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On the Dielectric Susceptibility of Classical Coulomb Systems

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This paper reports exact and numerical results on the shape dependence of the dielectric susceptibility of the one-component plasma (O.C.P.) in two dimensions. Some apparently conflicting predictions of phenomenological electrostatics and statistical mechanics are resolved. We prove indeed that, for a disk shaped two-dimensional one-component plasma at the particular temperature $T_0 = q^2(2K_B)^{-1}$, the Clausius–Mossotti relation is exactly fulfilled. It yields a value of the susceptibility which is twice that given by the second moment Stillinger–Lovett sum rule. Similar results are reported for the strip geometry. These discrepancies are explained in terms of shape dependent versus shape independent thermodynamic limits. We report also exact and numerical results on the size dependence of the dielectric susceptibility of the systems quoted above.

KEY WORDS: Dielectric susceptibility; Clausius–Mossotti relation; phenomenological electrostatics; Stillinger–Lovett sum rule; linear response theory; statistical mechanics; one-component plasma; disk and strip geometry; thermodynamic limit.

Let us consider an assembly of n species of charged particles confined in a domain Λ, of volume $|\Lambda|$, in the ν-dimensional euclidean space $\mathbb{R}^\nu$ ($\nu = 2, 3$). The system is assumed to be in thermal equilibrium at the inverse temperature $\beta = 1/K_B T$, where β is Boltzmann's constant.

We know that much information regarding the equilibrium properties of such systems can be derived from the truncated charge–charge correlation function

$$S_\Lambda(x, y) = \langle Q(x)\, Q(y) \rangle - \langle Q(x) \rangle \langle Q(y) \rangle \tag{1}$$

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where x and y are ν-dimensional vectors in Λ, $Q(x)$ is the instantaneous charge density

$$Q(x)=\sum_{\alpha,j} q_{\alpha,j}\delta(x-x_{\alpha,j}) \qquad \begin{array}{l}\alpha=1, 2,..., n\\ j=1, 2,..., N_\alpha\end{array} \tag{2}$$

and where the bracket means ensemble average.

In terms of the one- and two-particle correlation functions

$$\rho_{\alpha,\Lambda}(x)=\sum_{j}\langle\delta(x-x_{\alpha,j})\rangle \quad \text{and} \quad \rho_{\alpha\beta,\Lambda}(x, y)=\sum_{j,k}\langle\delta(x-x_{\alpha,j})\,\delta(y-x_{\beta,k})\rangle$$

with $j\neq k$ if $\alpha=\beta$ and of the truncated two-particle correlation functions

$$\rho^T_{\alpha\beta,\Lambda}(x, y)=\rho_{\alpha\beta,\Lambda}(x, y)-\rho_{\alpha,\Lambda}(x)\,\rho_{\beta,\Lambda}(y)$$

$S_\Lambda(x, y)$ becomes

$$S_\Lambda(x, y)=\sum_{\alpha} q^2_\alpha\rho_{\alpha,\Lambda}(x)\,\delta(x-y)+\sum_{\alpha,\beta} q_\alpha q_\beta\rho^T_{\alpha\beta,\Lambda}(x, y) \tag{3}$$

We consider next the response of the system to an homogeneous external field $E_{1,\text{ext}}$ applied in the x_1 direction. According to the linear response theory, the dielectric susceptibility component $\chi_{11,\Lambda}$ takes the form

$$\chi_{11,\Lambda}=\frac{\beta}{|\Lambda|}\left(\langle P^2_1\rangle-\langle P_1\rangle^2\right) \tag{4}$$

where P_1 is the x_1 component of the instantaneous polarization of the system

$$P=\sum_{\alpha,j} q_{\alpha,j}x_{\alpha,j}=\int_\Lambda dx\, xQ(x) \tag{5}$$

Using Eqs. (5) and (1), Eq. (4) becomes

$$\chi_{11,\Lambda}=\frac{\beta}{|\Lambda|}\int_\Lambda dx\, dy\, x_1 y_1 S_\Lambda(x, y)$$

which can also be written, using Eq. (3)

$$\chi_{11,\Lambda}=\frac{\beta}{|\Lambda|}\int_\Lambda dx\, dy\, x_1 y_1 \left\{\sum_{\alpha} q^2_\alpha\rho_{\alpha,\Lambda}(x)\,\delta(x-y)+\sum_{\alpha,\beta} q_\alpha q_\beta\rho^T_{\alpha\beta,\Lambda}(x, y)\right\} \tag{6}$$

For neutral systems, one can replace the product $x_1 y_1$ by $-\frac{1}{2}(y_1-x_1)^2$ in the integrand of Eq. (6). In this case, the first term of $\chi_{11,\Lambda}$ vanishes and Eq. (6) takes the form

$$\chi_{11,\Lambda} = -\frac{1}{2}\frac{\beta}{|\Lambda|}\sum_{\alpha,\beta} q_\alpha q_\beta \int_\Lambda dx\, dy (y_1 - x_1)^2 \rho^T_{\alpha\beta,\Lambda}(x, y) \tag{7}$$

For isotropic systems, $(y_1 - x_1)^2$ can be replaced by $(y-x)^2/\nu$. Equations (6) and (7) constitute the basic definitions of the susceptibility for finite systems. How to proceed to their thermodynamic limit will be discussed later and will be one of the main objects of this paper.

The interest of the dielectric susceptibility resides in the fact that it gives us information on the state of the system considered. This occurs via the relation between the susceptibility and the dielectric constant ε of the system. We recall that a dielectric state is characterized by $0 < \varepsilon^{-1} \leqslant 1$ and a plasma state by $\varepsilon^{-1} = 0$. According to the phenomenological laws of electrostatics the relation between the dielectric constant and the susceptibility is shape dependent.

If Λ is a ν-dimensional sphere immersed in a vacuum then the susceptibility is isotropic and its relation to the dielectric constant should be governed by the Clausius–Mossotti equation,[1,2] namely

$$\varepsilon^{-1} = \frac{1 - \left(\dfrac{\nu-1}{\nu}\right) 2\pi\chi_D}{1 + \left(\dfrac{(\nu-1)^2}{\nu}\right) 2\pi\chi_D} \qquad \nu = 2, 3 \tag{8}$$

Here the index D means disk or sphere.

It follows from Eq. (8) that the value of the susceptibility, in the plasma state, χ^P_D, is given by

$$\chi^P_D = \frac{\nu}{(\nu-1)\, 2\pi} \qquad \nu = 2, 3 \tag{9}$$

Besides the facts recalled above, there are results given by the statistical mechanics of infinite Coulomb systems related in particular to the perfect screening sum rules, valid for the plasma state.[3,4]

Under the assumptions that (1) the state of the finite system converges to a state of the infinite system defined by correlation functions $\rho_\alpha(x)$, $\rho_{\alpha\beta}(x, y)$, which are stationnary solutions of the BBGKY hierarchy with Maxwellian velocity distribution and that (2) $\rho^T_{\alpha\beta}(x, y)$ decays faster than $|x-y|^{-(\nu+2)}$ then, it is proved that the susceptibility tensor is isotropic and is given by the second moment Stillinger–Lovett sum rule

$$\chi^P_{SL} = -\frac{1}{2\nu}\beta \sum_{\alpha,\beta} q_\alpha q_\beta \int_{\mathbb{R}^\nu} dr\, r^2 \rho^T_{\alpha\beta}(r) = \frac{1}{(\nu-1)\, 2\pi} \tag{10}$$

Notice that in the proof of Refs. 3 and 4, the thermodynamic limit has been taken for the integrand first and then for the integral. This sum rule tells us that, in a perfect conductor, a local excess charge is shielded by a quadrupole free cloud of opposite charge.

We notice at this point that χ_D^P of Eq. (9) is v times χ_{SL}^P of Eq. (10)!

To resolve this contradiction it appeared to us imperative to calculate $\chi_{11,\Lambda}$ explicitly for a given model and to proceed to the thermodynamic limit in a way preserving the shape of the system.

The model considered here is the two-dimensional one-component plasma (O.C.P.), which consists of N identical particles of charge q embedded in a uniform neutralizing background of opposite charge. The Coulomb potential between two particles, at a distance r from one another, is, in two dimensions, given by

$$v(r) = -q^2 \ln\left(\frac{r}{L}\right)$$

where L is a length scale. The dimensionless coupling constant is $\gamma = \beta q^2$ where $\beta = 1/K_B T$ (K_B is Boltzman's constant and T is the temperature).

At the special value $\gamma = 2$, the equilibrium statistical mechanics of the model can be worked out exactly.[5]

We begin with a finite system of N particles immersed in a disk of radius R filled with a background of uniform charge density $-q\rho_b$. Let $Q = -q\pi\rho_b R^2$ be the total charge of the background and let $M = -Q/q = \pi\rho_b R^2$, which may be different from N.

Our aim is to calculate $\chi_{11,\Lambda}(N, M)$ and then to proceed to the thermodynamic limit with $M = N + S$, S finite and $N \to \infty$.

For $\gamma = 2$, it has been shown[6] that $\rho_{1,\Lambda=D}(x)$ and $\rho_{11,\Lambda=D}^T(x, y)$ are given by the following functions of the dimensionless variables $z = \sqrt{\pi\rho_b}(x_1 + ix_2)$, $z' = \sqrt{\pi\rho_b}(y_1 + iy_2)$ and $M = \pi\rho_b R^2$; namely

$$\rho_{1,\Lambda=D}(|z|) = \rho_b e^{-|z|^2} \sum_{l=0}^{N-1} \frac{(|z|^2)^l}{\gamma(l+1, M)} \tag{11}$$

and

$$\rho_{11,\Lambda=D}^T(z, z') = -\rho_b^2 e^{-(|z|^2+|z'|^2)} \sum_{l_1=0}^{N-1} \sum_{l_2=0}^{N-1} \frac{(zz'^*)^{l_1}}{\gamma(l_1+1, M)} \frac{(z^*z')^{l_2}}{\gamma(l_2+1, M)} \tag{12}$$

where z^* is the complex conjugate of z, $|z|^2 = zz^*$, and where $\gamma(l+1, M)$ is the incomplete gamma function defined by

$$\gamma(l+1, M) = \int_0^M e^{-u} u^l \, du \tag{13}$$

Taking advantage of the structure of the above correlation functions, we proceed with the calculation of $\chi_{11,A=D}$ in the form given by Eq. (6). Setting $\sqrt{\pi\rho_b}\,x_1=\frac{1}{2}(z+z^*)$, $\sqrt{\pi\rho_b}\,y_1=\frac{1}{2}(z'+z'^*)$, and $dx=|z|\,d\,|z|\,d\theta/\pi\rho_b$, the first term of Eq. (6), called $\chi^1_{11,A=D}$, becomes

$$\frac{2}{\pi^2 M}\int_0^{\sqrt{M}}|z|\,d\,|z|\,d\theta\left(\frac{z+z^*}{2}\right)^2 e^{-|z|^2}\sum_{l=0}^{N-1}\frac{|z|^{2l}}{\gamma(l+1,M)}$$

Noticing next that the cross terms of the integrand only contribute to the integral, we find, in using definition (13)

$$\chi^1_{11,A=D}=\frac{1}{\pi M}\sum_{l=0}^{N-1}\frac{\gamma(l+2,M)}{\gamma(l+1,M)} \tag{14}$$

Calling $\chi^2_{11,A=D}$ the second term of Eq. (6), and using Eq. (12) for $\rho^T_{11,A=D}(z,z')$, we find

$$\chi^2_{11,A=D}=-\frac{2}{\pi^3 M}\int_0^{\sqrt{M}}\int_0^{2\pi}|z|\,|z'|\,d\,|z|\,d\,|z'|\,d\theta\,d\theta'\left(\frac{z+z^*}{2}\right)\left(\frac{z'+z'^*}{2}\right)$$
$$\cdot\exp(-|z|^2-|z'|^2)\sum_{l_1=0}^{N-1}\frac{(zz'^*)^{l_1}}{\gamma(l_1+1,M)}\sum_{l_2=0}^{N-1}\frac{(z'z^*)^{l_2}}{\gamma(l_2+1,M)}$$

Integrating first over the angular variables and then over the radial ones, we find

$$\begin{aligned}\chi^2_{11,A=D}&=-\frac{1}{2\pi M}\sum_{l_1,l_2=0}^{N-1}\frac{\gamma^2\left(\dfrac{l_1+l_2+1}{2}+1,M\right)}{\gamma(l_1+1,M)\,\gamma(l_2+1,M)}\cdot(\delta_{l_2,l_1+1}\,\delta_{l_1,l_2+1})\\&=-\frac{1}{\pi M}\sum_{l=0}^{N-2}\frac{\gamma^2(l+2,M)}{\gamma(l+1,M)\,\gamma(l+2,M)}\\&=-\frac{1}{\pi M}\sum_{l=0}^{N-2}\frac{\gamma(l+2,M)}{\gamma(l+1,M)}\end{aligned} \tag{15}$$

Notice here the crucial action of the Kronecker δ functions on the upper limit of summation in Eq. (15).

Gathering the results of Eqs. (14) and (15), we find

$$\begin{aligned}\chi_{11,A=D}(N,M)&=\frac{1}{\pi M}\sum_{l=0}^{N-1}\frac{\gamma(l+2,M)}{\gamma(l+1,M)}-\frac{1}{\pi M}\sum_{l=0}^{N-2}\frac{\gamma(l+2,M)}{\gamma(l+1,M)}\\&=\frac{1}{\pi}\left[\frac{1}{M}\frac{\gamma(N+1,M)}{\gamma(N,M)}\right]\end{aligned} \tag{16}$$

This result is valid for any positive numbers N and M. For a neutral system $M = N$ and for $N \to \infty$ the asymptotic expansion of Eq. (16) yields

$$\chi_{11,\Lambda = D}(N, N) = \frac{1}{\pi}\left(1 - \sqrt{\frac{2}{\pi N}} + \frac{2}{N} + O(N^{-3/2})\right) \tag{17}$$

This result proves that, in the thermodynamic limit of an infinite and neutral disk, $\chi_{11,\Lambda = D} = \pi^{-1}$, thus confirming the prediction of electrostatics.

It is appropriate to recall here that if we had used, in Eq. (10), the truncated pair distribution function of the infinite O.C.P. at $\gamma = 2$, we would have obtained

$$\chi = \frac{1}{2}\int_{\mathbb{R}^2} d^2r\, r^2 \rho_b^2 \exp(-\pi\rho_b r^2) = \frac{1}{2\pi}\int_0^\infty du\, u \exp(-u) = \frac{1}{2\pi}$$

which is the Stillinger–Lovett value.

It is instructive to plot the N or size dependence of $\chi_{11,\Lambda = D}(N, N)$ in order to estimate how close a finite system approaches the electrostatics limit. For numerical analysis, Eq. (16) is conveniently written in the form

$$\pi\chi_{11,\Lambda = D}(N, N) = \frac{\int_0^1 dx[e^{1-x} \cdot x]^N}{\int_0^1 dx[e^{(N/N-1)(1-x)} \cdot x]^{N-1}} \tag{18}$$

and the results are plotted in Fig. 1. The relatively slow approach to saturation, proportional to $N^{-1/2} = (\pi\rho_b)^{-1/2} R^{-1}$, is apparent.

We can also investigate the influence of an excess or defect charge of the background. Setting $M = N + S$, the generalization of Eq. (18) reads

$$\pi\chi_{11,\Lambda = D}(N, N+S) = \left(\frac{N}{N+S}\right) \frac{\int_0^{1+S/N} [e^{1-x} \cdot x]^N\, dx}{\int_0^{1+S/N} [e^{(N/N-1)(1-x)} \cdot x]^{N-1}\, dx} \tag{19}$$

and the results are also plotted on Fig. 1 for $S = \pm 10$.

We observe that for negative (positive) values of S the saturation is reached more (less) rapidly.

On Fig. 2, numerical results, obtained by Monte Carlo simulation, are plotted for different values of γ ($\gamma = 0.5, 1, 2, 4, 10$) and N ($N = 10, 30, 44, 100, 176$). It appears clearly that, for $\gamma = 2$, exact and numerical results are very close and that for the other values of γ the susceptibility exhibits a behavior similar to those of $\gamma = 2$. This shows that, althought $\gamma = 2$ is the only exactly soluble case, the result of a susceptibility going like $1/\pi$ in the thermodynamic limit is valid for any γ. We observe finally that for values of γ greater (smaller) than 2 the saturation is reached more (less) rapidly.

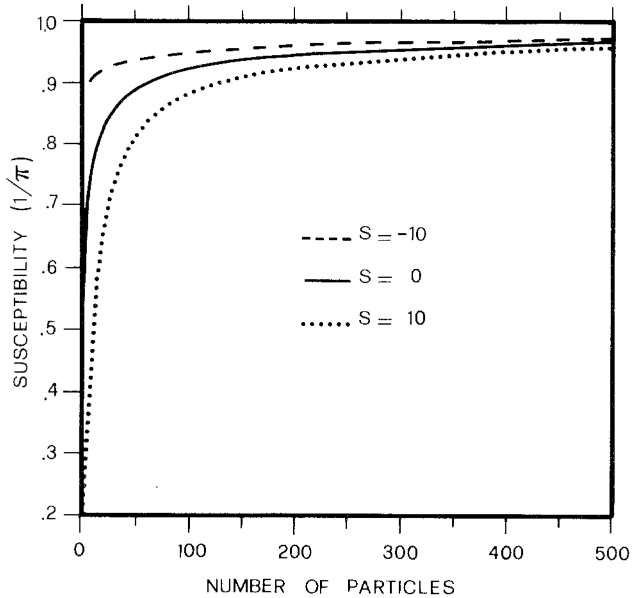

Fig. 1. Dielectric susceptibility of the O.C.P. on a disk at $\gamma = 2$ as a function of the number of particles and for three values of the excess charge of the background.

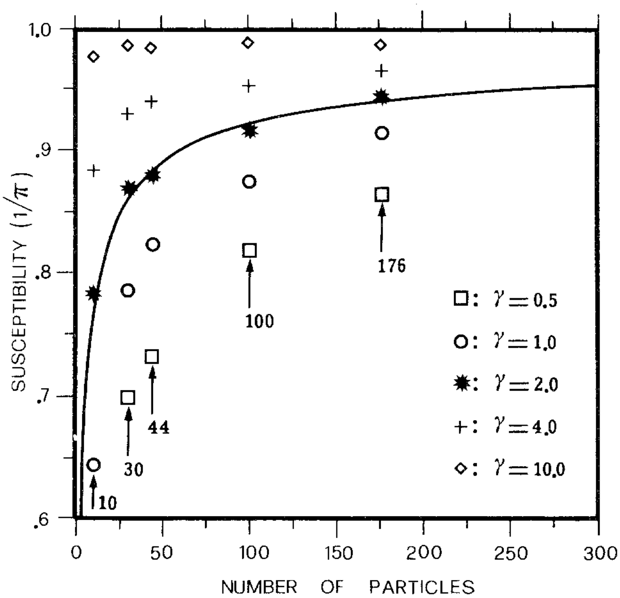

Fig. 2. Dielectric susceptibility of the O.C.P. on a neutral disk as a function of the number of particles and for five values of the coupling parameter γ. The full line corresponds to the soluble case $\gamma = 2$.

The results which are summarized on Figs. 1 and 2 demonstrate conclusively that χ_D tends toward the electrostatics limit. Yet, neither the exact calculation nor the numerical results reported above tell us why χ_D^P is ν times χ_{SL}^P!

We believe that this difference is due to the fact that the susceptibility consists of two parts: a shape-independent bulk part and a shape-dependent surface part. Since, on the basis of Eq. (7), the susceptibility can be viewed as the second moment of a suitably defined truncated pair distribution function, the question amounts to analyze the contributions from pairs of particles of given separation which belong to a surface layer or to the interior of a given domain Λ. This subject will be taken up in a forthcoming paper.

Let us mention finally, that, as in the case of the disk geometry presented above, the results of electrostatics concerning the susceptibility for a strip geometry can also be exactly reproduced by statistical mechanics. Indeed, it has been shown[7] that for the O.C.P. at $\gamma = 2$ and for such a geometry, the one- and two-particle functions can be given explicitly. The details of the proof will be given up in a forthcoming paper.

Here, we shall only briefly recall what is predicted by electrostatics concerning the susceptibility in the plasma state and we shall mention the results obtained by statistical mechanics.

If we consider a strip geometry ($\nu = 2, 3$), electrostatics tells us that the susceptibility tensor is anisotropic. Therefore, we have to make a distinction between the perpendicular component $\chi_\perp$ and the parallel component(s) $\chi_\parallel$ of the susceptibility, whether the external electric field is applied perpendicularly to the surfaces of the strip or parallel. In the first case, the relation between the dielectric constant and the perpendicular component of the susceptibility is given by

$$\varepsilon^{-1} = 1 - (\nu - 1)\, 2\pi\chi_\perp \qquad \nu = 2, 3 \tag{20}$$

and in the second case, we have

$$\varepsilon = 1 + (\nu - 1)\, 2\pi\chi_\parallel \qquad \nu = 2, 3 \tag{21}$$

It follows from the previous relations that the values of the susceptibility in the plasma state are, respectively, given by

$$\chi_\perp^P = \frac{1}{(\nu - 1)\, 2\pi} \qquad \nu = 2, 3 \tag{22}$$

and

$$\chi_\parallel^P = \infty \tag{23}$$

The proof of Eq. (23), using statistical mechanics, is obvious. Indeed, it has been shown rigorously[6] that, for the O.C.P. at $\gamma=2$ and along the surfaces of the strip the truncated two-particle distribution function decays only as an inverse power of the distance r, namely, as r^{-2} for a two-dimensional system. Then it is clear, using Eq. (7), that the parallel component(s) of the susceptibility diverge(s).

As for the perpendicular component of the susceptibility, we prove that it is given by

$$\chi_{\perp}=\frac{1}{2\pi}-\frac{C}{2KL}, \qquad L>0 \tag{24}$$

where

$$K=(2\pi\rho_b)^{1/2} \qquad \lim_{L\to\infty} C=\frac{1}{2\pi^{3/2}}\left(1+\frac{1}{2\sqrt{2}}\right)>0$$

and $2L$ is the distance between the surfaces of the strip.

Thus we see that in the thermodynamic limit ($L\to\infty$), Eq. (24) gives Eq. (22).

Finally, let us point out that in the case of the strip geometry, the Stillinger–Lovett sum rule does not apply, since the susceptibility is anisotropic.

After completion of this work, we learned that, in an unpublished work, B. Jancovici had also obtained the result given by Eq. (16).

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