

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 , $\alpha = 1, 2, \dots, m$, $\sum_\alpha e_\alpha N_\alpha = 0$, in a finite region V . The total potential energy of the system is

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

where \mathbf{r}_i^α 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 follows¹ from the definition of ρ 's that

$$\begin{aligned} \frac{\partial \rho_\alpha(\mathbf{r}_1; \mathbf{N})}{\partial \sigma} &= -\beta \frac{\partial w_\alpha(\mathbf{r}_1; \sigma)}{\partial \sigma} \rho_\alpha(\mathbf{r}_1; \mathbf{N}) \\ &\quad - \beta \sum_\gamma \int_V \frac{\partial w_\gamma(\mathbf{r}_2; \sigma)}{\partial \sigma} \rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2; \mathbf{N}) d\mathbf{r}_2, \end{aligned} \quad (2)$$

where

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

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

Let V tend toward some infinite region \mathfrak{D} in such a way that the bulk densities $N_\alpha/|V| \rightarrow n_\alpha$, $\rho_\alpha(\mathbf{r}_1; \mathbf{N}) \rightarrow \rho_\alpha(\mathbf{r}_1)$, 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.

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

Letting $R' \rightarrow \infty$ 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 $R \rightarrow \infty$ after R' has become infinite. The reason for doing this is that it is well known¹ that if $w_\alpha(\mathbf{r}; \sigma)$ does not decay as $|\mathbf{r}| \rightarrow \infty$ then in general the limit $V \rightarrow \mathfrak{D}$ 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 expect¹ that, in the limit $R' \rightarrow \infty$, Eq. (2) will take the form

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

This expectation is further reinforced by noting that screening gives^{2,3}

$$\begin{aligned} \sum_\gamma e_\gamma \int_{\mathfrak{D}} \rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 &= -e_\alpha \rho_\alpha(\mathbf{r}_1) \\ &= \lim_{V \rightarrow \mathfrak{D}} \sum_\gamma e_\gamma \int_V \rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2; \mathbf{N}) d\mathbf{r}_2. \end{aligned} \quad (6)$$

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

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

for $r_1 > R$.

It has been shown³ 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 occur⁵ when $R \rightarrow \infty$ 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_2^{d-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

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

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 Jancovici⁵ 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

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

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

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

Hence

$$\frac{\epsilon E}{4\pi} = \sum_{\alpha\gamma} e_{\gamma} \int (x_2 - d_{\alpha}/2) \rho_{\alpha\gamma}^T(d_{\alpha}/2, x_2, r_{12}) dr_2. \quad (11)$$

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

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

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

$$1/C_D = \frac{16\pi^2\beta}{\epsilon^2} \sum_{\alpha\gamma} e_{\alpha} e_{\gamma} \int x_1 (x_2 - x_1) \rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2) dx_1 dr_2 \\ = \frac{8\pi^2\beta}{\epsilon^2} \sum_{\alpha\gamma} e_{\alpha} e_{\gamma} \int (x_2 - x_1)^2 \rho_{\alpha\gamma}^T(\mathbf{r}_1, \mathbf{r}_2) dx_1 dr_2. \quad (13)$$

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The role of the Criegee intermediate in the matrix thermoluminescence study of the CH₂ + O₂ reaction

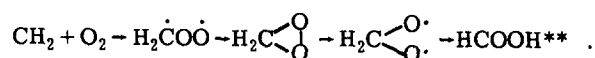
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In a matrix thermoluminescence study of the reaction of CH₂ with O₂, Lee and Pimentel¹ observed two new progressions which they assigned to the $a^3A'' - X^1A'$ (310–360 nm) and $A'^1A' - A^1A''$ (390–490 nm) transitions of HCOOH. They concluded that these observations provide the first evidence that one or more excited electronic states of formic acid are populated by the reaction: CH₂(³B₁) + O₂(³Σ_g⁻) → HCOOH**. This reaction between CH₂ and O₂ probably proceeds through the initial formation of the dioxymethylene adduct H₂C $\dot{O}O$ which then rearranges to the excited formic acid through

a series of CH₂O₂ intermediates;



This is similar to the mechanism suggested by Hsu and Lin for the gas-phase reaction of CH₂ with O₂.² 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 + O₂ reactions, all of which have been reviewed recently⁷ with reference to the involvement of