Hydrodynamic and surface interaction forces on a particle in a pore

Citation for published version (APA):

Hofman, J. A. M. H., & Stein, H. N. (1992). Hydrodynamic and surface interaction forces on a particle in a pore. *Journal of Colloid and Interface Science*, 154(2), 359-368. [https://doi.org/10.1016/0021-9797\(92\)90150-K](https://doi.org/10.1016/0021-9797(92)90150-K)

DOI:

[10.1016/0021-9797\(92\)90150-K](https://doi.org/10.1016/0021-9797(92)90150-K)

Document status and date:

Published: 01/01/1992

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Hydrodynamic and Surface Interaction Forces on a Particle in a Pore

J. A. M. H. HOFMAN¹ AND H. N. STEIN²

*Laboratory of Colloid Chemistry, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

Received November 18, 1991; accepted March 23, 1992

The interaction between a spherical particle in a pore near a constriction and the wall is calculated in order to understand the behavior of dispersions on their transport through a porous medium. A simplified geometry of the pore is assumed which permits, for a spherical particle:

- (a) Analytical calculation of the London-van der Waals attraction;
- (b) Calculation of electrostatic repulsion by numerical solution of the Poisson-Boltzmann equation and application of the Langmuir equation for the repulsive pressure; and
- (c) Calculation of hydrodynamic interactions by numerical solution of the Navier-Stokes equation by means of a finite element method.

The method permits solution of the Navier-Stokes equation, in the low Reynolds number range (e.g., $Re = 5 \times 10^{-4}$), as long as the closest distance between the particle and the wall is at least $0.3 \mu\text{m}$. The results indicate that under the conditions covered by the present calculations, for a stationary particle near a pore constriction, the hydrodynamic interactions by far predominate over colloid chemical interactions. © 1992 Academic Press, Inc.

INTRODUCTION

The behavior of dispersions in a porous medium is of practical interest for its relevance to filtration theory and to emulsions passing through a geological sediment. The situation is of theoretical interest because there is competition between various types of forces (colloid chemical, hydrodynamic) acting on the particle when it approaches a pore constriction. This situation therefore affords an opportunity to compare the influence of such forces.

Experimentally, large permeability reductions have been observed, e.g., in the case of emulsions flowing through porous media (1, 2, 3), even if the emulsions are stable, while there is a pronounced electrostatic repulsion between droplets and pore wall, and while the emulsion droplet size is smaller than the av-

erage pore diameter. Similar phenomena are known in filtration theory.

For particles larger than the average pore diameter, a mechanical sieving action would suffice for understanding the permeability reduction. Similarly, the permeability reduction can be understood if particles larger than the average pore diameter originate in the pores during transport of the dispersion through them; in other words, if we are dealing with an unstable dispersion which coagulates (or even coalesces) under the influence of shear. Nor is such a permeability reduction surprising if the particles can be considered to adhere to the pore walls. However, a permeability reduction has been observed in cases in which neither of these explanations seems to be applicable.

In order to understand such cases, we performed some calculations of the most important forces acting on a stationary particle near a pore constriction. The stationary particle condition was chosen because it is the most

¹ Present address: KIWA, Nieuwegein, The Netherlands.

² To whom correspondence should be addressed.

interesting one from the standpoint of blocking of pores. The calculations have been restricted to particles which are large enough for Brownian motion to be neglected (which is the case of interest when dealing with emulsions, and with many suspensions in which pore blocking has been observed).

The present investigation treats this problem for the case of a stationary spherical particle and the pore constriction that has a funnel-like shape. In order to approach theoretically the situation of pore blocking, the boundary conditions were chosen to refer to a stationary particle near a pore constriction. The particle in the pore will be subject to five different forces: attraction due to London-van der Waals forces; repulsion on partial overlap of the electrical double layers of the particle and the pore wall; drag forces induced by the flow of the continuous phase around the particle; buoyancy; and capillary forces. The last two forces are ignored. There are no indications that such forces play a dominant role in pore blocking, and inclusion of them would make the equations unnecessarily complicated, distracting attention from the central issue of this paper, the competition between hydrodynamic and surface forces.

For brevity, we restrict ourselves in the present paper to the case of Hamaker constants >0 , because this is the case of most interest to pore blocking.

A simplified geometry of the pore constriction is assumed (see Fig. 1), which permits analytical calculation of the London-van der Waals attractive energy and numerical calculation of electrostatic repulsion and hydrodynamic drag. In this geometry, the particle is assumed to occupy an axial position in the cylindrical pore.

LONDON-VAN DER WAALS ATTRACTION

With the geometry of the situation near a pore constriction described in Fig. 1, the attractive forces between the wall material and the particle can be treated analytically as long as the Hamaker constant is taken to be inde-

FIG. 1. Pore geometry assumed for calculation of the interaction between a particle and the pore wall, near a pore constriction.

pendent of distance. Thus, retardation effects are neglected; the impact of this approximation on the final result will be discussed later.

By an approach in essence similar to that employed by Hamaker (4) we obtain the total attractive energy by integrating the attraction between two atoms, one in the pore wall and one in the particle, over the volume both of the particle and of the wall material:

$$E = - \int dV_1 \int dV_2 \frac{Q^2 \lambda}{r^6}. \quad [1]$$

Here λ is the London-van der Waals constant describing the attraction between two atoms, one in the volume element dV_1 of the pore wall material, the other in the volume element dV_2 of the particle; r is the distance between the two volume elements concerned; and Q is the number of atoms per unit volume in dV_1 and dV_2 (taken equal for simplicity). The product $\pi^2 Q^2 \lambda$ is usually indicated as the Hamaker constant A_{Ham} .

An analytical integration of this equation is described in Appendix 1. In this treatment, the interaction energy between particle and pore wall is divided into three parts:

E_1 referring to the interaction of the particle with the material in the wide part of the pore wall;

E_2 concerning the interaction with the wall material where the pore is narrowing; and

E_3 concerning the interaction with the narrow part of the pore wall.

The total attractive force exerted by the pore wall on a particle approaching the constriction is then obtained by differentiating the total attractive energy with respect to the distance:

$$F_{\text{attraction}} = - \frac{d(E_1 + E_2 + E_3)}{dh} \quad [2]$$

Here h is the parameter indicating the position of the particle in relation to the pore constriction; $h = 0$ indicates that the particle center is at the beginning of the narrow part of the pore.

Figures 2 and 3 show some results obtained for values of the parameters as indicated in the legends to the figures. These results are obtained using positive values of the Hamaker constant. The latter may be negative, however. This will result in repulsive forces equal in magnitude but opposite in sign, compared with those shown in the Figs. 2 and 3.

Qualitatively, these figures can be understood as follows: a particle in a homogeneous pore (an infinite straight cylinder) does not experience any net attractive force from the pore wall, although the interaction energy between wall and particle is nonzero. There are equal amounts of material in the pore wall

FIG. 2. Attractive force for different particle radii. $A_{\text{Hamaker}} = 2.5 \times 10^{-21}$ J, $R_1 = 5 \mu\text{m}$, $R_2 = 1 \mu\text{m}$, $z_0 = 14 \mu\text{m}$, $R_p =$ (1) $0.75 \mu\text{m}$; (2) $0.95 \mu\text{m}$; (3) $1.5 \mu\text{m}$; (4) $2 \mu\text{m}$; (5) $3 \mu\text{m}$.

FIG. 3. Attractive force for different heights of the conical part of the pore. $A_{\text{Hamaker}} = 2.5 \times 10^{-21}$ J, $R_1 = 5 \mu\text{m}$, $R_2 = 1 \mu\text{m}$, $R_p = 0.95 \mu\text{m}$, z_0 : (1) $3 \mu\text{m}$; (2) $5 \mu\text{m}$; (3) $7 \mu\text{m}$; (4) $9 \mu\text{m}$; (5) $11 \mu\text{m}$; (6) $13 \mu\text{m}$.

above and below the particle, exerting forces which compensate each other. However, the interaction energy is larger when the particle is in a narrow pore than when the particle is in a wide pore, and therefore a net attractive force arises near a pore constriction. This force is at its maximum when the particle is near the entrance of the narrow part of the pore ($h = 0$).

ELECTROSTATIC REPULSION

For calculating the electrostatic repulsion between the particle and the pore wall material, first the electrical potential in a cylindrical gap is calculated. Both particle and wall, in the conical part of the pore, are divided into slices (Fig. 4). Every section is then approximated, as in the Derjaguin method for calculating the electrostatic repulsion between two spherical particles for large κa values (5), as having cylindrical symmetry. In this symmetry, the Poisson-Boltzmann equation,

$$\nabla^2 \psi = - \frac{\rho}{\epsilon_0 \epsilon_r} \quad [3]$$

with

ψ = electrical potential;

ρ = space charge density = $-2 z e_0 n_0 \times \sinh(z e_0 \psi / kT)$;

z = valence of the ions present (symmetrical electrolyte assumed),

e_0 = absolute value of charge of an electron;

FIG. 4. Division of pore and particle into slices for calculation of electrostatic repulsion.

n_0 = electrolyte concentration in the bulk liquid;

ϵ_0 = permittivity of vacuum;

ϵ_r = relative dielectric constant of the medium;

is expressed in cylindrical coordinates. In the expansion of $\nabla^2\psi$ in these coordinates, the terms in Θ and φ disappear, leading to the following equation:

$$\frac{\partial^2\psi}{\partial r^2} + \frac{1}{r} \frac{\partial\psi}{\partial r} = \frac{2ze_0n_0\sinh(ze_0\psi/kT)}{\epsilon_0\epsilon_r} \quad [4]$$

After making this equation dimensionless by the substitutions

$$y = ze_0\psi/kT, \quad \alpha = ze_0/kT,$$

$$\beta = \kappa(R - R_p),$$

where R_p = the radius of the inner cylinder; R = the radius of the outer cylinder; $t = \kappa(r - R_p)/\beta$; κ = the Debye-Hueckel parameter, we obtain the equation

$$\frac{d^2y}{dt^2} + \frac{\alpha\beta}{\beta t + \kappa R_p} \frac{dy}{dt} - \beta^2 \sinh y = 0. \quad [5]$$

This equation was numerically solved, using a finite difference relaxation scheme (NAG library subroutine D02GAF). For the potential determining electrostatic repulsion, at the pore

wall -0.08 V has been taken; at the particle -0.07 V (see later).

A typical solution of Eq. [7] is shown in Fig. 5. Similar curves were calculated for all slices in Fig. 4. The minimum in absolute value of such a curve was used to calculate the contribution of the slice concerned to the repulsive pressure, by using the Langmuir equation (6)

$$p = 2n_0kT(\cosh y_{\min} - 1). \quad [6]$$

The total repulsive force experienced by a particle approaching the pore constriction was calculated by multiplying this pressure by the surface area of the slice concerned at its minimum absolute potential value, and by summing all contributions of these slices,

$$F_R = \sum \pi R_{\text{slice}} p_i \sin 2\vartheta_i \Delta z, \quad [7]$$

where Δz is the height of a slice, R_{slice} is its radius, and ϑ_i is the angle between the direction of the r axis (i.e., the direction of the osmotic pressure) and the normal of the particle surface.

Figures 6 and 7 show typical results. The height of the conical pore section appears to have much less influence than the pore diameter. Separately, the influence of the number of slices was checked and found to be negligible as soon as this number was 31 or larger.

FIG. 5. Typical solution of the Poisson-Boltzmann equation in a cylindrical gap. $\psi_p = \psi_0 = -0.08$ V; electrolyte concentration: (1) 1×10^{-4} mole/liter; (2) 5×10^{-4} mole/liter; (3) 1×10^{-3} mole/liter.

FIG. 6. Influence of particle radius on electrostatic repulsive force. $R_1 = 5 \mu\text{m}$, $R_2 = 1 \mu\text{m}$, $z_0 = 14 \mu\text{m}$, $\psi_0 = \psi_p = -0.08 \text{ V}$, electrolyte concentration = $5 \times 10^{-4} \text{ mole/liter}$. R_p : (1) $0.95 \mu\text{m}$; (2) $1 \mu\text{m}$; (3) $2 \mu\text{m}$; (4) $3 \mu\text{m}$.

HYDRODYNAMIC FORCE

The Navier-Stokes equation was solved for the geometry depicted in Fig. 8 (to be considered axisymmetric), using the finite element method with the penalty function approach (7, 8), with the following boundary conditions:

FIG. 7. Influence of height of conical part of the pore on electrostatic repulsive force. $R_1 = 5 \mu\text{m}$, $R_2 = 1 \mu\text{m}$, $R_p = 0.95 \mu\text{m}$, $\psi_0 = \psi_p = -0.08 \text{ V}$, electrolyte concentration = $5 \times 10^{-4} \text{ mole/liter}$. z_0 : (1) $5 \mu\text{m}$; (2) $7 \mu\text{m}$; (3) $9 \mu\text{m}$; (4) $11 \mu\text{m}$; (5) $13 \mu\text{m}$.

FIG. 8. Domain and boundary conditions for the calculation of the hydrodynamic force acting on a particle in a funnel-like pore. Boundary 1: outlet; boundaries 2, 3, and 4: pore wall; boundary 5: inlet; boundaries 6 and 8: z axis; boundary 7: particle.

- (a) no slip at the pore wall (boundaries 2, 3, and 4);
- (b) no slip at the particle surface (boundary 7);
- (c) the velocity at the inlet boundary 5 has a parabolic profile;
- (d) to prevent oscillations in the solution, Neumann boundary conditions were used at the outlet of the pore (boundary 1).

The resulting velocity profile was used to calculate the drag coefficient.

The starting point therefore is the Navier-Stokes equation,

$$-\eta \nabla^2 u + \rho(u \cdot \nabla u) + \nabla p = \rho f, \quad [8]$$

in combination with the continuity equation

$$\nabla u = 0. \quad [9]$$

Here u is the velocity of the fluid phase, p is the pressure, ρ is the density of the liquid, and f comprises external forces acting on a volume element. The coordinate system employed is again a cylindrical one, with the z axis = the direction of flow.

Equations [8] and [9] can be made dimensionless by introducing a characteristic length L (= the particle diameter) and a characteristic velocity U_0 (= the maximum velocity at the inlet). These quantities are employed to make linear parameters dimensionless by dividing them by L , velocities by dividing them by U_0 , pressures by dividing them by ρU_0^2 , and volume forces f by dividing them by U_0^2/L . Indicating henceforth dimensionless quantities by u , p , and f , we obtain

$$-\frac{1}{\text{Re}} \nabla^2 u + (u \cdot \nabla u)u + \nabla p = f, \quad [10]$$

where Re is the Reynolds number $\rho U_0 L / \eta$. The form of this equation indicates that it is not applicable at $Re = 0$. In our calculations we used $Re = 5 \times 10^{-4}$.

The axisymmetry of the geometry implies that derivatives with respect to the coordinate ψ , and u_ψ are assumed to be zero. In addition, it implies that for the z axis the boundary conditions $u_r = 0$, $\partial u_z / \partial r = 0$ hold.

The other boundary conditions mentioned amount to $u_r = 0$ and $u_z = 0$ at boundaries 2, 3, 4, and 7, while the inlet velocity profile is given by

$$u_z = \left[\frac{2R_p r}{R_1} \right]^2 - 1, \quad u_r = 0. \quad [11]$$

The Neumann boundary conditions at boundary 1 in Fig. 8 can be expressed by

$$u_r = 0, \quad \frac{\partial u_z}{\partial z} = 0, \quad [12]$$

at this boundary.

In addition, for the pressure the boundary condition $p = 0$ at boundary 1 is applied.

The velocity profile calculated thus leads to the normal and tangential stresses in the liquid. To calculate the drag force, the vertical z components of the normal and tangential stresses at the particle surface must be integrated over the particle surface. The normal stress is equal to the hydrodynamic pressure, and the tangential stress is equal to the vorticity at the particle surface. This leads to the following equation to calculate the drag coefficient C_d :

$$C_d = \frac{F}{0.5 \rho A U_0^2} = -2 \int_0^\pi p_s \sin 2\psi d\psi - \frac{4}{Re} \int_0^\pi \xi_2 \sin^2 \psi d\psi. \quad [13]$$

In Eq. [13], F is the drag force acting on the sphere, $A = \pi R_p^2$ is the area of a section through the center of the particle, and ψ is the angle between the z axis and the normal to a surface element. Here, p_s is the hydrodynamic pressure at the surface of the particle, and $\xi_s = \nabla \times u$ at the particle surface.

A typical result is shown in Fig. 9.

FIG. 9. Hydrodynamic force acting on a particle. $R_1 = 5 \mu\text{m}$, $R_2 = 1 \mu\text{m}$, $z_0 = 14 \mu\text{m}$. R_p : (▲) $0.95 \mu\text{m}$; (●) $2 \mu\text{m}$.

DISCUSSION

The formulae derived in the preceding section have been applied under the conditions of a repulsive potential equal to the ζ potential at the surfaces concerned found in emulsions under some conditions resembling practical ones (3) ($\zeta_{\text{emulsion}} \approx -0.08 \text{ V}$; $\zeta_{\text{wall}} \approx -0.07 \text{ V}$ (3)). As to their order of magnitude, these data agree with data presented by Soo *et al.* (1, 2). Although the ζ potential is conceptually different from the potential determining electrostatic repulsion, in practice it appears to be a good indication for the double layer repulsion, at least in the absence of adsorbed polymer layers at the phase boundary concerned (9, 10).

Figures 10 and 11 present some data obtained for a particle smaller than the narrow part of the pore. Note in these figures the difference in vertical scale, necessitated by the difference in the order of magnitude of the forces involved. It is seen that the hydrodynamic drag force by far surpasses colloid chemical interactions. It should be noted that this has been calculated for electrostatic repulsions at about their maximum values (ζ potentials larger than 0.08 V in absolute sense are rare). In addition, the calculations refer to

FIG. 10. Attractive (▲), repulsive (●), and hydrodynamic (▼) forces as function of the position of the particle. $R_1 = 5 \mu\text{m}$, $R_2 = 1 \mu\text{m}$, $z_0 = 14 \mu\text{m}$, $R_p = 0.95 \mu\text{m}$.

the equilibrium electrical double layer not disturbed by flow. This means restriction of the results of this calculation to cases of low flows, or to cases in which the thickness of the double layer ($1/\kappa$) is small compared to the dimensions of the particle considered.

If the assumptions mentioned are fulfilled,

$$F_{\text{attraction}} < F_{\text{repulsion}} \ll F_{\text{hydrodynamic drag}}. \quad [14]$$

FIG. 11. Colloid chemical interactions as shown in Fig. 10, but on a different scale to show more detail (cf. the different scale on the y axis). Symbols as in Fig. 10.

The former part of this statement will not come as a surprise, at the given repulsive potentials introduced into the calculations. It should be remarked that our calculations of the London-van der Waals attraction refer to *unretarded* interactions; the relatively modest character of the role of attraction will in reality be even more pronounced when retardation is taken into account.

For lower values of the potential responsible for electrostatic repulsion, the sequence of the first two items in Eq. [14] may be reversed. Therefore, our general conclusion should read that, for a stationary particle at low but non-zero Reynolds numbers, the hydrodynamic forces predominate over colloid chemical forces.

Similar data for the case that the particle is larger than the smaller pore radius are presented in Figs. 12 and 13. As might be anticipated, the electrostatic repulsion rises steeply when the particle and the pore wall nearly make contact. On very close approach, the numerical solution of the equations becomes increasingly difficult. A typical practical limit in our calculations was a distance of closest approach between particle and pore wall of about $0.3 \mu\text{m}$ for a particle with radius = 1

FIG. 12. Attractive (▲), repulsive (●), and hydrodynamic (▼) forces as a function of the position of the particle. $R = 5 \mu\text{m}$, $R_2 = 1 \mu\text{m}$, $z_0 = 14 \mu\text{m}$, $R_p = 2 \mu\text{m}$.

μm ; it should be noted, however, that this limit is expected to be dependent on the computer facilities used. As a practical consequence of this it is expected that the closest distance between a particle and the pore wall will become significantly less than $0.3 \mu\text{m}$.

For the case of deformable particles (droplets of disperse phase in an emulsion), the schematization of the geometry as indicated in Fig. 1 will lose its applicability when particle and pore wall nearly make contact. On mutual approach of two emulsion droplets, deformation of the droplets may occur when the interfacial tension is low enough ($< \text{about } 0.0001 \text{ N/m}$ (11)). In the case discussed in the present paper, because of the large operative hydrodynamic forces, deformation of the droplet as schematically indicated in Fig. 14 is to be expected, even in cases when the interfacial tension does not attain very low values. In the case of pronounced electrostatic repulsion between droplets and wall discussed here, the distance between droplet and wall will be of the order of 10 nm (the distance of the secondary minimum to be expected). Such a close approach will effectively prevent liquid transport between droplet and wall, and this will lead to pronounced pore clogging when

FIG. 13. Colloid chemical interactions as shown in Fig. 12, but on a different scale to show more detail. Symbols as in Fig. 12.

FIG. 14. Schematic of deformation of emulsion droplet to be expected close to the pore constriction, when the droplet is larger than the narrow part of the pore.

part of the emulsion droplets are larger than the pore constrictions, even if the electrostatic repulsion between wall and droplet is large enough to prevent direct contact between droplet and wall.

APPENDIX 1:

DERIVATION OF THE FORMULAS FOR CALCULATION OF THE VAN DER WAALS INTERACTION

Starting from Eq. [1], first the integration over dV_2 referring to the particle is performed. This leads to the energy of interaction between the particle and one atom of the wall material situated at a distance a from the center of the particle, as shown in Fig. A1:

$$E_p = -\frac{4\pi\lambda Q}{3} \left[\frac{R_p}{a^2 - R_p^2} \right]^3. \quad [\text{A1}]$$

FIG. A1. Distances in the calculation of attraction between an emulsion droplet and the pore wall.

The integration over dV_1 , referring to the wall material, is best performed in cylindrical coordinates:

$$E_A = \int_0^{2\pi} \int_{-\infty}^{\infty} \int_{R(z)}^{\infty} E_p q r dr dz d\varphi. \quad [A2]$$

In order to perform the integration [A2], a is eliminated from [A1] through

$$a = \sqrt{r^2 + (z - h)^2}. \quad [A3]$$

We consider the particle to be situated in the upper part of the pore (as shown in Fig. 1). The attractive energy is then additively composed of three parts:

(a) E_1 , the attraction between the particle and the part of the pore material *lower* than the pore constriction;

(b) E_2 , the attraction between the particle and the *middle* (i.e., the conical) part of the pore material; and

(c) E_3 , the attraction between the particle and the *upper* part of the pore wall material.

Part (a): If the particle is smaller than the lower (narrow) part of the pore, E_1 is given by

$$E_1 = \frac{b}{4qa} + \frac{1}{2q\sqrt{q}} \left[2 \arctan \frac{b}{\sqrt{q}} + \pi \right], \quad [A4a]$$

where $q = 4(R_2^2 - R_p^2)$; $b = -2h$; $a = R_2^2 - R_p^2 - R_p^2 + h^2$.

If the particle is of the same size as the lower part of the pore, then E_1 is given by

$$E_1 = \frac{1}{12h^3}. \quad [A4b]$$

If the particle is larger than the narrow part of the pore, then E_1 is given by

$$E_1 = \frac{b}{4qa} + \frac{2}{4q\sqrt{-q}} \ln \left[\frac{(b - \sqrt{-q})}{(b + \sqrt{-q})} \right]. \quad [A4c]$$

Part (b): If the particle is smaller than the narrow part of the pore, E_2 is given by

$$E_2 = \frac{c_1 z_0 + b_1/2}{2q_1 Z_0} - \frac{b_1}{4q_1 a_1} + \frac{c_1}{q_1 \sqrt{q_1}} \left[\arctan \{ (2c_1 z_0 + b)/\sqrt{q} \} - \arctan \{ b/\sqrt{q} \} \right]. \quad [A5a]$$

Here,

$$\begin{aligned} a_1 &= R_2^2 - R_p^2 + h^2; \\ b_1 &= 2 \left[R_2 \left(\frac{R_1 - R_2}{z_0} \right) - h \right]; \\ c_1 &= 1 + \left[\frac{R_1 - R_2}{z_0} \right]^2; \\ q_1 &= 4a_1 c_1 - b_1^2; \quad \text{and} \\ Z_0 &= a_1 + b_1 z_0 + c_1 z_0^2. \end{aligned}$$

For the meaning of R_1 , R_2 , R_p , h , and z_0 , see Fig. 1.

If the particle is of the same size as the lower part of the pore, E_2 is given by

$$E_2 = \frac{2c_1}{3b_1^2} - \frac{1}{12c_1^2(z_0 + b_1/2c_1)}. \quad [A5b]$$

If the particle is larger than the narrow part of the pore, then E_2 is given by

$$E_2 = \frac{2c_1z_0 + b_1}{4q_1Z_0} - \frac{b_1}{4q_1a_1} + \frac{c_1}{q_1\sqrt{-q_1}} \\ \times \left[\ln \frac{2c_1z_0 + b_1 - \sqrt{-q_1}}{2c_1z_0 + b_1 + \sqrt{-q_1}} - \ln \frac{b_1 - \sqrt{-q_1}}{b_1 + \sqrt{-q_1}} \right]. \quad [\text{A5c}]$$

Part (c): For the calculation of E_3 , only the case of a particle smaller than the pore diameter is of interest. In this case, E_3 is given by

$$E_3 = -\frac{2z_0 + b_2}{4q_2Z_0} + \frac{2}{4q_2\sqrt{q_2}} \\ \times \left[\pi - 2 \arctan \frac{2z_0 + b_2}{\sqrt{q_2}} \right]. \quad [\text{A6}]$$

Here $q_2 = 4(R_1^2 - R_p^2)$, and $b_2 = -2h$.

The combination of equations [A4a], [A4b], or [A4c] with [A5a], [A5b], or [A5c], and with [A6], then gives the total attractive energy. On differentiating the energy of attraction, we obtain the attractive force:

$$F_{\text{attr}} = -\frac{d(E_1 + E_2 + E_3)}{dh}. \quad [\text{A7}]$$

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support for this investigation by Stichting Technische Wetenschappen, and by the Koninklijke Shell Exploratie en Productie Laboratorium. Professor van Steenhoven contributed significantly to the discussions on finite element methods.

REFERENCES

1. Soo, H., and Radke, C. J., *Chem. Eng. Sci.* **41**, 263 (1986).
2. Soo, H., Williams, M. C., and Radke, C. J., *Chem. Eng. Sci.* **41**, 273 (1986).
3. Hofman, J. A. M. H., and Stein, H. N., *Colloids Surf.* **61**, 317 (1991).
4. Hamaker, H. C., *Physica* **4**, 1058 (1937).
5. Derjaguin, B., *Kolloid Z.* **69**, 155 (1934); *Acta Physicochim. URSS* **10**, 333 (1939).
6. Verwey, E. J. W., and Overbeek, J. Th. G., "Theory of Stability of Lyophobic Colloids." Elsevier, Amsterdam, 1948.
7. Cuvelier, C., Segal, A., and van Steenhoven, A. A., "Finite Element Methods and Navier-Stokes Equations," Reidel, Dordrecht, 1986.
8. Pluijm, M. J. F. P., "The Development of a Micro-anemometer," Ph. D. Thesis, Eindhoven, 1987.
9. McGown, D. N. L., and Parfitt, G. D., *Disc. Faraday Soc.* **42**, 225 (1966).
10. Horn, R. G., and Smith, D. T., *J. Non Cryst. Solids* **120**, 72 (1990).
11. Hofman, J. A. M. H., and Stein, H. N., *J. Colloid. Interface Sci.* **147**, 508 (1991).