



**HAL**  
open science

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

Myroslav Holovko, Vojko Vlachy, Dung Di Caprio

## ► To cite this version:

Myroslav Holovko, Vojko Vlachy, Dung Di Caprio. On the contact conditions for the density and charge profiles in the theory of electrical double layer: From planar to spherical and cylindrical geometry. *Journal of Molecular Liquids*, 2023, 371, pp.121040. 10.1016/j.molliq.2022.121040 . hal-04281972

**HAL Id: hal-04281972**

**<https://hal.science/hal-04281972>**

Submitted on 13 Nov 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Holovko Vlachy di Caprio

2

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

6

M. Holovko

7

*Institute for Condensed Matter Physics, National Academy of Sciences*

8

*1 Svientsitskii Str., 79011 Lviv, Ukraine*

9

V. Vlachy

10

*Faculty of Chemistry and Chemical Technology, University of Ljubljana,*

11

*Vecna pot 113, SI-1000 Ljubljana, Slovenia*

12

D. di Caprio

13

*Chimie ParisTech, Institut de Recherche de Chimie Paris (IRCP),*

14

*Université PSL, CNRS, Paris, France*

## 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 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)

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

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

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

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

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

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

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

38 where

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

39 is the charge profile,  $P_\alpha$  is the bulk partial pressure for the ions of type  $\alpha$ .

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

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

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

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

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

49 where  $\chi$  is the inverse Debye length.

50 The connection between expressions (5) and (6) was the subject of discussions in [11, 12].  
 51 In particular, it was shown that for a symmetrical electrolyte at small surface charge both  
 52 expressions give similar results which are in good agreement with computer simulation data  
 53 [11]. In [12], it has been established that expression (6) can be obtained from Eq. (5) as a  
 54 result of two approximations. The first approximation is connected with the replacement in  
 55 the integral in Eq. (5) of the density profile  $\rho(z)$  by its contact value Eq. (1). As a result

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

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

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

65 a consequence, the density profile can be obtained as the pair distribution function between  
66 this particle representing the wall in the limit and a fluid particle. It was also shown in  
67 [16, 17] that in order to take into account the surface curvature effect, a surface term should  
68 be added to the pressure in expression (1). This means that the excess chemical potential  
69 for the particle created can be presented in the form

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

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

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

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

80 where is  $\rho_s$  is the total density distribution in the case of the spherical surface, where  
81  $\eta = \frac{1}{6}\pi\rho d^3$  is the packing fraction of hard sphere fluid. As usual, in the SPT approach  
82 [18–20], the hard sphere pressure is given by the Percus-Yevick compressibility.

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

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

85 where is  $\rho_c$  is the total density distribution in the case of the cylindrical surface,

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

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

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

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

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

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

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

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

111

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

115 relation in the following form

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

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

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

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

124 where

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

125 corresponds to the average force on a particle of type  $\alpha$  at point 1.

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

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

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

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

129 where

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

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

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

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

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

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

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

140 where

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

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

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

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

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



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

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

$$\nabla_1 \rho_\alpha(1) = -\beta q(1) \nabla_1 \psi(1) - \beta \sum_\alpha \rho_\alpha(1) \nabla_1 W_\alpha(1) \quad (25)$$

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

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

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

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

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

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

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

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

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

166 or in the form

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

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

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

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

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

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

173 In [27], it was noted that the electroneutrality condition for the spherical and the cylin-  
 174 drical double layers has respectively the following forms

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

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

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

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

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

179 can be presented also in the form

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

180 Since

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

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

183

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

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

198 [29]

### 199 **Acknowledgments**

200 M. Holovko and D. di Caprio, acknowledge funding from the European Union's Horizon  
201 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement  
202 N ° 734276. V. Vlachy acknowledges a support of the Slovenian Research Agency fund  
203 (ARRS) through project J1-1708.

- 
- 204 [1] D. Henderson and L. Blum. Some exact results and the application of the mean spherical  
205 approximation to charged hard spheres near a charged hard wall. *J. Chem. Phys.*, 69:5441–  
206 5449, 1978.
- 207 [2] D. Henderson, L. Blum, and J.L. Lebowitz. An exact formula for the contact value of the  
208 density profile of a system of charged hard spheres near a charged wall. *J. Electroanal. Chem.*,  
209 102:315–319, 1979.
- 210 [3] S.L. Carnie and D.Y.C. Chan. The statistical mechanics of the electrical double layer: Stress  
211 tensor and contact conditions. *J. Chem. Phys.*, 74:1293–1297, 1981.
- 212 [4] J. Yvon. *La théorie statistique des fluides et l'équation d'état*. Actualités scientifiques et  
213 industrielles : hydrodynamique, acoustique: Théories mécaniques. Hermann & cie, 1935.
- 214 [5] M. Born and H.S. Green. *A General Kinetic Theory of Liquids*. University Press, Cambridge,  
215 UK, 1949.

- 216 [6] M. Holovko, J.P. Badiali, and D. di Caprio. Contact conditions for the charge in the theory  
217 of the electrical double layer. J. Chem. Phys., 123:234705–1 – 234705–5, 2005.
- 218 [7] M. Holovko, J.P. Badiali, and D. di Caprio. New results from the contact theorem for the  
219 charge profile for symmetric electrolytes. J. Chem. Phys., 127:014106–1 – 014106–3, 2007.
- 220 [8] M. Holovko and D. di Caprio. On the contact condition for the charge profile in the theory  
221 of the electrical double layer for non symmetrical electrolytes. J. Chem. Phys., 128:174702–1  
222 – 174702–5, 2008.
- 223 [9] W. R. Fawcett and D. J. Henderson. A simple model for the diffuse double layer based on a  
224 generalized mean spherical approximation. J. Phys. Chem. B, 104(29):6837–6842, 2000.
- 225 [10] D. Henderson and D. Boda. On a conjecture of Fawcett. J. Electroanal. Chem., 582:16, 2005.
- 226 [11] L. B. Bhuiyan and D. Henderson. Comment on “Contact conditions for the charge in the  
227 theory of the electrical double layer” [J. Chem. Phys. 123, 234705 (2005)]. J. Chem. Phys.,  
228 128(11):117101, 2008.
- 229 [12] M. Holovko, J. P. Badiali, and D. di Caprio. Response to “Comment on ‘Contact conditions  
230 for the charge in the theory of the electrical double layer’ ” [J. Chem. Phys. 128, 117101  
231 (2008)]. J. Chem. Phys., 128(11):117102–1 – 117102–2, 2008.
- 232 [13] G. Gouy. Sur la constitution de la charge électrique à la surface d’un électrolyte. J. Phys.,  
233 9:457, 1910.
- 234 [14] D.L. Chapman. A contribution to the theory of electrocapillarity. Phil. Mag., 25:475, 1913.
- 235 [15] D. Henderson, F. F. Abraham, and J. A. Barker. The Ornstein-Zernike equation for a fluid  
236 in contact with a surface. Mol. Phys., 31(4):1291–1295, 1976.
- 237 [16] J.R. Henderson. Statistical mechanics of fluids at spherical structureless walls. Mol. Phys.,  
238 50(4):741–761, 1983.
- 239 [17] J. R. Henderson and J. S. Rowlinson. Statistical mechanics of fluid interfaces in cylindrical  
240 symmetry. J. Chem. Phys., 88(26):6484–6487, 1984.
- 241 [18] H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz. Aspects of the statistical thermody-  
242 namics of real fluids. J. Chem. Phys., 32(1):119–124, 1960.
- 243 [19] H. Reiss and D. M. Tully-Smith. Further development of scaled particle theory for rigid  
244 spheres: Application of the statistical thermodynamics of curved surfaces. J. Chem. Phys.,  
245 55(4):1674–1689, 1971.

- 246 [20] M. Holovko, T. Patsahan, and W. Dong. Fluids in random porous media: Scaled particle  
247 theory. Pure Appl. Chem., 85(1):115–133, 2012.
- 248 [21] P. Bryk, R. Roth, K. R. Mecke, and S. Dietrich. Hard-sphere fluids in contact with curved  
249 substrates. Phys. Rev. E, 68:031602–1 – 031602–8, Sep 2003.
- 250 [22] V. Vlachy and D. Bratko. An alternative approach to the osmotic coefficient of polyelectrolyte  
251 solutions. J. Chem. Phys., 75(9):4612–4614, 1981.
- 252 [23] V. Vlachy. On the virial equation for the osmotic pressure of linear polyelectrolytes. J. Chem.  
253 Phys., 77(11):5823–5825, 1982.
- 254 [24] H. Wennerström, B. Jönsson, and P. Linse. The cell model for polyelectrolyte systems. ex-  
255 act statistical mechanical relations, Monte Carlo simulations, and the Poisson–Boltzmann  
256 approximation. J. Chem. Phys., 76(9):4665–4670, 1982.
- 257 [25] E. Trizac and J.-P. Hansen. Wigner-Seitz model of charged lamellar colloidal dispersions.  
258 Phys. Rev. E, 56:3137–3149, Sep 1997.
- 259 [26] J. P. Mallarino, G. Téllez, and E. Trizac. The contact theorem for charged fluids: from planar  
260 to curved geometries. Mol. Phys., 113(17-18):2409–2427, 2015.
- 261 [27] W. Silvestre-Alcantara, D. Henderson, and L. B. Bhuiyan. Contact condition for the density  
262 profiles in spherical and cylindrical double layers. Mol. Phys., 113(22):3403–3405, 2015.
- 263 [28] M. Holovko and D. di Caprio. Contact theorems for anisotropic fluids near a hard wall.  
264 J. Chem. Phys., 142(1):014705, 2015.
- 265 [29] ©2022. Licensed under the Creative Commons CC-BY-NC-ND 4.0 license [https://](https://creativecommons.org/licenses/by-nc-nd/4.0/)  
266 [creativecommons.org/licenses/by-nc-nd/4.0/](https://creativecommons.org/licenses/by-nc-nd/4.0/).