Correlation Functions in the Cavity Model of Ionic Fluids

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The dominant long-range contribution of the solute–solvent interaction to ion–ion distribution functions is assessed in a limit that yields the cavity model of ionic solutions.

We have considered[1] the contribution of charge–dipole interactions to the thermodynamics and structure of ionic solutions from the standpoint of two models—the quasicontinuum cavity model of charged spheres of dielectric constant ε_0 in a continuum of dielectric constant ε as well as a molecular model consisting of charged-sphere solute particles and dipolar-sphere solvent particles. With suitable scaling of the interaction potentials one expects to obtain the cavity-model description from the molecular model in the limit $\sigma_d/\sigma_i \to 0$, where σ_d and σ_i are the dipolar-particle and ion diameters, respectively. In this limit, one keeps $\rho_d \sigma_d^3$ fixed, where ρ_d is the dipolar solvent-particle number density. Thus if one considers σ_i to be fixed, the solvent particles shrink in size and become more dense, to define in the limit what is effectively a continuum solvent that remains external to the ionic cores. One keeps $\beta \mu^2 \rho_d$ fixed, where $\beta = 1/kT$ and μ is dipole moment strength. (To ensure that one obtains the cavity-model result in this limit, one must also scale the dipole–dipole pair interaction between solvent particles; one can do this by cutting it off or tempering it for $r < L$,

where r is the distance between particle centers and $\sigma_d/L \to 0$, $L/\sigma_i \to 0$, as $\sigma_d/\sigma_i \to 0$.) We recover for the first time the full r^{-4} "cavity term" of the ion–ion cavity-model pair potential $\varphi_{\alpha\beta}^{CAV}(r)$ in such a limit as well as a corresponding screened r^{-4} term in the effective (i.e., solvent-averaged) direct correlation function $c_{\alpha\beta}^{eff}(r)$, which is screened by the factor $e^{-2\lambda r}$ and multiplied by the prefactor $(1 + \lambda r)^2$, where λ is the ion–ion inverse screening length. We also show that if one makes the usual approximation of pairwise additivity of the n-ion potentials of mean force at infinite dilution, one loses both the screening and the prefactor. This is thermodynamically significant; if there were no screening of the r^{-4} term, there could not be a critical point in the ionic fluid, as one of us has pointed out in earlier work.[2]

Our expression for $c_{\alpha\beta}^{eff}$ in the limit $\sigma_d/\sigma_i \to \infty$ is

$$\lim_{r \to \infty} c_{\alpha\beta}^{eff}(r) = -\beta \frac{q_\alpha q_\beta}{\varepsilon_\rho r} - \beta \frac{(\varepsilon_\rho - 1)(q_\alpha^2 R_\alpha^3 + q_\beta^2 R_\beta^3)}{2\varepsilon_\rho(2\varepsilon_\rho + 1)}$$
$$\times \frac{1 + 2\lambda r + \lambda^2 r^2}{r^4} e^{-2\lambda r} + \cdots \tag{1}$$

where subscripts α and β label ionic species and q_α and R_α are the ionic charge and solvent–ion interaction diameter, respectively. The ε_ρ is an effective dielectric constant. In the $\sigma_d/\sigma_i \to \infty$ limit our ion–ion potential of mean force has exactly this form, but with ε_ρ replaced by ε and λ replaced by zero. This quantity coincides with the pair potential of the cavity model, while the $c_{\alpha\beta}^{eff}$ coincides with the cavity-model direct correlation function. The pair correlation function of the cavity model in the Debye–Hückel limiting-law regime has independently been considered recently by Li et al.[3]

ACKNOWLEDGMENTS

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