AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **145**, 084103 (2016); doi: 10.1063/1.4961091
View online: http://dx.doi.org/10.1063/1.4961091
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/145/8?ver=pdfcov
Published by the AIP Publishing

Electrostatic interactions between charged dielectric particles in an electrolyte solution

Ivan N. Derbenev,[1,2] Anatoly V. Filippov,[2] Anthony J. Stace,[1] and Elena Besley[1,a)]
[1]*School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom*
[2]*Troitsk Institute for Innovation and Fusion Research, Pushkovykh Street 12, Troitsk, Moscow 142190, Russia*

(Received 9 June 2016; accepted 1 August 2016; published online 23 August 2016)

Theory is developed to address a significant problem of how two charged dielectric particles interact in the presence of a polarizable medium that is a dilute solution of a strong electrolyte. The electrostatic force is defined by characteristic parameters for the interacting particles (charge, radius, and dielectric constant) and for the medium (permittivity and Debye length), and is expressed in the form of a converging infinite series. The limiting case of weak screening and large inter-particle separation is considered, which corresponds to small (macro)ions that carry constant charge. The theory yields a solution in the limit of monopole and dipole terms that agrees exactly with existing analytical expressions, which are generally used to describe ion-ion and ion-molecular interactions in a medium. Results from the theory are compared with DLVO theory and with experimental measurements for the electrostatic force between two PMMA particles contained in a nonpolar solvent (hexadecane) with an added charge control agent. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4961091]

I. INTRODUCTION

The study of interactions between charged particles in a medium, which includes charge carriers, such as electrons, and ions, is of considerable importance to many scientific applications including coalescence and self-assembly of colloidal systems,[1] complex plasmas,[2] biochemical interactions,[3] and atmospheric physics and chemistry.[4] The majority of experimental observations are interpreted using the standard Derjaguin-Landau-Verwey-Overbeek (DLVO) theory[5,6] of colloidal stability assuming polarisation effects can be neglected. For low values of the surface electrostatic potential, $\psi_S < 25$ mV, the electrostatic force between two small particles or ions is typically described within the Debye-Hückel approximation,

$$F = \frac{Q_1 Q_2}{4\pi\varepsilon_0 k_m R^2}(1+\kappa R)\,e^{-\kappa R},$$

where κ^{-1} is the characteristic decay length of the electrostatic potential (the Debye length), R is the separation distance between the particles carrying the charges of Q_1 and Q_2, k_m is the dielectric constant of the medium, and ε_0 is the dielectric permittivity of vacuum.

Since publication of the Debye-Hückel theory of dilute electrolytes,[7] a number of attempts have been made to extend the theory to finite, polarisable particles. The solubility of glycine Zwitterions in alcohol-water mixtures has been investigated[8] within the Debye-Hückel approach, where the Zwitterions were represented as dielectric spheres containing discrete point charges inside and the potential was expanded up to the fourth order multipole moment. A similar problem has been solved in terms of an infinite series[9] using an expansion of modified Bessel functions, and the interaction energy has been deduced asymptotically to give a familiar expression for two finite-size ions. The problem of two identical colloidal particles with a continuous distribution of surface charge has been solved up to the quadrupole term.[10] The electrostatic force between two uniformly charged spheres in a finite region of an ionized medium has been derived[11] using an infinite multipole expansion, however the interaction turned out to be dependent on the form of external boundary. Analytical solutions for an infinite ionized medium have also been given for the case of a point charge interacting with either a conducting[12] or a dielectric sphere.[13]

It has been shown recently that contributions arising from polarisation effects can strongly influence the overall electrostatic interaction between dielectric particles, leading to a rather unusual behaviour, such as attraction between like-charged particles at close interaction distances.[14,15] These studies presented analytical models to account for the interaction between charged dielectric spheres either in the absence[14] or the presence of an external electric field.[15] Bichoutskaia *et al.*[14] solved the problem in the spherical coordinate system through re-expansion of Legendre polynomials, whilst Munirov *et al.*[15] arrived at the same solution using bi-spherical coordinates. The bi-spherical coordinate system was later adopted to derive an analytical expression for the electrostatic force between a charged dielectric sphere and a planar surface.[16]

As an alternative to the boundary value problem, a multiple scattering formalism has been used to study many-body systems containing spheres of the same charge and dielectric constants.[17] Other approaches based on a description of individual particles rather than a mean field include an image-charge method[18] and a boundary-element method.[19] Benchmarking of the latter two methods was performed by Gan *et al.*,[20] and their application to pair interactions in

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[a)] Author to whom correspondence should be addressed. Electronic mail: Elena.Besley@nottingham.ac.uk electrolyte solution demonstrated the strong effect ions have on the forces between colloidal particles.

In this work, we present a new analytical solution, which extends our understanding of how charged dielectric particles interact with one another to situations where the particles are suspended in an electrolyte solution. The electrostatic problem of two polarizable particles in solution has been solved for a relatively low concentration of electrolyte, and the methodology is validated using experimental measurements[21] performed on two PMMA spheres in a nonpolar solvent (hexadecane). At a more general level, the proposed solution can be used to study colloidal systems with high and/or widely different dielectric constants, when suspended in an electrolyte.

II. MODEL

A. Problem statement and basic assumptions

The electrostatic interaction between two dielectric particles is assumed to take place in a medium described by a dielectric constant and a Debye length. The dielectric constant represents the characteristic polarisation response of an isotropic and uniform medium. The Debye length is related to both the electrostatic and the thermodynamic properties of the medium, and it describes the shielding effect of an electrically neutral subsystem of charge carriers on propagation of the electric field. In this case it is necessary to define a self-consistent potential, (r), for both the interacting spheres and the ionic subsystem. If the ionic subsystem is in thermodynamic equilibrium (a Boltzmann distribution holds for ions at all distances from the charged surface of a particle) and the ions are assumed to be point charges interacting in accordance with Coulombs law, then the electrostatic potential is the solution of the well-known Poisson-Boltzmann (PB) equation. The PB equation is a general non-linear second-order differential equation; however to solve it for (r), the potential must satisfy a superposition principle that requires the PB equation to become linear with respect to (r). The PB equation is solved within the Debye-Hückel approximation, and in the case of an added electrolyte, low ionic concentrations are assumed. The Debye length is defined primarily by ionic strength (or molar concentration) as temperature cannot be varied over a wide range. Finally, within the framework of the electrostatic problem, the effects of electrostriction, solvation and mechanical deformation are excluded from consideration.

The assumptions made above allow us to state the problem as follows. Two dielectric spherical particles are suspended in an isotropic and uniform dielectric medium, which contains an electrolyte. The system is kept at constant temperature, and the interacting particles are placed sufficiently far from any wall to negate the effect of an external boundary. A graphical representation of the particle-particle interaction and the associated physical parameters is shown in Fig. 1. Two spherical dielectric particles with surface charge densities $_i$, radii a_i, and dielectric constants k_i, $(i = 1,2)$ are suspended in a medium with a dielectric constant k_m and a Debye length $^{-1}$. The medium is assumed to be electrically neutral and the electrolyte concentration sufficiently low for the interaction energy to be small in comparison to that associated with the thermal motion. Under these conditions, the self-consistent electrostatic potential due to the presence of the particles in the surrounding medium, $_{\text{out},i}(r)$, is described by the linearized PB equation,

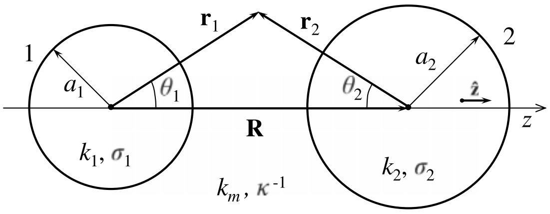

FIG. 1. A general geometry representation of the problem of two interacting dissimilar colloidal particles suspended in an electrolyte solution with dielectric constant k_{m} and Debye length $^{-1}$. Dielectric constants, surface charge densities, and the radii for particles 1 and 2 are denoted as k_1, $_1$, a_1, and k_2, $_2$, a_2, respectively.

$$_{\text{out},i}(r_i) - {}^2 \; _{\text{out},i}(r_i) = 0, \tag{1}$$

and the potential inside the particles, $_{\text{in},i}(r)$, can be described by the Laplace equation,

$$_{\text{in},i}(r_i) = 0. \tag{2}$$

The linearity of the problem means that the total potential can be expressed as

$$= \begin{cases} _{\text{in},i}, & r_i < a_i, \\ _{\text{out},1} + \; _{\text{out},2} \qquad _{\text{out}}, & r_i > a_i. \end{cases} \tag{3}$$

Introducing a dimensionless radial coordinate, $\tilde{r}_i = \; r_i$, Eqs. (1) and (2) can be expressed in the following form:

$$_{\tilde{r}_\text{i}} \; _{\text{in},i}(\tilde{r}_i) = 0, \quad _{\tilde{r}_\text{i}} \; _{\text{out}}(\tilde{r}_i) - \; _{\text{out}}(\tilde{r}_i) = 0,$$

where $_{\tilde{r}_\text{i}}$ is the Laplace operator with $\tilde{r}_i$ as the radial coordinate.

The boundary conditions for constant surface charge can then be written as follows:

$$\begin{cases} _{\text{in},i}\;_{\tilde{r}_\text{i}=\tilde{a}_\text{i}} = \; _{\text{out}}\Big|_{\tilde{r}_\text{i}=\tilde{a}_\text{i}}, \\ k_i \dfrac{_{\text{in},i}}{\tilde{r}_i}\Bigg|_{\tilde{r}_\text{i}=\tilde{a}_\text{i}} - k_m \dfrac{_{\text{out}}}{\tilde{r}_i}\Bigg|_{\tilde{r}_\text{i}=\tilde{a}_\text{i}} = \dfrac{\tilde{}_i}{_0}, \end{cases} \tag{4}$$

where the radii and the surface charge densities are expressed as $\tilde{a}_i = \; a_i$, $\tilde{}_i = \; _i/ \;$.

B. Analytical solution

1. Expansion of the potential and the surface charge density in terms of Legendre polynomials

Since the linearized PB equation with $\,, 0$ is a particular case of the Helmholtz equation, it cannot be solved through a separation of variables in the bi-spherical coordinate system, therefore, two spherical coordinate systems have been adopted, each with an origin at the centre of spheres. The potential inside each sphere that satisfies the Eq. (4) can be expanded in terms of Legendre polynomials[22]

$$\Phi_{\text{in},i} = \sum_{n=0}^{\infty} B_{n,i} P_n(\mu_i)\,\tilde{r}_i^n, \quad \mu_i = \cos\theta_i. \tag{5}$$

The potential outside each sphere that satisfies Eq. (1) and vanishes at infinity, takes the form[23,24]

$$\Phi_{\text{out},i} = \sum_{n=0}^{\infty} A_{n,i} P_n(\mu_i) \frac{K_{n+1/2}(\tilde{r}_i)}{\sqrt{\tilde{r}_i}}, \tag{6}$$

where $K_{n+1/2}(\tilde{r})$ are the modified Bessel functions of the third kind. In the case of a non-uniform surface charge distribution, but with azimuthal symmetry, the charge density can also be expanded in Legendre polynomials,

$$\frac{\tilde{\sigma}_i}{\varepsilon_0} = \sum_{n=0}^{\infty} \sigma_{i,n} P_n(\mu_i). \tag{7}$$

In order to apply the boundary conditions (4) and find the coefficients $A_{n,i}$ and $B_{n,i}$ it is necessary to re-expand Eqs. (5) and (6) for the potential in order to use just one set of spherical coordinates for each sphere. Equation (6) can be re-expanded by introducing a dimensionless distance between the centres of the interacting particles in the form of $\tilde{R} = \kappa R$, such that the modified Bessel functions now take the following form:[24]

$$\frac{K_{n+1/2}(\tilde{r}_i)}{\sqrt{\tilde{r}_i}} = \tilde{r}_i^n (2n-1)!! \sqrt{\frac{\pi}{2}} \sum_{l=0}^{\infty} (2n+2l+1) \times \frac{K_{n+l+1/2}(\tilde{R})}{\tilde{R}^{n+1/2}} \frac{I_{n+l+1/2}(\tilde{r}_j)}{\tilde{r}_j^{n+1/2}} C_l^{n+1/2}(\mu_j), \tag{8}$$

where $j = 3 - i$, $I_{n+l+1/2}(\tilde{r})$ are the modified Bessel functions of the first kind and $C_l^{n+1/2}(\mu)$ are the Gegenbauer polynomials. At the surface, $r_j = a_j < R$, a solution is sought only for the force along the z axis (Fig. 1). The Legendre polynomial in Eq. (6) can be represented as

$$\tilde{r}_i^n P_n(\mu_i) = \sum_{k=0}^{n} (-1)^k \frac{n!}{k!(n-k)!} \tilde{r}_j^k \tilde{R}^{n-k} P_k(\mu_j). \tag{9}$$

Substituting Eqs. (8) and (9) into Eq. (6) the potential outside each sphere is given by

$$\Phi_{\text{out},i} = \sum_{n=0}^{\infty} A_{n,i}(2n-1)!! \times \sum_{l=0}^{\infty} \Lambda_{n+l+1/2}(\tilde{r}_j,\tilde{R})\, C_l^{n+1/2}(\mu_j) \times \sum_{k=0}^{n} (-1)^k \frac{n!}{k!(n-k)!} \frac{1}{\tilde{R}^k \tilde{r}_j^{n-k}} P_k(\mu_j),$$

where

$$\Lambda_{l+1/2}(\tilde{r},\tilde{R}) = \frac{\pi}{2}\left(l + \frac{1}{2}\right) \frac{K_{l+1/2}(\tilde{R})}{\tilde{R}^{1/2}} \frac{I_{l+1/2}(\tilde{r})}{\tilde{r}^{1/2}}. \tag{10}$$

As proposed previously,[25] it is necessary to re-expand the product of Gegenbauer and Legendre polynomials in terms of Legendre polynomials in order to obtain a series linear in $P_n(\mu_j)$. Using explicit expressions for Legendre and Gegenbauer polynomials in terms of μ_j[26]

$$P_k(\mu) = \sum_{\nu=0}^{[k/2]} \frac{(-1)^{\nu}(2k-2\nu)!}{\nu!(k-\nu)!(k-2\nu)!} \frac{\mu^{k-2\nu}}{2^k} \equiv \sum_{\nu=0}^{k} \lambda_{k\nu}\mu^{\nu},$$

$$C_l^{n+1/2}(\mu) = \sum_{i=0}^{[l/2]} \frac{[2n-1+2(l-i)]!!}{(2n-1)!!} \times \frac{(-1)^i}{i!(l-2i)!} \frac{\mu^{l-2i}}{2^i} \equiv \sum_{i=0}^{l} \gamma_{nli}\mu^i,$$

and expanding each power of μ_j in terms of Legendre polynomials[27]

$$\mu^k = \sum_{l=0}^{[k/2]} \frac{k!(2k+1-4l)}{(2l)!!(2k+1-2l)!!} P_{k-2l}(\mu) \equiv \sum_{l=0}^{k} p_{kl} P_l(\mu),$$

an expression for the potential is obtained in the following form:

$$\Phi_{\text{out},i} = \sum_{n=0}^{\infty} P_n(\mu_j) \sum_{l=0}^{\infty} b_{nl}(\tilde{r}_j,\tilde{R}) A_{l,i}, \tag{11}$$

where

$$b_{nl}(\tilde{r},\tilde{R}) = (2l-1)!! \sum_{m=0}^{\infty}\sum_{k=0}^{l} (-1)^k \frac{l!}{k!(l-k)!} \times \frac{\Lambda_{l+m+1/2}(\tilde{r},\tilde{R})}{\tilde{R}^k \tilde{r}^{l-k}} \sum_{\nu=0}^{k} \lambda_{k\nu} \sum_{i=0}^{m} \gamma_{mli}\, p_{i+\nu,n}.$$

In order to apply the boundary conditions (4), the first derivatives of the potential are also required; inside the spheres, this is given by

$$\left.\frac{\partial\Phi_{\text{in},i}}{\partial\tilde{r}_i}\right|_{\tilde{r}_i=\tilde{a}_i} = \sum_{n=0}^{\infty} nB_{n,i}P_n(\mu_i)\,\tilde{a}_i^{n-1}, \tag{12}$$

whereas in the medium, the derivative of the potential takes the following form:[24]

$$\left.\frac{\partial\Phi_{\text{out},i}}{\partial\tilde{r}_i}\right|_{\tilde{r}_i=\tilde{a}_i} = \sum_{n=0}^{\infty} A_{n,i}P_n(\cos\theta_i) \times \frac{nK_{n+1/2}(\tilde{a}_i) - \tilde{a}_i K_{n+3/2}(\tilde{a}_i)}{(\tilde{a}_i)^{3/2}}. \tag{13}$$

The derivatives $\left.\frac{\partial\Phi_{\text{out},i}}{\partial\tilde{r}_j}\right|_{\tilde{r}_j=\tilde{a}_j}$ are expressed as

$$\left.\frac{\partial\Phi_{\text{out},i}}{\partial\tilde{r}_j}\right|_{\tilde{r}_j=\tilde{a}_j} = \sum_{n=0}^{\infty} P_n(\mu_j) \sum_{l=0}^{\infty} A_{l,i} \frac{b_{nl}(\tilde{a}_j,\tilde{R})}{\tilde{a}_j}. \tag{14}$$

Rewriting the boundary conditions (4) in accordance with the Eqs. (11)–(14) gives

$$\alpha_n(\tilde{a}_i,k_i)\,A_{n,i} + \sum_{l=0}^{\infty} \beta_{nl}(\tilde{a}_i,k_i)\,A_{l,j} = \sigma_{i,n}, \tag{15}$$

where

$$\begin{aligned} \alpha_n(\tilde{a}_i,k_i) &= k_m \frac{K_{n+3/2}(\tilde{a}_i)}{\tilde{a}_i^{1/2}} + n(k_i - k_m)\frac{K_{n+1/2}(\tilde{a}_i)}{\tilde{a}_i^{3/2}}, \\ \beta_{nl}(\tilde{a}_i,k_i) &= k_i n \frac{1}{\tilde{a}_i} b_{nl}(\tilde{a}_i,\tilde{R}) - k_m \frac{b_{nl}(\tilde{a}_i,\tilde{R})}{\tilde{a}_i}. \end{aligned} \tag{16}$$

2. An expression for the electrostatic force

The Maxwell stress tensor is used to calculate the interaction force acting on each sphere.[28] The force acting on sphere 1 by the presence of sphere 2 is expressed as

$$\mathbf{F}_1 = \square_{S_1} \mathbf{T}_{1\mathbf{n}} dS, \tag{17}$$

where

$$\begin{aligned}\mathbf{T}_{1\mathbf{n}} &= {}_0 k_m \left(E_{\mathbf{n}}\mathbf{E} - \frac{1}{2}\mathbf{n}E^2 \right) \\ &= {}_0 k_m \square \frac{1}{2} \square E_{\mathbf{n}}^2 - E^2 \square \mathbf{n} + E_{\mathbf{n}} E \square\end{aligned}$$

is the normal component of the Maxwell stress tensor, which represents the electrostatic shear stress and the pressure on the "medium-sphere" boundary in the absence of any mechanical deformation and electrostriction. Here

$$E_{\mathbf{n}} = -\frac{{}_{\text{out}}}{r_1}\square_{1=a_1}, \quad E \ = -\frac{1}{r_1}\frac{{}_{\text{out}}}{1}\square_{1=a_1} \tag{18}$$

are the normal and the tangential components of the self-consistent electric field, respectively. Using Eqs. (3), (6), and (11) an expansion for the self-consistent potential outside the spheres in terms of Legendre polynomials can be obtained,

$$\begin{aligned}{}_{\text{out}}(\tilde r_1, \ {}_1) = \square \square_{n=0} & A_{n,1}\frac{K_{n+1/2}(\tilde r_1)}{\tilde r_1} \\ & + \square_{l=0} b_{nl} \square \tilde r_1, \tilde R \square A_{l,2} \square P_n(\cos \ {}_1).\end{aligned} \tag{19}$$

Substituting (19) into (18) gives

$$\begin{aligned} E_{\mathbf{n}} &= -\frac{1}{a_1}\square_{n=0} \ {}_n P_n(\mu_1), \\ E \ &= \frac{\square\overline{1-\mu_1^2}\square}{a_1} \square_{n=1} \ {}_n \frac{}{\mu_1} P_n(\mu_1), \end{aligned} \tag{20}$$

where

$$\begin{aligned} {}_n &= A_{n,1}\frac{nK_{n+1/2}(\tilde a_1) - \tilde a_1 K_{n+3/2}(\tilde a_1)}{\tilde a_1^{1/2}} \\ &\quad + \tilde a_1 \square_{l=0} A_{l,2}\frac{b_{nl} \square \tilde a_1, \tilde R \square}{\tilde a_1}, \\ {}_n &= A_{n,1}\frac{K_{n+1/2}(\tilde a_1)}{\tilde a_1} + \square_{m=0} b_{nl} \square \tilde a_1, \tilde R \square A_{l,2}. \end{aligned} \tag{21}$$

Due to the axial symmetry of the problem, only the z-component of the force is non-zero leading to

$$\begin{aligned}(\mathbf{T}_{1\mathbf{n}})_z = {}& {}_0 k_m \\ & \times \square \frac{1}{2} \square E_{\mathbf{n}}^2 - E^2 \square \mu_1 - E_{\mathbf{n}} E \ \square \overline{1-\mu_1^2} \square .\end{aligned} \tag{22}$$

Combining (17), (20), and (22) a final expression for the electrostatic force is given by

$$\begin{aligned} F_{1z} = 4 \ {}_0 k_m \square_{n=1} & \frac{n}{(2n-1)(2n+1)} \\ & \times [\ {}_{n-1} - (n-1) \ {}_{n-1}][\ {}_n + (n+1) \ {}_n]. \end{aligned} \tag{23}$$

A complimentary expression for the electrostatic force acting on sphere 2 can be obtained by simultaneous interchanging of subscripts 1 and 2 in Eqs. (17)–(23). Stringent convergence tests for the electrostatic force represented by an infinite series of multipole moments have been reported by Lindgren *et al.*[29] In the present evaluation of the force, expansion (23) was truncated after the first 20 terms. However, more terms will be required at very short separation for particles that are dissimilar in size and charge.[29]

III. MODEL VERIFICATION

A. Interaction of small charged particles

Eq. (23) represents a general expression for the electrostatic force acting between two charged dielectric particles suspended in a solution which contains an electrolyte in low concentration. However it is instructive to consider special cases in order to reveal the physical meaning of low order terms in Eq. (23). First consider the case of weak screening and large inter-particle separation when the Debye length and separation are much greater than particle size, i.e., $a_i \quad R \quad 1$ or $\tilde a_i \quad \tilde R \quad 1$. This case corresponds to (macro)ions that do not undergo charge exchange with the solution. For small a_i (or R), the modified Bessel functions can be approximated as[24]

$$\begin{aligned} K_{n+1/2}(\tilde a_i) & \quad \square\overline{\frac{\tilde a_i}{2}} \frac{(2n-1)!!}{\tilde a_i^{n+1}}, \\ K_{n+1/2}\square\tilde R\square & = \square\overline{\frac{}{2\tilde R}} e^{-\tilde R} \square^{l}_{l=0} \frac{(n+l)!}{l!(n-l)!\square 2\tilde R \square^{l}}, \\ I_{n+1/2}(\tilde a_i) & \quad \square\overline{\frac{2\tilde a_i}{}} \frac{\tilde a_i^n}{(2n+1)!!}. \end{aligned} \tag{24}$$

This yields

$$\begin{aligned} {}_{n+1/2}\square\tilde a_i, \tilde R\square = {}& \square\overline{\frac{}{2}} \frac{\tilde a_i^n}{\tilde R} \frac{e^{-\tilde R}}{(2n-1)!!} \\ & \times \square^{l}_{l=0} \frac{(n+l)!}{l!(n-l)!\square 2\tilde R\square^{l}}. \end{aligned} \tag{25}$$

Approximations (24) and (25) make it possible to use the ratio a_i/R as an expansion parameter in Eq. (11) and to limit the number of terms, $n_{\max}$, in the expansion up to a certain number. It is assumed that the charge distribution on the surface of each sphere is uniform, i.e., ${}_i = \frac{Q_i}{4 \ a_i^2}$. This means that the only one non-zero term in Eq. (7) is

$${}_{i,n} = \frac{1}{4 \ {}_0}\frac{Q_i}{\tilde a_i^2} \ {}_{n,0}. \tag{26}$$

Next consider the two important cases of ion-ion interaction and ion-molecule interaction, respectively, in an electrolyte solution, where account is taken of the first monopole term ($n_{\max} = 1$) and the monopole and dipole terms ($n_{\max} = 2$) in expansion (23).

1. Ion-ion interaction

Ion-ion interaction can be represented as two non-polarizable charged spheres, and it corresponds to the expansion of all infinite sums up to $n_{\max} = 1$. The first term in the expansion series for the electrostatic force in Eq. (23) gives

$$F_{1z} = \frac{4 \quad {}_0 k_m}{3} \; {}_0 (\; {}_1 + 2 \; {}_1), \tag{27}$$

where, with reference to Eqs. (21), (24), and (25), at $n_{\max} = 1$

$$\begin{aligned} {}_0 &= - \frac{}{2} \frac{1}{\tilde{a}_1} A_{0,1}, \\ {}_1 &= -A_{1,1} \frac{}{2} \frac{2}{\tilde{a}_1^2} + \tilde{a}_1 A_{0,2} \frac{}{2} \frac{1+\tilde{R}}{\tilde{R}^2} e^{-\tilde{R}}, \\ {}_1 &= A_{1,1} \frac{}{2} \frac{1}{\tilde{a}_1^2} + A_{0,2} \frac{}{2} \tilde{a}_1 \frac{1+\tilde{R}}{\tilde{R}^2} e^{-\tilde{R}}. \end{aligned} \tag{28}$$

Here coefficients $A_{n,i}$ are the solution of the linear system (15), where with approximations (24) and (25) taken into account,

$$\begin{aligned} A_{0,i} & \quad \frac{1}{4 \quad {}_0} \frac{}{2} \frac{Q_i}{k_m}, \\ A_{1,i} & \quad -\frac{1}{4 \quad {}_0} \tilde{a}_i^3 \frac{k_i - k_m}{k_i + 2k_m} e^{-\tilde{R}} \frac{1+\tilde{R}}{\tilde{R}^2} \frac{}{2} \frac{}{k_m} Q_j. \end{aligned} \tag{29}$$

Finally, using (28) and (29) in Eq. (27) an explicit expression for the electrostatic force between two (macro)ions is obtained as follows:

$$\begin{aligned} F_{ion-ion} = &-\frac{Q_1 Q_2}{4 \quad {}_0 k_m R^2} (1 + \quad R)\, e^{- \quad R} \\ &-\frac{Q_1 Q_2}{4 \quad {}_0 k_m R^2} \frac{(1 + \quad R)\, e^{- \quad (R - a_1 - a_2)}}{1 + \quad (a_1 + a_2)}. \end{aligned} \tag{30}$$

Expression (30) contains only the first monopole term of expansion (23), which corresponds to the shielded Coulomb force between two finite-size ions of radii a_1 and a_2 in a medium with permittivity k_m and Debye length $^{-1}$. The presence of minus sign indicates that the force acting along the z axis is repulsive, when Q_1 has the same sign as Q_2.

2. Ion-molecule interaction

Next consider the interaction between an ion and a non-polar molecule. The ion is represented by a small charged non-polarizable sphere ($k_1 = k_m$), whereas the molecule is introduced as a polarizable sphere with zero charge ($Q_2 = 0$). These assumptions mean that the monopole term in Eq. (23) is zero, and in order to obtain a non-zero monopole-dipole force $n_{\max} = 2$. Expansion of (23) up to the second term yields the following simple expression for the force:

$$\begin{aligned} F_{1z} = 4 \quad & {}_0 k_m \\ \times & \; \frac{1}{3} \; {}_0 (\; {}_1 + 2 \; {}_1) + \frac{2}{15} (\; {}_1 - \; {}_1)(\; {}_2 + 3 \; {}_2) \; . \end{aligned} \tag{31}$$

Here

$$\begin{aligned} {}_0 &= -A_{0,1} \frac{}{2} \frac{1}{\tilde{a}_1}, \\ {}_1 &= -A_{1,1} \frac{}{2} \frac{2}{\tilde{a}_1^2} + \frac{}{2} \tilde{a}_1 e^{-\tilde{R}} \\ &\times A_{0,2} \frac{1+\tilde{R}}{\tilde{R}^2} + A_{1,2} \frac{2 + 2\tilde{R} + \tilde{R}^2}{\tilde{R}^3}, \\ {}_2 &= -A_{2,1} \frac{}{2} \frac{9}{\tilde{a}_1^3} + A_{0,2} \frac{}{2} \frac{2\tilde{a}_1^2}{\tilde{R}^2} e^{-\tilde{R}}, \\ {}_1 &= A_{1,1} \frac{}{2} \frac{1}{\tilde{a}_1^2} + \frac{}{2} \tilde{a}_1 e^{-\tilde{R}} \\ &\times A_{0,2} \frac{1+\tilde{R}}{\tilde{R}^2} + A_{1,2} \frac{2 + 2\tilde{R} + \tilde{R}^2}{\tilde{R}^3}, \\ {}_2 &= A_{2,1} \frac{}{2} \frac{3}{\tilde{a}_1^3} + A_{0,2} \frac{}{2} \frac{\tilde{a}_1^2}{\tilde{R}^3} \; 1 + \tilde{R} \; e^{-\tilde{R}}. \end{aligned} \tag{32}$$

Similar to the previous case, using approximations (28) and (29) in the system (15) gives the following solution:

$$\begin{aligned} A_{0,1} & \quad \frac{}{2} \frac{Q_1}{4 \quad {}_0 k_m}, \; A_{0,2} \quad \frac{\tilde{a}_2^3}{3\tilde{R}} e^{-\tilde{R}} \frac{}{2} \frac{Q_1}{4 \quad {}_0 k_m}, \\ A_{1,2} & \quad -\frac{1+\tilde{R}}{\tilde{R}^2} \tilde{a}_2^3 e^{-\tilde{R}} \frac{k_2 - k_m}{k_2 + 2k_m} \frac{}{2} \frac{Q_1}{4 \quad {}_0 k_m}, \\ A_{2,2} & \quad -\frac{2}{3} \frac{\tilde{a}_2^5}{\tilde{R}^3} \; 1 + \tilde{R} \; e^{-\tilde{R}} \frac{k_2 - k_m}{2k_2 + 3k_m} \frac{}{2} \frac{Q_1}{4 \quad {}_0 k_m}, \\ A_{1,1} & = A_{2,1} = 0. \end{aligned} \tag{33}$$

From Eqs. (32) and (33) it follows that the second term in the force expression (31) is zero, whereas the first term gives

$$\begin{aligned} F_{ion-molecule} & \\ = & \frac{Q_1^2 a_2^3}{4 \quad {}_0 k_m R^5} (1 + \quad R)\, e^{-2 \quad R} \\ \times & -\frac{(\quad R)^2}{3} + \frac{k_2 - k_m}{k_2 + 2k_m} \; 2\,(1 + \quad R) + (\quad R)^2 \; . \end{aligned} \tag{34}$$

In the absence of screening ($= 0$), Eq. (34) is reduced to

$$F_{ion-molecule} = 2\,(4 \quad {}_0 k_m) \frac{k_2 - k_m}{k_2 + 2k_m} a_2^3 \frac{Q_1^2}{(4 \quad {}_0 k_m)^2 R^5}. \tag{35}$$

Eq. (35) is in agreement with an expression given by Israelachvili[30] for the force between a non-polarisable ion and a neutral molecule, with the latter having a polarizability of $4 \quad {}_0 k_m \frac{k_2 - k_m}{k_2 + 2k_m} a_2^3$ as defined by the Clausius-Mossotti formula.[31,32] Eq. (34) can be also obtained using the force between a point charge and a dielectric microparticle.[13] The first term in Eq. (34) represents the electrolyte polarization around the molecule due to its finite size, and the force remains nonzero even in case $k_2 = k_m$. The second term can be reproduced exactly by derivation of the interaction energy between a point charge and a dipole in ionized medium[33] using the Clausius-Mossotti formula.

Note that in expressions (34) and (35) the effect of shielding is included twice: a shielding factor $e^{-2 \quad R}$ and the dielectric constant for the medium appearing as k_m^2. This dependence is derived from the origin of the electrostatic force: first the screened charge on particle 1 induces a dipole moment on particle 2 *via* a polarisable medium; in turn, this now screened dipole moment generates a second interaction with particle 1 through the same medium.

B. Comparison with experiments

As a test of the above theory, comparisons have been made with data taken from optical trap experiments on polymer particles by Sainis *et al.*[21] Experiments[21] have been performed on pairs of poly-methylmethacrylate (PMMA) spheres of radius 600 nm and dielectric constant 2.6 held in an optical trap in the presence of a nonpolar solvent (hexadecane) and a charge control agent (AOT). The electrostatic force has been measured for different molar concentrations of AOT corresponding to different values of particle charge and Debye length. Comparisons between the experimental data and the force calculated using both Eq. (23) and DLVO theory are shown in Fig. 2. The results show that at inter-particle separations exceeding the Debye length the experimental results are correctly described both by the present model (Eq. (23)) and DLVO theory. However, a discrepancy between DLVO theory and the proposed more accurate solution begins to emerge at shorter separations. Polarization contributions to the electrostatic force (fully described in the proposed model) are governed by a difference between the values of the dielectric constants of the interacting particles and the solvent. If the dielectric constants of the particles in the Dufresne experiment[21] were much greater than 2, it would lead to an enhancement of polarization effects, and DLVO theory would be even less accurate (see below).

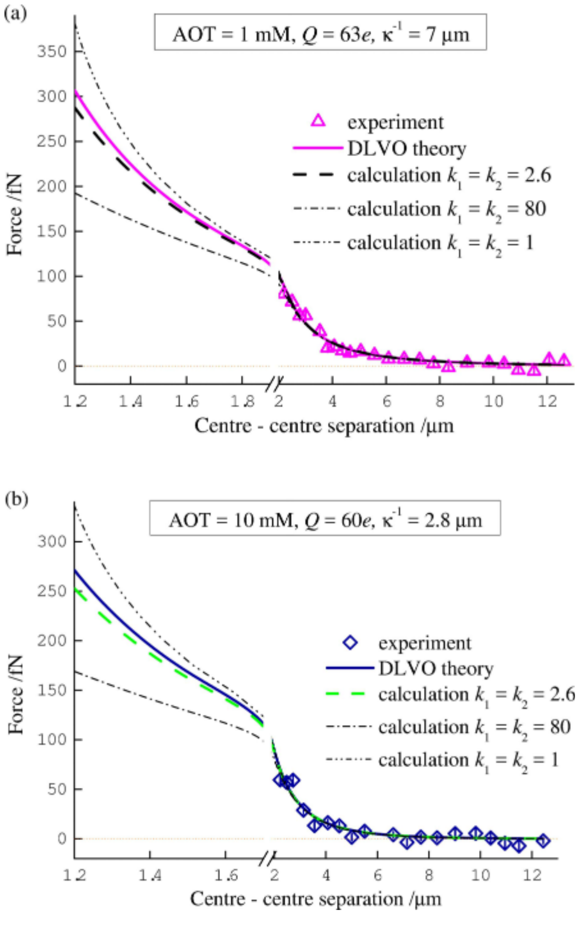

FIG. 2. Electrostatic force between two identical 600 nm PMMA particles ($k_1 = k_2 = 2.6$) in hexadecane ($k_{\mathrm{m}} = 2.06$) with AOT, measured in experiments at different AOT concentrations. The force is approximated by the present model and the electrostatic force from DLVO theory. Two additional curves at $k_1 = k_2 = 1$ and $k_1 = k_2 = 80$ correspond to hypothetical cases of whole particles filled with air and water, respectively.

Since no experimental data are currently available in the region of small inter-particle separations, a detailed numerical analysis has been performed in order to illustrate the interplay between polarization and shielding effects. The total charge density on a particle can be obtained using the boundary condition for the electric field strength,

$$ {}_{i,\mathrm{full}} = {}_0 \left[\frac{{}_{\mathrm{in},i}}{r_i} \bigg|_{r_i=a_i} - \frac{{}_{\mathrm{out,i}} + {}_{\mathrm{out,j}}}{r_i} \bigg|_{r_i=a_i} \right]. \tag{36}$$

Applying Eqs. (12) and (13) the following expression is obtained to provide a numerical evaluation of the total charge density:

$$ {}_{i,\mathrm{full}} = {}_0 \sum_{n=0} \left[A_{n,i} \frac{K_{n+3/2}(\tilde{a}_i)}{\tilde{a}_i^{1/2}} + \sum_{l=0} A_{l,2} \left(\frac{n}{\tilde{a}_1} b_{nl}\left(\tilde{a}_i, \tilde{R}\right) - \frac{b_{nl}\left(\tilde{a}_i, \tilde{R}\right)}{\tilde{a}_i} \right) \right] \times P_n(\mu_i). \tag{37}$$

Fig. 3 shows a numerical solution to Eq. (37) corresponding to a 10 mM molar concentration of AOT (as used in Fig. 2(b)) at an inter-particle separation equal to the Debye length (Fig. 3(a)) and at the point of contact (Fig. 3(b)), where there is zero surface-to-surface separation between particles. When the particles are separated by the Debye length, shielding from the electrolyte does not allow the particles to influence one another, and the surface charge distribution is almost uniform; hence, DLVO theory works well in this region. At zero separation reduction in the magnitude of the electrostatic force due to polarization (relative to DLVO theory) amounts to just 7%. For the experiments described in Fig. 2, there is little difference between the dielectric constants of the colloid particles and that of the solvent, and the magnitude of the charge is not high enough to cause significant polarization. In addition, the separation range studied does not include inter-particle distances where short-range forces (e.g., the van der Waals forces) dominate.

In order to further demonstrate the possible effects of polarization, two additional curves have been plotted in Fig. 2. The dashed-dotted curve denotes the electrostatic force between two spheres of the same charge and size as colloidal particles in the experiment[21] but with greater permittivity ($k_1 = k_2 = 80$). In this case, polarization effects lead to a strongly non-uniform distribution of surface charge (Fig. 3(c)) and a considerable reduction (37%) in electrostatic force relative to the force between non-polarizable spheres. The double dashed-dotted curve in Fig. 2 represents the case of less polarizable spheres ($k_1 = k_2 = 1$), for which the magnitude of the force at zero surface-to-surface separation is 24% greater than the electrostatic force predicted with DLVO theory. Calculations using Eq. (37) show that an increase in

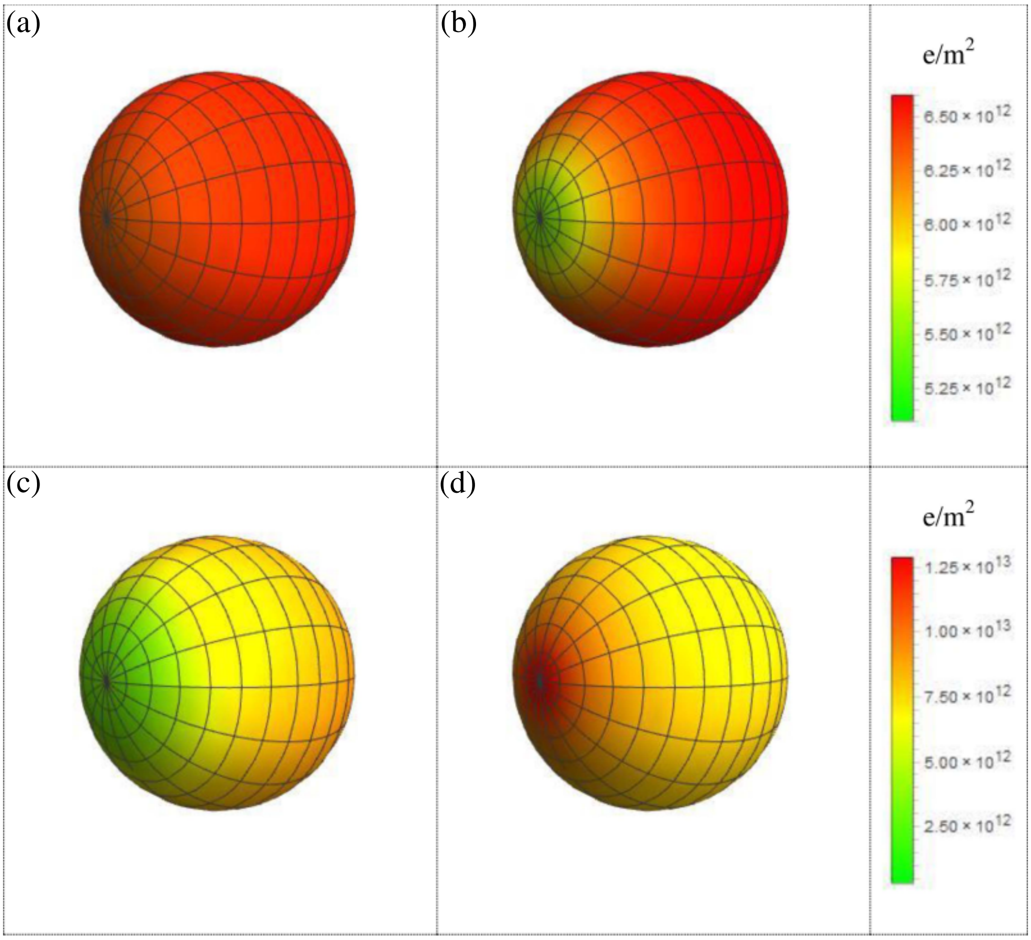

FIG. 3. Total charge distribution on the surface of a 600 nm PMMA sphere in hexadecane with 10 mM of AON (a) at a center-to-center separation equal to the Debye length for $k_1 = k_2 = 2.6$, (b) at zero surface-to-surface separation for $k_1 = k_2 = 2.6$, (c) at zero surface-to-surface separation for $k_1 = k_2 = 80$ and (d) at zero surface-to-surface separation for $k_1 = k_2 = 1$.

the magnitude of the force is caused by positive charge concentrated around the contact point (Fig. 3(d)). These two cases show that taking into account polarization effects can give a completely different character to the electrostatic interaction.

C. Comparison with the non-shielded model

A further analysis of the current solution has been undertaken in the limit of infinite Debye length ($= 0$) in order to compare results with the earlier methodology,[14] where the electrostatic force between particles was calculated in a vacuum. The corresponding electrostatic force between two spheres 1.25 nm in diameter, carrying charges of $Q_1 = -1e$ and $Q_2 = -7e$ and with dielectric constants $k_1 = k_2 = 20$ has been calculated and plotted in Fig. 4(a). Calculations of the electrostatic force have also been performed for a finite value of the Debye length of 2.5 nm (Fig. 4(b)), and these results are compared with the non-shielded force[14] multiplied by a factor of $(1 + \; R)\, e^{- \; R}$. As can be seen, the present model is in excellent agreement with the methodology developed for two polarizable spheres in a vacuum.[14] The calculations shown in Fig. 4(b) also reveal that the product of the force obtained using the non-shielded medium and the factor $(1 + \; R)\, e^{- \; R}$ gives a very good approximation for the interaction force in an electrolyte. This result is not unlike predictions obtained by DLVO theory, where the Coulomb force between two ions is multiplied by the same factor. Shielding effects become significant at separations greater than the Debye length, where mutual polarization of the interacting particles is negligible, whereas at short separations, polarization effects dominate.

D. Van der Waals force and conclusive remarks

Thus far only the electrostatic part of DLVO theory has been taken into account. However, interactions in DLVO theory consist both of an electrostatic repulsion and an attraction due to van der Waals forces. Since the attraction between like-charged particles is already captured by electrostatic model, it is useful to investigate if the van der Waals force overlaps with electrostatic attraction. For this purpose, calculations from Fig. 4(c) are compared with van der Waals force between two colloidal particles, calculated as follows:[30]

$$F_{\mathrm{vdW}} = \frac{Aa}{12s^2}, \tag{38}$$

where $A \quad 10^{-19}$ J is the Hamaker constant, a is the particle radius, and $s = R - 2a$ is the surface-to-surface separation. A comparison between the present model and DLVO theory

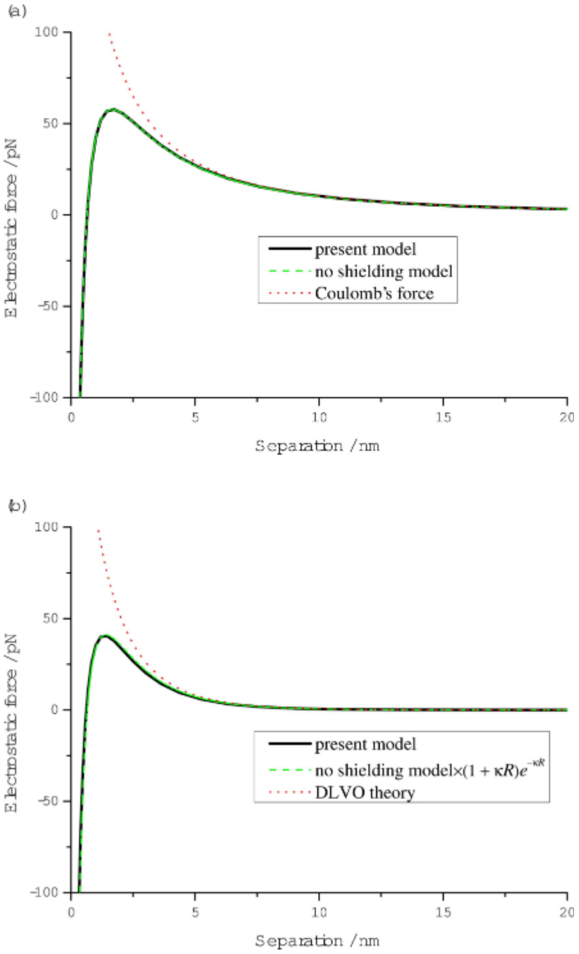

FIG. 4. Calculated electrostatic force between two colloidal particles in (a) vacuum, (b) and in electrolyte with $^{-1} = 2.5$ nm as a function of separation $R - a_1 - a_2$. In each case, $a_1 = a_2 = 1.25$ nm, $k_1 = k_2 = 20$, $Q_1 = -1e$, and $Q_2 = -7e$. The force has been calculated using the full present model and the approximation involving separately polarization and shielding terms. For reference purposes, the Coulomb force (a) and the double-layer force from DLVO theory (b) have also been plotted.

including the van der Waals force is shown in Fig. 5. It shows that in the present model the van der Waals force overlaps almost entirely with the attractive part of the electrostatic force, whereas in DLVO theory it is the van der Waals force that is responsible for attraction and the possible coalescence of colloidal particles.

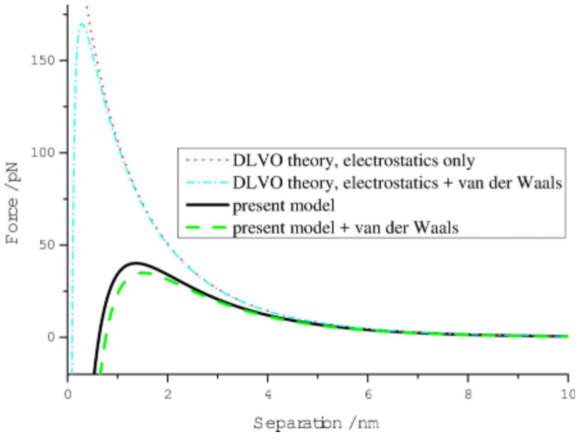

FIG. 5. Calculated electrostatic and the van der Waals forces between two colloidal particles in electrolyte $^{-1} = 2.5$ nm as a function of separation $R - a_1 - a_2$. The parameters of colloidal particles are the same as in Fig. 4.

In conclusion, the electrostatic problem for two polarizable colloidal particles in solution has been solved for low concentration of electrolyte such that the Debye-Hückel approximation is valid. The force is expressed as an infinite series, and the monopole and dipole terms are extracted to compare with literature expressions for ion-ion and ion-molecule interactions. It is shown that when the Debye length is much greater than the size of colloid particles it is possible to approximate the force at large distances by the shielding factor, whereas at short separations, the methodology developed for a non-ionized medium is sufficiently accurate. The presented methodology can be used to interpret experimental data for colloids and/or solvents with sufficiently different values of dielectric constant. It can also be used to study colloidal particles of high permittivity in order to obtain more accurate results for the electrostatic force at short separation. Calculations using the present model reveal particular cases where electrostatic attraction dominates over the van der Waals force, which may be essential in the study of coalescence processes.

ACKNOWLEDGMENTS

ERC Consolidator Grant No. ERC-2012-StG 307755 FIN and EPSRC Impact Acceleration Account grant are gratefully acknowledged. I.N.D. and A.V.F. also acknowledge support in part by a grant from Russian Science Foundation (Grant No. 16-12-10424).

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