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On the applicability of the Brinkman equation in soft surface electrokinetics

Stanislav S. Dukhin [a], Ralf Zimmermann [b,*], Jérôme F.L. Duval [c], Carsten Werner [b,d]

[a] New Jersey Institute of Technology, Newark, NJ 07102-1982, USA
[b] Leibniz Institute of Polymer Research Dresden & The Max Bergmann Center of Biomaterials Dresden, Hohe Strasse 6, 01069 Dresden, Germany
[c] Laboratoire Environnement et Minéralurgie, Nancy-Université, CNRS UMR 7569, 15 Avenue du Charmois, B.P. 40, 54501 Vandoeuvre-lès-Nancy Cedex, France
[d] Technische Universität Dresden, Center of Regenerative Therapies Dresden, Tatzberg 47, 01307 Dresden, Germany

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ABSTRACT

The Stokes equation is commonly used within the field of electrokinetics of hard impermeable surfaces while the Brinkman equation is adopted for tackling hydrodynamics in the framework of soft (permeable) surface electrokinetics (SSE). The latter was initially proposed for modeling the hydrodynamics in so-called hybrid systems that consist of a porous medium and an adjacent fluid phase basically because the conventional Darcy law or Debye and Bueche model initially proposed for that purpose failed to provide the required velocity and shear stress-continuity conditions at the porous media–fluid interface. However, even though the physical background of the Brinkman equation and its boundary conditions have been discussed when applied to the hydrodynamics of hybrid systems, controversy still remains with respect to their applicability in the field of SSE. Indeed, recent experiments pointed out better agreement between shear flow into a regular array of rods oriented across the flow and the solution of the Brinkman equation for hybrid systems providing a stress-jump boundary condition is taken into account (M.F. Tachie et al., J. Fluid. Mech. 493 (2003) 319). As there is identity in the Brinkman model for hybrid systems and for SSE, the question arises whether the above discontinuity of viscous stress must be incorporated or not into SSE modeling. Recent determination of hydrodynamic penetration length λ_o^{-1} of swollen and collapsed thermo-responsive films (J.F.L. Duval, R. Zimmermann, A.L. Cordeiro, N. Rein, C. Werner, Langmuir 25 (2009) 10691) suggests that there is no need for a cardinal revision of the Brinkman model, although further experimental investigations are required to support such a conclusion. With regard to these experiments, almost complete agreement between independent determination of λ_o^{-1} by swelling experiments and its derivation according to Brinkman model was obtained.

1. Introduction

In the last decades, the electrokinetics of soft (permeable) surfaces has been the topic of numerous publications [1–28], while the interpretation of electrokinetic measurements at hard (impermeable) surfaces has been established over a century [29–36]. First approximate analytical solutions of the Brinkman equation for grafted polymer layers were proposed about 20 years ago. Both, polyelectrolyte layers immobilized on a uncharged surface and uncharged polymers attached to charged surfaces were considered [1–5,7–9]. At the same time, first numerical solutions of the Brinkman equation were published [6]. A rigorous theory for the solution of the Brinkman equation specified for polyelectrolyte layers with uniform distribution of polymer segments was elaborated by Ohshima [10–12]. On the contrary, Duval and co-workers [22–24] proposed an analytical formalism for the electrokinetics of charged soft hydrogels that includes the possibility for modeling a gradual decay of the segment density. Hill et al. [18] also considered a nonuniform segment distribution, although the authors propose only a numerical solution of the Brinkman equation. In this work [18], the double layer polarization was incorporated in the electrophoresis theory of soft particles as well. In distinction from [18], the analytical solution for the electrophoresis of soft particles was developed in [26,27] using the method of thin double layer polarization [31]. Solutions of the Poisson–Boltzmann equation for linear and exponential distributions of fixed charges are obtained in Ref. [14]. So far, the majority of the experimental data were obtained for polyelectrolyte layers grafted to flat surfaces [15,26], but also colloidal systems, e.g., liposome surface grafted with polymers [17], were studied. Surface conductivity measurements have been proven to be a versatile tool for the characterization of polymer layers grafted to flat surfaces [25,28]. The corresponding theory was recently developed by Dukhin et al. [28] and successfully applied for the characterization of Na-acrylate gels [13].

The increasing interest in soft surface electrokinetics (SSE) is motivated by the growing importance of soft surfaces in many

* Corresponding author. Fax: +49 351 4658 533.
E-mail address: zimmermn@ipfdd.de (R. Zimmermann).

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colloidal and biocolloidal systems, e.g., grafted polymers [37], adsorbed biomolecules or polyelectrolyte layers [38], and biological cells [39]. In addition, polymer coatings are used in widespread technological and medical applications like biosensors [40], protein-resistant surfaces [41], tissue engineering scaffolds [42], antifoaming coatings [43], microfluidic systems [44], liquid displays [45], and drug delivery [46]. Appropriate theoretical models are required for the consistent interpretation of experimental results to achieve a quantitative understanding of the electro-hydrodynamic interfacial properties of soft surfaces.

No essential difficulties arose in the modeling of the electrostatics at soft surfaces. The concept of Donnan potential has been proven very helpful for soft surface coatings whose thickness considerably exceeds the Debye length. Despite the inherent complexity of soft polymeric surface layers in terms of local segment distribution from bulk layer to outer electrolytic medium, simple models that consist in assimilating soft layers to polyelectrolyte layers (PL) have attracted much attention, essentially because they allow the evaluation of hydrodynamic flow field profiles under conditions of SSE. These models were mostly developed for charged and uncharged hydrogel layers with uniform distribution of polymer segments. This basically implies that the transition between the surface layer and the outer electrolyte solution is sharp, step-function like, and that the gel layer is defined by a constant density of polymer segments. Similarly, in the model developed by Debye and Bueche [47] for the Darcy law, polymer segments are considered as resistance centers distributed uniformly in the PL and exerting frictional force on the water flowing inside the polymer layer.

When reviewing the literature on SSE from initial work by Donath and Pastushenko [1] and Dukhin et al. [2] to most recent developments, it is striking to note that the authors have insufficiently underlined the inadequacy of the sole application of the Darcy law for consistent interpretation of SSE. The Darcy equation necessitates indeed an unusual boundary condition describing a jump in tangential velocity at the interface when used within the so-called hybrid zone that encompasses the interface between the porous medium and the liquid phase. The governing hydrodynamic equations of SSE are formulated for this hybrid zone, a term that is used exclusively in the context of hydrodynamics of porous media. Instead, more consistent theories for the hydrodynamics of porous particles [52,55] explain the mandatory requirement for adopting the Brinkman equation [48] rather than the Darcy equation.

In Ref. [52], the authors emit criticism with regard to the Saffman condition by correctly arguing that any appropriate model for hydrodynamics in the hybrid zone should avoid the necessity of introducing parameters of which determination can be carried out from experiments only. The Brinkman model fulfills this condition. Compared to Darcy's law, this equation has an additional second-order viscous term, very similar to that involved in the Stokes equation. Therefore, if the Brinkman equation, which reads as

$$\mu^1 \Delta \mathbf{u} - \frac{\mu}{K}\mathbf{u} - \mathrm{grad}\, p = 0, \tag{1.1}$$

is used instead of Darcy's law for modeling the flow in the interfacial region, no inconsistencies in shear stress are encountered at the interface [52]. The parameter μ^1 in Eq. (1.1) is the effective medium viscosity, μ the liquid viscosity, $\mathbf{u}$ the liquid velocity, p the pressure, and K the hydrodynamic permeability of the porous body.

Although the Brinkman equation has been proposed by several authors in the context of SSE [1–24], a proper physical analysis of its adequacy is, to the best of our knowledge, absent from electrokinetic literature. One reason may be that the Brinkman equation was initially derived [48] for the hydrodynamics of the so-called "hybrid systems" [49,50,52–56], consisting of a porous medium filled with liquid and adjacent clear liquid, and not within the field of electrokinetics. The liquid flow along the porous body is accompanied by motion of the liquid inside the pores, called "hydrodynamic penetration."

Due to such penetration of flow into the medium, a hydrodynamic boundary layer of thickness λ_o^{-1}, called penetration length, exists in the interfacial region. For the modeling of this boundary layer, the Brinkman equation may be applied, while at some distance from the porous medium–clear liquid interface that exceeds λ_o^{-1}, the Darcy equation is sufficient. Since this equation is of lower order than the Brinkman equation, it is impossible to match the tangential and normal components of the velocity $\mathbf{u}$ within the porous medium with those of the velocity $\mathbf{U}$ in the liquid phase. The same limitation exists for stresses at the interface. Instead, only the normal components (u_n, U_n) are equated, while the tangential velocities (u_t, U_t) are allowed to slip by an amount proportional to the tangential stress exerted by the external fluid on the interface [49,50]:

$$u_n = U_n, \quad z = 0, \tag{1.2}$$

$$U_t - u_t = \frac{K^{0.5}}{\alpha\mu}\frac{dU_t}{dz}, \quad z = 0, \tag{1.3}$$

where z is the distance to the porous medium–clear liquid interface (the position $z = 0$ stands for that of the interface), K the hydrodynamic permeability of the porous medium, α denotes a dimensionless constant, and μ is the viscosity of the liquid. The constant α characterizes the structure of the porous medium and can be determined by experimental means only.

The Saffman condition [50] (Eq. (1.3)) is quantitatively consistent with experimental data of Beavers and Joseph [49] collected for various planar permeable surfaces. Values in the range $0.25 < \alpha < 10$ are reported for several low-porosity consolidated porous media. To our knowledge, there is only one publication where the electroosmosis theory was developed using the Saffman condition [51] with a concomitant criticism of the Brinkman equation.

The solution of the Brinkman equation (1.1) enables one to obtain a simple expression for the hydrodynamic penetration length, also called softness parameter,

$$\lambda_o = \left(\frac{9\phi_o}{2a_s^2}\right)^{\frac{1}{2}}, \tag{1.4}$$

where ϕ_o is the volume fraction of the segments given by $\phi_o = 4\pi n_s a_s^3/3$, a_s the segment radius, and n_s the segment concentration.

In order to address the hydrodynamics of porous media [52–56], researchers generally resort to the Brinkman equation even though the possibility of discontinuity for the interfacial stress [49,50] has never been rejected completely yet.

The consistency of the Brinkman equation for modeling the hydrodynamics of porous media has been largely debated in hydrodynamic literature, whereas this problem has, to our knowledge, deserved too little attention within the field of SSE. Starting from the introduction of the Brinkman equation in SSE in [1] for polyelectrolyte layers and in [2] for uncharged layers, there was no discussion regarding its physical adequacy for permeable surface layers.

As the revision of the boundary conditions for the Brinkman equation, recently performed in the hydrodynamics of hybrid systems, is unknown, to our knowledge, in SSE, we devote the next section to this topic and show the necessity in the discussion of this topic in colloid science. In Section 3, we make a first step in this direction and support our discussion with recently obtained experimental data [57] that quantitatively agree with predictions issued from the Brinkman model. The simplification of the boundary conditions for the Brinkman equation in the case of diffuse soft surfaces is discussed in Section 4.