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On the contact conditions for the density and charge profiles in the theory of electrical double layer: from planar to spherical and cylindrical geometry

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Abstract

In this paper, from the Born-Green-Yvon equations of the liquid-state theory, we formulate two equivalent approaches for the calculation of the charge and density profiles of ionic fluids near charged nonplanar surfaces. The contact theorems for the density and charge profiles are formulated by ~~the~~ direct integration of this system of equations. Both theorems have nonlocal character. It is shown that the contact value of the density profile for noncharged surfaces is characterized by the bulk pressure and the surface tension. The obtained results are applied to spherical and ~~and~~ cylindrical surfaces. It is shown that the contact theorem for the density profile coincides with the recent results obtained by W. Silvester-Alcantara, D. Henderson and L.B. Bhuiyan (*Mol. Phys.*, 113, 3403, 2015)

The contact theorems are one of the few exact results in the theory of the electrical double layer. They establish the exact expressions for the contact values of the density and of the charge profiles in the interface between an electrolyte and a charged electrode. The first contact theorem was formulated more than fourty years ago by D. Henderson, L. Blum and J.L. Lebowitz [1, 2] for the density profile in a planar electrical double layer formed by a primitive model of electrolyte and a uniformly charged planar hard electrode. According to their results, the contact value of the density profile is given by the sum of the bulk osmotic pressure P of the electrolyte and the Maxwell stress tensor contribution

$$\rho^{ct} = \sum_{\alpha} \rho_{\alpha} \left(\frac{d_{\alpha}}{2} \right) = \beta P + \beta \frac{\varepsilon E^2}{8\pi} \tag{1}$$

where $\rho_{\alpha}(z)$ are the density distribution functions for ions of type α at a normal distance z from the wall, d_{α} are the ion diameters, $\beta = 1/(k_B T)$ with k_B the Boltzmann constant, T the absolute temperature, ε is the dielectric constant of the solvent, where E is the electric field and $\dfrac{\varepsilon E}{4\pi} = q_s$ is the surface charge density per unit area on the wall.

We note that in order to avoid the problem of electrostatic image effects between the electrode and the electrolyte, identical dielectric constant ε in the electrode and in the electrolyte was assumed. A little later, it was shown in [3] that a formal derivation of the contact theorem for the density profile can be obtained by the direct integration of the Born-Yvon-Green (BGY) [4, 5] equation between singlet and pair distribution functions for electrolytes in the presence of a charged electrode. In our previous papers [6–8], in the framework, of a similar approach based on the integration of the BGY equation, the contact theorem for the charge profile was formulated for the planar electrical double layer. In contrast to the contact theorem for the density profile, the contact value of the charge profile has a non local character and can be presented in the following form

$$q^{ct} = \sum_{\alpha} e_{\alpha} \rho_{\alpha} \left(\frac{d_{\alpha}}{2} \right) = \beta \sum_{\alpha} e_{\alpha}^2 \int_{d_{\alpha}/2}^{\infty} \rho_{\alpha}(z) \frac{\partial \psi(z)}{\partial z} dz + \beta \sum_{\alpha} e_{\alpha} P_{\alpha} \tag{2}$$

where e_{α} is the charge of the ion of type α, $\psi(z)$ is the electrical potential defined as

$$\psi(z) = -\frac{4\pi}{\varepsilon} \int_{z}^{\infty} q(z_1)(z_1 - z) dz_1 \tag{3}$$

where

$$q(z) = \sum_{\alpha} e_{\alpha} \rho_{\alpha}(z) \tag{4}$$

is the charge profile, P_α is the bulk partial pressure for the ions of type α.

For the symmetrical electrolyte with $d_+ = d_- = d$ and $e_+ = -e_- = e$, the first term in Eq. (2) equals zero due to the electroneutrality condition. As a result, the contact theorem Eq. (2) reduces to the more simple form

$$q\left(\frac{d}{2}\right) = \beta e^2 \int_{d/2}^{\infty} \rho(z) \frac{\partial \psi(z)}{\partial z} dz \tag{5}$$

where $\rho(z)$ is the density profile.

From the analysis of the effects of the ionic size on the properties of the diffuse double layer, using experimental and computer simulations results for symmetrical electrolytes for small charge at the wall, the semi empirical local expression for the contact value $q(d/2)$, the so called Fawcett-Henderson-Boda conjecture [9, 10] has been proposed. According to this expression

$$q\left(\frac{d}{2}\right) = \beta e^2 \frac{1}{\chi} PE \tag{6}$$

where χ is the inverse Debye length.

The connection between expressions (5) and (6) was the subject of discussions in [11, 12]. In particular, it was shown that for a symmetrical electrolyte at small surface charge both expressions give similar results which are in good agreement with computer simulation data [11]. In [12], it has been established that expression (6) can be obtained from Eq. (5) as a result of two approximations. The first approximation is connected with the replacement in the integral in Eq. (5) of the density profile $\rho(z)$ by its contact value Eq. (1). As a result

$$q^{ct}\left(\frac{d}{2}\right) = \beta e^2 \rho^{ct}\left(\frac{d}{2}\right) \psi\left(\frac{d}{2}\right) \tag{7}$$

where $\psi(d/2)$ is the potential at the surface. The second approximation is connected with the use of the linear Gouy–Chapman theory [13, 14] for the description of $\psi(d/2)$.

The generalization of the contact theorems for charged non planar surfaces is one of the challenges in the theory of the electrical double layer. In particular, after the formulation of the contact theorem for the density profile in the case of the planar double layer, relation (1), significant efforts have been focused on the generalization of this contact theorem for the double layers with spherical, cylindrical and more complex non planar geometries. We note that according to the Henderson-Abraham-Barker approach [15] the surface in the fluid can be considered as an additional particle in the infinite radius and infinite dilution limit. As

a consequence, the density profile can be obtained as the pair distribution function between this particle representing the wall in the limit and a fluid particle. It was also shown in [16, 17] that in order to take into account the surface curvature effect, a surface term should be added to the pressure in expression (1). This means that the excess chemical potential for the particle created can be presented in the form

$$\mu_i^{ex} = P\mathcal{V}_i + \gamma_i \left(\frac{d}{2} + R_i\right) S_i \tag{8}$$

where $\gamma_i(r)$ is the surface tension defined as the surface part of the chemical potential, $\mathcal{V}_i$ is the volume accessible to the system, S_i is the surface area of the curved wall. The subscript $i = s$ or c denotes the spherical or cylindrical wall with the radius $R_i = R_s$ or $R_i = R_c$ respectively.

We note that an expression similar to (8) was also used in the scaled particle theory (SPT) [18–20] for the description of the chemical potential of the scaled particle in the hard sphere fluid. As for the SPT, $\gamma_i(d/2 + R_i)$ can be expanded around $(d/2)/(d/2 + R_i)$. In a similar way, in the case of the hard sphere fluid near a spherical surface, Bryk et al. [21] obtained the following expression for the contact value of the density profile near a non charged wall ($E = 0$)

$$\begin{aligned} \rho_s^{E=0}\left(\frac{d}{2} + R_s\right) &= \rho_s^{HS}\left(\frac{d}{2} + R_s\right) \\ &= \beta P^{HS} - \frac{9\eta^2}{4\pi(1-\eta)^3(d/2)^3}\left\{(1+\eta)\frac{d/2}{R_s + d/2} - \eta\frac{(d/2)^2}{(R_s + d/2)^2}\right\} \end{aligned} \tag{9}$$

where is ρ_s is the total density distribution in the case of the spherical surface, where $\eta = \frac{1}{6}\pi\rho d^3$ is the packing fraction of hard sphere fluid. As usual, in the SPT approach [18–20], the hard sphere pressure is given by the Percus-Yevick compressibility.

Comparably to [21], the expression for the contact value of the density profile for the hard sphere fluid near a non charged cylindrical wall was obtained in the following form

$$\begin{aligned} \rho_c^{E=0}\left(\frac{d}{2} + R_c\right) &= \rho_c^{HS}\left(\frac{d}{2} + R_c\right) \\ &= \beta P^{HS} - \frac{9\eta^2}{4\pi(1-\eta)^3(d/2)^3}\left\{\frac{1}{2}(1+\eta)\frac{d/2}{R_c + d/2}\right\} \end{aligned} \tag{10}$$

where is ρ_c is the total density distribution in the case of the cylindrical surface,

We should note that in the case of ionic fluids near a non charged wall, the pressure P and the surface tension $\gamma_i(r)$ will include also the corresponding Coulombic contributions.

The second aspect of the generalization of the contact theorem eq. (8) for the non planar case is associated to detailing the second term in the expression (8). So far, the activity in such direction was focused on the generalization of the Maxwell tensor for the double layer with charged spherical and cylindrical surfaces, charged membranes and charged surfaces with more complex geometries [22–26]. However, in these publications, the ionic sizes were not taken into account neither explicitly nor implicitly in the calculation of the Maxwell stress tensor. It was shown that for electrolytes with point ions, the Maxwell stress tensor contribution to the contact values of the density profile for walls with different geometries has a similar form as in the case of the planar wall.

The exact formulation of the contact theorem for the density profile for electric double layers in spherical and cylindrical geometries was obtained by Silvestre-Alcantara, Henderson and Bhuiyan [27]. According to their results, the contact theorem for the density profile for the surface of nonplanar geometry can be presented in the form

$$\rho_i\left(R_i+\frac{d}{2}\right)=\rho_i^{E=0}\left(R_i+\frac{d}{2}\right)-\beta E\int_{R_i+d/2}^{\infty}q(r)dr \tag{11}$$

where $q(r)=\sum_\alpha e_\alpha\rho_\alpha(r)$ is the charge profile, $\rho_i^{E=0}\left(R_i+d/2\right)$ is the contact value of the density profile near the non charged surface. The hard sphere contribution to the contact value of the density profile is given by expressions (9) and (10) for spherical and cylindrical surfaces respectively. As we can see the second term in (11) has a nonlocal character and is more universal than the first term.

In [27], it was shown that in the limit $R_i\to\infty$, the contact theorem (11) reduces to

$$\rho\left(\frac{d}{2}\right)=\beta P+\frac{\beta E^2\varepsilon}{4\pi} \tag{12}$$

which differs from ~~the~~ expression (1) by the second term which has a missing factor 1/2 compared to expression (1). The authors explained this difference by the fact that in the planar case one must assume a second parallel electrode of opposite charge at infinite separation from the first electrode.

In this note, we will show that the contact theorem for the density profile in the form (11) can be obtained from the BGY equation. Starting from the BGY equation, we will also obtain the exact relation for the charge profile. For convenience, we present the BGY

relation in the following form

$$\nabla_1\rho_\alpha(1) = -\beta\nabla_1 V_\alpha(1)\rho_\alpha(1) - \beta\rho_\alpha(1)\sum_\gamma \int \rho_\gamma(2) g_{\alpha\gamma}(12)\nabla_1 u_{\alpha\gamma}(r_{12})d2 \tag{13}$$

where 1 and 2 stand for the position of the corresponding particles, $V_\alpha(1) = e_\alpha V_\alpha^{coul}(1) + V_\alpha^{sh}(1)$ is the external potential, $u_{\alpha\gamma}(r_{12}) = e_\alpha e_\gamma u^{coul}(r_{12}) + u_{\alpha\gamma}^{sh}(r_{12})$ is the interaction pair potential. The subscripts α and γ stand for ions having charges e_α and e_γ, the superscripts *coul* and *sh* indicate the electrostatic and non electrostatic short-range contributions. $\rho_\alpha(1)$ is the density distribution of the particle of type α at point 1, $g_{\alpha\gamma}(12)$ is the pair distribution function between particles of type α and γ.

We consider here two equivalent approaches, where in both cases, we start from the BGY equation. In the first approach, we start from the BGY equation in the form

$$\nabla_1\rho_\alpha(1) = -\beta e_\alpha\rho_\alpha(1)\nabla_1 V^{coul}(1) - \beta\rho_\alpha(1)\nabla_1 V_\alpha^{sh}(1) - \beta\rho_\alpha(1)\nabla_1 W_\alpha(1) \tag{14}$$

where

$$\nabla_1 W_\alpha(1) = \sum_\gamma \int d2\rho_\gamma(2) g_{\alpha\gamma}(12)\left[e_\alpha e_\gamma \nabla_1 u^{coul}(r_{12}) + \nabla_1 u_{\alpha\gamma}^{sh}(r_{12})\right] \tag{15}$$

corresponds to the average force on a particle of type α at point 1.

In the second approach, in a similar way as in [3, 6], we introduce the standard mean electrostatic potential $\psi(1)$ defined by

$$\nabla_1\psi(1) = \nabla_1 V^{coul}(1) + \int \sum_\gamma e_\gamma\rho_\gamma(2)\nabla_1 u^{coul}(12)d2 \tag{16}$$

In this case, as in [6], we can rewrite the BGY equation in the following form

$$\nabla_1\rho_\alpha(1) = -\beta e_\alpha\rho_\alpha(1)\nabla_1\psi(1) - \beta\rho_\alpha(1)\nabla_1 V_\alpha^{sh}(1) - \beta\rho_\alpha(1)\nabla_1 W_\alpha(1) \tag{17}$$

where

$$\nabla_1 W_\alpha(1) = \sum_\gamma \int d2\rho_\gamma(2)\left[e_\alpha e_\gamma h_{\alpha\gamma}(12)\nabla_1 u^{coul}(r_{12}) + g_{\alpha\gamma}(12)\nabla_1 u_{\alpha\gamma}^{sh}(r_{12})\right] \tag{18}$$

corresponds to the average force on a particle of type α at point 1 with the exception of the contribution from the mean electrical potential and $h_{\alpha\gamma}(12) = g_{\alpha\gamma}(12) - 1$ is the pair correlation function.

Now we will formulate the equations for the density and the charge profiles

$$\rho(1) = \sum_{\alpha} \rho_{\alpha}(1) \quad \text{and} \quad q(1) = \sum_{\alpha} e_{\alpha}\rho_{\alpha}(1). \tag{19}$$

To continue, we can use the BGY equation in the standard form (14) which includes the Coulomb interaction between wall and ions, $V^{coul}(1)$, or in the form (17) which includes the mean electrostatic potential $\psi(1)$. We note that in both cases, we can omit the term related to the external potential $V_{\alpha}^{sh}(1)$ which we consider as equivalent to a hard wall. As a result from equation (14), we can formulate the following system of equations for the density and charge profiles

$$\nabla_1\rho_{\alpha}(1) = -\beta\nabla_1 V^{coul}(1)q(1) - \beta\sum_{\alpha}\rho_{\alpha}(1)\nabla_1 W_{\alpha}(1) \tag{20}$$

$$\nabla_1 q(1) = -\beta\nabla_1 V^{coul}(1)\hat{\rho}(1) - \beta\sum_{\alpha} e_{\alpha}\rho_{\alpha}(1)\nabla_1 W_{\alpha}(1) \tag{21}$$

where

$$\hat{\rho}(1) = \sum_{\alpha} e_{\alpha}^2\rho_{\alpha}(1) \tag{22}$$

After integration of relations (20) and (21), we obtain the contact theorem for the density and charge profiles generalizing the corresponding relations we obtained in [6] for the planar case. We note that the first term in relations (20) and (21), the Coulomb potential reads $V_s^{coul}(1) \propto \frac{1}{\varepsilon r}Q_s$ for spherical surfaces, and $V_c^{coul}(1) \propto -\frac{1}{\varepsilon}Q_c\ln(r/r_c)$ for cylindrical surfaces, where Q_s and Q_c are the charge of the corresponding surfaces. Since $\nabla_1 V_s^{coul}(1) \propto -\frac{1}{\varepsilon r^2}Q_s$ and $\nabla_1 V_c^{coul}(1) \propto -\frac{1}{\varepsilon r}Q_c$ after integration of equations (20) and (21), we can present the generalization of the contact theorems for the density and charge profiles near a nonplanar wall. For simplicity, we assume $d_+ = d_- = d$ and we obtain the contact theorems in the following form

$$\rho_i\left(R_i + \frac{d}{2}\right) = \rho_{i,\alpha}^{E=0}\left(R_i + \frac{d}{2}\right) - \beta E\sum_{\alpha}\int_{R_i+d/2}^{\infty} q_i(r)dr \tag{23}$$

$$q_i\left(R_i + \frac{d}{2}\right) = \sum_{\alpha} e_{\alpha}\rho_{i,\alpha}^{E=0}\left(R_i + \frac{d}{2}\right) - \beta E\sum_{\alpha}\int_{R_i+d/2}^{\infty}\hat{\rho}_{\alpha}(r)dr \tag{24}$$

where $\rho_{i,\alpha}^{E=0}(R_i + d_{\alpha}/2)$ is the contact value of the density profile for the noncharged surface of type i (=c or s) and particle of type α, $\rho_{i,\alpha}^{E=0}(R_i + d_{\alpha}/2)$ is the partial contact value of the density profile for the ion of type α near non charged surface type i.

We note that the contact theorem (23) for the density profile is identical to the relation (11) obtained by Silvester-Alcantara, Henderson and Bhuiyan [27].

Starting from the BGY equation in the form (17), which includes the mean electrostatic potential $\psi(1)$ instead of the Coulombic potential $V^{coul}(1)$, we can write the equations (20) and (21) for the density and charge profiles in the following equivalent form

$$\nabla_1 \rho_\alpha(1) \;=\; -\beta q(1) \nabla_1 \psi(1) - \beta \sum_\alpha \rho_\alpha(1) \nabla_1 W_\alpha(1) \tag{25}$$

$$\nabla_1 q(1) \;=\; -\beta \hat{\rho}(1) \nabla_1 \psi(1) - \beta \sum_\alpha e_\alpha \rho_\alpha(1) \nabla_1 W_\alpha(1) \tag{26}$$

Now after integration of these equations, we can present the contact theorems for the density and charge profiles near a nonplanar wall in in the following form

$$\rho_i\left(R_i + \frac{d}{2}\right) \;=\; \rho_i^{E=0}\left(R_i + \frac{d}{2}\right) - \beta \int_{R_i+d/2}^{\infty} q_i(r) \frac{\partial \psi(r)}{\partial r} r^{\delta_i} dr \tag{27}$$

$$q_i\left(R_i + \frac{d}{2}\right) \;=\; \sum_\alpha e_\alpha \rho_{i,\alpha}^{E=0}\left(R_i + \frac{d}{2}\right) - \beta \int_{R_i+d/2}^{\infty} \hat{\rho}(r) \frac{\partial \psi(r)}{\partial r} r^{\delta_i} dr \tag{28}$$

where $\delta_i = 2$ for spherical wall and $\delta_i = 1$ for cylindrical wall.

For charge symmetric electrolytes $e_+ = -e_- = e$ and the first term in the contact theorem for the charge profile in the form (24) or (28) vanishes. Moreover $\hat{\rho}(1)$ is proportional to the density profile

$$\hat{\rho}(1) = e^2 \rho(1) \tag{29}$$

and we have a simple nonlocal relation between the contact value of the charge profile and the density profile

$$q_i\left(R_i + \frac{d}{2}\right) \;=\; -\;\beta e^2 E \int_{R_i+d/2}^{\infty} \rho(r)\, dr \tag{30}$$

or in the form

$$q_i\left(R_i + \frac{d}{2}\right) \;=\; -\;\beta e^2 \int_{R_i+d/2}^{\infty} \rho(r) \frac{\partial \psi}{\partial r}\, r^{\delta_i}\, dr \tag{31}$$

In the limit $R_s \to \infty$ for the spherical surface or in the limit $R_c \to \infty$ for the cylindrical surface, the contact theorems for the charge and the density profiles reduce to the planar case. In particular in [27], it was shown that due to the local electroneutrality condition

$$-\int_{d/2}^{\infty} q(z) dz = \frac{\varepsilon E}{4\pi}, \tag{32}$$

the last term in expression (23) for the contact value of the density profile can be presented, in this limit, in the following form

$$-\beta E \int_{R_i+d/2}^{\infty} q(r)dr \xrightarrow[R_i\to\infty]{} -\beta E \int_{d/2}^{\infty} q(z)dz = \beta\frac{\varepsilon E^2}{4\pi} \tag{33}$$

which differs from the corresponding term in relation (1) by a factor 1/2.

In [27], it was noted that the electroneutrality condition for the spherical and the cylindrical double layers has respectively the following forms

$$-\int_{R_s+d/2}^{\infty} q_s(r)r^2dr = \frac{R_s^2\varepsilon E^2}{4\pi}, \tag{34}$$

$$-\int_{R_c+d/2}^{\infty} q_c(r)rdr = \frac{R_c\varepsilon E^2}{4\pi}. \tag{35}$$

Due to this, for the nonplanar case, the contact theorem for the density profile cannot be presented in simple local forms as for the planar case.

We should note that the last term in the contact theorem in the form (27) due to the Poisson equation

$$\nabla_1^2\psi(1) = -\frac{4\pi}{\varepsilon}q(1) \tag{36}$$

can be presented also in the form

$$-\beta\int_{R_i+d/2}^{\infty} q_i(r)\frac{\partial\psi}{\partial r}r^{\delta_i}dr = \beta\frac{\varepsilon}{4\pi}\int_{R_i+d/2}^{\infty}\nabla_1^2\psi_i(1)\nabla_1\psi_i(1)r^{\delta_i}dr \tag{37}$$

Since

$$\nabla^2\psi_i(1) = \frac{\partial^2\psi(1)}{\partial r^2} + \frac{\delta_i}{r}\frac{\partial\psi_i(1)}{\partial r} \tag{38}$$

we see that the integral in (37) cannot give the simple Maxwell stress term as in the case of the planar wall [6].

Thus in this paper starting from the BGY equation between the singlet and pair distribution functions of ionic fluids near a noncharged planar surface, we formulated two equivalent approaches to calculate the charge and the density ionic profiles. The first one includes the direct Coulomb interaction between ions and surface. In the second approach, this direct ion-surface interaction is transformed through the Poisson equation into the mean electrical potential. The contact theorems for the density and charge profiles are then formulated

for nonplanar surfaces by direct integration of this system of equations. The results are presented then applied to spherical and cylindrical surfaces. Both theorems have nonlocal character. It is shown that the contact value of the density profile for noncharged surfaces is characterized by bulk pressure and surface tension. The expressions of the contact theorem for the density profile are identical to the result recently formulated by Silvestre-Alcantara, Henderson and Bhuiyan [27]. By using our previous result for the contact theorems for anisotropic fluids near a hard planar wall [28], we can also generalize the obtained results for the orientationally ordered charged dispersions case.

[29]

Acknowledgments

M. Holovko and D. di Caprio, acknowledge funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement N ° 734276. V. Vlachy acknowledges a support of the Slovenian Research Agency fund (ARRS) through project J1-1708.

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