Charge Inversion in Spherical Colloids with Salt, Cationic and Anionic Surfactants

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Abstract

Solutions of spherical colloids with cationic surfactant, anionic surfactant, and monovalent salt, are studied in the framework of Debye-Hückel and Bjerrum theories of simple electrolytes. At equilibrium we have the formation of complexes of one colloid molecule and associated ions and cationic surfactants. The interactions in the process are electrostatic between charged particles and hydrophobic between surfactants. Besides complexes there is the formation of mixed micelles of cationic and anionic surfactants in solution. Since the micelles may have a net charge, association of ions at micelles can also occur. At colloids the association of surfactants can lead to charge inversion of complexes, due to hydrophobic interaction between associated cationic surfactants. All charged species are monovalent.

Keywords: Thermodynamics and statistical mechanics, Thermodynamic functions and equations of state, Structure of associated liquids: electrolytes, molten salts, etc.

1 Introduction

Charged systems are extremely hard to understand, mainly due to the long ranged Coulomb interaction, although important advances have been made in the last decades [1]-[16]. The theory of Debye and Hückel on dilute electrolyte solutions has been a major advance in the study of these systems [17]-[23]. The formation of dipoles in solution has been included by Bjerrum [24], making another important progress. The development of integral equations and Monte Carlo simulations have also contributed to the understanding of the problem [25]-[31]. The theoretical coexistence curve [22, 23] in closest

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agreement with Monte Carlo simulations is based on the fundamental ideas of Debye, Hückel and Bjerrum. The simplicity of Debye-Hückel-Bjerrum (DHBj) theory allows its application to other charged systems [1]-[2].

In this work we present a simple description of spherical colloids with salt and surfactants. The approach is very similar to that in [32, 33], but we have another component here, the surfactants in solution. We have then the hydrophobic attraction between chains in the association processes that leads to complex formation, beyond the Coulomb interaction. The electrostatic interaction between colloids and the ions and surfactants in solution is evaluated following Debye-Hückel theory. The polyion-polyion interaction is considered in a way similar to that in [33, 34] for linear micelles (see also [35]). The interaction between infinitesimal elements of polyions is assumed to be of Yukawa form, or Debye-Hückel, and then we integrate over the polyions. Another important feature to be considered is the formation of micelles in solution, since surfactants associate among themselves, besides complex formation with the colloids. We follow the same procedure we adopted in [36], where we studied linear polyelectrolytes with salt and cationic and anionic surfactants, leading to formation of polyelectrolyte complexes and mixed micelles.

The Helmholtz free energy is based on Debye-Hückel theory, and the equilibrium configuration is found through the usual minimization process, where the complex distribution is found. In this process we also find the number density and charge of micelles. An important result is that for some values of the parameters we find charge inversion of the colloids, due to hydrophobic attraction between associated surfactants at the complexes with colloids. This leads to a total number of associated particles larger than the number of charged sites of the colloid, resulting in charge inversion of the complexes. All charged species here are monovalente. Charged spherical colloids have been studied for example in [37, 38] in ionic solutions. Interaction of surfactants with surfaces has been studied in [39]-[44]. Charged inversion in colloid solutios with multivalent ions has been studied in [45]-[48]. To our knowledge this is the first place where isotherms of surfactant association in spherical colloids leading to charge inversion are evaluated.

2 The system

We consider a solution of N_p spherical polyions of radius a and Z negative sites equally spaced on its surface, in a system of total volume V, hence with number density $\rho_p = N_p/V$. Thus, if the colloid molecule is completely ionized, it has a charge $-Zq$, where q is the proton charge, and we have Z positive ions in solution for each colloid. The area per site is $a_1 = A/Z = 4\pi a^2/Z$. The corresponding superficial density of sites is then $\sigma_s = Z/A = 1/a_1$. Furthermore, there is monovalent salt with number density $\rho_s = N_s/V$, cationic surfactants with number density $\rho_{a1} = N_{a1}/V$, and anionic surfactants with number density $\rho_{a2} = N_{a2}/V$. There are N_s positive ions and N_s negative ions from the added salt, each with diameter σ. The surfactant is also a neutral pair molecule, which after dissociation presents a positive surfactant chain and a negative ion in solution. The cationic surfactant chain has z_{a1} neutral hydrophobic monomers and a charged monomer at the extremity with charge $+q$, and a counterion with charge $-q$. Similarly, the anionic surfactant chain has z_{a2} neutral hydrophobic monomers and a charged monomer at the extremity with charge $-q$, and a counterion with charge $+q$. All ions and monomers in surfactant chain have diameter $\sigma = 3$ Å. The solvent is a continuum medium with permittivity ε. We consider here water at 25°C.

At equilibrium the positive ions and surfactants associate on the colloids, and we have clusters or complexes in solution (fig. 1). We denote by N_{ij} the number of colloids with i associated positive ions and j positive surfactant chains, and the corresponding number density by $\rho_{ij} = N_{ij}/V$. We then evaluate the complex distribution ρ_{ij} minimizing the Helmholtz free energy of the system. We also consider the possibility of charge inversion. If $i + j = Z$ the colloid becomes neutral, and the hydrophobic attraction between surfactant tails allows the association to proceed, with the formation of a second layer of associated surfactants. In this case the charge of the complex becomes positive and we have charge inversion of the colloid.

Besides complexes of colloids we have the formation of mixed micelles of cationic and anionic surfactants in solution. Following [36, 49], we consider polidispersivity in the size of micelles given by a Gaussian distribution. The micelles are assumed to be spheres with g surfactant molecules. Among these pg are cationic and ng are anionic. Hence p and n represent the fraction of cationic and anionic surfactant at micelles, and $p + n = 1$. At equilibrium we have association of n_g ions at the surface of the micelles. The associated ions are positive if $p < n$ and negative if $p > n$. The net charge of a micelle of size g is $(p - n)gq$, before ion association. The corresponding association fraction of ions is $m_g = n_g/Z_g$, where $Z_g = |p - n|g$. The distribution $\rho_g = N_g/V$ of micelles and the association fraction m_g are also obtained from minimization of the corresponding free energy. Since in general the density of colloids is much less than the surfactant density, we make these minimizations independent from each other. That is, we first evaluate the number of micelles neglecting colloids, and with these values we then evaluate the complex distribution of colloids. Next we consider micelle formation.

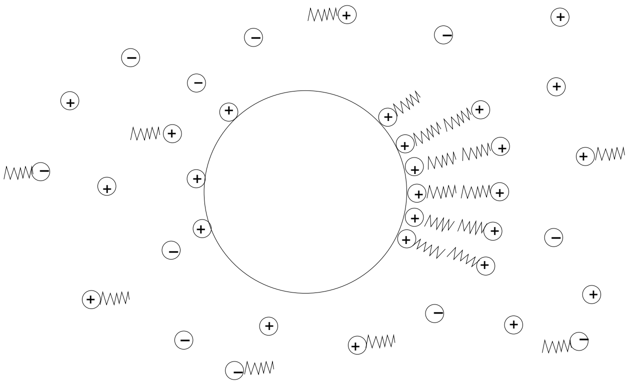

Figure 1: The spherical negative colloids form complexes with associated positive counterions and surfactants. A second layer of associated surfactants can be formed, inverting the charge of the complex. The bare charge of the colloid is $-Zq$. Mixed micelles, not shown, can also be formed.

3 Micelle formation

The surfactant molecules in aqueous solution become ionized, and due to electrostatic and hydrophobic interactions mixed micelles are formed. A micelle with g surfactants has pg cationic and ng anionic, with [49],

$$\begin{aligned} p &= \frac{\rho_{a1} f_{m2} X_2^*}{\rho_{a1} f_{m2} X_2^* + \rho_{a2} f_{m1} X_1^*} \\ n &= \frac{\rho_{a2} f_{m1} X_1^*}{\rho_{a1} f_{m2} X_2^* + \rho_{a2} f_{m1} X_1^*} \, . \end{aligned} \tag{1}$$

The quantities f_{m1} and f_{m2} are the activity coefficients of cationic and anionic surfactants in the mixed micelle, respectively. In our model we consider the mixed micelles as ideal, hence we fix $f_{m1} = f_{m2} = 1$ [49]. The quantities X_1^* and X_2^* are the CMC estimates of pure cationic and anionic surfactants, respectively.

We define the fraction of cationic and anionic surfactants in the micelles respectively by,

$$x_1 = \frac{p \sum_g g\rho_g}{\rho_{a1}} \, , \quad x_2 = \frac{n \sum_g g\rho_g}{\rho_{a2}} = x_1 \frac{n}{p} \frac{\rho_{a1}}{\rho_{a2}} \, . \tag{2}$$

The corresponding number densities of free cationic and anionic surfactants are,

$$
\begin{aligned}
\rho_{a1}^{f} &= \rho_{a1} - x_1 \rho_{a1}\,, \\
\rho_{a2}^{f} &= \rho_{a2} - x_2 \rho_{a2}\,.
\end{aligned} \tag{3}
$$

The number densities of free ions are, for $p > n$,

$$
\begin{aligned}
\rho_{+} &= \rho_s + \rho_{a2}\,, \\
\rho_{-} &= \rho_s + \rho_{a1} - \sum_g n_g \rho_g\,,
\end{aligned} \tag{4}
$$

and for $p < n$,

$$
\begin{aligned}
\rho_{+} &= \rho_s + \rho_{a2} - \sum_g n_g \rho_g\,, \\
\rho_{-} &= \rho_s + \rho_{a1}\,,
\end{aligned} \tag{5}
$$

where n_g is the number of associated ions at a micelle. We neglect the presence of colloids here. The corresponding association fraction is $m_g = n_g / Z_g$, with,

$$
Z_g = |p - n| g\,. \tag{6}
$$

We suppose all micelles with the same value of m_g.

The inverse Debye screening length is defined in the usual way by the relation,

$$
\kappa = \sqrt{4\pi\lambda_B(\rho_{+} + \rho_{-} + \rho_{a1}^{f} + \rho_{a2}^{f})}\,, \tag{7}
$$

where $\lambda_B = \beta q^2 / 4\pi\varepsilon$ is the Bjerrum length and $\beta = 1/kT$.

The size distribution of micelles is supposed to be described by a Gaussians distribution,

$$
\rho_g \sigma^3 = c \exp[-a(g - \bar{g})^2]\,, \tag{8}
$$

where $\bar{g}$ is the average size of the micelles. We take a and $\bar{g}$ as given parameters, and determine c by equation (2), aproximating the sum by an integral,

$$
\sum_g g \rho_g \sigma^3 \cong \int_0^{\infty} g \rho_g \sigma^3 dg = \frac{c}{2a} \exp[-a\bar{g}^2] + \frac{c\bar{g}}{2}\sqrt{\frac{\pi}{a}}[\mathrm{erf}(\sqrt{a}\bar{g}) + 1]\,. \tag{9}
$$

In this way we can obtain c for a given value osf x_1. The parameter a is related to the deviation from the mean value $\bar{g}$,

$$\left[\overline{(g-\bar{g})^2}\right]^{1/2} = \left(\frac{1}{2a}\right)^{1/2} . \tag{10}$$

The volume occupied by a micell with g surfactants is,

$$V_g = \frac{4\pi}{3} R_g^3 \,, \tag{11}$$

where R_g is the radius of a closed-packed spherical micelle,

$$R_g = \left(\frac{3}{4\pi} g v_m\right)^{1/3} . \tag{12}$$

In this expression the average volume of one surfactant in a micelle is,

$$v_m = \frac{\pi}{6} \sigma_m^3 \,, \tag{13}$$

with the mean effective diameter of one molecule given by,

$$\sigma_m = p\sigma_{ef}^1 + n\sigma_{ef}^2 \,, \tag{14}$$

and

$$\begin{aligned} \sigma_{ef}^1 &= z_{a1}^{1/3} \,, \\ \sigma_{ef}^2 &= z_{a2}^{1/3} \,. \end{aligned} \tag{15}$$

These are the effective diameters of spheres with the volume as one cationic or anionic surfactant, respectively.

The Helmholtz free energy for micelles is,

$$F_m = F_{id}^m + F_{int}^m + F_{dh}^m \,, \tag{16}$$

The ideal gas free energy is,

$$\begin{aligned} \beta F_{id}^m &= N_+(\ln \rho_+^* - 1) + N_-(\ln \rho_-^* - 1) \\ &\quad + N_{a1}^f(\ln \rho_{a1}^f - 1) + N_{a2}^f(\ln \rho_{a2}^f - 1) \\ &\quad + \sum_g N_g(\ln \rho_g^* - 1) \,, \end{aligned} \tag{17}$$

where the dimensionless reduced density of species s is $\rho_s^* = \rho_s \sigma^3$.

The free energy corresponding to the internal partition function of micelles is,

$$F^m_{int} = F^m_{ent} + F^m_{ion} + F^m_a + F^m_h \, . \tag{18}$$

The entropic contribution is [32, 33],

$$\begin{aligned} \beta F^m_{ent} &= |p-n| m_g \ln(m_g) \sum_g g N_g \\ &\quad + |p-n|(1-m_g)\ln(1-m_g) \sum_g g N_g \, , \end{aligned} \tag{19}$$

The electrostatic term is the usual energy of a charged surface [33, 50],

$$\beta F^m_{ion} = \frac{\lambda_B}{2\sigma} |p-n|^2 (1-m_g)^2 \sum_g \frac{g^2 N_g}{R_g} \, . \tag{20}$$

The free energy describing association of negative ions to positive surfactants in micelles is given by,

$$\beta F^m_a = -\ln\zeta \, |p-n| m_g \sum_g g N_g \, , \tag{21}$$

where ζ is the association constant of Bjerrum [3, 22, 23, 24],

$$\begin{aligned} \zeta &= \frac{2\pi\sigma^3}{3t^3} \left[\mathrm{Ei}(1/t) - \mathrm{Ei}(2) + e^2 \right] \\ &\quad - \frac{2\pi\sigma^3}{3} e^{1/t} \left[2 + \frac{1}{t} + \frac{1}{t^2} \right] \, , \end{aligned} \tag{22}$$

valid for $t < 0.5$, with $t = \sigma/\lambda_B$.

The hydrophobic free energy is given by a van der Waals term [18, 51],

$$\beta F^m_h = -\frac{a_m}{v_m} \sum_g g N_g \, , \tag{23}$$

with,

$$a_m = \frac{2\pi\sigma^3_m}{3} (\lambda^3 - 1) \varepsilon_m \, . \tag{24}$$

We use $\lambda = 2$. The hydrophobic energy interaction ε_m above is,

$$\varepsilon_m = p\varepsilon_1 + n\varepsilon_2 \, , \tag{25}$$

with ε_1 the hydrophobic energy interaction between neutral chains of cationic surfactants, and ε_2 the hydrophobic energy interaction between neutral chains of anionic surfactants.

Hence, with the above definitions the hydrophobic attraction between surfactants in micelles is represented by a square well of depth ε_m,

$$u = \begin{cases} \infty\,, & r < \sigma_m\,, \\ -\varepsilon_m\,, & \sigma_m \le r \le \lambda\sigma_m\,, \\ 0\,, & r > 2\sigma_m\,. \end{cases} \tag{26}$$

The electrotatic contribution describing the interaction between the ionic solution and micelles is [18, 19, 33],

$$\beta F_{dh}^m = -\frac{\lambda_B}{\sigma}(1-m_g)^2|p-n|^2\frac{\kappa\sigma}{2}\sum_g \frac{g^2 N_g}{1+\kappa R_g}\,. \tag{27}$$

The above expression is explained below (see eq.(38)).

The free energy of micelles F_m is a function of x_1 and m_g. The equilibrium configuration is obtained minimizing the free energy for given concentrations of cationic and anionic surfactants, and salt.

4 The Helmholtz free energy for colloids with salt and surfactants

We consider here the solution with spherical colloids. At equilibrium we have the formation of complexes, or clusters, of different sizes. The number density $\rho_{ij} = N_{ij}/V$ denotes complexes with i associated positive ions and j associated positive surfactants. Conservation of particle number leads to the equations,

$$\begin{aligned} \rho_{a1}^f &= \rho_{a1} - x_1\rho_{a1} - \sum_{ij} j\rho_{ij}\,, \\ \rho_{a2}^f &= \rho_{a2} - x_2\rho_{a2}\,. \end{aligned} \tag{28}$$

For $p > n$,

$$\begin{aligned} \rho_+ &= \rho_s + \rho_{a2} + \rho_m - \sum_{ij} i\rho_{ij}\,, \\ \rho_- &= \rho_s + \rho_{a1} - \sum_g n_g\rho_g\,, \end{aligned} \tag{29}$$

and for $p < n$,

$$\begin{aligned}\rho_+ &= \rho_s + \rho_{a2} + \rho_m - \sum_{ij} i\rho_{ij} - \sum_g n_g \rho_g \,, \\ \rho_- &= \rho_s + \rho_{a1} \,. \end{aligned} \tag{30}$$

The inverse Debye screening length is,

$$\kappa^2 = 4\pi\lambda_B(\rho_+ + \rho_- + \rho_{a1}^f + \rho_{a2}^f) \,. \tag{31}$$

We consider the values of x_1 and m_g obtained from minimization of the free energy F_m, eq.(16).

The Helmholtz free energy for colloids and the solution is a sum of terms,

$$F = F_{id} + F_{int} + F_{pc} + F_{pp} \,, \tag{32}$$

with the internal contribution due to complexes,

$$F_{int} = F_{ent} + F_{ion} + F_h \,. \tag{33}$$

The ideal gas free energy is,

$$\begin{aligned}\beta F_{id} &= \sum_{ij} \rho_{ij}^* \ln \rho_{ij}^* - \rho_p^* + \rho_+^*(\ln \rho_+^* - 1) \\ &\quad + \rho_-^*(\ln \rho_-^* - 1) + \rho_{af}^*(\ln \rho_{af}^* - 1) \,. \end{aligned} \tag{34}$$

The entropic free energy is [32, 33],

$$\beta F_{ent} = -\sum_{ij} N_{ij} \ln \Omega_{ij} \,,$$

where Ω_{ij} is the number of combinations of i ions and j surfactants in a complex ij,

$$\Omega_{ij} = \frac{Z!}{i!j!(Z-i-j)!} \,.$$

We obtain then, after using Stirling approximation,

$$\begin{aligned}\beta F_{ent} &= -\sum_{ij} N_{ij} \ln \Omega_{ij} \,, \\ &= Z \sum_{ij} N_{ij}[m_i \ln m_i + m_j \ln m_j \\ &\quad + (1 - m_i - m_j)\ln(1 - m_i - m_j)] \,, \end{aligned} \tag{35}$$

and the association fractions are $m_i = i/Z$, $m_j = j/Z$. The free energy describing electrostatic interaction between charged sites in a complex is the energy of a charged surface [33, 50],

$$\beta F_{ion} = \frac{Z^2 \lambda_B}{2a} \sum_{ij} \rho^*_{ij} p^2_{ij} \,, \tag{36}$$

with $p_{ij} = -1 + m_i + m_j$ the net valence of each colloid site. The hydrophobic interaction between associated surfactants is writen as in [32], taking the number of nearest neighbors approximately as four. For one colloid we have,

$$\beta F^1_h = -\frac{1}{2} \beta \varepsilon_1 \sum_{\substack{k \neq l \\ n.n.}}^{Z} \sigma_k \sigma_l \,,$$

where σ_k is the number occupation of surfactant at site k, and n.n. denotes sum over nearest neighbors. In the uniform approximation, for a complex with j associated surfactants, the occupation number at site k is $\sigma_k = \sigma = m_j$, for any site $1 \leq k \leq Z$,

$$\beta F^1_h = -\frac{1}{2} \beta \varepsilon_1 (4Z) m^2_j \,.$$

Summing over all complexes,

$$\beta F_h = -2Z \beta \varepsilon_1 \sum_{ij} N_{ij} m^2_j \,. \tag{37}$$

The hydrophobic energy above is ε_1, since only cationic surfactants associate at the spherical colloids. The free energy describing electrostatic interaction between colloids and the ionic solution is [18, 19, 33],

$$\beta F_{pc} = -Z^2 \frac{\lambda_B}{2a} \frac{\kappa a}{1 + \kappa a} \sum_{ij} N^*_{ij} p^2_{ij} \,. \tag{38}$$

The above expression is obtained in the following way. The electrostatic potential around a spherical colloid of radius a and charge Q, obtained from Debye-Hückel theory, is,

$$\phi = \begin{cases} \dfrac{Q}{4\pi\varepsilon a} \dfrac{1}{1 + \kappa a} \,, & r \leq a \,, \\ \dfrac{Q}{4\pi\varepsilon} \dfrac{e^{\kappa a}}{1 + \kappa a} \dfrac{e^{-\kappa r}}{r} \,, & r \geq a \,, \end{cases}$$

where Q, the charge of the colloid, is uniformly distributed over the surface. The potential ψ to be used in the charging process is,

$$\psi = \phi(a) - \phi(a)\Big|_{\kappa=0} = -\frac{Q\kappa}{4\pi\varepsilon(1+\kappa a)}\,.$$

The corresponding free energy for one colloid is given by,

$$\begin{aligned} F^1_{pc} &= \int \psi dQ = -\frac{\kappa}{4\pi\varepsilon(1+\kappa a)}\int_0^Q QdQ\,, \\ &= -\frac{Q^2}{8\pi\varepsilon}\frac{\kappa}{(1+\kappa a)}\,. \end{aligned}$$

For a complex ij, $Q = p_{ij}Zq$, hence,

$$F^1_{pc} = -\frac{p_{ij}^2 Z^2 q^2}{8\pi\varepsilon}\frac{\kappa}{1+\kappa a}\,.$$

Summing over all colloids,

$$\beta F_{pc} = -Z^2\frac{\lambda_B}{2a}\frac{\kappa a}{1+\kappa a}\sum_{ij} N_{ij}p_{ij}^2\,, \tag{39}$$

as in equation (38). Equation (27) is obtained in the same way.

The last contribution to the free energy is due to interaction between colloid molecules. We do this in the same manner as in [33, 34] for linear molecules. The electrostatic interaction between charge elements in two colloids is given by the Debye-Hückel potential,

$$du = dqdq'\frac{e^{-\kappa r'}}{4\pi\varepsilon r'}\,,$$

where dq and dq' are charge elements on the surfaces of two colloids distant r'. Integrating the above element over the surfaces of the colloids we obtain, after some algebra (see Appendix),

$$u = \frac{Z^2q^2}{16\pi\varepsilon}p_{ij}p_{kl}(e^{\kappa a} - e^{-\kappa a})^2\frac{1}{\kappa^2 a^2}\frac{e^{-\kappa r}}{r}\,,$$

where r is the distance between the centers of the colloids of radius a, and the two colloids are a ij complex and a kl complex. The above energy is evaluated in detail in section 6. We evaluate the corresponding free energy as in van der Waals theory [1, 18, 19, 33],

$$\beta F_{pp} = \frac{1}{2}\sum \rho_{ij}\rho_{kl}V\int \beta u d^3r\,.$$

The result is,

$$\beta F_{pp} = \frac{\pi \lambda_B}{4\sigma^3}(Za)^2 f(\kappa a)\frac{V}{\sigma^3}\sum_{ijkl}\rho^*_{ij}\rho^*_{kl}p_{ij}p_{kl}\,, \tag{40}$$

where,

$$f(x) \equiv [\exp(x) - \exp(-x)]^2 \exp(-2x)(1+2x)\frac{1}{x^4}\,.$$

The total number of complexes with $i+j \leq Z$ can be seen to be $(Z+1)(Z+2)/2$.

4.1 Charge inversion

We consider here the possibility of charge inversion of the colloid. This could happen due to the hydrophobic interaction between surfactant tails, since in our approximation the electrostatic interaction could at most neutralize the molecule. In this case we have to rewrite the entropic contribution to the internal free energy. The other terms remain unchanged in our approximation, with $p_{ij} = -1 + m_i + m_j > 0$ if $i + j > Z$.

The entropic contribution for $i+j \leq Z$, with no charge inversion, is given as before essentially by the term,

$$\Omega = \frac{Z!}{i!j!(Z-i-j)!}\,.$$

Charge inversion occurs if $i+j > Z$. We consider no empty sites in this case and denote $j = j' + k$, where $j' = Z - i$ surfactants bound directly to the colloid, and the remaining $k = j - j'$ surfactants are supposed to associate at the j' surfactants due to hydrophobic attraction. This gives rise to a bilayer over the colloid, partially covering the molecule. Now the entropic term has two terms, one due to the j' surfactants associated directly to the surfactant, and one due to the k surfactants associated to the j' surfactants. We denote the first term by Ω_1 and the second by Ω_2,

$$\Omega_1 = \frac{Z!}{i!j'!(Z-i-j')!}\,, \quad \Omega_2 = \frac{j'!}{k!(j'-k)!}\,,$$

and $\Omega_{ij} = \Omega_1\Omega_2$.

Hence, since $j' = Z - i$ and $k = j - j' = i + j - Z$,

$$\begin{aligned}\ln\Omega_{ij} &= \ln\Omega_1+\ln\Omega_2\,, \\ &= -Z[m_i\ln m_i+(1-m_i)\ln(1-m_i)] \\ &\quad -Z(1-m_i)\left[\frac{m_i+m_j-1}{1-m_i}\ln\frac{m_i+m_j-1}{1-m_i}\right. \\ &\quad \left.+\frac{2-2m_i-m_j}{1-m_i}\ln\frac{2-2m_i-m_j}{1-m_i}\right]\,,\end{aligned}$$

with $j \leq 2(Z-i)$. This means that $k \leq j'$, i.e. the second surfactant layer has size limited by the first layer to a maximum k equals to j'. The entropic free energy is then,

$$\beta F_{ent} = -\sum_{ij} N_{ij}\ln\Omega_{ij}\,, \tag{41}$$

The total number of possible complexes can be seen to be,

$$Z_{cl} = (Z+1)^2\,. \tag{42}$$

4.2 Pressure, chemical potentials and Gibbs free energy

In this section we state the expressions obtained from the free energy, namely the pressure, the chemical potentials, and the Gibbs free energy.

The pressure $p = -\partial F/\partial V$ is,

$$p = p_{id} + p_{pc} + p_{pp}\,, \tag{43}$$

corresponding to ideal contribution, polyion-counterion, and polyion-polyion contributions. These terms are,

$$\beta p_{id} = \sum_{ij}\rho_{ij} + \rho_+ + \rho_- + \rho_{af}\,. \tag{44}$$

$$\beta p_{pc} = -Z^2\frac{\lambda_B}{4a}\frac{\kappa a}{(1+\kappa a)^2}\sum_{ij}\rho_{ij}p_{ij}^2\,, \tag{45}$$

$$\begin{aligned}\beta p_{pp} &= \frac{\pi\lambda_B}{4\sigma^3}(Za)^2\frac{1}{\sigma^3}\left[f(\kappa a)+\frac{1}{2}\kappa a f'(\kappa a)\right]\times \\ &\quad \times\left(\sum_{ij}\rho_{ij}^* p_{ij}\right)^2\,.\end{aligned} \tag{46}$$

The chemical potentials $\mu_s = \partial F/\partial N_s$ are,

$$\beta\mu_{id,s} = \ln\rho_s^*\,, \tag{47}$$

In the case $i+j \leq Z$, with no overcharging, we have,

$$\begin{aligned}\beta\mu_{ij}^{ent} \;&=\; Zm_i\ln m_i + Zm_j\ln m_j \\ &\quad +Z(1-m_i-m_j)\ln(1-m_i-m_j)\,, \\ &\quad i+j\leq Z\,,\end{aligned} \tag{48}$$

If overcharging is allowed, then $i+j > Z$ and,

$$\begin{aligned}\beta\mu_{ij}^{ent} \;&=\; Zm_i\ln m_i + Z(1-m_i)\ln(1-m_i) \\ &\quad +Z(m_i+m_j-1)\ln\left(\frac{m_i+m_j-1}{1-m_i}\right) \\ &\quad +Z(2-2m_i-m_j)\ln\left(\frac{2-2m_i-m_j}{1-m_i}\right)\,, \\ &\quad i+j > Z\,.\end{aligned} \tag{49}$$

The other contributions are,

$$\beta\mu_{ij}^{ion} = \frac{(Zp_{ij})^2\lambda_B}{2a}\,, \tag{50}$$

$$\beta\mu_{ij}^{pc} = -(Zp_{ij})^2\frac{\lambda_B}{2a}\frac{\kappa a}{1+\kappa a}\,, \tag{51}$$

$$\beta\mu_{ij}^{pp} = \frac{1}{2}\pi\lambda_B(Za)^2\rho_{ij}f(\kappa a)\,, \tag{52}$$

$$\beta\mu_{ij}^{h} = -\beta\varepsilon(2Z)m_j^2\,, \tag{53}$$

$$\beta\mu_{+}^{pc} = -\frac{\pi Z^2}{\kappa a}\frac{\lambda_B^2}{\sigma^2}\frac{1}{(1+\kappa a)^2}\sum_{ij}\rho_{ij}^*p_{ij}^2\,, \tag{54}$$

$$\mu_{af}^{pc} = \mu_{+}^{pc}\,, \tag{55}$$

$$\beta\mu_{+}^{pp} = \frac{(\pi\lambda_B Za^2)^2}{2\kappa a\sigma^6}f'(\kappa a)\left(\sum_{ij}p_{ij}\rho_{ij}^*\right)^2\,, \tag{56}$$

$$\mu_{af}^{pp} = \mu_{+}^{pp}\,, \tag{57}$$

The Gibbs free energy is given by the usual expression, involving the pressure and chemical potentials,

$$G = F + pV = \sum_s N_s \mu_s\,. \tag{58}$$

4.3 Evaluation of complex distribution

The equilibrium configuration of the system is given by,

$$\delta F = 0\,, \tag{59}$$

that leads to,

$$\mu_{ij} = \mu_{00} + i\mu_{+} + j\mu_{af}\,, \tag{60}$$

or,

$$\rho_{ij}^{*} = \rho_{00}^{*}(\rho_{+}^{*})^{i}(\rho_{af}^{*})^{j} \exp\left\{\mu_{00}^{ex} - \mu_{ij}^{ex} + i\mu_{+}^{ex} + j\mu_{af}^{ex}\right\}\,, \tag{61}$$

which is the mass action law. The above equations are solved iteratively, and the resulting equilibrium distribution allows the evaluation of $\bar{m}_i$ and $\bar{m}_j$ for given values of densities and $\beta\varepsilon$. The mean values are defined in the usual manner. The mean association fraction of positive ions $\bar{m}_i$ is, for example,

$$\bar{m}_i = \frac{1}{Z}\frac{\sum_j i\rho_{ij}}{\sum_{ij}\rho_{ij}} = \frac{\sum_j i\rho_{ij}}{Z\rho_p}\,, \tag{62}$$

since,

$$\sum_{ij}\rho_{ij} = \rho_p\,. \tag{63}$$

5 Results and Conclusions

We consider the number density of colloids fixed at $\rho_m = Z\rho_p = 1\,\mu$M. This low density justify the neglecting of colloids in the determination of x_1 and m_g in the minimization process of micelle free energy. The salt density is $\rho_s = 1$ mM. The surface area per site at colloids is $a_1 = A/Z$, where $A = 4\pi a^2$. We consider two values of a_1, 20 Å^2 and 40 Å^2. Several values of Z are also considered below. We take the size of micelles as $\bar{g} = 100$ and

$a = 0.005$ in equations (8)-(10), resulting in a deviation of 10 in the size of micelles, following [36, 51]. We consider three values for surfactant chains in the results below: $(z_{a1}, z_{a2}) = (12, 8), (16, 14), (12, 12)$. With these values we find the equilibrium distribution ρ_{ij} of colloids from equation (61).

5.1 Area per site $a_1 = 20$ Å^2

Surfactant sizes $z_{a1} = 12$ and $z_{a2} = 8$

The surfactant chains have length $z_{a1} = 12$ and $z_{a2} = 8$, for cationic and anionic surfactants, respectively. The critical micelle concentrations are $X_1^* = 16$ mM and $X_2^* = 0.13$ M [52]. The above equations (61) are solved iteratively, and the resulting equilibrium distributions for some cases are obtained. Figures 2 and 3 refer to this case. The corresponding mean association fractions as functions of ρ_{a1} are shown in figure 2. The parameters are: $Z = 100$, $\beta\varepsilon_1 = 4.5$, $\beta\varepsilon_2 = 1.0$, $\rho_{a2} = 0.13$ M. We have charge inversion at $\rho_{a1} \cong 0.034$ M. The fraction of surfactants at micelles are $x_1 \cong 0.9$ and $x_2 \cong 1$.

In figure 3 we have the number density ρ_{a1} of cationic surfactant for charge inversion, as function of ε_1, for some values of Z. The curves may be fitted to the function $y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 = \sum_{i=0}^{4} a_i x^i$. The results for the constants a_i are shown in table 1.

Surfactant sizes $z_{a1} = 16$ and $z_{a2} = 14$

For these values of surfactant chains we have the critical micelle concentrations $X_1^* = 0.92$ mM, $X_2^* = 2.1$ mM. Figure 4 shows the critical density ρ_{a1}^c (M) at charge inversion for several values of Z. The density of anionic surfactant is $\rho_{a2} = 2.1$ mM. The curves may be fitted as before with a polynomial of the fourth degree, $y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4$. The results for the constants a_i are shown in table 1.

Surfactant sizes $z_{a1} = 12$ and $z_{a2} = 12$

The critical micelle concentrations are $X_1^* = 16$ mM, $X_2^* = 8.3$ mM. Figure 5 shows the critical density ρ_{a1}^c (M) at charge inversion for several values of Z. The density of anionic surfactant is $\rho_{a2} = 8.3$ mM. The curves may be fitted as before to a polynomial of the fourth degree, $y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4$. The results for the constants a_i are shown in table 1.

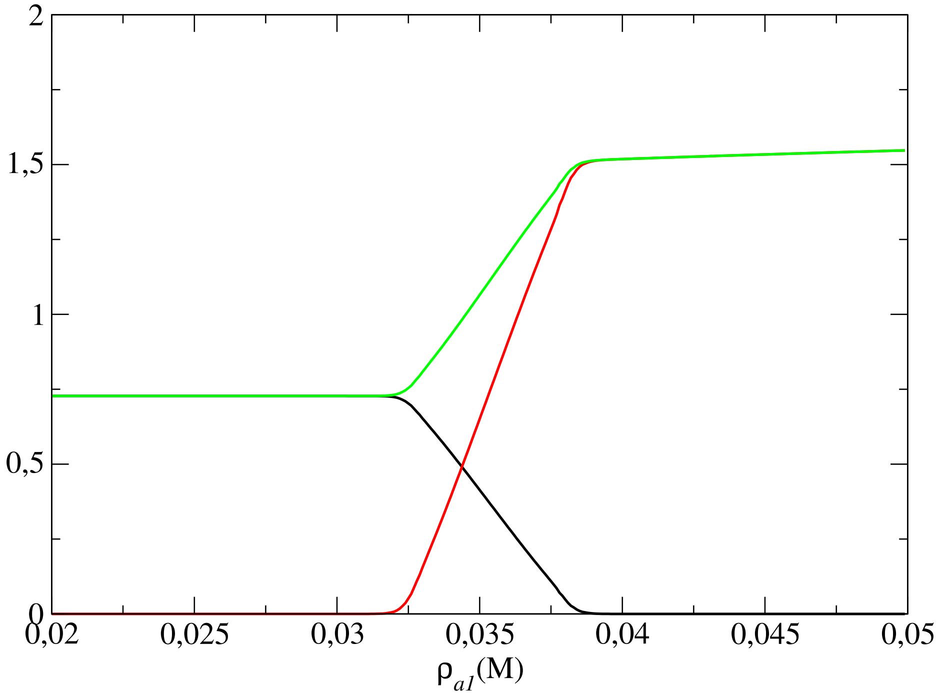

Figure 2: Mean association fractions $\bar{m}_i$ and $\bar{m}_j$ of positive ions and surfactants, respectively, at the colloids, as functions of ρ_{a1}(M), for $Z = 100$, $\rho_{a2} = 0.13$ M, $\beta\varepsilon_1 = 4.5$, $\beta\varepsilon_2 = 1$ (black line, $\bar{m}_i$; red line, $\bar{m}_j$; green line, $\bar{m}_i + \bar{m}_j$). The others parameters are as in figure 2. We have charge inversion at $\rho_{a1} \cong 0.034$ M. The surfactant chain sizes are $z_{a1} = 12$ and $z_{a2} = 8$, and $a_1 = 20$ Å^2.

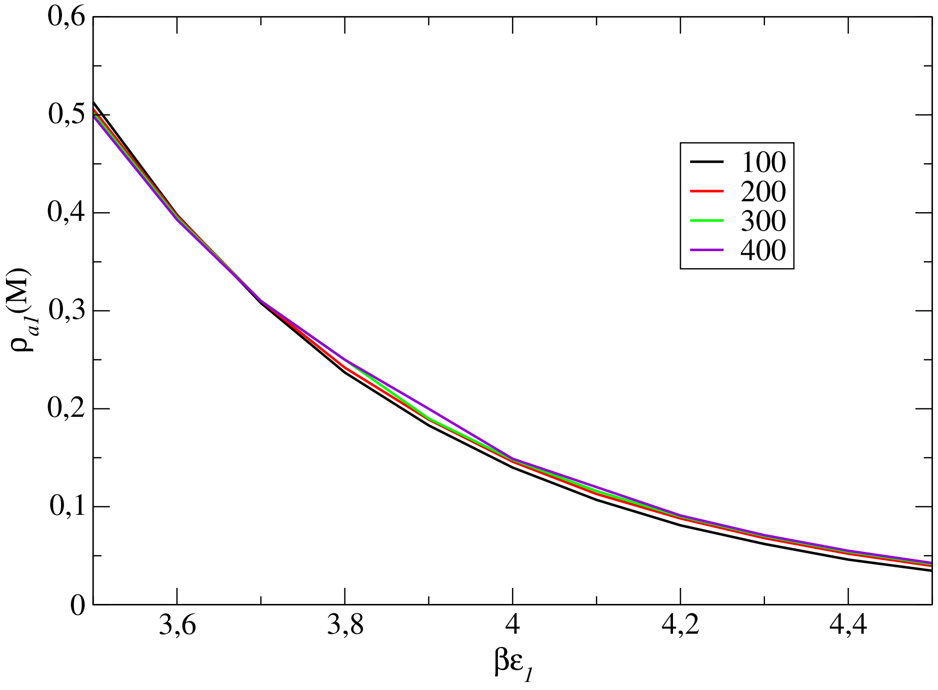

Figure 3: Number density of cationic surfactant for charge inversion, as function of ε_1, for some values of Z. The surfactant chain sizes are $z_{a1} = 12$ and $z_{a2} = 8$, and $a_1 = 20$ Å^2.

Z	a_0	a_1	a_2	a_3	a_4
100	98.626	- 86.813	28.931	- 4.3201	0.24359
200	82.654	- 71.542	23.451	- 3.4452	0.19114
300	74.824	- 64.479	21.082	- 3.095	0.17191
400	108.73	- 99.264	34.403	- 5.352	0.31469
Z	a_0	a_1	a_2	a_3	a_4
100	43.899	- 43.955	16.5	- 2.7501	0.17163
200	36.724	- 36.714	13.761	- 2.2901	0.14271
300	33.415	- 33.424	12.536	- 2.0876	0.13019
400	32.159	- 32.189	12.079	- 2.0125	0.12556
Z	a_0	a_1	a_2	a_3	a_4
100	5.0396	- 9.2172	6.2596	- 1.8656	0.20564
200	4.6582	- 8.5102	5.7702	- 1.7166	0.18886
300	4.5369	- 8.3222	5.6628	- 1.6899	0.18642
400	4.5098	- 8.3184	5.6874	- 1.7042	0.18866

Table 1: Constants a_i in the function $y = \sum_{i=0}^{4} a_i x^i$ that reproduce the curves in figures 3-5 for the density ρ_{a1} of positive surfactant for charge inversion, as function of $\beta\varepsilon_1$. From top to bottom, the values of z_{a1}, z_{a2} are (12,8), (16,14) and (12,12). The value of area per site is $a_1 = 20$ Å^2.

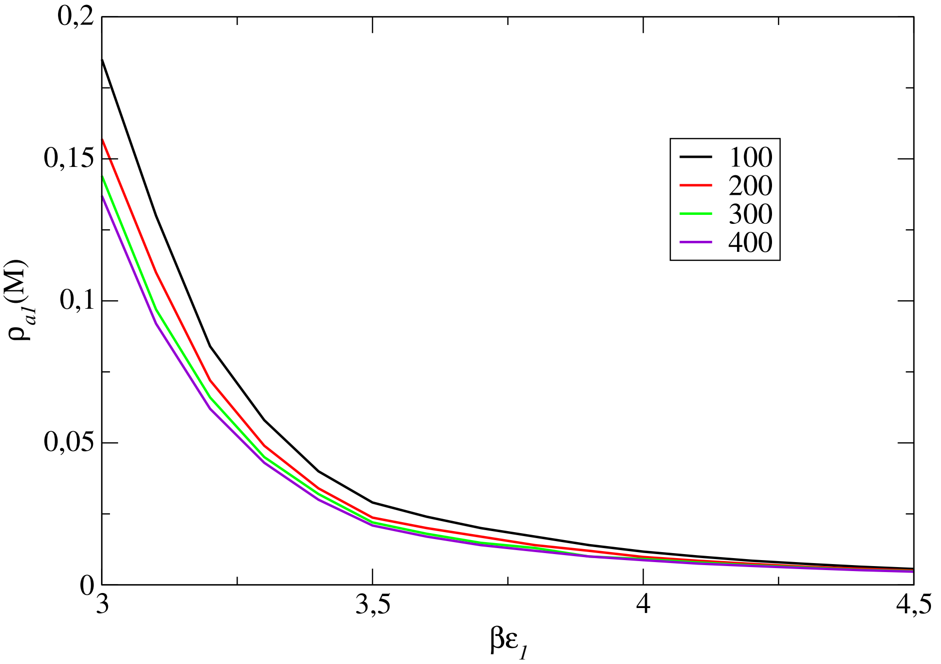

Figure 4: Number density of cationic surfactant for charge inversion, as function of ε_1, for some values of Z. The surfactant chain sizes are $z_{a1} = 16$ and $z_{a2} = 14$, and $a_1 = 20$ Å^2.

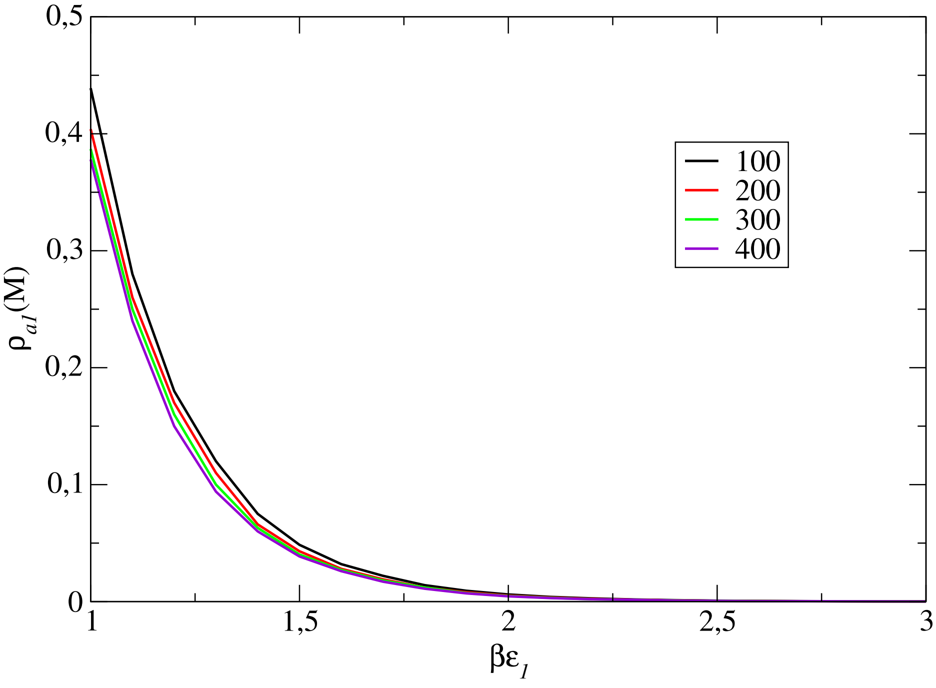

Figure 5: Number density of cationic surfactant for charge inversion, as function of ε_1, for some values of Z. The surfactant chain sizes are $z_{a1} = 12$ and $z_{a2} = 12$, and $a_1 = 20$ Å^2.

a_1	Z	a	a_1	Z	a
20	100	12.62	40	100	17.84
20	200	17.84	40	200	25.23
20	300	21.85	40	300	30.90
20	400	25.23	40	400	35.68

Table 2: Radius of the colloid for the values of a_1 and Z. The surface density of sites is $\sigma_s = 0.05$ Å^{-2} for $a_1 = 20$ Å^2, and $\sigma_s = 0.025$ Å^{-2} for $a_1 = 40$ Å^2.

5.2 Area per site $a_1 = 40$ Å^2

The above results were obtained for $a_1 = 20$ Å^2, the surface area per charged site of the colloid. We consider also $a_1 = 40$ Å^2. The radius a of the colloid depends on Z and a_1. Table 2 shows the corresponding radius in each case, in Angstrons.

We determine the conditions for overcharging as before. The density of cationic surfactant ρ_{a1} for overcharging, as function of $\beta\varepsilon_1$ can be determined as previously, and this function adjusted to the $y = \sum_{i=0}^{4} a_i x^i$, as before. The results are summarized in table 3.

6 Appendix - Polyion-polyion interaction

To evaluate the electrostatic interaction between two colloid molecules we take the interaction between two point particles or infinitesimal volumes in the Debye-Hückel theory as,

$$u = \lambda \frac{e^{-\kappa r}}{r} \,, \tag{64}$$

where λ is a constante with the dimensions of energy times length, and κ is the inverse Debye screening length. For two point charges $q, q,'$, $\lambda = qq'/4\pi\varepsilon$. Figure 6 shows a spherical shell with radius a interacting with a particle at P. The area element is,

$$dA = a^2 \mathrm{sen}\,\theta \, d\theta \, d\varphi = 2\pi a^2 \mathrm{sen}\,\theta \, d\theta \,,$$

since we have symmetry in the angle φ.

The interaction between the particle at P and the area element dA is,

$$du = \rho_s dA \lambda \frac{e^{-\kappa r}}{r} \,,$$

Z	a_0	a_1	a_2	a_3	a_4
100	166.25	- 152.83	52.857	- 8.1472	0.47203
200	155.04	- 140.63	48.033	- 7.319	0.41958
300	137.73	- 123.16	41.481	- 6.2341	0.35256
400	124.09	- 109.64	36.495	- 5.4207	0.30303
Z	a_0	a_1	a_2	a_3	a_4
100	10.454	- 9.6212	3.356	- 0.52428	0.030886
200	2.6079	- 1.979	0.55562	- 0.067405	0.0029138
300	3.1249	- 2.6762	0.8763	- 0.12958	0.0072844
400	6.6954	- 6.2225	2.1889	- 0.34433	0.020396
Z	a_0	a_1	a_2	a_3	a_4
100	2.7801	- 4.5627	2.8064	- 0.76492	0.07783
200	2.15	- 3.4473	2.075	- 0.55452	0.055425
300	2.0624	- 3.3068	1.9894	- 0.53112	0.053019
400	1.9175	- 3.0606	1.8342	- 0.48809	0.048593

Table 3: Constants a_i in the function $y = \sum_{i=0}^{4} a_i x^i$ for the case $a_1 = 40$ Å^2. From top to bottom, the values of z_{a1}, z_{a2} are (12,8), (16,14) and (12,12).

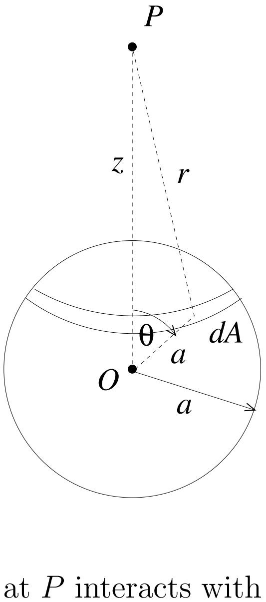

Figure 6: A particle located at P interacts with a spherical shell with radius a.

where ρ_s is the particle number surface density in the shell. The number of particles in dA is therefore $\rho_s dA$, and all of them are at the same distance r from P. Substituting dA,

$$du = 2\pi a^2 \rho_s \lambda \text{sen}\, \theta\, d\theta \frac{e^{-\kappa r}}{r}\,.$$

The variables r and θ are related by,

$$r^2 = a^2 + z^2 - 2za\cos\theta\,,$$

hence,

$$2rdr = 2za\text{sen}\,\theta\, d\theta\,,$$

and,

$$\text{sen}\,\theta\, d\theta = \frac{rdr}{za}\,.$$

Substituting this in du we obtain,

$$du = 2\pi\rho_s\lambda\frac{a}{z}dre^{-\kappa r}\,. \tag{65}$$

The interaction energy between the spherical shell and the particle at P is then,

$$u = \int du = 2\pi\rho_s\lambda\frac{a}{z}\int_{z-a}^{z+a} dre^{-\kappa r}\,,$$

or,

$$u = 2\pi a\rho_s\lambda\frac{e^{-\kappa z}}{\kappa z}(e^{\kappa a} - e^{-\kappa a})\,. \tag{66}$$

Two spherical shells

We consider now two spherical shells of radius a and b, and surface densities of particles ρ'_s, ρ_s (fig. 7). We write du as the interaction energy between one of the spherical shells and an element of area dA in the other spherical shell. Using (66) we have,

$$du = 2\pi\rho'_s(\rho_s dA)\lambda\frac{a}{\kappa r}e^{-\kappa r}[e^{\kappa a} - e^{-\kappa a}]\,.$$

Substituting $dA = 2\pi b^2\,\text{sen}\,\theta\, d\,\theta$,

$$du = 4\pi^2 b^2\rho'_s\rho_s\,\lambda\frac{a}{\kappa}\text{sen}\,\theta\, d\,\theta\frac{e^{-\kappa r}}{r}[e^{\kappa a} - e^{-\kappa a}]\,. \tag{67}$$

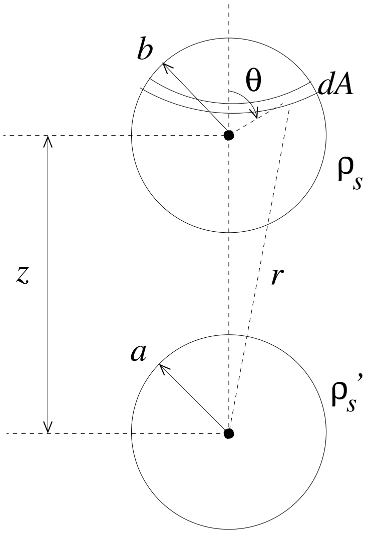

Figure 7: Two spherical shells with distance z between the centers.

The relation between the variables r, θ are,

$$r^2 = b^2 + z^2 + 2zb\cos\theta\,,$$

therefore,

$$rdr = -zb\,\mathrm{sen}\,\theta\,d\,\theta\,.$$

The interaction energy u is then,

$$u = \int du = -4\pi^2 ab\rho'_s\rho_s\,\lambda\frac{1}{\kappa z}[e^{\kappa a} - e^{-\kappa a}]\int_{z+b}^{z-b} dre^{-\kappa r}\,,$$

or,

$$u = 4\pi^2 ab\rho'_s\rho_s\,\frac{\lambda}{\kappa^2}(e^{\kappa a} - e^{-\kappa a})(e^{\kappa b} - e^{-\kappa b})\frac{e^{-\kappa z}}{z}\,. \tag{68}$$

7 Statements and Declarations

The author has no relevant financial or non-financial interests to disclose.

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