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Critical Behavior of the Correlation Function of a Coulombic Fluid[1]

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An extension of the Ornstein–Zernike theory of critical scattering by a simple fluid to include a type of coulombic system is suggested. The relation between the oscillations of the charge distribution predicted by the second moment condition of Stillinger and Lovett in the restricted primitive model and the critical behavior of the correlation function is also discussed.

KEY WORDS: Electrolyte solutions; critical point; Ornstein–Zernike theory; restricted primitive model; correlation function.

1. INTRODUCTION

Certain evidence has recently been given$^{(1)}$ on the existence of a critical point in the restricted primitive model (RPM) of an ionic solution. The existence of this critical point has been shown through approximate and Monte Carlo calculations of the equation of state.$^{(1)}$ One wonders if it is possible to relate such a critical behavior with a corresponding long-range behavior of the correlation function in an Ornstein–Zernike fashion—in other words, if it is possible to set up a hypothesis, adequate for Coulombic systems, corresponding to the main hypothesis of the (simple fluid) Ornstein–Zernike theory.

In this paper, we consider one possibility for such a hypothesis which seems, at least, reasonable and which provides a qualitative picture of the critical behavior in this type of system.

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Upon introducing the matrices H and C defined as

$$H_{ij}(r) \equiv (\rho_i\rho_j)^{1/2}h_{ij}(r), \qquad C_{ij}(r) \equiv (\rho_i\rho_j)^{1/2}c_{ij}(r), \qquad i,j = 1,2 \tag{1}$$

we obtain the Ornstein–Zernike (OZ) equation for a multicomponent system in the form

$$H(r) = C(r) + \int C(r')H(|\mathbf{r} - \mathbf{r}'|)\, d^3r' \tag{2}$$

Let us consider only systems of particles interacting via a potential of the form

$$u_{ij}(r) = u^s(r) + q_iq_j/\epsilon r, \qquad i,j = 1,2 \tag{3}$$

where u^s is a strictly short-ranged term (the RPM uses a hard-sphere potential for u^s). We now set up the main hypothesis of the OZ theory for this type of Coulombic system by assuming that: $c_{ij}(r) = -\beta q_iq_j/\epsilon r + s_{ij}(r)$, where $s_{ij}(r)$ is short-ranged at, and near, the critical point.

Let us introduce now the matrices R and E defined as

$$R_{ij} \equiv (\rho_i\rho_j)^{1/2}, \qquad E_{ij} \equiv q_iq_jR_{ij}, \qquad i,j = 1,2 \tag{4}$$

Since we suppose overall electroneutrality, $\sum_{i=1}^{2} \rho_iq_i = 0$, R and E satisfy the following relations:

$$ER = RE = 0 \tag{5}$$

$$RR = \rho R \qquad \left(\rho \equiv \sum_{i=1}^{2} \rho_i\right) \tag{6}$$

$$EE = \gamma E \qquad \left(\gamma \equiv \sum_{i=1}^{2} \rho_iq_i^2\right) \tag{7}$$

If we now define the "particle" correlation function $h^s(r)$ with its corresponding direct correlation function $c^s(r)$ as

$$h^s(r) = \tfrac{1}{2}[h_{11}(r) + h_{12}(r)], \qquad c^s(r) = \tfrac{1}{2}[c_{11}(r) + c_{12}(r)] \tag{8}$$

and the "charge" correlation function $h^a(r)$ with its corresponding direct correlation function $c^a(r)$ as

$$h^a(r) = \frac{1}{2q^2}[h_{11}(r) - h_{12}(r)], \qquad c^a(r) = \frac{1}{2q^2}[c_{11}(r) - c_{12}(r)] \tag{9}$$

then we can write H and C as

$$H(r) = h^s(r)R + h^a(r)E \tag{10a}$$

$$C(r) = c^s(r)R + c^a(r)E \tag{10b}$$

By using Eqs. (10), along with Eqs. (5)–(7), we can write the OZ equation in two separate (but coupled, in general) OZ integral equations, one involving h^s and c^s, and the other involving h^a and c^a:

$$h^s(r) = c^s(r) + \rho \int c^s(r')h^s(|\mathbf{r} - \mathbf{r}'|)\, d^3r' \tag{11}$$

$$h^a(r) = c^a(r) + \gamma \int c^a(r')h^a(|\mathbf{r} - \mathbf{r}'|)\, d^3r' \tag{12}$$

Let us now write the OZ integral equation [Eqs. (10a), (11), and (12)] in Fourier space, where we now have

$$\hat{H}(k) = \frac{\hat{c}^s(k)}{1 - \rho\hat{c}^s(k)} R + \frac{\hat{c}^a(k)}{1 - \gamma\hat{c}^a(k)} E \tag{13}$$

with

$$\hat{C}(k) = \hat{c}^s(k)R + \hat{c}^a(k)E \tag{14}$$

According to our above OZ assumption, we also have

$$\hat{C}(k) = -(4\pi\beta/\epsilon)(1/k^2)E + \hat{S}(k) \tag{15}$$

where

$$S_{ij}(r) = (\rho_i\rho_j)^{1/2} s_{ij}(r) \tag{16}$$

Also, with the notation of Eqs. (8) and (15), we have

$$\hat{S}(k) = \hat{c}^s(k)R + \left[\hat{c}^a(k) + \frac{4\pi\beta}{\epsilon}\frac{1}{k^2}\right]E \tag{17}$$

Thus, our main hypothesis can also be stated as: $\hat{C}(k)$ is a meromorphic function in k^2, with $-(4\pi\beta/\epsilon)(1/k^2)E$ as its only singular term at $k^2 = 0$. Or, in other words, $\hat{S}(k)$ is analytic in a neighborhood of $k^2 = 0$ and consequently $\hat{c}^s(k)$ and $\hat{c}^e(k)$ can be expanded in a Taylor series around $k^2 = 0$:

$$\hat{c}^s(k) = c_0{}^s + c_1{}^s k^2 + \cdots, \qquad \hat{c}^e(k) = \hat{c}_0{}^e + \hat{c}_1{}^e k^2 + \cdots \tag{18}$$

where $\hat{c}^e(k)$ is defined as

$$\hat{c}^e(k) \equiv \hat{c}^a(k) + (4\pi\beta/\epsilon)(1/k^2) \tag{19}$$

We now eliminate the function $\hat{c}^a$ (which is singular at $k = 0$) from Eq. (13) in favor of the function $\hat{c}^e$ (which, according to our hypothesis, is analytic at $k = 0$), thus obtaining

$$\begin{aligned}\hat{H}(k) &= \hat{h}^s(k)R + \hat{h}^a(k)E \\ &= \frac{\hat{c}^s(k)}{1 - \rho\hat{c}^s(k)} R + \frac{-(4\pi/\epsilon kT) + k^2\hat{c}^e(k)}{\kappa^2 + [1 - \gamma\hat{c}^e(k)]k^2} E\end{aligned} \tag{20}$$

where $\kappa^2 = (4\pi/\epsilon kT)\gamma$.

From this equation and from our main hypothesis it is already obvious that if any long-range behavior is expected in $H(r)$ it should be related to the approach to the origin $k = 0$ of a pole of $\hat{h}^s(k)$ since the other term in Eq. (20), $\hat{h}^a(k)$, does not have such a possibility, except in the trivial case $\kappa = 0$ $(T = \infty)$.

Let us now complete the analogy with the simple fluid case by expanding $\hat{c}^s$ and $\hat{c}^e$ in their Taylor series. Since, as far as the critical behavior is concerned, we are interested not in h^s or h^a in particular but in $H(r)$, we perform the sum in Eq. (20) and keep only the lowest approximation, i.e., we neglect terms of order k^4 in the denominator of $H(k)$ [thus excluding, as in the simple fluid case, any oscillatory behavior for $H(r)$]. Thus, we get

$$H(k) \approx \frac{(\kappa^2 c_0{}^s)R - [(4\pi/\epsilon kT)(1 - \rho c_0{}^s)]E + O(k^2)}{\kappa^2(1 - \rho c_0{}^s) + [(1 - \rho c_0{}^s)(1 - \gamma c_0{}^e) - \kappa^2 \rho c_1{}^s]k^2} \qquad (k \to 0) \tag{21}$$

or, by Fourier-transforming and returning to our original notation,

$$h_{ij}(r) \approx \frac{(1/4\pi)\kappa^2 c_0{}^s - (q_i q_j/\epsilon kT)(1 - \rho c_0{}^s)}{(1 - \rho c_0{}^s)(1 - \gamma c_0{}^e) - \kappa^2 \rho c_1{}^s} \frac{e^{-\alpha r}}{r} \qquad (r \to \infty) \tag{22}$$

where

$$\alpha^2 = \frac{\kappa^2(1 - \rho c_0{}^s)}{(1 - \rho c_0{}^s)(1 - \gamma c_0{}^e) - \kappa^2 \rho c_1{}^s} \tag{23}$$

On the other hand, the compressibility equation for multicomponent systems reads

$$\beta\rho(\partial p/\partial\rho) = \rho - \sum_{i,j} \rho_i \rho_j \int c_{ij}(r)\, d^3r \tag{24}$$

or, by using Eqs. (1) and (10b) along with the electroneutrality condition $\sum \rho_i q_i = 0$,

$$\beta(\partial p/\partial\rho) = 1 - \rho c_0{}^s \tag{25}$$

In the approach to the critical point, characterized by the divergence of the compressibility, i.e., by the limit $\beta(\partial p/\partial\rho) \to 0$, we have that Eq. (22) becomes

$$h_{ij}(r) \to [c_0{}^s/(-4\pi\rho c_1{}^s)]e^{-\alpha r}/r \tag{26}$$

$$\alpha = [(1 - \rho c_0{}^s)/(-\rho c_1{}^s)]^{1/2} \tag{27}$$

with a striking resemblance to the simple fluid case. The identification of the correlation length ξ with α^{-1} gives again the critical exponents relation $2\nu = \gamma$. Thus, the analogy has been completed.

Some comments are in order with respect to the extension of the Ornstein–Zernike theory just presented. First of all, our hypothesis so far does not have any formal justification, and so we take it literally as a hypothesis. However, this hypothesis has proved to be a useful one in the respect that we have just employed it, and, as we will see below, it provides a general scheme in which some particular, but important, approximate theories of ionic solutions fall. Let us mention that the conditions stated by our hypothesis imply the second moment condition of Stillinger and Lovett,(2) since from Eq. (18) we have that

$$\lim_{k\to 0} k^2 \hat{c}^e(k) = 0 \tag{28}$$

which is a sufficient condition for the Stillinger–Lovett moment condition to be satisfied.(3)

The second moment condition predicts that for values of κ above a certain value κ_0, the "charge" correlation function $h^a(r)$ will show oscillations. However, since in the approach to the critical point the asymptotic form of $h_{ij}(r)$ is dominated by the $h^s(r)$ term, as was shown above, we conclude that there is not any direct relation between the mentioned oscillations and the critical behavior.

Let us discuss now how some well-known approximate theories of ionic solutions that satisfy our main hypothesis fit into this scheme.

First we consider the mean spherical approximation (MSA),(4) whose defining equations for the restricted primitive model are

$$c_{ij}(r) = -\beta q_i q_j/\epsilon r, \qquad r > R \tag{29}$$

$$h_{ij}(r) = -1, \qquad r < R \tag{30}$$

which complement the OZ integral equation. Since this approximation can be solved analytically, we have analytic expressions for c^s and c^e. The above equations for $c_{ij}(r)$ and $h_{ij}(r)$ can be written as

$$\begin{aligned} c^s(r) &= 0, && r > R \\ h^s(r) &= -1, && r < R \end{aligned} \tag{31}$$

$$\begin{aligned} c^a(r) &= -\beta/\epsilon r, && r > R \\ h^a(r) &= 0, && r < R \end{aligned} \tag{32}$$

and so, Eq. (11), complemented with Eq. (31), becomes the OZ equation for a hard sphere ("reference") system in the mean spherical (Percus–Yevick) approximation. The quantity $1 - \rho c_0{}^s$ will then be the same as $1 - \rho c_0$ for the "reference" system:

$$1 - \rho c_0{}^s = (1 - \rho c_0)^{\mathrm{HS(PY)}} \tag{33}$$

and so there is no possibility for $1 - \rho c_0{}^s$ to be zero, or, in other words, no critical point can be observed in the correlation function of the restricted primitive model in this approximation. {However, we must notice that if

$\beta(\partial p/\partial\rho)$ for the restricted primitive model is evaluated through the energy, instead of the compressibility equation, the result is⁽⁴⁾

$$\beta(\partial p/\partial\rho) = \beta(\partial p/\partial\rho)^{\mathrm{HS}} + \beta\,\Delta(\partial p/\partial\rho) \tag{34}$$

where

$$\beta\left(\Delta\frac{\partial p}{\partial\rho}\right) = \frac{x}{8\pi R^3\rho}\left[1 - (1+2x)^{1/2} + \frac{x}{(1+2x)^{1/2}}\right] \tag{35}$$

with $x = \kappa R$ and now $\beta(\partial p/\partial\rho)$ can be zero for certain values of T and ρ ($T^* = \epsilon kTR/q^2 = 78.5 \times 10^{-3}$, $\rho^* = R^3\rho = 1.4 \times 10^{-2}$); in fact this was one of the ways by which the critical point was first detected⁽¹⁾.}

Another approximation closely related to the one just discussed is the so-called generalized mean spherical approximation,⁽⁵⁾ which is defined by the "boundary conditions"

$$\begin{aligned} c_{ij}(r) &= -\beta q_i q_j/\epsilon r + Ke^{-zr}/r, & r > R \\ h_{ij}(r) &= -1, & r < R \end{aligned} \tag{36}$$

where K and z are parameters determined by the requirement of thermodynamic consistency. One of the equations of consistency is precisely⁽⁵⁾

$$\beta\left(\frac{\partial p}{\partial\rho}\right)^{\mathrm{GMSA}} = 1 - \rho c_0{}^s(K, z, \rho) \tag{37}$$

along with the prescription that the left-hand side of this equation be given by the corresponding quantity in the mean spherical approximation obtained via the energy equation, i.e., by Eq. (34). Thus, with respect to the critical behavior, the result of this approximation is only to "legitimize" the critical point that already appeared in the thermodynamics of the mean spherical approximation, and to force it to appear also in the correlation functions.

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