Chapter 2
Diffusiophoresis of Spherical Colloidal Particles Parallel to the Plane Walls

Abstract A semi-analytical and semi-numerical calculation is used in single spherical colloidal particles in a nonelectrolyte solution, to calculate the diffusiophoresis velocity without considering the solute convection effect of fluid inertia. The fixed value of the concentration gradient to a parallel plate is the driving force. The boundary conditions for plate can be a solute linear distribution of the two situations that cannot penetrate or solute. When the particle radius is much larger than the thickness of particles and solute interaction layer plate, one part of the boundary effect is from the interaction effect produced by the concentration gradients and the colloidal particles, while the other part is from the viscosity of the fluid. The mobility velocity boundary is used to take point velocity under different polarization parameters and separation parameters to verify the reflection method. Due to the surface characteristics of the particles and the relative distance of the plate from the different boundary conditions on the plate, the plate effect can reduce or increase the motion velocity of particles.

2.1 Theoretical Analysis

This chapter concerns the situation of diffusiophoresis parallel to the two flat plane walls of spherical colloidal particles with radius a, which is influenced by a nonionic solute concentration gradient.

The distances of central point of spherical particles from the two plane walls are b and c, respectively, as shown in Fig. 2.1. In this figure, (x, y, z), $(p, \emptyset, z)$ and (r, θ, φ) represent the Cartesian coordinates with the center of particle as the origin, cylindrical coordinates, and spherical coordinate systems. At infinity, the solute concentration $C_\infty(x)$ displays linear distribution and the concentration gradient $E_\infty e_x$ ($= \nabla C_\infty$, in which E_∞ is positive), while e_x, e_y, and e_z are the three unit vectors of Cartesian coordinate. With respect to the radius of curvature of the interface and the distance of particles from the boundary, the interaction between fluid and solid interface is negligible. Therefore, the solution around the particles

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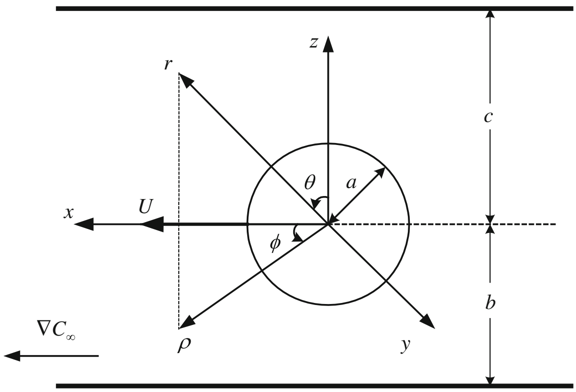

Fig. 2.1 Geometrical sketch for the diffusiophoresis of a *spherical particle* parallel to two plane walls at an arbitrary position between them

can be divided into inner region and outer region: the inner region is the interface layer of the adjacent layers, and the outer region is the main layer other than the interaction layer. This is estimated based on theoretical calculations to find out with the presence of plane walls, the correction of the velocity of individual particle diffusiophoresis represented by (Eq. 1.2). Before calculating the particle velocity and the fluid velocity, the distribution of the solute concentration of the solution must be found out.

2.1.1 Distribution Solute Concentration

Under the circumstance that Reynolds number and Peclet number are quite small and negligible, the mobility state considered can be regarded as a quasisteady state system. In the outer region, the Laplace equation and the Stokes equation can be used, respectively, to represent the conservation equations of fluid concentration and fluid momentum. The distribution of fluid concentration C satisfies

$$\nabla^2 C = 0 \tag{2.1}$$

The boundary conditions required to be met by the outer layer interaction external to the dominating equations are to figure out the internal fluid concentration and the distribution of fluid velocity, and to ensure that in the entire fluid phase, the fluid velocity and fluid concentration are required to have the results of continuity, so that the outcome can be obtained as follows (O'Brien 1983; Anderson and Prieve 1991):

$$r = a: \quad \frac{\partial C}{\partial r} = -\beta[\nabla^2 - \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})]C \tag{2.2}$$

In the above formula, β is the relaxation coefficient also known as polarization coefficient, and the definition is as follows:

$$\beta = (1 + v\,Pe)K \tag{2.3}$$

where,

$$Pe = \frac{kT}{\eta D} L * KC_0 \tag{2.4a}$$

$$K = \int_0^\infty [\exp(-\Phi(y_n)/kT) - 1]dy_n \tag{2.4b}$$

$$L^* = K^{-1} \int_0^\infty y_n[\exp(-\Phi(y_n)/kT) - 1]dy_n \tag{2.4c}$$

$$v = (L^* K^2)^{-1} \int_0^\infty \{\int_{y_n}^\infty [exp(-\Phi(y_n')/kT) - 1]dy_n'\}^2 dy_n \tag{2.4d}$$

In (2.4a–d), Φ represents a solute molecule with the surface of the particles due to the interaction potential arising letter number; D is the fluid diffusion coefficient; Yn is the distance along the particle surface which points to the direction of fluid; C_0 is the bulk fluid concentration when particle central location, while the particles do not exist. Fluid concentration away from the particles is not influenced, therefore,

$$z = c,\ -b: \quad \frac{\partial C}{\partial z} = 0 \tag{2.5}$$

$$\rho \to \infty: \quad C = C_\infty = C_0 + E_\infty x \tag{2.6}$$

where, formula (2.5) is the boundary condition that the fluid cannot penetrate the two plane walls, and the relaxation effect of the plate surface has to be ignored. As for the boundary condition of the two flat plane walls which are of linear distribution, formula (2.5) should be changed to

$$z = c,\quad -b: \quad C = C_0 + E_\infty x \tag{2.7}$$

Since both governing equation and boundary conditions are linear, fluid concentration of C can be represented as

$$C = C_w + C_p \tag{2.8}$$

where, due to the existence of plate and disturbance caused by the general solution to the double Fourier integral in Cartesian coordinates, as well as the concentration distribution of particles which is undisturbed by the motion, C_w can be expressed as:

$$C_w = C_0 + E_\infty x + E_\infty \int_0^\infty \int_0^\infty (Xe^{\kappa z} + Ye^{-\kappa z}) \sin(\hat{\alpha} x) \cos(\hat{\beta} y) d\hat{\alpha}\, d\hat{\beta} \tag{2.9}$$

wherein, X and Y are determinable functions, while $\kappa = (\hat{\alpha}^2 + \hat{\beta}^2)^{1/2}$. While C_p satisfies formula (2.1), the spherical coordinate's general solution caused by existence and influence of particles is defined as spherical harmonic function, and is expressed as follows:

$$C_p = E_\infty \sum_{n=1}^{\infty} R_n\, r^{-n-1} P_n^1(\mu) \cos\phi \tag{2.10}$$

wherein, P_n^1 is associated Legendre function, μ represents cosθ for the purpose of conciseness, and R_n stands for the unknown coefficient. The concentration distribution of C expressed by formulas (2.8)–(2.10) already satisfies the boundary condition of the infinity formula (2.6).

Apply the fluid concentration distribution C of formulas (2.8)–(2.10) into the boundary condition of formula (2.5) (or (2.7)), and take x and y as the Fourier sine and cosine transforms, then X and Y can be converted into the equation represented by Rn. Then, apply its solution into formula (2.9), so the distribution of fluid concentration in Figure C as modified Bessel functions of the second kind is as follows:

$$C = C_0 + E_\infty x + E_\infty \sum_{n=1}^{\infty} R_n\, \delta_n^{(1)}(r, \mu) \cos\varphi \tag{2.11}$$

wherein the detailed definition of the function $\delta_n^{(1)}(r, \mu)$ is in Appendix D of the formula [D1]. Applying Formula (2.11) into the boundary formula (2.2), the following can be obtained:

$$\sum_{n=1}^{\infty} R_n \left[\left(\frac{2\beta}{a} - 1\right)\delta_n^{(2)}(a, \mu) + \beta\delta_n^{(4)}(a, \mu)\right] = \left(1 - \frac{2\beta}{a}\right)(1 - \mu^2)^{1/2} \tag{2.12}$$

wherein functions $\delta_n^{(2)}(r, \mu)$ and $\delta_n^{(4)}(r, \mu)$ are defined as [D2] and [D4]. The integrals in the formulas $\delta_n^{(1)}$, $\delta_n^{(2)}$ and $\delta_n^{(4)}$ can be obtained by the number integrals.

In every particle surface, there will be a need for an infinite number of undetermined coefficients R_n, so that the boundary conditional (2.12) can be really met. However, using boundary collocation method people can convert infinite series (2.11) into a finite series, and can take a finite number of points on the surface of each particle to satisfy the boundary conditions (O'Brien 1968; Ganatos et al. 1980; Keh and Jan 1996). For each infinite series $\sum_{n=0}^{\infty}$, the first M item is taken, and then Formula (2.12) involves unknown coefficients R_n which have the number of M. Using the M different θ_i values in each surface of the spherules in formula

(2.11), we can generate M equations which can be used appropriately to solve the undetermined coefficients R_n.

2.1.2 Distribution of Fluid Velocity

The distribution of the fluid concentration obtained in the previous chapter can be used to further calculate the fluid velocity distribution in this system. Suppose the fluid is incompressible Newtonian fluid, which is creeping flow based on diffusiophoresis, then the outer flow field of diffusion can be conveyed by Stokes equation as follows:

$$\eta\nabla^2 v - \nabla p = 0 \tag{2.13a}$$

$$\nabla \cdot v = 0 \tag{2.13b}$$

wherein, v is the velocity distribution of the fluid, while p is its pressure distribution.

Particle surface and the fluid velocity boundary condition at infinity are (Anderson and Prieve 1991):

$$r = a \;:\; v = U + a\Omega \times e_r - \frac{kT}{\eta} L^* K(e_\theta e_\theta + e_\varphi e_\varphi) \cdot \nabla C \tag{2.14}$$

$$z = c, -b : \; v = 0 \tag{2.15}$$

$$\rho \to \infty : v = 0 \tag{2.16}$$

wherein, e_r, e_θ ,and e_φ are the unit vectors of the spherical coordinates, and $\mathrm{U} = Ue_x$ and $\Omega = \Omega e_y$ are the moving velocity and the rotational velocity of the colloidal particles in the diffusion mobility, respectively. Due to the ignorance of the inertial effect, under the symmetrical circumstance (when $b \neq c$), the diffusion velocity of spherical colloidal particles remains parallel to the concentration gradient of the fluid. Since the governing equations and boundary conditions are both linear, the outer region v of the particles can be divided into (Ganatos et al. 1980):

$$v = v_w + v_s \tag{2.17}$$

wherein, in Formula (2.13a, b), v_w is the Cartesian caused by the influence of the existence of the plane walls.

$$v_w = v_{wx} e_x + v_{wy} e_y + v_{wz} e_z \tag{2.18}$$

However, e_x, e_y, and e_z, are the three unit vectors of the Cartesian coordinates, respectively, while v_{wx}, v_{wy} and v_{wz} are Double Fourier integral.

$$v_{wx} = \int_0^\infty \int_0^\infty D_1(\alpha, \beta, z) \cos(\alpha x) \cos(\beta y) \mathrm{d}\alpha \ \mathrm{d}\beta \tag{2.19a}$$

$$v_{wy} = \int_0^\infty \int_0^\infty D_2(\alpha, \beta, z) \sin(\alpha x) \sin(\beta y) \mathrm{d}\alpha \ \mathrm{d}\beta \tag{2.19b}$$

$$v_{wz} = v_{wy} = \int_0^\infty \int_0^\infty D_3(\alpha, \beta, z) \sin(\alpha x) \sin(\beta y) \mathrm{d}\alpha \ \mathrm{d}\beta \tag{2.19c}$$

In Formula (2.19a–c),

$$\begin{aligned} D_1 = {} & [X^*(1 + \frac{\alpha^2}{\kappa} z) - X^{**} \frac{\alpha\beta}{\kappa} z - X^{***} \alpha z] e^{\kappa z} \\ & + [Y^*(1 - \frac{\alpha^2}{\kappa} z) + Y^{**} \frac{\alpha\beta}{\kappa} z - Y^{***} \alpha z] e^{-\kappa z} \end{aligned} \tag{2.20a}$$

$$\begin{aligned} D_2 = {} & [-X^* \frac{\alpha\beta}{\kappa} z + X^{**}(1 + \frac{\beta^2}{\kappa} z) + X^{***} \beta z] e^{\kappa z} \\ & + [Y^* \frac{\alpha\beta}{\kappa} z + Y^{**}(1 - \frac{\beta^2}{\kappa} z) + Y^{***} \beta z] e^{-\kappa z} \end{aligned} \tag{2.20b}$$

$$D_3 = [X^* \alpha z - X^{**} \beta z + X^{***}(1 - \kappa z)] e^{\kappa z} + [Y^* \alpha z - Y^{**} \beta z + Y^{***}(1 + \kappa z)] e^{-\kappa z} \tag{2.20c}$$

wherein according to the asterisk mark, X and Y are unknown functions, while $\kappa = (\alpha^2 + \beta^2)^{1/2}$. V_s is the spherical coordinate solution caused by the influence of the presence of the plane walls in formula (2.13a, b) shown as follows:

$$\mathrm{v}_s = v_{sx} \mathrm{e}_x + v_{sy} \mathrm{e}_y + v_{sz} \mathrm{e}_z \tag{2.21}$$

wherein,

$$v_{sx} = \sum_{n=1}^{\infty} (A_n A_n' + B_n B_n' + C_n C_n') \tag{2.22a}$$

$$v_{sy} = \sum_{n=1}^{\infty} (A_n A_n'' + B_n B_n'' + C_n C_n'') \tag{2.22b}$$

$$v_{sz} = \sum_{n=1}^{\infty} (A_n A_n''' + B_n B_n''' + C_n C_n''') \tag{2.22c}$$

For Formula (2.22a–c), according to the marks above, A_n, B_n, and C_n all involve the Ray built function accompanied by μ or $\cos\theta$ as variables, the detailed definition of which is provided in Formula (2.6) of the dissertation of Ganatos et al. (1980) (see instructions in Appendix D of this chapter). A_n, B_n and C_n are the undetermined coefficients, while formulas (2.17)–(2.22a–c) have been satisfied in the boundary conditions of Formula (2.16) at infinity.

To solve the X, Y, and, coefficients as well as A_n, B_n, and C_n from the unknown function, the process is approximated to the process to solve the fluid concentration field. First of all, apply the velocity field v into the boundary conditions of Formula (2.15), and decide the solution of superscripts X and Y. Then, apply the general solutions into Formula (2.14), so as to satisfy the boundary conditions of the particle surface, thereby obtaining A_n, B_n and C_n.

Apply Formulas (2.17)–(2.22a–c) into the boundary conditions of Formula (2.15), and apply Fourier sine and cosine transform to x and y, respectively, then D1, D2, and D3 can be converted into the function of the equations represented by the coefficients, A_n, B_n, and C_n. Then applying this solution back to formula (2.20a–c), Formulas (2.17)–(2.22a–c) can be converted into the modified Bessel functions of the second kind of A_n, B_n, and C_n. The integral types are as follows:

$$\mathrm{v} = v_x e_x + v_y e_y + v_z e_z \tag{2.23}$$

wherein,

$$v_x = \sum_{n=1}^{\infty} [A_n(A_n' + \alpha_n') + B_n(B_n' + \beta_n') + C_n(C_n' + \gamma_n')] \tag{2.24a}$$

$$v_y = \sum_{n=1}^{\infty} \left[A_n\left(A_n'' + \alpha_n''\right) + B_n\left(B_n'' + \beta_n''\right) + C_n\left(C_n'' + \gamma_n''\right)\right] \tag{2.24b}$$

$$v_z = \sum_{n=1}^{\infty} [A_n(A_n''' + \alpha_n''') + B_n(B_n''' + \beta_n''') + C_n(C_n''' + \gamma_n''')] \tag{2.24c}$$

In this situation, the marked α_n, β_n and γ_n are integral position functions (they must be obtained by numerical integration), and for their detailed definitions cf the formula [C1] in the chapter of Ganatos et al. (1980) (see the Appendix D of this chapter for instructions).

In order to satisfy the boundary conditions of the particle surface, apply Formulas (2.11) and (2.23) in Formula (2.14), then the outcome is:

$$\begin{aligned}&\sum_{n=1}^{\infty} [A_n(A_n' + \alpha_n') + B_n(B_n' + \beta_n') + C_n(C_n' + \gamma_n')] \\ &\quad = U + a\Omega\mu - U^{(0)}(H_1 \mu \cos\varphi + H_2 \sin^2\varphi)\end{aligned} \tag{2.25a}$$

$$\begin{aligned}&\sum_{n=1}^{\infty} [A_n(A_n'' + \alpha_n'') + B_n(B_n'' + \beta_n'') + C_n(C_n'' + \gamma_n'')] \\ &= -U^{(0)}(H_1 \mu \sin\varphi - H_2 \cos\varphi \sin\varphi)\end{aligned} \tag{2.25b}$$

$$\sum_{n=1}^{\infty}[A_n(A_n''' + \alpha_n''') + B_n(B_n''' + \beta_n''') + C_n(C_n''' + \gamma_n''')] \\ = -a\Omega(1-\mu^2)^{1/2}\cos\varphi + U^{(0)}H_1(1-\mu^2)^{1/2} \tag{2.25c}$$

Therein,

$$H_1 = \mu\cos\varphi + \frac{1}{a}\sum_{n=1}^{\infty}R_n\delta_n^{(3)}(a,\mu)\cos\varphi \tag{2.26a}$$

$$H_2 = 1 + \frac{1}{a(1-\mu^2)^{1/2}}\sum_{n=1}^{\infty}R_n\delta_n^{(1)}(a,\mu) \tag{2.26b}$$

$U^{(0)} = kTL * KE_{\infty}/\eta$, while the definitions of equation $\delta_n^{(3)}(r,\mu)$ can be found in Formula [D3]. The item M before coefficient R_n can be obtained by the formulas in the previous chapter.

Observing Formula (2.25a–c) in detail, it can be found that in the spherical surface, when the $r = a$ boundary takes point, all the simultaneous formulas are irrelevant with the selection of the value of φ. Therefore, Formula (2.25a–c) satisfies N different θ_i values of the grain surface of each particle (θ values range between 0 and π) hence results in 3 N linear equations, and can solve 3 N unknown A_n, B_n and C_n. At the same time, when N is large enough, it can be used to successfully solve the flow distribution.

2.1.3 The Deduction of Particle Diffusiophoresis Velocity

The drag force of fluid applied to the spherical particles can be expressed as (Ganatos et al. 1980):

$$F = -8\pi\eta A_1 e_x \tag{2.27a}$$

$$T = -8\pi\eta C_1 e_y \tag{2.27b}$$

From the above equation, it can be known that in Formula (2.24a–c), only low-order coefficients A_1 and C_1 have contributions to the drag forces and moments applied to spherical particles.

Since the particles can freely suspend in fluid, the particles have received a net force and net torque of zero. Applying this limit to Formula (2.27a–b), the outcome is as follows:

$$A_1 = C_1 = 0 \tag{2.28}$$

Combining Formula (2.28) and the 3 N linear equations generated by Formula (2.25a–c), the moving velocity of the particles U and the rotational velocity Ω can be successfully obtained.

2.1.4 *Calculation Methods of Figures*

This chapter explains when the particles move parallel to the two plane walls, and how to find a point on the particle surface to calculate the velocity of the motion of the particles for single particle diffusion. When finding the point on the boundary, I use any meridian plane of the particle (use the z-axis as a symmetry axis) to find point on semicircular surface so as to satisfy the boundary conditions. In the first place, I select three points of $\theta_i = 0$, $\pi/2$ and π, because these points mainly control the particle size in the direction of motion of the projection plane and the distance between the particles and the plane walls, but examining the linear algebraic equations carefully, I found that, if the point positions fall on $\theta_i = 0$, $\pi/2$ or π, then a set of singular coefficient matrixes will be generated. To avoid this obstacle, four basic points $\theta i = \alpha$, $\pi/2$-α, $\pi/2 + \alpha$, and π-α are selected on the semicircular surface, and the rest of the points are selected along the semicircular arc with $\theta_i = \pi/2$ as the mirror-image pair, and dividing this semicircular arc into the same length. Third in this case, I found that the best value of α is 0.1°. Under this circumstance, all the undetermined coefficients will have satisfactory convergence values. All the numerical calculations in the estimating functions α_n, β_n and γ_n and $\delta_n^{(i)}$ will be obtained by the 80-points approach of Gauss-Laguerre quadrature.

2.2 Results and Discussions

Based on this, it will be used to explore the usage of the method of border point in terms of solving a single spherical particle parallel to the two plane walls, and to find out the calculation results of diffusion mobility.

2.2.1 *Diffusiophoresis of Particle Parallel to One Single Plate*

The collocation solutions for the translational and rotational velocities of a spherical particle undergoing diffusiophoresis parallel to a plane wall (with c approaches infinite) for different values of the relaxation parameter and separation parameter a/b are presented in Table 2.1 and 2.2 for the cases of an impermeable wall and a wall with the imposed far-field solute concentration gradient, respectively.

Both the tables use the border method to take point and converge numerical calculations to present effective digits. When the convergence velocity has a/b value, the greater a/b, the slower convergence velocity is, and the more the number

Table 2.1 Diffusiophoretic motion and rotating velocity of *spherical particles* parallel to a single plate that cannot penetrate through the solute

a/b	U/U_0			$-a\Omega/U_0$		
	Exact solution†		Asymptotic solution	Exact solution†		Asymptotic solution
$\beta/a = 0$						
0.2	0.99953	(0.99953)	0.99953	0.00030	(0.00030)	0.00031
0.4	0.99684	(0.99684)	0.99688	0.00492	(0.00492)	0.00540
0.6	0.99172	(0.99172)	0.99166	0.02669	(0.02669)	0.03455
0.8	0.98853	(0.98853)	0.98336	0.10164	(0.10164)	0.15360
0.9	0.99789	(0.99789)	0.97635	0.20389	(0.20389)	0.29818
0.95	1.0223	(1.02231)	0.97135	0.3189	(0.31890)	0.40846
0.99	1.1450	(1.14536)	0.96629	0.6162	(0.61832)	0.52144
0.995	1.230	(1.23060)		0.761	(0.76533)	
0.999	1.449			1.075		
$\beta/a = 10$						
0.2	0.99816		0.99816	0.00030		0.00030
0.4	0.98558		0.98563	0.00496		0.00483
0.6	0.95065		0.95099	0.02723		0.02484
0.8	0.87024		0.87445	0.10440		0.08088
0.9	0.78727		0.80822	0.20427		0.13233
0.95	0.7117		0.76452	0.3033		0.16632
0.99	0.5737		0.72318	0.4851		0.19826
0.995	0.536			0.538		
0.999	0.501			0.596		

of points required to be taken. When $a/b = 0.999$, its boundary points need to reach $M = 36$ and $N = 36$, or more, for convergence.

Through the use of spherical bipolar coordinates, Keh and Chen (1988) obtained semianalytical-seminumerical solutions for the normalized translational and rotational velocities of a dielectric sphere surrounded by an infinitesimally thin electric double layer undergoing electrophoresis parallel to a nonconducting plane wall. These solutions, which can apply to the case of diffusiophoresis of a sphere with relaxation parameter is equal to zero parallel to an impermeable plane wall, are also presented in Table 2.1 for comparison. It can be seen that our collocation solutions for the particle velocities agree excellently with the bipolar-coordinate solutions.

In Appendix C1, I have demonstrated the reflection method to obtain the spherical particles that are parallel to a flat plate, and the analytical solution of diffusion mobility. The motion and the velocity of rotation of particles found is represented in Formula [C1-11a, b], and the results of this calculation are also listed in the table to be compared with the correct numerical results obtained with border access. The results show that the numerical results are very consistent when $\lambda = a/b \leq 0.8$, in addition, when valuing the reflection method with the boundary collocation method regularization mobile velocity, it can be shown that its error is less than 1.1 %. However, the accuracy of Formula [C1-11a, b] decreases with the increase of λ.

Table. 2.2 Diffusiophoretic motion and rotating velocity of *spherical particles* parallel to a single plate appear in linear distribution

a/b	U/U_0		$-a\Omega/U_0$	
	Exact solution	Asymptotic solution	Exact solution	Asymptotic solution
$\beta/a = 0$				
0.2	0.99853	0.99853	0.00030	0.00030
0.4	0.98840	0.98846	0.00498	0.00480
0.6	0.95922	0.95993	0.02767	0.02422
0.8	0.88358	0.89274	0.10880	0.07619
0.9	0.79405	0.83125	0.21593	0.12162
0.95	0.7074	0.78952	0.3200	0.15067
0.99	0.5509	0.74938	0.4940	0.17738
0.995	0.510		0.539	
0.999	0.468		0.584	
$\beta/a = 10$				
0.2	0.99990	0.99990	0.00030	0.00030
0.4	0.99973	0.99977	0.00494	0.00536
0.6	1.00126	1.00132	0.02715	0.03393
0.8	1.00835	1.00571	0.10687	0.14890
0.9	1.01621	1.00762	0.22178	0.28746
0.95	1.0216	1.00774	0.3556	0.39282
0.99	1.0251	1.00708	0.6874	0.50057
0.995	1.036		0.826	
0.999	1.098		1.040	

The exact numerical solutions for the normalized velocities U/U_0 and $a\Omega/U_0$ of a spherical particle undergoing diffusiophoresis parallel to a plane wall as functions of *a/b* are depicted in Fig. 2 for various of *β/a*. It can be seen that the wall-corrected normalized diffusiophoretic mobility U/U_0 of the particle decreases with an increase in *β/a* for the case of an impermeable wall (the boundary condition (2.5) is used), but increases with an increase in *β/a* for the case of a plane wall prescribed with the far-field solute concentration distribution (the boundary condition (2.7) is used), keeping the ratio *a/b* unchanged. This decrease and increase in the particle mobility becomes more pronounced as *a/b* increases.

This behavior is expected knowing that the solute concentration gradients on the particle surface near an impermeable wall decrease as the relaxation parameter *β/a* increase and these gradients near a wall with the imposed far-field concentration gradient increase as *β/a* increases (see the analysis in Appendix C1).

When $\beta/a = 1/2$ under the boundary conditions, two different plane walls will have the same particle diffusion mobility. Under this special circumstance, the fluid concentration between the plane walls and particle interactions disappears. As for the flow force effects caused by the presence of the plane walls for particle, the diffusion of the colloidal particles' movable degrees will monotonously decrease with the increase of *a/b*.

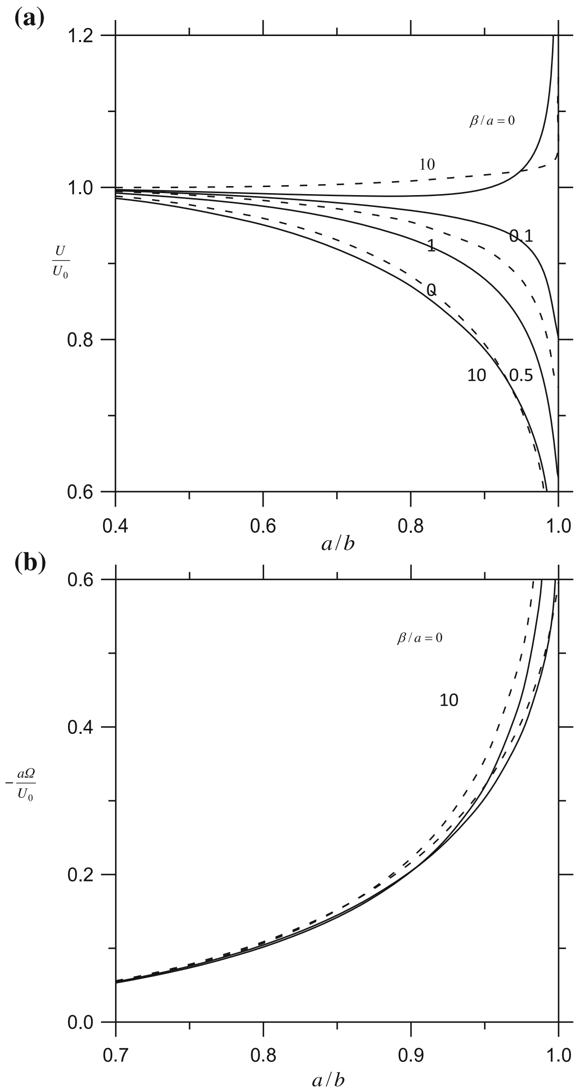

Fig. 2.2 **a** Plots of the normalized translational velocity $U = U_0$ of a *spherical particle* undergoing diffusiophoresis parallel to a plane wall versus the separation parameter $a = b$. **b** Figure of velocity $a\Omega/U_0$ to *a/b* of colloidal particles parallel diffusiophoresis of the single plate

When examining Tables 2.1 and 2.2 and Fig. 2.2a, we find an interesting phenomenon: the plate that is qualitatively dissolved is nonpenetrable, while the polarization coefficient β/a is minimum (such as $\beta/a = 0$) of the case, when the *a/b* decreases, the diffusion of the particles' movable degrees with *a/b* increases while decreasing extremely to a small value, and later with the increase of the *a/b*, it increases. When the gap between the particles and the plane walls is small enough, the velocity of motion of the particles is even larger than in the situation when plane walls are present. For example, when $\beta/a = 0$ and $a/b = 0.999$, the velocity of motion of the colloidal particles will be 45 % faster than the values in the absence of plane walls. In the case of higher *β/a*, the velocity of motion of the plane walls particles is parallel to the fluid which cannot be penetrated; with increase of *a/b*, the velocity decreases monotonically. In the case of the flat surface as a fluid distribution of linear polarization, parameter *β/a* is relatively larger (such as the $\beta/a = 10$); when *a/b* is smaller, the diffusion of the particles' movable degrees with *a/b* drops to a small value, and then increases with the increase of *a/b*. When the gap between the particles and the plane walls is small enough, the velocity of motion of the particles will also be greater than the situation when there are no plane walls. In the case when *β/a* is smaller, the velocity of motion of the particles' parallel fluid distribution plate is linear; with the increase of *a/b*, the velocity decreases monotonously.

For the interesting case that U/U_0 is not monotone decreasing, it is understood that due to the flow force of resistance effect and fluid concentration gradient growth of the interactions of reasoning result, for cause when plate for fluid does not penetrate and polarization parameter *β/a* is extremely small, and when the plate for fluid is in a linear distribution, while polarization parameter *β/a* larger circumstances, the particle motion velocity is increased with *a/b*, which appears to decrease first and then increase (Please check the sentence for clarity in meaning). Through the reflection method, the U/U_0 (formula C1-11 a) is the same as the situation described in the figure.

In the same geometry situation, spherical colloidal particles as diffusion in Tables 2.1 and 2.2 and Fig. 2.2b are influenced by body force field, (such as gravitational field) and the influence caused by the motion of rotation, while the directions of rotation are opposite. This is a comparison with a thin electric double layer of charged particle parallel to an insulating plate of electrophoresis, which is quite approximate (see Keh and Chen 1988). For any polarization parameter *β/a*, particle diffusiophoresis is normalized rotational velocity as $a\Omega/U_0$ for *a/b* of the monotone increasing function, however, when *a/b* is not big, the influence of *β/a* to $a\Omega/U_0$ is not significant.

O 'Neill (1964) and Ganatos et al. (1980) had respectively used spherical bipolar coordinates and boundary take point method to solve the subcritical flow motion parallel to the infinite plane walls of a single spherical particle which was influenced by body force Fe_x. Comparing the spherical particle by gravitational field (at this time, $U_0 = F/6\pi\eta a$) and the effect of diffusion force, we can find the situation of particles in diffusiophoresis when they are influenced by the plane walls which is far less than that of settlement motion.

In parenthesis is the calculated value based on the results of double spherical coordinates according to Keh and Chen (1988).

In Fig. 2.2b, the colloidal particles parallel to the single plate of the diffusion rotational velocity display $a\Omega/U_0$ to *a/b* mapping (the solid line for solute does not penetrate the plate, while the dashed line for solute is a linear distribution of plate).

Table 2.3 Diffusiophoretic motion of *spherical particles* parallel to two single plane walls

a/b	U/U_0			
	$\beta/a = 0$		$\beta/a = 10$	
	Exact solution	Asymptotic solution	Exact solution	Asymptotic solution
For impermeable plane walls				
0.2	0.99796	0.99796	0.99470	0.99470
0.4	0.98597	0.98617	0.96038	0.96083
0.6	0.96339	0.96661	0.87952	0.88817
0.8	0.94684	0.96326	0.74486	0.81008
0.9	0.96662	0.98325	0.64927	0.79933
0.95	1.0163	1.00270	0.5839	0.81018
0.99	1.2243	1.02412	0.4935	0.82992
0.995	1.363		0.481	
0.999	1.718		0.494	
For plane walls prescribed with the far-field concentration profile				
0.2	0.99586	0.99587	0.99832	0.99832
0.4	0.96931	0.96975	0.98877	0.98899
0.6	0.90602	0.91448	0.97215	0.97605
0.8	0.79069	0.85485	0.96200	0.98514
0.9	0.69390	0.84471	0.97401	1.01389
0.95	0.6184	0.85078	0.9974	1.03838
0.99	0.5075	0.86316	1.0550	1.06415
0.995	0.490		1.113	
0.999	0.497		1.256	

2.2.2 Diffusiophoresis of Particle Parallel to Two Plane Walls

Table 2.3 compares when a spherical particle is placed in two parallel plane walls (when $c = b$), and is parallel to two plane walls, the diffusiophoresis for different polarization ratio *β/a* and separating parameters (separation Parameter) *a/b* in two different boundary conditions of the plane walls, the outcomes of which are under the boundary condition using point method, and with the reflection method for approximate results proved by each other (see Appendix C type (C1-20)).

Approximate to the motion situation of single particle parallel to the plate, in order to take the boundary collocation method for correct outcomes and the reflection method for approximate results (Formula (C1-20)), when $\lambda \leq 0.6$, the two kinds of calculations are very approximate. But when $\lambda \geq 0.8$, with reflection method the approximate result is considerably different. Generally speaking, Formula (C1-20) overestimates the particle diffusion velocity. Comparing Table 2.3 with Tables 2.1 and 2.2, we can see that when *a/b* is relatively small and as a single plate of the boundary effect directly added into, it will underestimate the two-plate boundary effect; however, when *a/b* is very large and as a single

Fig. 2.3 Plots of the normalized diffusiophoretic mobility $U = U_0$ of a *spherical particle* migrating on the median plane between two parallel plane walls (with $c = b$) versus the separation parameter $a = b$ for several values of $r = a$

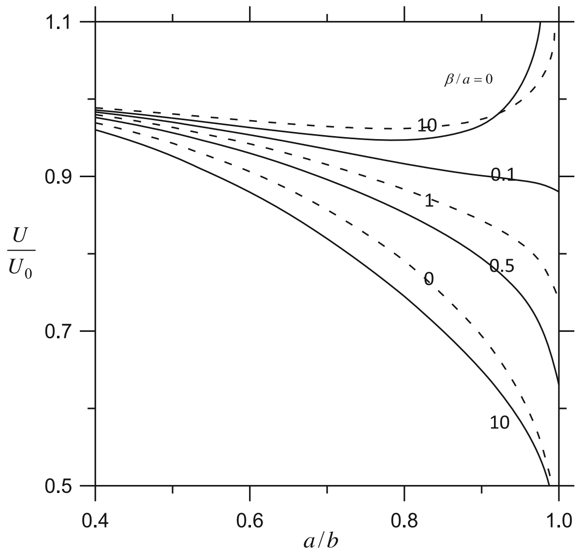

plate boundary effect of direct additive into, it will overestimate the two-plate boundary effect.

For different polarization ratios *β/a*, with separate parameters *a/b* of the particle regularization diffusion, the shift motion velocity U/U_0 and rotational velocity $a\Omega/U_0$ to boundary take point method for numerical results are shown in Fig. 2.3. According to the figure, it is known that the plate in which the fluid cannot penetrate, its regularization diffusiophoresis velocity U/U_0 will also increase with the polarization ratio *β/a* gradually reducing. However, in the plate for linear concentration distribution of cases, the normalized diffusiophoresis velocity U/U_0 will also increase when the polarization ratio *r/a* increasing. Approximately, when plate for fluid does not penetrate, and polarization ratio *β/a* is minimum (such as $\beta/a = 0$), where *a/b* is relatively small, the particle of the diffusion mobility increases with the increase of *a/b* and declines to a minimum, then when *a/b* increases, it increases. In addition, when the gap between particles and plane walls is small enough, the particle's motion velocity is also larger than the situation without plane walls. Therefore, when the gap between particles and plane walls is extremely small, fluid concentration gradient effect of growth will be larger than the power of flow resistance effect, therefore causing the particle motion velocity to increase. Through the reflection method for approximate results (type (C1-20)), its trend corresponds with the outcomes obtained from the boundary take point method.

Comparing Figs. 2.3 and 2.2a, we can conclude that when the second plate is added, it does not necessarily enhance the particle due to influence of diffusion swimming velocity (even if two plane walls and particles are of equal distance). Because when joining the second plate, the flow force of resistance effect and the fluid concentration gradient effect of growth although increased have different

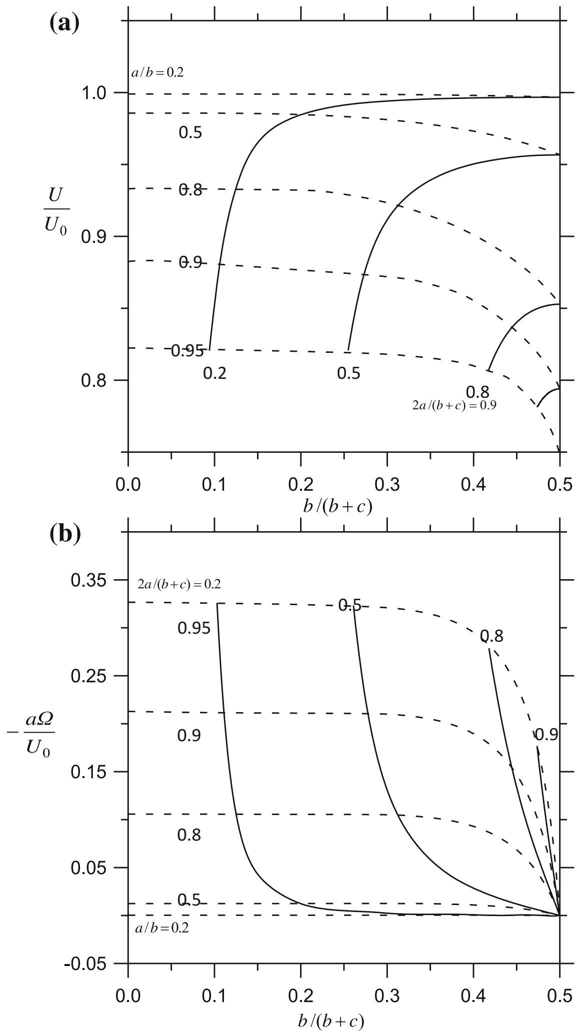

Fig. 2.4 **a** Plots of the normalized translational velocities $U = U_0$ of a *spherical particle* undergoing diffusiophoresis parallel to two plane walls versus the ratio $b = (b + c)$. **b** When $\beta/a = 1/2$, the diffusiophoresis rotational velocity of colloidal particles $a\Omega/U_0$, make figure for $b/(\mathrm{b} + c)$ between two parallel plane walls

degrees, so that the total influence does not necessarily enhance the particles of the diffusiophoresis velocity influence, which is the so-called "Phoretic Migration Enhancing Effect (PMEE)."

Colloidal particles are located at any position between two plane walls, for different separation parameters a/b, when the polarization parameter $\beta/a = 1/2$ (now for two kinds of different boundary conditions of plane walls, they have the same numerical results), particle regularization diffusiophoresis velocity U/U_0 and rotational velocity of $a\Omega/U_0$ numerical results as shown in Fig. 2.4.

The dotted line in the figure represents distance between the fixed one of the plane walls and the particles (a/b = constant), and the influence caused by the change of another plate (in $z = c$) for the diffusiophoresis of colloidal particles. The line represents the fixed distance between two plane walls ($2a/(b + c) =$ constant); when the particle is located at different locations between two plane walls, the influence they cause is to colloid particle diffusiophoresis. From Fig. 2.4a, we know that under this circumstance, plate net effect will reduce particle diffusion velocity U/U_0. When $2a/(b + c)$ is a fixed value, and particle is located in the middle between two plane walls ($c = b$), the drag force is minimum, and it has the largest mobile velocity (the rotational velocity is zero). While when the particle gradually moves toward a plate (when $b/(b + c)$ decrease), the drag force of fluid increases, and the motion velocity decreases but the rotational velocity increases.

With a fixed particle and at a distance from one of the plane walls (when a/b is a fixed value), the existence of another plate will reduce particle motion velocity and rotating velocity, and with the particles and another flat gradually moving toward each other (when $b/(b + c)$ gradually increases), particle motion velocity and rotating velocity gradually decreases as well.

On the other hand, for some cases such as the diffusiophoresis of a colloidal sphere with a small value of β/a parallel to two impermeable plane walls or with a large value of β/a parallel to two plates prescribed with the far-field solute concentration distribution, the net wall effect can increase the diffusiophoretic mobility of the particle relative to its isolated value.

If we compare different $2a/(b + c)$ cases with each other, it can be found that when the particle is located in the middle of two plane walls, at this time there is relatively maximum particle velocity value; while when the particle is near any one of the plane walls the relative velocity decreases. What is worth mentioning is that in fixed particle and the distance of a flat (fixed a/b value), another plate to the effect of particle motion velocity is not monotone function, however, for the sake of conciseness, I do not provide a figure to illustrate this.

Ganatos et al. (1980) used the boundary collocation method to solve when a single spherical particle is located at any position in between two flats, parallel plane walls will display falling motion. Compared with this chapter, we can see that in general cases, the effect of plane walls diffusiophoresis is much smaller than a falling motion.

2.3 Conclusions

This study considers single spherical colloidal particles in the case of low Reynolds number and low picogram number of columns, parallel in a single infinite plate or infinite plate of diffusiophoretic motion behavior, respectively, taking point method (boundary collocation method) and reflection method for solving particle swimming velocity and comparing particle phoretic motion in the case.

In this chapter, I consider a single spherical colloidal particle diffusion in the electrolyte solution. The boundary conditions of the plates are solute impermeable and solute linear distribution of the two cases. The results found that the diffusiophoresis boundary effects varied. Generally speaking, the diffusiophoretic velocity of separation parameters has a monotonic decreasing function. However, when a/b is close to 1, under different parameters of polarization ($= \beta/a$), the boundary effects of plates could accelerate or decelerate motion velocity of particles (compared with a single particle at infinity condition); this phenomenon of the acceleration effect of concentration gradient and the effect of viscosity of fluid mechanics should make a situation of competition for both.

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