

## Charge oscillations in Debye-Hückel theory

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**Abstract.** – The recent generalized Debye-Hückel (GDH) theory is applied to the calculation of the *charge-charge* correlation function,  $G_{ZZ}(\mathbf{r})$ . The resulting expression satisfies both i) the charge neutrality condition *and* ii) the Stillinger-Lovett second-moment condition for all  $T$  and  $\rho_N$ , the overall ion density, and iii) exhibits charge oscillations for densities above a “Kirkwood line” in the  $(\rho_N, T)$ -plane. This corrects the normally assumed DH charge correlations, and, when combined with the GDH analysis of the density correlations, leaves the GDH theory as the *only* complete description of ionic correlation functions, as judged by i)–iii), iv) exact low-density  $(\rho_N, T)$  variation, and v) reasonable behavior near criticality.

A complete theory of ionic fluids, and in particular one which describes the ionic critical region, remains an outstanding challenge for statistical physics [1]. Recent progress has been made at the mean-field level by studies based on the Debye-Hückel (DH) theory of the restricted primitive model (RPM) of electrolytes [2], supplemented with ion pairing, free-ion depletion, and the concomitant dipolar-ionic interactions [3]. A satisfactory theory must also include a description of the ionic correlation functions. However, the conventionally *assumed* DH ion-ion correlation functions, of which there appear to be three varieties, have several shortcomings: the most significant is the absence of a diverging density-density correlation length at the DH critical point, which renders the theory totally uninformative as regards the relevant order-parameter fluctuations. Further, although the predicted charge-charge correlation function,  $G_{ZZ}(\mathbf{r})$ , with the familiar screening decay as  $e^{-\kappa_D r}/r$ , is exact in the low-density limit, it violates the Stillinger-Lovett second-moment condition [4]. Furthermore, there is much evidence indicating that the charge correlations become oscillatory at moderately high densities [5], [6], a phenomenon also missed by the simple screening form.

Similar difficulties arise with the oft-used mean-spherical approximation (MSA), which exhibits, in particular, a complete cancellation of Coulombic effects from the density-density correlation function,  $G_{NN}(\mathbf{r})$ . In this case some improvement has been found by adding an *ad*

*hoc* term to the assumed direct correlation functions and adjusting it to gain consistency with various sum rules; this generalized MSA, or GMSA, yields non-trivial density correlations, including a diverging correlation length at the MSA critical point [7].

However, it fails badly at low densities [8]-[10] and, as explained elsewhere [3], [8], [11], the MSA (and GMSA) appears to be inferior to DH-based theories for describing the critical region. Hence, we have sought to remedy the deficiencies of the DH correlation functions as well and, specifically, to do so in a more natural way. By following the spirit of the DH approximation, we extended the theory to the case of non-uniform, slowly varying ionic densities,  $\rho_{\pm}(\mathbf{r})$ , thus enabling derivation of a Helmholtz free-energy *functional* [8], [10]. Ion correlations may then be obtained by functional differentiation techniques. This generalized Debye-Hückel (GDH) theory was applied to the calculation of  $G_{NN}(\mathbf{r})$ , and provided not only the expected critical divergence of the second-moment density correlation length,  $\xi$ , but also the surprising, *universal* and *exact* divergence of  $\xi$  in the low-density limit [8], [12] (where the GMSA fails by predicting a finite, non-universal value [9]). This testament to the physical validity of the GDH approach motivated the calculation of the charge-charge correlations via GDH theory that is reported here.

We find an expression for  $G_{ZZ}(\mathbf{r}) \equiv \langle [\rho_+(\mathbf{r}) - \rho_-(\mathbf{r})] [\rho_+(\mathbf{0}) - \rho_-(\mathbf{0})] \rangle$  which in the low-density limit approaches the conventional and exact DH result, but which *also* explicitly satisfies the Stillinger-Lovett second-moment condition. Furthermore, it exhibits charge oscillations for densities above a “Kirkwood line” in the density-temperature plane [7]. More concretely, we find for the RPM (equisized hard-spheres with diameters  $a$ , charges  $\pm q_0$ , and solvent dielectric constant  $D$ ) the closed-form, Fourier transform expression for the charge-charge correlation function

$$\hat{G}_{ZZ}(\mathbf{k}; \rho_N, T) = \rho_N k^2 / [\kappa_D^2 + k^2 + a^{-2} g_0(\kappa_D a, ka)], \quad (1)$$

where  $\rho_N = \rho_+ + \rho_-$  is the total ion density, while the Debye parameter is given, as usual, by  $\kappa_D^2 = 4\pi q_0^2 \rho_N / D k_B T$ , and

$$g_0(x, q) = x^2(\cos q - 1) - [2 \ln(1 + x) - 2x + x^2](\cos q - \sin q/q). \quad (2)$$

Expansion in powers of  $k$  yields  $\hat{G}_{ZZ}(\mathbf{k}; \rho_N, T) = (D k_B T / 4\pi q_0^2) k^2 + O(k^4)$ , which demonstrates satisfaction of both the Stillinger-Lovett second-moment condition [4],

$$\int d\mathbf{r} r^2 G_{ZZ}(\mathbf{r}) = -6\rho_N / \kappa_D^2, \quad (3)$$

and the “zeroth-moment” or charge-neutrality condition [2b], [4],

$$\int d\mathbf{r} G_{ZZ}(\mathbf{r}) = 0 \Rightarrow \int_{|\mathbf{r}| > a} d\mathbf{r} G_{ZZ}(\mathbf{r}) = -\rho_N, \quad (4)$$

for all  $\rho_N$  and  $T$ . In the low-density limit (1) becomes  $\hat{G}_{ZZ}(\mathbf{k}) \approx \rho_N k^2 / (\kappa_D^2 + k^2)$ , the exact, universal limiting behavior. By analyzing the poles of (1) we may obtain the predicted large-distance behavior of  $G_{ZZ}(\mathbf{r}; \rho_N, T)$ : from that we find that simple exponential decay persists only up to  $x \equiv \kappa_D a = x_K$ ; for  $x > x_K$  the decay is oscillatory. Numerically we obtain the “Kirkwood value”

$$x_K \simeq 1.17832, \quad (5)$$

which lies in the usually expected range [4]-[7].

Before presenting the GDH calculation, we summarize briefly the conventional DH correlation functions for comparison. Debye-Hückel theory provides an approximate result for  $\phi_\sigma(\mathbf{r})$ ,

the mean electrostatic potential at  $\mathbf{r}$  due to both a charge of type  $\sigma$  fixed at the origin and the corresponding induced charge distribution [2], namely,

$$\begin{aligned}\phi_\sigma^{\text{DH}}(\mathbf{r}) &= q_\sigma/Dr - q_\sigma\kappa_D/D(1 + \kappa_D a), & r < a, \\ \phi_\sigma^{\text{DH}}(\mathbf{r}) &= q_\sigma e^{\kappa_D(r-a)}/D(1 + \kappa_D a), & r \geq a.\end{aligned}\quad (6)$$

The DH thermodynamics uses only the self-potential  $\lim_{\mathbf{r} \rightarrow 0} [\phi_\sigma^{\text{DH}}(\mathbf{r}) - q_\sigma/Dr] = q_\sigma\kappa_D/D(1 + \kappa_D a)$ . In a first effort to obtain correlations, one may supplement the treatment of Debye and Hückel with the formally exact statistical Poisson's equation which, for the RPM, states [2b]

$$\nabla^2 \phi_\sigma(\mathbf{r}) = -(4\pi q_\sigma/D) G_{ZZ}(\mathbf{r})/\rho_N \quad (\sigma = \pm). \quad (7)$$

This yields a  $G_{ZZ}^{\text{Poiss}}$  with a simple screening decay that i) satisfies (4) for all  $\rho_N$  and  $T$ , but ii) violates the second-moment condition everywhere except in the low density,  $\kappa_D a \rightarrow 0$  limit. Furthermore, this Poisson route says nothing whatsoever about the density-density correlations.

A second approach is to parallel the derivation of (6) [2] by putting  $\phi_\sigma^{\text{DH}}(\mathbf{r})$  into a Boltzmann form,  $g_{\sigma\tau}(\mathbf{r} \neq \mathbf{0}) \equiv \langle \rho_\sigma(\mathbf{r}) \rho_\tau(\mathbf{0}) \rangle / \rho_\sigma \rho_\tau \simeq \exp[-\beta q_\sigma \phi_\tau(\mathbf{r})]$  for  $r > a$  with  $g_{\sigma\tau}(\mathbf{r}) = 0$  for  $r < a$ . Then both  $G_{ZZ}^{\text{Bltz}}$  and  $G_{NN}^{\text{Bltz}}$  may be obtained, although the latter displays no sign of the proper critical behavior. However, a more glaring defect of this approach is that  $G_{ZZ}^{\text{Bltz}}(\mathbf{r})$  violates not only the second-moment condition, but *also* the charge-neutrality sum rule! (This follows readily from the inequality  $\sinh x > x$  (when  $x > 0$ ).)

A third path, perhaps the most travelled in the literature, is to linearize the Boltzmann form to get  $g_{\sigma\tau}(\mathbf{r}) \simeq 1 - \beta q_\sigma \phi_\tau(\mathbf{r})$ , for  $r > a$ . This gives the same charge correlations as does the Poisson route, but for  $G_{NN}^{\text{lin}}$  the Coulombic terms cancel completely, as in the MSA.

Now, although (7) is an exact relation, approximate theories are generally inconsistent with respect to some identities; indeed, only the exact solution can satisfy all possible relations. Our GDH theory [8] provides an alternate, formally exact approach to the correlations, which more closely follows the thermodynamic theory and may then be judged on its relative merits.

Our guiding motivation is that a free-energy-functional formulation ensures density correlations that are sensitive to the critical point (*i.e.* the compressibility relation is satisfied by construction); thus, we are led to develop a DH theory for an inhomogeneous electrolyte. As detailed elsewhere [10], the approach is sufficiently general to allow the calculation, via functional differentiation techniques, of all the  $\sigma, \tau$  correlation functions  $G_{\sigma\tau}(\mathbf{r})$  for an arbitrary multi-component, equisized hard-sphere electrolyte; see [10]. For brevity, however, we restrict consideration here to the RPM, for which the *imposed* density variations

$$\rho_\pm(\mathbf{r}) = \bar{\rho}_\pm [1 \pm \Delta \cos \mathbf{k} \cdot \mathbf{r}], \quad (8)$$

(*i.e.* in response to an external potential) result in the Helmholtz free energy

$$\bar{f}[\rho_\sigma(\mathbf{r})] - \bar{f}[\bar{\rho}_\sigma] = -\frac{1}{4} \rho_N^2 \hat{G}_{ZZ}^{-1}(\mathbf{k}) \Delta^2 + O(\Delta^4), \quad (9)$$

where  $\bar{f} \equiv -\beta F/V$  [8], [10]. Thus  $G_{ZZ}$  may be found by expansion in  $\Delta$ .

The generalized Debye charging process yields the free energy [2b], [10], [13]

$$F[\rho_\sigma(\mathbf{r})] = F^{\text{HC}}[\rho_\sigma(\mathbf{r})] + \int_0^1 d\lambda \sum_\sigma \int d^d r' \rho_\sigma(\mathbf{r}') \psi_\sigma(\mathbf{r}', \{\lambda q_\sigma\}), \quad (10)$$

where  $F^{\text{HC}}$  denotes the pure hard-core Helmholtz free energy functional, while the mean electrostatic potential seen by an ion of type  $\sigma$  fixed at  $\mathbf{r}'$  is found from

$$\psi_\sigma(\mathbf{r}') \equiv \lim_{\mathbf{r} \rightarrow \mathbf{r}'} [\phi_\sigma(\mathbf{r}; \mathbf{r}') - q_\sigma/D|\mathbf{r} - \mathbf{r}'|], \quad (11)$$

in which  $\phi_\sigma(\mathbf{r}; \mathbf{r}')$  is the potential at  $\mathbf{r}$  due to *both* the fixed charge at  $\mathbf{r}'$  and the induced charge distribution [8], [10]. (Compare with (6) above, *et seq.*) To calculate  $\phi_\sigma(\mathbf{r}; \mathbf{r}')$ , we begin with the exact *inhomogeneous* version of the statistical Poisson's equation [10],

$$\nabla_r^2 \phi_\sigma(\mathbf{r}; \mathbf{r}') = -(4\pi/D) \sum_\tau q_\tau \rho_\tau(\mathbf{r}) g_{\tau\sigma}(\mathbf{r}; \mathbf{r}'). \quad (12)$$

The DH approximation is to replace the  $g_{\tau\sigma}$  with Boltzmann factors which depend on the potential. However, it is crucial to note that the varying ionic charge densities carry along an imposed overall electrostatic potential  $\Phi(\mathbf{r})$ , determined simply by

$$\nabla^2 \Phi(\mathbf{r}) = -4\pi q_0 \rho_Z(\mathbf{r})/D \equiv -(4\pi/D) \sum_\tau q_\tau \rho_\tau(\mathbf{r}), \quad (13)$$

with appropriate boundary conditions. This is independent of the fixed charge of type  $\sigma$  at  $\mathbf{r}'$ , and therefore should not contribute to the Boltzmann factor for  $g_{\tau\sigma}$ . Hence, we take

$$g_{\tau\sigma}(\mathbf{r}; \mathbf{r}') \simeq \exp[-\beta q_\tau \tilde{\phi}_\sigma(\mathbf{r}; \mathbf{r}')], \quad |\mathbf{r} - \mathbf{r}'| > a, \quad (14)$$

in the spirit of DH, with the “local induced potential”

$$\tilde{\phi}_\sigma(\mathbf{r}; \mathbf{r}') \equiv \phi_\sigma(\mathbf{r}; \mathbf{r}') - \Phi(\mathbf{r}), \quad (15)$$

and, as before,  $g_{\tau\sigma} = 0$  for  $|\mathbf{r} - \mathbf{r}'| < a$ . The need for the separation of  $\phi_\sigma(\mathbf{r}; \mathbf{r}')$  into a background  $\Phi(\mathbf{r})$  and an induced piece  $\tilde{\phi}_\sigma(\mathbf{r}; \mathbf{r}')$  is clear in the limit  $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$ , in which  $\ln[g_{\tau\sigma}(\mathbf{r}; \mathbf{r}')] \rightarrow 0$  while  $\phi_\sigma(\mathbf{r}; \mathbf{r}') \rightarrow \Phi(\mathbf{r})$  [14].

Next one inserts (14) into (12) and makes the second approximation of the DH procedure, namely linearization. This results in the full GDH equation

$$\begin{aligned} \nabla_r^2 \tilde{\phi}_\sigma(\mathbf{r}; \mathbf{r}') &= -(4\pi/D) [q_\sigma \delta(\mathbf{r} - \mathbf{r}') - q_0 \rho_Z(\mathbf{r})], \quad |\mathbf{r} - \mathbf{r}'| \leq a, \\ \nabla_r^2 \tilde{\phi}_\sigma(\mathbf{r}; \mathbf{r}') &= \tilde{\kappa}_D^2(\mathbf{r}) \tilde{\phi}_\sigma(\mathbf{r}; \mathbf{r}'), \quad |\mathbf{r} - \mathbf{r}'| \geq a, \end{aligned} \quad (16)$$

where the spatially varying Debye parameter [6], [8], [10] is defined by  $\tilde{\kappa}_D^2(\mathbf{r}) \equiv (4\pi\beta/D) \sum_\tau q_\tau^2 \rho_\tau(\mathbf{r})$ . The second term on the right-hand side for  $|\mathbf{r} - \mathbf{r}'| \leq a$ , *i.e.* *inside* the hard sphere, is needed to cancel the background charge density  $\rho_Z(\mathbf{r})$  there; it represents an effective “cavity source” term.

To obtain  $G_{ZZ}$  for the RPM we choose the spatially varying densities (8), for which  $\tilde{\kappa}_D^2(\mathbf{r})$  reduces simply to  $\kappa_D^2$ . The resulting GDH equation (16) can be solved readily by Green's function methods [8], [10]. Integrating the self-potential  $\psi_\sigma(\mathbf{r}')$  against the density and charging according to (10) gives the free energy to order  $\Delta^2$ , from which our main result (1) follows by use of (9). Note that the  $q_\sigma \delta(\mathbf{r} - \mathbf{r}')$  source does not contribute directly to the charge-charge correlation function in the simple case of the RPM; rather it is the cavity term and  $\Phi(\mathbf{r})$  that serve to determine  $G_{ZZ}$ .

To elucidate the long-distance behavior of  $G_{ZZ}(\mathbf{r})$ , we solve for the pole,  $k_0$ , of  $\hat{G}_{ZZ}(\mathbf{k})$  that lies closest to the origin in the complex  $k$  plane. The real and imaginary parts of  $k_0$  plotted in fig. 1 were found by solving the coupled equations  $\text{Re}[\hat{G}_{ZZ}^{-1}(k_0)] = \text{Im}[\hat{G}_{ZZ}^{-1}(k_0)] = 0$  numerically, using the Newton-Raphson method. When this pole is purely imaginary, corresponding to the leftmost part of curve (a) in fig. 1,  $G_{ZZ}$  decays monotonically as  $e^{-r/\xi_Z}/r$ , where the screening length is  $\xi_Z = 1/\text{Im}(k_0)$ . In the low-density limit one finds  $\xi_Z^{-1} = \kappa_D [1 + \frac{1}{4}x^2 - \frac{1}{9}x^3 + \frac{19}{96}x^4 + \dots]$  so that  $\xi_Z$  approaches the Debye value  $\xi_D \equiv 1/\kappa_D$ : see the line (c). As  $\kappa_D$  and  $\rho_N/T$  increase, the pole  $k_0$  and a nearby, purely imaginary pole  $k_1$ , curve (d), approach: at the Kirkwood value,  $\kappa_{D,a} = x_K$  (see (5)), they merge, with  $a/\xi_Z = 2.266_0$ , and for larger  $\kappa_D$

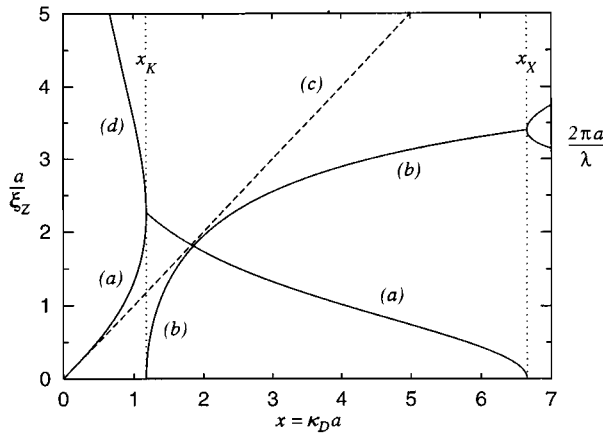


Fig. 1. – Plots versus  $x = (4\pi q_0^2 \rho_N a^2 / D k_B T)^{1/2}$  of (a)  $\text{Im}(k_0 a) = a/\xi_Z$ , the inverse charge-charge correlation length, (b)  $\text{Re}(k_0 a) = 2\pi a/\lambda$ , the inverse charge oscillation wavelength, (c)  $x = \kappa_D a$ , the inverse Debye length, and (d)  $\text{Im}(k_1 a)$ , the subleading pole. Note that within pure DH theory the critical point occurs at  $x_c = 1$  and  $T_c^* = 1/16$ ; in pairing theories based on DH theory  $x_c = 0.9\text{--}1.1$  and  $T_c^* = 0.052\text{--}0.057$  [1], [3], [15].

they become complex, implying the oscillatory decay  $G_{ZZ}(\mathbf{r}) \sim \cos[(2\pi r/\lambda) - \theta_{\kappa_D}] e^{-r/\xi_Z}/r$ , with  $\lambda = 2\pi/\text{Re}(k_0)$  (see plot (b)) and  $\theta_{\kappa_D}$  a phase shift. Hence, charge oscillations occur for densities  $\rho_N^* = \rho_N a^3 > x_K^2 T^*/4\pi \simeq 0.110 T^*$ , where  $T^* \equiv D k_B T a / q_0^2$ . Finally, at  $x = x_X = 6.6523_2$  the poles move to the real axis, *i.e.* they merge with their complex conjugates. Here the oscillations, with wavelength  $\lambda_X \simeq 1.847a$ , are no longer damped; this is suggestive of the onset of crystallization [6] although this region certainly lies beyond the limits of validity of our approximation.

Let us also remark on the inclusion of dipolar ion pairing. Following [3] and [8], one may straightforwardly add pairing to the calculation of  $G_{ZZ}$ . However, in this case, as opposed to the density-density correlations, one expects there to be no major contribution from the pairs, since, in the center-of-mass approximation, the dipolar ion pairs, of density  $\rho_2$ , appear as neutral objects that cannot contribute directly to the charge-charge correlations. One important role of pairing, however, concerns the location of the Kirkwood line in the  $(\rho_N, T)$  plane: owing to the *depletion* of the free ion density,  $\rho_1 \equiv \rho_+ + \rho_- = \rho_N - 2\rho_2$ , the onset of charge oscillations is expected to lie close to the critical region: see [11], [15] for the critical parameters and degree of pairing in the various approximations. Lastly, we mention that the charge-charge correlations in the GDH formulation with pairing still satisfy the sum rules (3) and (4); however, in the Stillinger-Lovett rule (3) the “background” dielectric constant  $D$  that enters the definition of  $\kappa_D$  acquires a linear dependence on  $\rho_2(\rho_N, T)$ . In general, the state-dependence of  $D$  seems an open question [4] although most authors seem to hold that it should be totally absent in the RPM. If that is correct the pairing treatment would require further improvement. (See also [11].)

In conclusion, we have shown how the original theory of Debye and Hückel [2] can be generalized in a natural way, by considering imposed spatially varying ionic densities, to obtain not only the density-density correlations,  $G_{NN}(\mathbf{r})$  [8], but also the charge-charge correlation function  $G_{ZZ}(\mathbf{r})$ . This GDH theory is the only one available that satisfies the important sum rules (3) and (4), gives *exact* low-density results [8], [12], and behaves sensibly in the critical region [8]. The charge correlations exhibit *oscillations* for densities such that  $\kappa_D a > x_K \simeq 1.178$ ; see fig. 1.

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