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Electrophoresis of solid particles embedded in an unbounded electrolyte

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Abstract. We consider an assemblage of $N \geqslant 1$ solid and charged particles embedded in an unbounded electrolyte. This work examines the rigid-body motion of such solids in an imposed electric field $\boldsymbol{E}_\infty$. The advocated approach rests on the treatment of $6N+1$ boundary integral equations and circumvents determining the electric field $\boldsymbol{E}$ and the fluid flow within the electrolyte. Numerical results for assemblages of nine uniformly charged spheres or ellipsoids are reported. The interaction between near-contact particles may be very strong and deeply depends on the cluster nature. © 2001 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

electrophoresis / integral equations / boundary elements

Electrophorèse d'une assemblée de particules en milieu électrolyte infini

Résumé. *On détermine le mouvement de $N \geqslant 1$ particules solides et chargées en milieu electrolyte infini, sous l'action d'un champ électrostatique imposé $\boldsymbol{E}_\infty$. La méthode proposée repose sur la résolution de $6N+1$ équations intégrales de frontière et s'affranchit de l'évaluation du champ électrostatique effectif $\boldsymbol{E}$ et de l'écoulement dans l'électrolyte. Les résultats numériques, fournis ici pour neuf sphères ou ellipsoides uniformément chargés, révèlent que l'intéraction entre les particules devient cruciale lorsque celles-ci sont proches et s'avère très sensible à la configuration étudiée. © 2001 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS*

electrophorèse / equations intégrales / éléments de frontière

Version française abrégée

Soient $N \geqslant 1$ particules solides $\mathcal{P}_n$ (voir *figure 1a*) en milieu électrolyte infini de permittivité ϵ et de viscosité μ. La surface S_m de $\mathcal{P}_m$ admet ζ_m pour potentiel «zéta» et en présence d'un champ électrique $\boldsymbol{E}_\infty$ imposé, $\mathcal{P}_n$ acquiert des vitesses $\boldsymbol{U}^{(n)}$ de translation (celle d'un point O_n de $\mathcal{P}_n$) et de rotation $\boldsymbol{\omega}^{(n)}$ à déterminer en fonction de ϵ, μ, $\boldsymbol{E}_\infty$ et des ζ_m [1]. Pour $\boldsymbol{E}_\infty$ uniforme, la célèbre solution [2–4] de Smoluchowski (1), obtenue pour $N=1$ et ζ_1 constant, a été étendue [9] au cas $N \geqslant 2$ si $\zeta_m = \zeta_1$ constant. Cette Note propose une méthode procurant les inconnues $(\boldsymbol{U}^{(n)}, \boldsymbol{\omega}^{(n)})$ dans le cas le plus général ($\boldsymbol{E}_\infty$ et ζ_m quelconques).

On adopte des coordonnées cartésiennes d'origine O et la convention de sommation des indices. Sous des hypothèse classiques [10], le champ effectif $\boldsymbol{E}$ dans le domaine fluide Ω, de frontière $S := \bigcup_{n=1}^{N} S_n$, s'écrit $\boldsymbol{E} = \boldsymbol{E}_\infty - \nabla\phi$ où le potentiel de perturbation ϕ vérifie (2) avec $r := OM$ tandis que l'électrolyte présente un écoulement $(\boldsymbol{u}, p)$ de Stokes permanent, de tenseur des contraintes $\boldsymbol{\sigma}$, sujet à (3)–(4). Les

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vitesses $U^{(n)}$ et $\omega^{(n)}$ sont obtenues en exigeant [1] un torseur des efforts hydrodynamiques nul sur chaque solide, c'est-à-dire (5) où σ s'exprime, via (2)–(4), en fonction des inconnues $(U^{(n)}, \omega^{(n)})$. Considérons, pour $L \in \{T, R\}$, $6N$ écoulements $(u_L^{(n),i}, p_L^{(n),i})$ exercant sur S les densités surfaciques d'efforts $f_L^{(n),i}$ et sujets à (3) et (8) où δ désigne le symbole de Kronecker (T ou R correspondant respectivement à une translation ou une rotation de $\mathcal{P}_n$). Les inconnues $U^{(n)} = U_j^{(n)} e_j$ et $\omega^{(n)} = \omega_j^{(n)} e_j$ obéissent alors [9] au système (6) de coefficients définis par (7). La détermination du mouvement des particules ne requiert ainsi que la connaissance sur S des vecteurs $\nabla\phi$ et $f_L^{(n),i}$. Ces grandeurs s'obtiennent par résolution d'équations intégrales de Fredholm sur S : la première, (9), de première espèce et bien posée [13], procure ϕ (et donc $\nabla\phi$) sur S et les $6N$ autres, (10), de seconde espèce et bien posées [14,12], fournissent les densités $f_L^{(n),i}$ et découlent d'une généralisation de résultats exposés dans [14].

La résolution numérique de (9)–(10) utilise des éléments triangulaires curvilignes sur S [11], une représentation isoparamétrique des inconnues et une factorisation LU de chaque système discrétisé. On envisage (voir *figures 1a–b*) quatre configurations A_l, $l \in \{1, \ldots, 4\}$, à neuf sphères ou ellipsoides, définies par (11)–(14) où $d \geqslant 2$ désigne la variable de séparation de A_l (pour des particules en contact $d = 2$). De plus, $E_\infty = E e_i$ est uniforme, chaque fonction ζ_m est séparément constante et 74 points de collocation sont disposés sur chaque S_m (sauf 242 points sur la grosse sphère S_5 pour A_2). Si $\zeta_m = \zeta_1 \neq 0$ pour tout m, ces maillages conduisent à des erreurs numériques $\mathrm{Max}_{(n,j)} |\mu U_j^{(n)}/(\epsilon\zeta_1 E) - \delta_{ij}|$ et $\mathrm{Max}_{(n,j)} |\mu\omega_j^{(n)} c_n(l)/(\epsilon\zeta_1 E)|$ de l'ordre du pourcent pour $d \geqslant 2{,}3$. Si les fonctions ζ_n diffèrent, la mobilité $v_i^{(m)} := \mu U^{(m)}/(\epsilon\zeta_m E)$ de $\mathcal{P}_m$ dans la direction e_i s'avère dépendre de la configuration et de sa « séparation » d. Pour illustrer ce point, examinons les cas $\zeta_n = \delta_{nm}$ pour (par linéarité et en raison de symétries) les seules valeurs $m \in \{1, 2, 4, 5\}$. Les résultats révèlent que $v_3^{(m)} - 1$ est négligeable pour $d \sim 10$ mais, comme le montrent les *figures 2a–b*, devient pour $d \to 2$ non seulement appréciable mais très sensible à la configuration et à la position de la particule ($v_3^{(m)} - 1$ est positif si $m = 2$ pour A_2 ou si $m = 4$ pour A_3 et négatif sinon !). Ces conclusions dépendent aussi de la direction e_i : les *figures 2c–d* montrent ainsi que la particule centrale $\mathcal{P}_5$ est accélérée (par rapport à la solution de Smoluchowski $v_i^{(5)} = 1$) selon e_2 et ralentie selon e_3 pour chaque configuration, le cas de A_1 (neuf sphères identiques) conduisant aux effets les plus prononcés.

1. Introduction

The transport of $N \geqslant 1$ solid particles $\mathcal{P}_n$ (see *figure 1a*) by an external electric field E_∞ (Electrophoresis) admits many physical and biological applications.

Each solid $\mathcal{P}_n$ experiences a rigid-body motion, of unknown translational and angular velocities $U^{(n)}$ and $\omega^{(n)}$, and we denote by ζ_n the so-called zeta potential on its surface S_n. Under the usual "thin double-layer" assumptions and for nonconducting particles [1], the vectors $U^{(n)}$ and $\omega^{(n)}$ only depend

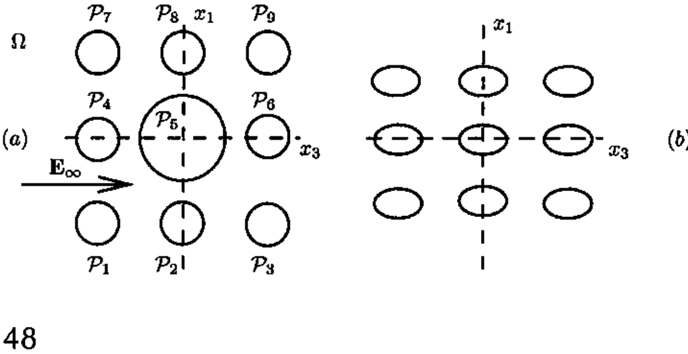

Figure 1. (a) Nine-sphere assemblage A_2. (b) Nine-ellipsoid assemblage A_4.

Figure 1. *(a) Configuration à neuf sphrères A_2. (b) Confirguration à neuf ellipsooides A_4.*

on the functions ζ_m, the imposed electric field $\boldsymbol{E}_\infty$ and the constant permittivity and viscosity ϵ and μ of the electrolyte. Many available works consider a single particle $\mathcal{P}_1$. In this direction, the celebrated Smoluchowski solution [2–4]:

$$\boldsymbol{U}^{(1)} = \frac{\epsilon\zeta_1 \boldsymbol{E}_\infty}{\mu}, \qquad \boldsymbol{\omega}^{(1)} = \mathbf{0} \tag{1}$$

holds, for any particle's shape, as soon as both $\boldsymbol{E}_\infty$ and ζ_1 are uniform. Unfortunately, collections of particles are encountered in particle separation and, to the author's very best knowledge [5–8], only clusters of uniformly charged spheres have been addressed for $N \geqslant 2$ and $\boldsymbol{E}_\infty$ uniform. As recently established in [9], the solution (1) still holds for any particle and any assemblage provided that $\zeta_n = \zeta_1$ with ζ_1 and $\boldsymbol{E}_\infty$ uniform. Whenever one of these conditions breaks down a numerical approach seems unavoidable. This Note reduces such a procedure to the treatment of $6N+1$ boundary integral equations and reports, for nine-particle assemblages, our very first numerical results.

2. The governing system and the relevant boundary integral equations

Henceforth, Cartesian coordinates and the tensor summation convention are adopted whereas $r := OM$ and $S := \bigcup_{n=1}^{N} S_n$. In the unbounded flow domain Ω, the electric field reads $\boldsymbol{E} = \boldsymbol{E}_\infty - \nabla\phi$ and the perturbation potential ϕ obeys the well-posed Neumann-type problem [10]:

$$\nabla^2\phi = 0 \quad \text{in } \Omega, \quad \nabla\phi \to \mathbf{0} \quad \text{as } r \to \infty \quad \text{and} \quad \nabla\phi.\boldsymbol{n} = \boldsymbol{E}_\infty.\boldsymbol{n} \quad \text{on } S \tag{2}$$

In addition, for a weak applied field $\boldsymbol{E}_\infty$ and small particles, the electrolyte flow $(\boldsymbol{u}, p)$ is governed by the quasi-static creeping motion problem:

$$\mu\nabla^2\boldsymbol{u} = \nabla p \quad \text{and} \quad \nabla.\boldsymbol{u} = 0 \quad \text{in } \Omega, \quad (\boldsymbol{u}, p) \to (\mathbf{0}, 0) \quad \text{as } r \to \infty, \quad \boldsymbol{u} = \boldsymbol{u}_d \quad \text{on } S \tag{3}$$

where the prescribed velocity $\boldsymbol{u}_d$ reads, for the "thin double-layer" model [10]:

$$\boldsymbol{u}_d(M) = \boldsymbol{U}^{(n)} + \boldsymbol{\omega}^{(n)} \wedge \boldsymbol{O_n M} - \frac{\epsilon\zeta_n(M)[\boldsymbol{E}_\infty - \nabla\phi]}{\mu} \quad \text{on } S_n \tag{4}$$

if $\boldsymbol{U}^{(n)}$ denotes the velocity of the point O_n of $\mathcal{P}_n$. Solving (2)–(4) provides $(\boldsymbol{u}, p)$ and the stress tensor $\boldsymbol{\sigma}$ versus the velocities $\boldsymbol{U}^{(n)} = U_j^{(n)}\boldsymbol{e}_j$ and $\boldsymbol{\omega}^{(n)} = \omega_j^{(n)}\boldsymbol{e}_j$. Finally, such velocities are obtained [1] by requiring zero net hydrodynamic force and torque on each particle $\mathcal{P}_m$:

$$\int_{S_m} \boldsymbol{e}_i.\boldsymbol{\sigma}.\boldsymbol{n}\,\mathrm{d}S_m = 0, \qquad \int_{S_m} [\boldsymbol{e}_i \wedge \boldsymbol{O_n M}].\boldsymbol{\sigma}.\boldsymbol{n}\,\mathrm{d}S_m = 0; \quad i \in \{1,2,3\} \text{ and } m \in \{1,\ldots,N\} \tag{5}$$

As explained in [9], the conditions (5) actually yield the key $6N$-equation linear system:

$$A_{(m),L}^{(n),i,j} U_j^{(m)} + B_{(m),L}^{(n),i,j} \omega_j^{(m)} = \frac{\epsilon}{\mu}\int_S \zeta[\boldsymbol{E}_\infty - \nabla\phi].\boldsymbol{f}_L^{(n),i}\,\mathrm{d}S \tag{6}$$

where summations over indices j and m hold, $L \in \{T, R\}$, $i \in \{1,2,3\}$, $n \in \{1,\ldots,N\}$ and:

$$A_{(m),L}^{(n),i,j} = \int_{S_m} \boldsymbol{e}_j.\boldsymbol{f}_L^{(n),i}\,\mathrm{d}S_m, \qquad B_{(m),L}^{(n),i,j} = \int_{S_m} [\boldsymbol{e}_j \wedge \boldsymbol{O_m M}].\boldsymbol{f}_L^{(n),i}\,\mathrm{d}S_m \tag{7}$$

Moreover, in (6)–(7), the vector $\boldsymbol{f}_L^{(n),i}$ denotes the hydrodynamic surface force arising on S for the Stokes flow $(\boldsymbol{u}_L^{(n),i}, p_L^{(n),i})$ that obeys (3) with the conditions (δ is the Kronecker delta):

$$\boldsymbol{u}_T^{(n),i} = \delta_{nm}\boldsymbol{e}_i, \qquad \boldsymbol{u}_R^{(n),i} = \delta_{nm}[\boldsymbol{e}_i \wedge \boldsymbol{O}_n\boldsymbol{M}] \quad \text{on } S_m \tag{8}$$

where letters T or R actually pertain to a translation or a rotation of the solid $\mathcal{P}_n$. According to (6)–(7), one only needs to determine the previous fields $\boldsymbol{f}_L^{(n),i}$ and the tangential derivatives of ϕ (since $\nabla\phi.\boldsymbol{n} = \boldsymbol{E}_\infty.\boldsymbol{n}$ on S) on the surfaces S_m only. In other words, it is no use gaining the fluid motion $(\boldsymbol{u}, p)$ and ϕ in Ω. Furthermore, the required vectors $\boldsymbol{f}_L^{(n),i}$ and $\nabla\phi$ on S may be obtained by solving $6N+1$ boundary integral equations on S. First, as solution to (2), the function ϕ obeys on S the well-known Fredholm boundary integral equation of the second kind [11]:

$$-4\pi\phi(M) + \int_S [\phi(P) - \phi(M)]\frac{\boldsymbol{PM}.\boldsymbol{n}(P)}{PM^3}\,\mathrm{d}S = \int_S \frac{[\boldsymbol{E}_\infty.\boldsymbol{n}](P)}{PM}\,\mathrm{d}S \tag{9}$$

By extending the material available in [12], the components of each force $\boldsymbol{f}_L^{(n),i}$ are also seen to satisfy the following system of coupled Fredholm boundary integral equations of the first kind:

$$[\boldsymbol{u}_L^{(n),i}.\boldsymbol{e}_k](M) = -\int_S \left\{\frac{\delta_{jk}}{PM} + \frac{(\boldsymbol{PM}.\boldsymbol{e}_j)(\boldsymbol{PM}.\boldsymbol{e}_k)}{PM^3}\right\}\left[\frac{\boldsymbol{f}_L^{(n),i}.\boldsymbol{e}_j}{8\pi\mu}\right](P)\,\mathrm{d}S; \quad k \in \{1,2,3\} \tag{10}$$

For $\boldsymbol{E}_\infty.\boldsymbol{n} \in \mathcal{H}^{-1/2}(S)$ the solution to (9) is unique in $\mathcal{H}^{-1/2}(S)$ (see [13]) and permits us to compute the tangential derivatives of ϕ on S. The solution to (9) in $(\mathcal{H}^{-1/2}(S))^3$ is defined up to any constant multiple of $\boldsymbol{n}$ if $N=1$ [12] and unique if $N \geqslant 2$ [14].

3. Numerical method and results

Our basic integral equations (9)–(10) are treated by using the classical boundary element method [11]. More precisely, we used on each surface S_n isoparametric triangular and curvilinear boundary elements and resorted to a standard LU factorization algorithm in solving the resulting matrix systems and (6). Henceforth, i_1 or i_3 belong to $\{1,2,3\}$ and we restrict our attention to four nine-ellipsoid assemblages A_l, $l \in \{1,\ldots,4\}$, such that

$$OO_n = x_j^n(l)\boldsymbol{e}_j = (i_1 - 1)d_1(l)\boldsymbol{e}_1 + (i_3 - 1)d_3(l)\boldsymbol{e}_3 \quad \text{for } n = 3(i_1 - 1) + i_3 \tag{11}$$

$$\frac{[x_1 - x_1^n(l)]^2}{a_n^2(l)} + \frac{[x_2]^2}{b_n^2(l)} + \frac{[x_3 - x_3^n(l)]^2}{c_n^2(l)} = 1 \quad \text{if } M(x_1,x_2,x_3) \in S_n \tag{12}$$

with (see *figures 1a–b* for clusters A_2 and A_4) the following settings, for $k \in \{1,2,3\}$,

$$a_n(k) = b_n(k) = c_n(k) = 1 + \delta_{n5}(k-1)[-4]^{2-k}, \quad d_1(k) = d_3(k) = d\left[1 + \frac{\delta_{k2}}{2}\right] \tag{13}$$

$$a_n(4) = 0.8, \quad b_n(4) = 1, \quad c_n(4) = 1.2, \quad d_1(4) = 1.6 + 1.2(d-2), \quad d_3(4) = 1.2d \tag{14}$$

where the *separation variable* $d \geqslant 2$ equals 2 for touching particles. Thus, A_1 and A_4 consist of nine identical spheres or ellipsoids while eight spheres of unit radii surrounder a big or a small sphere S_5 for clusters A_2 or A_3. Each solid $\mathcal{P}_n$ is uniformly charged (ζ_n is constant) and the external field $\boldsymbol{E}_\infty = E\boldsymbol{e}_i$ is uniform. By superposition and for symmetry reasons, only cases $\zeta_n = \delta_{nm}$ with $m \in \{1,2,4,5\}$ are addressed. The surface S_n is discretized by using a 74-node mesh except in the case of the 242-node mesh used on S_5 for cluster A_2. If $\zeta_n = \zeta_1$ (see (1)), such choices yield numerical

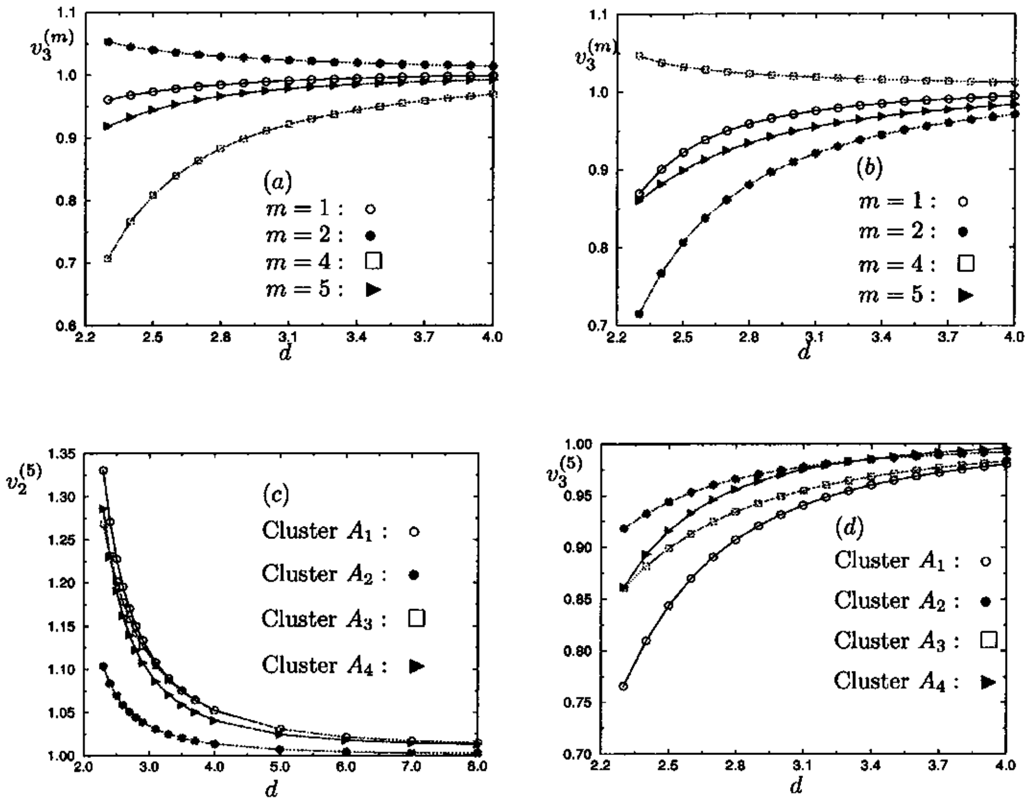

Figure 2. Electrophoretic mobility $v_i^{(m)}$ for $\boldsymbol{E}_\infty = E\boldsymbol{e}_i$, $\zeta_n = \delta_{nm}$ and $d \geqslant 2.3$. (a) $i = 3$ and cluster A_2. (b) $i = 3$ and cluster A_3. (c) $m = 5$, $i = 2$. (d) $m = 5$, $i = 3$.

Figure 2. *Mobilité $v_i^{(m)}$ pour $\boldsymbol{E}_\infty = E\boldsymbol{e}_i$, $\zeta_n = \delta_{nm}$ et $d \geqslant 2{,}3$. (a) $i = 3$ and cluster A_2. (b) $i = 3$ and cluster A_3. (c) $m = 5$, $i = 2$. (d) $m = 5$, $i = 3$.*

errors $\mathrm{Max}_{(n,j)} |\mu U_j^{(n)}/(\epsilon\zeta_1 E) - \delta_{ij}|$ and $\mathrm{Max}_{(n,j)} |\mu\omega_j^{(n)} c_n(l)/(\epsilon\zeta_1 E)|$ of order of one percent in the range $d \geqslant 2.3$. For $\boldsymbol{E}_\infty = E\boldsymbol{e}_i$ and uniform but different zeta potentials ζ_n the electrophoretic mobilities $v_i^{(m)} = \mu U_i^{(m)}/(\epsilon\zeta_m E)$ differ from one and deeply depend on the cluster nature and its separation variable.

As reported in *figures 2a–b*, the difference $v_3^{(m)} - 1$ quickly vanishes as the separation variable d increases (actually, for $d \sim 10$ each particle seems isolated) while the interactions become dramatic for near-contact particles ($d \to 2.$). In these latter circumstances, $v_3^{(m)} - 1$ is very sensitive to the location of the particle and to the cluster: it is positive if $m = 2$ for A_2 or if $m = 4$ for A_3 and negative in other cases. The results also highly depend on the direction of $\boldsymbol{E}_\infty = E\boldsymbol{e}_i$. For instance, as depicted in *figures 2c–d* for $m = 5$, the particle $\mathcal{P}_5$ is speeded up (with respect to the Smoluchowski solution $v_i^{(5)} = 1$) in the direction $\boldsymbol{e}_2$ while it is slowed down in the direction $\boldsymbol{e}_3$. In both directions the assemblage A_1 of identical spheres yields the stronger interactions.

4. Conclusions

The enclosed numerical results reveal strong interactions for near-contact particles of unequal and uniform zeta potentials. The present method also applies to the general case of non-uniformly charged particles embedded in an arbitrary field $\boldsymbol{E}_\infty$. In addition, the use of iterative methods allows us to deal with a great number of particles (about one hundred). Such basic tasks are currently under investigation.

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