Journal of Statistical Physics, Vol. 89, Nos. 1/2, 1997

Variational Extension of the Mean Spherical Approximation to Arbitrary Dimensions

Esov S. Velázquez,[1,2] Lesser Blum,[1] and Harry L. Frisch[3]

Received May 15, 1996; final November 8, 1996

We generalize a variational principle for the mean spherical approximation for a system of charged hard spheres in 3D to arbitrary dimensions. We first construct a free energy variational trial function from the Debye–Hückel excess charging internal energy at a finite concentration and an entropy obtained at the zero-concentration limit by thermodynamic integration. In three dimensions the minimization of this expression with respect to the screening parameter leads to the mean spherical approximation, usually obtained by solution of the Ornstein-Zernike equation. This procedure, which interpolates naturally between the zero concentration/coupling limit and the high-concentration/coupling limit, is extended to arbitrary dimensions. We conjecture that this result is also equivalent to the MSA as originally defined, although a technical proof of this point is left for the future. The Onsager limit $T\,\Delta S^{\mathrm{MSA}}/\Delta E^{\mathrm{MSA}} \to 0$ for infinite concentration/coupling is satisfied for all $d \neq 2$, while for $d = 2$ this limit is 1.

KEY WORDS: Ionic mixtures; mean spherical approximation; variational approach.

1. INTRODUCTION

It is a pleasure to contribute to this issue in honor of Bernard Jancovici, a true great man in the theory of Coulomb systems.

The mean spherical approximation (MSA) was originally formulated in 3 dimensional space[1,2] as a linearized closure to the Ornstein–Zernike

[1] Department of Physics, University of Puerto Rico, P.O. Box 23343, Rio Piedras, Puerto Rico 00931.

[2] On leave from Department of Physics, University of Puerto Rico, Mayagüez Campus, Mayagüez, Puerto Rico 00681.

[3] Department of Chemistry, University at Albany, State University of New York, Albany, New York 12222.

equation. For ionic system MSA closure is the linearized Poisson–Boltzmann equation, which is also the starting equation of the Debye–Hückel (DH) approximation,[3] since the Fourier transforms of the MSA equations and the DH equations are the same, except for the discontinuities contributions coming from the boundaries. For the most general case of arbitrary mixtures of charged hard spheres the analytic solution of the MSA in 3 dimensions is given in terms of a single scaling (screening) parameter Γ.[4] Furthermore the thermodynamic-electrostatic excess properties such as the internal energy, Helmholtz free energy and entropy, derived from the internal energy by thermodynamic integration yield explicit formulas[5,6] which are isomorphic with those of Debye and Hückel, except for the fact that the Debye parameter κ is replaced by the scaling (screening) parameter Γ. In spite of this similarity in the thermodynamics, the MSA pair correlation functions are not simple exponentials, as is the case in the DH theory, but reflect the excluded volume of the ions in the ionic cloud, and are therefore oscillating functions.[5] The excluded volume effect makes the ionic cloud larger, and in fact in the high density-high coupling limit

$$\kappa \simeq \Gamma^{1/2}. \tag{1}$$

One of the remarkable facts of the MSA-like theories is that for a variety of systems in 3D, which includes systems with not only hard cores but other types of interactions such as associating interactions,[7,8] the thermodynamic charging excess functions obtained from the internal energy by integration of

$$\frac{\partial \beta\, \Delta A^{\mathrm{MSA}}}{\partial \beta} = \Delta E^{\mathrm{MSA}}. \tag{2}$$

are of the general form:

$$\Delta A^{\mathrm{MSA}} = \Delta E^{\mathrm{MSA}} - T\, \Delta S^{\mathrm{MSA}}, \tag{3}$$

where

$$\Delta E^{\mathrm{MSA}} = -\frac{e^2}{\varepsilon} \sum_i \rho_i (z_i^*)^2 \frac{\Gamma}{1+\Gamma \sigma_i}, \tag{4}$$

and

$$\Delta S^{\mathrm{MSA}} = -k \frac{\Gamma^3}{3\pi}, \tag{5}$$

where the symbols are those of ref. 7, namely ρ_i, z_i^*, σ_i are the density, effective charge and diameter of ion i, ε is the dielectric constant, T is the absolute temperature and k is the Boltzmann constant.

In a previous paper[9] the observation was made that all the MSA results Eqs. (3–5) could be obtained by minimization of a functional which is identical to the MSA excess free energy ΔA^{MSA}

$$\frac{\partial\, \Delta A^{\mathrm{MSA}}}{\partial \Gamma}=0. \tag{6}$$

The MSA is the variational problem in which an approximate (the so-called ring sum) free energy ΔA^{MSA} is minimal[10]

$$\delta[\Delta A^{\mathrm{MSA}}]=0. \tag{7}$$

This interpretation was already present in the original work of Percus and Yevick.[3] Differentiation of equation (6) yields explicitly

$$\frac{\partial\, \Delta A^{\mathrm{MSA}}}{\partial \Gamma}=\frac{\partial\, \Delta E^{\mathrm{MSA}}}{\partial \Gamma}-\frac{\partial T\, \Delta S^{\mathrm{MSA}}}{\partial \Gamma}=-\sum_i \frac{\rho_i (e z_i^*)^2}{\epsilon}\left[\frac{1}{(1+\sigma_i \Gamma)^2}\right]+\frac{\Gamma^2}{\pi}=0. \tag{8}$$

which is an algebraic equation for the new scaling parameter Γ, and is the correct closure equation for the MSA.

When all the ions have the same diameter $\sigma_i=\sigma$ then Eq. (8) simplifies considerably, and we recover the primitive model result,[2] which is a simple quadratic for Γ

$$(1+2\kappa\sigma)=(1+2\Gamma\sigma)^2. \tag{9}$$

The solution of this equation is

$$\Gamma=(1/2\sigma)(\sqrt{(1+2\kappa\sigma)}-1). \tag{10}$$

For low concentrations we get back the DH theory. At infinite coupling we get Eq. (1).

A more formal justification of this result can be found using the variational principle for the ring diagram sum[10] in which the minimization of the ring diagrams sum with respect to the direct correlation function yields the MSA, in combination with the scaling principle for the MSA, which requires a single parameter for any given mixture of charged hard spheres. We extend this principle to arbitrary dimensions. The conjecture is that this generalization of the 3 dimensional variational derivation of the MSA to arbitrary dimensions should correspond to the Ornstein–Zernike based MSA.

The limit of infinite dimensions has been investigated for different many body problems[11, 12, 13, 14] because it represents considerable simplifications in the computational algorithms, and also because of insights that it gives for problems such as criticality and percolation. We consider here the restricted primitive model for a ionic mixture of d-dimensional hard hyperspheres of diameter σ with centrally located charges ez_i, where e is the fundamental charge. The medium and the ions have uniform dielectric constant ε. The method is a generalization of the variational method proposed in earlier work[9] to arbitrary dimensions. In Section 2, we review the Debye–Hückel theory,[15] which is the exact limiting theory of ionic solutions for low concentrations, but which does not properly include hard-core interaction condition

$$g(r) = 0, \qquad r < \sigma. \tag{11}$$

In the MSA, the hard-core interactions are properly included, while the same linearized Boltzmann approximation is used for the charged part. The hard core exclusion interactions prevent the collapse of the system, since the volume occupied by the ions prevents the formation of pairs of unbounded energy. As it was recently shown, a variational method[9] will reproduce exactly the results obtained by analytic solution of the MSA integral equations in 3 dimensions. We assume then that this is true for any dimensionality. This conjecture is based on the analysis of Chandler and Andersen,[10] who showed that the minimization of an approximation to the Helmholtz free energy, consisting of the sum of ring diagrams, is equivalent to the MSA ring diagrams, which we conjecture to be valid in any dimensionality. A detailed proof of this conjecture is left for a future publication. This point was is also discussed by Percus.[3] We derive the DH expressions in any dimension, using an extension of the variational principle[9] to derive the closure relation for the screening parameter Γ. Finally, we study the Onsager limit[16, 17] $T\Delta S/\Delta E$ for the infinite density limit.

2. DEBYE–HÜCKEL THEORY

Since our results are based on the generalization of the Debye–Hückel theory we give a short account of these results:[18] The electrostatic potential at a distance r from ion i, $\phi_i(r)$, must satisfy Poisson's equation:

$$\nabla_d^2 \phi_i(r) = -\frac{\Omega_d}{\varepsilon} q_i(r), \tag{12}$$

where ∇_d^2 is the Laplacian in d-space,

$$\Omega_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} \tag{13}$$

is the surface of the d-dimensional unit sphere, and $q_i(r)$ is the charge density at r, which is found by adding the contributions of all ions surrounding i:

$$q_i(r) = e \sum_{j \neq i} z_j \rho_j^{(i)}(r). \tag{14}$$

The density of ions in the neighborhood of i can be expressed in terms of the pair correlation function,

$$g_{ij}(r) = \frac{\rho_j^{(i)}(r)}{\rho_j} = \frac{\rho_i^{(j)}(r)}{\rho_i}. \tag{15}$$

From an analogy to the compressible fluid model with density proportional to the pressure, the pair correlation function is

$$g_{ij}(r) = e^{-\beta w_{ij}(r)}, \tag{16}$$

where $w_{ij}(r)$ is the potential energy due to the interaction of i and j. We write this potential energy as

$$w_{ij}(r) = u_{ij}(r) + \zeta_{ij}(r) \qquad u_{ij}(r) = ez_j\phi_i(r), \tag{17}$$

the first term being purely electrostatic interactions. If all non-electrostatic interactions (including hard cores) are small compared to the electrostatic interactions ($\zeta_{ij}(r) \approx 0$), and since when r is very large $\phi_i(r)$ must be small, we can linearize the exponential:

$$g_{ij}(r) \simeq 1 - \beta ze_j\phi_i(r). \tag{18}$$

Substituting into Poisson's Eq. (12) we obtain the DH equation:[15]

$$\nabla_d^2\phi_i(r) = \kappa^2\phi_i(r) \qquad r > \sigma, \tag{19}$$

where

$$\kappa^2 = \frac{\Omega_d \beta a^2}{\varepsilon} \sum_j \rho_j z_j^2, \tag{20}$$

and σ is the diameter of the hyperspheres. The solution of the DH equation is accomplished transforming to spherical coordinates.[19] The radial part of the Laplacian is

$$\nabla_d^2 = \frac{1}{r^{d-1}} \frac{\partial}{\partial r}\left(r^{d-1} \frac{\partial}{\partial r}\right), \tag{21}$$

and we find

$$\frac{d^2\phi_i}{dr^2} + \frac{d-1}{r}\frac{d\phi_i}{dr} - \kappa^2 \phi_i = 0 \qquad r > \sigma, \tag{22}$$

whose general solution is

$$\phi_i(r) = \frac{1}{r^{d/2-1}} \left[A_i K_{d+2-1}(\kappa r) + B_i I_{d/2-1}(\kappa r)\right] \qquad r > \sigma, \tag{23}$$

where $K_\nu(x)$ and $I_\nu(x)$ are the modified or hyperbolic Bessel functions. The boundary condition when $r \to \infty$ requires that $B_i = 0$. For $r < \sigma$, the centers of the ions surrounding i are not included and the potential must satisfy Laplace's equation:

$$\nabla_d^2 \phi_i(r) = 0 \qquad r < \sigma, \tag{24}$$

which yields, for $0 < r < \sigma$

$$\phi_i(r) = \begin{cases} C_i \ln(D_i r) & d = 2 \\ -\dfrac{C_i}{(d-2)\, r^{d-2}} + D_i & d > 2 \end{cases} \tag{25}$$

The values of the constants are determined by the boundary conditions at $r = \sigma$ (continuity of the potential and of the electric displacement), and Gauss' law. We find

$$\phi_i(r) = \begin{cases} -\dfrac{e z_i}{\varepsilon}\left[\ln\dfrac{r}{\sigma} - \dfrac{K_0(\kappa\sigma)}{\kappa\sigma K_1(\kappa\sigma)}\right] & 0 < r < \sigma \quad d = 2 \\ \dfrac{e z_i}{\varepsilon (d-2)\, r^{d-2}} + \dfrac{e z_i}{\varepsilon \sigma^{d-2}}\left[\dfrac{K_{d/2-1}(\kappa\sigma)}{\kappa\sigma K_{d/2}(\kappa\sigma)} - \dfrac{1}{d-2}\right] & 0 < r < \sigma \quad d > 2 \\ \dfrac{e z_i K_{d/2-1}(\kappa r)}{\varepsilon \kappa \sigma^{d/2} K_{d/2}(\kappa\sigma)\, r^{d/2-1}} & r > \sigma \end{cases} \tag{26}$$

where the average electrostatic potential acting on the ith ion fixed at the origin due to all other ions in the solution is

$$\langle \phi_i \rangle = \begin{cases} \dfrac{ez_i K_0(\kappa\sigma)}{\varepsilon\kappa\sigma K_1(\kappa\sigma)} & d=2 \\ \dfrac{ez_i}{\varepsilon\sigma^{d-2}} \left[\dfrac{K_{d/2-1}(\kappa\sigma)}{\kappa\sigma K_{d/2}(\kappa\sigma)} - \dfrac{1}{d-2} \right] & d>2 \end{cases} \tag{27}$$

This charge distribution satisfies the local electroneutrality condition

$$-ez_i = \int_\sigma^\infty dr\, \Omega_d r^{d-1} q_i(r), \tag{28}$$

which can be verified by direct substitution. The expression for the excess energy per unit volume is[4, 5]

$$\Delta E^{\text{MSA}} = \tfrac{1}{2} \sum_{i,j} \rho_i \rho_j \int_\sigma^\infty dr\, \Omega_d r^{d-1} u_{ij}(r)\, g_{ij}(r). \tag{29}$$

Therefore, we find

$$\Delta E^{\text{MSA}} = \begin{cases} \dfrac{-\kappa K_0(\kappa\sigma)}{4\pi\sigma\beta K_1(\kappa\sigma)} & d=2 \\ -\dfrac{\kappa^2 \Gamma(d/2)\, K_{d/2-2}(\kappa\sigma)}{4(d-2)\pi^{d/2}\sigma^{d-2}\beta K_{d/2}(\kappa\sigma)} & d>2 \end{cases} \tag{30}$$

To identify the behavior of ΔE^{MSA} in the limit of infinite dimensions, we use the asymptotic expression for large order ν[20]

$$K_\nu(\nu z) \sim \sqrt{\frac{\pi}{2\nu}} \frac{d^{-\nu\eta}}{(1+z^2)^{1/4}} \left\{ 1 + \sum_{k=1}^{\infty} (-1)^k \frac{u_k(t)}{\nu^k} \right\}, \tag{31}$$

where

$$u_0(t) = 1, \tag{32}$$

$$u_{k+1}(t) = t^2(1-t^2) \frac{u_k'(t)}{2} + \frac{1}{8} \int_0^t (1-5x^2)\, u_k(x)\, dx \qquad k=0, 1, 2,..., \tag{33}$$

$$t = \frac{1}{\sqrt{1+z^2}}, \tag{34}$$

$$\eta = \sqrt{1+z^2} + \ln \frac{z}{1+\sqrt{1+z^2}}, \tag{35}$$

to find

$$K_\nu(z) \sim \sqrt{\frac{\pi}{2}} \frac{e^{-\sqrt{z^2+\nu^2}}}{(z^2+\nu^2)^{1/4}} \left(\frac{\nu+\sqrt{z^2+\nu^2}}{4}\right)^\nu (1+O(\nu^{-1})), \tag{36}$$

and, to leading order in ν^{-1}

$$\frac{K_{\nu-a}(z)}{K_\nu(z)} \sim \left(\frac{z}{2(\nu-a)}\right)^a \qquad z \ll \nu - a \to \infty. \tag{37}$$

With the appropriate substitution in the previous equation, (30) becomes

$$\Delta E^{\mathrm{MSA}} \sim -\frac{\kappa^4 \sigma^4 \Gamma(D/2)}{4(d-2)(d-4)^2 \pi^{d/2} \sigma^d \beta} \qquad d \to \infty, \tag{38}$$

and since d is large, Stirling's approximation for the Gamma function can be readily used to find

$$\Delta E^{\mathrm{MSA}} \sim -\frac{\kappa^4 \sigma^4 \pi^{1/2} e}{2(d-2)^{3/2} (d-4)^2 \beta} \left(\frac{d-2}{2\pi e \sigma^2}\right)^{d/2} \tag{39}$$

3. LIMIT FOR DILUTED SOLUTIONS

For very diluted solutions, where κ is very small, we may approximate the hyperbolic Bessel functions in (30) by their asymptotic form to obtain

$$\Delta E^{\mathrm{MSA}} = \begin{cases} \dfrac{\kappa^2}{4\pi\beta}\,[\ln(\kappa\sigma/2)+\gamma] + O(\kappa^4) & d=2 \\ -\dfrac{\kappa^d \Gamma(2-d/2)}{2^d (d-2)\,\pi^{d/2}\beta} + O(\kappa^4) & 2<d<4 \\ \dfrac{\kappa^4}{16\pi^2\beta}\,[\ln(\kappa\sigma/2)+\gamma] + O(\kappa^6) & d=4 \\ -\dfrac{\kappa^4 \Gamma(d/2-2)}{16(d-2)\,\pi^{d/2}\sigma^{d-4}\beta} + O(\kappa^d) & 4<d<6 \\ -\dfrac{\kappa^4 \Gamma(d/2-2)}{16(d-2)\,\pi^{d/2}\sigma^{d-4}\beta} + O(\kappa^6) & d \geqslant 6 \end{cases} \tag{40}$$

We now consider

$$\Delta A^{\mathrm{MSA}} = \Delta E^{\mathrm{MSA}} - T\,\Delta S^{\mathrm{MSA}}, \tag{41}$$

where ΔA^{MSA} is the excess Helmholtz's free energy and ΔS^{MSA} is the excess entropy due to the charges. From this expression, we obtain

$$\Delta A^{\text{MSA}} = \frac{1}{\beta} \int_0^\beta d\beta' \, \Delta E^{\text{MSA}}(\beta'), \tag{42}$$

which is equivalent to the charging process used in the DH theory to derive thermodynamic functions. After using (40)

$$\Delta A^{\text{MSA}} = \begin{cases} \dfrac{\kappa^2}{4\pi\beta} [\ln(\kappa\sigma/2) + \gamma - 1/2] + O(\kappa^4) & d=2 \\ -\dfrac{\kappa^d \Gamma(2-d/2)}{2^{d-1} d(d-2)\pi^{d/2}\beta} + O(\kappa^4) & 2<d<4 \\ \dfrac{\kappa^4}{32\pi^2\beta} [\ln(\kappa\sigma/2) + \gamma - 1/4] + O(\kappa^6) & d=4 \\ -\dfrac{\kappa^4 \Gamma(d/2-2)}{32(d-2)\,\pi^{d/2}\sigma^{d-4}\beta} + O(\kappa^d) & 4<d<6 \\ -\dfrac{\kappa^4 \Gamma(d/2-2)}{32(d-2)\,\pi^{d/2}\sigma^{d-4}\beta} + O(\kappa^6) & d \geqslant 6 \end{cases} \tag{43}$$

Now we return to (41) to find

$$\Delta S^{\text{MSA}} = \begin{cases} \dfrac{\kappa^2}{8\pi\beta T} + O(\kappa^4) & d=2 \\ -\dfrac{\kappa^d \Gamma(2-d/2)}{2^d d\pi^{d/2}\beta T} + O(\kappa^4) & 2<d<4 \\ \dfrac{\kappa^4}{32\pi^2\beta T} [\ln(\kappa\sigma/2) + \gamma + 1/4] + O(\kappa^6) & d=4 \\ -\dfrac{\kappa^4 \Gamma(d/2-2)}{32(d-2)\,\pi^{d/2}\sigma^{d-4}\beta T} + O(\kappa^d) & 4<d<6 \\ -\dfrac{\kappa^4 \Gamma(d/2-2)}{32(d-2)\,\pi^{d/2}\sigma^{d-4}\beta T} + O(\kappa^6) & d \geqslant 6 \end{cases} \tag{44}$$

Onsager[16] observed that the internal energy of charged, conducting systems consisting of convex particles with a hard repulsive core has an exact lower bound. The Onsager result also implies that the excess entropy diverges at a slower rate than the excess energy in the limit of infinite coupling,[17] thus in the Onsager limit

$$\lim_{\kappa \to \infty} \frac{T \, \Delta S^{\text{MSA}}}{\Delta E^{\text{MSA}}} = 0. \tag{45}$$

It can be verified that this limit is verified for the multidimensional generalization of the MSA. In other words the MSA interpolates between the Debye–Hueckel low density limit, where both theories are identical, to the high density/high coupling limit where the internal energy is the dominating contribution, given by the finite size capacitor model.

4. THE MEAN SPHERICAL APPROXIMATION

The MSA is introduced to satisfy both the low coupling limit given by the DH theory and the infinite coupling limit determined by the Onsager limit.[17] The theory is developed using the spherical capacitor model. The radius of the capacitor is the radius of the central ion plus the width of the ionic cloud, $\lambda_c = 1/2\Gamma$. The value of the screening parameter, Γ, is obtained by minimizing the excess Helmholtz's free energy in the form

$$\Delta A^{\text{MSA}} = \Delta E^{\text{MSA}} - T\,\Delta S^{\text{MSA}}. \tag{46}$$

The excess internal energy (30) is written in terms of Γ and the excess entropy is obtained from Eq. (44) by simply substituting $\kappa = 2\Gamma$:

$$\Delta S^{\text{MSA}} = \begin{cases} \dfrac{\Gamma^2}{2\pi\beta T} & d=2 \\ -\dfrac{\Gamma^d \Gamma(2-d/2)}{d\pi^{d/2}\beta T} & 2<d<4 \\ \dfrac{\Gamma^4}{2\pi^2\beta T}\left[\ln(\Gamma\sigma)+\gamma+1/4\right] & d=4 \\ -\dfrac{\Gamma^4\Gamma(d/2-2)}{2(d-2)\,\pi^{d/2}\sigma^{d-4}\beta T} & d>4 \end{cases} \tag{47}$$

The excess Helmholtz's free energy is found to be

$$\Delta A^{\text{MSA}} =$$

$$\begin{cases} -\dfrac{e^2 K_0(2\Gamma\sigma)}{4\Gamma\sigma\varepsilon K_1(2\Gamma\sigma)}\sum_i \rho_i z_i^2 - \dfrac{\Gamma^2}{2\pi\beta} & d=2 \\ -\dfrac{e^2 K_{d/2-2}(2\Gamma\sigma)}{2(d-2)\,\sigma^{d-2}\varepsilon K_{d/2}(2\Gamma\sigma)}\sum_i \rho_i z_i^2 + \dfrac{\Gamma^d\Gamma(2-d/2)}{d\pi^{d/2}\beta} & 2<d<4 \\ -\dfrac{e^2 K_0(2\Gamma\sigma)}{4\sigma^2\varepsilon K_2(2\Gamma\sigma)}\sum_i \rho_i z_i^2 - \dfrac{\Gamma^4}{2\pi^2\beta}\left[\ln(\Gamma\sigma)+\gamma+1/4\right] & d=4 \\ -\dfrac{e^2 K_{d/2-2}(2\Gamma\sigma)}{2(d-2)\,\sigma^{d-2}\varepsilon K_{d/2}(2\Gamma\sigma)}\sum_i \rho_i z_i^2 + \dfrac{\Gamma^4\Gamma(d/2-2)}{2(d-2)\,\pi^{d/2}\sigma^{d-4}\beta} & d>4 \end{cases} \tag{48}$$

The MSA is the minimization of the excess free energy:[10]

$$\delta(\Delta A^{\mathrm{MSA}}) = 0, \tag{49}$$

which reduces to

$$\frac{\partial\, \Delta A^{\mathrm{MSA}}}{\partial \Gamma} = 0, \tag{50}$$

since ΔA^{MSA} is a function of the single parameter Γ. Substituting (48) into the previous equation, we find

$$\kappa^2 \Gamma(d/2)\, \Psi_d(2\Gamma\sigma) = \begin{cases} 4\Gamma^d \sigma^{d-2} \Gamma(2-d/2) & 2 \leqslant d < 4 \\ -4\Gamma^4\sigma^2[2\ln(\Gamma\sigma) + 2\gamma + 1] & d = 4 \\ \dfrac{8\Gamma^4\sigma^2\Gamma(d/2-2)}{d-2} & d > 4 \end{cases} \tag{51}$$

where

$$\Psi_d(x) = 1 - \frac{(d-2)\, K_{d/2-1}(x)}{x K_{d/2}(x)} - \frac{K^2_{d/2-1}(x)}{K^2_{d/2}(x)}. \tag{52}$$

For odd d, $\Psi_d(x)$ becomes a rational function of x:

$$\Psi_{2n+3}(x) = 1 - \frac{2(2n+1)\, G_n(x)}{G_{n+1}(x)} - \frac{4x^2 G_n^2(x)}{G^2_{n+1}(x)} \qquad n = 0, 1, 2, 3,... \tag{53}$$

where

$$G_n(x) = \sqrt{\frac{2x}{\pi}}\, (2x)^n\, e^x K_{n+1/2}(x) = \sum_{j=0}^{n} \frac{(2n-j)!}{(n-j)!\, j!} (2x)^j \qquad n = 0, 1, 2, 3,... \tag{54}$$

and (51) becomes an algebraic equation in Γ. To obtain the behavior of the quotient in (45) in the infinite coupling limit, we use the asymptotic form of (51),

$$\lim_{\Gamma \to \infty} \kappa^2 \Gamma(d/2) \simeq \begin{cases} \dfrac{4\Gamma^4\sigma^2}{2\Gamma\sigma + 1} & d = 2 \\ -\dfrac{8\Gamma^{d+1}\sigma^{d-1}\Gamma(2-d/2)}{d-2} & 2 < d < 4 \\ 4\Gamma^5\sigma^3[2\ln(\Gamma\sigma) + 2\gamma + 1] & d = 4 \\ -\dfrac{16\Gamma^5\sigma^3\Gamma(d/2-2)}{(d-2)^2} & d > 4 \end{cases} \tag{55}$$

into (30) and (47) to find

$$\lim_{\Gamma \to \infty} \frac{T\Delta S^{\text{MSA}}}{\Delta E^{\text{MSA}}} \simeq \begin{cases} 1 & d=2 \\ \Gamma^{-1} \to 0 & d>2 \end{cases} \tag{56}$$

and therefore, the MSA satisfies the Onsager limit for infinite coupling for all $d \neq 2$.

ACKNOWLEDGMENTS

E. S. V. thanks the U.S. Department of Education Hispanic Faculty Development Fellowship and the University of Puerto Rico, Mayagüez Campus, for his support. L. B. thanks the Office of Naval Research, NSF CHE-9513558 and NSF-EPSCoR OSR-94-52893 for support. H. L. F. acknowledges NSF support through grant DMR-90-23541.

REFERENCES

1. J. L. Lebowitz and J. K. Percus, *Phys. Rev.* **144**:251 (1966).
2. E. Waisman and J. L. Lebowitz, *J. Chem. Phys.* **52**:4307 (1970).
3. J. K. Percus and G. J. Yevick, *Phys. Rev.* **136**:B290 (1964).
4. L. Blum, *Mol. Phys.* **30**:1529 (1977).
5. L. Blum and J. S. Høye, *J. Phys. Chem.* **81**:1311 (1977).
6. K. Hiroike, *Mol. Phys.* **33**:1195 (1977).
7. J. N. Herrera and L. Blum, *J. Chem. Phys.* **94**:5077 (1991).
8. L. Blum, Yu. Kalyuzhnyi, O. Bernard, and J. N. Herrera, *J. Phys. Cond. Matter* **8**:A143 (1966).
9. L. Blum and Y. Rosenfeld, *J. Stat. Phys.* **63**:1177 (1991).
10. H. C. Andersen and D. Chandler, *J. Chem. Phys.* **57**:1918 (1972).
11. H. O. Carmesin, H. L. Frisch, and J. K. Percus, *Phys. Rev. B* **40**:9416 (1989).
12. H. L. Frisch, N. Rivier, and D. Wyler, *Phys. Rev. Lett.* **54**:2061 (1985).
13. T. R. Kirkpatrick, *J. Chem. Phys.* **85**:3515 (1986).
14. M. Schulz and H. L. Frisch, *Phys. Rev. E* **52**:442 (1995).
15. P. Debye and E. Hückel, *Phys. Z.* **24**:185 (1923).
16. L. Onsager, *J. Phys. Chem.* **43**:189 (1939).
17. Y. Rosenfeld and L. Blum, *J. Chem. Phys.* **85**:1556 (1986).
18. Y. Levin, X. Li, and M. E. Fisher, *Phys. Rev. Lett.* **73**:2716 (1994). (Note that Eq. (6) is missing a term for $d \neq 2$, $C_d a^d \beta f^{\text{DH}} = \ln[C_d(x/2\pi)^{d/2} K_{d/2}(x)] + x^2/2(d-2)$).
19. N. J. Vilenkin, *Special Functions and the Theory of Group Representations*, p. 435–440, American Mathematical Society (1968).
20. F. W. J. Olver, in *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Segun, Dover Publications, (1968).