A sum rule for an inhomogeneous electrolyte

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

$$U(\mathbf{N}) = \sum_{i,\alpha} w_\alpha (\mathbf{r}_i^\alpha; \sigma) + {\sum_{i,j,\alpha\gamma}}' e_\alpha e_\gamma |\mathbf{r}_i^\alpha - \mathbf{r}_j^\gamma|^{-1} + \hat{U}(\mathbf{N}) , \qquad (1)$$

where $\mathbf{r}_i^\alpha$ is the coordinate of particle i of species α, $w_\alpha(\mathbf{r}; \sigma)$ is an external potential which depends on a parameter σ, and $\hat{U}(\mathbf{N})$ is some "short range" (pair) interaction between the particles.

Let $\rho_{\alpha_1}(\mathbf{r}_1; \mathbf{N})$, $\rho_{\alpha_1\alpha_2}(\mathbf{r}_1; \mathbf{r}_2; \mathbf{N})$, etc., be the one particle, pair, etc., densities for this system in the canonical ensemble at some reciprocal temperature β. It then follows[1] from the definition of ρ's that

$$\frac{\partial \rho_\alpha(\mathbf{r}_1; \mathbf{N})}{\partial \sigma} = -\beta \frac{\partial w_\alpha(\mathbf{r}_1; \sigma)}{\partial \sigma} \rho_\alpha(\mathbf{r}_1; \mathbf{N})$$

$$- \beta \sum_\gamma \int_v \frac{\partial w_\gamma(\mathbf{r}_2; \sigma)}{\partial \sigma} \rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2; \mathbf{N}) d\mathbf{r}_2 , \qquad (2)$$

where

$$\rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2; \mathbf{N}) \equiv \rho_{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{N}) - \rho_\alpha(\mathbf{r}_1; \mathbf{N})\rho_\gamma(\mathbf{r}_2; \mathbf{N}) \qquad (3)$$

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

Let V tend toward some infinite region $\mathfrak{D}$ in such a way that the bulk densities $N_\alpha/|V| \to n_\alpha$, $\rho_\alpha(\mathbf{r}_1; \mathbf{N}) \to \rho_\alpha(\mathbf{r}_1)$, $\ldots$, etc. We wish to study Eq. (2) when $w_\alpha(\mathbf{r}; \sigma)$ is an electrostatic potential due to an external surface charge density on some boundaries of V. For example, V could be the region between two spheres of radius R and R', σ the large density on the surface of the inner sphere.

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

Letting $R' \to \infty$ produces the region $\mathfrak{D}$ 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 $\mathfrak{D}$ is the half space $x \geq 0$ and $w_\alpha(\mathbf{r}; \sigma)$ is equal to $-4\pi\sigma e_\alpha x$. We shall treat this case as a limit of the first example when $R \to \infty$ *after* R' has become infinite. The reason for doing this is that it is well known[1] that if $w_\alpha(\mathbf{r}; \sigma)$ does not decay as $|\mathbf{r}| \to \infty$ then in general the limit $V \to \mathfrak{D}$ may not be taken inside the integral sign—

no matter how fast the infinite volume $\rho_\alpha^T(\mathbf{r}_1, \mathbf{r}_2)$ decays. For the charged sphere, however, there is decay in w and we certainly expect[1] that, in the limit $R' \to \infty$, Eq. (2) will take the form

$$\frac{\partial \rho_\alpha(\mathbf{r}_1)}{\partial \sigma} = \frac{4\pi\beta e_\alpha R^2}{|\mathbf{r}_1|} \rho(\mathbf{r}_1) - 4\pi\beta R^2 \sum_\gamma e_\gamma \int_{|\mathbf{r}_2| > R} \frac{\rho_{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_2|} d\mathbf{r}_2. \qquad (5)$$

This expectation is further reinforced by noting that screening gives[2,3]

$$\sum_\gamma e_\gamma \int_{\mathfrak{D}} \rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -e_\alpha \rho_\alpha(\mathbf{r}_1)$$

$$= \lim_{V \to \mathfrak{D}} \sum_\gamma e_\gamma \int_V \rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2; \mathbf{N}) d\mathbf{r}_2 . \qquad (6)$$

An interchange of limits *not* valid for uncharged systems.[1] Combining Eqs. (5) and (6) yields

$$\frac{\partial \rho_\alpha(\mathbf{r}_1)}{\partial \sigma} = 4\pi\beta R^2 \int_{r_2 > R} \left[\frac{1}{r_2} - \frac{1}{r_1}\right]\left[\sum_\gamma e_\gamma \rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2)\right] d\mathbf{r}_2 , \qquad (7)$$

for $r_1 > R$.

It has been shown[3] that a sufficient condition for Eq. (6) to be valid is that $\rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2)$ decay *faster* than $(r_{12})^{-d}$, d the number of space dimensions, $d = 3$ 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 $R \to \infty$ and $\mathfrak{D}$ 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_{12}^{d-1}, uniformly in R, then we can set $r_1 = R + x_1$, $x_1 > 0$ and pass to the limit of $R \to \infty$. We then obtain the situation of a semi-infinite system in contact with a charged wall and Eq. (7) takes the form

$$\frac{\partial \rho_\alpha(x_1)}{\partial E} = \beta \sum_\gamma e_\gamma \int_{x_2 > 0} (x_2 - x_1)\rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 , \qquad (8)$$

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 $\rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2)$ decays *faster* than $(r_{12})^{-(d+1)}$ then the *excess* charge density, $\sum_\gamma e_\gamma$ $\sum_\gamma e_\gamma \rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2)$, caused by the particle at $\mathbf{r}_1$, 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 $\rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2)$ for the semi-infinite system does *not* decay faster than $r_{12}^{-(d+1)}$ in *every* direction, e.g., if both $\mathbf{r}_1$ and $\mathbf{r}_2$ stay close to the surface of the sphere then the decay is slow.

This conclusion was dramatically confirmed by some exact calculations of Jancovici[5] in a one component plasma (jellium) 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

$$p = kT \sum_{\alpha=1}^{m} \rho_\alpha(d_\alpha/2) - \frac{\epsilon E^2}{8\pi} \quad , \tag{9}$$

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

$$\frac{\epsilon E}{4\pi} = kT \sum_\alpha \frac{\partial \rho_\alpha(d_\alpha/2)}{dE} \quad . \tag{10}$$

Hence

$$\frac{\epsilon E}{4\pi} = \sum_{\alpha\gamma} e_\gamma \int (x_2 - d_\alpha/2) \rho_{\alpha\gamma}^T(d_\alpha/2, x_2, r_{12}) d\mathbf{r}_2 \quad . \tag{11}$$

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

$$1/C_D = \frac{16\pi^2}{\epsilon^2} \sum_\alpha e_\alpha \int x_1 \frac{\partial \rho_\alpha(x_1)}{\partial E} dx_1 \quad . \tag{12}$$

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

$$1/C_D = \frac{16\pi^2 \beta}{\epsilon^2} \sum_{\alpha\gamma} e_\alpha e_\gamma \int x_1 (x_2 - x_1) \rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2) dx_1 d\mathbf{r}_2$$

$$= \frac{8\pi^2 \beta}{\epsilon^2} \sum_{\alpha\gamma} e_\alpha e_\gamma \int (x_2 - x_1)^2 \rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2) dx_1 d\mathbf{r}_2. \tag{13}$$

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# The role of the Criegee intermediate in the matrix thermoluminescence study of the CH₂+O₂ 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 $a^3A'' \rightarrow X^1A'$ (310–360 nm) and $A'^1A' \rightarrow A^1A''$ (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: $CH_2(^3B_1) + O_2(^3\Sigma_g^-) \rightarrow HCOOH^{**}$. This reaction between CH_2 and O_2 probably proceeds through the initial formation of the dioxymethylene adduct $H_2\dot{C}O\dot{O}$ which then rearranges to the excited formic acid through

a series of CH_2O_2 intermediates;

$$CH_2 + O_2 \rightarrow H_2\dot{C}O\dot{O} \rightarrow H_2C{<}^O_O \rightarrow H_2C{<}^{O\cdot}_{O\cdot} \rightarrow HCOOH^{**} \quad .$$
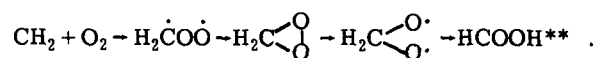
This is similar to the mechanism suggested by Hsu and Lin for the gas-phase reaction of CH_2 with O_2.[2] The evidence in support of this mechanism comes from recent theoretical[3,4] and experimental[5,6] studies of the ozonolysis of alkenes, and from experimental studies of carbene $+O_2$ reactions, all of which have been reviewed recently[7] with reference to the involvement of