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# Addendum to Henderson and Smith's Exact Formulas for the Pair Correlation Functions of Charged Hard Spheres in the Mean Spherical Approximation

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Henderson and Smith[(1)] have derived analytical expressions for the pair correlation functions of a system of charged hard spheres of equal size in the bulk and also near a charged wall, in the mean spherical approximation.

The purpose of this note is to show that a very similar expression is valid for the case of unequal-size hard ions, if certain terms that are small for most electrolytic solutions are neglected. This was suggested by Henderson and Smith.

We use the results of Blum and Høye[(2)] for this case [Eq. (4.26)]. The Laplace transform of the pair correlation function is

$$G_{ij}(s) = G_{ij}^{\mathrm{HS}}(s) - A_{ij}e^{-s\sigma_{ij}}\left(s^2 + 2\Gamma s + 2\Gamma^2 - \frac{2\Gamma^2}{\alpha^2}\sum_l p_l a_l{}^2 e^{-s\sigma_l}\right)^{-1} \tag{1}$$

where we are using the notation of Ref. 2. Here

$$A_{ij} = z_i z_j(\alpha^2/4\pi)[(1 + \Gamma\sigma_i)(1 + \Gamma\sigma_j)]^{-1} \tag{2}$$

$$\alpha^2 = 4\pi\beta e^2/\epsilon_0 \tag{3}$$

with $z_i$ the electrovalence, $e$ the elementary charge, and $\beta = 1/kT$ the Boltzmann thermal factor. The screening parameter $\Gamma$ and the charge parameter $\alpha$ are obtained from the solution of the mean spherical approximation[(2,3)]; $\sigma_i$ is the hard ion diameter and $\sigma_{ij} = (1/2)(\sigma_i + \sigma_j)$.

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Equation (1) is strikingly similar to Eqs. (9) and (10) of Henderson and Smith, so that clearly

$$g_{ij}(r) = g_{ij}^{\mathrm{HS}}(r) - \frac{A_{ij}}{r} \sum_{m=0}^{\infty} \frac{2\Gamma^{m+1}}{m!\,\alpha^{2m}} \times \left[ \sum_{\{l_t\}} \prod_{t=1}^{m} \rho_{l_t} a_{l_t}^2 F_m\left(r - \sigma_{ij} - \sum \sigma_{l_t}\right) \right] \tag{4}$$

where $F_m(r) = 0$ for $r < 0$, and

$$F_m = r^{m+1} e^{-\Gamma_r} [j_{m-1}(\Gamma_r) - j_m(\Gamma_r)]$$

Also, the sum is over all $\{l_t\} = l_1, \ldots, l_m$; $j_m(x)$ is the spherical Bessel function; and $j_{-1}(x) = \cos(x)/x$.

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## REFERENCES

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