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AN EXACT FORMULA FOR THE CONTACT VALUE OF THE DENSITY PROFILE OF A SYSTEM OF CHARGED HARD SPHERES NEAR A CHARGED WALL

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ABSTRACT

An exact formula for the contact value of the density of a system of charged hard spheres near a charged hard wall is obtained by means of a general statistical mechanical argument. In addition, a formula for the contact value of the charge profile in the limit of large field is obtained. Comparison with the corresponding expressions in the Poisson-Boltzmann theory of Gouy and Chapman shows that these latter expressions become exact for large fields, independent of the density of the hard spheres.

INTRODUCTION

It is well-known that the contact value of the density, $\rho(x)$, of a fluid in contact with a flat hard wall at $x = 0$ is equal to the momentum transfer to the wall divided by kT. Hence the pressure p of the fluid is given by

$$p = kT\,\rho(0) \tag{1}$$

where T is the temperature of the fluid and k is Boltzmann's constant.

The extension of eqn. (1) to the case where the interaction of the fluid with the wall is not hard is used here to obtain an expression for $\rho(0)$ for charged hard spheres, in a medium whose dielectric constant is ϵ, in contact with a charged hard wall. This charged hard sphere/charged hard wall system is a simple but useful model of an electrolyte solution near an electrode. Our analysis shows

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that the Poisson-Boltzmann theory results for the contact values of the density and charge profiles are exact for high fields, independent of the density of the charged hard spheres (i.e., the electrolyte concentration).

BASIC EQUATION

To derive the extension of eqn. (1) we consider a fluid bounded by two semi-infinite smooth walls separated by a distance L. Let us obtain the force balance on a slab of fluid of thickness l adjacent to the wall at $x = -\sigma/2$. Provided that there is no longer range force acting on this slab from the right (this includes the wall at $x = L$ and any fluid layer near it) we have

$$p_{xx}(l) = -\int_0^l \frac{\partial U(x)}{\partial x} \rho(x)\,\mathrm{d}x \tag{2}$$

where $U(x)$ is the potential due to the wall at $x = -\sigma/2$ and $p_{xx}(l)$ is the x-x component of the stress tensor at $x = l$. If the integral on the right is independent of l as would certainly be the case when the range of U is less than l then letting $p_{xx}(l) = p$, the bulk pressure, and l and $L \to \infty$, we obtain

$$p = -\int_0^\infty \frac{\partial U(x)}{\partial x} \rho(x)\,\mathrm{d}x \tag{3}$$

We believe that, due to shielding, eqn. (3) (or its analogue eqn. 6) remains valid also for the charged fluid-charged wall system. It is the basic equation used in this paper.

If the wall is hard, it is convenient to write eqn. (3) in the form

$$p = kT \int_0^\infty R(x) \frac{\partial}{\partial x} \exp(-\beta U)\,\mathrm{d}x \tag{4}$$

where $R(x) = \rho(x)\exp(\beta U)$ is continuous and $\beta = 1/kT$. For a hard wall, the derivative in eqn. (4) can and should be interpreted as a delta function and, using $\rho(0) = R(0)$, eqn. (1) follows. Hence eqn. (3) is the desired extension of eqn. (1). If the wall is hard but also has an additional "soft" interaction with the system particles,

$$U(x) = \begin{cases} \infty & x < 0 \\ W(x) & x > 0 \end{cases} \tag{5}$$

then eqn. (3) becomes

$$p = kT\,\rho(0) - \int_0^\infty \frac{\partial W(x)}{\partial x} \rho(x)\,\mathrm{d}x \tag{6}$$

ELECTRIFIED INTERFACE

Consider a system of charged hard spheres near a charged wall at $x = -\sigma/2$. That is, the origin of the coordinate system is a plane through the centers of the spheres in contact with the wall. The dielectric constant of the medium is constant throughout the whole system. No solvent or image forces are considered. For simplicity, we assume that there are equal numbers of hard spheres of charge $\pm ze$. For this system, eqn. (6) becomes

$$p = kT \sum_i \rho_i(0) - \sum_i \int_0^\infty \frac{\partial W_i}{\partial x} \rho_i(x)\,\mathrm{d}x \tag{7}$$

If $\epsilon E/4\pi$ is the surface charge density on the wall at $x = -\sigma/2$ then $E/2$ is the unscreened electric field due to this wall and $\partial W_1/\partial x = zeE/2$ and $\partial W_2/\partial x = -zeE/2$. Hence

$$p = kT\,\rho(0) - \frac{E}{2} \int_0^\infty q(x)\,\mathrm{d}x \tag{8}$$

where $\rho(x) = \rho_1(x) + \rho_2(x)$ is the particle density and $q(x) = -ze[\rho_1(x) - \rho_2(x)]$ is the charge density. We note that $q(x) \to 0$ as $x \to \infty$ so that we need not worry about the upper limit in the integral or about the other wall even though $\partial W/\partial x$ is constant.

The integral of $q(x)$ must be equal in magnitude, but opposite in sign, to the charge on the wall (screening). Thus

$$\int_0^\infty q(x) = -\epsilon E/4\pi \tag{9}$$

Substitution of eqn. (9) into (8) yields

$$kT\,\rho(0) = p + \epsilon E^2/8\pi \tag{10}$$

Equation (10) has been obtained earlier by Henderson and Blum [1] by adding the Maxwell stress to eqn. (1).

There is no corresponding exact expression for $q(0)$. However, when E is large the hard spheres whose charge has the same sign as the charge on the wall will have zero density near the wall. Thus, for large E,

$$\frac{kT}{ze}|q(0)| \simeq \epsilon E^2/8\pi \tag{11}$$

It is instructive to compare eqns. (10) and (11) with the corresponding results in the Poisson-Boltzmann (PB) theory of Gouy [2] and Chapman [3]. In this theory

$$\rho(0) = \rho \cosh(\beta ze\phi_0) \tag{12}$$

$$\rho_1(0) - \rho_2(0) = \rho \sinh(\beta ze\phi_0) \tag{13}$$

Here ϕ_0 is the potential drop across the diffuse double layer, given by

$$\phi_0 = \frac{2}{\beta ze} \sinh^{-1}\left(\frac{\beta zeE}{2\kappa}\right) \tag{14}$$

where κ is the Debye screening parameter, given by $\kappa^2 = 4\pi\beta z^2e^2\rho/\epsilon$, and ρ is the density of the bulk hard sphere fluid. For comparison with eqns. (10) and (11)

TABLE 1

Values of $N_a\sigma^2$ for a charged hard sphere model of an electrolyte solution (z = 1, σ = 2.76 × 10^{-10} m, T = 298 K, ϵ = 78.4) near a charged wall with a surface density of 1.2 Cm^{-1} calculated from PB theory

Conc./M	ϕ_0(v)	$\rho(0)\,\sigma^3$	$N_a\sigma^2$
0.0001	0.43	5.31	0.47
1.0	0.16	5.33	0.48

it is convenient to eliminate ϕ_0 from eqns. (12) and (13). The result is

$$kT\,\rho(0) = kT\,p + \epsilon E^2/8\pi \tag{15}$$

$$\rho_1(0) - \rho_2(0) = \frac{\epsilon E}{4\pi z e}\,\kappa\left[1 + \left(\frac{\beta z e E}{2\kappa}\right)^2\right]^{1/2} \tag{16}$$

Thus, the PB result satisfies eqn. (10) but with p replaced by the ideal gas approximation, ρkT. At large E, the PB result satisfies eqn. (11).

When E = 0, the PB expression for $\rho(0)$ will be reliable only at very low densities or very low electrolyte concentrations where $p \simeq \rho kT$. However, at high field, the PB expressions for $\rho(0)$ and $q(0)$ will be exact, *independent* of the density of the charged hard spheres (i.e., the electrolyte concentration).

This latter point may not be generally known since conventional wisdom is that the PB theory fails as E is increased because unreasonably large values of $\rho(0)$ are obtained. In reality, for any density the PB values for $\rho(0)$ and $q(0)$ become more accurate as E is increased and ultimately become exact.

A large value of $\rho(0)$ does not mean that there are excessive numbers of spheres near the wall. The number of spheres per unit area near the wall N_a is given by the integral of $\rho(x)$:

$$N_a \simeq \int_0^{\sigma/2} \rho(x)\,\mathrm{d}x \tag{17}$$

where σ is the hard-sphere diameter. The upper limit in eqn. (17) is somewhat arbitrary. However, eqn. (17) is at least qualitatively correct. If the density profile falls off quickly enough, N_a will be reasonable even when $\rho(0)$ is large. Values of N_a, calculated from the PB $\rho(x)$, for a value of E, larger than is experimentally attainable, are listed in Table 1. Even though $\rho(0)$ is large, N_a is still less than half the density of a close-packed layer.

SUMMARY

We obtained an exact general expression for the contact value, $\rho(0)$, of the density profile of a fluid near a wall which was applied to a system of hard charged spheres near a charged hard wall. In addition, an exact result for the high field limit of the contact value, $q(0)$, of the charge profile was obtained. The corresponding PB theory results are similar to these exact results. At low fields the PB $\rho(0)$ is satisfactory only at very low concentrations. However, at high fields both the PB $\rho(0)$ and $q(0)$ are satisfactory at all concentrations.

At very large fields the PB theory gives unphysically large values for N_a even though the PB $\rho(0)$ is exact. Evidently at very large fields the PB $\rho(x)$ does not fall off fast enough. However, the fields at which this occurs are beyond the ex experimentally accessible region. For experimentally attainable values of E, the calculations of Henderson and Blum [1,4] indicate that the PB $\rho(x)$ actually falls off too fast. Hence, the PB values for N_a may be too small for values of E which are of experimental interest. In any case by itself $\rho(0)$ is not relevant in accessing the accuracy of the PB theory.

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