A sum rule for an inhomogeneous electrolyte

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We consider an electrolyte consisting of \( m \) species with charges \( e_\alpha \), particle numbers \( N_\alpha, \alpha = 1, 2, \ldots, m, \) \( \sum e_\alpha N_\alpha = 0, \) in a finite region \( V \). The total potential energy of the system is

\[
U(N) = \sum_{i,s} u_\alpha(r_i^s; \sigma) + \sum_{s,s'} e_\alpha \epsilon_s \phi_{s,s'} |r_i^s - r_i^{s'}|^2 + \Lambda(N),
\]

where \( r_i^s \) is the coordinate of particle \( i \) of species \( \alpha \), \( u_\alpha(r; \sigma) \) is an external potential which depends on a parameter \( \sigma \) and \( \Lambda(N) \) is some "short range" (pair) interaction between the particles.

Let \( \rho_\alpha(r_1; N), \rho_{\alpha s}(r_1; r_2; N), \) etc., be the one particle, pair, etc., densities for this system in the canonical ensemble at some reciprocal temperature \( \beta \). It then follows \(^1\) from the definition of \( \rho_s \)'s that

\[
\frac{\delta U(N)}{\delta \sigma^\alpha(r_1; N)} = -\beta \frac{\delta u_\alpha(r_1; \sigma)}{\delta \sigma} \rho_\alpha(r_1; N) - \beta \sum_{s,s'} \int_\nu \frac{\delta u_\alpha(r_1; \sigma)}{\delta \sigma} \rho_{\alpha s}(r_1, r_2; N) dr_2,
\]

where

\[
\rho_{\alpha s}(r_1, r_2; N) = \rho_{\alpha r}(r_1, r_2; N) - \rho_{\alpha s}(r_1; N) \rho_{s r}(r_2; N)
\]

is the "truncated" pair correlation (Ursell) function.

Let \( V \) tend toward some infinite region \( \mathcal{D} \) in such a way that the bulk densities \( N_\alpha/|V| \rightarrow n_\alpha, \rho_\alpha(r_1; N) \rightarrow \rho_{\alpha r}(r_1) \), etc. We wish to study Eq. (2) when \( u_\alpha(r; \sigma) \) is an electrostatic potential due to an external surface charge density on some boundary of \( V \). For example, \( V \) could be the region between two spheres of radius \( R \) and \( R' \), \( \sigma \) the large density on the surface of the inner sphere.

\[
w_\alpha(r; \sigma) = e_\alpha \frac{4 \pi \sigma r^2}{r^3}, \quad R \leq r = |r| \leq R'.
\]

Letting \( R \rightarrow \infty \) produces the region \( \mathcal{D} \) external to the sphere of radius \( R \). Another example, which is of particular interest, is the case of a charged wall at \( x = 0 \), where \( \mathcal{D} \) is the half space \( x \geq 0 \) and \( w_\alpha(r; \sigma) \) is equal to \(-4 \pi \sigma e x \). We shall treat this case as a limit of the first example when \( R \rightarrow \infty \) after \( R' \) has become infinite. The reason for doing this is that it is well known \(^1\) that if \( w_\alpha(r; \sigma) \) does not decay as \( |r| \rightarrow \infty \) then in general the limit \( V - \mathcal{D} \) may not be taken inside the integral sign—no matter how fast the infinite volume \( \rho_{\alpha s}(r_1, r_2) \) decays. For the charged sphere, however, there is decay in \( w \) and we certainly expect \(^1\) that, in the limit \( R' \rightarrow \infty \), Eq. (2) will take the form

\[
\frac{\delta \rho_\alpha(r_1)}{\delta \sigma} = \frac{4 \pi \beta e_\alpha R^2}{r_1} \rho(r_1) - \frac{4 \pi \sigma R^2}{r_1} \int_\nu \epsilon_s \phi_{s,s'} \frac{\delta \rho_{\alpha s}(r_1, r_2; N)}{\delta \sigma} dr_2.
\]

This expectation is further reinforced by noting that screening gives \(^1\)

\[
\sum_{s,s'} \epsilon_s \int_\nu \rho_{\alpha s}(r_1, r_2; N) dr_2 = \int_\nu \rho_{\alpha s}(r_1, r_2; N) dr_2 = \lim_{R \rightarrow \infty} \sum_{r_2 \in \mathcal{D}} \epsilon_s \rho_{\alpha s}(r_1, r_2; N) dr_2.
\]

An interchange of limits not valid for uncharged systems. \(^1\) Combining Eqs. (5) and (6) yields

\[
\frac{\delta \rho_\alpha(r_1)}{\delta \sigma} = \frac{4 \pi \beta e_\alpha R^2}{r_1} \rho(r_1) \left[ \frac{1}{r_2} - \frac{1}{r_1} \right] \sum_{s,s'} \epsilon_s \rho_{\alpha s}(r_1, r_2; N) dr_2,
\]

for \( r_1 > R \).

It has been shown \(^3\) that a sufficient condition for Eq. (6) to be valid is that \( \rho_{\alpha s}(r_1, r_2) \) decay faster than \( r_2^{-d} \), \( d \) the number of space dimensions, \( d = \beta \) here, (and that a similar clustering property holds for the three-particle correlations). We now argue heuristically that if we are in a regime of temperature and bulk density where the uniform infinite system has strong clustering, e.g., in the Debye screening regime, \(^4\) then the worst case (slowest decay) for the nonuniform system should occur \(^5\) when \( R \rightarrow \infty \) and \( \mathcal{D} \) becomes the half space \( x \geq 0 \). There are two points we wish to make concerning such a semi-infinite system: (i) by a slight extension of the proof in Ref. (3) we can show that screening holds for this system even if the decay parallel to the wall is exactly \( r^{-d} \), and (ii) if in fact the truncated pair correlation function outside the sphere of radius \( R \) decays faster than \( r_2^{-1} \), uniformly in \( R \), then we can set \( r_1 = R + x_1, x_1 > 0 \) and pass to the limit of \( R \rightarrow \infty \). We then obtain the situation of a semi-infinite system in contact with a charged wall and Eq. (7) takes the form

\[
\frac{\delta \rho_\alpha(r_1)}{\delta \sigma} = \beta \sum_{r_2 > 0} \epsilon_s \int_{r_2 > 0} (x_2 - x_1) \rho_{\alpha s}(r_1, r_2) dr_2.
\]
where we have set $4\pi\sigma = E$, the external field produced by the wall.

Equation (8) has some very interesting implications. It was shown in Ref. (3) that if $\rho_{sr}(r_1, r_2)$ decays faster than $\gamma_{r1}^{(d+1)}$ then the excess charge density, $\Sigma e_r \rho_{sr}(r_1, r_2)$, caused by the particle at $r_1$, has no dipole moment. This would mean in our case that the right-hand side of Eq. (8) should vanish in such a case but this is clearly unreasonable for the left-hand side of Eq. (8) when $x_1$ is near the wall so that the validity of Eq. (8) must imply that $\rho_{sr}(r_1, r_2)$ for the semi-infinite system does not decay faster than $\gamma_{r1}^{(d+1)}$ in every direction, e.g., if both $r_1$ and $r_2$ stay close to the surface of the sphere then the decay is slow.

This conclusion was dramatically confirmed by some exact calculations of Jancovici$^4$ in a one component plasma (krypton) in two dimensions at the temperature $\beta e^2 = 2$. The pair correlation decays only as $r^{-d}$ ($d = 2$) parallel to the wall. As already noted, screening does hold and we have verified that Eq. (8) is also valid in that case.

The contact theorem of Henderson et al.$^6$ is

$$p = kT \sum_{a=1}^{\infty} \rho_a (d_a/2) - \frac{eE^2}{8\pi},$$

(9)

where $\rho_a (d_a/2)$ is the density at the wall, $p$ is the bulk pressure, and $d_a$ is the hard sphere diameter. Differentiating and using $\partial \rho / \partial E = 0$ gives

$$\frac{eE}{4\pi} = kT \sum_{a=1}^{\infty} \frac{\partial \rho_a (d_a/2)}{dE}.$$ 

(10)

Hence

$$\frac{eE}{4\pi} = \sum_{aT} \sigma_r (x_2 - d_a/2) p_{sr} (d_a/2, x_2, r_1) dr_1.$$ 

(11)

Finally, Eq. (8) can be used to obtain a new expression for the differential capacitance of a double layer.

$$1/C_D = \frac{16\pi^2}{\epsilon^2} \sum_{aT} e_r \int x_1 \frac{\partial \rho_a (x_1)}{\partial E} dx_1.$$ 

(12)

Substitution of Eq. (8) into Eq. (12) gives

$$1/C_D = \frac{16\pi^2}{\epsilon^2} \sum_{aT} e_r \int x_1 (x_2 - x_1) \rho_{sr} (r_1, r_2) dx_1 dr_2 = \frac{8\pi^2}{\epsilon^2} \sum_{aT} e_r \int (x_2 - x_1)^2 \rho_{sr} (r_1, r_2) dx_1 dr_2.$$ 

(13)

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The role of the Criegee intermediate in the matrix thermoluminescence study of the CH$_2$ + O$_2$ reaction

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In a matrix thermoluminescence study of the reaction of CH$_2$ with O$_2$, Lee and Pimentel$^1$ observed two new progressions which they assigned to the $a^3A'' - X^1A'$ (310–360 nm) and $A^1A' - A^3A''$ (390–490 nm) transitions of HCOOH. They concluded that these observations provide the first evidence that one or more excited electronic states of formic acid are populated by the reaction: CH$_3$($B_1$) + O$_2$(5 $\Sigma^+$) $\rightarrow$ HCOOH**. This reaction between CH$_2$ and O$_2$ probably proceeds through the initial formation of the oxymethylene adduct H$_2$C=O which then rearranges to the excited formic acid through a series of CH$_2$O intermediates;

$$\text{CH}_3 + \text{O}_2 \rightarrow \text{H}_2\text{C}=\text{O} \rightarrow \text{H}_3\text{C}=\text{O} \rightarrow \text{H}_2\text{C} \leftrightarrow \text{O} \rightarrow \text{HCOOH}^*.$$ 

This is similar to the mechanism suggested by Hsu and Lin for the gas-phase reaction of CH$_3$ with O$_2$. The evidence in support of this mechanism comes from recent theoretical$^3$ and experimental$^5$ studies of the ozoneonolysis of alkenes, and from experimental studies of carbene + O$_2$ reactions, all of which have been reviewed recently$^4$ with reference to the involvement of