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Electrical properties of a charged surface in a general electrolyte solution

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Abstract

The electrical properties of a planar charged surface in a general electrolyte solution are examined. Analytical expressions for the electrical potential, surface excess of co-ions, double-layer free energy, and entropy are derived. A perturbation method is proposed for the resolution of the Poisson–Boltzmann equation governing the electrical potential distribution. The analysis extends the classic Gouy–Chapman's result to an arbitrary a:b electrolyte solution. The present approach yields a system of linear ordinary differential equations, which can be solved to an arbitrary order, in principle. The performance of the present perturbation solution is satisfactory for conditions normally encountered in practice. For example, if the second-order solution is adopted, deviations in the electrical potential and thermodynamic properties examined are less than 5%. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The electrical potential distribution for a charged surface immersed in an electrolyte solution at equilibrium is approximately described by the Poisson–Boltzmann equation [1]. Solving this equation represents a first step in describing the basic properties of a colloidal suspension such as its stability and thermodynamic properties. Unfortunately, due to its non-linear nature, the only solvable case is a planar surface in a symmetric electrolyte solution. The problem was solved by Gouy and Chapman [1] for the case of constant surface potential about one century ago. Since then, a considerable amount of effort has been exerted to extend their result to a more realistic case, such as curved surfaces, asymmetric electrolytes, and various surface conditions. La Mer et al. [2], for example, solved the Poisson–Boltzmann equation in spherical geometry for a general electrolyte. The solution takes the form of a complicated infinite series; each term involves an integral which needs to be determined numerically. Dukhin et al. [3,4] considered a spherical surface in a 1:1 electrolyte solution. A perturbation method is proposed in which the electrical potential is expanded in terms of the negative powers of

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the position variable. The same approach was adopted by Sigal and Shamansky [5] to derive the electrical potential for a cylindrical surface and 1:1 electrolytes. By applying the same perturbation method, Lekkerkerker [6] was able to obtain the electrical free energy for both cylindrical and spherical surfaces and 1:1 electrolytes. In a study of a charged sphere in v:v, 1:2, and 2:1 electrolyte solutions, Stokes [7] suggested a perturbation method in which the derivative of the electrical potential is expanded in a negative power series of the position variable. An approximate solution, which is based on an empirical parameter was derived by Parlange [8] for the case of a spherical surface and 1:1 electrolytes. The same approach was adopted by Ohshima et al. [9] for a spherical surface in 1:1 and 2:1 electrolyte solutions. Bentz [10] considered a sphere in a solution containing any combination of monovalent and divalent ions. An approximate closed form for the electrical potential was derived. Hsu and Kuo [11] were able to obtain an approximate expression for the electrical potential for planar surfaces and a:b electrolytes. The derivation is based on a semi-empirical polynomial function, which is characterized by the valences of ions. Similar approach was also adopted for the case of cylindrical and spherical surfaces [12]. Some other studies about the resolution of Poisson–Boltzmann equation include, for instance, spherical surface in v:v electrolytes [13], spherical surface in 1:1 electrolytes [14–17], cylindrical and spherical surfaces in a:b electrolytes [18], and planar surface in 1:2, 2:1 and v:v electrolytes [19].

As can be seen from the above discussions, although relevant analyses are ample in the literature, most of them are limited to symmetric electrolytes, especially 1:1 electrolytes. The problem of a general a:b electrolyte has not been solved satisfactorily. The available results are either of numerical nature or involve some empirical assumptions. In the present study, this problem is solved through a perturbation method. The solution procedure is mathematically rigorous.

2. Analysis

The distribution of the scaled electrical potential ψ in the electrical double layer near a planar charged surface in an a:b electrolyte solution can be described by [1]

$$\frac{d^2\psi}{dX^2} = \frac{g}{a+b} \tag{1}$$

where $\psi = F\phi/RT$, $X = \kappa r$, $g = \exp(b\psi) - \exp(-a\psi)$, and $\kappa^2 = F^2 a(a+b)C_a^0/\varepsilon_r\varepsilon_0 RT$. In these expressions, ϕ is the electrical potential, F and R denote, respectively, the Faraday constant and the gas constant, ε_r and ε_0 are the relative permittivity of the liquid phase and the permittivity of a vacuum, respectively, C_a^0 is the bulk concentration of cation, T is the absolute temperature, κ is the reciprocal Debye length, and r is the distance from the surface. The boundary conditions associated with Eq. (1) are

$$\psi = \psi_0 \text{ at } X = 0 \tag{2a}$$

$$\psi \to 0 \text{ and } d\psi/dX \to 0 \text{ as } X \to \infty \tag{2b}$$

where ψ_0 denotes the scaled surface potential. Integrating Eq. (1) once and applying Eq. (2b) gives, after some algebraic manipulations,

$$\frac{dY}{dX} = -\operatorname{sgn}(\psi_0)\left(\frac{af}{k}\right)^{1/2} \tag{3}$$

where $k = 2 + 2b/a$, and

$$Y = \exp(a\psi/2) \tag{3a}$$

$$f = \frac{1}{a}\left(1 - \frac{k}{k-2}Y^2 + \frac{2}{k-2}Y^k\right). \tag{3b}$$

Eq. (3) can be recast as

$$\frac{\mathrm{d}Y}{\mathrm{d}X} = -\operatorname{sgn}(\psi_0)Q^{1/2} \tag{4}$$

where

$$Q = \frac{1-\varepsilon}{4}\left(1 - \frac{2}{1+\varepsilon}Y^2 + \frac{1-\varepsilon}{1+\varepsilon}Y^{4/(1-\varepsilon)}\right) \tag{4a}$$

$$\varepsilon = \frac{k-4}{k} = \frac{b-a}{b+b}. \tag{4b}$$

The last expression suggests that $|\varepsilon| < 1$. The boundary condition associated with Eq. (3) is

$$Y = Y_0 \text{ at } X = 0 \tag{5}$$

where $Y_0 = \exp(a\psi_0/2)$. Suppose that Y can be expanded as

$$Y = K_0 + \sum_{n=1}^{\infty} \varepsilon^n K_n. \tag{6}$$

Substituting Eq. (6) into Eq. (4) gives

$$\frac{\mathrm{d}K_0}{\mathrm{d}X} + \sum_{n=1}^{\infty} \varepsilon^n \frac{\mathrm{d}K_n}{\mathrm{d}K} = A_0 + \sum_{n=1}^{\infty} \varepsilon^n A_n \tag{7}$$

where

$$A_0 = \frac{1-K_0^2}{2} \tag{7a}$$

$$A_1 = -K_0K_1 - \left(1 - 4K_0^2 + 3K_0^4 - 4K_0^4 \ln K_0\right)/8A_0 \tag{7b}$$

$$\begin{aligned} A_2 = {} & -K_0K_2 - \left[\left(1 - 3K_0^2\right)K_1^2 - 4K_0\left(1 - K_0^2 + 2K_0^2 \ln K_0\right)K_1 \right. \\ & \left. + 2K_0^2\left(1 - K_0^2 + 2K_0^2 \ln K_0 - 2K_0^2 \ln^2 K_0\right)\right]/4A_0 - A_1^2/2A_0 \end{aligned} \tag{7c}$$

$$\ldots$$

Eq. (7) leads to the following system of linear differential equations:

$$\frac{\mathrm{d}K_n}{\mathrm{d}X} = A_n, \qquad n = 0, 1, 2, \ldots \tag{8}$$

The associated boundary conditions can be obtained by substituting Eq. (5) into Eq. (6). We have

$$K_0 = \exp(a\psi_0/2) \text{ at } X = 0 \tag{8a}$$

$$K_n = 0, \qquad n = 1, 2, \ldots, \text{ at } X = 0. \tag{8b}$$

It can be shown that the solution to Eq. (8) subject to Eqs. (8a) and (8b) is (Appendix A)

$$K_0 = \frac{1+Z}{1-Z} \tag{9a}$$

$$K_1 = K_{1,Z} - K_{1,Z}(X=0) \tag{9b}$$

$$K_2 = K_{2,Z} - K_{2,Z}(X=0) \tag{9c}$$

$$\ldots$$

where

$$Z = \left[\tanh\left(\frac{a\psi_0}{4}\right)\right]\exp(-X) \tag{9d}$$

$$K_{1,Z} = \frac{4Z^2}{3(1-Z)^2} = \left(2 + Z + \tfrac{2}{5}Z^2 + \tfrac{1}{5}Z^3 + \tfrac{22}{175}Z^4 + \ldots\right) \tag{9e}$$

$$\begin{aligned} K_{2,Z} = \frac{8}{3(1-Z)^2}\Big[&\left(Z^2 + \tfrac{5}{2}Z^3 + \tfrac{217}{45}Z^4 + \tfrac{187}{30}Z^5 + \ldots\right) \\ &- \left(Z^2 + \tfrac{11}{12}Z^3 + \tfrac{13}{8}Z^4 + \tfrac{211}{120}Z^5 + \ldots\right)K_{1,Z}(X=0) \\ &- \left(\tfrac{3}{16} + \tfrac{3}{8}Z\ln Z - \tfrac{3}{16}Z^2\right)K_{1,Z}^2(X=0)\Big] \end{aligned} \tag{9f}$$

Often, the surface potential as a function of surface charge density is required [18]. We define the scaled surface charge density, p, as [20]

$$p = -aF\sigma/2\varepsilon_0\varepsilon_r RT\kappa \tag{10}$$

where σ is the surface charge density. It can be shown that

$$p = \frac{a}{2}\left(\frac{\mathrm{d}\psi}{\mathrm{d}X}\right)_{X=0} \tag{11}$$

On the basis of Eqs. (3a), (6), (7) and (11), we obtain

$$\begin{aligned} p &= \left(\frac{1}{Y}\frac{\mathrm{d}Y}{\mathrm{d}X}\right)_{X=0} = \exp(-a\psi_0/2)\left[A_0(X=0) + \sum_{n=1}^{\infty}\varepsilon^n A_n(X=0)\right] \\ &\cong -\sinh(a\psi_0/2) + \varepsilon B_1 + \varepsilon^2 B_2 \end{aligned} \tag{12}$$

where

$$B_1 = \frac{\exp(-a\psi_0) - 4 + 3\exp(a\psi_0) - 2a\psi_0\exp(a\psi_0)}{8\sinh(a\psi_0/2)} \tag{12a}$$

$$B_2 = \frac{B_1^2 + 1 - \exp(a\psi_0) + a\psi_0\exp(a\psi_0) - a^2\psi_0^2\exp(a\psi_0)/2}{2\sinh(a\psi_0/2)} \tag{12b}$$

Applying the method proposed by Hsu and Kuo [18], Eq. (12) can be solved for ψ_0 to yield (Appendix A)

$$\psi_0 \cong \frac{2}{a}\left[\ln(q-p) + \varepsilon C_1 + \varepsilon C_2\right] \tag{13}$$

where

$$q^2 = (p^2 + 1) \tag{13a}$$

$$C_1 = -C_3/8pq \tag{13b}$$

$$C_2 = -\left(C_4 - \frac{C_3^2}{8p^2} + 4C_5 + 4C_3^2 C_6\right)/8pq \tag{13c}$$

$$C_3 = (q+p)^2 - 4 + 3(q-p)^2 - 4(q-p)^2 \ln(q-p) \tag{13d}$$

$$C_4 = C_3\left\{1 + \left[(q-p)^2 \ln(q-p)\right]/pq\right\} \tag{13e}$$

$$C_5 = \frac{C_3^2}{64p^2} + 1 - (q-p)^2 + 2(q-p)^2 \ln(q-p) - 2(q-p)^2 \ln^2(q-p) \tag{13f}$$

$$C_6 = \left[1 - \frac{1}{q(q-p)}\right]/64pq = \frac{-1}{64q^2}\,. \tag{13g}$$

The free energy of an electrical double layer, F_{el}, can be calculated by (Appendix A)

$$\begin{aligned} F_{\mathrm{el}} &= \int_0^{\sigma} \phi_0 \mathrm{d}\sigma \\ &= \frac{-2(a+b)C_a^0 RT}{\kappa} \int_0^{p} \psi_0 \mathrm{d}p \\ &\cong \frac{4(a+b)}{a\kappa} C_a^0 RT \left(D_0 + \varepsilon D_1 + \varepsilon^2 D_2\right) \end{aligned} \tag{14}$$

where ϕ_0 is the surface potential, and

$$D_0 = p \ln(p+q) - q + 1 \tag{14a}$$

$$D_1 = \left[-\tfrac{1}{2}\ln\left(\frac{1+q}{p}\right) + q - p\right]\ln(q+p) + 2q - \tfrac{3}{2}q + \frac{\alpha_1}{2} - 2 + \frac{\pi^2}{8} \tag{14b}$$

$$\begin{aligned} D_2 = {} & \tfrac{1}{16}\left[\ln\left(\frac{1+q}{p}\right) + \frac{q^3}{p^2} - q - \frac{2}{q}\right]\ln^2(p+q) \\ & + \tfrac{1}{8}\left[8\ln\left(\frac{1+q}{p}\right) - 6q - \frac{4}{q} + 8p - \frac{1}{p}\right]\ln(p+q) \\ & + \tfrac{1}{8}\left(-18q - \frac{4}{q} + 22p - 8\alpha_1 - \alpha_4\right) + \tfrac{1}{16}\left(45 - 4\pi^2 - \frac{7\pi^2 B_{3/2}}{3}\right). \end{aligned} \tag{14c}$$

In these expressions, α_1 and α_4 are defined in Appendix A, and $B_{3/2}$ is the Bernoulli number of order 3/2.

The entropy of an electrical double layer, S_{el}, is calculated by [11]

$$\begin{aligned} S_{\mathrm{el}} &= -\frac{\partial F_{\mathrm{el}}}{\partial T} \\ &\cong -\frac{3F_{\mathrm{el}}}{2T} + \frac{2(a+b)}{a\kappa} C_a^0 R\left(F_0 + \varepsilon F_1 + \varepsilon^2 F_2\right) \end{aligned} \tag{15}$$

where

$$F_0 = p\ln(p+q) \tag{15a}$$

$$F_1 = \left(q - \frac{1}{2q} - p\right)\ln(p+q) + \frac{p^2}{q} - \frac{p}{2} \tag{15b}$$

$$\begin{aligned} F_2 = {} & \tfrac{1}{16}\left(2q - \frac{2q^3}{p^2} + \frac{2p^2}{p^3}\right)\ln^2(p+q) \\ & + \tfrac{1}{8}\left(\frac{q^2+1}{p} - 6q + \frac{2}{q} - \frac{2p}{q^2} - \frac{4}{q^3} + 7p\right)\ln(p+q) \\ & + \tfrac{1}{8}\left(\frac{13}{q} - 10q - \frac{4p}{q^2} - \frac{4}{q^3} + 16p\right) \end{aligned} \tag{15c}$$

The surface excess of co-ions, Γ, can be evaluated by [11]

$$\begin{aligned} \Gamma &= \frac{-2}{k}\left(\frac{-\sigma}{aF} + \frac{\kappa}{2RT}\frac{\partial F_{\mathrm{el}}}{\partial \kappa}\right) \\ &\cong -2C_a^0\left(G_0 + \varepsilon G_1 + \varepsilon^2 G_2\right)/\kappa \end{aligned} \tag{16}$$

where

$$G_0 = p - q + 1 \tag{16a}$$

$$G_1 = \left[\tfrac{1}{2q} - \tfrac{1}{2}\ln\left(\frac{1+q}{p}\right)\right]\ln(p+q) + 2q - \frac{p^2}{q} - p + \frac{\alpha_1}{2} - 2 + \frac{\pi^2}{8} \tag{16b}$$

$$\begin{aligned} G_2 = {} & \tfrac{1}{16}\left[\ln\left(\frac{1+q}{p}\right) + \frac{3q^3}{p^2} - 3q - \frac{2}{q} - \frac{2p^2}{q^3}\right]\ln^2(p+q) \\ & + \tfrac{1}{8}\left[8\ln\left(\frac{1+q}{p}\right) - \frac{q^2+2}{p} - \frac{6}{q} + \frac{2p}{q^2} + \frac{4}{q^3} + p\right]\ln(p+q) \\ & + \tfrac{1}{8}\left(-8q - \frac{17}{q} + \frac{4p}{q^2} + \frac{4}{q^3} + 6p - 8\alpha_1 - \alpha_4\right) \\ & + \tfrac{1}{16}\left(45 - 4\pi^2 - \frac{7\pi^3 B_{3/2}}{3}\right). \end{aligned} \tag{16c}$$

The amount of co-ions adsorbed near the solid–liquid interface can be calculated by [11]

$$\Gamma = \frac{a}{b\kappa} C_a^0 \int_0^\infty [\exp(b\psi) - 1] \mathrm{d}X. \tag{17}$$

3. Discussion

According to Eq. (4b), ε vanishes for the case of a symmetric electrolyte. In this case, Eqs. (6), (9a) and (9d) lead to

$$\psi = \frac{1 + [\tanh(a\psi_0/4)]\exp(-X)}{1 - [\tanh(a\psi_0/4)]\exp(-X)}. \tag{18}$$

This is consistent with the classic result of Gouy and Chapmann [1]. Note that for electrolytes often encountered in practice, $a,b \leq 3$, and $|\varepsilon| \leq 1/2$. The rate of convergence of Eq. (6) is satisfactory.

Compared with the solution derived by La Mer et al. [2] for the case of a:b electrolytes, the result obtained in the present analysis is more simpler in both mathematical representation and numerical calculation. The former involves an infinite series, and each term contains an integral which needs to be determined numerically. The approach adopted by Hsu and Kuo [11] involves an empirical fourth-order polynomial, which is assumed on the basis of the qualitative behavior of the electrical potential distribution. In contrast, the present perturbation method is mathematically rigorous, and provides essentially the exact solution, if sufficient terms are used in Eq. (6).

If ε is positive, then b > a by Eq. (4b). In this case, a surface is negatively charged and K_n is smaller than unity. The electrical potential increases from a negative value to 0 as the distance from the surface increases from 0 to ∞. The greater the ε, the slower the rate of increase of the electrical potential. That is, for two values of ε, ε_1 and ε_2, if $\varepsilon_1 > \varepsilon_2$, then $|\psi(\varepsilon_1)| > |\psi(\varepsilon_2)|$ at a fixed position.

The performance of the present perturbation method in the prediction of the electrical potential and thermodynamic properties of an electrical double layer is illustrated in Tables 1 and 2. An uncharged surface is chosen as the reference state. The second-order perturbation solution is used, and the exact values are based on the numerical solution of Eq. (1). For the electrical potential, t equally spaced points in the range $0 \leqslant X \leqslant 2$ are

Table 1
Averaged percent deviations (%) of the present perturbation method from the corresponding exact values in the electrical potential and thermodynamic properties of an electrical double layer

a:b	ε	E_ψ	$E_{F_{el}}$	$E_{S_{el}}$	E_Γ
1:2	1/3	3.18	2.31	2.76	2.03
1:3	1/2	4.06	3.49	3.82	2.11
2:1	−1/3	3.22	1.86	2.23	1.59
2:3	1/5	2.47	1.08	1.41	0.93
3:1	−1/2	4.29	3.04	3.26	2.75
3:2	−1/5	2.55	0.82	1.25	0.69

An uncharged surface is chosen as the reference state in the evaluation of the thermodynamic properties. The second-order perturbation solution is used, and the exact values are based on the numerical solution of Eq. (1). Parameters used are: ionic strength = 1 mol/m^3, $T = 298.15$ K, $\varepsilon_r = 78$, and $\psi_0 = -1$. E_ψ, $E_{F_{el}}$, $E_{S_{el}}$, and E_Γ are defined in Eqs. (19) and (20).

Table 2
Averaged percent deviations (%) of the present perturbation method from the corresponding exact values in the electrical potential and thermodynamic properties of an electrical double layer

a:b	ε	E_ψ	$E_{F_{el}}$	$E_{S_{el}}$	E_Γ
1:2	1/3	3.42	2.48	2.82	2.15
1:3	1/2	4.11	3.67	3.94	2.41
2:1	−1/3	2.78	1.61	2.05	1.37
2:3	1/5	2.63	1.15	1.43	1.03
3:1	−1/2	3.96	2.89	3.10	2.60
3:2	−1/5	2.47	0.74	1.02	0.48

An uncharged surface is chosen as the reference state in the evaluation of the thermodynamic properties. The second-order perturbation solution is used, and the exact values are based on the numerical solution of Eq. (1). Parameters used are the same as those in Table 1 except that: ionic strength = 100 mol/m^3. $\psi_0 = -1$. E_ψ, $E_{F_{el}}$, $E_{S_{el}}$, and E_Γ are defined in Eqs. (19) and (20).

chosen, and the electrical potentials at these points are evaluated. The averaged percent deviation in ψ, E_ψ, is defined as

$$E_\psi = \left(\sum_{j=1}^{t} \left| \frac{\psi_j^* - \psi_j}{\psi_j^*} \right| / t \right) \times 100\% \tag{19}$$

where ψ_j is the scaled electrical potential at point j estimated by the second-order perturbation solution, and ψ_j^* the corresponding exact value. The percent deviation in the thermodynamic property P, E_P, is defined as

$$E_P = \left| \frac{P^* - P}{P^*} \right| \times 100\%, \qquad P = F_{el}, S_{el}, \text{or } \Gamma \tag{20}$$

where P denotes the value of the thermodynamic property based on the second-order perturbation solution, and P^* is the corresponding exact value. As can be seen from Tables 1 and 2, the deviations based on the second-order perturbation solution are less than 5% for both low and high ionic strength.

It can be shown that D_0, D_1, and D_2 defined in Eqs. (14a), (14b) and (14c) are of the same sign. Therefore, if ε is positive, then the perturbation result for free energy approaches to the corresponding exact value monotonically, and if ε is negative, then it approaches to that in an oscillating manner. Similar arguments can be applied to the cases of entropy and surface excess of co-ions.

For a positively charged surface, if we define $Y = \exp(-b\psi/2)$, $k = 2 + 2a/b$, and $\varepsilon = (a-b)/(a+b)$, the present analysis leads to the same results as those obtained for a negatively charged surface.

In a study of the effect of ion size on the spatial variation of electrical potential, Bhuiyan et al. [19] considered the case of a planar surface in 1:2, 2:1, and v:v electrolyte solutions. The governing Poisson–Boltzmann equation was solved through direct integration, and an iterative procedure proposed. In contrast to their analysis, an arbitrary a:b electrolyte solution is considered in the present study. A perturbation method is adopted for the resolution of the Poisson–Boltzmann equation, and an approximate analytical solution derived. Compared with the iterative expression of Bhuiyan et al. for the electrical potential, the present analytical result is more desirable. This is because that mathematical manipulations on the electrical potential such as integration and differentiation are necessary in the subsequent estimation of the thermodynamic properties of the system under consideration.

4. Conclusion

In summary, the Poisson–Boltzmann equation for the case a planar charged surface immersed in a general a:b electrolyte solution is solved analytically by adopting a perturbation method. The result obtained is used to derive the free energy, entropy, and surface excess of co-ions of an electrical double layer. We show that the rate of convergence of the present perturbation solution is satisfactory. For example, if the second-order solution is adopted, the deviations in the electrical potential and the thermodynamic properties examined are less than 5%.

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Appendix A

The relations necessary for the derivation of Eq. (7) are summarized as below:

$$\ln Y = \ln\left(\sum_{n=0}^{\infty} \varepsilon^n K_n\right) \cong \ln K_0 + \varepsilon\left(\frac{K_1}{K_0}\right) + \varepsilon^2\left(\frac{K_2}{K_0} - \frac{K_1^2}{2K_0^2}\right) \tag{A1}$$

$$\begin{aligned}\frac{1-\varepsilon}{2(1+\varepsilon)}Y^2 &\cong \tfrac{1}{2}(1-\varepsilon)\left[\sum_{n=0}^{\infty}(-1)^n\varepsilon^n\right]\left[K_0^2 + \varepsilon(2K_0K_1) + \varepsilon^2(2K_0K_2 + K_1^2)\right] \\ &\cong \tfrac{1}{2}K_0^2 + \varepsilon\left(K_0K_1 - K_0^2\right) + \varepsilon^2\left(K_0^2 - 2K_0K_1 + K_0K_2 + \tfrac{K_1^2}{2}\right)\end{aligned} \tag{A2}$$

$$\begin{aligned}\frac{(1-\varepsilon)^2}{4(1+\varepsilon)}Y^{4/(1-\varepsilon)} &\cong \tfrac{1}{4}(1-\varepsilon)^2\left[\sum_{n=0}^{\infty}(-1)^n\varepsilon^n\right]Y^4\left[1 + \frac{4\varepsilon}{1-\varepsilon}\ln Y + \frac{8\varepsilon^2}{(1-\varepsilon)^2}\ln^2 Y\right] \\ &\cong \frac{K_0^4}{4} + \varepsilon\left(K_0^3K_1 - \tfrac{3}{4}K_0^4 + K_0^4\ln K_0\right) \\ &\quad + \varepsilon^2\Big(K_0^4 - 2K_0^3K_1 + \frac{3}{2}K_0^2K_1^2 + K_0^3K_2 \\ &\quad + 4K_0^3K_1\ln K_0 - 2K_0^4\ln K_0 + 2K_0^4\ln^2 K_0\Big)\end{aligned} \quad . \tag{A3}$$

The derivation of Eqs. (9a)–(9c) are based on the expressions below:

$$\mathrm{d}X = -\mathrm{d}Z/Z \tag{A4a}$$

$$K_0 = 1 + 2\sum_{n=1}^{\infty} Z^n \tag{A4b}$$

$$1 - K_0^2 = \frac{-4Z}{(1-Z)^2} = -4\sum_{n=0}^{\infty} nZ^n \tag{A4c}$$

$$\ln K_0 = 2\sum_{n=0}^{\infty}\frac{Z^{2n+1}}{2n+1} \tag{A4d}$$

$$\ln Z = -\sum_{n=1}^{\infty}\frac{(1-Z)^n}{n} \tag{A4e}$$

$$1-3K_0^2=\frac{-2(Z^2+4Z+1)}{(1-Z)^2} \tag{A4f}$$

$$\begin{aligned} P_1 &= \frac{1}{8A_0}\left(1-4K_0^2+3K_0^4-4K_0^4\ln K_0\right)\\ &= \frac{-1}{2(1-Z)^2}\left[(Z^2+4Z+1)-(1+Z)^4\sum_{n=0}^{\infty}\frac{Z^{2n+1}}{2n+1}\right]\\ &= \frac{8Z^2}{3(1-Z)^2}\left(1+Z+\tfrac{3}{5}Z^2+\tfrac{2}{5}Z^3+\tfrac{11}{35}Z^4+\ \dots\right) \end{aligned} \tag{A4g}$$

$$K_{1,Z}=\frac{-1}{I}\int P_1 I\,\mathrm{d}X \tag{A4h}$$

$$P_1^2=\frac{64Z^4}{9(1-Z)^4}\left(1+2Z+\tfrac{11}{5}Z^2+2Z^3+\tfrac{313}{175}Z^4+\ \dots\right) \tag{A4i}$$

$$K_{1,Z}^2=\frac{64Z^4}{9(1-Z)^4}\left(1+Z+\tfrac{13}{20}Z^2+\tfrac{2}{5}Z^3+\tfrac{93}{350}Z^4+\ \dots\right) \tag{A4j}$$

$$P_2=\frac{A_1^2}{2A_0}=-\frac{(1+Z)^2}{4Z}K_1^2-\frac{(1-Z)^2}{4Z}P_1^2-\frac{(1-Z)^2}{2Z}K_1P_1 \tag{A4k}$$

$$\begin{aligned} P_3 &= \frac{1}{4A_0}\left[\left(1-3K_0^2\right)K_1^2-4K_0\left(1-K_0^2+2K_0^2\ln K_0\right)K_1\right.\\ &\quad \left.+2K_0^2\left(1-K_0^2+2K_0^2\ln K_0-2K_0^2\ln^2 K_0\right)\right]\\ &= \frac{Z^2+4Z+1}{4Z}K_1^2-2\frac{1+Z}{1-Z}K_1+2\frac{(1+Z)^3}{Z(1-Z)}\left(\sum_{n=0}^{\infty}\frac{Z^{2n+1}}{2n+1}\right)K_1+\left(\frac{1+Z}{1-Z}\right)^2-\frac{(1+Z)^4}{Z(1-Z)^2}\\ &\quad\times\left[\sum_{n=0}^{\infty}\frac{Z^{2n+1}}{2n+1}-2Z^2\left(1+\tfrac{2}{3}Z^2+\tfrac{23}{45}Z^4+\tfrac{44}{105}Z^6+\ \dots\right)\right] \end{aligned} \tag{A4l}$$

$$K_{2,Z}=\frac{-1}{I}\int(P_3+P_4)I\,\mathrm{d}X \tag{A4m}$$

$$I=(1-Z)^2/Z. \tag{A4n}$$

The expressions necessary for the derivation of Eq. (13) are summarized as below:

$$C_7=-p\left(C_{10}^{-2}-4+3C_{10}^2-4C_{10}^2\ln C_{10}\right)/\left[\left(8p^2+\varepsilon C_3\right)q\right] \tag{A5a}$$

$$C_8=\frac{C_{10}}{q}+\frac{\{[1/q(q-p)]-1\}C_7^2}{2} \tag{A5b}$$

$$C_9=-4p\left(q^2C_7^2+1-C_{10}^2+2C_{10}^2\ln C_{10}-2C_{10}^2\ln^2 C_{10}\right)/\left(8p^2+\varepsilon C_3\right) \tag{A5c}$$

$$C_{10}=(q-p)-\varepsilon\frac{(q-p)C_3}{8pq}+\varepsilon^2\frac{C_3^2}{128p^2q^3} \tag{A5d}$$

Note C_{10} is the first-order approximation of Y_0. Substituting C_{10} into Eqs. (A5a), (A5b) and (A5c) gives

$$C_7 = -\left[C_3 + \varepsilon\left(C_4 - \frac{C_3^2}{8p^2}\right) + \varepsilon^2\left(C_{11} - \frac{C_3C_4}{8p^2} + \frac{C_3^3}{64p^4}\right)\right]\Big/8pq \tag{A6a}$$

$$\begin{aligned} C_8 = -\Bigg\{&\left(C_5 + C_3^2C_6\right) + \varepsilon\left[C_{12} - \frac{C_3C_5}{8p^2} + 2C_3C_6\left(C_4 - \frac{C_3^2}{8p^2}\right)\right] \\ &+ \varepsilon^2\left[C_{13} - \frac{C_3C_{12}}{8p^2} + \frac{C_3^2C_5}{64p^2} + 2C_3C_6\left(C_{11} - \frac{C_3C_4}{8p^2} + \frac{C_3^3}{64p^4}\right) + C_6\left(C_4 - \frac{C_3^2}{8p^2}\right)^2\right]\Bigg\}\Big/2pq \end{aligned} \tag{A6b}$$

$$C_9 = -\left[C_5 + \varepsilon\left(C_{12} - \frac{C_3C_5}{8p^2}\right) + \varepsilon^2\left(C_{13} - \frac{C_3C_{12}}{8p^2} + \frac{C_3^2C_5}{64p^4}\right)\right]\Big/2p \tag{A6c}$$

In these expressions,

$$C_{11} = C_3\left[6pq - \frac{1}{q(q-p)^3} + \frac{q-p}{q} - 4(q-p)\left(\frac{1}{q} + q - p\right)\ln(q-p)\right]\Big/64p^2q^2 \tag{A6d}$$

$$C_{12} = \frac{C_3\left(C_4 - C_3^2/8p^2\right)}{32p^2} + \frac{(q-p)^2C_3\left[\ln^2(q-p)\right]}{2pq} \tag{A6e}$$

$$\begin{aligned} C_{13} = {}& \frac{C_3\left(C_{12} - C_3C_4/8p^2 + C_3^3/64p^4\right)}{32p^2} + \frac{\left(C_4 - C_3^2/8p^2\right)^2}{64p^2} - \frac{(q-p)^2C_3^2}{32p^2q^2} \\ &+ \frac{(q-p)C_3^2\left[-(1/q + q - p)\ln^2(q-p) - 2(q-p)\ln(q-p) + 3(q-p)\right]}{32p^2q^2} \end{aligned} \tag{A6f}$$

Expressing $(\varepsilon C_7 + \varepsilon^2 C_8)$ in terms of the increasing order of ε, Eq. (13) can be recovered.

In the integration of Eq. (14), C_1 and C_2 needed to be expressed in terms of p and q. We have

$$C_1 = \tfrac{1}{2} - \frac{q}{2p} - \frac{p}{2q} + \frac{1}{2pq} + \left(1 - \frac{q}{2p} - \frac{p}{2q}\right)\ln(p+q) \tag{A7a}$$

$$\begin{aligned} C_2 = {}& \left(\frac{q^3}{8p^3} - \frac{q^2}{4p^2} + \frac{q}{2p} - 1 + \frac{p}{2q} - \frac{p^2}{4q^2}\right. \\ &\left. + \frac{p^3}{8q^3} - \frac{q}{4p^3} - \frac{p}{4q^3} + \frac{1}{4p^2} - \frac{1}{2pq} + \frac{1}{4q^2} + \frac{1}{8p^3q} + \frac{1}{8pq^3}\right) \\ &+ \frac{\ln(p+q)}{2}\left(\frac{q^3}{2p^3} - \frac{q^2}{2p^2} + \frac{q}{2p} - 1 + \frac{p}{2q} - \frac{p^2}{2q^2} + \frac{p^3}{2q^3} - \frac{q}{2p^3} - \frac{p}{2q^3} + \frac{1}{pq}\right) \\ &+ \frac{\ln^2(p+q)}{8}\left(\frac{q^3}{p^3} - \frac{q}{p} - \frac{p}{q} + \frac{p^3}{q^3}\right) \end{aligned} \tag{A7b}$$

The following relations are useful:

$$p\,\mathrm{d}p = q\,\mathrm{d}q$$

$$\mathrm{d}\ln(q+p) = \mathrm{d}p/q$$

$$\ln[(1+q)/p] = 2\tanh^{-1}(q-p)$$

$$W = q-p$$

$$\ln W = -\ln(p+q)$$

$$p = (1-W^2)/2W$$

$$q = (1+W^2)/2W$$

$$\mathrm{d}p = -\left[(1+W^2)/2W^2\right]\mathrm{d}W$$

$$\alpha_1 \equiv \int \frac{\ln[(1+q)/p]}{q}\mathrm{d}p = -2\int \frac{\tanh^{-1}W}{W}\mathrm{d}W = -2\sum_{n=0}^{\infty}\frac{W^{2n+1}}{(2n+1)^2}$$

$$\alpha_2 \equiv \int \frac{\tan^{-1}p}{q}\mathrm{d}p = \left[\tan^{-1}p + 2\tan^{-1}(q-p)\right]\ln(p+q) + 2\sum_{n=0}^{\infty}\frac{(-1)^n W^{2n+1}}{(2n+1)^2}$$

$$\alpha_3 \equiv \int \frac{\alpha_1}{q}\mathrm{d}p = 2\sum_{n=0}^{\infty}\frac{W^{2n+1}}{(2n+1)^3}$$

$$\alpha_4 \equiv \int \frac{\ln[(1+q)/p]\ln(p+q)}{q}\mathrm{d}p = -\alpha_1\ln W - \alpha_3$$

$$\int (q^3/p^3)\mathrm{d}p = -\frac{q^3}{2p^2} + \frac{3q}{2} - \tfrac{3}{2}\ln\left(\frac{1+q}{p}\right)$$

$$\int (q^2/p^2)\mathrm{d}p = p - \frac{1}{p}$$

$$\int \frac{q}{p}\mathrm{d}p = q - \ln\left(\frac{1+q}{p}\right)$$

$$\int \frac{p}{q}\mathrm{d}p = q$$

$$\int \frac{p^2}{q^2}\mathrm{d}p = q - \tan^{-1}p$$

$$\int \frac{p^3}{q^3}\mathrm{d}p = q + \frac{1}{q}$$

$$\int \frac{q}{p^3}\mathrm{d}p = -\frac{q}{2p^2} - \tfrac{1}{2}\ln\left(\frac{1+q}{p}\right)$$

$$\int \frac{p}{q^3}\mathrm{d}p = -\frac{1}{q}$$

$$\int \frac{1}{p^2}\mathrm{d}p = -\frac{1}{p}$$

$$\int \frac{1}{pq} \mathrm{d}p = -\ln\left(\frac{1+q}{p}\right)$$

$$\int \frac{1}{q^2} \mathrm{d}p = \tan^{-1} p$$

$$\int \frac{1}{p^3 q} \mathrm{d}p = \frac{-q}{2p^2} + \frac{1}{2} \ln\left(\frac{1+q}{p}\right)$$

$$\int \frac{1}{pq^3} \mathrm{d}p = \frac{1}{q} - \ln\left(\frac{1+q}{p}\right)$$

$$\int \frac{q^3 \ln(p+q)}{p^3} \mathrm{d}p = \left[\frac{3q}{2} - \frac{q^3}{2p^2} - \frac{3}{2} \ln\left(\frac{1+q}{p}\right)\right] \ln(p+q) - p - \frac{1}{2p} + \frac{3\alpha_1}{2}$$

$$\int \frac{q^2 \ln(p+q)}{p^2} \mathrm{d}p = \left(p - \frac{1}{p}\right) \ln(p+q) - q - \ln\left(\frac{1+q}{p}\right)$$

$$\int \frac{q \ln(p+q)}{p} \mathrm{d}p = \left[q - \ln\left(\frac{1+q}{p}\right)\right] \ln(p+q) - p + \alpha_1$$

$$\int \ln(p+q) \mathrm{d}p = p \ln(p+q) - q$$

$$\int \frac{p \ln(p+q)}{q} \mathrm{d}p = q \ln(p+q) - p$$

$$\int \frac{p^2 \ln(p+q)}{q^2} \mathrm{d}p = (p - \tan^{-1} p) \ln(p+q) - q + \alpha_2$$

$$\int \frac{p^3 \ln(p+q)}{q^3} \mathrm{d}p = \left(q + \frac{1}{q}\right) \ln(p+q) - p - \tan^{-1} p$$

$$\int \frac{q \ln(p+q)}{p^3} \mathrm{d}p = \left[\frac{-q}{2p^2} - \tfrac{1}{2} \ln\left(\frac{1+q}{p}\right)\right] \ln(p+q) - \tfrac{1}{2p} + \frac{\alpha_1}{2}$$

$$\int \frac{p \ln(p+q)}{q^3} \mathrm{d}p = -\frac{\ln(p+q)}{q} + \tan^{-1} p$$

$$\int \frac{\ln(p+q)}{p^2} \mathrm{d}p = -\frac{\ln(p+q)}{p} - \ln\left(\frac{1+q}{p}\right)$$

$$\int \frac{\ln(p+q)}{q^2} \mathrm{d}p = (\tan^{-1} p) \ln(p+q) - \alpha_2$$

$$\int \frac{\ln(p+q)}{pq} \mathrm{d}p = -\left[\ln\left(\frac{1+q}{p}\right)\right] \ln(p+q) + \alpha_1$$

$$\int \frac{q^3 \ln^2(p+q)}{p^3} \mathrm{d}p = \left[\frac{3q}{2} - \frac{q^3}{2p^2} - \tfrac{3}{2} \ln\left(\frac{1+q}{p}\right)\right] \ln^2(p+q)$$
$$- \left(2p + \frac{1}{p}\right) \ln(p+q) + 2q - \ln\left(\frac{1+q}{p}\right) + 3\alpha_4$$

$$\int \frac{q\ln^2(p+q)}{p}\mathrm{d}p = \left[q - \ln\left(\frac{1+q}{p}\right)\right]\ln^2(p+q) - 2p\ln(p+q) + 2q + 2\alpha_4$$

$$\int \frac{p\ln^2(p+q)}{q}\mathrm{d}p = q\ln^2(p+q) - 2p\ln(p+q) + 2q$$

$$\int \frac{p^3\ln^2(p+q)}{q^3}\mathrm{d}p = \left(q + \frac{1}{q}\right)\ln^2(p+q) - 2p\ln(p+q) + 2q + 2\alpha_2 - 2(\tan^{-1}p)\ln(p+q)$$

$$\alpha_1(p=0) = -\pi^2/4$$

$$\alpha_2(p=0) = \pi^2 E_{1/2}/4$$

$$\alpha_3(p=0) = 7\pi^2 B_{3/2}/6$$

$$\alpha_4(p=0) = -\alpha_3(p=0)$$

$$\lim_{p\to 0}\left\{[\ln^n(p+q)]/p^n\right\} = 1, n \in R$$

$$\lim_{p\to 0}\left\{[\ln[(1+q)/p]]\ln(P+q)\right\} = 0$$

$$\partial p/\partial T = -p/2T$$

$$\partial p/\partial \kappa = -p/\kappa$$

In these expressions, $E_{1/2}$ and $B_{3/2}$ are, respectively, the Euler number of 1/2 order and the Bernoulli number of 3/2 order.

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