

Coulombic phase transitions in symmetrical quantum systems

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Stimulated by recent investigations of the Coulombic criticality of symmetrical classical charged hard sphere systems by M. E. Fisher and co-workers we undertake an analysis of a mass-symmetrical quantum system. The role of the “smallest distance” between charges plays here the thermal de Broglie wavelength $\Lambda(T) = h/[64\pi mkT]^{1/2}$. A critical point is found at the critical temperature $T_c \approx 7186$ K and density $n_c^* \approx 3.73 \times 10^{21} \text{ cm}^{-3}$. [S1063-651X(96)04809-X]

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I. INTRODUCTION

The discussion of Coulombic phase transitions in classical systems of spheres with equal diameter a and opposite charges $e = e_+ = -e_-$ has a long tradition with a rather controversial discussion about the existence of this transition and the location of the critical point [1–7]. Only precise experiments by Pitzer [8] and the above-mentioned analysis by Fisher and co-workers [1–4] led to some clarification of the situation. It seems to be more or less clear now that Coulombic phase transitions exist and that they are in a first approximation described by a refined Debye-Hückel theory in combination with an appropriate mass action law. Now the question comes up again of whether a corresponding phase transition in quantum plasmas exists or not and where it is located in the phase space T, n . This question also has a long and rather controversial history, which started with the hypothesis developed by Norman and Starostin [9] and led to several estimates of the critical point for gas plasmas [7,10–13] and for solid state plasmas [10,14,15]. Here we take up the question again considering not a real system but the most simple theoretical model we can imagine: light equal masses with opposite charged and equal densities [15]:

$$\begin{aligned} m &= m_+ = m_-, \\ e &= e_+ = -e_-, \\ n &= n_+ = n_-. \end{aligned} \quad (1)$$

We may imagine a system consisting of electrons and positrons (without pair annihilation). Another possible realization are electrons and holes in semiconductors, however, here the masses may not be completely equal and a dielectric constant $D > 1$ should be taken into account. The symmetrical Coulomb system possesses hydrogenlike bound states:

$$E_n = -\frac{me^4}{4D^2\hbar^2n^2}. \quad (2)$$

The two characteristic length scales are the Bohr orbit radius

$$a_B = \frac{2\hbar^2 D}{me^2} \quad (3)$$

and the thermal wavelength

$$\Lambda = (2\pi)^{1/2} \frac{\hbar}{(mkT)^{1/2}}. \quad (4)$$

In fact a_B denotes the distance of closest approach for bound charges and Λ is the corresponding distance for free charges. Thus the quantum case is more difficult than the classical one, where only one length, the diameter of the charges a , exists.

The big advantage of mass-symmetrical systems is that for symmetry reasons all the odd-power contributions (e^{2k} with k odd) to the thermodynamic functions cancel. This fact appears to be a large simplification of the theory and will be exploited below in a similar way as in our previous work on this problem [15].

II. CLASSICAL AND QUANTUM STATISTICS OF SYMMETRICAL COULOMB SYSTEMS

The basic quantity of the classical theory is the pair distribution function, which reads in the Debye-Hückel-Bjerrum approximation

$$\begin{aligned} F_{ab}(r) &= \Theta(r-a) \left[1 - \frac{e_a e_b}{kTD r(1+\kappa a)} \exp[\kappa(a-r)] \right] \\ &+ \sum_{k=2}^{\infty} \frac{1}{k!} \left(\frac{-e_a e_b}{kTD r} \right)^k. \end{aligned} \quad (5)$$

Here the first order contribution to the Boltzmann factor was screened according to Debye-Hückel theory and the other terms were left unscreened according to their short-range character. Carrying out the standard charging procedure we get for the free energy density [6,10]

$$\beta f = 2n[\ln(n\Lambda^3) - 1] - \frac{\kappa^3}{12\pi} \Phi(\kappa a) - n^2 a^3 K(b) + \dots, \quad (6)$$

with

$$b = \frac{e^2}{DkTa},$$

$$\kappa^2 = (8\pi n e^2 / DkT), \tag{7}$$

$$K(b) = 4\pi a^3 \sum_{k=2}^{\infty} \frac{b^{2k}}{(2k)!(3k-3)}, \tag{8}$$

and

$$\Phi(x) = \frac{3}{x^3} [\ln(1+x) - x + 0.5x^2] \approx 1 - \frac{3}{4}x + \frac{3}{5}x^2 - \dots \tag{9}$$

The last contribution to the free energy density in Eq. (6) is exponentially diverging in the bound state region $b \gg 1$. It is useful therefore to rescale according to a chemical picture [12], which introduces the density of free charges n^* and of bound pairs n_0^* with the conservation relations

$$n = n^* + n_0^*, \tag{10}$$

which are related by a Bjerrum-type mass action law

$$\frac{n_0^*}{(n^*)^2} = K(T) \exp[-\kappa abG(\kappa a)], \tag{11}$$

where

$$G(x) = (1+x)^{-1} \approx 1 - x + x^2 - \dots \tag{12}$$

In the chemical picture the free energy density is now

$$\begin{aligned} \beta f^*(\beta, n^*, n_0^*) &= 2n^* [\ln(n^* \Lambda^3) - 1] \\ &+ n_0^* \{ \ln[n_0 \Lambda_0^3 / K(T)] - 1 \} \\ &- \frac{(\kappa)^3}{12\pi} \Phi(\kappa a). \end{aligned} \tag{13}$$

The thermodynamics based on Eqs. (10)–(13) possesses a first order phase transition below the critical temperature [1–6,13]

$$T_c = \frac{1}{b_c} = \frac{1}{16}. \tag{14}$$

The quantum statistics may be developed in analogy to the classical case. Let us first neglect symmetry effects. Then the analogue of Eq. (5) will be the density matrix:

$$\begin{aligned} \rho_{ab} &= \rho_{ab}^{\text{free}} - \left\langle ab \left| \frac{e_a e_b}{kTr} \exp(-\kappa r) \right| ba \right\rangle \\ &+ \left\langle ab \left| \sum_{k=2}^{\infty} \frac{1}{k!} \left(\frac{-e_a e_b}{kTr} \right)^k \right| ba \right\rangle. \end{aligned} \tag{15}$$

Here, ρ_{ab}^{free} is the free particle contribution to the density matrix. The linear contribution was approximated by the matrix element of the Debye potential (i.e., static screening). The higher contributions with respect to the interaction parameter e^2 were not screened at all. The free energy is again in analogy to the classical treatment, found by a charging procedure leading to quantum versions of the involved functions Φ , K , and G . The methods to carry out the traces were ex-

plained in detail in earlier work [10]. It seems remarkable that the result of the explicit calculations may be represented in exactly the same shape as the classical result (6), namely,

$$\beta f = \beta f_{\text{id}} - \frac{\kappa^3}{12\pi} \Phi_q(B) - n^2 a_q^3 K_q(B),$$

with

$$B = \frac{4\sqrt{2}e^2}{DkT\Lambda} = \frac{4e^2 m^{1/2}}{\sqrt{\pi} h (kT)^{1/2}}, \tag{16}$$

$$\Phi_q(x) = {}_1F_1\left(1, \frac{5}{2}, \frac{4}{\pi} x^2\right) + \frac{3\pi}{8x} + \frac{3\pi^2}{32x^3} \left[1 - \exp\left(\frac{4x^2}{\pi}\right) \right], \tag{17}$$

$$K_q(T) = \Lambda^3 \sum_{k=2}^{\infty} \frac{\pi^k \zeta(2k-2)}{k!} \left(\frac{B}{8}\right)^{2k}, \tag{18}$$

where ${}_1F_1$ is a confluent hypergeometric function. The difference between the classical and the quantum case is therefore in the concrete meaning of the parameters and functions: Instead of the classical Bjerrum parameter b we now get the Born parameter by the replacement

$$b \rightarrow B.$$

Furthermore, the classical length is replaced by the quantum length

$$a_q = \frac{\Lambda}{4\sqrt{2}} = \frac{h}{\sqrt{64\pi m kT}}.$$

The classical Bjerrum mass action constant is transformed to a quantum version by

$$K(T) \rightarrow K_q.$$

By introducing the definition of Riemann's ζ function $\zeta(x)$ we get an expression of remarkable simplicity:

$$K_q(T) = \Lambda^3 \sum_{s=1}^{\infty} s^2 [\exp(-\beta E_s) - 1 + \beta E_s], \tag{18'}$$

where E_s are the energy levels defined by Eq. (2). The expression (18') was discussed already by Planck and Brillouin as a convergent version of the hydrogenic partition function and later derived more rigorously by Larkin and others [10]. At this point we wish to stress again that the above considerations lead to the remarkable result that the quantum partition function (18') is in full analogy to the Bjerrum mass action constant.

Finally the mass action function is derived from the free energy as

$$\frac{n_0^*}{(n^*)^2} = K_q(T) \exp[-\kappa a_q B G_q(\kappa a_q)],$$

where G_q is defined as

$$G_q(x) = \frac{\pi}{4x} \left\{ 1 - \exp\left(\frac{4x^2}{\pi}\right) \left[1 - \operatorname{erf}\left(\frac{2x}{\sqrt{\pi}}\right) \right] \right\}, \quad (18'')$$

with $\operatorname{erf}(x)$ denoting the error function.

The quantum versions of the Debye-Hückel functions have a similar shape to the classical ones since their first two terms in the Taylor expansion are identical:

$$\begin{aligned} G_q &= 1 - x + \frac{20}{3\pi} x^2 - \dots, \\ \Phi_q &= 1 - \frac{3}{4}x + \frac{4}{\pi}x^2 - \dots. \end{aligned} \quad (19)$$

The differences appear only in the second order and in the higher order terms. The condition of thermodynamic stability leads to the inequality

$$xB[G(x) + xG'(x)] \leq 4. \quad (20)$$

In the region where the inequality (20) is violated, a first order phase transition of Coulombic type may appear.

Forgetting for a moment the differences between the classical and the quantum expressions for the G functions, i.e., assuming

$$G_q = [1 + x]^{-1} \quad (21)$$

we can repeat the classical analysis [1,6] and find by solving a quadratic equation

$$\begin{aligned} x_c &= 1, \\ B_c &= 16, \\ T_c &= \frac{|E_1|}{4\pi D^2 k_B}, \\ n_c &= \frac{1}{16\pi^4} a_B^{-3}. \end{aligned} \quad (22)$$

More explicitly this gives

$$T_c = 6282/D^2 \quad \text{K}, \quad (23)$$

$$n_c = 5.24 \times 10^{20}/D^2 \quad \text{cm}^{-3}.$$

Without the approximation (21) the stability condition (20) can be analyzed only numerically. We get for the critical parameters the condition

$$B_c = \frac{4}{x_c [G(x_c) + x_c G'(x_c)]}.$$

An approximate solution is

$$x_c = 0.728, \quad B_c = 18.4.$$

We will show in the next section that symmetry effects due to the Fermi character of the charges modify this result.

III. SYMMETRY EFFECTS

A. Structure of thermodynamical functions

In the semiclassical discussion of the previous paragraphs the quantum character of the charges' statistics has so far been neglected. Taking into account the Fermionic antisymmetry into the binary density matrix Eq. (15) leads to rather complicated formulas. By careful analysis of the individual terms, however, it is possible to refer the whole problem more or less to the electron fluid [or one component plasma (OCP)]. Let us—in the spirit of the chemical picture—start with the extensiveness of the free energy density with respect to the different particle species:

$$\beta f = \frac{F(n_0, n_+, n_-)}{k_B T V} = \beta f_0 + \beta f_+ + \beta f_-. \quad (24)$$

Here, the index refers to the charge of the particle. The model system—the vacuum electron-positron plasma, with $D=1$ —consists, as described above, of neutral bosonic bound states and its positive and negative Fermionic constituents of equal mass m_e and charges $\pm e$. For the first term on the right-hand side (rhs) of Eq. (24), then, the classical expression from above can be directly used:

$$\beta f_0 = n_0 [\ln(n_0 \Lambda_0^3) - 1 - \ln \sigma_{\text{PBL}}(T)]. \quad (25)$$

The de Broglie wavelength is given by

$$\Lambda_0 = \frac{h}{\sqrt{2\pi m_0 k_B T}}, \quad (26)$$

where

$$m_0 = \frac{m_+ m_-}{m_+ + m_-} = \frac{1}{2} m_e \quad (27)$$

is the effective mass.

The Planck-Brillouin-Larkin (PBL) sum of states has already been introduced. For bound states of equal masses (which can be scaled onto the hydrogen problem with $m_e/2$) it can be written as

$$\sigma_{\text{PBL}}(\tau) = \sum_s s^2 \left[\exp\left(\frac{1}{2s^2 \tau}\right) - 1 - \frac{1}{2s^2 \tau} \right], \quad (28)$$

where the dimensionless temperature

$$\tau = \frac{k_B T}{|E_1|} \quad (29)$$

in terms of the hydrogen ground state has been introduced.

Note that in βf_0 no interaction has been included. This assumption not only disregards polarizabilities and phase space occupation, but it also assumes a constancy of the bound state itself throughout the density-temperature plane, which cannot be expected in nature. The correlation length of the bound state, the Bohr radius a_B , should be thought of as a variable. A theoretical approach on such a basis has been carried out in [16]. In the presented model, however, the emphasis is put on discussing the principal fermionic effects

in a quantum plasma and not on realistic modeling of the interactions. Thus the given form of βf_0 shall be sufficient.

The basis for the discussion of βf_{\pm} shall be the expansion

$$f_{\pm} = f_{\text{id}} + f_{e^2} + f_{e^4}, \quad (30)$$

representing the first two terms of an expansion with respect to the Coulomb interaction.

The ideal parts of the free energy of distinguishable particles obviously superpose and are given for Fermions as

$$f_{\pm}^{\text{id}} = n^* \tau [I_{1/2}^{-1}(y) - I_{3/2}(\mu = I_{1/2}^{-1}(y))/y], \quad (31)$$

where the degeneracy parameter

$$y = \frac{1}{2} n^* \Lambda_e^3 = 3 \sqrt{\pi} r_s^{-3} \tau^{-3/2} \quad (32)$$

is given in the dimensionless temperature τ and density parameter

$$r_s = \left(\frac{4\pi}{3} n^* \right)^{-1/3} / a_B. \quad (33)$$

Note that the free energy density in Eq. (31) is measured in $|E_1|$ as will be the energy scale from now on. The density n^* shall be shorthand for $n^* = n_+ = n_-$.

The functions I in Eq. (31) are the Fermi functions and their inverses of the indicated order:

$$I_{k/2}(\xi) = \frac{1}{\Gamma(k/2+1)} \int_0^{\infty} \frac{z^{k/2} dz}{e^{z-\xi} + 1}. \quad (34)$$

There is a long history of fit formulas for the Fermi functions. We use a formula given by Zimmermann [17]:

$$I_{1/2}^{-1}(y) = \begin{cases} \ln y + 0.3536y - 0.000495y^2 + 0.000125y^3 & \text{if } y < 5.5 \\ 1.209y^{2/3} - 0.6803y^{-2/3} - 0.85y^{-2} & \text{if } y \geq 5.5, \end{cases} \quad (35)$$

$$I_{3/2}(\mu = I_{1/2}^{-1}(y)) = \begin{cases} y + 0.1768y^2 - 0.0033y^3 + 0.000094y^4 & \text{if } y < 5.5 \\ 0.4836y^{5/3} + 1.3606y^{1/3} - 1.7y^{-1} & \text{if } y \geq 5.5. \end{cases} \quad (36)$$

The e^2 term in Eq. (30) in systems of overall neutrality reduces to the so-called Hartree-Fock term, which describes first order interaction with exchange (see, e.g., [10] and references to earlier work therein). Since exchange can only occur between indistinguishable particles, the Hartree-Fock term decouples for both charged subsystems:

$$f_{e^2} = 2f_{\pm}^{\text{HF}}.$$

For the first two cumulants of the expansion on the rhs of Eq. (30) thus the OCP contributions of the subsystems simply superpose and the following trivial scaling law is established:

$$(f_+(n^*, \tau) + f_-(n^*, \tau))|_{\text{id, HF}} = 2(f_{\pm}^{\text{id}}(n^*, \tau) + f_{\pm}^{\text{HF}}(n^*, \tau)). \quad (37)$$

If in the e^4 term in Eq. (30) the exchange contribution is explicitly excluded, one arrives at the so-called Montroll-Ward (MW) term. For this term in [18] a scaling has been given, referring general symmetrical plasmas to the OCP. The mathematical origin of this scaling is invariance properties of the occurring integrals with respect to the number of species, the charges, the mass ratio, and the dielectric constant in a general multispecies plasma. For our simple model system this scaling reads

$$f_+^{\text{MW}}(n^*, \tau) + f_-^{\text{MW}}(n^*, \tau) = 2f_{\text{OCP}}^{\text{MW}}\left(n^*, \frac{\tau}{2}\right). \quad (38)$$

The form in which the known expansions of the interaction contributions to the free energy shall be incorporated are Padé approximants, which converge correctly to the limiting cases. For the OCP the following structure has been proposed by Ebeling [19] and optimized by Ebeling and Lehmann [15]:

$$\eta_{\text{xc}}^{\text{OCP}} = \frac{U \eta_{\text{xc}}^{(0)} - d_0 r_s^{-3/2} \tau^{-1/2} - d_2 r_s^{-3} \tau^{-1}}{1 + U + R} \quad (39)$$

with the switch functions

$$U = \frac{6}{\pi} c_1 r_s^{-3} \tau^{-3} + 36\pi c_2 r_s^{-6} \tau^{-3}, \quad (40)$$

$$R = c_3 \ln[1 + d_1 r_s^{-3/2} \tau^{-1} / c_3],$$

and the low-temperature limit

$$\eta_{\text{xc}}^{(0)} = -\frac{a_H}{r_s} - 2b_0 \ln \left[1 + \frac{\exp(b_1/2b_0) r_s^{-1/2}}{1 + 2b_0 r_s^{1/2} / (a_M - a_H)} \right]. \quad (41)$$

The Madelung constant a_M has been fitted by Baus, Hansen, Galam, and DeWitt [20–22] in terms of the interaction parameter $\Gamma = 2/(r_s \tau)$:

$$a_M = a_H + [a_1 - a_2 \Gamma^{-3/4} + a_3 \Gamma^{-1} \ln \Gamma + a_4 \Gamma^{-1}] \frac{2}{1 + (1/3\Gamma)^3}. \quad (42)$$

In (39), η can be any of the specific thermodynamical potentials F/N , $G/N = \mu$, E/N (free energy, Gibbs potential, and internal energy per particle). The physical constants a_i , b_i , and d_i as well as the optimized numerical constants c_i are given in Table I for $\eta = \mu$, the chemical potential, since the mass action law below will be expressed in terms of μ .

The formula (39) mixes the different types of terms wherefore the scaling laws (37) and (38) have to be put in by hand in order to achieve the desirable superposition form

$$\eta_{\text{xc},+} + \eta_{\text{xc},-} = 2 \eta_{\text{xc}}^{\text{OCP, scal}}. \quad (43)$$

Deviation from the simple superposition concerns only the constants $d_0^{\text{scal}} = \sqrt{2} d_0$ and $d_1^{\text{scal}} = 2^{3/2} d_1$, referring to the Debye-Hückel static screening term and the so-called ring sum, respectively, which are the low density, high tempera-

TABLE I. Numerical constants for the Padé approximant for the chemical potential μ_{xc} .

a_H	2.389
a_1	1.167
a_2	3.7347
a_3	0.55513
a_4	3.1806
b_0	0.06218
b_1	0.1140
d_0	3.46341
d_1	4.34164
d_2	3
c_1	2.0
c_2	1.5
c_3	6.8

ture limit of the Montroll-Ward term. In the zero temperature limit the temperature scaling as in (38), obviously, becomes meaningless.

In summary we may state that the exchange and correlation contributions to the thermodynamical functions of a symmetrical quantum plasma are largely given (i.e., in low orders of perturbation theory) by the well-studied OCP expressions. Where the simple superposition symmetry is broken at least the formal dependencies on densities and temperature remain intact. Thus, by altering the respective constants, the available fit formulas for the OCP may be employed. We note that in the nondegenerate low density regions the formulas given here are consistent with those given in Sec. II.

B. Mass action law, stability, and critical point

The mass action law (MAL) is, in the chemical picture, a consequence of the equilibrium request $\delta F(n_0, n^*) = 0$. With $\mu^* = \mu^{\text{id}}(n^*, \tau) + \mu_{xc}^{\text{OCP, scal}}(n^*, \tau)$ from Eq. (43) it reads for our symmetrical plasma simply

$$\mu_0 = 2\mu^*. \quad (44)$$

The chemical potential of the bound states is obtained immediately from Eq. (25) as

$$\mu_0 = \tau \ln \left(\frac{n_0 \Lambda_0^3}{\sigma_{\text{PBL}}} \right). \quad (45)$$

If a dimensionless density parameter $r_s^{(0)}$ is defined in analogy to (33) for the bound state density, the MAL can be solved analytically:

$$r_s^{(0)}(r_s, \tau) = \sqrt[3]{12\sqrt{2}\pi\tau^{-1/2}\sigma_{\text{PBL}}^{-1/3}\exp\left[-\frac{2}{3\tau}\mu^*(r_s, \tau)\right]}. \quad (46)$$

It has to be reiterated at this point that this analytical solution is entirely due to the fact that there is no nonideality contribution to μ_0 . Figure 1 shows the solution of Eq. (46) in the critical region, which will be discussed further below.

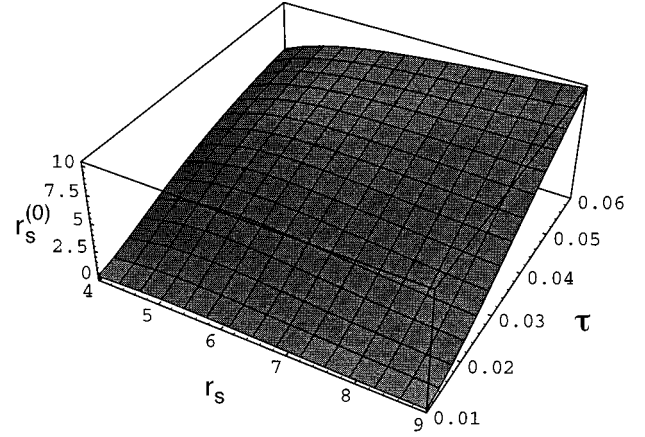


FIG. 1. Critical region; bound states density $r_s^{(0)}$.

If in (46) the nonideality part vanishes and μ^{id} reduces the classical logarithmic expression, the above equation turns into the well-known Saha equation.

By means of Eq. (46) it is also possible to give an expression for the degree of ionization, α , which is the ratio of unbound electron density to overall electron density:

$$\alpha = \frac{n^*}{n^* + n_0}. \quad (47)$$

It is then straightforward to obtain

$$\alpha^{-1} = 1 + \frac{1}{12\sqrt{2}\pi} r_s^3 \tau^{3/2} \sigma_{\text{PBL}} \exp\left(\frac{2\mu^*}{\tau}\right). \quad (48)$$

It may be of interest to observe that Eq. (48) can also be written in terms of the degeneracy parameter:

$$\alpha^{-1} = 1 + \frac{1}{4\sqrt{2}} y^{-1}(r_s, \tau) \sigma_{\text{PBL}} \exp\left(\frac{2\mu^*}{\tau}\right). \quad (49)$$

Figure 2 shows the degree of ionization in vicinity of the critical point.

The stability condition

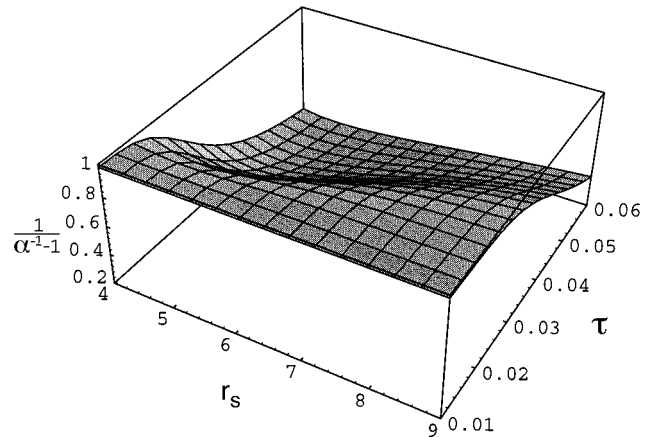


FIG. 2. Critical region; inverse degree of ionization.

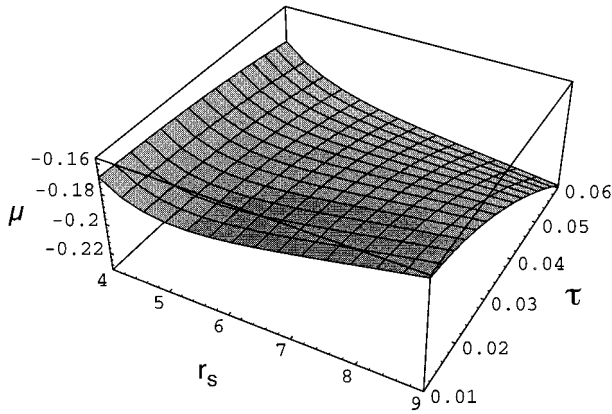


FIG. 3. Critical region; chemical potential $\mu^* = \mu^{\text{id}} + \mu_{\text{xc}}$ in $|E_1|$.

$$\frac{\partial p}{\partial V} \leq 0 \quad (50)$$

can be, using the MAL (44), rewritten as [10]

$$\frac{\partial \mu^*}{\partial r_s} \leq 0, \quad (51)$$

where the equality refers to the critical point (CP), the uniqueness of which is secured by the demand that in any vicinity of it a stable state may be found. In topological terms, the critical point is a saddle point of the μ^* surface over the density-temperature plane. Figure 3 shows the chemical potential μ^* in the vicinity of the critical point, which is found to be located at

$$r_s^{\text{crit}} = 7.562, \quad \tau^{\text{crit}} = 0.045486. \quad (52)$$

Due to the flatness of the μ^* surface, it had been necessary to iterate up to five digits in τ^{crit} in order to have stable four digits in r_s^{crit} . Going back to dimensional entities, one has

$$n_c^* \approx 3.73 \times 10^{21} \text{ cm}^{-3}, \quad T_c \approx 7186 \text{ K}, \quad (53)$$

which is in close correspondence to the critical data estimated in Sec. II.

Bearing in mind that the degree of ionization has above been given in the form $\alpha = \alpha(n^*, n_0(n^*))$, the condition of criticality can also be expressed in terms of α :

$$\alpha_{\text{CP}}(1 - \alpha_{\text{CP}}) = n^* \left. \frac{\partial \alpha}{\partial n^*} \right|_{\text{CP}}, \quad (54)$$

where again the solutions in any nonstable domain have to be disregarded. Condition (56), however, is in Fig. 2 much harder to detect than the saddle point of the chemical potential in Fig. 3. The critical degree of ionization is found as $\alpha_{\text{CP}} \approx 0.445$.

Finally, the degeneracy and interaction parameters at the critical point are evaluated as

$$\begin{aligned} y_c(r_s^{\text{crit}}, \tau^{\text{crit}}) &\approx 1.27, \\ \Gamma_c(r_s^{\text{crit}}, \tau^{\text{crit}}) &\approx 5.81. \end{aligned} \quad (55)$$

This establishes that the CP is located in a region where the Boltzmann statistics already have to be substantially degeneracy corrected and the Padé approximant (39) has already switched to the strongly coupled, low temperature regime.

It can be concluded that the criticality of a vacuum electron-positron plasma is due to an intricate interplay of Coulomb interaction and Fermi statistics. The value of the critical degree of ionization *a posteriori* justifies our theory buildup, which—in terms of interaction—takes into account only the free charges. For other symmetrical plasmas, such electron-hole plasmas in semiconductors, where a dielectric constant ϵ weakens the Coulomb interaction, separate studies have to be carried out.

IV. DISCUSSION

We exploited in this work the formal analogy between the classical Debye-Hückel-Bjerrum theory for symmetrical charged spheres and the corresponding quantum problem of point charges with equal masses. The quantum functions corresponding to the Debye-Hückel-Bjerrum expressions are found. As we have shown, the main difference is the replacement of the hard-sphere diameter by a temperature-dependent distance proportional to the de Broglie wavelength:

$$a \rightarrow a_q(T) = \Lambda / (4\sqrt{2}). \quad (56)$$

In all other respects the classical and the quantum functions have rather similar structure and properties. In order to take into account symmetry effects we exploited the scaling properties of the Hartree-Fock and Motroll-Ward approximations. On this basis the thermodynamical functions of symmetrical plasmas may be reduced to those of electron plasmas for which reliable Padé approximants are available. We have further shown that the critical point is located in the moderately degenerate region, the effect of the Fermion character on the phase transition is studied.

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