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# Electrophoresis of a 2-particle cluster near a plane boundary

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## Abstract

Particle–boundary and particle–particle interactions in Electrophoresis are examined by considering a 2-particle cluster near a plane boundary. The advocated treatment holds for two insulating particles of arbitrary shapes and zeta potential functions and resorts to 13 boundary-integral equations. Preliminary results reveal that, depending upon the addressed velocity nature (translational or angular), wall–particle may be stronger or weaker than particle–particle interactions. **To cite this article:** A. Sellier, C. R. Mecanique 331 (2003).

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## Résumé

**Électrophorèse de deux particules en présence d’une paroi plane.** On examine l’électrophorèse d’une particule isolante, sous l’action d’un champ électrique uniforme  $\mathbf{E}_\infty$ , en présence d’une seconde particule isolante et d’une paroi plane parfaitement conductrice et normale à  $\mathbf{E}_\infty$  ou isolante et parallèle à  $\mathbf{E}_\infty$ . La méthode préconisée utilise 13 équations intégrales de frontière et on montre que, selon la nature (translation ou rotation) de la vitesse examinée, les interactions paroi–particule peuvent être plus fortes ou moindres que les interactions particule–particule. **Pour citer cet article :** A. Sellier, C. R. Mecanique 331 (2003).

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**Keywords:** Fluid mechanics; Electrophoresis; Wall–particle interactions; Particle–particle interactions

**Mots-clés :** Mécanique des fluides ; Électrophorèse ; Paroi plane ; Interactions

## Version française abrégée

On place au dessus du plan  $\Sigma$ , d’équation  $x_3 = 0$  en coordonnées cartésiennes  $x_j = \mathbf{OM} \cdot \mathbf{e}_j$ , deux particules solides  $\mathcal{P}_n$  ( $n = 1, 2$ ) dans un électrolyte de viscosité  $\mu$  et permittivité  $\varepsilon$  uniformes (voir la Fig. 1). La surface isolante  $\mathcal{S}_n$  de  $\mathcal{P}_n$  admet le zéta potentiel  $\zeta_n$  et sous le champ électrique  $\mathbf{E}_\infty$  uniforme  $\mathcal{P}_n$  acquiert une vitesse de translation  $\mathbf{U}^{(n)}$  (celle d’un point  $O_n$  de  $\mathcal{P}_n$ ) et de rotation  $\boldsymbol{\Omega}^{(n)}$ , fonctions de  $\varepsilon \mathbf{E}/\mu$ ,  $O_1 O_2$ ,  $h_n = \mathbf{OO}_n \cdot \mathbf{e}_3$ ,  $\zeta_n$  et du plan  $\Sigma$  : isolant, de zéta potentiel uniforme  $\zeta_w$  et parallèle à  $\mathbf{E}_\infty$  (Cas 1) ou parfaitement conducteur et normal à  $\mathbf{E}_\infty$  (Cas 2). Les cas d’une sphère sans [2–5] ou avec [9–12]  $\Sigma$  et de deux sphères [6–8] sans  $\Sigma$  ont été

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résolus (avec  $\zeta_1$  et  $\zeta_2$  uniformes sauf dans [12]). Cette Note envisage deux particules de formes et de zéta potentiels arbitraires en présence de  $\Sigma$ .

Dans le domaine fluide  $\Omega$  le champ électrique est  $\mathbf{E} = \mathbf{E}_\infty - \nabla\phi$ . Le potentiel  $\phi$  et l'écoulement  $(\mathbf{u}, p)$ , de tenseur des contraintes  $\boldsymbol{\sigma}$ , vérifient [10] le problème (2)–(5) où  $\mathbf{n}$  est la normale sortante sur  $\mathcal{S} = \mathcal{S}_1 \cup \mathcal{S}_2$  et  $r = OM$ . La particule  $\mathcal{P}_n$  d'inertie négligeable migre librement ce qui conduit [1] à (6). Le théorème de réciprocité [13] étendu aux 12 écoulements de Stokes  $(\mathbf{u}_L^{(n,i)}, p_L^{(n,i)})$ , assujettis pour  $L \in \{T, R\}$  à (7) où  $\delta$  est le symbol de Kronecker et induisant sur  $\mathcal{S}$  les efforts surfaciques  $\mathbf{f}_L^{(n,i)}$ , permet de réécrire (2)–(6) sous la forme de (8), (9) avec  $\zeta' = \zeta_n - \zeta_w$  sur  $\mathcal{S}_n$  (Cas 1) ou  $\zeta' = \zeta_n$  sur  $\mathcal{S}_n$  (Cas 2) et  $U_j^{(n)} = \mathbf{U}^{(n)} \cdot \mathbf{e}_j$ ,  $\Omega_j^{(n)} = \boldsymbol{\Omega}^{(n)} \cdot \mathbf{e}_j$ . Le système (8), de matrice symétrique et définie négative [13], admet une solution unique  $(\mathbf{U}^{(1)}, \boldsymbol{\Omega}^{(1)}, \mathbf{U}^{(2)}, \boldsymbol{\Omega}^{(2)})$  obtenue en calculant  $\nabla\phi$  et  $\mathbf{f}_L^{(n,i)}$  sur  $\mathcal{S}$  par résolution numérique de 13 équations intégrales de Fredholm de seconde ((10)) ou de première ((11); voir [15]) espèce si  $M'(x_1, x_2, -x_3)$  est le symétrique de  $M(x_1, x_2, x_3)$  par rapport à  $\Sigma$ . En effet, l'approximation de  $\phi$  via (10) et donc de ses dérivées tangentielles conduit, grâce à  $\nabla\phi \cdot \mathbf{n} = \mathbf{E}_\infty \cdot \mathbf{n}$ , à celle de  $\nabla\phi$  sur  $\mathcal{S}$ . La discrétisation (isoparamétrique avec un maillage à  $N_n$  noeuds de triangles curvilignes sur  $\mathcal{S}$  [16]) de (10), (11) débouche sur des systèmes linéaires traités par factorisation  $LU$ .

Pour  $\mathbf{E}_\infty = E\mathbf{e}_1 \neq \mathbf{0}$  (Cas 1) et deux sphères de rayon  $a$ , de centres  $O_n$  et de zéta potentiels uniformes  $\zeta_n$  astreints à (14), traçons les mobilités non nulles  $u_i^{(n)}(d, \lambda)$  et  $w_i^{(n)}(d, \lambda)$ , introduites par (15), où  $d$  et  $\lambda$  sont des paramètres de séparation sphère–sphère et  $\Sigma$ -sphère. Notons que pour  $\mathcal{P}_n$  seule (voir (1))  $u_i^{(n)}(0, 0) = \delta_{i1}\delta_{n1}$ ,  $w_i^{(n)}(0, 0) = 0$  à savoir que  $u_i^{(n)}(d, \lambda) - \delta_{i1}\delta_{n1}$  et  $w_i^{(n)}(d, \lambda)$  représentent l'influence des seules interactions paroi–sphère ( $\Sigma S$ ) si  $d = 0$  et combinées paroi–sphère et sphère–sphère ( $\Sigma S - SS$ ) si  $d > 0$  sur la migration de  $\mathcal{P}_n$  seule. Les cas d'une sphère avec  $\Sigma$  ( $d = 0$ , [11]) et de deux sphères sans  $\Sigma$  ( $\lambda = 0$ , [7]) montrent (voir le Tableau 1) que le choix  $N_1 = N_2 = 866$  assure une précision de l'ordre de  $5 \times 10^{-4}$  pour  $\text{Max}(d, \lambda) \leq 0,9$ . La Fig. 2 procure sous ce choix, en fonction de  $\lambda$  et pour  $d = 0; 0,3; 0,6; 0,8$  et  $0,9$ , les seules fonctions non nulles  $u_1^{(n)}, w_2^{(2)}, w_2^{(1)}(0, \lambda)$  et  $w_2^{(1)}(d, \lambda) = 10[w_2^{(1)}(0, \lambda) - w_2^{(1)}(d, \lambda)]$  si  $d > 0$ . Les interactions combinées  $\Sigma S - SS$  sont ainsi plus importantes pour  $u_1^{(n)}$  et  $w_2^{(2)}$  (voir Figs. 2 (a), (b), (d)) mais moindres pour  $w_2^{(1)}$  (voir Fig. 2(c)) que les interactions  $\Sigma S$ . Les interactions paroi–sphère sont faibles pour  $u_1^{(n)}$  (à  $d$  fixé  $u_1^{(n)}$  varie peu avec  $\lambda$  aux Figs. 2 (a) et (b) et les interactions combinées  $\Sigma S - SS$ , positives pour  $u_1^{(1)}$  et négatives pour  $u_1^{(2)}$ , croissent jusqu'à 20% avec  $d$ . A l'opposé, pour  $w_2^{(n)}$  les interactions  $\Sigma S - SS$  s'avèrent faibles (au plus 3%), positives pour  $\mathcal{P}_1$  (voir  $w_2^{(1)}$ ) mais positives ou négatives pour  $\mathcal{P}_2$  (voir  $w_2^{(2)}$ ).

## 1. Introduction

We consider two solid and insulating particles  $\mathcal{P}_n$  ( $n = 1, 2$ ) freely suspended above a plane boundary  $\Sigma$  in a viscous electrolyte of constant dielectric permittivity  $\varepsilon$  and viscosity  $\mu$  (see Fig. 1).

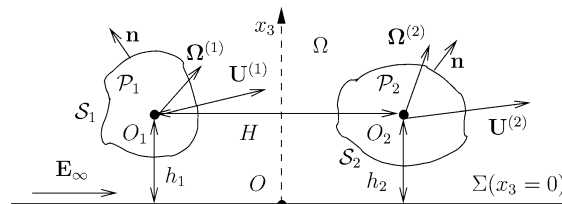


Fig. 1. Two solid particles  $\mathcal{P}_1$  and  $\mathcal{P}_2$  lying near the insulating plane  $\Sigma$ .  
Fig. 1. Deux particules solides  $\mathcal{P}_1$  et  $\mathcal{P}_2$  au voisinage du plan isolant  $\Sigma$ .

Particle–electrolyte interactions induce on the surface  $\mathcal{S}_n$  of  $\mathcal{P}_n$  a so-called “zeta potential” function  $\zeta_n$  and applying a uniform external electric field  $\mathbf{E}_\infty$  results in a motion of  $\mathcal{P}_n$  [1] of unknown translational velocity  $\mathbf{U}^{(n)}$  (the velocity of one point  $O_n$  of  $\mathcal{P}_n$ ) and angular velocity  $\boldsymbol{\Omega}^{(n)}$ . Since this migration, termed electrophoresis, plays a key role in particle analysis and/or separation it is of prime interest to determine  $(\mathbf{U}^{(n)}, \boldsymbol{\Omega}^{(n)})$ . If  $h_n = d(O_n, \Sigma)$  and  $H = O_1 O_2$  respectively denote typical  $\mathcal{P}_n$ -wall and  $\mathcal{P}_1 - \mathcal{P}_2$  separations, available works [2–12] only deal, for  $\mathbf{E}_\infty$  uniform, with the following cases:

- (i) A single particle  $\mathcal{P}_1 (h_1 = h_2 = H = \infty)$ . If  $\zeta_1$  is uniform the Smoluchowski solution

$$\mathbf{U}^{(1)} = \varepsilon \zeta_1 \mathbf{E}_\infty / \mu, \quad \boldsymbol{\Omega}^{(1)} = \mathbf{0} \tag{1}$$

holds [2–4]. If  $\zeta_1$  is non-uniform  $\mathcal{P}_1$  may both rotate and translate [5].

- (ii) Two particles without boundaries ( $h_1 = h_2 = \infty$ ). Such circumstances focus on  $\mathcal{P}_1 - \mathcal{P}_2$  interactions and has only received attention for two spheres of uniform  $\zeta_n$  [6–8].
- (iii) One particle  $\mathcal{P}_1$  near a plane wall  $\Sigma (H = \infty)$ . The available literature ([9–11] for a sphere with  $\zeta_1$  uniform and [12] for any shape and  $\zeta_1$  function) handles two cases:  
 Case 1:  $\Sigma$  is insulating, of uniform zeta potential  $\zeta_w$  and parallel to  $\mathbf{E}_\infty$ .  
 Case 2:  $\Sigma$  is normal to  $\mathbf{E}_\infty$  and perfectly conducting.

This Note extends the method advocated in [12] to a 2-particle cluster near the wall  $\Sigma$  in above Cases 1 and 2. It also both encloses and discusses our preliminary results.

## 2. Relevant boundary-integral equations and numerical treatment

We use cartesian coordinates  $x_j = \mathbf{OM} \cdot \mathbf{e}_j$  with  $\Sigma$  located at  $x_3 = 0$  and the usual summation convention with  $r = OM = (x_j x_j)^{1/2}$ ,  $\mathbf{U}^{(n)} = U_j^{(n)} \mathbf{e}_j$  and  $\boldsymbol{\Omega}^{(n)} = \Omega_j^{(n)} \mathbf{e}_j$ . In the fluid domain  $\Omega$  the electric field becomes  $\mathbf{E} = \mathbf{E}_\infty - \nabla \phi$ . If  $\mathbf{n}$  denotes the unit outward normal on  $\mathcal{S} = \mathcal{S}_1 \cup \mathcal{S}_2$  the perturbation potential  $\phi$  and the fluid flow  $(\mathbf{u}, p)$  obey [10]

$$\nabla^2 \phi = \nabla \cdot \mathbf{u} = 0 \quad \text{and} \quad \mu \nabla \mathbf{u} = \nabla p \quad \text{in } \Omega, \quad (\nabla \phi, p) \rightarrow (\mathbf{0}, 0) \quad \text{as } r \rightarrow \infty \tag{2}$$

$$\nabla \phi \cdot \mathbf{n} = \mathbf{E}_\infty \cdot \mathbf{n} \quad \text{and} \quad \mathbf{u} = \mathbf{U}^{(n)} + \boldsymbol{\Omega}^{(n)} \wedge \mathbf{O}_n \mathbf{M} - \varepsilon \zeta_n \mathbf{E} / \mu \quad \text{on } \mathcal{S}_n \tag{3}$$

$$\text{Case 1: } \nabla \phi \cdot \mathbf{e}_3 = \mathbf{E}_\infty \cdot \mathbf{e}_3 = 0 \quad \text{and} \quad \mathbf{u} = -\frac{\varepsilon \zeta_w}{\mu} \mathbf{E} \quad \text{on } \Sigma, \quad \mathbf{u} \rightarrow -\frac{\varepsilon \zeta_w}{\mu} \mathbf{E}_\infty \quad \text{as } r \rightarrow \infty \tag{4}$$

$$\text{Case 2: } \phi = 0 \quad \text{and} \quad \mathbf{u} = \mathbf{0} \quad \text{on } \Sigma, \quad \mathbf{u} \rightarrow \mathbf{0} \quad \text{as } r \rightarrow \infty \tag{5}$$

According to [1],  $\mathbf{E}$  applies zero net force and torque on the freely-suspended particle  $\mathcal{P}_n$ . If  $\boldsymbol{\sigma} = \boldsymbol{\sigma}(\mathbf{u}, p)$  denotes the stress tensor one thus supplements (2)–(5) with the relations

$$\int_{\mathcal{S}_n} \mathbf{e}_i \cdot \boldsymbol{\sigma} \cdot \mathbf{n} dS_n = 0; \quad \int_{\mathcal{S}_n} [\mathbf{e}_i \wedge \mathbf{O}_n \mathbf{M}] \cdot \boldsymbol{\sigma} \cdot \mathbf{n} dS_n = 0 \quad \text{for } i \in \{1, 2, 3\}, n \in \{1, 2\} \tag{6}$$

For  $L \in \{T, R\}$ , let us consider twelve Stokes flows  $(\mathbf{u}_L^{(n),i}, p_L^{(n),i})$  such that

$$\mathbf{u}_L^{(n),i} = \mathbf{0} \quad \text{on } \Sigma \quad \text{and} \quad \text{as } r \rightarrow \infty, \quad \mathbf{u}_T^{(n),i} = \delta_{nm} \mathbf{e}_i \quad \text{and} \quad \mathbf{u}_R^{(n),i} = \delta_{nm} [\mathbf{e}_i \wedge \mathbf{O}_n \mathbf{M}] \quad \text{on } \mathcal{S}_m \tag{7}$$

where  $\delta$  denotes the Kronecker delta and subscripts  $T$  or  $R$  respectively hold for a translation or a rotation of  $\mathcal{P}_n$ . Designating by  $\mathbf{f}_L^{(n),i}$  the surface stress induced on  $\mathcal{S}$  by  $(\mathbf{u}_L^{(n),i}, p_L^{(n),i})$  and extending to our multiply-connected

and semi-infinite domain  $\Omega$  the Lorentz reciprocal theorem [13], one arrives, under velocity boundary conditions (3)–(5), at the equations

$$A_{(m),L}^{(n),i,j} U_j^{(m)} + B_{(m),L}^{(n),i,j} \Omega_j^{(m)} = \frac{\varepsilon}{\mu} \int_S \zeta' [\mathbf{E}_\infty - \nabla\phi] \cdot \mathbf{f}_L^{(n),i} dS \tag{8}$$

with  $\zeta' = \zeta_n - \zeta_w$  on  $S_n$  in Case 1,  $\zeta' = \zeta_n$  on  $S_n$  in Case 2 and

$$A_{(m),L}^{(n),i,j} = \int_{S_m} \mathbf{e}_j \cdot \mathbf{f}_L^{(n),i} dS_m, \quad B_{(m),L}^{(n),i,j} = \int_{S_m} (\mathbf{e}_j \wedge \mathbf{O}_m \mathbf{M}) \cdot \mathbf{f}_L^{(n),i} dS_m \tag{9}$$

Note [13] that (8) admits a symmetric and negative-definite  $12 \times 12$  matrix. By virtue of (8), (9), the unique solution  $(\mathbf{U}^{(1)}, \boldsymbol{\Omega}^{(1)}, \mathbf{U}^{(2)}, \boldsymbol{\Omega}^{(2)})$  is gained by evaluating  $\nabla\phi$  and  $\mathbf{f}_L^{(n),i}$  on  $S = S_1 \cup S_2$  only. If  $M'(x_1, x_2, -x_3)$  is the symmetric of  $M(x_1, x_2, x_3)$  with respect to the plane  $\Sigma$ , the function  $\phi$  obeys in Case  $l$  ( $l = 1, 2$ ) the boundary-integral equation

$$\begin{aligned} & -4\pi\phi(M) + \int_S [\phi(P) - \phi(M)] \frac{\mathbf{PM} \cdot \mathbf{n}(P)}{PM^3} dS_P + (-1)^{l+1} \int_S \phi(P) \frac{\mathbf{PM}' \cdot \mathbf{n}(P)}{PM'^3} dS_P \\ & = \int_S [\mathbf{E}_\infty \cdot \mathbf{n}](P) \left\{ \frac{1}{PM} + (-1)^{l+1} \frac{1}{PM'} \right\} dS_P \end{aligned} \tag{10}$$

A non-trivial generalization to two particles of results established for one particle [14,15] shows that the required surface stress  $\mathbf{f}_L^{(n),i}$  fulfills the boundary-integral equation

$$-8\pi\mu[\mathbf{u}_L^{(n),i} \cdot \mathbf{e}_j](M) = \int_S [G_{jk}^0 + G_{jk}^b](P, M) [\mathbf{f}_L^{(n),i}(P) \cdot \mathbf{e}_k] dS_P \tag{11}$$

$$G_{jk}^0(P, M) = \delta_{jk}/PM + (\mathbf{PM} \cdot \mathbf{e}_j)(\mathbf{PM} \cdot \mathbf{e}_k)/PM^3 \tag{12}$$

$$\begin{aligned} G_{jk}^b(P, M) = G_{jk}^0(P, M') - 2c_j [(\mathbf{OM} \cdot \mathbf{e}_3)/PM'^3] \\ \times \{ \delta_{k3} \mathbf{PM}' \cdot \mathbf{e}_j - \delta_{j3} \mathbf{PM}' \cdot \mathbf{e}_k + \mathbf{OP} \cdot \mathbf{e}_3 [\delta_{jk} - 3(\mathbf{PM}' \cdot \mathbf{e}_j)(\mathbf{PM}' \cdot \mathbf{e}_k)/PM'^2] \} \end{aligned} \tag{13}$$

with  $c_1 = c_2 = 1, c_3 = -1$ . Thus, inverting one and twelve Fredholm boundary-integral equations (10) and (11) respectively yields  $\phi$  and  $\mathbf{f}_L^{(n),i}$  on  $S$ . The numerical implementation uses a  $N_n$ -node mesh of isoparametric, curvilinear and triangular 6-node boundary elements on  $S_n$  [16] and solves the linear systems associated to (10), (11) by Gaussian elimination. Finally,  $\nabla\phi$  is deduced on  $S$  from the link  $\nabla\phi \cdot \mathbf{n} = \mathbf{E}_\infty \cdot \mathbf{n}$  and the calculation of its tangential derivatives from the numerical approximation of  $\phi$ .

### 3. Preliminary results and discussion

We report numerical results for an “horizontal” 2-sphere cluster with  $\mathbf{E}_\infty = E\mathbf{e}_1 \neq \mathbf{0}$  (Case 1). Each sphere  $\mathcal{P}_n$  has radius  $a$ , center  $O_n$  and uniform zeta potential  $\zeta_n$  with

$$\mathbf{OO}_n = \frac{(-1)^n a}{d} \mathbf{e}_1 + \frac{a}{\lambda} \mathbf{e}_3, \quad 0 \leq d < 1, \quad 0 \leq \lambda < 1, \quad \zeta'_1 = \zeta_1 - \zeta_w \neq 0, \quad \zeta'_2 = \zeta_2 - \zeta_w = 0 \tag{14}$$

where  $d$  and  $\lambda$  denote sphere–sphere and sphere–wall separation parameters. The case of  $\zeta'_1$  and  $\zeta'_2$  uniform and non-zero may be easily deduced from the above choice of  $(\zeta'_1, \zeta'_2)$  by symmetry properties. Non-zero and so-called electrophoretic “mobilities”

$$u_i^{(n)}(d, \lambda) = \mu[\mathbf{U}^{(n)} \cdot \mathbf{e}_i]/[\varepsilon E \zeta'_1], \quad w_i^{(n)}(d, \lambda) = \mu[\boldsymbol{\Omega}^{(n)} \cdot \mathbf{e}_i]/[\varepsilon E \zeta'_1] \tag{15}$$

are computed with  $N = 2N_1 = 2N_2$  collocations points on  $\mathcal{S} = \mathcal{S}_1 \cup \mathcal{S}_2$ . If  $\lambda = 0$  or  $d = 0$  one recovers circumstances (ii) or (iii) (two spheres free from boundaries or one sphere with a plane boundary). As shown in Table 1, using a refined 866-node mesh on each sphere yields numerical errors of order of  $5 \times 10^{-4}$  in the range  $\text{Max}(d, \lambda) \leq 0.9$ .

Table 1

Comparison between theoretical [7,11] and computed non-zero mobilities  $u_1^{(1)}(0, 0.9)$ ,  $w_2^{(1)}(0, 0.9)$  and  $u_1^{(1)}(0.9, 0)$  for different settings  $N_1 = N_2$

Tableau 1

Mobilités non nulles  $u_1^{(1)}(0; 0,9)$ ,  $w_2^{(1)}(0; 0,9)$  et  $u_1^{(1)}(0,9; 0)$  pour différents choix de  $N_1 = N_2$ . Comparaisons avec [7,11]

$N_1 = N_2$	$u_1^{(1)}(0, 0.9)$	$u_1^{(1)} [11]$	$w_2^{(1)}(0, 0.9)$	$w_2^{(1)} [11]$	$u_1^{(1)}(0.9, 0)$	$u_1^{(1)} [7]$
74	0.99869	0.99789	-0.20454	-0.20389	0.82046	0.79031
242	0.99625	0.99789	-0.20563	-0.20389	0.79455	0.79031
530	0.99794	0.99789	-0.20354	-0.20389	0.79199	0.79031
866	0.99779	0.99789	-0.20338	-0.20389	0.79023	0.79031

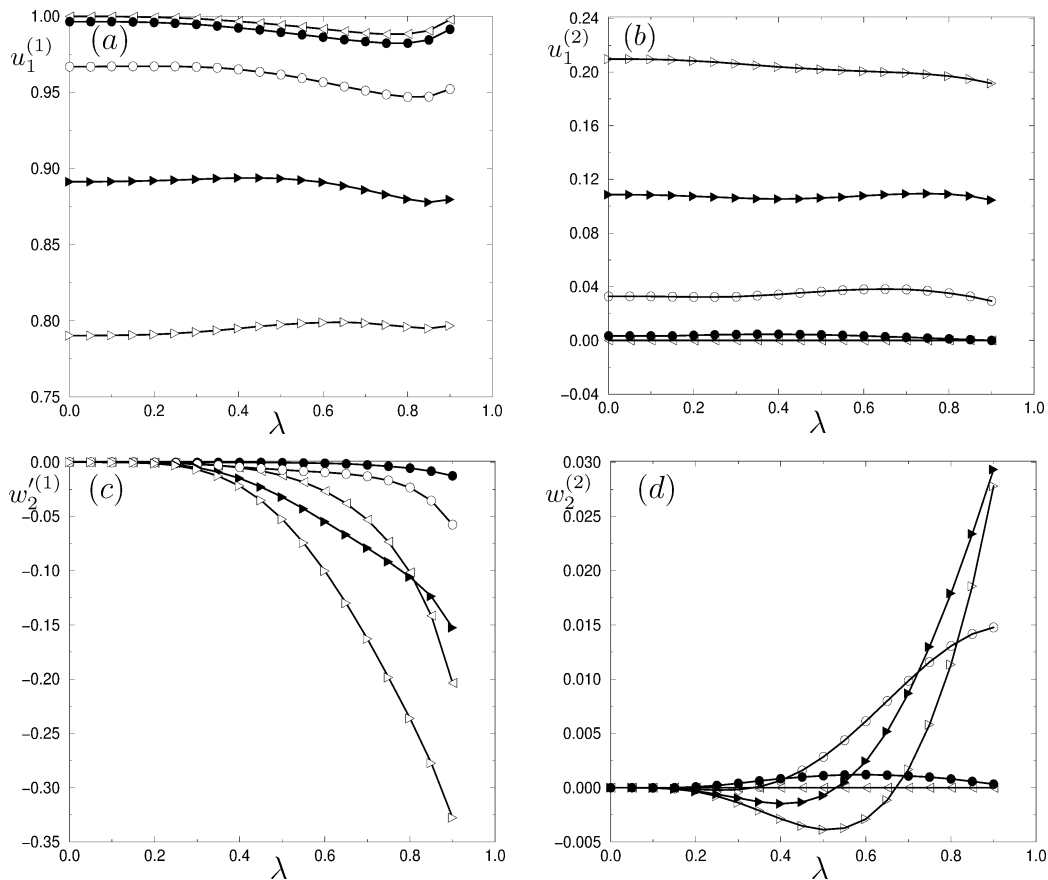


Fig. 2. Non-zero electrophoretic mobilities  $u_1^{(n)}$ ,  $w_2^{(2)}$  and  $w_2'^{(1)}$  for  $d = 0$  ( $\triangleleft$ ),  $d = 0.3$  ( $\bullet$ ),  $d = 0.6$  ( $\circ$ ),  $d = 0.8$  ( $\blacktriangleright$ ) or  $d = 0.9$  ( $\triangleright$ ). (a):  $u_1^{(1)}$ . (b):  $u_1^{(2)}$ . (c):  $w_2'^{(1)}$ . (d):  $w_2^{(2)}$ .

Fig. 2. Mobilités non nulles  $u_1^{(n)}$ ,  $w_2^{(2)}$  et  $w_2'^{(1)}$  pour  $d = 0$  ( $\triangleleft$ ),  $d = 0,3$  ( $\bullet$ ),  $d = 0,6$  ( $\circ$ ),  $d = 0,8$  ( $\blacktriangleright$ ) ou  $d = 0,9$  ( $\triangleright$ ). (a) :  $u_1^{(1)}$ . (b) :  $u_1^{(2)}$ . (c) :  $w_2'^{(1)}$ . (d) :  $w_2^{(2)}$ .

Non-zero mobilities  $u_1^{(n)}(d, \lambda)$  and  $w_2^{(n)}(d, \lambda)$ , computed with  $N_1 = N_2 = 866$ , are plotted versus  $\lambda$  and for  $d = 0, 0.3, 0.6, 0.8$  and  $0.9$  in Figs. 2(a)–(d). For clarity, our Fig. 2(c) actually displays functions  $w_2^{\prime(1)}(0, \lambda) = w_2^{(1)}(0, \lambda)$  and  $w_2^{\prime(1)}(d, \lambda) = 10[w_2^{(1)}(0, \lambda) - w_2^{(1)}(d, \lambda)]$  for  $d > 0$ . In view of (1), a single sphere  $\mathcal{P}_n$  has mobilities  $u_i^{(n)}(0, 0) = \delta_{n1}\delta_{i1}$ ,  $w_i^{(n)}(0, 0) = 0$  (since  $\zeta'_n = \delta_{n1}$ ). Thus, functions  $u_1^{(n)} - \delta_{n1}$  and  $w_1^{(n)}$  are due to pure sphere–wall (SW) interactions if  $d = 0$  and combined sphere–wall and sphere–sphere (SW-SS) interactions if  $d > 0$ . Note that SW-SS interactions are greater (for  $u_1^{(n)}$  and  $w_1^{(2)}$ ; see Figs. 2(a), (b), (d)) or weaker (for  $w_1^{(1)}$ ; see Fig. 2(c)) than SW interactions. For  $u_1^{(n)}$  sphere–wall interactions are weak for  $0 \leq \lambda \leq 0.9$  (each curve is nearly flat) whereas combined SW-SS interactions, negative for  $u_1^{(1)}$  and positive for  $u_1^{(2)}$ , increase with  $d$  up to 20% of the unit Smoluchowski mobility. Mobilities  $w_2^{(n)}$  exhibit opposite trends: combined SW-SS interactions (reducing to quantities  $w_2^{(n)}$ ) are weak (less than 3%), positive for  $\mathcal{P}_1$  (remind definition of  $w_2^{\prime(1)}$  and see Fig. 2(c)) and either positive or negative for  $\mathcal{P}_2$  (see Fig. 2(d)).

#### 4. Concluding remarks

Even for our simple “horizontal” 2-sphere cluster, the relative magnitude of particle–particle and particle–wall interactions deeply depends upon the velocity nature (translational or angular). A strong accuracy is needed in all computations and the boundary-integral treatment is quite suitable for such a refined analysis. Finally, particle–particle and wall–particle interactions depend upon the cluster nature (shape and zeta potential of each particle) and orientation relative to  $\mathbf{E}_\infty$  and  $\Sigma$ . Such issues are currently investigated.

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