Fluid-mechanical and electrical fluctuation forces in colloids

D. Drosdoff and A. Widom
Physics Department, Northeastern University, Boston, Massachusetts 02115, USA
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Fluctuations in fluid velocity and fluctuations in electric fields may both give rise to forces acting on small particles in colloidal suspensions. Such forces in part determine the thermodynamic stability of the colloid. At the classical statistical thermodynamic level, the fluid velocity and electric field contributions to the forces are comparable in magnitude. When quantum fluctuation effects are taken into account, the electric-fluctuation-induced van der Waals forces dominate those induced by purely fluid-mechanical motions. The physical principles are applied in detail for the case of colloidal particle attraction to the walls of the suspension container and more briefly for the case of forces between colloidal particles.

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I. INTRODUCTION

Fluctuations in thermodynamic field parameters may give rise to forces [1–6] acting on colloidal particles. Examples of such field parameters include velocity fields [7] within the fluid surrounding the particle and local electric fields. Our purpose is to examine the magnitudes of these two force effects. We seek to ascertain which of these forces has the dominant effect on the thermodynamic properties of colloidal suspensions.

The classical statistical thermodynamic contribution to fluctuations forces is scaled by the thermal energy k_BT. The forces due to quantum-mechanical zero-point fluctuations involve a frequency scale ω_∞ of motion and are thereby scaled by the energy quantum $\hbar\omega_\infty$. The total magnitude of such forces depends upon whether or not the fluctuations are classical or quantum mechanical in nature. We find for temperatures in the neighborhood of room temperature that the electric field fluctuation force [8–15] dominates the hydrodynamic fluctuation force [16] in the fully quantum-mechanical theory.

The Einstein theory of purely *classical* statistical thermodynamic fluctuation forces will be reviewed in Sec. II. The general results are employed for the specific example of the force on a colloidal spherical particle due to a neighboring hard wall. The hydrodynamic case is discussed in Sec. III while the electric field case is discussed in Sec. IV. The general theory of quantum-mechanical fluctuations is explored in Sec. V and the frequency scales of both fluid mechanical and electrical fluctuations are considered in Sec. VI. The frequency scales are such that the fluid-mechanical fluctuation forces are classical while the electric dipole fluctuation forces are quantum mechanical. The latter thereby dominate the former as discussed in Sec. VII. Although the electric field *static* quantum fluctuation forces dominate the classical fluid *static* fluctuation forces, the fluid forces are nonetheless observable. If the bandwidth of experimental observations of Brownian motion coincides with a frequency regime wherein fluid mechanics holds true, then fluid fluctuation forces may be (and have been) measured. This point is discussed in Sec. VIII wherein the formula for the fluid and electrical fluctuation forces are exhibited for two well separated spheres. In the concluding section, the electric fluctuation forces are shown to more strongly determine the phase properties of a colloid, i.e., whether the colloidal particles will form a smooth colloidal suspension or whether the colloidal particles will undergo phase separation.

II. STATISTICAL THERMODYNAMICS

Consider two coordinate sets $Q=(Q_1,\ldots,Q_m)$ and $X=(X_1,\ldots,X_n)$. For the moment, let us fix Q and assume that X undergoes classical thermal fluctuations [17]. The Einstein probability [18] P of exhibiting a deviation $\Delta X=(\Delta X_1,\ldots,\Delta X_n)$ from thermal equilibrium has a Gaussian form determined by an activation free energy ΔF. The activation free energy is the minimum isothermal work done on the system by the environment in order to produce the fluctuation ΔX, whence it follows that

$$P \propto e^{-\Delta F/k_BT},$$

$$\Delta F = \frac{1}{2}\sum_{j,k}^{n} G^{-1}{}_{jk}(Q)\Delta X_j \Delta X_k, \tag{1}$$

wherein the matrix $\|G_{jk}(Q)\|$ describes an effective Hooke's law compliance. The static classical fluctuation-response theorem dictates that

$$\overline{\Delta X_i \Delta X_j} = k_BTG_{ij}(Q), \tag{2}$$

which follows directly from Eq. (1). The forces $f=(f_1,\ldots,f_m)$ conjugate to $Q=(Q_1,\ldots,Q_m)$ may be derived from the free energy

$$f_l = -\frac{\partial \Delta F}{\partial Q_l} = -\frac{1}{2}\sum_{j,k}^{n} \frac{\partial G^{-1}{}_{jk}(Q)}{\partial Q_l}\Delta X_j \Delta X_k. \tag{3}$$

The mean value of this fluctuation force

$$\bar{f}_l = -\frac{1}{2}\sum_{j,k}^{n} \frac{\partial G^{-1}{}_{jk}(Q)}{\partial Q_l}\overline{\Delta X_j \Delta X_k} \tag{4}$$

may be evaluated via Eq. (2) as

$$\bar{f}_l = -\frac{k_BT}{2}\sum_{j,k}^{n} G_{kj}(Q)\frac{\partial G^{-1}{}_{jk}(Q)}{\partial Q_l},$$

$$\bar{f}_l = \frac{k_BT}{2}\frac{\partial}{\partial Q_l}\ln[\det\|G_{jk}(Q)\|]. \tag{5}$$

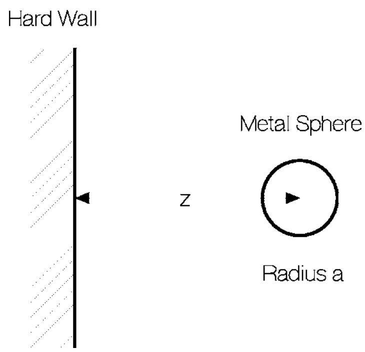

FIG. 1. Shown is a metal sphere of radius a submerged in a fluid at a distance z from a hard wall. We seek to compute the fluctuation forces on the sphere due to the presence of the wall in part to establish the physically dominant contributions.

Employing a reference matrix $\|G_{jk}^{(0)}\|$ that is *independent* of Q, we may write Eq. (5) in terms of an effective potential $U(Q)$, i.e.,

$$\bar{f}_l = -\frac{\partial U(Q)}{\partial Q_l},$$

$$U(Q) = \frac{k_B T}{2} \ln \det[G^{-1}(Q) G^{(0)}]. \tag{6}$$

If $G(Q)$ obeys the Green's function matrix equation

$$G(Q) = G^{(0)} + G^{(0)} \Sigma(Q) G(Q), \tag{7}$$

then

$$U(Q) = \frac{k_B T}{2} \ln \det[1 - G^{(0)} \Sigma(Q)]$$

$$U(Q) = -\frac{k_B T}{2} \sum_{n=1}^{\infty} \frac{1}{n} \mathrm{Tr}[G^{(0)} \Sigma(Q)]^n. \tag{8}$$

The central result of this section resides in Eqs. (6)–(8) which describe the effective potential $U(Q)$ of *classical* statistical thermodynamic fluctuation forces in terms of the determinants of the compliance matrices. The quantum-mechanical version of fluctuation forces will be briefly discussed in the following work where we will explicitly compute the situation shown in Fig. 1. We consider two contributions to the fluctuation forces between the sphere and the wall, namely, (i) fluid velocity fluctuations and (ii) electric field fluctuations.

III. FLUID VELOCITY FLUCTUATIONS

For a single metal sphere (in a fluid) with momentum $\mathbf{p}$ and position $\mathbf{r}$, the minimum isothermal work required to produce the momentum is given by the total kinetic energy

$$\Delta F = \mathbf{p} \cdot \frac{1}{2\mathsf{M}(\mathbf{r})} \cdot \mathbf{p} = \frac{1}{2} \sum_{j,k}^{3} M^{-1}{}_{jk}(\mathbf{r}) p_j p_k, \tag{9}$$

where the mass matrix $\|M_{jk}(\mathbf{r})\|$ plays the role of the compliance in Eq. (1). The static fluctuation response Eq. (2) now reads as the equipartition theorem

$$\overline{p_j p_k} = k_B T M_{jk}(\mathbf{r}). \tag{10}$$

Let us consider the mass matrix $\|M_{jk}(\mathbf{r})\|$ in more detail.

If the sphere were very far from the wall $z=\infty$, then the mass matrix would be given by

$$M^{(0)}{}_{jk} = \delta_{jk}(M + \mu) = \delta_{jk}\left(M + \frac{2\pi\rho a^3}{3}\right), \tag{11}$$

wherein ρ is the mass density of the fluid and M is the mass of the sphere. The Euler mass μ, which is half the mass of the displaced fluid, has the following physical interpretation [19]. The kinetic energy of a sphere moving slowly with velocity $\mathbf{v}$ through an infinite bulk fluid is given by

$$K_{total} = K_{particle} + K_{fluid} = \frac{1}{2} \sum_{j,k}^{3} M_{jk}^{(0)} v_j v_k,$$

$$K_{total} = \frac{1}{2} M |\mathbf{v}|^2 + \frac{1}{2} \mu |\mathbf{v}|^2. \tag{12}$$

The mass M enters into the particle kinetic energy $K_{particle} = (1/2) M |\mathbf{v}|^2$. If the particle moves through the fluid, then the fluid exhibits a dipolar back flow contribution $K_{fluid} = (1/2) \mu |\mathbf{v}|^2$ to the total kinetic energy.

When the sphere is at distance $z < \infty$ from the wall, the back-flow fluid mass current vector must have a zero component normal to the boundaries. The fluid kinetic energy thereby depends on z. In the limit in which $z \gg a$, the mass matrix $\|M_{jk}(z)\|$ of the sphere is well known [20]. It is

$$\begin{pmatrix} M + \mu_\perp(z) & 0 & 0 \\ 0 & M + \mu_\perp(z) & 0 \\ 0 & 0 & M + \mu_\parallel(z) \end{pmatrix}, \tag{13}$$

wherein

$$\mu_\perp(z) = \mu\left[1 + \frac{3}{16}\left(\frac{a}{z}\right)^3 + \cdots\right],$$

$$\mu_\parallel(z) = \mu\left[1 + \frac{3}{8}\left(\frac{a}{z}\right)^3 + \cdots\right]. \tag{14}$$

The potential energy of the sphere induced by fluid momentum fluctuations is thereby

$$U_{fluid}(z) = \frac{k_B T}{2} \ln \det[M^{-1}(z) M^{(0)}], \tag{15}$$

which reads

$$U_{fluid}(z) = -\frac{3\mu k_B T}{8(M + \mu)}\left(\frac{a}{z}\right)^3 + \cdots$$

$$\text{with} \quad \mu = \frac{2\pi\rho a^3}{3} \quad \text{and} \quad a \ll z. \tag{16}$$

From fluid velocity thermodynamic fluctuations, it follows that the sphere will be attracted to the wall with a potential proportional to the temperature and inversely proportional to the third power of the distance from the wall.

IV. ELECTRIC DIPOLE MOMENT FLUCTUATIONS

If one places a neutral conducting sphere in the neighborhood of a perfectly conducting wall, then charge rearrangements within the sphere will create fluctuating electric dipole moments. The fluctuating dipole moments will induce an attraction between the sphere and the wall as will now be shown. We again assume that the sphere radius is much less than the distance between the sphere and the wall $a \ll z$. The dipole moment $\mathbf{d}$ of the conducting sphere will induce a surface charge on the perfectly conducting wall usually described in terms of an "image" dipole moment $\mathbf{d}_i$. The interaction between the dipole moment and the image is given by

$$\Delta F = \frac{\mathbf{d} \cdot \mathbf{d}_i - 3(\mathbf{d} \cdot \mathbf{n})(\mathbf{d}_i \cdot \mathbf{n})}{16z^3}. \tag{17}$$

The image dipole moment is related to the dipole moment of the sphere via

$$d_z = d_{iz}, \quad d_x = -d_{ix}, \quad \text{and} \quad d_y = -d_{iy}, \tag{18}$$

so that the interaction free energy reads

$$\Delta F = -\left(\frac{d_x^2 + d_y^2 + 2d_z^2}{16z^3}\right). \tag{19}$$

Taking the thermodynamic average $U_{dipole} = \overline{\Delta F}$ yields

$$U_{dipole}(z) = -\left(\frac{C_T}{16z^3}\right) + \cdots \quad (a \ll z),$$

$$C_T = \overline{d_x^2 + d_y^2 + 2d_z^2}, \tag{20}$$

wherein the Hamaker constant [21] C_T is determined by the polarizability α_T via

$$k_B T \alpha_T = \overline{d_x^2} = \overline{d_y^2} = \overline{d_y^2} \quad (a \ll z),$$

$$C_T = 4\alpha_T = 4a^3 \quad \text{(conducting sphere)}. \tag{21}$$

Altogether, the final attractive potential energy is

$$U_{dipole}(z) = -\frac{k_B T}{4}\left(\frac{a}{z}\right)^3 + \cdots \quad (a \ll z). \tag{22}$$

Note the similarity between the fluid fluctuation potential in Eq. (16) and the dipole fluctuation potential in Eq. (22). Both potentials obey $U \propto -[k_B T(a/z)^3]$ with proportionality constants of similar order unity. It would at this stage appear that the strengths of electrical and fluid-mechanical fluctuation forces are comparable in magnitude. However, this has only been proven at the classical statistical thermodynamic level of computation. Let us now consider quantum-mechanical fluctuations.

V. QUANTUM FLUCTUATIONS

In the quantum-mechanical theory of fluctuations, the *static* response function $k_B T G_{ij}(Q)$ at zero temperature in Eq. (2) is replaced by a complex-frequency- (ζ-) dependent response function $k_B T G_{ij}(Q,\zeta)$ which obeys a dispersion relation with $\Im m \zeta > 0$ of the form

$$G_{ij}(Q,\zeta) = \frac{2}{\pi}\int_0^\infty \frac{\omega \, \mathrm{Im}\, G_{ij}(Q,\omega + i0^+) d\omega}{(\omega^2 - \zeta^2)}. \tag{23}$$

The static response function is then the zero-frequency limit

$$G_{ij}(Q) \equiv \lim_{\zeta \to 0} G_{ij}(Q,\zeta),$$

$$G_{ij}(Q) \equiv \frac{2}{\pi}\int_0^\infty \mathrm{Im}\, G_{ij}(Q,\omega + i0^+)\frac{d\omega}{\omega}. \tag{24}$$

The power spectrum of quantum noise corresponding to the frequency-dependent response function $G_{ij}(Q,\zeta)$ obeys the quantum-mechanical fluctuation dissipation theorem

$$\frac{1}{2}\langle\{\Delta X_i(t), \Delta X_j(0)\}\rangle = \int_{-\infty}^{\infty} S_{ij}(Q,\omega) e^{-i\omega t} d\omega,$$

$$S_{ij}(Q,\omega) = \frac{E_T(\omega)}{\pi\omega}\, \mathrm{Im}\, G_{ij}(Q,\omega + i0^+),$$

$$E_T(\omega) = \left(\frac{\hbar\omega}{2}\right)\coth\left(\frac{\hbar\omega}{2k_B T}\right). \tag{25}$$

Employing the identity

$$\frac{E_T(\omega)}{k_B T} = \sum_{n=-\infty}^{\infty} \frac{\omega^2}{\omega^2 + \omega_n^2},$$

$$\omega_n = \frac{2\pi k_B T n}{\hbar}, \tag{26}$$

along with Eqs. (23), (25), and (26), implies

$$\frac{1}{2}\langle \Delta X_i \Delta X_j + \Delta X_j \Delta X_i \rangle = k_B T \sum_{n=-\infty}^{\infty} G_{ij}(Q, i|\omega_n|). \tag{27}$$

It is worthwhile to compare the quantum-mechanical fluctuation Eq. (27) to the classical Eq. (2):

$$\overline{\Delta X_i \Delta X_j} = k_B T G_{ij}(Q,0) \equiv k_B T G_{ij}(Q). \tag{28}$$

For a single fluctuating variable, say $X = \Sigma_i a_i X_i$, one obtains from Eq. (27) the expression

$$\langle \Delta X^2 \rangle = k_B T \sum_{n=-\infty}^{\infty} G(Q, i|\omega_n|),$$

$$G(Q,\zeta) = \frac{2}{\pi}\int_0^\infty \frac{\omega \, \mathrm{Im}\, G_{ij}(Q,\omega + i0^+) d\omega}{\omega^2 - \zeta^2}. \tag{29}$$

Employing the inequality

$$\frac{1}{\omega^2 + \omega_n^2} \leq \frac{1}{\omega_n^2}, \tag{30}$$

and the definition for the X-motion frequency scale ω_∞,

$$\omega_\infty^2 = \left(\frac{2}{\pi G(Q,0)}\right)\int_0^\infty \omega \,\mathrm{Im}\, G(Q,\omega+i0^+)d\omega, \qquad (31)$$

in Eq. (29) yields the upper bound

$$|\langle \Delta X^2\rangle - k_B T G(Q,0)| \le 2\omega_\infty^2 k_B T G(Q,0)\sum_{n=1}^{\infty}\frac{1}{\omega_n^2}, \qquad (32)$$

i.e.,

$$\left|\frac{\langle \Delta X^2\rangle}{k_B T G(Q,0)} - 1\right| \le \frac{1}{12}\left(\frac{\hbar\omega_\infty}{k_B T}\right)^2. \qquad (33)$$

From the inequality in Eq. (33) we find that a sufficient condition for employing *classical* fluctuations is

$$\langle \Delta X^2\rangle \approx k_B T G(Q,0) \quad \text{if } \hbar\omega_\infty \ll k_B T \qquad (34)$$

in agreement with the classical Eq. (2).

VI. FLUCTUATION FREQUENCIES

Our purpose is to estimate ω_∞ for both the fluid-mechanical and the electrical fluctuation forces. We conclude for "room temperature" that

$$\hbar\omega_\infty \ll k_B T, \quad \text{fluid mechanics (classical)},$$

$$\hbar\omega_\infty \gg k_B T, \quad \text{dipole moments (quantum)}. \qquad (35)$$

The derivations follow.

A. Effective mass sum rule

If $\mathbf{p}$ denotes the momentum of a colloidal particle within a fluid, then the dynamical mass of the particle obeys the Kubo formula

$$\mathsf{M}_{ij}(\zeta) = \frac{i}{\hbar}\int_0^\infty \langle [p_i(t),p_j(0)]\rangle e^{i\zeta t}dt. \qquad (36)$$

From Eq. (36) one finds

$$\frac{i}{\hbar}\langle [p_i(t),p_j(0)]\rangle = \frac{2}{\pi}\int_0^\infty \mathrm{Im}\,\mathsf{M}_{ij}(\omega+i0^+)\sin(\omega t)d\omega, \qquad (37)$$

from which follows the equal time commutation sum rule

$$\frac{i}{\hbar}\langle [\dot{p}_i,p_j]\rangle = \frac{2}{\pi}\int_0^\infty \omega\,\mathrm{Im}\,\mathsf{M}_{ij}(\omega+i0^+)d\omega. \qquad (38)$$

The imaginary part of the mass given in Eq. (38) is related to the real part of the mechanical impedance by

$$\mathrm{Im}\,\mathsf{M}_{ij}(\omega+i0^+) = \frac{\mathrm{Re}\,\mathsf{Z}_{ij}(\omega+i0^+)}{\omega}, \qquad (39)$$

where Z_{ij} is the mechanical impedance. For example, a single sphere in a bulk fluid will have a mechanical impedance appropriately derived from a frequency-dependent viscosity in the form of Stokes law

$$\mathsf{Z}_{ij}(\zeta) = 6\pi a\,\eta(\zeta)\delta_{ij}. \qquad (40)$$

For static colloidal particles, the viscosity is not directly measured through the diffusion coefficient [22],

$$\mathsf{D}_{ij} = k_B T \mathsf{Z}_{ij}^{-1}. \qquad (41)$$

However, the viscosity contributes to the interacting fluctuation forces via the nonzero Matsubara frequency [23,24] terms in Eq. (27). If the microscopic force $\dot{\mathbf{p}}=\mathbf{f}$ on the colloidal particle is derivable from a potential $\mathbf{f}=-\mathrm{grad}V$, then the sum rule Eq. (38) obeys

$$\frac{2}{\pi}\int_0^\infty \omega\,\mathrm{Im}\,\mathsf{M}(\omega+i0^+)d\omega = \langle \mathrm{grad}\,\mathrm{grad}\,V\rangle. \qquad (42)$$

On the other hand, from the dispersion relation

$$\mathsf{M}(\zeta) = \frac{2}{\pi}\int_0^\infty \frac{\omega\,\mathrm{Im}\,\mathsf{M}(\omega+i0^+)d\omega}{(\omega^2-\zeta^2)} \quad \text{if Im } \zeta > 0, \qquad (43)$$

it follows that the static mass obeys

$$\mathsf{M} = \frac{2}{\pi}\int_0^\infty \mathrm{Im}\,\mathsf{M}(\omega+i0^+)\frac{d\omega}{\omega}. \qquad (44)$$

From Eqs. (42) and (44) one computes the Hooke's law frequency tensor

$$\mathbf{\Omega}_\infty^2 = \mathsf{M}^{-1}\cdot\langle \mathrm{grad}\,\mathrm{grad}\,V\rangle. \qquad (45)$$

For a given principal X direction of the tensor, the hydrodynamic frequency scale is given by

$$\omega_\infty^2 = \frac{1}{M}\left\langle \frac{\partial^2 V}{\partial X^2}\right\rangle. \qquad (46)$$

The mass of the colloidal particle is proportional to the volume of the particle. The interaction V between the colloidal particle and the fluid is spatially nonzero only in the neighborhood of the particle surface. Thus, $\langle \partial^2 V/\partial X^2\rangle$ is proportional to the contact surface area. If the number of atoms within the colloidal particle is denoted by N, then the number of atoms on the colloidal particles surface is proportional to $N^{2/3}$. The frequency in Eq. (46) may be estimated by

$$\omega_\infty^2 \sim N^{-1/3}\omega_{vib}^2 \qquad (47)$$

where ω_{vib} is a typical atomic vibrational (say phonon) frequency. As a numerical example, let us consider a colloidal particle with $N\sim 10^{10}$ and with a vibrational frequency obeying $\hbar\omega_{vib}\sim k_B T$ at room temperature. For such a colloidal particle $\hbar\omega_\infty \sim 0.02 k_B T$ which is in the classical regime of Eq. (35).

B. Polarizability sum rule

If $\mathbf{d}$ denotes the electric dipole moment of a colloidal particle within a fluid, then the polarizability of the particle obeys

$$\alpha_{ij}(\zeta) = \frac{i}{\hbar}\int_0^\infty \langle [d_i(t),d_j(0)]\rangle e^{i\zeta t}dt. \qquad (48)$$

From Eq. (48) one finds

$$\frac{i}{\hbar}\langle[d_i(t),d_j(0)]\rangle = \frac{2}{\pi}\int_0^\infty \text{Im}\,\alpha_{ij}(\omega+i0^+)\sin(\omega t)d\omega, \tag{49}$$

from which follows the equal time commutation sum rule

$$\frac{i}{\hbar}\langle[\dot{d}_i,d_j]\rangle = \frac{2}{\pi}\int_0^\infty \omega\,\text{Im}\,\alpha_{ij}(\omega+i0^+)d\omega. \tag{50}$$

The electric dipole moment and its rate of change, summed over all the charges within the colloidal particle, is given by

$$\mathbf{d} = e\sum_k z_k\mathbf{r}_k,$$

$$\dot{\mathbf{d}} = e\sum_k z_k\dot{\mathbf{r}}_k = e\sum_k z_k\mathbf{v}_k. \tag{51}$$

The equal time commutators $[\mathbf{v}_k,\mathbf{r}_l]=-i\hbar 1\,\delta_{kl}(1/M_k)$ and $[\dot{d}_i,d_j]=-i\hbar\delta_{ij}\Sigma_k(e^2z_k^2/M_k)$ imply

$$\frac{2}{\pi}\int_0^\infty \omega\,\text{Im}\,\alpha_{ij}(\omega+i0^+)d\omega = \delta_{ij}\sum_k\left(\frac{e^2z_k^2}{M_k}\right). \tag{52}$$

From the dispersion relation (with $\Im\mathrm{m}\zeta>0$)

$$\alpha_{ij}(\zeta) = \frac{2}{\pi}\int_0^\infty \frac{\omega\,\text{Im}\,\alpha_{ij}(\omega+i0^+)d\omega}{(\omega^2-\zeta^2)}, \tag{53}$$

it follows that the static polarizability obeys

$$\alpha_{ij} \equiv \alpha_{ij}(0) = \frac{2}{\pi}\int_0^\infty \text{Im}\,\alpha_{ij}(\omega+i0^+)\frac{d\omega}{\omega}. \tag{54}$$

For a spherical colloidal particle,

$$\omega_\infty^2 = \left(\frac{2}{\pi\alpha_T}\right)\int_0^\infty \omega\,\text{Im}\,\alpha(\omega+i0^+)d\omega. \tag{55}$$

For a conducting sphere of volume $V=(4\pi a^3/3)$ the frequency scale

$$\omega_\infty^2 = \frac{e^2}{\alpha_T}\sum_k\left(\frac{z_k^2}{M_k}\right) = \frac{4\pi e^2}{3V}\sum_k\left(\frac{z_k^2}{M_k}\right). \tag{56}$$

The plasma frequency for a portion of condensed matter

$$\Omega_p^2 = \frac{4\pi e^2}{V}\sum_k\left(\frac{z_k^2}{M_k}\right), \tag{57}$$

is dominated by electronic oscillations $\Omega_p^2 \approx (4\pi ne^2/m)$ wherein m and n represent, respectively, the electron mass and density of electrons per unit volume. The frequency scale for dipolar fluctuations is then

$$\omega_\infty^2 = \frac{\Omega_p^2}{3}. \tag{58}$$

A metallic plasma frequency is of order $(\hbar\Omega_p/k_B)\sim 10^5$ K. Equation (58) then implies $\hbar\omega_\infty \gg k_BT$, as in Eq. (35), for temperatures near room temperature.

VII. QUANTUM DIPOLAR FORCES

It has been found at room temperature that fluid fluctuation forces are classical and electric fluctuation forces are quantum mechanical. An estimate of the quantum-mechanical dipolar potential follows. The energy of interaction between a conducting sphere and wall due to dipole quantum fluctuations is found by summing the polarizability over Matsubara frequencies as in Sec. V; i.e.,

$$U_{dipole}(z) = \frac{\varpi_0}{z^3},$$

$$\varpi_0 = -\frac{k_BT}{4}\sum_{-\infty}^{\infty}\alpha(i|\omega_n|). \tag{59}$$

If we take into account the dielectric response function $\varepsilon(\zeta)$ of the fluid then

$$U_{dipole}(z) = \frac{\varpi}{z^3},$$

$$\varpi = -\frac{k_BT}{4}\sum_{-\infty}^{\infty}\frac{\alpha(i|\omega_n|)}{\varepsilon(i|\omega_n|)}. \tag{60}$$

The inclusion of the screening dipoles of the liquid in between the sphere and the wall leads to a reduction of the coupling strength by the fraction

$$f = \frac{\varpi}{\varpi_0} = \frac{\sum_{-\infty}^{\infty}[\alpha(i|\omega_n|)/\varepsilon(i|\omega_n|)]}{\sum_{-\infty}^{\infty}\alpha(i|\omega_n|)} \tag{61}$$

which (as will be shown in what follows) only slightly decreases the attractive effect.

A simple model for the polarizability will be found in order to estimate the potential energy in Eq. (59). We assume that the polarizability has a single pole at frequency ω_∞; i.e.,

$$\alpha(\zeta) \approx \frac{\alpha_T\omega_\infty^2}{\omega_\infty^2-\zeta^2}. \tag{62}$$

The residue at the pole has been fixed so that $\alpha(0)\equiv\alpha_T$. Substituting Eq. (62) in Eq. (59) one finds for the interaction potential

$$U_{dipole}(z) \approx -\left(\frac{k_BT}{4z^3}\right)\sum_{n=-\infty}^{\infty}\frac{\alpha_T\omega_\infty^2}{\omega_\infty^2+\omega_n^2},$$

$$U_{dipole}(z) \approx -\left(\frac{\hbar\omega_\infty\alpha_T}{8z^3}\right)\coth\left(\frac{\hbar\omega_\infty}{2k_BT}\right). \tag{63}$$

Since $\hbar\omega_\infty \gg k_BT$ one finds

$$U_{dipole}(z) = -\frac{\hbar\omega_\infty\alpha_T}{8}\left(\frac{1}{z}\right)^3 = -\frac{\hbar\omega_\infty}{8}\left(\frac{a}{z}\right)^3. \tag{64}$$

A simple pole model for the inverse dielectric response of the fluid $\varepsilon^{-1}(\zeta)$ takes the form $\varepsilon(\zeta)=1-(\tilde{\Omega}_p/\zeta)^2$ wherein $\tilde{\Omega}_p$ is the plasma frequency of the liquid. Employing this approximation in Eqs. (61) and (62) yields (after some tedious algebra) the quantum interaction reduction factor

$$\lim_{T\to 0} f \approx \frac{1}{1+|\tilde{\Omega}_p/\omega_\infty|} \sim 1 \tag{65}$$

since the plasma frequency entering into the insulating fluid $\varepsilon(\zeta)$ is much smaller than the plasma frequency entering into the conducting spherical $\alpha(\zeta)$.

By comparing Eq. (64) to Eq. (16), it seems that the dipole fluctuation forces are much larger than the fluid fluctuation forces. We find that

$$\frac{U_{fluid}(z)}{U_{dipole}(z)} = \left(\frac{3\mu}{f(M+\mu)}\right)\frac{k_BT}{\hbar\omega_\infty}. \tag{66}$$

The term on the right-hand side of Eq. (66) in large parentheses is of order unity. Thus

$$\frac{U_{fluid}(z)}{U_{dipole}(z)} \sim \frac{k_BT}{\hbar\omega_\infty} \ll 1. \tag{67}$$

Using typical plasma frequencies for metals, $\omega_\infty=(\Omega_p/\sqrt{3}) \sim (10^{16}/\text{s})$ we see that the inequality in Eq. (67) holds by a very large margin. If the colloidal particle mass density is large compared with the fluid mass density, i.e., $M \gg \mu$, then fluid fluctuation forces are further reduced relative to the already dominant electrodynamic fluctuation forces.

We note, in passing, that the thermal quantum coherence length scale for electromagnetic fluctuations is $\lambda_T = (\hbar c/k_BT)$ which is $\sim 7\ \mu\text{m}$ at room temperature. Retardation effects imply that for distances large compared with the thermal quantum coherence length λ_T, fluctuation forces are purely classical. For distances less than λ_T quantum fluctuations are important. For length scales of importance in colloids, electromagnetic quantum fluctuations are thereby dominant. For example, if the distance to the wall is $z\sim 5\ \mu\text{m}$ and the sphere radius is $a\sim 0.5\ \mu\text{m}$, then the electromagnetic fluctuation force is quantum mechanical. On the other hand, to obtain λ_T for fluid fluctuations one must replace light velocity by sound velocity, which makes $\lambda_T(\text{fluid})$ extremely small. We again conclude that fluid fluctuation forces arise *only* from classical thermal fluctuations. As for the quantum electrodynamic fluctuations, for distances less than the thermal coherence length but possibly larger than an optical wavelength scale λ_0, retardation would lessen the effect of quantum fluctuations by a factor (λ_0/z) which at the micrometer length scales of interest is not much less than unity. Equation (67) is thereby still valid.

VIII. FLUID MOTION

The static classical fluid force between two spherical colloidal particles separated by r may be shown to be derived from the potential

$$U_{fluid}(r) = -3\pi^2\left(\frac{k_BT\rho^2a^6}{(\mu+M)^2}\right)\left(\frac{a}{r}\right)^6 \quad (r \gg a), \tag{68}$$

wherein ρ is the fluid mass density, μ is the Euler mass, and M, is the bare mass of the colloidal particle. The above potential is derived from a long time scale statistical averaging over those fluid-mechanical fluctuations which otherwise induce colloidal particle Brownian motion. Direct observation [25,26] of Brownian motion forces require shorter time scales. Typical experimental bandwidths for micrometer scale colloidal particle size are about 0.1 MHz.

For two identical metallic colloidal particles separated by r, the quantum electric field fluctuation potential is given by

$$U_{dipole}(r) = -\frac{3k_BT}{r^6}\sum_{n=-\infty}^{\infty}\alpha(i|\omega_n|)\alpha(i|\omega_n|) \quad \text{for } r \gg a. \tag{69}$$

In the single-pole approximation for $\alpha(\zeta)$ with the metallic $\alpha(0)=a^3$ we find that

$$U_{dipole}(r) \approx -\left(\frac{3\hbar\omega_\infty}{2}\right)\left(\frac{a}{r}\right)^6 \quad \text{for} \quad r \gg a \quad \text{and} \quad \hbar\omega_\infty \gg k_BT. \tag{70}$$

Note that

$$\frac{U_{fluid}(r)}{U_{dipole}(r)} \sim \left(\frac{\rho^2a^6}{(\mu+M)^2}\right)\left(\frac{k_BT}{\hbar\omega_\infty}\right) \ll 1. \tag{71}$$

The very large magnitude of ω_∞ forbids direct observation of the fluid fluctuations.

It is difficult, but not impossible, to estimate both electrodynamic and fluid-mechanical fluctuation forces in a regime wherein the sphere is very close to the wall ($z=a+h$ with $h \ll a$) and/or two spheres are very close to each other ($r=2a+h$ with $h \ll a$). We refer to this regime as the "close regime." For the sphere quite close to the wall

$$U_{fluid\ wall}(h) \approx -\frac{k_BT}{2}\ln\left(\frac{a}{h}\right) + \text{const} \quad (h \ll a), \tag{72}$$

yielding the fluid fluctuation force

$$F_{fluid\ wall} \approx -\frac{k_BT}{2h} \quad (h \ll a). \tag{73}$$

In the close regime for the electrodynamic fluctuation forces

$$U_{electric\ wall}(h) \approx -\frac{27}{192}\left(\frac{\hbar\omega_\infty a}{h}\right) \quad (h \ll a), \tag{74}$$

yielding the force of attraction

$$F_{electric\ wall} \approx -\frac{27}{192}\left(\frac{\hbar\omega_\infty a}{h^2}\right) \quad (h \ll a). \tag{75}$$

The force ratio in the close regime is

$$\frac{F_{fluid\ wall}}{F_{electric\ wall}} \sim \left(\frac{k_BTh}{\hbar\omega_\infty a}\right) \ll 1, \tag{76}$$

since both inequalities $k_BT \ll \hbar\omega_\infty(\text{electric})$ and $h \ll a$ hold true by a large margin. Similarly, for two spheres wherein the closest point from one sphere to another is given by $h \ll a$, one finds a similar ratio

$$\frac{F_{fluid\ spheres}}{F_{electric\ spheres}} \sim \left(\frac{k_B T h}{\hbar \omega_\infty a}\right) \ll 1. \qquad (77)$$

In regimes in which colloidal objects are very close to one another, the dominance of electrodynamic fluctuation forces over fluid fluctuation forces is complete due to both coupling strengths $k_B T \ll \hbar\omega_\infty$ and geometry $h \ll a$. The electrical fluctuation forces are thereby of more importance for applications on a micrometer to nanometer length scale.

IX. CONCLUSIONS

The general theory of quantum-mechanical fluctuations was discussed with particular emphasis on computing the frequency scales of motion from sum rules. The frequency scales determine whether the fluctuations and thereby the forces are classical or quantum mechanical in nature. We have shown how fluctuations in fluid velocity fields and in electric fields give rise to forces exerted on colloidal particles. Fluctuation forces were computed in detail for the case of colloidal particles attracted to the walls of the suspension container. The resulting van der Waals force has the form

$$U_{wall}(z) = -U_1(a/z)^3 \quad \text{for } z \gg a. \qquad (78)$$

The electric field fluctuation contribution to U_1 dominates the fluid-mechanical contribution to U_1 as in Eq. (67). The long ranged static attraction between two spherical particles of radius a separated by a distance r has the van der Waals form

$$U_{particle}(r) = -U_0(a/r)^6 \quad \text{for } r \gg a. \qquad (79)$$

The electric field fluctuation contribution to U_0 dominates the fluid-mechanical contribution to U_0 as in Eq. (71).

For the case of the fluid-mechanical fluctuation-induced forces, we have employed a model with a frequency-dependent mass which is equivalent to a frequency-dependent viscous damping coefficient. Previous fluid-mechanical experiments allow the Brownian particles to move and measure the dynamic correlations in the displacements and velocities. These occur on a time scale very slow compared with the time scales of electric field fluctuations. For that very reason, the quantum fluid fluctuations contribute a smaller amount to the static (long time averaged) fluid-induced Casimir forces. At the level of *classical* statistical thermodynamics, the fluid velocity and electric field contributions to the static potential are comparable. When quantum fluctuation effects are taken into account, the electric fluctuation contribution to the potentials dominates the fluid-mechanical contribution to the potentials as in Eqs. (67) and (71). The electric field fluctuation long ranged forces can be, and have been [27,28], observed by measuring phase separations in some colloidal suspensions. Further work on colloidal forces in still other geometries would be of general interest.

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