Many-Body Functions of Nonprimitive Electrolytes in One Dimension

Fernando Vericat[1] and Lesser Blum[2]

The statistical mechanics of a mixture of hard-core ions and dipoles in one dimension, namely, the one-dimensional version of the so-called nonprimitive model of an electrolyte, is considered by stressing the effect of the charge–dipole interactions and the hard-core repulsions on the thermodynamics and, especially, on the many-body functions of the systems. The adaptation of Baxter's generating function technique to this model lets us express the thermodynamic and structural functions in terms of a non-Hermitian generalized Hill-type Hamiltonian. The eigenvalues and eigenfunctions of this differential operator yield, in closed form, the n-body correlation functions in the bulk and near the container's walls. We also comment on the screening of the electric fields by the system ions and study the Donnan equilibrium when one of the ionic species in the mixture cannot diffuse through a semipermeable membrane.

KEY WORDS: One-dimensional systems; non-nearest-neighbor forces; many-body functions; nonprimitive electrolytes.

1. INTRODUCTION

Exactly solvable models of interacting particles in one dimension are good "laboratories" in order to check approximate theories designed to describe their more realistic three-dimensional analogs.[1] Obviously, one-dimensional models are, in general, physically poorer than their three-dimensional counterparts. Thus, the Van Hove theorem[2] establishes that no phase transitions can occur in one dimension for many-body systems with pairwise nonsingular forces of finite range. For forces of infinite range, however, the possibility of first-order transitions remains open.[3,4]

---

[1] Instituto de Física de Líquidos y Sistemas Biológicos (IFLYSIB), Universidad Nacional de La Plata, Le Plata, Argentina.
[2] Department of Physics, Faculty of Natural Sciences, University of Puerto Rico, Río Piedras, Puerto Rico 00931.

Classical one-dimensional Coulomb systems, though belonging to this last class (of systems), do not show phase transitions. This was conjectured by Edwards and Lenard[5] for mixtures of point charges of opposite sign, and demonstrated by Kunz[6] for point charges of the same sign in a neutralizing background (the one-component plasma). Despite the lack of phase transitions, classical Coulomb systems in 1D still show many interesting aspects that deserve further study. Moreover, they are among the few known examples of exactly solvable many-body interacting models with non-nearest-neighbor forces.

The calculation of the many-body correlation functions for systems with non-nearest-neighbor forces is in general a nontrivial problem. The correlation functions for the one-component plasma (OCP) of point particles were obtained with different techniques by Baxter[7] and later by Kunz.[6] Baxter also use his method to obtain the correlations in a mixture of point charges of opposite sign in 1D,[7] a problem previously considered by Edwards and Lenard by means of a functional integral technique.[5]

In 3D, the Coulomb force between point charges of opposite sign is unbounded at small distances. In order to avoid this singularity, a harsh repulsive term is usually added to the pair potential. In 1D, this pole does not exist. However, if the one-dimensional systems are to be used as "laboratories" for approximations to be applied in 3D, it is natural to include an equivalent repulsive term in the one-dimensional pair potential. The statistical mechanics in 1D of Coulomb particles with hard core was first considered by Baxter,[8] who calculated the thermodynamics of the one-dimensional version of the primitive model of an electrolyte (PME), namely a mixture of charged hard rods in the line.

The PME mimics electrolytic solutions, considering the solvent as continuous. A more realistic model takes the solvent as a new discrete component. In the so-called nonprimitive model of an electrolyte (NPME), the solvent is modeled as hard spheres with an imbedded dipole. The corresponding version in 1D is a mixture of hard rods with opposite charges (ions) and hard rods with dipoles (the solvent). It should be pointed out here that, unlike the one-dimensional PME (where hard rods are not necessary for the system's stability), in the one-dimensional NPME the lack of hard repulsions makes the system unstable.[9]

In general, the presence of hard-core interactions in systems whose particles interact via non-nearest-neighbor forces complicates the evaluation of the correlation functions even more. For charged hard rods in a neutralizing background (the OCP with hard core), such an evaluation is possible for the one[10]- and two[11]-body correlation functions by extending the analysis Kunz has done for the OCP of point particles.[6] For the PME in 1D, Baxter suggests the possibility of evaluating the

correlation functions by applying the same technique he employs for the mixture of point charges of opposite sign.[8]

In this work we use Baxter's method for studying the correlations of the NPME in 1D. In a previous paper[12] we exactly solved the system's thermodynamics and confirmed the necessity of the hard cores in order to avoid unstabilities. Here we are mainly interested in the many-body functions, but we also discuss some other aspects related to the thermodynamic behavior of the system.

In the next section we present the one-dimensional version of the NPME and define a hierarchy of generalized canonical and grand-canonical functions. These many-body functions are the basis of our description of the system's thermodynamics and structure. Each of the generalized grand-canonical functions is written in terms of an abstract operator which satisfies a difference-differential equation, whose solution [Eq. (37)] is the main result of this paper.

The main thermodynamic results are summarized in Section 3. We stress the effect of external electric fields on the thermodynamic magnitudes and briefly discuss how the electric fields inside the fluid are shielded by the mobile charges. Section 4 is the paper's core. There we use Eq. (37) in order to evaluate the many-body correlation functions in two different situations: far enough from the walls (where the system is translational invariant) and near them (where it is inhomogeneous). In Section 5 we apply the results of the previous sections to study the Donnan equilibrium when one of the charged species cannot diffuse through a selective membrane dividing the system's container.

The operators associated with the generalized functions are written in Eq. (37) in terms of the eigenvalues and eigenfunctions of a Hill-type differential operator. We devote Section 6 to study its characteristic value problem. We particularly consider the simplest case of detailed charge balancing, for which the solution is expressed in terms of continued fractions. In the especially simple case of point particle at high temperatures, the generalized Mathieu operator reduces to the harmonic oscillator Hamiltonian. Fully analytic expressions are obtained in this particular case, as is shown in Section 7.

2. NONPRIMITIVE ELECTROLYTE IN 1D

2.1. The System

Let us consider the nonprimitive model for electrolytes in 1D.[12] The system is a mixture of s species; $s - 1$ constitute the solute and the remaining one is the solvent. All particles in the mixture are hard rods and

we assume for simplicity that all of them have the same length b. The ions of species α ($\alpha = 1,..., s-1$) have a point charge of strength $Z_\alpha q$ in the hard-rod center, where q is the unit charge and Z_α the electrovalence. The solvent hard rods have a dipole of moment μ.

The particles are free to move along the segment $[0, L]$ on the x axis. We assume that they are subject to the electric field generated by two point charges $+Q$ and $-Q$ placed at the extremes $x = -b/2$ and $x = L + b/2$.

Denote by N_α ($\alpha = 1,..., s$) the number of particles of species α, and by x_{α_i} ($i = 1,..., N_\alpha$) the position of the ith particle of species α. The configuration of the solvent particles is given by the position and the orientation of the point dipole. The orientation of the ith dipole is given by a scalar e_i, which can take the values $+1$ or -1.

The basic long-range interactions are derived from the Coulomb potential $\Phi(x)$, which is solution of the one-dimensional Poisson equation

$$\frac{d^2\Phi(x)}{dx^2} = -\delta(x) \tag{1}$$

Explicitly, the pair interactions in the model are

$$\Phi_{\alpha\gamma}(x_{\alpha_i}; x_{\gamma_j}) = \infty \qquad (\alpha, \gamma = 1,..., s-1, s) \tag{2a}$$

for $|x_{\alpha_i} - x_{\gamma_j}| < b$, and

$$\Phi_{\alpha\gamma}(x_{\alpha_i}; x_{\gamma_j}) = \tfrac{1}{2} Z_\alpha Z_\gamma q^2 |x_{\alpha_i} - x_{\gamma_j}| \qquad (\alpha, \gamma = 1,..., s-1)$$

$$\Phi_{\alpha s}(x_{\alpha_i}; x_{s_j} e_j) = \tfrac{1}{2} Z_\alpha q e_j \mu (x_{\alpha_i} - x_{s_j})/|x_{\alpha_i} - x_{s_j}| \qquad (\alpha = 1,..., s-1)$$

$$\Phi_{ss}(x_{s_i} e_i; x_{s_j} e_j) = 0 \tag{2b}$$

for $|x_{\alpha_i} - x_{\gamma_j}| > b$.

The hard-core condition (2a) imposes a restriction on the number of particles,

$$b \sum_{\alpha=1}^{s} N_\alpha \leqslant L \tag{3}$$

Besides for this steric restriction, we consider, according to Baxter's technique,[7,8] that N_α is arbitrary. To ensure the overall electroneutrality of the system, the total charge $-q\sigma$, where

$$\sigma \equiv \sum_{\alpha=1}^{s-1} Z_\alpha N_\alpha \tag{4}$$

is fixed at $x = L$. The inclusion of this extra charge is equivalent to assuming that the system is in contact with an infinite reservoir which exchanges ions with it. Clearly the system plus the reservoir is globally

electroneutral. In the case of interest, however, the system by itself must be electroneutral:

$$\sigma = 0 \tag{5}$$

Following Baxter,[7] we will reach condition (5) at the end of the calculations in a somehow artificial manner: a term containing a new variable t is introduced in the expression of the total potential energy in such a way that by integrating with respect to t, the integral representation of the Kronecker delta $\delta_{\sigma,0}$ appears in the grand-canonical functions.

We denote by $\Phi_{\{N_\alpha\}}$ the potential energy for an arbitrary composition $\{N_\alpha\}$ $(\alpha = 1,..., s-1, s)$ of the system, which in general will not be neutral. $\Phi_{\{N_\alpha\}}$ is the sum of four contributions: (i) the pair interactions among all possible pairs of particles, (ii) the interaction between each particle and charges $\pm Q$, (iii) the interaction between each particle and the extra boundary charge $-q\sigma$, and (iv) the t-dependent term which contains the system electroneutrality. We have

$$\Phi_{\{N_\alpha\}} = \frac{1}{2} \sum_{\alpha,\gamma}^{s-1} \sum_{\alpha_i \neq \gamma_j}^{N_\alpha N_\gamma} \Phi_{\alpha\gamma}(x_{\alpha_i}; x_{\gamma_j}) + \frac{1}{2} \sum_{\alpha=1}^{s-1} \sum_{\alpha_i s_j}^{N_\alpha N_s} \Phi_{\alpha s}(x_{\alpha_i}; x_{s_j} e_j)$$

$$+ \frac{1}{2} \sum_{s_i \neq s_j}^{N_s} \Phi_{ss}(x_{s_i} e_i; x_{s_j} e_j)$$

$$+ \sum_{\alpha=1}^{s-1} \sum_{\alpha_i}^{N_\alpha} Z_\alpha q Q |L - x_{\alpha_i}| + \mu Q \sum_{i=1}^{N_s} e_i$$

$$+ \frac{1}{2} q^2 \sigma \sum_{\alpha=1}^{s-1} \sum_{\alpha_i}^{N_\alpha} Z_\alpha |L - x_{\alpha_i}| + \frac{1}{2} q\mu\sigma \sum_{i=1}^{N_s} e_i$$

$$- q\sigma i k T t \tag{6}$$

The t-dependent term can be interpreted as the interaction of the system ions with an imaginary point dipole of moment $i2kTt$ located inside the reservoir $(x > L)$. Here $i = \sqrt{-1}$ is the imaginary unit, k the Boltzmann constant, and T the absolute temperature. The explicit dependence of the potential on L and t is

$$\Phi_{\{N_\alpha\}}(L, t) = \tfrac{1}{2}(q\sigma)^2 L + qQ\sigma L - ikT\sigma q t$$

$$+ \text{terms of zeroth order in } L \text{ and } t \tag{7}$$

When $\exp[-\Phi_{\{N_\alpha\}}(L, t)/kT]$ is integrated over t between $-\pi$ and π, we get

$$\int_{-\pi}^{\pi} \exp(iq\sigma t) \, dt = 2\pi\delta_{\sigma,0} \tag{8}$$

which is equivalent to the electroneutrality condition (5). We then obtain the thermodynamic and structural functions of interest, such as the parti-

tion and the correlation functions for the electroneutral system, by first considering $\Phi_{\{N_\alpha\}}$ arbitrary and eventually integrating over t.

2.2. Generalized Grand-Canonical Functions

We proceed to define a set of auxiliary functions which are functionals of $\Phi_{\{N_\alpha\}}$.

Consider that n_α $(\alpha = 1,..., s-1, s)$ particles are kept fixed. Define the generalized canonical functions $S_{\{N_\alpha\};\{n_\alpha\}}$:

$$S_{\{N_\alpha\};\{n_\alpha\}}(L, t, Q; \mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s})$$

$$= \left(\prod_{\alpha=1}^{s} \frac{1}{(N_\alpha - n_\alpha)!} \right)$$

$$\times \sum_{\{\mathbf{e}^{(N_s - n_s)}\}} \int_0^L \cdots \int_0^L d\mathbf{x}^{\{N_\alpha - n_\alpha\}} \exp\left(\frac{-\Phi_{\{N_\alpha\}}}{kT} \right) \tag{9}$$

where we use the compact notation $\mathbf{x}^{\{n_\alpha\}}$ for the position of all the root particles and $d\mathbf{x}^{\{N_\alpha - n_s\}}$ for the integration over all field particles. Furthermore, $\mathbf{e}^{n_s}$ denotes the orientation of all the fixed dipoles and the sum is over all possible orientations of the free dipoles.

Following Baxter, we obtain a recurrence relation for $S_{\{N_\alpha\};\{n_\alpha\}}$ by differentiation with respect to L. We must thus consider the possibility of L being less than some or all of the fixed particle coordinates $\mathbf{x}^{\{n_\alpha\}}$, although, of course, the functions of interest will be evaluated only when L is greater than all them.

In order to take that possibility into account, the summations in Eq. (6) include all the field particles, but only the root particles which lie between 0 and L.

Differentiation of $S_{\{N_\alpha\};\{n_\alpha\}}$ with respect to L gives

$$\frac{\partial S_{\{N_\alpha\};\{n_\alpha\}}(L, t, Q; \mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s})}{\partial L}$$

$$= \sum_{\gamma=1}^{s-1} \exp(iZ_\gamma t) \exp\left(\tau \frac{\partial^2}{\partial t^2} \cdot + i\eta \frac{\partial}{\partial t} \cdot \right)$$

$$\times S_{\{N_\alpha - 1\}_\gamma; \{n_\alpha\}}(L - b, t \cdot Q; \mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s})$$

$$+ 2 \cos\left(\kappa \frac{\partial}{\partial t} \cdot + i\xi \right) \exp\left(\tau \frac{\partial^2}{\partial t^2} \cdot + i\eta \frac{\partial}{\partial t} \cdot \right)$$

$$\times S_{\{N_\alpha - 1\}_s; \{n_\alpha\}}(L - b, t, Q; \mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s})$$

$$+ \frac{\tau}{b} \left(\frac{\partial^2}{\partial t^2} \cdot + i \frac{\eta}{\tau} \frac{\partial}{\partial t} \cdot \right) S_{\{N_\alpha\};\{n_\alpha\}}(L, t, Q; \mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s}) \tag{10}$$

Here $\{N_\alpha - 1\}_\gamma$ means that we must eliminate a particle of type γ from the set of mobile particles. We have further defined

$$\tau = q^2 b/2kT; \qquad \kappa = \mu q/kT$$
$$\eta = qQb/kT; \qquad \xi = \mu Q/kT$$
(11)

Equation (10) is a difference-differential equation for the generalized canonical function $S_{\{N_\alpha\};\{n_\alpha\}}$.

Since the definition of $S_{\{N_\alpha\};\{n_\alpha\}}$ depends on the number of fixed particles whose coordinates are smaller than L, we see that it is a function of L with discontinuities at the position of each fixed particle. Therefore, for $L = x_{\gamma_j}$ ($\gamma = 1,..., s - 1$, s; $j = 1, n_\gamma$), we have the boundary conditions

$$\lim_{\delta \to 0} S_{\{N_z\};\{n_\alpha\}}(L = x_\gamma + \delta, t, Q; \mathbf{x}^{\{n_z\}} \mathbf{e}^{n_s})$$

$$= K_\gamma \lim_{\delta \to 0} S_{\{N_\alpha - 1\}_\gamma;\{n_\alpha - 1\}_\gamma}(L = x_\nu - b - \delta, t, Q; \mathbf{x}^{\{n_z\}} \mathbf{e}^{n_s}) \qquad (12)$$

where

$$K_\gamma = \exp(iZ_\gamma t) \exp\left(\tau \frac{\partial^2}{\partial t^2} \cdot + i\eta \frac{\partial}{\partial t} \cdot\right), \qquad (\gamma = 1,..., s - 1)$$

$$K_s = K_s(e_j) = \exp\left[ie_j\left(\kappa \frac{\partial}{\partial t} \cdot + i\xi\right)\right] \exp\left(\tau \frac{\partial^2}{\partial t^2} \cdot + i\eta \frac{\partial}{\partial t} \cdot\right)$$
(13)

If the fixed particle is a dipole, K_s depends on its orientation e_j.

We also have the normalization condition

$$S_{\{N_\alpha\};\{n_\alpha\}}(L = \sigma^-, t, Q; \mathbf{x}^{\{n_z\}} \mathbf{e}^{n_s}) = \delta_{\{N_z\};\{n_z\}} \delta_{0,\{n_\alpha\}}$$
(14)

From the generalized canonical functions we can define the generalized grand-canonical functions:

$$f_{\{n_\alpha\}}(L, t, Q; \mathbf{x}^{\{n_z\}} \mathbf{e}^{n_s})$$

$$= \sum_{\{N_\alpha\} \geqslant \{n_\alpha\}} \prod_{\alpha = 1}^s \omega_\alpha^{N_\alpha - n_\alpha} S_{\{N_\alpha\};\{n_\alpha\}}(L, t, Q; \mathbf{x}^{\{n_z\}} \mathbf{e}^{n_s})$$
(15)

where ω_α is a positive parameter which will be later identified with the fugacity of particles of species α. Here the compact notation $\{N_\alpha\} \geqslant \{n_\alpha\}$ means that the sums are over $N_\alpha \geqslant n_\alpha$ ($\alpha = 1,..., s$). The sums must also be limited to those sets $\{N_\alpha\}$ that satisfy the condition (3).

In terms of these new functions, Eqs. (10), (12), and (14) yield the following results.

(i)   Between fixed particle positions

$$\frac{\partial}{\partial L} f_{\{n_\alpha\}}(L,\, t,\, Q;\, \mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s})$$

$$= H_1 f_{\{n_\alpha\}}(L - b,\, t,\, Q;\, \mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s}) + H_2 f_{\{n_\alpha\}}(L,\, t,\, Q;\, \mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s}) \qquad (16)$$

where

$$H_1 = \sum_{\gamma = 1}^{s-1} \omega_\gamma K_\gamma + \omega_s [K_s(e = 1) + K_s(e = -1)] \qquad (17)$$

$$H_2 = \frac{\tau}{b} \left(\frac{\partial^2}{\partial t^2} \cdot + i \frac{\eta}{\tau} \frac{\partial}{\partial t} \cdot \right) \qquad (18)$$

(ii)   Across the position x_γ of a fixed particle

$$f_{\{n_\beta\}}(L,\, t,\, Q;\, \mathbf{x}^{\{n_\beta\}} \mathbf{e}^{n_{s'}}) = K_\gamma f_{\{n_\beta - 1\}}(L - b,\, t,\, Q;\, \mathbf{x}^{\{n_\beta - 1\}} \mathbf{e}^{n_s}) \qquad (19)$$

where $\mathbf{x}^{\{n_\beta - 1\}}$ means that we have eliminated the coordinate x_γ from the set $\mathbf{x}^{\{n_\beta\}}$.

(iii)   At $L = 0$

$$f_0(L = 0^-,\, t,\, Q) = 1 \qquad (20)$$

We will later see how the functions f_0 and $f_{\{n_\alpha\}}$ give the grand-canonical partition function $\Xi(L,\, Q)$ and the $\{n_\alpha\}$-body correlation functions $g_{\{n_\alpha\}}(Q;\, \mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s})$. Now we obtain $f_{\{n_\alpha\}}(L,\, t,\, Q;\, \mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s})$ from Eqs. (16)–(20).

The generalized grand-canonical functions $f_{\{n_\alpha\}}$ can be written in terms of the mean value of an operator $\hat{f}_{\{n_\alpha\}}$, using the formalism of operators and vectors in Hilbert space:

$$f_{\{n_\alpha\}}(L,\, t,\, Q;\, \mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s}) = \int_{-\pi}^{\pi} \langle t | \hat{f}_{\{n_\alpha\}} | t' \rangle \, dt' \qquad (21)$$

where the kets $|t\rangle$ represent the eigenvectors of the operator $\hat{t}$ with continuous spectrum $t \in [-\pi, \pi]$: $\hat{t}|t\rangle = t|t\rangle$.

Equation (16), with boundary conditions (19) and (20), also holds in operator language. To solve it for the operator $\hat{f}_{\{n_\alpha\}}$, we assume that the

positions of the fixed particles (without considering to which species they belong) are ordered

$$x_r < \cdots < x_2 < x_1 \qquad \left(r = \sum_{\alpha=1}^{s} n_\alpha \right) \tag{22}$$

Furthermore, we take into account condition (3). This condition limits the number of particles between fixed particles or between the fixed particle located at x_1 (at x_r) and the container's right (left) wall. Therefore the operator $\hat{f}_{\{n_\alpha\}}$ is formally given by

$$\hat{f}_{\{n_\alpha\}} = \sum_{n=0}^{\infty} \frac{(\hat{H}'')^n}{n!} \left[(L - x_1) - nb \right]^n \theta[(L - x_1) - nb] \cdot \hat{B}$$

$$\times \sum_{k=0}^{\infty} \frac{(\hat{H}'')^k}{k!} \left[x_r - kb \right]^k \theta[x_r - kb] \tag{23}$$

with θ the Heaviside step function and

$$\hat{B} = \hat{K}_1 \cdot \prod_{j=1}^{r-1} \sum_{k_j=0}^{\infty} \frac{(\hat{H}'')^{k_j}}{k_j!} \left[(x_j - x_{j+1}) - (k_j + 1)b \right]^{k_j}$$

$$\times \theta[(x_j - x_{j+1}) - (k_j + 1)b] \cdot \hat{K}_{j+1} \tag{24}$$

Here K_γ $(\gamma = 1,...,r)$ are operators which, in t-representation, yield Eq. (13). Using the operator $\hat{P} \equiv -id \cdot /d\hat{t}$ we have

$$\hat{K}_\gamma = \exp(iZ_\gamma \hat{t}) \exp[-\tau(\hat{P} + Q/q)^2] \exp(\tau Q^2/q^2) \qquad \text{for ions}$$

$$\hat{K}^s(e_j) = \exp[-e_j \kappa(\hat{P} + Q/q)] \exp[-\tau(\hat{P} + Q/q)^2] \tag{25}$$

$$\times \exp(\tau Q^2/q^2) \qquad \text{for dipoles}$$

In Eqs. (23) and (24), the operator $\hat{H}''$ is defined by

$$\hat{H}'' \equiv \hat{H}_1 + \hat{H}_2 \exp(b\hat{H}') \tag{26}$$

where $\hat{H}'$ satisfies

$$[\exp(b\hat{H}')]\hat{f}_{\{n_\alpha\}}(L - b) = \hat{f}_{\{n_\alpha\}}(L) \tag{27}$$

The operators $\hat{H}_1$ and $\hat{H}_2$ are defined so that, in the t-representation, they yield Eqs. (17) and (18). Therefore

$$\hat{H}_1 = \sum_{\gamma=1}^{s-1} \omega_\gamma \hat{K}_\gamma + \omega_s[\hat{K}_s(e_j = 1) + \hat{K}_s(e_j = -1)] \tag{28}$$

$$\hat{H}_2 = -(\tau/b)[\hat{P}^2 + 2(Q/q)\hat{P}] \tag{29}$$

We now consider that $L - x_1 > nb$. This condition implies that the container's "right wall" is far enough to disturb the bulk of the system (semi-infinite system). Then

$$\hat{H}' \equiv \hat{H} = \hat{H}_1 \exp(-b\hat{H}) + \hat{H}_2 \tag{30}$$

and

$$\hat{H}'' = \hat{H} \exp(b\hat{H}) \tag{31}$$

Equation (30) implicitly defines the operator $\hat{H}$, which will play a central role in the remainder of the paper. In general it is non-Hermitian and can be spectrally decomposed into the form

$$\hat{H} = \sum_m \gamma_m |\phi_m\rangle\langle\psi_m| \tag{32}$$

where $\{|\phi_m\rangle\}$ and $\{|\psi_m\rangle\}$ denote biorthogonal vectors which satisfy

$$\hat{H}|\phi_m\rangle = \gamma_m |\phi_m\rangle \tag{33}$$

and

$$\hat{H}^\dagger |\psi_m\rangle = \gamma_m^* |\psi_m\rangle \tag{34}$$

respectively, with $\hat{H}^\dagger$ being the Hermitian adjoint of the operator $\hat{H}$. The sum in Eq. (32) is, of course, over all the eigenvector indices.

In the t-representation the (abstract) eigenvalue equation (33) yields

$$(H_1 e^{-\gamma_m b} + H_2)\, \phi_m(t) = \gamma_m \phi_m(t) \tag{35}$$

where H_1 and H_2 are given by Eqs. (17)–(18) and (13), while $\phi_m(t) = \langle t|\phi_m\rangle$.

The expansion of the abstract operator $\hat{f}_{\{n_\alpha\}}$ corresponding to Eq. (32) is

$$\hat{f}_{\{n_\alpha\}} = \sum_{mm'} |\phi_m\rangle \frac{e^{\gamma_m(L-x_1)}}{1 + \gamma_m b} \langle\psi_m| \hat{B}|\phi_{m'}\rangle$$

$$\times \sum_{k=0}^{\infty} \frac{(\gamma_{m'} e^{\gamma_{m'} b})^k}{k!} [x_r - kb]^k \theta[x_r - kb]\langle\psi_{m'}| \tag{36}$$

In the thermodynamic limit $L \to \infty$, $N_\alpha \to \infty$, $N_\alpha/L = \rho_\alpha = \text{const}$, Eq. (37) yields

$$\hat{f}_{\{n_\alpha\}} = \sum_m |\phi_0\rangle - \frac{e^{\gamma_0(L-x_1)}}{1+\gamma_0 b} \langle \psi_0| \hat{B} |\phi_m\rangle$$

$$\times \sum_{k=0} \frac{(\gamma_m e^{\gamma_m b})^k}{k!} [x_r - kb]^k \theta[x_r - kb] \langle \psi_m| \qquad (37)$$

where γ_0 represents the largest real eigenvalue of Eq. (35).

For the thermodynamic properties we have $\{n_\alpha\} \equiv 0$. Consequently, in the same way as we obtain Eq. (37), we deduce

$$\hat{f}_0 = \frac{e^{\gamma_0(L+b)}}{1+\gamma_0 b} |\phi_0\rangle\langle\psi_0| \qquad (38)$$

3. THERMODYNAMICS

The thermodynamics of the system under study has been discussed in previous work.[12] Here we review some of the main results.

The grand partition function is

$$\Xi(L, Q) = \frac{1}{2\pi} e^{-Q^2 L/2kT} \int_{-\pi}^{\pi} f_0(L, t, Q) \, dt$$

$$= \frac{1}{2\pi} e^{-Q^2 L/2kT} \int_{-\pi}^{\pi} dt \int_{-\pi}^{\pi} dt' \langle t| \hat{f}_0 |t'\rangle \qquad (39)$$

Taking into account Eq. (38), we find for the bulk pressure

$$\frac{P(Q)}{kT} = \lim_{L \to \infty} \frac{1}{L} \ln \Xi(L, Q)$$

$$= \gamma_0(Q) - \frac{Q^2}{2kT} \qquad (40)$$

The eigenvalue γ_0 is an analytic monotonic function of the thermodynamic variables. Then, from Eq. (40), we see that no phase transitions can occur for the ion–dipole mixture, a common feature with other one-dimensional Coulomb systems.[5,6]

The operator H is an periodic function of t of period 2π (we are here assuming that all the ionic electrovalences are $+1$ or -1). Then the eigenvectors of Eq. (35) are Bloch wave functions

$$\phi_m(t, Q) = \phi_m(t, 0) e^{-i(Q/q)t} \qquad (41)$$

where $k = Q/q$ is the Bloch momentum and $\phi_m(t, 0)$ (the zero-external-field eigenfunction) is a periodic function of period 2π.

Since the eigenfunctions must satisfy the periodicity condition

$$\phi_m(t + 2\pi, Q) = \phi_m(t, Q) \tag{42}$$

we see that relation (41) is valid for external fields that satisfy $D = Q = nq$, with n being an integer. In this case, the eigenvalues that correspond to the eigenvectors (41) satisfy

$$\gamma_m(Q) - \frac{Q^2}{2kT} = \gamma_m(0) \tag{43}$$

The particle number density for different species is also given in terms of the maximum eigenvalue

$$\rho_\alpha(Q) = \lim_{L \to \infty} \frac{1}{L} \omega_\alpha \frac{\partial \ln \Xi}{\partial \omega_\alpha}$$

$$= \omega_\alpha \frac{\partial \gamma_0(Q)}{\partial \omega_\alpha} \tag{44}$$

According to Eqs. (43) and (44), we have for $Q = nq$ $(n \in \mathbb{Z})$

$$\Delta\rho_\alpha \equiv \rho_\alpha(Q) - \rho_\alpha(0) = 0 \tag{45}$$

The fact that densities are in this case the same either with or without the external field is a consequence of ionic screening.

Since in general $\gamma_0(Q) - Q^2/2kT$ is a periodic function of Q of period q, we see that not only the pressure [Eq. (40)] and the densities [Eq. (44)], but also other state functions are periodic in the external field. In particular, the average electric field

$$E(Q) - kT \lim_{L \to \infty} \left[\frac{1}{L} \frac{\partial \ln \Xi(L, Q)}{\partial Q} \right]$$

$$Q - kT \frac{\partial \gamma_0(Q)}{\partial Q} \tag{46}$$

is null for $Q = nq$, since it is zero for $Q = 0$. This means that charges which are multiples of the ionic charge are perfectly shielded.

If the external charge Q is not a multiple of the ionic charge q, then the ionic screening is not perfect. In this case Eqs. (43) and (45) are no longer valid, and the system shows electrostriction. In any case the system structurally behaves as a dielectric, since ions tend to form neutral pairs. Screening requires the separation of a number of such pairs. Thus, only integral multiples of the ionic charges can be perfectly shielded.[13,14]

It should be noted that in real electrode–electrolyte interfaces, Q and q are always multiples of the elementary charge. Moreover, $Q \gg q$, so that if we consider that Q is an integral multiple of q, there is no limitation of the real physical situation. This is implicit in our earlier work[12] and was explicitly used in Eq. (36) of that work. We also remark that, from the point of view of electrolyte theory, one is interested in those situations in which the system screens, because that is what happens in the real 3-dimensional case.

4. STRUCTURE

We use the generalized $\{n_\alpha\}$-body functions to compute the correlation functions, which are given by

$$g_{\{n_\alpha\}}(\mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s}) = \left(\prod_{\alpha=1}^{s} \frac{L^{n_\alpha}(N_\alpha - n_\alpha)!}{N_\alpha!} \right) \frac{\int_{-\pi}^{\pi} S_{\{N_\alpha\};\{n_\alpha\}}(L, t, Q; \mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s})\, dt}{\int_{-\pi}^{\pi} S_{\{N_\alpha\};0}(L, t, Q)\, dt} \tag{47}$$

Thus, in the thermodynamic limit, we have

$$g_{\{n_\alpha\}}(\mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s}) = \prod_{\alpha=1}^{s} \left(\frac{\omega_\alpha}{\rho_\alpha} \right)^{n_\alpha} \frac{\int_{-\pi}^{\pi} dt \int_{-\pi}^{\pi} dt' \langle t| \hat{f}_{\{n_\alpha\}} |t' \rangle}{\int_{-\pi}^{\pi} dt \int_{-\pi}^{\pi} dt' \langle t| \hat{f}_0 |t' \rangle} \tag{48}$$

We now specialize to the bulk region and the region near the walls.

4.1. Bulk Correlations

Here we consider that all the fixed particles are far from the container's walls. We assume that the positions of the fixed particles satisfy $Nb < x_r < \cdots < x_2 < x_1 < L - Nb$, where $N = \sum_{\alpha=1}^{s} N_\alpha$. Equation (36) gives

$$\hat{f}_{\{n_\alpha\}} = \sum_{mm'} |\phi_m\rangle \frac{e^{\gamma_m(L - x_1)}}{1 + \gamma_m b} \langle \psi m| \hat{B} |\phi_{m'}\rangle \frac{e^{\gamma_{m'} x_r}}{1 + \gamma_{m'} b} \langle \gamma \psi_{m'}| \tag{49}$$

In the thermodynamic limit,

$$\hat{f}_{\{n_\alpha\}} = |\phi_0\rangle \frac{e^{\gamma_0(L - x_1)}}{1 + \gamma_0 b} \langle \psi_0| \hat{B} |\phi_0\rangle \frac{e^{\gamma_0 x_r}}{1 + \gamma_0 b} \langle \psi_0| \tag{50}$$

From Eq. (48) and taking into account Eq. (38), we have

$$g_{\{n_\alpha\}}(\mathbf{x}^{\{n_\alpha\}} \mathbf{e}^{n_s}) = \prod_{\alpha=1}^{s} \left(\frac{\omega_\alpha}{\rho_\alpha} \right)^{n_\alpha} \frac{e^{\gamma_0(x_r - x_1)} e^{-\gamma_0 b}}{1 + \gamma_0 b} \langle \psi_0| \hat{B} |\phi_0\rangle \tag{51}$$

It is seen that, like the thermodynamic quantities, the correlation functions are periodic functions of the external field of period q.

Consider the singlet and pair correlation functions. Since the expressions for ions and dipoles are similar, we will omit (in the arguments) the dipole orientation $\mathbf{e}^{ns}$, though it is understood that for dipolar correlations these variables must be present.

The one-body correlation function is

$$g_\alpha(x_1) \qquad \text{(for all values of } x_1\text{)} \tag{52}$$

so that the bulk density is

$$\rho_\alpha = \frac{\omega_\alpha e^{-\gamma_0 b}}{1 + \gamma_0 b} \langle \psi_0 | \hat{K}_\alpha | \phi_0 \rangle \tag{53}$$

In the bulk region the one-body correlation function is translationally invariant.

The pair correlation function is

$$g_{\alpha\gamma}(x_1 x_2) = \frac{\omega_\alpha \omega_\gamma}{\rho_\alpha \rho_\gamma} \frac{e^{-\gamma_0 b} e^{\gamma_0(x_2 - x_1)}}{1 + \gamma_0 b} \langle \psi_0 | \hat{B}_{\alpha\gamma} | \phi_0 \rangle \tag{54}$$

Here the operator $\hat{B}_{\alpha\gamma}$ is

$$\hat{B}_{\alpha\gamma} = \hat{K}_\alpha \sum_{k=0}^{\infty} \frac{(\hat{H} \exp(b\hat{H}))^k}{k!} [(x_1 - x_2) - (k+1)b]^k$$
$$\times \theta[(x_1 - x_2) - (k+1)b] \hat{K}_\gamma \tag{55}$$

In the t-representation the matrix element yeilds

$$\langle \psi_0 | \hat{B}_{\alpha\gamma} | \phi_0 \rangle$$
$$= \sum_{k=0}^{\infty} \frac{[(x_1 - x_2) - (k+1)b]^k}{k!} \theta[(x_1 - x_2) - (k+1)b]$$
$$\times \int_{-\pi}^{\pi} dt\, \psi_0^*(t) K_\alpha (He^{bH})^k K_\gamma \phi_0(t) \tag{56}$$

Using the spectral decomposition (32), the matrix element can be written in the equivalent form

$$\langle \psi_0 | \hat{B}_{\alpha\gamma} | \phi_0 \rangle$$
$$= \sum_{mk} \frac{(\gamma_m e^{\gamma_m b})^k}{k!} [(x_1 - x_2) - (k+1)b]^k \theta[(x_1 - x_2) - (k+1)b]$$
$$\times \langle \psi_0 | \hat{K}_\alpha | \phi_m \rangle \langle \psi_m | \hat{K}_\gamma | \phi_0 \rangle \tag{57}$$

where

$$\langle \psi_0 | \hat{K}_\alpha | \phi_m \rangle = \int_{-\pi}^{\pi} dt \, \psi_0^*(t) \, K_\alpha \phi_m(t) \tag{58}$$

Provided that (57) is absolutely convergent, for large $|x_1 - x_2|$,

$$\rho_\alpha \rho_\gamma \, g_{\alpha\gamma}(x_1 x_2) \sim \frac{\omega_\alpha \omega_\gamma e^{-2\gamma_0 b}}{(1 + \gamma_0 b)^2} \langle \psi_0 | \hat{K}_\alpha \hat{K}_\gamma | \phi_0 \rangle \tag{58}$$

Thus, the pair correlation function is a constant in the translational-invariant central region when x_1 and x_2 are far enough from each other.

It should be noted that, for neutral hard rods ($q = 0$, $\mu = 0$)—say, for a Tonks gas[15]—we recover the classical result of Salsburg et al.,[16] previously found by Zernike and Prins.[17] Using $\omega_\alpha = \omega_\gamma = \omega = \gamma_0 e^{\gamma_0 b}$ and $\gamma_0 = \rho/(1 - \rho b)$, with ρ the total number density, we have

$$\rho^2 g(x_1 x_2) = \frac{\rho^2}{1 - \rho b} \sum_{k=0}^{\infty} \frac{[a(y-k)]^k}{k!} e^{-a(y-k)} \theta(y - k) \tag{60}$$

where

$$y = (x_1 - x_2 - b)/b, \qquad a = \gamma_0 b = \rho b/(1 - \rho b) \tag{61}$$

Moreover, for $b = 0$, Baxter's result for point ions[7] is recovered from Eqs. (54) and (56),

$$\rho_\alpha \rho_\gamma \, g_{\alpha\gamma}(x_1 x_2) = \omega_\alpha \omega_\gamma \int_{-\pi}^{\pi} dt \, \phi_0^*(t) \, K_\alpha e^{(H - \gamma_0)|x_1 - x_2|} K_\gamma \phi_0(t) \tag{62}$$

where we consider that $\psi_0(t) = \phi_0(t)$, since, in this case, the operatyor H is self-adjoint.

Using Eqs. (57) and (58), we can write the point particle correlations in the alternative form given by Edwards and Lenard[5]:

$$\rho_\alpha \rho_\gamma \, g_{\alpha\gamma}(x_1 x_2) = \sum_m B_{m,\alpha} B_{m,\gamma} e^{-(\gamma_0 - \gamma_m)(x_1 - x_2)} \tag{63}$$

where

$$B_{m,\alpha} = \omega_\alpha \int_{-\pi}^{\pi} dt \, \phi_0(t) \, K_\alpha \phi_m(t) \tag{64}$$

4.2. The Near-Wall Region

We consider the one-body correlation function $g_\alpha(x_1)$ for values of x_1 so that $0 \leqslant x_1 \leqslant Nb$:

$$\rho_\alpha g_\alpha(x_1) = \omega_\alpha \frac{\int_{-\pi}^{\pi} dt \int_{-\pi}^{\pi} dt' \, \langle t | \hat{f}_1 | t' \rangle}{\int_{-\pi}^{\pi} dt \int_{\pi}^{\pi} dt' \, \langle t | \hat{f}_0 | t' \rangle} \tag{65}$$

The relation between the eigenvectors of operators $\hat{t}$ and $\hat{P}$ is

$$\langle t | P \rangle = \frac{1}{(2\pi)^{1/2}} e^{iPt} \tag{66}$$

Thus, we see that Eq. (65) can be written

$$\rho_\alpha g_\alpha(x_1) = \omega_\alpha \frac{\langle \rho = 0 | \hat{f}_1 | P = 0 \rangle}{\langle P = 0 | \hat{f}_0 | P = 0 \rangle} \tag{67}$$

In the thermodynamic limit, using Eqs. (23) and (24), we have

$$\rho_\alpha g_\alpha(x_1) = \frac{\omega_\alpha e^{-\gamma_{0b}} e^{-\gamma_0 x_1}}{\langle \psi_0 | P = 0 \rangle}$$
$$\times \sum_{k=0}^{\infty} \langle \psi_0 | \hat{K}_\alpha \frac{(\hat{H} \exp(b\hat{H}))^k}{k!} | P = 0 \rangle [x_1 - kb] \, \theta[x_1 - kb] \tag{68}$$

We are in a region that is not translational invariant and the one-body correlation function dependens on x_1. Furthermore, we observed that for $x_1 \to \infty$ the bulk density (53) is recovered.

The one-body correlations, when evaluated at $x_1 = 0$, satisfy the contact value theorem.[18] To show this, we consider that, since

$$\hat{H}_2 | P = 0 \rangle = \left(-\frac{q^2}{2kT} \hat{P}^2 - \frac{qQ}{kT} \hat{P} \right) | P = 0 \rangle$$
$$= 0 | P = 0 \rangle \tag{69}$$

then

$$\hat{H}_1 [\exp(-b\hat{H}) | P = 0 \rangle = \hat{H} | P = 0 \rangle \tag{70}$$

At $x_1 = 0$, Eq. (68) yields

$$\rho_\alpha g_\alpha(xs_1 = 0) = \omega_\alpha e^{-\gamma_0 b} \frac{\langle \psi_0 | \hat{K}_\alpha | P = 0 \rangle}{\langle \psi_0 | P = 0 \rangle} \tag{71}$$

Therefore, using Eqs. (28), (29), and (70) and defining

$$\rho_s \, g_s(x=0) = \rho_s \sum_{e=\pm 1} g_s(x=0; e) \tag{72}$$

we have

$$\sum_{\gamma=1}^{s} \rho_\gamma \, g_\gamma(x=0) = \frac{\langle \psi_0 | \hat{H} | P=0 \rangle}{\langle \psi_0 | P=0 \rangle}$$

$$= \gamma_0(Q) \tag{73}$$

and, using Eq. (40),

$$kT \sum_{\gamma=1}^{s} \rho_\gamma \, g_\gamma(x=0) = P(\infty) + \frac{Q^2}{2} \tag{74}$$

which is the contact values theorem for the ion–dipole mixture[19] in 1D. In this last equation $P(\infty)$ denotes the pressure in the bulk far from the wall located at the origin.

5. DONNAN EQUILIBRIUM

In this section we consider that the electrolyte solution is in a container divided by a semipermeable membrane. The solvent and all the solute species, except one, can permeate through this membrane. We use the results of the previous section to study the one-dimensional Donnan equilibrium in this system.

In order to simplify the notation, let us consider a mixture of just three ionic species, namely $+$, $-$, and P ("protein") dissolved in the dipolar solvent S. All the components in the mixture can stay in the intervals $[-(L_2+b/2), \, -b/2]$ (side 1) and $[b/2, \, L_2+b/2]$ (side 2) of the axis x except for ions of species P, which are constrained to be only in the side 2. Thus we are assuming that a Donnan membrane of width b is symmetrically located at $x=0$. Although particles of species $+$, $-$, and S can permeate through the membrane, their centers cannot remain inside it.

As before, all the particles are hard rods of length b. The solvent particles are dipoles of dipolar moment μ. We assume that the cations and anions have point charge $+q$ and $-q$, respectively, while proteins P have a charge Zq.

The system is subject to an external electric field generated by a charge $Q = Q_1 + Q_2$ located at $x=0$ and two charges $-Q_1$ and $-Q_2$ placed at the container walls $-(L_1+b)$ and L_2+b, respectively.

The whole system is neutral. Furthermore, in equilibrium each side of the membrane must be neutral by itself. We impose the electroneutrality condition in the same way as before: by means of a fluctuating charge ensemble.

Suppose that there are M, m, n, and r particles of type P, $+$, $-$, and S, respectively. The numbers of particles in the two compartments ($M_2 = 0$, m_1, n_1, r_2) and ($M_2 = M$, m_2, n_2, r_2) must satisfy $m_1 + m_2 = m$, $n_1 + n_2 = n$, and $r_1 + r_2 = r$. As in Section 2, we introduce the auxiliary charges $-q\sigma_1$ and $-q\sigma_2$ with $\sigma_1 = m_1 - n_1$ and $\sigma_2 = ZM_2 + m_2 - n_2$ at the points $x = -(L_1 + b/2)$ and $x = L_2 + b/2$, respectively.

Because of the nature of the charge–charge and charge–dipole interactions in 1D, we find that the two sides of the interface behave, from the electrostatic point of view, in a completely independent way. Moreover, the hard-core parts of particles located on both sides of the membrane do not interfere, bgecause they see a gap of length h at the membrane position. Thus, the total potential energy can be written as the sum of two separate contributions:

$$\Phi_{Mm_2n_2r_2}^{0m_1n_1r_1}(L_1 Q_1 t_1; L_2 Q_2 t_2) = \Phi_{(L_1 Q_1 t_1)}^{0m_1n_1r_1} + \Phi_{(L_2 Q_2 t_2)}^{nm_2n_2r_2} \qquad (75)$$

where $\Phi_{(L_\alpha Q_\alpha t_\alpha)}^{n_\alpha m_\alpha n_\alpha r_\alpha}$ ($\alpha = 1, 2$) denotes the potential energy on side α. As in Section 2, the variables t_α are introduced so that the container side α is electroneutral after we integrate the generating functions over the interval $[-\pi, \pi]$.

We see from Eq. (75) that the grand-partition function factorizes,

$$\Xi_{\omega_P \omega_+ \omega_- \omega_S}(L_1 Q_1; L_2 Q_2; T) = \Xi_{\omega_+ \omega_- \omega_S}^{(1)}(L_1 Q_1 T) \, \Xi_{\omega_P \omega_+ \omega_- \omega_S}^{(2)}(L_2 Q_2 T) \qquad (76)$$

where

$$\Xi^{(\alpha)}(L_\alpha Q_\alpha T) = \frac{1}{2\pi} e^{-Q_\alpha^2 L_\alpha / 2kT} \int_{-\pi}^{\pi} dt \int_{-\pi}^{\pi} dt' \, \langle t | \hat{f}_0^{(\alpha)} | t' \rangle \qquad (77)$$

ω_α ($\alpha = $ P, $+$, $-$, S) are the fugacities of the protein, cation, anion, and solvent, respectively.

The density profiles at each side of the membrane are

$$\rho_\gamma^{(\alpha)} g_\gamma^{(\alpha)}(x) = \omega_\gamma \frac{\int_{-\pi}^{\pi} dt \int_{-\pi}^{\pi} dt' \, \langle t | \hat{f}_\gamma^{(\alpha)}(x - (-)^\alpha b/2) | t' \rangle}{\int_{-\pi}^{\pi} dt \int_{-\pi}^{\pi} dt' \, \langle t | \hat{f}_0^{(\alpha)} | t' \rangle} \qquad (78)$$

where $\alpha = 1, 2$ and $\gamma = +$, $-$, S. The same relation with $\alpha = 2$ and $\gamma = $ P is valid for particles P on side 2. On side 1 we have, instead,

$$\rho_P^{(1)} g_P^{(1)}(x) \equiv 0 \qquad (79)$$

Using property (69), we have $(\alpha = 1, 2)$

$$\sum_{\gamma = P, +, -, S} \rho_\gamma^{(\alpha)} g_\gamma^{(\alpha)}(x = (-)^\alpha b/2) = \gamma_0^{(\alpha)}(Q_\alpha) \tag{80}$$

From this we obtain the sum rule

$$kT \sum_{\gamma = P, +, -, S} \rho_\gamma^{(2)} g_\gamma^{(2)}(x = b/2) - kT \sum_{\gamma = +, -, S} \rho_\gamma^{(1)} g_\gamma^{(1)}(x = -b/2)$$
$$= \Pi + \tfrac{1}{2}(Q_2^2 - Q_1^2) \tag{81}$$

where

$$\Pi = P_2(\infty) - P_1(-\infty) \tag{82}$$

is the osmotic pressure, with P_α the bulk pressure on side α.

Equation (81) is the contact value theorem for the Donnan membrane.[20,21] It can be written in the form given by Zhou and Stell[21]:

$$kT\rho_P \, g_P\left(x = \frac{b}{2}\right) = \Pi + \frac{1}{2} \left[E^2(x = 0^+) - E^2(x = 0^-) \right]$$

$$+ kT \sum_{\gamma = +, -, S} \rho_\gamma \int_{-\infty}^{\infty} g_\gamma(x) \frac{dv_{\gamma m}(x)}{dx} \, dx \tag{83}$$

Here $v_{\gamma m}(x)$ is the particle–membrane interaction for the diffusible species γ,

$$v_{\gamma m}(x) = \begin{cases} \infty & -b/2 < x < b/2 \\ 0 & \text{otherwise} \end{cases} \tag{84}$$

and $E(X)$ is the electric field.

6. THE CHARACTERISTIC VALUE PROBLEM

We now consider the solution of the characteristic value problem associated with the operator $\hat{H}$ [Eq. (33) or, in the t-representation, Eq. (35)]. Because of Eqs. (41) and (43), we see that in the case $Q/q =$ integer it is enough to solve the zero-field case.

Here we restrict ourselves to the simplest nonprimitive model of the electrolyte, namely a mixture of two species $(+, -)$ of charged hard rods, with electrovalences $Z_+ = -Z_- = 1$ and fugacities $\omega_+ = \omega_- = \omega_i$ (detailed

charge balance) in a solvent of dipolar hard rods. Thus, in the t-representation, the operator $\hat{H}$ reads

$$\hat{H} \equiv 2 \left[\omega_i \cos(t) + \omega_s \cos\left(\kappa \frac{d}{dt} \cdot \right) \right] e^{-\gamma b} e^{\tau(d^2/dt^2)} + \frac{\tau}{b} \frac{d^2}{dt^2} \cdot \qquad (85)$$

This is a generalized Mathieu-type Hamiltonian. Because of the periodicity of $\cos(t)$, the eigenfunctions satisfy the boundary condition [Eq. (42)]

$$\phi_m(t + 2\pi) = \phi_n(t) \qquad (86)$$

We assume that the eigenfunctions of the operator H are expanded

$$\phi_n(t) = \sum_{j=0}^{\infty} A_{n,j} \cos(jt) \qquad (n = 0, 1, \ldots) \qquad (87)$$

so that the coefficients $A_{n,j}$ satisfy a three-term recursion relation

$$x_{b,j+1} - v_{n,j} x_{n,j} + x_{n,j-1} = 0 \qquad (88)$$

where

$$x_{n,j} = e^{-j^2\tau} A_{n,j} \qquad (89)$$

and

$$v_{n,j} = \frac{(\tau j^2/b + \gamma_n) e^{\tau j^2} - 2\omega_s e^{-\gamma_n b} \cosh(\kappa j)}{\omega_i e^{-\gamma_n b}} \qquad (90)$$

From Eq. (88) we find a family of transcendent equations for the eigenvalues γ_n:

$$F_j^{(-)} - F_j^{(+)} = 0 \qquad (91)$$

where $F_j^{(-)}$ and $F_j^{(+)}$ are expressed as continued fractions:

$$F_j^{(-)} = v_j - \cfrac{1}{v_{j-1} - \cfrac{1}{v_{j-2} - \cfrac{1}{v_{j-3} - \cdots}}} \qquad (92)$$

and

$$F_j^{(+)} = \cfrac{1}{v_{j+1} - \cfrac{1}{v_{j+2} - \cfrac{1}{v_{j+3} - \cdots}}} \qquad (93)$$

Furthermore, from Eq. (88) we also have a recursion relation for the eigen-function coefficients $(n = 0, 1, 2,...; \; j = 0, 1, 2,...)$

$$A_{n,j} = \cfrac{A_{n,j-1} r^{\tau(2j-1)}}{v_{n,j} - \cfrac{1}{v_{n,j+1} - \cfrac{1}{v_{n,j+2} - \cdots}}} \tag{94}$$

Knowing the coefficients in the expansions of the eigenfunctions of $\hat{H}$, we can obtain directly the corresponding expansions of the eigenfunctions corresponding to the adjoint operator $\hat{H}^{\dagger}$:

$$\psi_n(t) = e^{\tau(d^2/dt^2)} \cdot \phi_n(t)$$

$$= \sum_{j=0}^{\infty} e^{-\tau j^2} A_{n,j} \cos(jt) \tag{95}$$

From Eqs. (91)–(95) and (90) it is seen that for $b = 0$

$$\gamma \sim 2\omega_s \cosh(\kappa j) - \frac{q^2}{2kT} j^2 \tag{96}$$

as j grows. This explicitly shows that for $\kappa \neq 0$ the maximum eigenvalue is unbounded.

7. THE PLASMA LIMIT FOR POINT PARTICLES

A mixture of point ions $(b = 0)$ moving in a continuous medium has two well-defined regimes.[5,21] For small couplings, namely for small values of $q^2/2kT$ (high temperatures or small charges) the system behaves (from a thermodynamic point of view) as a charged plasma, whereas for strong couplings it is a neutral dipolar gas with a density half of the total density. It should be remembered, however, that despite the thermodynamic validity of the Debye–Hückel theory, the system is structurally a dielectric.

We have just seen that when the solvent is modeled by an ensemble of point dipoles the eigenvalues are unbounded except for $\kappa \to 0$ $(q \to 0$ or $T \to \infty)$. Thus, the pressure grows without limit (Fig. 1) and the system is thermodynamically unstable.[12] The physical reason for this behavior is that for finite temperatures an infinite number of point dipoles are drawn near the point charges, causing a sort of catastrophic solvation.

In the plasma limit, operator (85) is written in abstract space

$$\hat{H} \equiv 2\omega_i \cos(\hat{t}) + 2\omega_s \cos(i\kappa \hat{P}) - \lambda^2 \hat{P}^2 \tag{97}$$

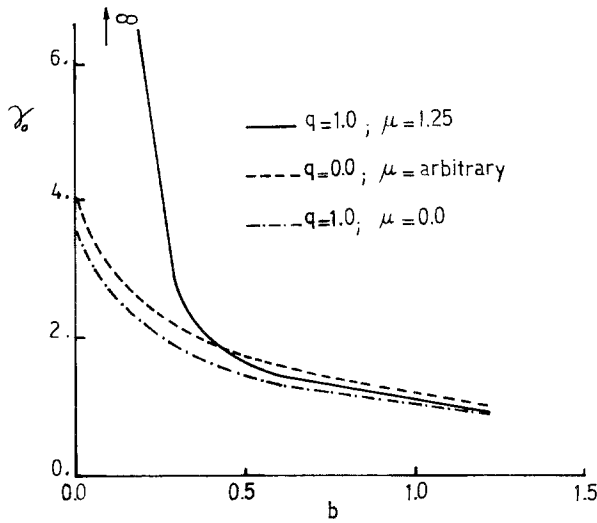where $\lambda^2 = \tau/b = q^2 2kT$ is the ion–ion coupling parameter.

Fig. 1. Typical behavior of the pressure $\gamma_0 = P/kT$ versus the hard-rod length b for a non-primitive electrolyte in 1D. The remaining parameters are $\omega_s = 1.5$, $\omega_i = 0.5$, and $1/kT = 1.0$ (arbitrary units).

We approximate

$$\cos(\hat{t}) \sim \hat{1} - \hat{t}^2/2$$
$$\cos(i\kappa\hat{P}) \sim \hat{1} + \kappa\hat{P}^2/2 \tag{98}$$

Therefore,

$$\hat{H} = -\lambda^2\hat{P}^2/c - \omega_i\hat{t} + 2(\omega_i + \omega_s)\hat{1} \tag{99}$$

where the constant c is

$$c = (1 - 2\omega_s\mu^2/kT)^{-1} \tag{100}$$

and $\hat{1}$ is the unit operator.

We consider the "annihilation" operator

$$\hat{a} = \frac{1}{\sqrt{2}}\left[(\lambda/c\omega_i)^{-1/2}\hat{t} + i(\lambda/\omega_i)^{1/2}\hat{P}\right] \tag{101}$$

and the "creation" operator $\hat{a}^\dagger$. then $\hat{H}$ is written in terms of the "particle number" operator $\hat{n} = \hat{a}^\dagger\hat{a}$:

$$\hat{H} = -(\lambda^2\omega_i/c)^{1/2}(2\hat{n} + \hat{1}) + 2(\omega_i + \omega_s)\hat{1} \tag{102}$$

Since $\hat{n}|\phi_n\rangle = n|\phi_n\rangle$, the characteristic value problem (33) gives the eigenvalues

$$\gamma_n = -(\lambda^2\omega_i/c)^{1/2}(2n+1) + 2(\omega_i + \omega_s) \tag{103}$$

Thus, the system pressure is

$$\frac{P}{kT} = \gamma_0 = 2(\omega_i + \omega_s) - (\lambda^2\omega_i/c)^{1/2} \tag{104}$$

Using Eq. (44), we further obtain the number densities

$$\rho_i = 2\rho_+ = 2\rho_- = 2\omega_i - \tfrac{1}{2}(\lambda^2\omega_i/c)^{1/2} \tag{105}$$

and

$$\rho_s = 2\omega_s - \lambda(\omega_i)^{1/2}c(c-1)/2 \tag{106}$$

For the primitive model of electrolyte, Edwards and Lenard[6] found, in the small coupling (Debye–Hückel) limit $\lambda \ll 1$,

$$\rho_i = 2\omega_i - \tfrac{1}{2}(\lambda^2\omega_i/\varepsilon)^{1/2} \tag{107}$$

where ε is the dielectric constant of the continuous solvent. Then we identify parameter c in Eq. (105) with the electrolyte-concentration-dependent dielectric constant:

$$\varepsilon = \frac{1}{1 - 2\omega_s\mu^2/kT} \sim 1 + \frac{2\omega_s\mu^2}{kT} \tag{108}$$

Comparison of this result with the dielectric constant of a (pure) gas of point dipoles at high temperatures[23] shows that the effect of the ion–dipole coupling is included in ω_s, which replaces the dipolar density in the pure dipolar gas formula.

The osmotic pressure of the ions is given by

$$\frac{\Pi}{kT} = (\rho_+ + \rho_-) - \frac{\lambda_\varepsilon}{\sqrt{8}}(\rho_+ + \rho_-)^{1/2} \tag{109}$$

where $\lambda_\varepsilon = \lambda/\sqrt{\varepsilon}$. This expression has the form of the Debye–Hückel osmotic pressure.

8. REMARKS

We have obtained the exact many-body functions for the one-dimensional version of the nonprimitive model of an electrolyte. This implies

considering systems of hard-core particles interacting through non-nearest-neighbor forces of infinite range. To this end, we have adapted Baxter's generating function technique in order to take into account the finite size of the particles.

Because of the hard-core repulsions, the number of particles lying between each pair of root particles in the many-body functions is finite. As a consequence, the many-body functions are written as potential series with Heaviside step functions. In the point particle limit these series sum to exponential functions.

The hard cores also cause the operator $\hat{H}$ associated with the system to be non-self-adjoint. A factor $\exp(-\tau\hat{P}^2)$ is responsible for this behavior. The eigenvalues of this operator are always bounded, in contrast with the point particle case, for which the presence of the dipoles produces the system's instability at any finite temperature and any dipole fugacity.

When the system is subjected to the field generated by external changer $\pm Q$, it is seen that the thermodynamic and correlation functions are periodic functions of Q of equal period to the ionic charge q. In particular, charges Q which are multiples of q are perfectly screened, so that the bulk system behaves as in the complete absence of external charges. However, from a structural point of view, the system behaves always as a dielectric.

ACKNOWLEGMENTS

REFERENCES

1. J. K. Percus, in *Simple Models of Equilibrium and Nonequilibrium Phenomena,* J. L. Lebowitz, ed. (North-Holland, Amsterdam, 1987).
2. L. Van Hove, *Physica* **16**:137 (1950).
3. M. Kac, *Phys. Fluids* **2**:8 (1959).
4. G. A. Baker, Jr., *Phys. Rev.* **122**:1477 (1961).
5. S. F. Edwards and A. Lenard, *J. Math. Phys.* **3**:778 (1962).
6. H. Kunz, *Ann. Phys.* (NY) **85**:303 (1974).
7. R. Baxter, *Phys. Fluids* **7**:38 (1964).
8. R. Baxter, *Phys. Fluids* **8**:687 (1965).
9. J. L. Lebowitz, Private communication.
10. F. Vericat and L. Blum, *Physica* **145A**:190 (1987).
11. F. Vericat and L. Blum, unpublished.

12. F. Vericat and L. Blum, *J. Chem. Phys.* **82**:1492 (1985).
13. M. Aizenman and P. A. Martin, *Commun. Math. Phys.* **78**:99 (1980).
14. M. Aizenman and J. Fröhlich, *J. Stat. Phys.* **26**:347 (1981).
15. L. Tonks, *Phys. Rev.* **50**:955 (1936).
16. Z. W. Salsburg, R. W. Zwanzig, and J. G. Kirkwood, *J. Chem. Phys.* **21**:1098 (1953).
17. F. Zernike and J. Prins, *Z. Phys.* **41**:184 (1927).
18. D. Hendersom, L. Blum, and J. L. Lebowitz, *J. Electroanalyt. Chem.* **102**:315 (1979).
19. L. Blum and D. Henderson, *J. Chem. Phys.* **74**:1902 (1981).
20. E. Martina, *Chem. Phys. Lett.* **94**:205 (1983).
21. Y. Zhou and G. Stell, *J. Chem. Phys.* **89**:7020 (1988).
22. Ph. Choquard, H. Kunz, Ph. A. Martin, and M. Navet, in *Physics in One Dimension*, J. Bernasconi and T. Schneider, eds. (Springer, Berlin, 1981).
23. H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, London, 1958).