Electric microfield distribution at an ion in the classical multicomponent plasma

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A physically motivated criterion for the validity of the Gaussian approximation for the electric microfield distribution at an arbitrary ion in the general multicomponent classical plasma is presented. The exact second moment is obtained from the Onsager proper energy for a unit dipole at the center of a cavity, of radius equal to the ion-sphere radius, embedded in a uniform conducting fluid. A connection between scaling behaviors of the plasma-mixture thermodynamics and its electric microfield distribution is pointed out.

Many recent advances[1–11] in the calculation of the electric microfield distribution in strongly coupled plasmas are based on the Morita-Iglesias formulation[1,2] of the problem. The electric microfield distribution $W(\epsilon)$, namely, the probability density of finding an electric field $E=|\mathbf{E}|$ equal to ϵ at some point, is equivalent to finding the pair distribution function of a classical fluid interaction through a complex pair potential. This motivated two semiempirical types of approximations that are remarkably accurate also for strongly coupled plasmas, especially for $W(\epsilon)$ at a charged point. The first type[3] originates from the adjustable parameter exponential approximation, dubbed APEX. The second, the integral equation approach,[9,10] solves the modified hypernetted-chain equation[12] for the structure of the complex-interaction fluid, by employing a judicious guess for the form of the bridge function.[10] This form is suggested by the exact analytic solution[9] of the mean-spherical model equations for the complex potential. The distribution $W(\epsilon)$ as obtained from the mean-spherical model equations is always Gaussian.[11] It features the exact second moment when applied to evaluate $W(\epsilon)$ at a charged point in classical plasmas.[9] The Gaussian approximation with the exact second moment must be also the exact strong-coupling limit result upon using the hypernetted-chain integral equation for the structure of the complex-interaction fluid.[13]

In this Brief Report I present a criterion for the validity of the Gaussian approximation for the electric microfield distribution at an arbitrarily charged point in the general multicomponent plasma. It has a very simple physical interpretation in terms of the Onsager self-energy of a dipole at the center of a hard sphere with conducting boundary conditions.[14] In particular, I find that the Gaussian behavior of $W(\epsilon)$ at a relatively highly charged ion in a predominantly low-Z plasma may extend to relatively high fields ϵ even for a weakly coupled, experimentally accessible, plasma. The intimate connection between scaling behaviors of the plasma-mixture thermodynamics and its electric microfield distribution is demonstrated. The Gaussian form as the high-density limiting form was derived by Gans[15] and Jackson.[16]

Consider a D-dimensional classical multicomponent plasma, consisting of positive point ions of charges $Z_i e$ and relative concentrations ξ_i, of total number density $n=N/V$ and temperature T, embedded in a rigid, uniform, neutralizing background charge of density $\rho_b=(\sum_i \xi_i Z_i e)N/V=\langle Z\rangle ne$. Using the Wigner-Seitz radius a as the unit of length, define the dimensionless coupling parameter $\Gamma_0=e^2a^{2-D}/k_BT$, and let ea^{1-D} be the electric field unit. From both thermodynamic and structural point of view,[13] the behavior of the strongly coupled plasma is governed by the "confined-atom" (ion-sphere) picture. Specifically, when for any *particular* charged particle in the plasma, of charge Z_i, we have

$$\gamma_i=\Gamma_0\langle Z\rangle^{1-2/D}Z_i^{1+2/D}\gg 1 , \tag{1}$$

then the charge Z_i can be viewed (on the average) as "sitting" at the center of its own (effective hard-core) ion sphere of the background charge density, of radius

$$R_i=a(Z_i/\langle Z\rangle)^{1/D}r_0(\Gamma_{\text{eff}}) , \tag{2}$$

where $r_0(\Gamma_{\text{eff}})\lesssim 1$ varies slowly with the plasma conditions. It is important to note that as long as the particular charge Z_i obeys (1), i.e., $\gamma_i\gg 1$, then this ion-sphere picture for its vicinity holds even when the plasma is overall weakly coupled, namely, when $\Gamma_{\text{eff}}=\sum_j\xi_j\gamma_j<1$. This property can be observed from the analysis[13] of the hypernetted-chain equation for the multicomponent plasma structure, for which $r_0\to 1$ in the limits of $\Gamma_0\to\infty$ or $Z_i\to\infty$. $\Gamma_0(\Gamma_{\text{eff}})$ can be estimated from the variational hard-sphere theory or the "soft" mean-spherical approximation,[12,13] and is about $\frac{1}{2}$ even for $\Gamma_{\text{eff}}=1$.

The self-energy of the ion sphere, containing the point charge and its background, is given by

$$u_i=\alpha_D\gamma_i , \tag{3}$$

where α_D is the ion-sphere Madelung constant (e.g., $\alpha_D=-\frac{9}{10}$ for $D=3$). When the condition (1) is met for *all* the charges in the plasma, then the potential energy per ion of the system is tightly bound from below by the ion-sphere (Onsager) lower bound[17] given by

$$\langle u\rangle=\sum_i\xi_i U_i=\alpha_D\sum_i\xi_i\gamma_i=\alpha_D\Gamma_0\langle Z\rangle^{1-2/D}\langle Z^{1+2/D}\rangle , \tag{4}$$

where $\langle Z^k \rangle = \sum_i \xi_i Z_i^k$. Although formally holding when $\Gamma_{\rm eff} \gg 1$, the validity of the parameters γ_i as the "correct" scaling variables is manifested by, e.g., the linear law[18] for the excess free energy. Defining $f = F^{\rm ex}/NkT$, it reads

$$f_{\rm mix} = \sum_i \xi_i f_0(\gamma_i) \tag{5}$$

and holds remarkably accurately even down to $\Gamma_{\rm eff} \sim 1$. Here $f_0(\Gamma_0)$ is the one-component-plasma (OCP) excess free energy. This holds for the fluid plasma despite the fact that the heat capacity $c_V = \Gamma_0^2 \partial f_0(\Gamma_0)/\partial \Gamma_0$ is markedly different from $D/2$ which is the expected harmonic ion-sphere picture. The ion-sphere picture and the scaling variables γ_i are equally useful for the description of the electric microfield distribution at the charge Z_i.

Independent of the details of the spherically symmetric average distribution of ions around the (central) ion Z_i, the electric field (excluding that due to Z_i itself), inside any spherical cavity around Z_i in which there are no other ions, is given by (using the Newton-Gauss theorem for the enclosed background charge),

$$\mathbf{E} = -\langle Z \rangle \mathbf{x} \ . \tag{6}$$

Here $\mathbf{x} = \mathbf{r}/a$ is a vector from the central charge Z_i and E is in units of ea^{1-D}. The energy cost for a relatively small (see below) fluctuation of the charge distribution around Z_i such that Z_i is displaced from its central position by $\mathbf{x}$ is given by

$$\delta u_i / k_B T = -Z_i \mathbf{E}\cdot\mathbf{x}/2k_B T = \kappa x^2/\langle Z \rangle^2 = \kappa E^2 \ , \tag{7}$$

where

$$\kappa = \Gamma_0 Z_i / 2\langle Z \rangle \ . \tag{8}$$

The probability density for the charge Z_i to be acted upon by an electric field $\mathbf{E}$ is thus given by the Boltzmann factor

$$W(\mathbf{E}) = \exp(-\delta u_i/k_B T) = \exp(-\kappa \mathbf{E}\cdot\mathbf{E}) \ . \tag{9}$$

It is interesting to note that κ as obtained above from the cavity assumption connects well with an exact sum rule: Assuming that (9) holds for all $\mathbf{E}$ then the (normalized) probability for a field magnitude $\epsilon = E$ is

$$P(\epsilon) = 2\kappa^{D/2} \epsilon^{D-1} \exp(-\kappa\epsilon^2)/\Gamma(D/2) \ , \tag{10}$$

with a second moment

$$\langle \epsilon^2 \rangle = \int_0^\infty \epsilon^2 P(\epsilon) d\epsilon = D/2\kappa = D\langle Z \rangle / \Gamma_0 Z_i \tag{11}$$

which is identical to the exact second moment of the electric microfield distribution. In other words, the derived result (10) is identical to the Gaussian distribution tailored to satisfy the exact second moment. The cavity picture leading to (9) automatically limits its validity to fields smaller than the maximal field inside the cavity ϵ_c, i.e., using (2) and (6), we obtain

$$\epsilon < \epsilon_c = \langle Z \rangle (Z_i / \langle Z \rangle)^{1/D} r_0(\Gamma_{\rm eff}) \tag{12a}$$

which for the OCP with $Z=1$ takes the form

$$\epsilon < \epsilon_c = r_0(\Gamma_0) \ . \tag{12b}$$

It should be kept in mind that the physical picture leading to this criterion is tied to the validity of (1), namely, to $\gamma_i \gg 1$ for (12a) and $\Gamma_0 \gg 1$ for (12b). In order to estimate what is "large" γ_i in this context, $(\epsilon_c)^2$ should be compared to (11). The criterion (12) is valid as long as

$$\epsilon_c / (\langle \epsilon^2 \rangle)^{1/2} = r_0(\Gamma_{\rm eff})(\gamma_i/D)^{1/2} > 1 \ . \tag{13}$$

In three dimensions this corresponds roughly to $\gamma_i \geq 10$ (i.e., to $\Gamma_0 \geq 10$ for the OCP), while in two dimensions the range of validity of (12) extends roughly to $\gamma_i \geq 6$. We see from (13) that as D increases then (12) is limited to higher values of γ_i. This analysis is in full agreement with the results in Refs. 3–5. To make the comparison easier note that when (13) is satisfied then ϵ_M, the position of the maximum of $P(\epsilon)$, is well approximated by the Gaussian maximum given by $\epsilon_{{\rm max},G} = [(D-1)\langle Z \rangle / \Gamma_0 Z_i]^{1/2}$ so that (for $D > 1$)

$$\epsilon_c / \epsilon_M \cong r_0(\Gamma_{\rm eff})[\gamma_i/(D-1)]^{1/2} \ . \tag{14}$$

Indeed, the $Z_0 = 10$, $D=3$ results in Fig. 2 of Ref. 4, and the $D=2$ results of Fig. 4 in Ref. 5, corresponding to $\gamma_i = 49.68$ and 32, respectively, are almost perfect Gaussians despite the weak-coupling nature ($\Gamma_{\rm eff} = 1.56$, 2, respectively), of these plasmas. For the OCP with $\Gamma_0 = 10$ (Ref. 3) the ratio (14) is about 1.8, covering almost the full peak. For smaller γ_i when (13) does not hold then the criterion (12) is less accurate but still provides a useful estimate. On the other hand, we see from (12a) and (12b) that $P(\epsilon)$ becomes strictly Gaussian in the formal limit $\gamma_i \to \infty$. In analogy with the ion-sphere potential energy [Eqs. (3) and (4)] we obtain the Gaussian distribution as the natural leading contribution in a strong-coupling expansion for $W(\epsilon)$.

Since the ion-sphere picture for any charge Z_i is an exact asymptotic strong-coupling limit ($\gamma_i \to \infty$) of the hypernetted-chain and mean-spherical theories, then the Gaussian approximation must be their corresponding exact strong-coupling limit. The fact that the mean-spherical approximation maintains its Gaussian asymptotic result at all values of the plasma coupling parameter is an additional feature of this model.[11] The physical mechanism leading to (7) represents a fluctuation that creates a dipole at the test particle. This picture is manifested by the integral equation approach to the Morita-Iglesias formalism, provided we apply directly the Onsager description of the strong-coupling limit.

In the Morita-Iglesias formalism one considers the Fourier transform, $W(k)$, of the electric microfield distribution $W(\epsilon)$, which can be expressed in the form

$$\ln W(k) = -[F(\lambda) - F(\lambda=0)]/k_B T \ . \tag{15}$$

Here $F(\lambda)$ denotes the configurational free energy of the plasma when a "test" imaginary point dipole $i\boldsymbol{\lambda}$ is put at the charged point of type j in question, and eventually $\lambda = (k_B T)k$. The strong-coupling solution of the mean-spherical and hypernetted-chain equations, is described by the Onsager state in which the free-energy difference in (15) is given in terms of the self-energies of the Onsager "atoms." For plasmas these are composed of the point charges at the center of a neutralizing uniformly charged sphere of the ion-sphere radius, with conducting boundary conditions. All terms in (15) cancel out except the contribution of the test particle with the dipole, leading to

$$\ln W(k)_{\text{Onsager}} = k_B T u(\lambda, R_j) , \tag{16a}$$

where

$$u(\lambda, R) = -\lambda^2/2R^3 \tag{16b}$$

is the self-energy of the Onsager object (its proper energy) consisting of a point *real* dipole λ at the center of a sphere of radius R with conducting boundary conditions, i.e., it is the self-energy of the surface-induced charge. Substituting $\lambda=(k_B T)k$ in (16), using the relation $\ln W(k) = -\langle \epsilon \rangle k^2/6$ for the Gaussian distribution, and recalling R_j from (2), we finally obtain

$$\langle \epsilon^2 \rangle = 3k_B T/R_j^3 \tag{17}$$

in agreement with (11).

For any finite value of γ_i there is a small but nonzero probability for close encounters between ions. Thus, although the cavity picture is valid for a semiquantitative description of $W(\epsilon)$ for $\epsilon<\epsilon_c$, the large fields are obtained from nearest neighbors[19] with probability $g(x) = \exp(-\Gamma_0 Z_f Z_i/x)$ for a field $\epsilon = Z_f/x^2$, giving rise to the form

$$P(\epsilon) \sim \epsilon^{-5/2} \exp[-Z_i(\Gamma_0 \epsilon/Z_f)^{1/2}]$$

which vanishes in the formal limit of $\gamma_i \rightarrow \infty$. As γ_i decreases then ϵ_c also decreases while the range of validity of the large fields form (with appropriate screening corrections[19]) extends to lower fields. The transition from the weak-coupling, Holtzmark regime,[19] to the strong-coupling, Gaussian, regime of the electric microfield distribution is like the transition from Debye-Huckel to ion-sphere thermodynamics. Both transitions are gradually built up with increasing test charge and coupling, respectively, by the correlation-hole effect [Eqs. (1) and (2)] with the relevant length scale for the plasma gradually changing from Debye length to pair-exclusion (ion-sphere) radius.

The relevance of the thermodynamic scaling parameter γ_i to the microfield distribution can be further demonstrated. Let $\epsilon_{\max}$ and $P_{\max}$ be the position and value of $P(\epsilon)$ at its maximum, and let $\epsilon_{\max,G}$ and $P_{\max,G}$ be the corresponding values for the Gaussian approximation, namely (e.g., for $D=2,3$),

$$\begin{aligned} &\epsilon_{\max,G} = \kappa^{-1/2}, \quad P_{\max,G} = (4/e)(\kappa/\pi)^{1/2} \quad (D=3) \\ &\epsilon_{\max,G} = (2\kappa)^{-1/2}, \quad P_{\max,G} = (2\kappa/e)^{1/2} \quad (D=2) . \end{aligned} \tag{18}$$

Consider the ratios $y_\epsilon = \epsilon_{\max}/\epsilon_{\max,G}$, $y_p = P_{\max}/P_{\max,G}$ and let $y_\epsilon^{(0)}(\Gamma_0)$, $y_p^{(0)}(\Gamma_0)$ be the results for the one-component plasma (Fig. 1 in Ref. 3). In analogy with the linear law for the free energy (5), we expect that these one-component-plasma functions will describe the general case upon replacing Γ_0 b γ_i,

$$y_\epsilon = y_\epsilon^{(0)}(\gamma_i), \quad y_p = y_p^{(0)}(\gamma_i) . \tag{19}$$

Indeed for $\gamma_i > 1$ all the simulation data for $P(\epsilon)$ at a charged point in both the one- and two-component plasmas (taken, e.g., from the figures in Refs. 3–5) obey remarkably well the scaling relation (19). It should be noted that $y_\epsilon^{(0)}(\Gamma_0)$ and $y_p^{(0)}(\Gamma_0)$ take different forms in two (Ref. 5) and three (Ref. 4) dimensions.

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