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Macroion virial contribution to the osmotic pressure in charge-stabilized colloidal suspensions

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Our interest goes to the different virial contributions to the equation of state of charged colloidal suspensions. Neglect of surface effects in the computation of the colloidal virial term leads to spurious and paradoxical results. This pitfall is one of the several facets of the danger of a naive implementation of the so called one component model, where the microionic degrees of freedom are integrated out to only keep in the description the mesoscopic (colloidal) degrees of freedom. On the other hand, due incorporation of wall induced forces dissolves the paradox brought forth in the naive approach, provides a consistent description, and confirms that for salt-free systems, the colloidal contribution to the pressure is dominated by the microionic one. Much emphasis is put on the no salt case but the situation with added electrolyte is also discussed.

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I. INTRODUCTION

In a complex mixture where several species with widely different characteristic time and space scales coexist, it is common practice to resort to a coarse grained description integrating from the partition function all degrees of freedom that do not belong to the main (larger) constituent [1–4]. This leads to a state dependent effective Hamiltonian for the main constituent, thereby allowing a one component model (OCM) description. The motivation for such a procedure is not only to facilitate contact with experiments, where most of the time the small constituents cannot be probed directly, but also to simplify the theoretical treatment. Indeed, one can then use the well developed statistical mechanics tools from the theory of simple liquids to study the OCM. This transposition from simple to complex fluids is, however, paved with practical difficulties, see, e.g., [5,6]. It is the purpose of the present paper to discuss one such pitfall arising in the context of charged colloidal suspensions.

The system we will consider is made up of N_c charged spherical hard particles (colloids) immersed in a solvent with dielectric constant ε, which fills a box with volume V limited by a neutral hard wall. The colloid's interior is assumed to have the same dielectric constant as the solvent. Each colloid bears a charge $Z_c e$ where e is the elementary charge and $Z_c \gg 1$. The medium outside the container is a structureless dielectric continuum with dielectric constant ε'. To ensure electroneutrality, the solution contains $N_c Z_c$ microscopic counterions, assumed monovalent. Additional microions may also be present due to the dissociation of an added salt and the total number of microions is denoted N_{micro}. The particles interact through Coulomb forces and hard sphere exclusion, although in the subsequent analysis, the hard-core interaction will turn out to be irrelevant.

The paper is organized as follows. In the situation where $\varepsilon = \varepsilon'$, we consider in Sec. II the different virial contributions to the equation of state. In the salt-free case, we argue that the colloidal contribution P_{ocm} has to be negligible compared to the microionic one (P_{micro}). We then show that a naive implementation of the OCM picture leads to a violation of the constraint $P_{\mathrm{ocm}} \ll P_{\mathrm{micro}}$. Section III for $\varepsilon = \varepsilon'$ and Sec. IV for $\varepsilon' < \varepsilon$ are devoted to the resolution of this apparent paradox. It will be shown that in a closed cell, the surface contribution to the colloidal virial P_{ocm} is comparable to the bulk term, while only the latter is considered in the naive picture. Hence its failure, resulting from a gross overestimation of P_{ocm}. As a consequence, the knowledge of a good effective potential in the bulk is insufficient when it comes to directly computing the colloidal virial in a closed box. Concluding remarks are drawn in Sec. V, where we discuss in particular how the effective potential can be used—indirectly but from a standard procedure—to compute the total pressure of the system. While most of the analysis holds without salt, the situation of an added electrolyte is also briefly addressed.

II. EQUATION OF STATE, EFFECTIVE INTERACTIONS, AND ONE COMPONENT MODEL VIRIAL

A. Equation of state

We start by the simplest situation where $\varepsilon=\varepsilon'$ and consider *all* charged species in the solution. The virial theorem allows us to write the total osmotic pressure P (with respect to pure solvent) in the form

$$\beta PV = N_c + N_{\text{micro}} + \frac{\beta}{3}\left\langle \sum_{i\in col+micro} \boldsymbol{r}_i\cdot\boldsymbol{F}_i^{\text{int}}\right\rangle, \tag{1}$$

where $\beta=1/(kT)$ is the inverse temperature and the summation runs over colloids and microscopic ions, therefore involving N_c+N_{micro} terms. In Eq. (1) the angular brackets denote a statistical average (that coincides with time average) and $\boldsymbol{F}_i^{\text{int}}$ is the (internal) force exerted on particle i at position $\boldsymbol{r}_i$, due to hard-core and Coulombic interactions in the solution. Adding the force exerted by the wall to $\boldsymbol{F}_i^{\text{int}}$ would therefore provide the total force $\boldsymbol{F}_i^{\text{tot}}$ felt by particle i. We note here that it is possible to express the pressure in Eq. (1) as a surface integral over the wall of the total (colloid +microions) concentration. Applying the virial theorem to the microions only, we have

$$\begin{aligned} N_{\text{micro}}kT + \frac{1}{3}\left\langle \sum_{i\in micro} \boldsymbol{r}_i\cdot\boldsymbol{F}_i^{\text{tot}}\right\rangle &= 0 = N_{\text{micro}}kT \\ &+ \frac{1}{3}\left\langle \sum_{i\in micro} \boldsymbol{r}_i\cdot\boldsymbol{F}_i^{\text{int}}\right\rangle \\ &- \frac{kT}{3}\left\langle \oint_{\text{box}} \rho_{\text{micro}}(\boldsymbol{r})\boldsymbol{r}\cdot d^2\boldsymbol{S}\right\rangle, \end{aligned} \tag{2}$$

where the surface integral with normal oriented outward runs over the box confining the system. Inserting the latter equality into Eq. (1), we obtain

$$P = \rho_c kT + P_{\text{ocm}} + P_{\text{micro}} \quad \text{with } P_{\text{ocm}} = \frac{1}{3V}\left\langle \sum_{i\in col} \boldsymbol{r}_i\cdot\boldsymbol{F}_i^{\text{int}}\right\rangle; \tag{3}$$

$$P_{\text{micro}} = \frac{kT}{3V}\left\langle \oint_{\text{box}} \rho_{\text{micro}}(\boldsymbol{r})\boldsymbol{r}\cdot d^2\boldsymbol{S}\right\rangle,$$

where $\rho_c=N_c/V$ and $\rho_{\text{micro}}(\boldsymbol{r})$ denotes the total microion density at point $\boldsymbol{r}$. Within mean-field approximation, this equation may be found in [1]. The first term on the right hand side of Eq. (3) is the colloid ideal gas term which can be safely neglected in practice for the parameter range of interest here (see below). The second term—of central interest here—is the colloid-colloid virial contribution and is indexed by the subscript OCM since it would be the only term considered (apart from the ideal gas one) in the OCM approach, restricted to the mesoscopic degrees of freedom $\{\boldsymbol{r}_i\}_{1\leq i\leq N_c}$. Indeed, the statistical average $\langle\cdots\rangle$ may be performed in two steps:

$$\begin{aligned} P_{\text{ocm}} &= \frac{1}{3V}\left\langle \sum_{i=1}^{N_c} \boldsymbol{r}_i\cdot\boldsymbol{F}_i^{\text{int}}\right\rangle_{col+micro} \\ &= \frac{1}{3V}\left\langle \sum_{i=1}^{N_c} \boldsymbol{r}_i\cdot\langle\boldsymbol{F}_i^{\text{int}}\rangle_{micro}\right\rangle_{col} \\ &= \frac{1}{3V}\left\langle \sum_{i=1}^{N_c} \boldsymbol{r}_i\cdot\boldsymbol{F}_i^{\text{eff}}\right\rangle_{col}, \end{aligned} \tag{4}$$

where we have introduced the microion averaged effective force $\boldsymbol{F}_i^{\text{eff}}$ exerted on colloid i for a given colloid configuration.

The third term in Eq. (3), P_{micro}, accounts for the direct coupling between colloids and microions. In principle, this third term is to be averaged over the colloidal degrees of freedom. However, even at simplified or mean-field level, a full N_c-colloid simulation is computationally demanding [7–9], and further simplifications are helpful. Of particular interest are two such simplifications, both belonging to the Poisson-Boltzmann family, that reduce the initial N_c-body problem onto a $N_c=1$-body situation. The first one is the common cell model approach originating from a solid state point of view where the Wigner-Seitz cell around a colloid is constructed and then "sphericalized" for the sake of simplicity. The Poisson-Boltzmann equation is solved within this cell, and from the microionic density profile one can then estimate P_{micro}. The second model is the renormalized jellium model [10] where a liquid state point of view is adopted: the colloid-colloid pair distribution function $g_{cc}(r)$ is considered structureless so that other colloids around a tagged macroion behave as a continuous background. The charge of this background is *a priori* unknown, and enforced to coincide with the effective charge. This self-consistency requirement leads to a unique and well defined effective charge [10]. It has been shown that for salt-free suspensions, these two models—cell and jellium—both lead to a pressure P_{micro} that is in excellent agreement with existing experimental data [11] and primitive model simulations for P [12,13], see, e.g., [10,14,15]. We note that P_{micro} may be coined a "volume" term [2,17,18], since—at least, within the cell model and jellium approaches—it does not depend on the colloidal degrees of freedom but only on the mean colloidal density. The good agreement one obtains with the exact pressure P for both models implies that for salt-free systems $P\simeq P_{\text{micro}}$. This is corroborated by a recent study of finite stiff-chain polyelectrolytes [19]. From Eq. (3) where the ideal gas contribution ($\rho_c kT$) is neglected, this may be transposed into the following requirement:

$$P_{\text{ocm}} \ll P_{\text{micro}}. \tag{5}$$

A similar conclusion was reached in Ref. [20].

B. Effective interactions

Both Poisson-Boltzmann cell and jellium approaches are not only useful to estimate the pressure, but also to derive effective parameters for solvent+microions averaged colloid-colloid interactions. By construction, the effective potential is that which leads to the correct colloid-colloid pair structure encoded in the potential of mean force g_{cc}, *assuming pair-wise colloid-colloid interactions within the OCM model* (see, e.g., [1]). Although the effective potential has a clear-cut definition, there is no rigorous *operational* route to construct this object. In general, when microionic correlations do not invalidate the mean-field picture [13], a good approximation is to write the effective potential as a sum of pair-wise Yukawa terms of the form

$$\beta v_{\mathrm{eff}}(r) = Z_{\mathrm{eff}}^2 \lambda_B \left(\frac{\exp(\kappa_{\mathrm{eff}} a)}{1+\kappa_{\mathrm{eff}} a} \right)^2 \frac{\exp(-\kappa_{\mathrm{eff}} r)}{r} \tag{6}$$

with a the colloid radius, $\lambda_B = \beta e^2/\varepsilon$ the Bjerrum length, and Z_{eff} and κ_{eff} the effective charge and inverse screening length computed within the cell or jellium model [10,21–23]. Such a "DLVO"-like expression [1,2,4] would accurately reproduce the large distance interaction of two colloids in a salt sea [1,2,4]. Its relevance in the no-salt case will not be discussed. As will become clear below, we are interested here in orders of magnitude, that should not depend on the precise form of Eq. (6).

C. An apparent paradox

Within the jellium model, the salt-free equation of state takes a particularly simple form,

$$\beta P_{\mathrm{micro}} = Z_{\mathrm{eff}} \rho_c . \tag{7}$$

Within the cell model, this expression is not exact but approximately correct. For a highly charged macroion, one has $Z_{\mathrm{eff}} \gg 1$ which allows us to neglect the ideal gas term in Eq. (3). In spite of its simplicity, the expression $\beta P_{\mathrm{micro}} = \rho_c Z_{\mathrm{eff}}$ hides a complex density dependence through Z_{eff} and is in excellent agreement with the exact pressure P found experimentally or in primitive model simulations, as emphasized above. In addition, the effective screening length reads [10]

$$\kappa_{\mathrm{eff}}^2 = 4\pi \lambda_B \rho_c Z_{\mathrm{eff}} . \tag{8}$$

The constraint embodied in Eq. (5) may therefore be rewritten

$$\beta P_{\mathrm{ocm}} \ll Z_{\mathrm{eff}} \rho_c . \tag{9}$$

Alternatively, in the low electrostatic coupling regime (where Z_{eff} coincides with Z_c), one should recover the ideal gas pressure $\beta P \simeq \rho_c (1+Z_{\mathrm{eff}})$. Given that in this limit, $\beta P_{\mathrm{micro}} \simeq \rho_c Z_{\mathrm{eff}}$, we recover the requirement (9), that will be an important benchmark for the following analysis. We now turn to the formulation of the apparent paradox.

In the bulk of the suspension, the effective potential (6) provides the effective force acting on a colloid i,

$$\boldsymbol{F}_i^{\mathrm{eff}} = \sum_{j=1}^{N_c} \boldsymbol{F}_{ij}^{\mathrm{eff}} = - \sum_{j=1}^{N_c} \boldsymbol{\nabla}_{\boldsymbol{r}} v_{\mathrm{eff}}(r) \bigg|_{\boldsymbol{r}=\boldsymbol{r}_i-\boldsymbol{r}_j} . \tag{10}$$

Considering naively that P_{ocm} appearing in Eqs. (3) and (4) is dominated in a very large system by its bulk behavior, we insert Eq. (10) into Eq. (4) to approximate P_{ocm} by P_{ocm}^* with

$$P_{\mathrm{ocm}}^* = \frac{1}{3V} \left\langle \sum_{i,j=1}^{N_c} \boldsymbol{r}_i \cdot \boldsymbol{F}_{ij}^{\mathrm{eff}} \right\rangle_{col} = \frac{1}{6V} \left\langle \sum_{i,j=1}^{N_c} \boldsymbol{r}_{ij} \cdot \boldsymbol{F}_{ij}^{\mathrm{eff}} \right\rangle_{col} , \tag{11}$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$. We will subsequently omit the subscript "col" indicating the degrees of freedom involved in the average. Introducing the colloid-colloid pair correlation function $g_{cc}(r)$, we can write

$$\beta P_{\mathrm{ocm}}^* = -\frac{\rho_c^2}{6} \int_{r=2a}^{\infty} g_{cc}(r) \frac{d\beta v_{\mathrm{eff}}(r)}{dr} r d^3\boldsymbol{r} \tag{12}$$

$$= \frac{2\pi \rho_c^2 Z_{\mathrm{eff}}^2 \lambda_B}{\kappa_{\mathrm{eff}}^2} \left\{ 1 + \frac{(\kappa_{\mathrm{eff}} a)^2}{3(1+\kappa_{\mathrm{eff}} a)^2} \right\} + \frac{\rho_c^2}{6} \int_{r=2a}^{\infty} [g_{cc}(r) - 1](1 + \kappa_{\mathrm{eff}} r) \beta v_{\mathrm{eff}}(r) d^3\boldsymbol{r} . \tag{13}$$

To estimate the above quantity, it is sufficient to keep the dominant term only, which is the first one on the right hand side (rhs), arising from the long-range behavior of the pair correlation function ($g_{cc} \to 1$ at large distances). In this term, the curly brackets may be safely approximated by 1 since at low densities, $\kappa_{\mathrm{eff}} a \ll 1$. Remembering Eq. (8), we obtain

$$P_{\mathrm{ocm}}^* \simeq \frac{2\pi \rho_c^2 Z_{\mathrm{eff}}^2 \lambda_B}{\kappa_{\mathrm{eff}}^2} \tag{14}$$

$$\simeq \frac{1}{2} Z_{\mathrm{eff}} \rho_c . \tag{15}$$

The factor 1/2 which appears is classical (see, e.g., [1]). The important point here is that estimation (15) by far violates the constraint (9). A similar conclusion would be reached including the first correction in $Z_{\mathrm{eff}}^2 \exp(-\kappa_{\mathrm{eff}} r)/r$ to the long distance behavior $g=1$ when computing the integral on the rhs of Eq. (13): this yields $P_{\mathrm{ocm}}^* \simeq Z_{\mathrm{eff}} \rho_c / 2[1 + O(\kappa_{\mathrm{eff}} \lambda_B)]$ with $\kappa_{\mathrm{eff}} \lambda_B \ll 1$ in the dilute limit. The paradox here is that the very same approach that provides a contribution P_{micro} very close to the total pressure gives an effective potential that *apparently* spoils the previous agreement, by grossly overestimating the colloidal virial contribution to the pressure. We will see that this feature is not ascribable to a failure of the functional form of Eq. (6), which provides a decent approximation for the quantity P_{ocm}^*.

D. How can the paradox be resolved?

The root of the paradox reported above is that approximating P_{ocm} by P_{ocm}^* is *incorrect*: while P_{ocm}^* provides a reasonable estimate for the bulk contribution to P_{ocm}, *surface effects* make that in the vicinity of the wall, the effective force felt by a colloid, differ from Eq. (10). These surface induced terms play a key role here and contribute a large amount to the colloidal virial P_{ocm}, *no matter how large the system is*. It turns out that bulk and surface induced contributions almost cancel each other, so that the resulting expression for P_{ocm} is much smaller than P^{*}_{ocm} and therefore fulfills the requirement (9). Our goal in the remainder is to illustrate this cancellation explicitly, from a correct description of confinement effects. To this aim, it is judicious to simplify the problem by considering the limit of point colloids ($a=0$), and by identifying the effective charge with the bare one Z_c. Considering charge renormalization effects is here immaterial and focusing on dilute systems where κa is small, finite a effects do not affect our main conclusions. In the bulk of the suspension, the effective potential therefore takes a simple Yukawa form

$$\beta v_{\mathrm{eff}}(r) = Z_c^2 \lambda_B \frac{\exp(-\kappa r)}{r}, \tag{16}$$

with $\kappa^2 = 4\pi\lambda_B Z_c \rho_c$.

At this point, a comparison with simple electrolytes seems appropriate, for the aforementioned cancellation is already present. For our discussion, we may consider that the role of the colloids is played by the cations, and that the anions constitute the remaining "microions." The pressure has to be close to [1,4]

$$\beta P_{\mathrm{electrolyte}} \simeq \rho_{\mathrm{anion}} + \rho_{\mathrm{cation}} - \frac{\kappa^3}{24\pi}, \tag{17}$$

with equal mean densities $\rho_{\mathrm{anion}} = \rho_{\mathrm{cation}}$. From the contact theorem, we deduce the densities at the wall,

$$\rho_{\mathrm{anion}}(\mathrm{wall}) = \rho_{\mathrm{cation}}(\mathrm{wall}) \simeq \rho_{\mathrm{anion}} - \frac{\kappa^3}{48\pi}. \tag{18}$$

Rewriting Eq. (3) in the form

$$\beta P_{\mathrm{electrolyte}} = \rho_{\mathrm{cations}} + \frac{\beta}{3V}\left\langle \sum_{i\in cation} \boldsymbol{r}_i \cdot \boldsymbol{F}_i^{\mathrm{int}} \right\rangle + \rho_{\mathrm{anion}}(\mathrm{wall}) \tag{19}$$

we obtain from Eqs. (17) and (18)

$$\frac{\beta}{3V}\left\langle \sum_{i\in cation} \boldsymbol{r}_i \cdot \boldsymbol{F}_i^{\mathrm{int}} \right\rangle \simeq -\frac{\kappa^3}{48\pi}. \tag{20}$$

Given that $\kappa^2 = 8\pi\lambda_B Z^2 \rho_{\mathrm{cation}}$, we have $\kappa^3/(\beta P^{*}_{\mathrm{ocm}}) \propto \kappa\lambda_B$ which is a small quantity for a dilute system. We explicitly see here that the "colloidal" virial [left hand side (lhs) of Eq. (20) up to a factor β] is by far smaller than the estimation P^{*}_{ocm}.

III. WALL MEDIATED FORCES WITHOUT DIELECTRIC DISCONTINUITY

In the vicinity of the wall, the colloids do not see a spherically symmetric environment. As a consequence,

(i) the usual $\exp(-\kappa r)/r$ pair interaction is modified;

(ii) the mean force acting on a colloid does not vanish. This is a one body, wall induced effect, mediated by the microions. It is therefore an *internal* force, that should be taken into account in Eq. (4). It should not be confused with the *external* (and short range) direct colloid-wall interaction.

Evaluating the rhs of Eq. (4) therefore requires a careful computation of both types of microion averaged colloidal forces. To this end, we need the solution $\phi_z(\rho,z')$ of Debye-Hückel equation $\nabla^2\phi_z = \kappa^2\theta(z')\phi_z$ in the case where a test charge is located in the solution a distance z from an infinite neutral wall. We have introduced the Heaviside function θ and cylindrical coordinates (ρ,z') such that the test particle is located at $(0,z)$ with $z>0$. The planar geometry approximation for the wall is sufficient provided the cell size or radius of curvature is much larger than Debye length $1/\kappa$. We start by the situation of equal dielectric constants inside and outside the solution ($\varepsilon=\varepsilon'$). The electrostatic potential may be written in the form of a Hankel (two dimensional Fourier) transform [26] where q and ρ are conjugate quantities [24,25],

$$\phi_z(\rho,z') = Z_c\lambda_B \int_0^{\infty} \left(\frac{k-q}{k+q} e^{-k(z+z')} + e^{-k|z-z'|} \right) \frac{1}{k} J_0(q\rho) q\,dq; \tag{21}$$

$$k \equiv \sqrt{\kappa^2 + q^2}.$$

The second term in the integrand ($e^{-\kappa|z-z'|}$) gives exactly $Z_c\lambda_B \exp(-\kappa r)/r$ where $r=[\rho^2+(z-z')^2]^{1/2}$ is the distance to the source. This is the standard Debye-Hückel potential which dominates in the bulk. The remaining term, which vanishes at large distances (κz or $\kappa z' \gg 1$) is due to the presence of the interface.

A. One colloid ion average force

The force felt by a colloid located a distance z from the planar interface follows from Eq. (21), considering the electrostatic potential $\tilde{\phi}_z = \phi_z - Z_c^2\lambda_B e^{-\kappa r}/r$ where the self term has been subtracted:

$$\begin{aligned} \beta \boldsymbol{F}_{c\text{-}wall} &= \hat{\boldsymbol{n}} Z_c \frac{\partial}{\partial z'} \beta\tilde{\phi}_z(0,z') \bigg|_{z,z'=z} \\ &= Z_c^2 \lambda_B \int_0^{\infty} \frac{k-q}{k+q} e^{-2kz} q\,dq (-\hat{\mathbf{n}}). \end{aligned} \tag{22}$$

In this equation, $\hat{\boldsymbol{n}}$ denotes the unit vector perpendicular to the interface pointing outside the solution. We coin the force (22) "colloid wall" and for notational convenience, we henceforth omit the superscripts "int" and "eff." This force repels the colloid from the wall [$k=(\kappa^2+q^2)^{1/2}>q$], as a result of microions imbalance between the half of the colloid exposed to the wall, and the other hemisphere. Inserting Eq. (22) into Eq. (4) we have

$$\frac{1}{3V}\left\langle \sum_{i=1}^{N_c} \boldsymbol{r}_i \cdot \boldsymbol{F}_{i\text{-}wall} \right\rangle = \frac{1}{3V}\int_{wall} d^2S \int_0^{\infty} \rho_c(z) \boldsymbol{r} \cdot \boldsymbol{F}_{i\text{-}wall}(z) dz. \tag{23}$$

To leading order, the above integral may be computed assuming a uniform density of colloids $\rho_c(z)=\rho_c$. In Eq. (23), $\boldsymbol{r}$ denotes the absolute position with $\boldsymbol{r}=\boldsymbol{s}-z\hat{\boldsymbol{n}}$ ($\boldsymbol{s}$ is therefore the orthogonal projection of $\boldsymbol{r}$ onto the wall). We neglect the term in $-z\hat{\boldsymbol{n}}$ (that would contribute proportionally to the surface of the system), so that

$$\frac{1}{3V}\left\langle \sum_{i=1}^{N_c} \boldsymbol{r}_i\cdot\beta\boldsymbol{F}_{i\text{-}wall}\right\rangle \tag{24}$$

$$\simeq \frac{\beta\rho_c}{3V}\int_{wall} d^2S\int_0^\infty \boldsymbol{s}\cdot\boldsymbol{F}_{i\text{-}wall}(z)dz$$

$$\simeq -\frac{\rho_c}{3V}Z_c^2\lambda_B\left(\int_{wall}\boldsymbol{s}\cdot\hat{\mathbf{n}}\,d^2S\right)\times\int_0^\infty dz\int_0^\infty \frac{\sqrt{\kappa^2+q^2}-q}{\sqrt{\kappa^2+q^2}+q}e^{-2z\sqrt{\kappa^2+q^2}}qdq \tag{25}$$

$$\simeq -\frac{1}{6}\rho_c Z_c^2\kappa\lambda_B \tag{26}$$

$$\simeq -\frac{\kappa^3}{24\pi}. \tag{27}$$

Incidentally, this is exactly the Debye-Hückel form for the excess pressure of an electrolyte [see Eq. (17)]. For dilute systems, this quantity is small compared to $\rho_c Z_c$, as emphasized earlier. The constraint (9) is therefore fulfilled.

B. Colloid-colloid interactions

Within the simple Debye-Hückel treatment, the potential of interaction between two colloids near the wall (one at z, the other at z', with a lateral distance ρ between them) is $Z_c\phi_z(\rho,z')=Z_c\phi_{z'}(\rho,z)$. To calculate the force felt by the colloid at z due to all neighbors, we assume again a uniform distribution of neighbors:

$$\beta\boldsymbol{F}_{col\text{-}col}(z)=\hat{\mathbf{n}}\rho_c\int_{z'=0}^\infty dz'\int_0^\infty 2\pi\rho d\rho\left.\frac{\partial Z_c\beta\phi_z(\rho,z')}{\partial z}\right|_{z'} \tag{28}$$

$$=-\hat{\mathbf{n}}\rho_c Z_c^2\lambda_B\int_0^\infty dq\int_0^\infty 2\pi\rho d\rho\left(\frac{\sqrt{\kappa^2+q^2}-q}{\sqrt{\kappa^2+q^2}+q}-1\right)\times e^{-z\sqrt{\kappa^2+q^2}}\frac{1}{\sqrt{\kappa^2+q^2}}J_0(q\rho)qdq. \tag{29}$$

The component of the force parallel to the wall vanishes upon averaging.

Inserting this force into Eq. (4) and proceeding along similar lines as in Eq. (24), we have

$$\frac{\beta}{3V}\left\langle\sum_{i=1}^{N_c}\boldsymbol{r}_i\cdot\boldsymbol{F}_{i\text{-}coll}\right\rangle \simeq \rho_c^2 Z_c^2\lambda_B\int_0^\infty 2\pi\rho d\rho\int_0^\infty\left(-\frac{\sqrt{\kappa^2+q^2}-q}{\sqrt{\kappa^2+q^2}+q}+1\right)\times\frac{1}{\kappa^2+q^2}J_0(q\rho)qdq. \tag{30}$$

Both expressions (29) and (30) are of the form of a Hankel transform at the origin $q=0$ of the inverse Hankel transform of a function $A(q)$, with $A=(\cdots-1)e^{-kz}/k$ in Eq. (29) and $A=(-\cdots+1)/k^2$ in Eq. (30). This is nothing but $A(0)$ [26], which vanishes in both cases. Therefore, with the approximations proposed, the force in Eq. (29) and the virial term in Eq. (30) vanish. To be more specific, we compute explicitly the integrals in Eq. (30):

$$\frac{\beta}{3V}\left\langle\sum_{i=1}^{N_c}\boldsymbol{r}_i\cdot\boldsymbol{F}_{i\text{-}coll}\right\rangle\simeq\frac{1}{2}\rho_c Z_c(-1+1). \tag{31}$$

The term in +1 in the parentheses arises from the term in +1 in Eq. (30), which gives the usual "bulk" $e^{-\kappa r}/r$ pair interaction, as already mentioned. The associated virial is $\beta P^*_{\text{ocm}}=Z_c\rho_c/2$, as obtained in Eq. (15). The present calculation shows that this term is canceled by an opposite wall induced contribution. If the simplifying assumption $g_{cc}=1$ is relaxed, the resulting expression for Eq. (31) no longer vanishes but remains negligible with respect to $\rho_c Z_c$. On the other hand, relaxing the assumption of a uniform profile $\rho_c(z)$ leaves the result unaffected, as will be seen in Sec. IV.

We conclude here that summing the two contributions from Eqs. (27) and (31) provides a value for P_{ocm} that is compatible with the constraint (9).

IV. ANALYSIS IN PRESENCE OF A DIELECTRIC DISCONTINUITY

In this section, we extend the previous analysis to the situation where the dielectric constants are not matched: $\eta=\varepsilon'/\varepsilon\neq1$. The relevant parameter range corresponds to $\eta<1$, e.g., for water droplets in air in spray-drying experiments. The first important difference with the $\eta=1$ case is that the equation of state (3) takes a different form. The pressure is indeed not solely given by the contact densities of charged species at the wall, but contains additional electric contributions (polarization or image effects). On the other hand, Eqs. (1) and (2) are still formally correct provided one also includes in the "internal" forces the electric forces from the wall. The resulting equation of state reads

$$P=\rho_c kT+\frac{1}{3V}\left\langle\sum_{i\in col}\boldsymbol{r}_i\cdot\boldsymbol{F}_i^{\text{int}}\right\rangle+\frac{kT}{3V}\left\langle\oint_{\text{box}}\rho_{\text{micro}}(\boldsymbol{r})\boldsymbol{r}\cdot d^2\boldsymbol{S}\right\rangle+\frac{1}{3V}\left\langle\oint_{\text{box}}\boldsymbol{r}\cdot\boldsymbol{T}^{el}d\boldsymbol{S}\right\rangle. \tag{32}$$

Here

$$\boldsymbol{T}^{el}=\frac{\varepsilon}{8\pi}E^2\boldsymbol{I}-\frac{\varepsilon}{4\pi}\boldsymbol{E}\otimes\boldsymbol{E} \tag{33}$$

is the Maxwell tensor, with $\boldsymbol{E}$ the local electric field and $\boldsymbol{I}$ the isotropic tensor.

The counterpart of Eq. (21) now reads

$$\phi_z(\rho,z')=Z_c\lambda_B\int_0^\infty\left(\frac{k-\eta q}{k+\eta q}e^{-k(z+z')}+e^{-k|z-z'|}\right)\frac{1}{k}J_0(q\rho)qdq; \tag{34}$$

$$k \equiv \sqrt{\kappa^2 + q^2}.$$

As in the case $\eta=1$ and as long as $\eta \neq 0$, the corresponding interaction between two colloids decays as ρ^{-3} at large distances parallel to the wall (see [27] for a discussion of this dipolarlike term). When $\eta=0$, the wall can be formally removed considering the electric image located symmetric to the $z=0$ plane.

The colloid-colloid and colloid-wall interactions readily follow from Eq. (34). At short distances $z \to 0$, the latter diverges like $z^{-1}(1-\eta)/(1+\eta)$ [25], which corresponds to the unscreened interaction of a particle with its own image. This divergence means that the uniform colloid density cannot be invoked when it comes to computing Eq. (23). To obtain the leading order behavior, we can assume that the colloids are distributed with the Boltzmann weight $\rho_c(z)=\rho_c \exp[-\beta\phi_{c-wall}(z)]$, where $\boldsymbol{F}_{c-wall}=-\boldsymbol{\nabla}\phi_{c-wall}$ and the potential ϕ_{c-wall} deriving from Eq. (34) vanishes for $z \to \infty$. The precise knowledge of this potential is, however, not required since

$$\frac{1}{3V}\left\langle \sum_{i=1}^{N_c} \boldsymbol{r}_i \cdot \boldsymbol{F}_{i\text{-}wall} \right\rangle = \frac{\rho_c}{3V}\int_{wall} d^2S \int_0^\infty \boldsymbol{r} \cdot \boldsymbol{F}_{c\text{-}wall}(z)\exp[-\beta\phi_{c\text{-}wall}(z)]dz \tag{35}$$

$$\simeq \rho_c kT[\exp(-\beta\phi_{c\text{-}wall}(z))]_0^\infty \tag{36}$$

$$\simeq -\rho_c kT. \tag{37}$$

This term therefore cancels the ideal gas one on the rhs of Eq. (32).

The wall induced colloid-colloid contribution to the colloidal virial may be computed along similar lines as in Sec. III B. An expression involving again a Hankel transform composed with its inverse is again obtained, with now a function

$$A(q) = \left(\frac{\sqrt{\kappa^2+q^2}-\eta q}{\sqrt{\kappa^2+q^2}+\eta q} - 1\right)\frac{1}{\sqrt{\kappa^2+q^2}}\int_0^\infty dz \rho_c(z) e^{-z\sqrt{\kappa^2+q^2}}. \tag{38}$$

Since $A(0)=0$, we conclude here that

$$\left\langle \sum_{i=1}^{N_c} \boldsymbol{r}_i \cdot \boldsymbol{F}_{i\text{-}coll} \right\rangle \simeq 0, \tag{39}$$

so that the total colloidal virial (including colloid-colloid and colloid-wall interactions) is close to $-\rho_c kT$, which is a small quantity compared to the microionic contribution $Z_c\rho_c kT$. Equation (32) can finally be rewritten,

$$P \simeq \frac{kT}{3V}\left\langle \oint_{\text{box}} \rho_{\text{micro}}(\boldsymbol{r})\boldsymbol{r} \cdot d^2\boldsymbol{S} \right\rangle + \frac{1}{3V}\left\langle \oint_{\text{box}} \boldsymbol{r} \cdot \boldsymbol{T}^{el} d\boldsymbol{S} \right\rangle. \tag{40}$$

V. CONCLUDING REMARKS

Before briefly discussing the situation where a salt is added, two comments are in order.

A. Closed cells vs periodic boundary conditions

From the previous discussion, it appears that the equation of state (3) holds when the system is confined by a hard wall, and would fail if periodic boundary conditions (pbc) would be enforced. The inadequacy of P^*_{ocm} to approximate P_{ocm} may then be phrased in the following way:

$$3VP^*_{\text{ocm}} \equiv \frac{1}{2}\left\langle \sum_{i,j=1}^{N_c} \sum_{\boldsymbol{n}} \boldsymbol{r}_{ij} \cdot \boldsymbol{F}^{\text{eff}}_{ij}(\boldsymbol{r}_{ij} - \boldsymbol{R}_{\boldsymbol{n}}) \right\rangle_{pbc} \tag{41}$$

$$\neq \left\langle \sum_{i}^{N_c} \boldsymbol{r}_i \cdot \boldsymbol{F}^{\text{eff}}_i \right\rangle_{hard\ walls}, \tag{42}$$

where in Eq. (41), the sum involves all periodic images of the cell considered: $\boldsymbol{n}$ is a vector with components in $\mathbb{Z}^3$, which indexes the center $\boldsymbol{R}_{\boldsymbol{n}}$ of a given image of the "central" cell. The central cell has $\boldsymbol{R}_{\boldsymbol{0}}=\boldsymbol{0}$ and since we deal here with a short range effective potential, the sum over $\boldsymbol{n}$ may be truncated to retain only the seven terms with $|\boldsymbol{n}| \leq 1$.

However, for any simple fluid where the forces $\boldsymbol{F}_i$ are given, Eq. (42) would be an equality. Indeed we have

$$\left\langle \sum_i \boldsymbol{r}_i \cdot \boldsymbol{F}_i \right\rangle^{simple\ fluid}_{hard\ walls} \equiv \frac{1}{2}\left\langle \sum_{i,j} \boldsymbol{r}_{ij} \cdot \boldsymbol{F}_{ij} \right\rangle^{simple\ fluid}_{hard\ walls}, \tag{43}$$

where the rhs shows negligible dependence on the boundary conditions provided the system is large enough, and can then be computed with pbc provided the correct forces are considered $[\boldsymbol{F}_i=\Sigma_j\Sigma_{\boldsymbol{n}}\boldsymbol{F}_{ij}(\boldsymbol{r}_{ij}-\boldsymbol{R}_{\boldsymbol{n}})]$. Hence

$$\left\langle \sum_i \boldsymbol{r}_i \cdot \boldsymbol{F}_i \right\rangle^{simple\ fluid}_{hard\ walls} = \frac{1}{2}\left\langle \sum_{i,j} \sum_{\mathbf{n}} \boldsymbol{r}_{ij} \cdot \boldsymbol{F}_{ij}(\boldsymbol{r}_{ij} - \boldsymbol{R}_{\boldsymbol{n}}) \right\rangle^{simple\ fluid}_{pbc}. \tag{44}$$

The difference between Eqs. (42) and (44) illustrates the important role of microions. We may also consider that the ≠ sign in Eq. (42) arises from the density dependence of the effective pair potential.

A natural question at this point is does the knowledge of the "bulk" effective potential (6) between colloids allow to compute their virial P_{ocm} as it appears in Eq. (3)? The answer is positive in a closed cell, at the OCM level, provided that due account is taken for the dielectric images of the colloids. In the following section, we address a related question, and discuss how the full pressure of the colloidal system may be recovered, assuming again that the only information at hand is that of the bulk effective colloid-colloid interaction.

B. Back to the DLVO potential

We consider here a simple liquid that interacts with a pair-wise potential given by Eq. (6), with effective parameters $Z^*_{\text{eff}} \gg 1$ and $\kappa^{*2}_{\text{eff}}=4\pi\lambda_B Z^*_{\text{eff}}\rho^*_c$ (salt-free case, for simplicity). These parameters are fixed *a priori*, and chosen to coincide with those relevant for a colloidal suspension at $\rho_c = \rho_c^*$. The potential of interaction is therefore *density independent* and the system, later referred to as "auxiliary," can be studied for $\rho_c \neq \rho_c^*$.

We consider the parameter range (essentially low density) where the excess pressure of such a system is well approximated by P^*_{ocm} in Eq. (14):

$$\beta P^*_{\mathrm{ocm}} \simeq \frac{2\pi\rho_c^2 Z^{*2}_{\mathrm{eff}}\lambda_B}{\kappa^{*2}_{\mathrm{eff}}} = \frac{1}{2}\frac{\rho_c^2}{\rho_c^*}Z^*_{\mathrm{eff}}. \tag{45}$$

Incidentally, the contact theorem indicates that the contact density in the case where the system is confined by a closed box, reads $\rho_c(wall) \simeq \rho_c^2 Z^*_{\mathrm{eff}}/(2\rho_c^*)$. This quantity is much larger than the mean density ρ_c (except when ρ_c is extremely small, a limit of little interest here). This excess with respect to the mean density is to be contrasted with the *depletion* from the wall that is present in the original colloidal system containing microions: Eq. (22) for $\varepsilon = \varepsilon'$ shows a repulsive colloid-wall behavior, and the depletion is even stronger when $\varepsilon' < \varepsilon$ due to like-sign images; see the discussion after Eq. (34).

The pressure of the simple liquid with DLVO interactions, close to P^*_{ocm}, has *a priori* nothing to do with the pressure P^{original} of the real colloidal system. It has also nothing to do with the colloid virial contribution entering Eq. (3). However, for $\rho_c = \rho_c^*$, the colloid-colloid structural information is the same for both original and auxiliary systems. One may then invoke Kirkwood-Buff identity [28] which states that the inverse compressibility of the original colloidal suspension coincides with the long wavelength limit of the colloid-colloid structure factor $S_{cc}(k)$:

$$\chi = \left(\left.\frac{\partial \beta P^{\mathrm{original}}}{\partial \rho_c}\right|_T \right)^{-1} = S_{cc}(0). \tag{46}$$

The compressibility in our auxiliary simple liquid with *fixed* potential of interaction is therefore the same at $\rho_c = \rho_c^*$ (and only at this density)

$$\left.\frac{\partial P^{\mathrm{original}}}{\partial \rho_c}\right|_T \overset{\rho_c=\rho_c^*}{=} \left.\frac{\partial P^*_{\mathrm{ocm}}}{\partial \rho_c}\right|_{T,\kappa^*_{\mathrm{eff}},Z^*_{\mathrm{eff}}}. \tag{47}$$

This offers a means to compute the equation of state of the original colloidal system from integrating the inverse compressibility of the auxiliary one. In this integration, due account must be taken of the density dependence of both Z^*_{eff} and κ^*_{eff}. The previous integration procedure therefore requires us to consider the auxiliary system for several values of ρ_c for a given ρ_c^* [to compute the derivative in the rhs of Eq. (47)], before scanning the range of interest for ρ_c^*. Of course, the general procedure outlined here does not depend on the specific form of the effective potential, and is equally valid when salt is added. It turns out, however, that the DLVO potential together with the salt-free approximation (14)—which leads to Eq. (45)—provides a clear illustration of the procedure. From Eq. (45), we obtain the rhs of Eq. (47):

$$\left.\frac{\partial \beta P^*_{\mathrm{ocm}}}{\partial \rho_c}\right|_{T,\kappa^*_{\mathrm{eff}},Z^*_{\mathrm{eff}}} \simeq Z^*_{\mathrm{eff}} \quad \text{at} \quad \rho_c = \rho_c^*. \tag{48}$$

To compute the lhs of Eq. (47), we may come back to the jellium model which gives $\beta P^{\mathrm{original}} \simeq Z_{\mathrm{eff}}\rho_c$. In this expression, the effective charge may depend on the density, but for salt-free cases, this dependence is at most logarithmic for $\rho_c \to 0$ [10] and provides only a subdominant term to the compressibility, so that

$$\left.\frac{\partial \beta P^{\mathrm{original}}}{\partial \rho_c}\right|_T \simeq Z_{\mathrm{eff}}. \tag{49}$$

Evaluating this expression at $\rho_c = \rho_c^*$ where $Z_{\mathrm{eff}} = Z^*_{\mathrm{eff}}$, we recover Eq. (48). This not only illustrates the identity (47) but also the consistency of the underlying DLVO potential.

C. Situation with added salt

When the suspension is dialyzed against a salt reservoir, most of the technical analysis carried out earlier is still valid. We consider a similar auxiliary system as in Sec. V B, with effective screening length such that $\kappa^{*2}_{\mathrm{eff}} > 4\pi\lambda_B Z^*_{\mathrm{eff}}\rho_c$ due to the screening by salt ions [29]. The effective charge and screening lengths are again chosen to coincide with those of a colloidal system at a particular density ρ_c^*, but are otherwise density independent. Equation (47) still holds while P^*_{ocm} is given by Eq. (13). Neglecting again the integral on the rhs of Eq. (13), and inserting the resulting P^*_{ocm} in Eq. (47), we obtain

$$\left.\frac{\partial P^{\mathrm{original}}}{\partial \rho_c}\right|_T = \mathcal{A}\frac{4\pi\lambda_B\rho_c Z^2_{\mathrm{eff}}}{\kappa^2_{\mathrm{eff}}}, \tag{50}$$

where we have replaced Z^*_{eff} by Z_{eff} and κ^*_{eff} by κ_{eff} *after* computing the rhs of Eq. (47). Here, the prefactor $\mathcal{A}$ reads

$$\mathcal{A} = 1 + \frac{(\kappa_{\mathrm{eff}}a)^2}{3(1+\kappa_{\mathrm{eff}}a)^2}. \tag{51}$$

Is relation (50) compatible with $P_{\mathrm{ocm}} \ll P = P^{\mathrm{original}}$? Neglecting P_{ocm} (together with $\rho_c kT$) in Eq. (3), we have $P \simeq P_{\mathrm{micro}}$ which in the jellium model is given by $\kappa^2_{\mathrm{eff}}/(4\pi\lambda_B)$. With the help of [29], we arrive at

$$\left.\frac{\partial P_{\mathrm{micro}}}{\partial \rho_c}\right|_T = \frac{4\pi\lambda_B\rho_c Z^2_{\mathrm{eff}}}{\kappa^2_{\mathrm{eff}}}. \tag{52}$$

Equations (50) and (52) give the same result provided $\mathcal{A}$ is close to unity, which means $\kappa_{\mathrm{eff}}a < 1$. We conclude here that omitting the colloidal contribution to the pressure, P_{ocm}, is inconsistent when $\kappa_{\mathrm{eff}}a > 1$. It turns out, however, that $\mathcal{A}$ increases very mildly with $\kappa_{\mathrm{eff}}a$ (e.g., it is close to 1.2 for $\kappa_{\mathrm{eff}}a = 4$). A more precise discussion would require us to consider the full rhs in Eq. (13), which is beyond the scope of this paper. Finally, we note that in the salt-free case where $\kappa_{\mathrm{eff}}a = 3\eta_c Z_{\mathrm{eff}}\lambda_B/A$ with $\eta_c = 4\pi\rho_c a^3/3$ the colloidal volume fraction and $Z_{\mathrm{eff}}\lambda_B/a$ on the order of 10 for highly charged colloids, we have $\kappa_{\mathrm{eff}}a < 3$ and therefore $\mathcal{A}$ close to 1 even for packing fractions as high as 10%.

D. Summary

We have seen that for a salt-free colloidal suspension, the colloidal contribution P_{ocm} to the equation of state [as written in Eq. (3)] is a negligible quantity. This feature may easily be overlooked in a naive implementation of the one component model, where only P^*_{ocm}, the *bulk* contribution to P_{ocm}, is computed. The fact that P^*_{ocm} is of the same order of magnitude as the total pressure P of the suspension is not compatible with the requirement $P_{\text{ocm}} \ll P_{\text{micro}} \simeq P$, that has emerged as a central constraint in our analysis. We have shown that no matter how large the system is, surface effects that require the resolution of Poisson's equation in the vicinity of a confining wall contribute a large amount to P_{ocm}. To zeroth approximation, these surface terms cancel the bulk value P^*_{ocm}, so that one finally recovers $P_{\text{ocm}} \ll P$.

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