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A SUM RULE FOR AN INHOMOGENEOUS ELECTROLYTE

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ABSTRACT: We obtain a new sum rule for the density profile of an electrolyte in contact with a charged flat hard (nonconducting) wall. This, in turn, strongly implies that the decay of the pair correlation near the wall is *not faster* than (distance)^{-d-1}, where d is the dimension of the system.

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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

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

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

Let $\rho_\alpha(\underline{r}_1; \underline{N})$, $\rho_{\alpha\gamma}(\underline{r}_1, \underline{r}_2; \underline{N})$, 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

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

where

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

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

Let V tend toward some infinite region $\mathcal{D}$ in such a way that the bulk densities $N_\alpha/V \rightarrow n_\alpha$, $\rho_\alpha(\underline{r}; \underline{N}) \rightarrow \rho_\alpha(\underline{r})$, etc. We wish to study Eq. (2) when $w_\alpha(\underline{r}; \sigma)$ 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,

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

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 $w_\sigma(r; \sigma)$ is equal to $-4\pi\sigma x$. 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 $w_\sigma(r; \sigma)$ does not decay as $|\underline{r}| \rightarrow \infty$ then in general the limit $V \rightarrow \mathcal{D}$ may not be taken inside the integral sign --- no matter how fast the infinite volume $\rho_\sigma^T(\underline{r}_1, \underline{r}_2)$ 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

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

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

$$\sum_{\underline{r}} e_{\underline{r}} \int_{\mathcal{D}} \rho_\sigma^T(\underline{r}_1, \underline{r}_2) d\underline{r}_2 = -e_\sigma \rho_\sigma(\underline{r}_1) = \lim_{V \rightarrow \mathcal{D}} \sum_{\underline{r}} e_{\underline{r}} \int_V \rho_\sigma^T(\underline{r}_1, \underline{r}_2; N) d\underline{r}_2, \quad (6)$$

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

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

for $\underline{r}_1 > R$.

It has been shown³ that a sufficient condition for Eq. (6) to be valid is that

$\rho_\sigma^T(\underline{r}_1, \underline{r}_2)$ decay *faster* than $(\underline{r}_{12})^{-d}$, 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 $\mathcal{D}$ becomes the half space $x > 0$. 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 $\underline{r}_1 = R + \underline{x}_1$, $\underline{x}_1 > 0$ 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

$$\frac{\partial \rho_\sigma(\underline{x}_1)}{\partial \sigma} = \beta \sum_{\underline{r}} e_{\underline{r}} \int_{\underline{x}_2 > 0} (\underline{x}_2 - \underline{x}_1) \rho_\sigma^T(\underline{r}_1, \underline{r}_2) d\underline{r}_2 \quad (8)$$

where we have set $4\pi\sigma = F$, the external electric field produced by the wall.

Equation (8) has some very interesting implications. It was shown in Ref. (3) that if $\rho_\sigma^T(\underline{r}_1, \underline{r}_2)$ decays *faster* than $(\underline{r}_{12})^{-(d+1)}$ then the excess charge density, $\sum_{\underline{r}} e_{\underline{r}} \rho_\sigma^T(\underline{r}_1, \underline{r}_2)$, caused by the particle at $\underline{r}_1$, has *no* dipole moment. This would mean in our case that the right side of (8) should vanish in such a case but this is clearly unreasonable for the left side of (8) when $\underline{x}_1$ is near the wall so that the validity of (8) must imply that $\rho_\sigma^T(\underline{r}_1, \underline{r}_2)$ for the semi-infinite system does *not* decay faster than $r_{12}^{-(d+1)}$ in *every* direction, e.g., if both $\underline{r}_1$ and $\underline{r}_2$ 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

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

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

$$\begin{aligned} 1/C_D &= \frac{16\pi^2\beta}{\epsilon^2} \sum_{\alpha\gamma} e_{\alpha} e_{\gamma} \int x_1 (x_2 - x_1) \rho_{\alpha\gamma}^T(r_1, r_2) dx_1 dr_2 \\ &= \frac{8\pi^2\beta}{\epsilon^2} \sum_{\alpha\gamma} e_{\alpha} e_{\gamma} \int (x_2 - x_1)^2 \rho_{\alpha\gamma}^T(r_1, r_2) dx_1 dr_2. \end{aligned} \quad (13)$$

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