Exact solution of the mean spherical model for the electric microfield distribution in a plasma

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Iglesias [Phys. Rev. A 27, 2705 (1983)] has reformulated the problem of calculating the electric-microfield distribution in a plasma so that it is equivalent to finding the pair-distribution function of a fluid interacting through a complex potential. We solve the mean spherical model for such a fluid analytically and find that the microfield distribution so obtained is Gaussian with exact second moment.

I. INTRODUCTION

Iglesias¹ has recently demonstrated that the calculation of the fluctuating electric field at an ion in a plasma can be cast into a form that is analogous to the problem of determining the structure of a classical fluid. This formulation, which builds on an earlier observation by Morita,² thus invites the application of standard methods from the theory of fluids to the calculation of the electric-microfield distribution in a plasma. In this paper, we examine one such method, the exact solution of the mean spherical model.

Interest in the plasma electric microfield arises primarily from its influence on the intensity of radiation emitted by an ion immersed in the field. The resulting emission line shape contains information about the electric-microfield distribution in the plasma and so can be used as a probe of plasma conditions.³ A variety of theoretical methods⁴⁻¹¹ has been applied to this problem since it was first analyzed by Holtsmark.¹² Recently, Iglesias's formulation¹ of the question has been used to motivate an empirical but remarkably accurate approximation,¹³ APEX (adjustable parameter exponential approximation).

The mean spherical model (MSM), first proposed by Lebowitz and Percus,¹⁴ has been solved exactly for a variety of molecular potentials. Of particular relevance to the case studied here are the solutions of Palmer and Weeks¹⁵ for charged hard spheres and of Wertheim¹⁶ for dipolar hard spheres.

In the next section, we summarize Iglesias's formulation of the electric-microfield distribution calculation and simplify the generalized Ornstein-Zernike (OZ) equation that enters into it. To the simplified OZ equation we then couple in Sec. III the MSM closure and find that the equations can be readily solved to yield an analytic expression for the generalized direct correlation function and finally for the electric-microfield distribution. The microfield distribution obtained from the MSM turns out to be Gaussian with an exact second moment.

II. ANALYSIS OF THE ORNSTEIN-ZERNIKE EQUATION

The model consists of $N+1$ hard spheres (labeled 0 through N) of diameter σ , each with charge e and all con-

tained in a volume V at temperature $T=(k_B\beta)^{-1}$; a uniform background of the opposite charge serves to neutralize the assembly. (For simplicity, the background is allowed to permeate the spheres.) For a given configuration with no core overlap, the potential energy of the system is

$$U(\mathbf{r}^{N+1}) = \sum_{0 \leq i < j \leq N} e^2/r_{ij} + U_B, \quad (1)$$

where U_B is the contribution of the background and $r_{ij} = |\mathbf{r}_{ij}|$, with

$$\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i. \quad (2)$$

The focus of interest is on the electric field experienced by the charge at $\mathbf{r}_0$; again for a particular configuration, this is

$$\mathbf{E}(\mathbf{r}^{N+1}) = \sum_{j=1}^N \frac{e}{r_{0j}^3} \mathbf{r}_{j0} - e\rho \int d\mathbf{r} \frac{\mathbf{r}_0 - \mathbf{r}}{|\mathbf{r}_0 - \mathbf{r}|^3}, \quad (3)$$

where $\rho \equiv N/V$. The probability density for finding the value ϵ for $\mathbf{E}(\mathbf{r}^{N+1})$ is then

$$\begin{aligned} W(\epsilon) &= \langle \delta(\epsilon - \mathbf{E}(\mathbf{r}^{N+1})) \rangle \\ &= \frac{1}{(2\pi)^3} \int d\mathbf{K} e^{-i\mathbf{K} \cdot \epsilon} \langle \exp[i\mathbf{K} \cdot \mathbf{E}(\mathbf{r}^{N+1})] \rangle \\ &= \frac{1}{2\pi^2\epsilon} \int_0^\infty dK KT(K) \sin(K\epsilon), \end{aligned} \quad (4)$$

where

$$T(K) = \langle \exp[i\mathbf{K} \cdot \mathbf{E}(\mathbf{r}^{N+1})] \rangle \quad (5)$$

is the characteristic function corresponding to ϵ and in the last equality of (4) we have used the fact that it is isotropic in a bulk sample. The angular brackets here denote a canonical ensemble average over configurations weighted by a Boltzmann factor with the configuration energy of Eq. (1) plus the hard-sphere overlap exclusion. Iglesias¹ shows that Eq. (5) may be formally rewritten as

$$T(K) = \exp \left[i\rho \int_0^K d\lambda \int d\mathbf{r} [g(\mathbf{r}, \lambda) - 1] \frac{e\hat{\mathbf{K}} \cdot \hat{\mathbf{r}}}{r^2} \right], \quad (6)$$

where $\hat{\mathbf{K}}$ and $\hat{\mathbf{r}}$ are unit vectors in the $\mathbf{K}$ and $\mathbf{r}$ directions, respectively, and $g(\mathbf{r}_0, \lambda)$ is a generalized pair distribution

function (PDF) for a system interacting with "potential energy"

$$U(\mathbf{r}^{N+1}; \lambda) = U(\mathbf{r}^{N+1}) - i \sum_{j=1}^N \frac{e\lambda \cdot \mathbf{r}_{j0}}{\beta r_{0j}^3}, \quad (7)$$

with $\lambda = \lambda \hat{\mathbf{K}}$.

Equation (6) makes the computation of the electric-microfield distribution in a plasma formally equivalent to the determination of a PDF, albeit for a complex potential. To this end, one defines a corresponding direct correlation function (DCF) through the generalized Ornstein-Zernike equation¹

$$h(\mathbf{r}_{01}, \lambda) = C(\mathbf{r}_{01}, \lambda) + \rho \int d\mathbf{r}_2 h(\mathbf{r}_{02}, \lambda) C(\mathbf{r}_{21}), \quad (8)$$

where $h \equiv g - 1$ and $C(r)$ is the ordinary DCF for the system composed of charged hard spheres. The OZ equation for this latter case is

$$h(r_{12}) = C(r_{12}) + \rho \int d\mathbf{r}_3 h(r_{13}) C(r_{32}). \quad (9)$$

To proceed with the determination of the generalized PDF, one must first put Eq. (8) into a more manageable form. We note from the definition¹ of $g(\mathbf{r}, \lambda)$ that

$$g(\mathbf{r}, -\lambda) = g^*(\mathbf{r}, \lambda), \quad (10)$$

where the asterisk denotes complex conjugate, so that this function may be expanded in the form

$$\begin{aligned} g(\mathbf{r}_{01}, \lambda) &= g(r_{01}, \lambda, \cos\theta_1) \\ &= \sum_{l \text{ even}} g_l(r_{01}, \lambda) P_l(\cos\theta_1) \\ &\quad + i \sum_{l \text{ odd}} g_l(r_{01}, \lambda) P_l(\cos\theta_1). \end{aligned} \quad (11)$$

Here, $\cos\theta_1 = \hat{\mathbf{K}} \cdot \hat{\mathbf{r}}_{01}$ and $P_l(x)$ is the Legendre polynomial of order l ; $C(\mathbf{r}_{01}, \lambda)$ will have a similar expansion. Setting the origin of coordinates at $\mathbf{r}_0$ and orienting the z axis along $\mathbf{K}$, we have further that

$$\begin{aligned} C(r_{12}) &= C((r_{01}^2 + r_{02}^2 - 2r_{01}r_{02}\cos\theta_{12})^{1/2}) \\ &= \sum_l \xi_l(r_{01}, r_{02}) P_l(\cos\theta_{12}) \\ &= \sum_{l,m} \frac{4\pi}{2l+1} \xi_l(r_{01}, r_{02}) Y_{lm}^*(\omega_1) Y_{lm}(\omega_2), \end{aligned} \quad (12)$$

where $\omega_j = (\theta_j, \phi_j)$ is the orientation of $\mathbf{r}_{0j}$,

$$\begin{aligned} \xi_l(r_{01}, r_{02}) &= \frac{2l+1}{2} \int_{-1}^1 d(\cos\theta_{12}) C(r_{12}) P_l(\cos\theta_{12}) \\ &= \frac{2l+1}{2} \int_{|r_{01}-r_{02}|}^{r_{01}+r_{02}} dr_{12} \frac{r_{12}}{r_{01}r_{02}} C(r_{12}) \\ &\quad \times P_l \left[\frac{r_{01}^2 + r_{02}^2 - r_{12}^2}{2r_{01}r_{02}} \right] \end{aligned} \quad (13)$$

from the orthogonality of the Legendre polynomials, and we have used the spherical-harmonic addition theorem¹⁷ in the last equality of (12).

Inserting these expansions into Eq. (8) and again invoking the orthogonality of the Legendre polynomials, we have that

$$r_{01} h_l(r_{01}, \lambda) = r_{01} C_l(r_{01}, \lambda) + 2\pi\rho \int_0^\infty dr_{02} r_{02} h_l(r_{02}, \lambda) \int_{|r_{01}-r_{02}|}^{r_{01}+r_{02}} dr_{12} r_{12} C(r_{12}) P_l \left[\frac{r_{01}^2 + r_{02}^2 - r_{12}^2}{2r_{01}r_{02}} \right], \quad (14)$$

a form of the generalized OZ equation that now involves only real, spherically symmetric functions.

For $l=0$, (14) reduces to the same format as the usual OZ equation for simple liquids,

$$\begin{aligned} r h_0(r, \lambda) &= r C_0(r, \lambda) \\ &\quad + 2\pi\rho \int_0^\infty ds s h_0(s, \lambda) \int_{|r-s|}^{r+s} dt t C(t), \end{aligned} \quad (15)$$

though (15) is linear, rather than quadratic, in the unknowns, as is of course the original Eq. (8).

For $l=1$, we have

$$\begin{aligned} r h_1(r, \lambda) &= r C_1(r, \lambda) \\ &\quad + 2\pi\rho \int_0^\infty dt t C(t) \int_{|r-t|}^{r+t} ds s h_1(s, \lambda) \\ &\quad \times \frac{r^2 + s^2 - t^2}{2rs}, \end{aligned} \quad (16)$$

which can be further simplified as follows. We find first that

$$\begin{aligned} \frac{1}{r} \frac{d}{dr} [r^2 h_1(r, \lambda) - r^2 C_1(r, \lambda)] \\ = 2\pi\rho \int_0^\infty dt t C(t) \int_{|r-t|}^{r+t} ds \frac{1}{s} \frac{d}{ds} [s^2 h_1(s, \lambda)] \end{aligned} \quad (17)$$

after an integration by parts.

Now define a function $h_1^{(-1)}(r, \lambda)$ such that

$$\frac{d}{dr} [r h_1^{(-1)}(r, \lambda)] = \frac{1}{r} \frac{d}{dr} [r^2 h_1(r, \lambda)] \quad (18)$$

and similarly for $C_1^{(-1)}(r, \lambda)$. Then Eq. (17) becomes

$$\begin{aligned} \frac{d}{dr} [r h_1^{(-1)}(r, \lambda) - r C_1^{(-1)}(r, \lambda)] \\ = 2\pi\rho \int_0^\infty dt t C(t) [(r+t) h_1^{(-1)}(r+t, \lambda) \\ - |r-t| h_1^{(-1)}(|r-t|, \lambda)], \end{aligned} \quad (19)$$

which we shall take as the simplified form of the OZ equation for $l=1$, having eliminated $P_1(x)$.

With a generalization of Eq. (18), namely

$$\frac{d}{dr} \left[\frac{1}{r^{k-2}} f_l^{(k-2)}(r) \right] = \frac{1}{r^{2k-1}} \frac{d}{dr} [r^{k+1} f_l^{(k)}(r)], \quad (20)$$

applied recursively as needed, one can reduce all the l -even cases of Eq. (14) to the form (15) containing "lowered" functions $f_l^{(0)}(r)$ and all l -odd cases to the form (19) containing lowered functions $f_l^{(-1)}(r)$. Since no additional terms beyond $l=0$ and 1 will be needed in the sequel, however, we omit the proof. Equation (20) is equivalent to Blum's¹⁸ generalization of Wertheim's¹⁶ transformation.

III. THE MEAN SPHERICAL MODEL

The MSM is formally defined by joining the OZ equation (8) to the exact condition

$$g(r, \lambda) = 0, \quad r < \sigma \quad (21)$$

and the approximation

$$C(r, \lambda) = -\beta\phi(r, \lambda), \quad r > \sigma \quad (22)$$

where ϕ is here the coupling between particle 0 and any other:

$$\beta\phi(r, \lambda) = \beta e^2/r - ie\lambda \cdot \hat{r}/r^2. \quad (23)$$

In terms of coefficients, these equations yield

$$g_l(r, \lambda) = 0 \quad (24)$$

for $r < \sigma$, and

$$C_0(r, \lambda) = -\beta e^2/r, \quad (25a)$$

$$C_1(r, \lambda) = e\lambda/r^2, \quad (25b)$$

$$C_l(r, \lambda) = 0, \quad l > 1 \quad (25c)$$

for $r > \sigma$. With these conditions and Eq. (14), it is apparent that only $l=0$ and 1 terms will contribute to $g(r, \lambda)$.

The radial equation (15) with the closure (24) and (25a) is evidently equivalent to the MSM charged hard-sphere problem,¹⁵ so that

$$C_0(r, \lambda) = C(r), \quad (26)$$

$$g_0(r, \lambda) = g(r).$$

To proceed with the $l=1$ equation, we note first that, from (18),

$$h_1^{(-1)}(r, \lambda) = h_1(r, \lambda) - \frac{1}{r} \int_r^\infty dx h_1(x, \lambda), \quad (27)$$

so that with (24) we get

$$h_1^{(-1)}(r, \lambda) = -\gamma/r, \quad r < \sigma \quad (28)$$

where

$$\gamma = \int_\sigma^\infty dx h_1(x, \lambda), \quad (29)$$

while similarly

$$C_1^{(-1)}(r, \lambda) = 0, \quad r > \sigma. \quad (30)$$

Now define

$$G_1(r, \lambda) = h_1^{(-1)}(r, \lambda) + \gamma/r \quad (31)$$

so that

$$G_1(r, \lambda) = 0, \quad r < \sigma \quad (32)$$

and introduce the Laplace transforms

$$\hat{C}_1(s, \lambda) = \int_0^\infty dr r C_1^{(-1)}(r, \lambda) e^{-sr}, \quad (33)$$

$$\hat{h}_1(s, \lambda) = \int_0^\infty dr r h_1^{(-1)}(r, \lambda) e^{-sr} \quad (34)$$

and similarly for $\hat{C}(s)$, while

$$\hat{G}_1(s, \lambda) = \hat{h}_1(s, \lambda) + \gamma/s. \quad (35)$$

Then from the OZ equation (19) for $l=1$ we find

$$\begin{aligned} \frac{\hat{G}_1(s, \lambda)}{\gamma s} \left[1 + \frac{2\pi\rho}{s} [\hat{C}(s) - \hat{C}(-s)] \right] \\ = \frac{C_1(s, \lambda)}{\gamma s} - \frac{\alpha/\gamma}{s^2} - \frac{4\pi\rho\beta e^2}{s^4}, \end{aligned} \quad (36)$$

where

$$\begin{aligned} \alpha &= \lim_{r \rightarrow 0} [r C_1^{(-1)}(r, \lambda)] \\ &= - \int_0^\sigma dr C_1(r, \lambda) + \lambda e/\sigma. \end{aligned} \quad (37)$$

Equation (36) may be compared with the Laplace-transformed OZ equation for charged hard spheres,¹⁵

$$\hat{g}(s) \left[1 + \frac{2\pi\rho}{s} [\hat{C}(s) - \hat{C}(-s)] \right] = \hat{C}(s) - \frac{A}{s^2} - \frac{4\pi\rho\beta e^2}{s^4}, \quad (38)$$

which suggests a solution of (36) of the form

$$\hat{G}_1(s, \lambda) = \gamma s \hat{g}(s), \quad (39)$$

$$\hat{C}_1(s, \lambda) = \gamma s \hat{C}(s),$$

or

$$h_1^{(-1)}(r, \lambda) = \frac{\gamma}{r} \frac{d}{dr} [r g(r)] - \frac{\gamma}{r}, \quad (40)$$

$$C_1^{(-1)}(r, \lambda) = \frac{\gamma}{r} \frac{d}{dr} [r C(r)],$$

and finally

$$\begin{aligned} h_1(r, \lambda) &= \gamma h'(r), \\ C_1(r, \lambda) &= \gamma C'(r), \end{aligned} \quad (41)$$

where the prime denotes differentiation. The last of these were obtained from the inversion of Eq. (27),

$$h_1(r, \lambda) = h_1^{(-1)}(r, \lambda) - \frac{1}{r^2} \int_0^r dx x h_1^{(-1)}(x, \lambda). \quad (42)$$

More explicitly, we recall the Palmer-Weeks solution¹⁵

$$C(r) = \begin{cases} A + Br + Cr^2 + Dr^3 + Fr^5, & r < \sigma \\ -\beta e^2/r, & r > \sigma \end{cases} \quad (43)$$

to obtain, using (41)

$$C_1(r, \lambda) = \begin{cases} \gamma(B + 2Cr + 3Dr^2 + 5Fr^4), & r < \sigma \\ \gamma\beta e^2/r^2, & r > \sigma \end{cases} \quad (44)$$

which imposes the condition [cf. Eq. (25b)]

$$\gamma = \lambda/\beta e. \quad (45)$$

Further, from (37) and (44) we have

$$\begin{aligned} \alpha/\gamma &= A + \beta e^2/\sigma - C(\sigma^-) \\ &= A + g(\sigma^+). \end{aligned} \quad (46)$$

But for consistency between (36) and (38) we need $\alpha/\gamma = A$ or

$$g(\sigma^+) = 0. \quad (47)$$

This is the condition suggested by Gillan¹⁹ to impose continuity on $g(r)$ and $C(r)$ and uniquely fix the hard-sphere diameter σ when using charged hard spheres to model the one-component plasma. Here it is a requirement. With (47) it follows¹⁵ that $B=0$ in (44).

Our final expression for $C_1(r, \lambda)$ is then

$$C_1(r, \lambda) = \begin{cases} \frac{\lambda}{\beta e} (2Cr + 3Dr^2 + 5Fr^4), & r < \sigma \\ \frac{\lambda e}{r^2}, & r > \sigma \end{cases} \quad (48)$$

Expressions for the coefficients for $r < \sigma$ can be found in Ref. 15.

We note that while condition (47) makes $h_0(r, \lambda)$ and $C_0(r, \lambda)$ continuous, $h_1(r, \lambda)$ and $C_1(r, \lambda)$ still display a discontinuity at $r = \sigma$. In practice, $h_1(r, \lambda)$ is most easily computed using the Fourier transform of Eq. (16),

$$\tilde{h}_1(k, \lambda) = \frac{\tilde{C}_1(k, \lambda)}{1 - \rho \tilde{C}(k)}, \quad (49)$$

where

$$\begin{aligned} \tilde{h}_1(k, \lambda) &= 4\pi \int_0^\infty dr r^2 h_1(r, \lambda) j_1(kr), \\ h_1(r, \lambda) &= \frac{1}{2\pi^2} \int_0^\infty dk k^2 \tilde{h}_1(k, \lambda) j_1(kr), \end{aligned} \quad (50)$$

and similarly for C_1 ; here $j_1(x)$ is the spherical Bessel function of order one.

Finally, returning to Eq. (6), we can now evaluate $T(K)$ for the mean spherical approximation. With the expansion (11), we have in general

$$\ln T(K) = -\frac{4}{3} \pi \rho e \int_0^K d\lambda \int_0^\infty dr h_1(r, \lambda), \quad (51)$$

which yields from (41)

$$\begin{aligned} \ln T(K) &= -\frac{4}{3} \frac{\pi \rho}{\beta} \int_0^K d\lambda \lambda \int_0^\infty dr h'(r) \\ &= -\frac{1}{6} m_2 K^2, \end{aligned} \quad (52)$$

where

$$m_2 = \frac{4\pi \rho}{\beta} \quad (53)$$

is the exact second moment.¹³

IV. CONCLUSIONS

The main result of the foregoing discussion is the analytic expression

$$h(\mathbf{r}, \mathbf{K}) = h(r) + i \frac{K}{\beta e} h'(r) P_1(\cos \theta) \quad (54)$$

for Iglesias's generalized PDF in MSM approximation, along with a similar expression for the DCF. Used directly in Eq. (51), this result yields a Gaussian distribution for $T(K)$ and so also for $W(\epsilon)$. That the second moment of this distribution turns out to be exact is encouraging, but the Gaussian shape itself is an inadequate representation of $W(\epsilon)$.¹³

The inadequacy of the final result can be traced to the MSM closure, Eq. (22), which enforces a linearization of the correlation functions that contains the same harmonic terms as does the potential itself. A similar linearization, in this sense, occurs also in Wertheim's solution of the MSM for hard dipoles,¹⁶ which then goes on to predict a final result, the dielectric constant, that is also not very accurate. (It should be noted that the hard-sphere diameter makes no appearance in any of these results.)

The usefulness of Eq. (54) is to be found elsewhere, in what was in fact the motivation for this work. In his paper, Iglesias¹ plausibly suggested using the hypernetted-chain approximation, in which the exact relation

$$\begin{aligned} g(\mathbf{r}, \mathbf{K}) &= \exp[-\beta \phi(\mathbf{r}, \mathbf{K}) + h(\mathbf{r}, \mathbf{K}) \\ &\quad - C(\mathbf{r}, \mathbf{K}) + B(\mathbf{r}, \mathbf{K})] \end{aligned} \quad (55)$$

is approximated by neglecting the generalized bridge function $B(\mathbf{r}, \mathbf{K})$, to determine the generalized correlation functions. A calculation along these lines, or even one that includes a spherically symmetric $B(r)$ from the one-component plasma (OCP), leads however to mediocre results;²⁰ a better approximation is needed for $B(\mathbf{r}, \mathbf{K})$ for the integral equation approach to succeed. It is natural to look to the MSM solution for some guidance and to consider the analytic form of Eq. (54) to be "appropriate," in some sense, if not used directly in a linearized fashion. Thus, put for the generalized bridge function, which appears in the exponent of $g(\mathbf{r}, \mathbf{K})$ in Eq. (55),

$$B(\mathbf{r}, \mathbf{K}) = B(r) + i \frac{K}{\beta e} B'(r) P_1(\cos \theta), \quad (56)$$

where $B(r)$ is the bridge function of the OCP. Numerical solution of the integral equation that results from this ansatz is found to indeed yield results in excellent agreement with simulation data.²⁰

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