longitudinal motions, when the total free energy is a sum of energies of different sound modes. The spectrum of sound waves depends on the distance between bodies R due to hydrodynamic boundary conditions on the 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 $\vec{v} = \vec{\nabla} \phi / \partial t$, one can obtain from equation (2)

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

Through thermodynamic relations and the continuity equation, one can obtain $\delta p = -\rho s_0^2 \nabla^2 \phi$, where s_0 is the adiabatic sound velocity [67]. At the typical frequency $\omega \sim s_0/a$ (a is the particle radius) involved in the problem, the dissipative term in equation (3) is small, and one can write

$$\frac{\partial^2 \phi}{\partial t^2} - s_0^2 \nabla^2 \phi = 0. \quad (4)$$

For the case of small friction, the boundary condition $\nabla_n \phi = 0$ on equation (4) corresponds to the Euler equation [67]. Generally, the free energy of a system of harmonic oscillators does not depend on friction in the thermal limit.

Let us consider first the case of two infinite parallel plates, separated by the distance R , when the frequency spectrum has the form [67]

$$\omega_n^2(k) = s_0^2 \left(k^2 + \frac{\pi^2 n^2}{R^2} \right). \quad (5)$$

The free energy per unit area of the system now can be expressed as a sum of energies of independent oscillators:

$$F = T \int \frac{d^2k}{(2\pi)^2} \sum_{n=1}^{\infty} \ln \frac{\hbar \omega_n(k)}{T}. \quad (6)$$

This type of interaction has been considered in the literature [39]. The simplest way to calculate the energy (6) is to divide the whole interval R into small segments $a_0 = R/N$. Then

$$\sum_{n=1}^N \ln \left(k^2 + \frac{\pi^2 n^2}{a_0^2 N^2} \right) = 2 \sum_{n=1}^N \ln \frac{n}{N} + \ln \prod_{n=1}^{\infty} \left(1 + \frac{a_0^2 N^2 k^2}{\pi^2 n^2} \right). \quad (7)$$

Using the relation $x \prod_{n=1}^{\infty} (1 + x^2/\pi^2 n^2) = \sinh x$, the Stirling formula for $N!$, omitting constants and R -linear terms, can be obtained from equations (5)–(7):

$$F = \frac{T}{2} \int \frac{d^2k}{(2\pi)^2} \ln [1 - \exp(-2kNa_0)]. \quad (8)$$

Now one should put in equation (8) $Na_0 = R$, and after integration we obtain, according to equation (1), the van der Waals interaction per unit area of two infinite plates:

$$u_{\text{vdW}}(R) = -\frac{\zeta(3)}{16\pi} \frac{T}{R^2}. \quad (9)$$

The result (9) enables one to calculate the van der Waals energy $U_{\text{vdW}}(R)$ of two spheres of radii a , separated by the centre-to-centre distance R , when $(R - 2a) \ll a$. In this case the inter-surface distance, measured in the direction parallel to the centre-to-centre line, is $R - 2a + (x^2 + y^2)/a$, where x and y are the coordinates in the plane perpendicular to the centre-to-centre line. The procedure leads to an integration:

$$U_{\text{vdW}}(R) = \int dx dy u_{\text{vdW}} \left(R - 2a + \frac{x^2 + y^2}{a} \right). \quad (10)$$

The result of the integration at $(R - 2a) \ll 2a$ is

$$U_{\text{vdW}}(R) = -\frac{\zeta(3)}{16} T \frac{a}{R - 2a} \quad (\text{spheres}). \quad (11)$$

The interaction energy (11) is calculated under fixed boundaries of particles, which corresponds to zero sound velocity s of the particle material (infinite acoustic mismatch). Under reduction of the mismatch, U_{vdW} decreases, going to zero at $s = s_0$, if there are only longitudinal acoustic modes inside the particles. The sound velocities for polystyrene particles, $s \simeq 2.1 \times 10^5 \text{ cm s}^{-1}$, and for water, $s_0 \simeq 1.5 \times 10^5 \text{ cm s}^{-1}$, provide a finite mismatch, which reduces the result (11), as one can show, by approximately four times. But in reality this conclusion is not correct, since transverse acoustic modes of the particle material increase the mismatch, leading the interaction towards the result (11). An account of the finite mismatch is a matter for further study, but the exact U_{vdW} seems to be close to the result (11).

The above calculations are applicable, strongly speaking, only to uncharged particles like hard spheres. For charged particles the electric charge density of a fluid en is finite and decays

over the Debye length λ_D . This results in a modification of the spectrum of fluctuations, by adding the plasma frequency $s^2k^2 + \omega_p^2 n/n_0$, where $\omega_p^2 = 4\pi n e^2 / \varepsilon M$ (M is the mass of the fluid molecule) and $n_0 \sim 10^{23} \text{ cm}^{-3}$ is the molecular density of the fluid. The coefficient n/n_0 arises from the sound spectrum being formed by the whole fluid, while the Coulomb gap is determined only by a small number of ions: $n \sim Z/4\pi a \lambda_D^2 \sim 10^{17} \text{ cm}^{-3}$ (typically, $Z \sim 10^4$). Since the wave vector k is inversely proportional to the inter-particle distance, one can conclude from this that the Coulomb effects modify the above hard-sphere result (11) when $(R - 2a)$ exceeds $100 \mu\text{m}$.

3. The paradox

In the case of the conventional van der Waals interaction, mediated by electromagnetic fluctuations, the mean values of the electric and magnetic fields are zero $\langle \vec{E} \rangle = \langle \vec{H} \rangle = 0$. The stress tensor σ_{ik} for the electromagnetic field is quadratic with respect to fields and hence the mean value $\langle \sigma_{ik} \rangle$ is not zero. This makes the origin of the force due to electromagnetic fluctuations straightforward. The situation with hydrodynamic fluctuation forces is different. For the linearized Navier–Stokes equation the mean value of the velocity is zero, $\langle \vec{v} \rangle = 0$ (the same holds for the fluctuation part of p). The hydrodynamic stress tensor

$$\sigma_{ik} = \eta \left(\frac{\partial v_i}{\partial r_k} + \frac{\partial v_k}{\partial r_i} \right) - p \delta_{ik} \quad (12)$$

is linear in fluctuation variables, its fluctuation part is zero, and the fluctuation force has to be zero in this approximation. A non-zero contribution to $\langle \sigma_{ik} \rangle$ can result from the non-linear terms in the Navier–Stokes equation neglected in the above approach. This non-linearity has been accounted for in [68], and a finite fluctuation force has been obtained. This result was shown to be incorrect in [69], where the exact mean value of the stress tensor (12) was found to be zero on the basis of exact non-linearity of the Navier–Stokes equations. One conclusion of [69] is that a hydrodynamic fluctuation interaction is impossible, which contrasts with the result (9). What is going wrong?

To understand the situation, let us consider the linear chain of small particles, connected by elastic springs, shown in figure 1 and described by the dynamic equation

$$\frac{\partial^2 u_n}{\partial t^2} = \frac{s^2}{b_0^2} (u_{n+1} + u_{n-1} - 2u_n) \quad (13)$$

where s is the sound velocity and b_0 is the period. Two unmoving big particles substitute for small particles, as shown in figure 1. The system is elastic and the force acting on a big particle, placed on the site n , is

$$F_n = \frac{ms^2}{b_0^2} (u_{n+1} - u_{n-1}). \quad (14)$$

Here m is the mass of a small particle. The free energy of the fluctuation motion of the small particles U_{vdW} is determined by a sum over self-frequencies ω_i of the system $F = T \sum \ln(\hbar\omega_i/T)$, resulting in

$$U_{\text{vdW}} = \frac{T}{2} \ln 4N \quad (15)$$

where N is a number of springs between two big particles. Two different positions of big particles, ‘natural’ in figure 1(a) and ‘compressed’ in figure 1(b), have identical self-frequencies since the system is harmonic and hence $U_{\text{vdW}}^{(a)} = U_{\text{vdW}}^{(b)}$ (equal to N in equation (15)). In this situation there is no van der Waals force, which is clear, since the mean value of the linear

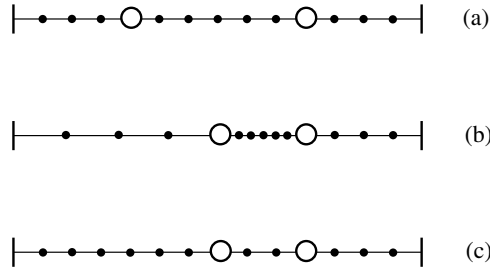


Figure 1. The linear chain of particles. Each horizontal segment between particles behaves like an elastic harmonic spring. The configuration (a) represents the ‘natural’ positions of two attached particles (open circles). The configuration (b) is obtained from (a) by a compressive motion of the attached particles without a destruction of harmonic bonds. (c) is another ‘natural’ position obtained from (a) by a destruction of harmonic bonds.

force (14) should be zero. On the other hand, for another ‘natural’ position in figure 1(c), the self-frequencies differ from those in figures 1(a) and (b); in this case $U_{\text{vdW}}^{(a)} \neq U_{\text{vdW}}^{(c)}$ (different from N in equation (15)) and the van der Waals force is non-zero. This is a consequence of the fact that a transition from the position (a) to the position (c) in figure 1 cannot occur within a harmonic approximation; one should destroy some harmonic springs and rearrange them again in a different way. The linear expression for force (14) is not valid for describing a transition from (a) to (c) and a real force is non-linear, which makes its average finite even for $\langle u_n \rangle = 0$.

An analogous situation takes place in hydrodynamics. According to its derivation, equation (9) is valid only for discrete $R = Nb_0$, where b_0 is the inter-atomic distance and N is an integer number. The full dependence of u_{vdW} on R has a structure on the atomic scale corresponding to removal of discrete atomic layers from the inter-plane region. The hydrodynamic expression for the stress tensor (12) is not valid at such a short scale—like equation (14) cannot describe the breaking of harmonic bonds. In contrast to the smooth van der Waals potential mediated by electromagnetic fluctuations, the interaction mediated by hydrodynamic ones has a structure as a function of distance on the atomic scale, superimposed on the smooth function (9). To some extent, this is analogous to the observation of the structured interaction potential [62], where the role of atoms was played by small particles. The resulting statement is that the hydrodynamic expression for the stress tensor (12) cannot be used for calculation of fluctuation forces since it becomes non-linear (and contributes to those forces) at short distances where the hydrodynamic approach is not valid. Hydrodynamic fluctuation forces should be calculated on the basis of energy as is done in this paper. The conclusion of [69] of the absence of hydrodynamic fluctuation forces based on use of the hydrodynamic stress tensor is incorrect.

4. Interaction mediated by fluctuations of particle position

The hydrodynamic van der Waals interaction is formed by fast density fluctuations with a typical frequency $\omega_L \sim s_0/a \sim 10^9 \text{ s}^{-1}$. Besides this longitudinal motion, there are also slow transverse fluctuations of the fluid driven by fluctuations of particle linear velocities \vec{u}_1 and \vec{u}_2 of the small frequency $\omega_T \sim \eta/\rho a^2 \sim 10^6 \text{ s}^{-1}$. This type of transverse fluctuation is independent of the longitudinal one. Thermal fluctuations of particle velocities mediate an important part of the total interaction, which supplements U_{vdW} .

Before consideration of this contribution, we focus at first on some aspects of the derivation of non-linear dissipative equations, which are useful for understanding the formation of the

interaction by fluctuations of particle velocities. Let us start with a one-dimensional motion in the potential $V(x)$ of a particle with the mass $m(x)$, attached to a heat bath, which provides a friction. A convenient way to proceed is to use the formalism of Caldeira and Leggett [70] of an infinite set of oscillators in thermal equilibrium. The Lagrangian has the form

$$L = \frac{m(x)}{2} \dot{x}^2 - V(x) + \frac{1}{2} \sum_i (m_i \dot{y}_i^2 - m_i \omega_i^2 y_i^2) - F(x) \sum_i c_i y_i \quad (16)$$

where $F(x) = \int^x dz \sqrt{\eta(z)}$ is a non-linear coupling to the thermostat. Using the formalism of Caldeira and Leggett, one can derive the Langevin equation in the limit of high temperatures:

$$m(x)\ddot{x} + \frac{1}{2} \frac{\partial m}{\partial x} \dot{x}^2 + \eta(x)\dot{x} + V'(x) = \sqrt{\eta(x)} f(t) \quad (17)$$

where the average is defined as $\langle f(t)f(t') \rangle = 2T\delta(t-t')$. Let us suppose the viscosity η to be sufficiently big; this separates the big frequency $\Omega \sim \eta/m$ from the low frequency V''/η of the viscous motion in the potential $V(x)$. One can also derive from the Lagrangian (16) the Fokker–Planck equation for the distribution function W , which in the low-frequency limit depends only on x and t :

$$\frac{\partial W(x, t)}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{W}{\eta(x)} \frac{\partial}{\partial x} [V(x) + I(x)] + \frac{T}{\eta(x)} \frac{\partial W}{\partial x} \right\}. \quad (18)$$

The additional potential in equation (18) is

$$I(x) = -\frac{T}{2} \ln m(x). \quad (19)$$

The Langevin (17) and the Fokker–Planck (18) equations are derived independently from the initial system (16) and do not contain uncertainties since the high-frequency limit is well defined by equation (17). If we omit two mass terms in equation (17), the high-frequency limit becomes indefinite ($\Omega = \infty$) and an attempt to derive the Fokker–Planck equation from the Langevin equation encounters the Ito–Stratonovich uncertainty [71] as a result of the loose definition of the high-frequency limit. Note that neither the Ito nor the Stratonovich approach results in the correct Fokker–Planck equation (18) for a massive particle with a variable viscosity $\eta(x)$.

To clarify the origin of the effective potential (19), let us represent the variable x in equation (17) as $x(t) + \delta x(t)$, where the small correction $\delta x(t)$ varies rapidly with frequencies $\Omega \sim \eta/m$ and $x(t)$ is a slowly varying variable. In equation (17) one can keep the second order of δx , considering $x(t)$ as an instant argument. After an averaging over high frequencies, equation (17) turns into a low-frequency part with two fluctuation-induced terms:

$$\eta(x)\dot{x} + \left[\frac{\partial V(x)}{\partial x} - \frac{1}{2} \frac{\partial m(x)}{\partial x} \langle \delta \dot{x}^2 \rangle - \frac{1}{2\sqrt{\eta(x)}} \frac{\partial \eta(x)}{\partial x} \langle \delta x f \rangle \right] = \sqrt{\eta(x)} f(t). \quad (20)$$

By means of the fluctuation-dissipation theorem [72] one can write (see also [73])

$$\langle \delta \dot{x}^2 \rangle = \frac{iT}{\pi} \int_{-\infty}^{\infty} \frac{d\omega}{m\omega + i\eta} = \frac{T}{m}. \quad (21)$$

The integration path in equation (21) can be deformed into the far semicircle in the upper half-plane of complex ω . Hence, $\langle \delta \dot{x}^2 \rangle$ is determined by high frequencies, and the use of instant variables, leading to the incorporation of $\langle \delta \dot{x}^2 \rangle$ into the low-frequency equation (20), is correct. Analogously,

$$\langle \delta x f \rangle = -\frac{T\sqrt{\eta}}{\pi} \text{P} \int_{-\infty}^{\infty} \frac{d\omega}{\omega(m\omega + i\eta)} = \frac{T}{\sqrt{\eta}}. \quad (22)$$

The letter ‘P’ stands for the principal value of the integral, which can be represented as the integral along the infinite contour consisting of the real axis plus a small circle around zero in

the upper half-plane and minus the integral around that small circle. The integration along the infinite contour can be shifted to the far upper half-plane and gives zero, but the integration around the small circle gives a finite result. Hence, $\langle \delta x f \rangle$ is determined by the zero-frequency limit; the use of instant arguments and incorporation of $\langle \delta x f \rangle$ into equation (20) are not appropriate. Among the two fluctuation-induced terms in equation (20), only one (with $\partial m / \partial x$) has meaning and it results in the potential (19). This remains true in a more general case, when the linearized form of the dynamic equation is

$$(-m\omega^2 - i\omega\eta(\omega) + V'')\delta x_\omega = 0. \quad (23)$$

In this case the mass m is strictly defined by the condition $\eta(\omega)/\omega \rightarrow 0$ at $\omega \rightarrow \infty$ and the potential (19) is determined by the high-frequency limit according to equation (21), when only a mass term plays a role.

The origin of the potential (19) can also be understood from the following non-rigorous arguments. One can write formally the free energy $F = -T \ln(\Delta p \Delta x / \hbar)$, where momentum fluctuations $(\Delta p)^2 \sim mT$ are formed on a short timescale Ω^{-1} and fluctuations of the coordinate $(\Delta x)^2 \sim Tt/\eta$ are slow. In the expression

$$F = -\frac{T}{2} \ln m + \frac{T}{2} \ln \frac{\hbar^2 \eta}{T^2 t} \quad (24)$$

the first term originates from fast fluctuations of the momentum and corresponds to equation (19).

The interaction (19) has a simple interpretation. Suppose a classical non-dissipative particle with the variable mass $m(x)$ moves with the total energy E in the harmonic potential αx^2 . For a variable mass the mean displacement $\langle x \rangle \neq 0$, since in the region with bigger mass the particle spends more time having a smaller velocity. One can easily show that, when $m(x)$ varies slowly on the scale of the particle amplitude, $\langle x \rangle$ can be calculated by making the mass $m(0)$ constant and adding the potential $-(E/2) \ln m(x)$. In other words, a particle tends to spend more time in a region with bigger mass. This conclusion remains correct for a dissipative case with fast fluctuations of velocity instead of harmonic oscillations, when the energy E can be replaced as an approximation by the temperature T . This corresponds to the potential (19).

One can easily generalize this method to the multi-dimensional case. Suppose that in the high-frequency limit the kinetic energy has the form

$$K = \frac{1}{2} m_{ij}(\vec{R}) \dot{R}_i \dot{R}_j \quad (\omega \rightarrow \infty). \quad (25)$$

Then in the equation of motion, where only the kinetic part is kept,

$$m_{ij}(\vec{R}) \ddot{R}_j + \left(\frac{\partial m_{ij}}{\partial R_k} - \frac{1}{2} \frac{\partial m_{kj}}{\partial R_i} \right) \dot{R}_k \dot{R}_j = F_i \quad (26)$$

one can consider the variables again as sums of slow and fast parts $R_i(t) + \delta R_i(t)$. Taking the average of the quadratic (with respect to δR) part produces the fluctuation-induced effective force

$$F_i^{ef} = F_i + \frac{1}{2} \frac{\partial m_{kj}}{\partial R_i} \langle \delta \dot{R}_k \delta \dot{R}_j \rangle. \quad (27)$$

Taking account of the average $\langle \delta \dot{R}_k \delta \dot{R}_j \rangle = T m_{kj}^{-1}$, the effective force reads

$$F_i^{ef} = F_i + \frac{T}{2} m_{kj}^{-1} \frac{\partial m_{kj}}{\partial R_i} = F_i + \frac{\partial}{\partial R_i} \left[\frac{T}{2} \ln(\det m) \right]. \quad (28)$$

From here the generalization of equation (19) follows:

$$I(\vec{R}) = -\frac{T}{2} \ln [\det m(\vec{R})]. \quad (29)$$

The additional potential energies (19) or (29) have a fluctuation origin and are mediated by fast fluctuations of velocity with the typical frequency $\Omega \sim \eta/m$, which form, for each instant coordinate, the quasi-equilibrium free energy. One can formulate a rule for calculating the effective fluctuation potential even for a system with a complicated dynamics: one has to find the kinetic energy (25) in the limit of high frequency and to insert the mass tensor into equation (29). The method in the form presented is applicable to classical systems with the kinetic energy proportional to the square of the velocities.

5. Two particles in a fluid and the Euler mass

Suppose that there are two particles in a fluid of radius a separated by the centre-to-centre distance R . If they perform an oscillatory motion with a high frequency ω , the fluid velocity obeys the Euler equation everywhere in a fluid excepting in a thin layer of thickness $\sim \sqrt{\eta/\rho\omega}$ close to the particle surfaces, where the full Navier–Stokes equation should be used [67]. Hence for finding the mass tensor (25) one has to solve the Euler equation with the 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 the Euler mass. For example, the Euler mass tensor of one particle is [67]

$$m_{ij} = \frac{2\pi}{3} a^3 (2\rho_0 + \rho) \delta_{ij} \quad (30)$$

where ρ_0 is the mass density of the particle.

In the case of two particles in a bulk fluid the Euler mass cannot be calculated analytically for an arbitrary relation between R and a . Nevertheless, there is a situation where an analytical calculation of $I(R)$ over the full range is possible. This is the case of two particles confined between two parallel plates separated by a distance equal to the particle diameter, which corresponds to the current experiments [75]. Let us suppose the particles to be of cylindrical shape with the axis of length $2a$ perpendicular to the plates. In this case, particle and fluid velocities are directed parallel to the plates and the problem becomes two dimensional. The velocity of the incompressible Euler fluid can be written as $\vec{v} = \vec{\nabla}\phi$ with the boundary condition that the normal derivative $\partial\phi/\partial\vec{n}$ cancels the normal components of the particle velocities. Since the scalar ϕ satisfies the Laplace equation $\nabla^2\phi = 0$ in two dimensions, one can use a conformal transformation to convert the geometry into a planar one. If the centres of two particles localize at the positions $\text{Re } z = \pm R/2$, $\text{Im } z = 0$ on the complex z -plane, the conformal transformation

$$z = \left(\frac{R^2}{4} - a^2 \right)^{1/2} \coth \frac{w}{2} \quad (31)$$

maps the two circles onto two infinite parallel lines:

$$\text{Re } w = \pm \ln \left(\frac{R}{2a} + \sqrt{\frac{R^2}{4a^2} - 1} \right) \quad (32)$$

in the complex w -plane. For the plane geometry, the problem can be solved in a straightforward way. The mass tensor is easily diagonalized by two centre-of-mass motions and two relative ones. Using the formula (29), one can obtain after some calculations

$$I(R) = -T \ln \left[1 - \frac{2(R^2 - 4a^2)}{a^2(1 + \rho_0/\rho)} \sum_{n=1}^{\infty} \frac{n(R - \sqrt{R^2 - 4a^2})^{2n}}{(R + \sqrt{R^2 - 4a^2})^{2n} + (2a)^{2n}} \right] - T \ln \left[1 + \frac{2(R^2 - 4a^2)}{a^2(1 + \rho_0/\rho)} \sum_{n=1}^{\infty} \frac{n(R - \sqrt{R^2 - 4a^2})^{2n}}{(R + \sqrt{R^2 - 4a^2})^{2n} - (2a)^{2n}} \right]. \quad (33)$$

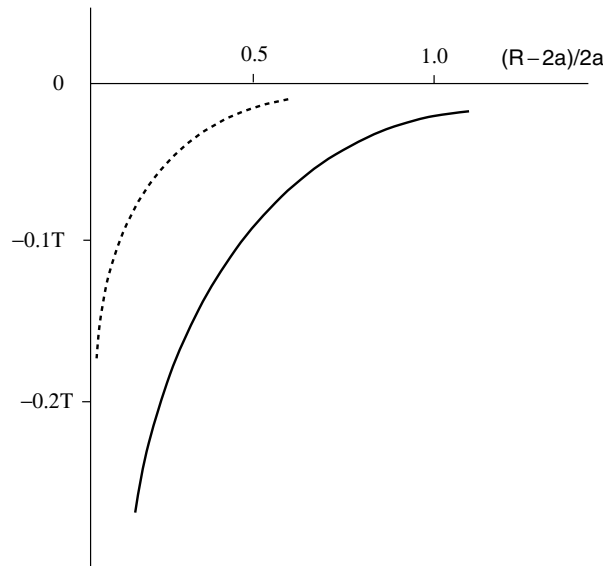


Figure 2. The fluctuation interactions of two cylindrical particles with the axes, of the same length as the diameter, directed perpendicular to two parallel plates, between which they are confined. The inter-plate distance is the same as the particle diameter. The dashed curve is $I(R)$ and the solid curve is the total fluctuation hydrodynamic interaction $U_{\text{vdW}}(R) + I(R)$.

At $\rho_0 = \rho$ in limiting cases one obtains

$$I(R) = T \begin{cases} -\ln(\pi^4/72) + (6/\pi^2)\sqrt{(R-2a)/a} & (R-2a) \ll 2a \\ -a^4/R^4 & 2a \ll R. \end{cases} \quad (34)$$

$I(R)$ is plotted in figure 2 as a dashed curve. The van der Waals interaction for cylindrical particles of length $2a$ can be obtained from equation (9) in the same way as equation (10) was derived. At $(R-2a) \ll 2a$, for two cylinders of length $2a$,

$$U_{\text{vdW}} = -\frac{\zeta(3)}{16} T \left(\frac{a}{R-2a} \right)^{3/2} \quad (\text{cylinders}). \quad (35)$$

The total interaction $U_{\text{vdW}}(R) + I(R)$ is shown in figure 2 by the solid curve, where the close-particles limit (35) is extrapolated up to the region $(R/2a - 1) \lesssim 1$. The interaction $I(R)$ is not influenced by the Coulomb effects in a bulk fluid, since it is mediated by fluctuations, corresponding to an incompressible fluid. Nevertheless, in a restricted geometry, for example between two charged plates, fluctuation motion in some direction can be restricted, which can modify the interaction $I(R)$.

6. The Fokker-Planck equation for two particles in a fluid

The low-frequency dynamic equation for particles

$$\zeta_0^{ij}(\vec{R})u_{1,2}^j + \zeta_1^{ij}(\vec{R})u_{2,1}^j = F_{1,2}^i \quad (36)$$

is non-linear due to a coordinate dependence of the friction coefficients in equation (36), which is called the hydrodynamic interaction [74]. The Fokker-Planck equation for the distribution function $W(\vec{R}, t)$ of two particles in a fluid can be derived similarly to equation (18).

The result is the following:

$$\frac{\partial W}{\partial t} = \frac{\partial}{\partial R_i} \zeta_{ij}^{-1} \left[W \frac{\partial U_{\text{tot}}(R)}{\partial R_j} + T \frac{\partial W}{\partial R_j} \right] \quad (37)$$

where $\zeta_{ij} = (\zeta_0^{ij} - \zeta_1^{ij})/2$ and the total interaction potential consists of a mean-field electrostatic part $U(R)$ and two fluctuation interactions:

$$U_{\text{tot}}(R) = U(R) + U_{\text{vdW}}(R) + I(R). \quad (38)$$

The friction tensor in the limit $a \ll R$ has the form [74]

$$\zeta_{ij} = 3\pi a \left[\left(1 + \frac{3a}{4R} + \frac{9a^2}{16R^2} \right) \delta_{ij} + \left(\frac{3a}{4R} + \frac{27a^2}{16R^2} \right) \frac{R_i R_j}{R^2} \right]. \quad (39)$$

For colloid experiments, which deal with long-time statistics [26, 27], the equilibrium distribution function $W \sim \exp(-U_{\text{tot}}(R)/T)$ is relevant. In optical tweezers experiments [28–31] two particles are initially fixed and the statistics of the initial motions after release is studied. If the friction coefficients $\zeta_{0,1}^{ij}$ were coordinate independent, the two methods would give the same interaction potential. But the situation becomes different for coordinate-dependent friction coefficients. If, at the moment $t = 0$, the distribution function was artificially localized by optical tweezers at the point \vec{R}_0 ($W = \delta(\vec{R} - \vec{R}_0)$), then the average inter-particle distance $\langle R_i \rangle = \int d^3 R_i W$ after release at $t = 0$ obeys the relation

$$\frac{\partial}{\partial t} \langle R_i \rangle = \zeta_{ij}^{-1} F_j^{ef} \quad (40)$$

where the effective force is

$$F_i^{ef} = -\frac{\partial U_{\text{tot}}}{\partial R_i} + T \zeta_{ip} \frac{\partial}{\partial R_q} \zeta_{pq}^{-1}. \quad (41)$$

This force consists of a potential part and the noise-induced drift; it is measured in the optical tweezers instant experiments rather than long-time-statistics experiments, which give only the first potential term. Under experimental conditions [29], the noise-induced drift is small. But if two particles are electrostatically fixed in the middle plane between two glass plates, separated by the length h ($R \ll h$), the effect of the noise-induced drift on the initial motion is not small:

$$F_i^{ef} = -\frac{\partial}{\partial R_i} \left[U_{\text{tot}}(R) + T \frac{3a}{4R} \right]. \quad (42)$$

This equation is valid in the limit of small particle radius compared to R . As one can see from equation (42), optical tweezers measurements can produce a deviation from a real interaction potential.

7. Discussion

As shown in this paper, for hard spheres (no mean-field interaction except an infinite repulsion on contact) in a fluid there are two types of hydrodynamic fluctuation force: (i) the van der Waals forces, mediated by fluctuations of sound waves (U_{vdW}), which are similar to the conventional (electromagnetic) van der Waals interactions, and (ii) forces due to a thermal drift of particles to the region with a bigger effective mass (I). Despite the van der Waals interaction (9) formally coinciding with the electromagnetic van der Waals formula at $\varepsilon \rightarrow \infty$ [65], the existence of such effect in hydrodynamics is not trivial, since a calculation on the basis of the hydrodynamic stress tensor leads to an incorrect conclusion in the absence of the effect (section 3). The interaction I is also of fluctuation origin. It has a simple mechanical explanation based on a particle spending more time in a region with a bigger mass, since there its velocity is

smaller. The proposed hydrodynamic fluctuation interactions provide a long-range (micron-scale) attraction of the order of kT in contrast to the conventional van der Waals attraction, which is negligible at the micron scale.

Charged colloidal particles in an electrolyte, strictly speaking, cannot be considered as hard spheres; nevertheless, the Coulomb effects weakly modify U_{vdW} , as shown in section 2. The interaction I is not modified by the Coulomb effects in a bulk fluid, but can be influenced by an electrostatic restriction of fluctuations in the direction perpendicular to charged confining plates.

The total interaction energy of two particles in a fluid is a sum of the Coulomb repulsive part (DLVO) [1,2] and the attractive potentials U_{vdW} and I , as plotted in figure 2. The character of the resulting interaction depends on the particle charges and the Debye length in a very delicate way. Formally, the power-law fluctuation attractions always prevail at some distance R_0 over the exponential repulsion. Nevertheless, when λ_D is not sufficiently small, the resulting potential minimum is far away and can be indistinguishable in experiments. Reference [76] reported an absence of attraction. A lucky choice of electrostatic parameters for observing fluctuation hydrodynamic forces corresponds to a close position of the minimum ($R_0 - 2a$) $\lesssim 2a$.

The experimentally observed attraction satisfies the $k_B T$ universality condition, i.e., it is of the order of $k_B T$ in various experiments. This universality is not a trivial property, since electrostatic and hydrodynamic mean-field energies are a few orders of magnitude bigger than those at room temperature. The kT universality leads to there being a selection of possible attraction mechanisms. Perhaps the best candidate satisfying this universality is an attraction mediated by thermal fluctuations of some physical quantities. Since the two mechanisms proposed above both lead to attraction of the order of $k_B T$, they are probably relevant in the interpretation of experimental data on attraction. The next step is to study U_{vdW} and I at all R for spherical particles in a bulk fluid and for a confined geometry. The contribution of fluctuating surface waves to the formation of an attraction of particles at liquid–air [8] and liquid–liquid [33] interfaces should increase the attraction effect.

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