Theory of symmetric electrolyte solutions: Field-theoretic approach

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We provide perturbative, nonperturbative, and renormalization-group treatments of the symmetric electrolyte problem which permits us to obtain the corrections to the known Debye-Hückel results in a systematic way. In addition, nonperturbative methods enabled us to obtain some results for the case of dense electrolyte systems. The renormalization-group method is used to investigate the possibility of phase transitions. Our results indicate the absence of phase transitions in three dimensions for a sufficiently diluted symmetric electrolyte in complete agreement with the results of Kosterlitz.

I. INTRODUCTION

Recently a number of papers[1–3] have appeared in which the authors investigate the possibility of a phase transition within the framework of the restricted primitive model (RPM) of a symmetric electrolyte. The transition is from a conducting state, where ions of opposite charge are not bound to each other, to an insulating state where such ions form dipoles, quadrupoles, etc., thus significantly reducing the conductivity of the electrolyte. This conclusion has been reached on the basis of analysis of solutions of an improved Ornstein-Zernike-type integral equation[3] and by analysis of a Padé resummed series expansion.[1,4] It is known,[5] however, that Ornstein-Zernike-type equations effectively correspond to the so-called random-phase approximation (RPA) and, hence, cannot give reliable results in the vicinity of the phase transition, if it exists. On the other hand, mathematical problems similar to the electrolyte problem were studied independently by many investigators. An example from solid-state physics is the electron-hole plasma in semiconductors which at certain conditions can form bound electron-hole pairs called Wannier excitons.[6] Formation of such pairs is possible, however, only under conditions far from equilibrium so that conventional methods of statistical mechanics cannot be used. Another example is from plasma physics.[7] For a two-component asymmetric ionic plasma, phase separation was observed within the RPA approximation. The third example is from general theoretical work on phase transitions. It was established some time ago by Kosterlitz and Thouless[8] and, independently, by Berezinsky[9] that the RPM in two dimensions does undergo a phase transition of the above described nature but above two dimensions it was shown later by Kosterlitz[10] that there is no phase transition.

In view of the diversity of results obtained by different researchers working independently in different fields we would like to present in this paper some sort of unified treatment of the electrolyte problem *written in a language accessible to the researchers in the field of electrolytes.* It is our purpose to demonstrate the connections between the standard statistical mechanical treatments and those which were developed in the context of field theory. More rigorous treatments of these connections can be found in Refs. 11–16. However, authors of these papers were concerned mostly with establishing rigourous connections rather than actual numerical results and none of these papers discusses the possibility of phase transitions in electrolytes.

In reality the situation may be even more complex than we might first realize, as it is explained in the review article by Hansen.[16] Only when the sizes of the ions (macroions) are sufficiently larger than the solvent molecules, so that ion-solvent correlations can be ignored, is the RPM model applicable. In this case solvent effects are effectively presented in the form of a dielectric constant which is assumed to be the same for all ionic concentrations. This might be too crude an assumption, but at present this is the only option for some sort of analytic development.

This paper consists of six sections. In Sec. II we provide the major parameters of the theory and establish the connection between the Poisson-Boltzmann equation and the Sine-Gordon equation. In Sec. III we provide the field-theoretic perturbation expansion calculations. We develop a systematic way to obtain the corrections to the Debye-Hückel theory for the case of the virial expansion and mean interparticle potential. We demonstrate that the corrections to the Debye-Hückel theory effectively lead to the renormalization (rescaling) of the ionic charges as well as the Debye-Hückel screening length. In Sec. IV we treat the same problem nonperturbatively by solving exactly the Sine-Gordon equation in one dimension and approximately in three dimensions. Then the standard technique of instanton calculations[17] is applied to obtain the fluctuation corrections in one dimension and in three dimensions we provide the leading terms only leaving the detailed calculations for future work. Section V is devoted to the renormalization-group calculations. We employ here a method[18] different from that used by Kosterlitz.[10] This method permits us not only to reproduce his final results but also clearly exemplify conditions under which his method is valid. Our presentation is made within the language accessible to the researchers in the electrolyte

theory so that all renormalization-group parameters are properly identified with corresponding parameters used in electrolyte theory. It is demonstrated that within the limits of validity of the Kosterlitz method there is no phase transition in the restricted primitive model of electrolytes in three dimensions which is in agreement with Kosterlitz's conclusions.[10] Section VI is devoted to a brief discussion of our results.

II. GENERAL RESULTS

The equilibrium theory of electrolyte solutions is developed in a close analogy with the statistical thermodynamics of plasma. However, there are some very important differences which do not permit us merely to copy results of plasma theory. Unlike the electron-ion plasma, in electrolyte solutions solvent effects must be properly taken into account,[16] and positive and negative carriers have the same or comparable masses (compared to the large difference between ion and electron masses in the plasma). Therefore, there is no small parameter associated with the mass ratio for the case of electrolytes and other small parameters must be introduced. To do so we would like to review some of the characteristic parameters of electrolytes.[19]

First, there is a Bjerrum length, defined by

$$\lambda_B=\frac{e^2}{\epsilon kT}\ , \tag{2.1}$$

where e has the dimensionality of charge, ϵ is the dielectric constant of the medium in which the charge is immersed, k is Boltzmann's constant, and T is the absolute temperature. Second, the Debye-Hückel screening length is defined as

$$\lambda_{\rm DH}=\left[4\pi\lambda_B\sum_i n_{0i}Z_i^2\right]^{-1/2}\propto\left[\sum_i n_{0i}\right]^{-1/2}\ , \tag{2.2}$$

where Z_i is the valence of the ith ion, n_{0i} is the equilibrium concentration of the ith ion component in solution, and the sum over i ranges over all types of ions present in solution. Using the definition of the ionic strength I,

$$I=\tfrac{1}{2}\sum_i c_i Z_i^2\ , \tag{2.3}$$

where c_i is the molar concentration of the ith component, relation (2.2) can be rewritten as follows:

$$\lambda_{\rm DH}=(8\pi\times10^{-3}N_A\lambda_B I)^{-1/2}\ , \tag{2.4}$$

where N_A is Avogadro's constant. The average distance between ions in solution r_{0i} is of the order

$$r_{0i}\sim(n_{0i})^{-1/3}\ , \tag{2.5}$$

and the size of the ions is of the order σ_i. Given these definitions we can construct some dimensionless quantities which will provide us with necessary expansion parameters. First among them is the nonideality parameter η,

$$\eta=\frac{\lambda_B Z_i Z_j}{(r_{0i}r_{0j})^{1/2}}\ . \tag{2.6}$$

The electrolyte is considered to be ideal when $\eta\ll1$. Second, we can define parameter ζ as

$$\zeta=\frac{r_{0i}}{\sigma_i}\ . \tag{2.7}$$

Evidently $\zeta\geq1$ and Eq. (2.6) can be considered only when $\zeta\gg1$, in which case ions in solution can be approximated by point charges interacting via a Coulomb potential. Finally, we can introduce the parameter ξ,

$$\xi=\frac{\lambda_{\rm DH}}{r_{0i}}\ . \tag{2.8}$$

It is clear that only when $\xi>1$, the Debye-Hückel theory can be of some predictive value. Given the above results we have the following inequalities:

$$\sigma_i<r_{0i}<\lambda_{\rm DH}\ . \tag{2.9}$$

All above estimates are based on the assumption that the dielectric constant ϵ entering Eq. (2.1) remains the same when the concentration of ions is changed. Hence, it should be considered to great extent as a phenomenological parameter of the theory. The so-called restricted primitive model of electrolytes implicitly includes the effects of short-range interactions by phenomenologically postulating the interaction potential $w_{ij}(r)$,

$$w_{ij}(r)=\begin{cases}\dfrac{q_iq_j}{\epsilon r}, & r\geqq\sigma_{ij}\\ \infty, & r<\sigma_{ij}=\frac{1}{2}(\sigma_i+\sigma_j)\end{cases} \tag{2.10}$$

where $q_{i,j}$ is the charge on the ions. For $r\gg\sigma_{ij}$ the hard-core portion of the potential (2.10) is of little importance and can be ignored as a first approximation.

We would like to consider in some detail the case of symmetric electrolytes, i.e., $Z=Z_1=-Z_2$, $\sigma=\sigma_1=\sigma_2$, $Z=1,2,\ldots,N$. The Poisson equation

$$\nabla^2\phi=-\frac{4\pi e}{\epsilon}\sum_\alpha Z_\alpha n_\alpha(r)\ , \tag{2.11}$$

supplemented with the electroneutrality condition

$$\sum_\alpha Z_\alpha n_{\alpha0}=0 \tag{2.12}$$

and closure relation

$$n_\alpha(r)=n_{\alpha0}\exp\left[-\frac{eZ_\alpha\phi}{kT}\right]\ , \tag{2.13}$$

produces for the case of 1-1 symmetric electrolytes the following result:

$$\nabla^2\phi=-\frac{4\pi e n_0}{\epsilon}\left[\exp\left[-\frac{e\phi}{kT}\right]-\exp\left[\frac{e\phi}{kT}\right]\right]$$

$$=\frac{8\pi e n_0}{\epsilon}\sinh\left[\frac{e\phi}{kT}\right],\quad r>R_0\ , \tag{2.14}$$

where we note $n_0=n_{0\alpha}$ for all α. Equation (2.14) upon the substitution $\phi\rightarrow i\bar{\phi}$ can also be written as

$$\nabla^2\bar{\phi}=\frac{8\pi e n_0}{\epsilon}\sin\left[\frac{e\bar{\phi}}{kT}\right]. \tag{2.15}$$

The last equation is the static case of the three-dimensional version of the famous sine-Gordon equation. Consideration of mixtures of 1-1 and 2-2 electrolytes, etc., would produce the double sine-Gordon and related equations. Here, for simplicity, we consider only the 1-1 case. The above change from the potential ϕ to $i\bar{\phi}$ turns out to be an important element in the subsequent field-theoretic formulation of the above problem.

III. SYMMETRIC 1-1 ELECTROLYTE IN THE GRAND CANONICAL ENSEMBLE: CONVERSION TO THE FIELD-THEORETIC FORM

We would like to consider the symmetric electrolyte problem within the grand canonical ensemble. Such treatment was first initiated by Edwards[20] in 1959. Many other authors made attempts to improve his results.[12–15] However, these authors were more interested in mathematical rigor and did not obtain numerical results beyond that given by Debye-Hückel (DH). Another attempt to go beyond the DH results within the framework of classical statistical methods was made by Stell and Lebowitz.[4] These authors, however, did not explicitly compute the correction terms in the perturbation expansion and, therefore, we are unable to use their results. An alternative approach to the problem via the correlation-function method was provided by Waisman and Lebowitz[21] who used the so-called mean spherical approximation to the Ornstein-Zernike integral equation. As it was noted by the authors themselves, their method is not applicable in the vicinity of the phase transition (if such exists) so that the question about the phase transition in the symmetric three-dimensional electrolyte is thus far not solved by conventional methods of statistical mechanics. It is our purpose to provide here an alternative route to the same problem which will enable us to study both the correction to the DH results as well as to study the possibility of the phase transition. The grand partition sum for the 1-1 electrolyte system can be written in the usual manner as follows:

$$\Xi=\sum_{n_+=0}^{\infty}\sum_{n_-=0}^{\infty}\frac{\lambda_+^{n_+}}{n_+!}\frac{\lambda_-^{n_-}}{n_-!}Q(n_+,n_-)\ , \tag{3.1}$$

$$Q(n_+,n_-)=\int_\Lambda\left[\prod_{i=1}^{n}d^d\mathbf{r}_i\right]\exp\left[-\frac{U^e}{kT}-\frac{U^{sr}}{kT}\right],$$

$$n=n_++n_-\ , \tag{3.2}$$

$$U^e=\frac{e^2}{2\epsilon}\sum_{\substack{i\neq j\\ i,j=1}}^{n_+}\frac{Z_+^2}{r_{ij}^{d-2}}\Theta(r_{ij}-\sigma_{ij})$$

$$+\sum_{\substack{i\neq j\\ i,j=1}}^{n_-}\frac{Z_-^2}{r_{ij}^{d-2}}\Theta(r_{ij}-\sigma_{ij})$$

$$+2\sum_{i=1}^{n_+}\sum_{j=1}^{n_-}\frac{Z_+Z_-}{r_{ij}^{d-2}}\Theta(r_{ij}-\sigma_{ij})\ , \tag{3.3a}$$

$$U^{sr}=\tfrac{1}{2}\sum_{\substack{i\neq j\\ i,j}}U(r_{ij})\Theta(\sigma_{ij}-r_{ij})\ , \tag{3.3b}$$

$\lambda_\pm=l_T^{-d}\exp(\mu_\pm/kT)$, the thermal wavelength $l_T=(h^2/2\pi mkT)^{1/2}$, m is the mass of the ion, σ_{ij} was defined in (2.10), $\Theta(x)$ is just the usual unit step function, and d is the dimensionality of space. In order to develop the field-theoretic treatment, we would like to present the partition sum, Eq. (3.1), as a sum on some d-dimensional hyperlattice (assuming, as usual, the periodic boundary conditions for volume Λ) with some lattice spacing a. Then the step functions in Eq. (3.3) become unnecessary, the integration over d^dr_i must be replaced by a summation, and the function r_{ij}^{2-d} must be replaced by some lattice propagator $G^{(d)}(i,j)$, the explicit form of which is of no importance to us at this moment. What is, however, important is the fact that each lattice site can be occupied with either a positive or negative charge which permits us to introduce the spin variables $S(i)=\{{}^{1}_{-1}$ for each lattice site by analogy with the Ising model. Following Glimm and Jaffe[15] we can write instead of Eq. (3.1) the expression for the grand partition sum of the symmetric electrolyte where $\lambda_+=\lambda_-=\lambda$,

$$\Xi=\sum_{n=0}^{\infty}\lambda^n\sum_{\{S_n\}}a^{nd}\sum_{\substack{i_k\in\Lambda\\ k=1,2,\ldots,n}}Q(n)\ , \tag{3.4}$$

where the symbol $\{S_n\}$ should be understood in the usual sense of the Ising model, and

$$Q(n)=\frac{1}{n!}\exp\left[-\frac{e^2}{2\epsilon kT}\sum_{\substack{k\neq l\\ k,l=1}}^{n}S(i_k)G^{(d)}(i_k,i_l)S(i_l)\right]. \tag{3.5}$$

In the continuum limit $G^{(d)}(i,j)$ will be represented by the logarithmic function in $d=2$ and by r^{-1} in $d=3$, as usual. The reasons for putting the Coulomb problem on the lattice are twofold. First, because $G^{(d)}(i_k,i_k)=G^{(d)}(0)$ is finite there is no need to introduce the repulsive short-range potential as was done in Eqs. (3.1)–(3.3b). Second, one is allowed to develop the field-theoretic formulation in close analogy with that given for the Ising model.[22] After standard manipulation,[12–15] we obtain, finally,

$$\Xi=\int D[\phi]\exp\left[-\int d^3r\left[\frac{1}{8\pi}(\nabla\phi)^2-2\lambda\cos(\alpha\phi)\right]\right]. \tag{3.6}$$

where $\alpha=e/\sqrt{\epsilon kT}$. It is convenient at this point to rescale the field ϕ ($\phi=\tilde{\phi}/\sqrt{4\pi}$), and we shall omit the tilde in the subsequent discussions and equations. Denoting $\alpha\sqrt{4\pi}=\beta$ we obtain

$$\Xi=\int D[\phi]\exp\left[-\int d^3r[\tfrac{1}{2}(\nabla\phi)^2-2\lambda\cos(\beta\phi)]\right]. \tag{3.7}$$

Expanding $\cos(\beta\phi)$ in Eq. (3.7) and keeping only terms up through quadratic order in ϕ, we obtain

$$\Xi_{\rm DH}\simeq\exp(2\lambda V)\int D[\phi]\exp\left[-\tfrac{1}{2}\int d^3r[(\nabla\phi)^2+\omega^2\phi^2]\right], \tag{3.8}$$

where

$$\omega^2=2\lambda\beta^2. \tag{3.9}$$

The functional integral in Eq. (3.8) is Gaussian and can be easily evaluated, producing the final result

$$\frac{PV}{kT}=\ln\Xi=2\lambda V-\tfrac{1}{2}\sum_{k<k_0}\ln\left[\frac{2\pi}{k^2+\omega^2}\right], \tag{3.10}$$

where cutoff k_0 is of order a^{-1}. Going from a summation to integration in the last term of (3.10) we obtain the following expression:

$$-\tfrac{1}{2}\sum_{k\le k_0}\ln\left[\frac{2\pi}{k^2+\omega^2}\right]=\frac{V}{2(2\pi)^3}\int_0^{k_0}dk\,k^2(2\pi)\ln\left[\frac{k^2+\omega^2}{2\pi}\right], \tag{3.11}$$

where it was taken into account that $\phi_{\underline{k}}=\phi_{-\underline{k}}$. In the limit when $k_0\to\infty$ (i.e., $a\to0$) the above integral becomes divergent. This divergence occurs because the partition sum implicitly includes both the interparticle interaction energy plus the sum of energies of the Coulombic interactions between the given charge and its own field. Such interactions should be excluded by some sort of regularization procedure, for example, by introduction of the upper cutoff k_0. Since there is no general method for assigning a well-defined value to k_0, the dimensional regularization procedure is used instead.[19,22,23] The implementation of this method can be illustrated by rewriting expression (3.11) in a space of arbitrary dimension d so that it is equal to

$$\frac{V}{4(2\pi)^3}\int d^dk\ln(k^2+\omega^2), \tag{3.12}$$

where we have ignored the factor $-\ln(2\pi)$ because it will contribute to the infinite energy and d is treated as an analytic parameter. Integral (3.12) can be easily calculated by noting

$$I=\int d^dk\ln(k^2+\omega^2)=\int d^dk\int^{\omega^2}dx\frac{1}{k^2+x}, \tag{3.13}$$

and using the standard result[24]

$$\int d^dk\frac{1}{k^2+x}=\pi^{d/2}\Gamma(1-d/2)x^{d/2-1}. \tag{3.14}$$

By analytic continuation to $d=3$ (3.11) becomes

$$-\frac{V}{24\pi}\omega^3. \tag{3.15}$$

For the general case, dimensional regularization may produce well-defined poles in d which may be removed by renormalization if the problem is renormalizable.

Returning now to Eq. (3.10) and recalling that

$$\langle 2N\rangle=\lambda\frac{\partial\ln\Xi}{\partial\lambda}, \tag{3.16}$$

we obtain in the limit where e (the charge) approaches zero the following result;

$$\langle 2N\rangle=2\lambda V, \tag{3.17a}$$

or

$$2\lambda=\frac{\langle 2N\rangle}{V}=2n_0. \tag{3.17b}$$

In this approximation $\omega^2=(8\pi e^2/\epsilon kT)n_0=\kappa^2$ where $\kappa=\lambda_{\rm DH}^{-1}$ is defined according to Eq. (2.2). Whence, using Eqs. (3.10), (3.15), and (3.17), we obtain back the already-known Debye-Hückel result.[25] This time, however, we clearly see how to improve it. Indeed, when we proceed from the total expression (3.7) to its abbreviated version (3.8) only the quadratic terms in ϕ were preserved. In order to obtain systematic corrections to the pressure we can now write

$$\Xi=\frac{\Xi}{\Xi_{\rm DH}}\Xi_{\rm DH}, \tag{3.18}$$

so that we obtain the following virial expansion:

$$\frac{P}{kT}=2\lambda-\frac{\omega^3}{24\pi}+\frac{1}{V}\ln\left[\frac{\Xi}{\Xi_{\rm DH}}\right]. \tag{3.19}$$

We now write for the exponent in Eq. (3.7),

$$\exp\left[-\int d^3r[\tfrac{1}{2}(\nabla\phi)^2-2\lambda\cos(\beta\phi)]\right]=\exp(2\lambda V)\exp\left[-\tfrac{1}{2}\int d^3r[(\nabla\phi)^2+\omega^2\phi^2]\right]\times\exp\left[+2\lambda\int d^3r\left[\cos(\beta\phi)-1-\frac{\beta^2}{2}\phi^2\right]\right]=\exp(-S_{\rm DH}[\phi]+S_{\rm int}[\phi]), \tag{3.20}$$

where S_{DH} is the Debye-Hückel portion of the above exponent as defined in Eq. (3.8) and $S_{int}=2\lambda\int d^3r[\cos(\beta\phi)-1-(\beta^2/2)\phi^2]$. Expanding $[\exp S_{int}(\phi)]$ in the power series, we obtain

$$\frac{PV}{kT}=2\lambda-\frac{\omega^3}{24\pi}+\frac{1}{V}\ln\left[\sum_{m=0}^{\infty}\frac{1}{m!}\langle(S_{int}[\phi])^m\rangle_{DH}\right], \tag{3.21}$$

where the functional average is understood in the sense that

$$\langle\cdots\rangle_{DH}=\frac{\int D[\phi]e^{-S_{DH}[\phi]}\cdots}{\int D[\phi]e^{-S_{DH}[\phi]}}. \tag{3.22}$$

Using results of the linked-cluster theorem[26] we conclude that in the diagrammatic expansion of Eq. (3.21) only the connected diagrams must be included.

In order to accomplish our general discussion, we would next like to show how to compute the correlation function $g^{(2)}$. In the DH approximation we must consider the following expression:[13]

$$g^{(2)}(l,m)\frac{n_0^2}{\lambda^2}=\left\langle\exp\left[\frac{ie}{\sqrt{\epsilon kT}}[\phi(l)-\phi(m)]\right]\right\rangle_{DH}$$
$$=\frac{\int D[\phi]\exp\left[-\frac{ie}{\sqrt{\epsilon kT}}[\phi(l)-\phi(m)]\right]\exp(-S_{DH}[\phi])}{\int D[\phi]\exp(-S_{DH}[\phi])}. \tag{3.23}$$

Using the expression for the density $\rho(r)=\sum_{i=1}^{n}\delta(r-r_i)S(r_i)$ we can rewrite Eq. (3.23) so that it equals

$$\frac{\int D[\phi]\exp\left[\frac{ie}{\sqrt{\epsilon kT}}\int\rho(\underline{r})\phi(\underline{r})d\underline{r}\right]\exp(-S_{DH}[\phi])}{\int D[\phi]\exp(-S_{DH}[\phi])}. \tag{3.24}$$

In Eq. (3.24) we have Gaussian integrals both in the numerator and denominator. The integral in the numerator can be calculated by the usual shift procedure. Remembering that $\lambda=l_T^{-d}\exp[\mu+(e^2/2\epsilon)G^{(3)}(0)]$,[15] we see for this case that the singular self-interaction terms [involving $G^{(3)}(0)$] are canceled and we are left with the expression

$$g^{(2)}(r_1,r_2)=\text{const}\times\exp\left[\frac{e^2}{\epsilon kT}\left[\frac{\exp(-\kappa r_{12})}{r_{12}}\right]\right]. \tag{3.25}$$

Using the relation between the correlation function and the potential of the mean force[27] $\omega_{12}^{(2)}$, we obtain

$$\omega_{12}^{(2)}=-\frac{e^2}{\epsilon}\left[\frac{\exp(-\kappa r_{12})}{r_{12}}\right], \tag{3.26}$$

i.e., the attractive screened Coulomb potential, as anticipated. In order to obtain corrections to this result we should follow exactly the same procedure as that for the "free energy" [Eqs. (3.19)—(3.21)]. Using formula (3.20), expanding $\cos(\beta\phi)$, and initially keeping only the quartic term, we obtain for the $S_{int}[\phi]$ the following expression:

$$S_{int}[\phi]=\frac{\lambda}{2}\beta^4\int\phi^4d^3r. \tag{3.27}$$

Computations with this expression go in exact analogy with one-component scalar ϕ^4 field theory,[22] so that there is no need to repeat here the diagrammatic rules. First- and second-order diagrams for this case are depicted in Fig. 1. Some of the higher-order diagrams are depicted in Fig. 2. Calculation of the diagrams (a) and (b) of Fig. 1 is trivial and is made with the help of Eq. (3.14) so that we obtain (in three dimensions), for Fig. 1(a),

$$12\frac{\lambda}{2}\beta^2V\left[\int\frac{d^3k}{(2\pi)^3}(k^2+\omega^2)^{-1}\right]^2=\frac{3}{32\pi^2}\frac{\omega^6}{\lambda}V, \tag{3.28}$$

and for Fig. 1(b)

$$(4\times3)^2\left[\frac{\lambda}{2}\beta^4\right]^2V\left[\int\frac{d^3k}{(2\pi)^3}(k^2+\omega^2)^{-1}\right]^2\left[\int\frac{d^3k}{(2\pi)^3}(k^2+\omega^2)^{-2}\right]=\frac{9}{128\pi^3}\frac{\omega^9}{\lambda^2}V. \tag{3.29}$$

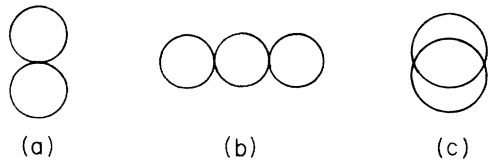

FIG. 1. First- (a) and second- [(b) and (c)] order Feynman diagrams for the virial expansion [Eq. (3.11)] resulting from a ϕ^4 interaction term coming from the cosine expansion in Eq. (3.20).

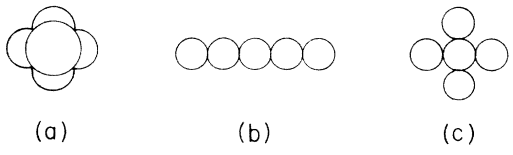

FIG. 2. Representative fourth-order Feynman diagrams for the virial expansion [Eq. (3.21)] resulting from a ϕ^4 field-theory approximation.

In the computation of the expression in Eq. (3.29) we used the formula

$$\int d^d k \frac{1}{(k^2+a^2)^\alpha} = \pi^{d/2} \frac{\Gamma(\alpha - d/2)}{\Gamma(\alpha)} (a^2)^{d/2-\alpha} , \tag{3.30}$$

and took account of the translational invariance of the free propagator. The latter produced the volume factors in Eqs. (3.28) and (3.29). Computation of the last diagram depicted in Fig. 1(c) is somewhat more lengthy and was already described in Kholodenko and Freed.[28] For this case we obtain

$$V 4\times 4\times 3\times 2 \left[\frac{\lambda}{2}\beta^4\right]^2 \frac{1}{(2\pi)^9} \int \left[\prod_{i=1}^{3} d^3 k_i\right] \frac{1}{[(k_i^2+\omega^2)][(\underline{k}_1+\underline{k}_2-\underline{k}_3)^2+\omega^2]} . \tag{3.31}$$

This integral is formally ultraviolet divergent as can be seen from the power counting described in Kholodenko and Freed.[28] Its computation would produce the sum of the singular $(3-d)^{-1}$ and the regular (nonsingular) terms. To remove the singularity, the renormalization procedure is needed.[28] This procedure is well defined in the case where only one coupling constant is present.[22] In our case $S_{\text{int}}[\phi]$, given by Eq. (3.27), is just an approximation to the true S_{int} and therefore it is necessary to perform the renormalization procedure with an infinite number of coupling constants. This is not possible in general, as is well known, with use of the standard field-theoretic methods. Thus we have three options: (a) artificially introduce an upper cutoff in Eq. (3.31); (b) use the method of insertions[22] treating higher-order terms as composite operators; (c) perform calculations of partition sum, Eq. (3.7), nonperturbatively. The last option will be discussed in some detail in Sec. IV. For the moment, we just ignore the singular diagrams so that we can write, using Eqs. (3.21), (3.28), and (3.29), the following approximation to the virial expansion:

$$\frac{P}{kT} = 2\lambda - \frac{\omega^3}{24\pi} + \frac{3}{32\pi^2}\frac{\omega^6}{\lambda} + \frac{9}{128\pi^3}\frac{\omega^9}{\lambda^2} + \cdots . \tag{3.32a}$$

If we choose an approximation in which $2\lambda \simeq 2n_0$ [see Eq. (3.17b)], then $\omega^2 \simeq \kappa^2$ and we finally obtain

$$\frac{PV}{kT} = 2n_0 - \frac{\kappa^3}{24\pi} + \frac{3}{32\pi^2}\frac{\kappa^6}{n_0} + \frac{9}{128\pi^3}\frac{\kappa^9}{n_0^2} + \cdots . \tag{3.32b}$$

It is relatively trivial to obtain a partial resummation of all nonsingular diagrams of the type given in Figs. 2(b), 2(c), etc., and we leave this procedure to the reader. This will create a subset of a countable infinity of nonsingular diagrams. Further expansion of $\cos(\beta\phi)$ would create diagrams like those depicted in Fig. 3. One can easily en-

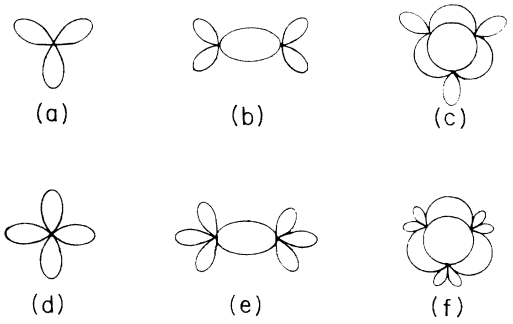

FIG. 3. Some representative Feynman diagrams for the virial expansion (3.21) resulting from terms of order ϕ^n ($n \geq 6$) in the expansion of $\cos(\beta\phi)$ in Eq. (3.20).

large the list of above diagrams and compute those of them which are nonsingular. Rather we would now like to concentrate our attention on some principal questions regarding the electrolyte problem.

Since the two-particle potential of the mean force plays a crucial role in the computation of all quantities of interest, we would like to compute the corrections to the Debye-Hückel result, Eq. (3.26), using the field-theoretic methods. This computation will reveal some physical features of the problem which are not accessible by other methods. If we restrict ourselves to just the quartic (3.27) and the ϕ^6-order terms, then the diagrammatic expansion of the Fourier-transformed binary potential formally coincides with that depicted in Fig. 3 of Kholodenko and Freed.[23] For convenience, this result is reproduced in Fig. 4. From Kholodenko and Freed[23,28] we already know that the result of the diagrammatic expansion for the full inverse propagator can be conveniently represented as

$$-\frac{\epsilon}{e^2}[\omega_{12}^{(2)}(k,\omega^2)]^{-1}\equiv w_{12}^{-1}(k,\omega^2)=k^2+\omega^2+\Sigma(k,\omega^2,\lambda)\ , \tag{3.33}$$

where the so-called mass operator Σ takes into account all interaction effects. It is known (see, for example, Kholodenko and Freed[23]) that $\Sigma(\kappa,\omega^2,\lambda)$ can be generally decomposed as follows:

$$\Sigma(\underline{k},\omega^2,\lambda)=k^2 f_1(\underline{k},\omega^2,\lambda)+\omega^2 f_2(\underline{k},\omega^2,\lambda)\ . \tag{3.34}$$

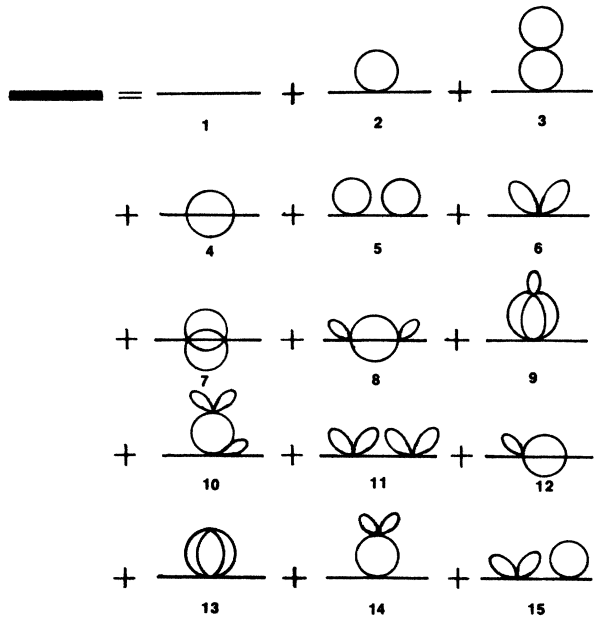

FIG. 4. Diagrammatic expansion for the Fourier-transformed potential of the mean interparticle force. Here only the ϕ^4 and ϕ^6 terms of the expansion for $\cos(\beta\phi)$ were used. The expansion is given without the combinational weights and correct signs thus only exhibiting the topology of the relevant diagrams. Combinational weights are the same as those in the standard ϕ^4–ϕ^6 field theory (Ref. 22).

Furthermore, dimensional analysis of Eq. (3.34), as compared with Eq. (3.33), would require functions f_1 and f_2 to be dimensionless. We already know that $[k^2]=[\omega^2]=L^{-2}$ where L is some arbitrary length and [ ] implies units. Now according to Eqs. (3.10) and (3.17b), $[\lambda]=L^{-3}$; therefore, we anticipate that the most general functional form of f_1 and f_2 should be

$$f_{1,2}(\underline{k},\omega^2,\lambda)=\phi_{1,2}\left[\frac{k^2}{\omega^2},\frac{\omega^3}{\lambda},\frac{k^2}{\lambda^{2/3}}\right]\ . \tag{3.35}$$

Because, by definition, $\omega=0$ if $k=0$, we can expand $\phi_{1,2}$ in the Taylor's series in k^2. For $k\to 0$ (large distances) we can preserve terms up to quadratic in k. This then would produce the following result for w_{12}^{-1}:

$$\begin{aligned} w_{12}^{-1}(k^2,\omega^2)&\approx k^2\tilde{f}_1\left[\frac{\omega^3}{\lambda}\right]+\omega^2\tilde{f}_2\left[\frac{\omega^3}{\lambda}\right]+O(k^4)\\ &\approx\tilde{f}_1\left[\frac{\omega^3}{\lambda}\right](k^2+\tilde{\omega}^2)+O(k^4)\ . \end{aligned} \tag{3.36}$$

Thus we can see that corrections to the Deybe-Hückel result effectively renormalize the value of the screening parameter κ and the coupling constant e (i.e., the electric charge) so that with good accuracy we can write

$$w_{12}(r)\propto(e^{\rm ren})^2\frac{\exp(-\kappa^{\rm ren}r)}{r}\ , \tag{3.37}$$

$$(e^{\rm ren})^2=e^2/\tilde{f}_1\left[\frac{\omega^3}{\lambda}\right]\ \text{and}\ (\kappa^{\rm ren})^2=\kappa^2\frac{\tilde{f}_2}{\tilde{f}_1}\ . \tag{3.38}$$

In order to demonstrate explicitly how this result is applied, consider the computation of the diagrams 2 and 3 in Fig. 4. Using the rules outlined in Kholodenko and Freed,[23,28] one sees that the above computations are basically the same as are done for the case of the virial expansion [see Eqs. (3.14) and (3.30)] so that we can write

$$\begin{aligned} w_{12}^{-1}(k,\omega)&=k^2+\omega^2-\frac{3}{8\pi}\frac{\omega^5}{\lambda}-\frac{9}{32\pi^2}\frac{\omega^8}{\lambda^2}+\cdots\\ &\approx k^2+\omega^2\left[1-\frac{3}{8\pi}\frac{\omega^3}{\lambda}-\frac{9}{32\pi^2}\frac{\omega^6}{\lambda^2}\right]+O(k^4)\\ &\approx k^2+\kappa^2\left[1-\frac{3}{8\pi}\frac{\kappa^3}{n_0}-\frac{9}{32\pi^2}\frac{\kappa^6}{n_0^2}\right]+O(k^4)\\ &\approx k^2+(\kappa^{\rm ren})^2+O(k^4)\ . \end{aligned} \tag{3.39}$$

Although in this example only κ gets renormalized, in general both κ and e^2 are effectively renormalized. These results permit us to systematically improve the Debye-Hückel theory.

At this point we would like to mention that because of the connection between the potential of the mean force $\omega_{ij}^{(2)}$ and the correlation function[27] the above results imply

$$g_{12}^{(2)} \sim \exp\left[\pm\frac{\exp(-\kappa^{\text{ren}}r)}{\epsilon kTr}\right] . \tag{3.40}$$

The above differs from the commonly accepted DH result[29]

$$g_{12}^{(2)} = 1-\frac{\exp(-\kappa r)}{\epsilon kTr} . \tag{3.41}$$

The Debye-Hückel $g_{12}^{(2)}$ is meaningless when $r\to 0$ because $g_{12}\to -\infty$. In contrast to this, expression (3.38) never becomes negative. We have to mention as well, a very close connection between the diagrammatic expansion for the potential of the mean force (Fig. 4) and the diagrammatic representation of the virial expansion (Fig. 1).

IV. NONPERTURBATIVE TREATMENT FOR THE 1-1 ELECTROLYTE MODEL

In Sec. III we obtained explicitly the first two perturbative corrections [see Eq. (3.32b)] to the Debye-Hückel virial expansion result.[25] Before we proceed with the nonperturbative approach, we would like to rewrite Equation (3.32b) in a somewhat more transparent form. Let V_{DH} be the volume of the Debye-Hückel sphere, i.e., $V_{\text{DH}}\propto\kappa^{-3}$. In Sec. II we had introduced [see Eq. (2.5)] the volume per ion $V_i\sim n_{0i}^{-1}$, now we can define the dimensionless parameter $\gamma=V_i/V_{\text{DH}}=\xi^{-3}$, where ξ was defined in Eq. (2.8). Using this parameter Eq. (3.32b) can be written as

$$\frac{PV}{kT}=2n_0\left[1-\frac{\gamma}{48\pi}+\frac{3}{64\pi^2}\gamma^2+\frac{9}{256\pi^3}\gamma^3+O(\gamma^4)\right] . \tag{4.1}$$

Equation (4.1) does not include the ion size. As it was demonstrated in Sec. III, ignoring the sizes of ions is implicitly responsible for various kinds of divergences like those coming from the diagrams depicted in Fig. 1(c) and these divergences can be eliminated by the introduction of cutoffs, as it was explained already. Consequently, expansion (4.1) should be replaced, in principle, by a double expansion in terms of parameters γ and ζ (or its inverse) defined in Eq. (2.7). However, we know that the explicit introduction of the cutoffs in the renormalizable field theory[22] can be completely eliminated by the appropriate redefinition (renormalization) of the initial parameters of the theory. An example of such redefinition was given in Eq. (3.38). This procedure is *not* entirely systematic, however, within the limits of the perturbation expansion based on Eqs. (3.20) and (3.21) even if the method of insertions is used.[22] Therefore we are forced to develop some sort of nonperturbative treatment. This will enable us, in principle, to obtain the equation of state where only one parameter γ, perhaps renormalized, is used. Unfortunately, the nonperturbative approach is associated with serious mathematical difficulties as well, so that systematic results have been obtained only for one- and two-dimensional models.[30–32] Here we just outline the method and provide a very crude nonperturbative solution solely for illustrative purposes. Systematic treatment would require a separate lengthy investigation that is beyond the scope of this work.

We begin with Eq. (3.7) which we can rewrite as follows:

$$\Xi=\exp(2\lambda V)\Xi_{\text{SG}} ,$$

$$\Xi_{\text{SG}}=\int D[\phi]\exp\left[-\int d^3r\{\tfrac{1}{2}(\nabla\phi)^2+2\lambda[1-\cos(\beta\phi)]\}\right] , \tag{4.2}$$

where SG means sine-Gordon. This name comes from the fact that the saddle point approximation to Ξ_{SG} produces the sine-Gordon equation which is the same as Eq. (2.15) with rescaling of the field and replacement of 2λ with $2n_0$ according to Eq. (3.17b). By replacement of ϕ with $\bar{\phi}+\delta\phi$ in Eq. (4.2) and assuming that $\delta\phi\ll\bar{\phi}$ we obtain with accuracy up through quadratic terms in $\delta\phi$,

$$\Xi_{\text{SG}}=\exp(-S_{Cl}[\bar{\phi}])\int D[\delta\phi]\exp\left[-\tfrac{1}{2}\int d^3r\,\delta\phi[-\nabla^2+2\lambda\beta^2\cos(\beta\bar{\phi})]\delta\phi\right] , \tag{4.3}$$

where $\bar{\phi}$ is determined from the solution of the sine-Gordon equation,

$$\nabla^2\bar{\phi}=2\lambda\beta\sin(\beta\bar{\phi}) . \tag{4.4}$$

This equation has the following infinite set of constant solutions:

$$\beta\bar{\phi}=n\pi,\quad n=0,\pm1,\pm2,\pm3,\text{ etc} . \tag{4.5}$$

We can select from among this infinite sequence a subset defined by $n=2m$, $m=0,\pm1,\pm2,\ldots$ such that the potential $U(\bar{\phi})=2\lambda[1-\cos(\beta\bar{\phi})]$ in (4.2) will be zero for all m. If we choose $m=0$ and expand $\cos(\beta\bar{\phi})$ around $\bar{\phi}=0$, i.e., we now have instead of $\phi=\bar{\phi}+\delta\phi$ just $\phi=\delta\phi$, then, keeping terms up through orders quadratic in $\delta\phi$ we shall recover the Debye-Hückel result using Eq. (4.3). The above infinity of constant solutions needs to be understood in physical terms. To accomplish this, we consider the one-dimensional case, where Eq. (4.4) acquires the form

$$\frac{d^2\bar{\phi}}{dx^2}=2\lambda\beta\sin(\beta\bar{\phi}) . \tag{4.6}$$

We first rescale our field $\phi:\bar{\phi}=\psi/\beta$ so that Eq. (4.6) can

be rewritten as

$$\frac{d^2\psi}{dx^2}=\omega^2\sin\psi\ , \tag{4.7}$$

where ω^2 is defined by Eq. (3.9). Finally we write $x=y/\omega$ so that Eq. (4.7) acquires the form

$$\frac{d^2\psi}{dy^2}=\sin\psi\ . \tag{4.8}$$

Let $\psi=i\hat{\psi}$ then we obtain,

$$\frac{d^2\hat{\psi}}{dy^2}=\sinh\hat{\psi}\ . \tag{4.9}$$

We made the last substitution in order to bring Eq. (4.9) to the form used in the conventional Debye-Hückel theory [see Eq. (2.15)]. Multiplying both sides of Eq. (4.9) out by $2d\hat{\psi}/dy$, we obtain

$$\left[\frac{d\hat{\psi}}{dy}\right]^2=2(\cosh\hat{\psi}-1)+\text{const}\ . \tag{4.10}$$

To choose the constant in Eq. (4.10) we appeal to our physical intuition connected with Eq. (2.15), namely, we require that $d\hat{\psi}/dy\to 0$ and $\hat{\psi}\to 0$ for $y\to\infty$, then we obtain const$=0$. Using this result Eq. (4.1) can be rewritten as

$$\frac{d\hat{\psi}}{dy}=\pm 2\sinh(\hat{\psi}/2)\ . \tag{4.11}$$

This then produces the following result:

$$\int^{\hat{\psi}(y)}dx\frac{1}{2\sinh(x/2)}=\pm(y-y_0)\ , \tag{4.12}$$

or

$$\ln|\tanh[\hat{\psi}(y)/4]|=\pm(y-y_0)\ . \tag{4.13}$$

Here y_0 represents some integration constant to be determined later. Going back to the variable ψ, we obtain

$$\psi(y)=\pm 4\tan^{-1}\{\exp[\pm(y-y_0)]\}\ . \tag{4.14a}$$

In one dimension y varies from $-\infty$ to $+\infty$. We choose the sign $+$ in the exponent in Eq. (4.14a) so that the function $\psi(y)$ varies from 0 to 2π. Going back to a normal system of units, we obtain

$$\bar{\phi}=\pm\frac{4}{\beta}\tan^{-1}\{\exp[\omega(x-x_0)]\}\ . \tag{4.14b}$$

Consider now once again the potential function defined in Eq. (4.2). It can now be written as

$$\frac{U(\bar{\phi})}{4\lambda}=\sin^2(\beta\bar{\phi}/2)\ . \tag{4.15}$$

The solution (4.14) brings the function $U(\phi)/(4\lambda)$ from one of its minima to the neighboring minima for x running from $+\infty$ to $-\infty$. Because of Eq. (4.5) and expression (4.14) we can construct the additional solutions of Eq. (4.6),

$$\bar{\phi}'=\bar{\phi}+\frac{2m\pi}{\beta}\ . \tag{4.16}$$

Solutions (4.14b) [or (4.16)] can be visualized as a soliton ($+$ sign) and antisoliton ($-$ sign) solution,[17] respectively, so that x_0 is the position of the soliton (antisolition) on the x axis. Hence we see from Eq. (4.16) that all the above soliton solutions can be divided into an infinite number of topological sectors which can be characterized by a pair of integers N_1 and N_2 (Ref. 17) corresponding to the asymptotic values $2N_1\pi/\beta$ and $2N_2\pi/\beta$ that the field $\bar{\phi}'$ must approach as x tends to $\pm\infty$, respectively. We define now the topological charge Q,

$$Q=N_1-N_2=\frac{1}{2\pi}\int_{-\infty}^{\infty}dx\,\beta\frac{d\bar{\phi}}{dx}\ , \tag{4.17}$$

where sign $Q=+1$ (or -1) corresponds to a soliton or antisoliton solution, respectively; the prime notation in the field $\bar{\phi}$ has been dropped. In the following paragraphs we shall discuss only solutions which belong to a particular topological sector thus excluding the possibility of tunneling between the sectors.[17] Without loss of generality, we can consider the case $n,m=0$ in Eq. (4.16). For this case we have two soliton solutions, Eq. (4.14), and one constant solution $\bar{\phi}=0$. When they are substituted into Eq. (4.3) the constant solution will produce the Debye-Hückel result as it was already explained, and substitution of either of the solutions of Eq. (4.14) into the fluctuation kernel (4.3) would produce an equation for the eigenmodes $\eta_n(x)$,

$$[-\nabla^2+2\lambda\beta^2\cos(\beta\bar{\phi})]\eta_n(x)=E_n^2\eta_n(x)\ . \tag{4.18}$$

The variation $\delta\phi$ can be expanded in terms of $\eta_n(x)$, i.e., $\delta\phi=\sum_{n=0}^{\infty}c_n\eta_n(x)$. Analysis of Eq. (4.18) shows that it has a discrete zero-mode $E_0=0$ followed by a continuous spectrum.[30] In order to analyze this spectrum, as well as the case $\bar{\phi}=0$, it is convenient to consider the above problem first for the case of a large box $-L/2\leq x\leq L/2$ with the subsequent limiting procedure $L\to\infty$. Then for the case $\bar{\phi}=0$ we obtain, according to Eq. (4.18),

$$E_n^2=k_n^2+\omega^2,\quad \omega^2=2\lambda\beta^2\ , \tag{4.19}$$

with $k_nL=2\pi n$, $n=0,\pm1,\pm2,\ldots$; and for the case $\bar{\phi}\neq 0$, we obtain

$$\tilde{E}_n^2=\tilde{k}_n^2+\omega^2\ , \tag{4.20}$$

with $\tilde{k}_nL+\Delta(k_n)=2n\pi$ where $\Delta(k)$ is the phase shift of the corresponding Schrödinger problem. Because of the zero mode, which is related to the translational symmetry, i.e., freedom of choice of x_0 in Eq. (4.14b) anywhere along the x axis, care must be taken when the functional integration over this mode is performed in Eq. (4.3). To overcome the zero-mode problem the collective coordinate method is used.[17] Instead of expansion of $\delta\phi$ in terms of the coefficients c_n [see Eq. (4.18)], the expansion is introduced in terms of b_n defined as follows:

$$\delta\phi=\bar{\phi}(x-x_0)+\sum_{n=1}^{\infty}b_n\eta_n(x-x_0)\ . \tag{4.21}$$

If for the case of c_n, the functional integration measure in (4.3) is just a product of c_n, i.e.,

$$D[\delta\phi]=\prod_{n=0}^{\infty} dc_n \ , \tag{4.22}$$

it should be replaced by the product of b_n, i.e.,

$$\prod_{n=0}^{\infty} dc_n=(S_{Cl})^{1/2}dx_0\prod_{n=1}^{\infty} db_n \ , \tag{4.23}$$

where the Jacobian of such a transformation is just $(S_{Cl}[\bar{\phi}])^{1/2}$, as was demonstrated by Coleman.[33] Going back to (4.3) and combining all above results we obtain, in one dimension,

$$\Xi_{SG}\sim\prod_{n=0}^{\infty}\left[\frac{2\pi}{E_n^2}\right]^{1/2}+[\exp(-S_{Cl})](S_{Cl})^{1/2}\left[\prod_{n=1}^{\infty}\int db_n\exp\left[-\frac{b_n^2\tilde{E}_n^2}{2}\right]\right]\int_{-L/2}^{L/2}dx_0$$

$$=\exp\left[-\frac{L}{2\pi}\int_{-\infty}^{\infty}dk\,\tfrac{1}{2}\ln\left[\frac{k^2+\omega^2}{2\pi}\right]\right]\left[1+\frac{L(S_{Cl})^{1/2}}{\sqrt{2\pi}}\exp(-S_{Cl})\exp\left[\tfrac{1}{2}\sum_{n=0}^{\infty}\ln E_n^2-\tfrac{1}{2}\sum_{n=1}^{\infty}\ln\tilde{E}_n^2\right]\right] , \tag{4.24}$$

where only the soliton solution is taken into account and S_{Cl} is determined, according to the one-dimensional version of Eq. (4.2), as follows:

$$S_{Cl}[\bar{\phi}]=\int_{-\infty}^{\infty}dx\left[\tfrac{1}{2}\left[\frac{d\bar{\phi}}{dx}\right]^2+2\lambda[1-\cos(\beta\bar{\phi})]\right] . \tag{4.25}$$

Using Eq. (4.10) written in normal units we can convert Eq. (4.25) into the following expression:

$$S_{Cl}[\bar{\phi}]=\int_{-\infty}^{\infty}dx\left[\frac{d\bar{\phi}}{dx}\right]^2=\int_{\bar{\phi}(-\infty)}^{\bar{\phi}(\infty)}d\bar{\phi}\frac{dx}{d\phi}\left[\frac{d\bar{\phi}}{dx}\right]^2$$

$$=2\sqrt{2\lambda}\int_{\bar{\phi}(-\infty)}^{\bar{\phi}(\infty)}d\bar{\phi}\sin(\beta\bar{\phi}/2)=\frac{8}{\beta}\sqrt{2\lambda}=\frac{16\lambda}{\omega} , \tag{4.26}$$

where in the last line we have used equations (4.11) and (4.14). To accomplish our calculations, we have to go back to Eq. (4.24) and consider the following expression:

$$\exp\left[\tfrac{1}{2}\sum_{n=0}^{\infty}\ln E_n^2-\tfrac{1}{2}\sum_{n=1}^{\infty}\ln\tilde{E}_n^2\right]$$

$$=\exp(\tfrac{1}{2}\ln\omega^2)\exp\left[\tfrac{1}{2}\sum_{n=1}^{\infty}\ln\left[\frac{k_n^2+\omega^2}{\tilde{k}_n^2+\omega^2}\right]\right] . \tag{4.27}$$

Using the fact that $k_nL=\tilde{k}_nL+\Delta(k_n)$, according to Eqs. (4.19) and (4.20), we have

$$k_n-\tilde{k}_n=\frac{\Delta(k_n)}{L} , \tag{4.28a}$$

and

$$k_n^2+\tilde{k}_n^2-2k_n\tilde{k}_n=\left[\frac{\Delta(k_n)}{L}\right]^2 . \tag{4.28b}$$

In the limit $L\to\infty$ we can write approximately

$$\tilde{k}_n^2\approx 2k_n(\tilde{k}_n-k_n)+k_n^2$$

$$\approx 2k_n\left[-\frac{\Delta(k_n)}{L}\right]+k_n^2 . \tag{4.29}$$

Substitution of this result into Eq. (4.27) then produces in the limit $L\to\infty$

$$\exp(\tfrac{1}{2}\ln\omega^2)\exp\left[-\tfrac{1}{2}\sum_{n=1}^{\infty}\ln\left[\frac{k_n^2+\omega^2+2k_n[-\Delta(k_n)/L]}{k_n^2+\omega^2}\right]\right]$$

$$\approx\exp(\tfrac{1}{2}\ln\omega^2)\exp\left[-\sum_{n=1}^{\infty}\frac{k_n[-\Delta(k_n)]/L}{k_n^2+\omega^2}\right]$$

$$=\exp(\tfrac{1}{2}\ln\omega^2)\exp\left[-\frac{1}{4\pi}\int_{-\infty}^{\infty}dk\left[\frac{d\Delta(k)}{dk}\right]\ln(k^2+\omega^2)\right] . \tag{4.30}$$

Here, in going from the summation to the k integration, we have performed an integration by parts. Going back to Eq. (4.24) and collecting all terms we can now write the following result ($d=1$):

$$\Xi_{SG}\cong\exp\left[-\frac{L}{4\pi}\int_{-\infty}^{\infty}dk\ln\left[\frac{k^2+\omega^2}{2\pi}\right]\right]$$

$$\times\left\{1+\frac{L\omega}{\sqrt{2\pi}}\left[\frac{16\lambda}{\omega}\right]^{1/2}\exp\left[-\frac{16\lambda}{\omega}\right]\exp\left[-\frac{1}{4\pi}\int_{-\infty}^{\infty}dk\left[\frac{d\Delta(k)}{dk}\right]\ln(k^2+\omega^2)\right]\right\}. \tag{4.31}$$

At this point we must take into account two things. First, we have to include not only solitons but antisolitons according to Eq. (4.14). Second, we have to take into account that position x_0 of the center of the soliton could be anywhere on the x axis. This then leads to a grand canonical ensemble of solitons and antisolitons so that the final result for Ξ_{SG} will be[30]

$$\Xi_{SG}=\exp\left[-\frac{L}{4\pi}\int dk\ln\left[\frac{k^2+\omega^2}{2\pi}\right]\right]\left[\sum_{N_1,N_2=0}^{\infty}\frac{1}{N_1!}\frac{1}{N_2!}\left[\frac{L\omega}{\sqrt{(2\pi)}}\exp(-S_{Cl}-\sigma)\right]^{N_1+N_2}\right], \tag{4.32}$$

or

$$\Xi_{SG}=\tilde{\Xi}_{DH}\exp\left[2L\frac{\omega}{\sqrt{2\pi}}\exp(-S_{Cl}-\sigma)\right], \tag{4.33}$$

where σ is defined as follows:

$$\sigma=-\tfrac{1}{2}\ln S_{Cl}+\frac{1}{4\pi}\int_{-\infty}^{\infty}dk\left[\frac{d\Delta(k)}{dk}\right]\ln(k^2+\omega^2). \tag{4.34}$$

S_{Cl} was given in Eq. (4.26) and Ξ_{DH} is the one-dimensional realization of the Debye-Hückel partition function [Eq. (3.10)]. Generalization of the above results to three dimensions is rather straightforward apart from the fact that Eq. (4.4) cannot be solved exactly in three dimensions. It is known,[34] however, that at large distances the numerical solution of Eq. (4.4) virtually coincides with the one-dimensional result, Eq. (4.14), with the replacement of $x-x_0$ by $|r-r_0|$.

If, for illustrative purposes, we adopt the three-dimensional version of Eq. (4.14) as a solution to Eq. (4.4), then r_0 must be interpreted as the position of the soliton in three-dimensional space. Instead of Eq. (4.26) for the classical action, we shall obtain

$$S_{Cl}[\bar{\phi}]=8\lambda\int d^3r\sin^2(\beta\bar{\phi}/2), \tag{4.35}$$

where Eqs. (4.2) and (4.10) were used. Since identifying $x-x_0$ with $|r-r_0|$ requires r be sufficiently large, we neglect r_0 relative to r, choose r_0 to be at the origin of the spherical system of coordinates, and obtain from (4.35)

$$S_{Cl}[\bar{\phi}]=32\pi\lambda\int_0^{\infty}dr\,r^2\sin^2(\beta\bar{\phi}/2). \tag{4.36}$$

Taking into account the explicit three-dimensional generalization of solution (4.14) and making an obvious change of variables, the following relation is obtained:

$$S_{Cl}[\bar{\phi}]=\frac{32\pi\lambda}{\omega^3}I, \tag{4.37}$$

where I is determined by the integral

$$I=\int_0^{\infty}dy\,y^2\sin^2\left[\frac{\beta\bar{\phi}(y)}{2}\right]$$

$$=4\int_0^{\infty}dy\,y^2\frac{e^{-2y}}{(1+e^{-2y})^2}=\frac{\pi^2}{12}=0.822. \tag{4.38}$$

If we accept S_{Cl} given in Eq. (4.36), then omitting fluctuation corrections, except the Debye-Hückel type, we can write instead of Eq. (4.33) the following three-dimensional result:

$$\Xi_{SG}\simeq\exp\left[-\frac{V}{24\pi}\omega^3+\frac{2\omega^3}{[(2\pi)^3]^{1/2}}V\exp(-S_{Cl})\right]. \tag{4.39}$$

Using the result (4.37) for S_{Cl} in the exponent of Eq. (4.39), the exponential can be expanded in a power series in λ/ω^3 which should be compared with that presented in Eq. (4.1). If we accept that $2\lambda\approx 2n_0$, we obtain instead of (4.1) the following result:

$$\frac{P}{kT}=2n_0\left[1-\frac{\gamma}{48\pi}+\frac{\gamma}{(\sqrt{2\pi})^3}\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\left[\frac{32\pi I}{\gamma}\right]^n\right]. \tag{4.40}$$

Here we explicitly see that now the small parameter is actually γ^{-1} (not γ) so that the above result is essentially nonperturbative.

More quantitative calculations, including the fluctuation corrections, are rather cumbersome and will be presented in subsequent publications. The difficulties presented by these calculations lie in the fact that, unlike

the one-dimensional case [Eq. (4.27)], the ratio of determinants would require some sort of renormalization procedure already encountered in similar two-dimensional calculations.[31,32] The systematic renormalization procedure would involve rather lengthy calculations and, therefore, is not presented.

V. THE RENORMALIZATION GROUP ANALYSIS OF THE 1-1 ELECTROLYTE MODEL

In Secs. III and IV we discussed various methods for the computation of the grand partition sum for the 1-1 electrolyte system. These methods permit us to write an equation of state as a power series in terms of the parameter γ, Eq. (4.1), or its inverse, Eq. (4.40). Because of the approximative nature of such expansions, it is illegitimate to draw any conclusions about the possible phase transition in the above electrolyte. This was confirmed later by more rigorous renormalization-group calculations for two-dimensions by Kosterlitz.[8,10] Since the three-dimensional case cannot be analyzed in closed form by methods described up to this point, the renormalization-group method is the only reliable alternative.

Kosterlitz[10] considered the problem of phase transition in d-dimensional Coulomb gas. He came to the conclusion that there are no phase transitions in the dimensionalities higher than two. We provide here an alternative renormalization-group method which was originally developed in the unpublished work by Raby and Ukawa and presented with some very minor numerical errors (for the case of two dimensions) in the review article by Kogut.[18] Here we generalize the method of Raby and Ukawa to study the same problem in d dimensions. We shall demonstrate here under what conditions results of Kosterlitz[10] can be reproduced and when his derivation becomes incorrect. For the cases where Kosterlitz's method fails, more sophisticated methods are needed[35] and they will not be presented here.

It is convenient to rewrite the partition sum (3.7) in somewhat different form,

$$\Xi_\Lambda=\int D[\phi]\exp\left[-\int d^dx\left[\tfrac{1}{2}\phi_\Lambda(-\nabla^2)\phi_\Lambda - 2\lambda\cos(\beta\phi_\Lambda)\right]\right], \tag{5.1}$$

where we have introduced field $\phi_\Lambda(\mathbf{x})$ via

$$\phi_\Lambda(\mathbf{x})=\int_{0<p<\Lambda}\frac{d^d\mathbf{p}}{(2\pi)^d}\exp(i\mathbf{p}\cdot\mathbf{x})\phi(\mathbf{p}), \tag{5.2}$$

$$\phi^*(\mathbf{p})=\phi(-\mathbf{p}). \tag{5.3}$$

The cutoff Λ implicitly takes into account the finite size of macroions in solution. Following the standard procedure described by Wilson and Kogut,[36] we subdivide the domain of momentum integration into two parts: a low-frequency part $0\leq p\leq\Lambda'$ and a high-frequency part $\Lambda'\leq p\leq\Lambda$. Then, as usual, define a field $\phi_{\Lambda'}$, according to

$$\phi_{\Lambda'}(\mathbf{x})=\int_{0<p<\Lambda'}d^dp\frac{1}{(2\pi)^d}\exp(i\mathbf{p}\cdot\mathbf{x})\phi(\mathbf{p}), \tag{5.4}$$

where the high-frequency part is obtained as

$$h(\mathbf{x})=\phi_\Lambda(\mathbf{x})-\phi_{\Lambda'}(\mathbf{x})=\int_{\Lambda'<p<\Lambda}d^dp\frac{1}{(2\pi)^d}\exp(i\mathbf{p}\cdot\mathbf{x})\phi(\mathbf{p}). \tag{5.5}$$

Use of the above definitions permit us to rewrite Eq. (5.1) as follows:

$$\Xi_\Lambda=\int D[\phi_{\Lambda'}]\exp\left[\tfrac{1}{2}\int d^dx\phi_{\Lambda'}\nabla^2\phi_{\Lambda'}\right]\exp\ln\Xi'(\phi_{\Lambda'}), \tag{5.6}$$

where

$$\Xi'(\phi_{\Lambda'})=\int D[h]\exp\left[\tfrac{1}{2}\int d^dx\, h\nabla^2h + 2\lambda\cos[\beta(\phi_{\Lambda'}+h)]\right]. \tag{5.7}$$

The orthogonality of $h(x)$ and $\phi_{\Lambda'}(x)$ with respect to integration over x (Ref. 36) eliminates the cross terms and $D[\phi]$ is replaced by $D[\phi_{\Lambda'}]D[h]$. We now want to compute $\Xi(\phi_{\Lambda'})$ perturbatively. Analogously to Eq. (3.22), we define now the averaging procedure as

$$\langle\cdots\rangle_h=\frac{\int D[h]\exp\left[\tfrac{1}{2}\int d^dx\, h\nabla^2h\right](\cdots)}{\int D[h]\exp\left[\tfrac{1}{2}\int d^dx\, h\nabla^2h\right]}. \tag{5.8}$$

Then by writing

$$\Xi'(\phi_{\Lambda'})=\frac{\Xi'(\phi_{\Lambda'})}{\mathcal{N}}\mathcal{N}, \tag{5.9}$$

where

$$\mathcal{N}=\int D[h]\exp\left[\tfrac{1}{2}\int d^dx\, h\nabla^2h\right], \tag{5.10}$$

and substituting Eq. (5.9) into Eq. (5.6) we obtain the following cumulant expansion by analogy with Eq. (3.21):

$$\ln\left[\frac{\Xi'(\phi_{\Lambda'})}{\mathcal{N}}\right]\approx 2\lambda\int d^dx\langle\cos[\beta(\phi_{\Lambda'}+h)]\rangle_h + \tfrac{1}{2}(2\lambda)^2\int d^dx\int d^dy\langle\cos\{\beta[\phi_{\Lambda'}(\mathbf{x})+h(\mathbf{x})]\}\cos\{\beta[\phi_{\Lambda'}(\mathbf{y})+h(\mathbf{y})]\}\rangle_h^c+\cdots. \tag{5.11}$$

Here $\langle\cdots\rangle_h^c$ means cumulant average, i.e.,

$$\langle\cos\{\beta[\phi_{\Lambda'}(x)+h(x)]\}\cos\{\beta[\phi_{\Lambda'}(y)+h(y)]\}\rangle_h^c$$
$$=\langle\cos\{\beta[\phi_{\Lambda'}(\mathbf{x})+h(\mathbf{x})]\}\cos\{\beta[\phi_{\Lambda'}(\mathbf{y})+h(\mathbf{y})]\}\rangle_h-\langle\cos\{\beta[\phi_{\Lambda'}(\mathbf{x})+h(\mathbf{x})]\}\rangle_h\langle\cos\{\beta[\phi_{\Lambda'}(\mathbf{y})+h(\mathbf{y})]\}\rangle_h\ . \quad (5.12)$$

The overall multiplicative constant $\exp(\ln\mathcal{N})$ appearing due to Eq. (5.9) can be dropped because it does not affect the renormalization procedure. Computation of averages can be done easily using the shift procedure, described after Eq. (3.24), by rewriting $\cos[\beta(\phi_{\Lambda'}+h)]$ in exponential form,

$$\cos[\beta(\phi_{\Lambda'}+h)]=\tfrac{1}{2}\{\exp[i\beta(\phi_{\Lambda'}+h)]+\exp[-i\beta(\phi_{\Lambda'}+h)]\}\ , \quad (5.13)$$

yielding the result

$$\langle\cos\beta(\phi_{\Lambda'}+h)\rangle_h=A(0)\cos[\beta\phi_{\Lambda'}(\mathbf{x})]\ , \quad (5.14)$$

where

$$A(\mathbf{x})=\exp\left[-\frac{\beta^2}{2}G_h^{(d)}(\mathbf{x})\right]\ , \quad (5.15)$$

and

$$G_h^{(d)}(\mathbf{x})=\int_{\Lambda'<p<\Lambda}d^dp\frac{1}{(2\pi)^d}\frac{\exp(i\mathbf{p}\cdot\mathbf{x})}{p^2}\ . \quad (5.16)$$

Obtaining the cumulant average of Eq. (5.12) using the shift procedure produces the following result:

$$\tfrac{1}{2}A^2(0)[A^2(\mathbf{x}-\mathbf{y})-1]\cos\{\beta[\phi_{\Lambda'}(\mathbf{x})+\phi_{\Lambda'}(\mathbf{y})]\}+\tfrac{1}{2}A^2(0)[A^{-2}(\mathbf{x}-\mathbf{y})-1]\cos\{\beta[\phi_{\Lambda'}(\mathbf{x})-\phi_{\Lambda'}(\mathbf{y})]\}\ . \quad (5.17)$$

Introducing the relative coordinates $\alpha=\mathbf{x}-\mathbf{y}$ and $\delta=\frac{1}{2}(\mathbf{x}+\mathbf{y})$, we take advantage of the weak spatial variation of the low-frequency field $\Phi_{\Lambda'}(\mathbf{x})$ by preserving only first-order terms in α,

$$\phi_{\Lambda'}(\mathbf{x})-\phi_{\Lambda'}(\mathbf{y})\approx\alpha\cdot\nabla\phi_{\Lambda}(\delta)\ . \quad (5.18)$$

Expression (5.17) can now be rewritten as

$$\tfrac{1}{2}A^2(0)[A^2(\alpha)-1]\cos[2\beta\phi_{\Lambda'}(\delta)]+\tfrac{1}{2}A^2(0)[A^{-2}(\alpha)-1]\{1-\beta^2[\alpha\cdot\nabla\phi_{\Lambda'}(\delta)]^2\}\ . \quad (5.19)$$

Substituting Eq. (5.11) into Eq. (5.6) with averages given by formulas (5.14) and (5.19) we obtain the final result (with accuracy up to terms of order λ^2)

$$\Xi_\Lambda\approx\exp\left[\tfrac{1}{4}(2\lambda)^2A^2(0)a_1\int d^d\mathbf{x}\right]\times\int D[\phi_{\Lambda'}]\exp\left[-[1+\tfrac{1}{2}(2\lambda)^2\beta^2a_2A^2(0)]\int d^dx[\tfrac{1}{2}(\nabla\phi_{\Lambda'})^2-2\lambda A(0)\cos(\beta\phi_{\Lambda'})]\right]\ . \quad (5.20)$$

Here a_1 and a_2 are defined as follows:

$$a_1=\int d^dy[A^{-2}(\mathbf{y})-1]\ , \quad (5.21)$$

and

$$a_2=\int d^dy\,y^2[A^{-2}(\mathbf{y})-1]\ . \quad (5.22)$$

In order to accomplish the renormalization transformations, we would like to specify Λ', defined in Eq. (5.4), as $\Lambda'=l\Lambda$, $0<l<1$. Now in order to bring the momentum integration in the expression (5.4) back to the form given by Eq. (5.2), we have to rescale the momentum variable $p=p'l$. After these preliminaries, we can rewrite Eq. (5.20) as follows:

$$\Xi_\Lambda(\lambda,\beta)=\exp\left[\lambda^2A^2(0)a_1\int d^dx\right]\Xi_\Lambda(\lambda',\beta')\ , \quad (5.23)$$

where we have redefined field ϕ_Λ in the following manner:

$$\phi_\Lambda\to[1+2\lambda^2\beta^2a_2A^2(0)]^{1/2}\phi_\Lambda\ . \quad (5.24)$$

We now must redefine β and λ accordingly,

$$(\beta')^2=\beta^2/[1+2\lambda^2\beta^2a_2A^2(0)]\ , \quad (5.25)$$

$$\lambda'=\lambda A(0)\ . \quad (5.26)$$

Equations (5.25) and (5.26) provide the necessary recurrence relations for the development of the renormalization-group method. Before we proceed, we have to notice that the factor $\int d^dx$ in the exponent of Eq. (5.23) is just the volume of the system. Taking a logarithm of both sides of Eq. (5.23), we obtain

$$\frac{\Omega(\lambda,\beta)}{VkT}=-\lambda^2A^2(0)a_1+\frac{\Omega'(\lambda',\beta')}{VkT}\ , \quad (5.27)$$

where the thermodynamic potential $\Omega=-PV$. Write $F=\Omega(\lambda,\beta)/VkT$, then we obtain

$$F=F'-\lambda^2A^2(0)a_1\ , \quad (5.28)$$

which provides the final recurrence relation. This latter recurrence plays an auxiliary role and will not be considered subsequently.

Using the fact that $S[\phi]$ must be dimensionless, we

conclude that ϕ varies inversely with the square root of the units of distance. If we rescale the distance $(x \to x/\beta^2)$ in Eq. (5.11), we find that the smallness parameter is $\lambda\beta^6 \sim \lambda\lambda_B^3 \sim \eta^3$. Thus this method of renormalization is valid when the nonideality parameter η is less than 1. For other conditions alternative renormalization[35] must be used. We will consider only the case $\eta < 1$ which then will effectively lead us to the result of Kosterlitz.[10] It is convenient to choose the parameter l defined above arbitrarily close to unity, then $l\Lambda \cong \Lambda - d\Lambda$. For the propagator $G_h^{(d)}$ defined in Eq. (5.16) we then can write the following expression:

$$G_h^{(d)}(x) \approx d\Lambda\, \Lambda^{d-3} f(\Lambda \mid \mathbf{x} \mid) , \tag{5.29}$$

where $f(\Lambda \mid \mathbf{x} \mid)$ is some function coming from the angular integration. To understand this result we recall the well-known formula

$$\int d^d q\, F(q^2, \mathbf{q}\cdot\mathbf{p}) = C_{d-1} \int_0^\infty dq\, q^{d-1} \int_0^\pi d\theta (\sin\theta)^{d-2} F(q^2, pq\cos\theta) , \tag{5.30}$$

where C_{d-1} is defined according to

$$C_d = 2\pi^{d/2}/\Gamma(d/2) , \tag{5.31}$$

and $\Gamma(x)$ is just an ordinary gamma function. Given Eq. (5.29) we now want to compute a_2 defined in Eq. (5.22). Using the definition of $A(x)$ given in Eq. (5.15) and combining it with result (5.29) we obtain, after rescaling of variables in Eq. (5.22), the following result:

$$a_2 = \beta^2 d\Lambda\, \Lambda^{-5} \alpha_2 , \tag{5.32}$$

where α_2 is just a simple number coming from the following integral:

$$\alpha_2 = \int d^d x\, x^2 f(x) . \tag{5.33}$$

The function $f(x)$ has been defined in Eq. (5.29). The dimensionality of space d does not appear explicitly in Eq. (5.32) (apart from the different value of α_2 in different dimensionalities). Consider now the approximation for $A(0)$. We have, according to Eq. (5.15),

$$A(x) \approx 1 - \frac{\beta^2}{2} G_h^{(d)}(x) \approx 1 - \frac{\beta^2}{2} f(\Lambda x) \Lambda^{d-3} d\Lambda . \tag{5.34}$$

To obtain $A(0)$, we need only to calculate $f(0)$ which can be obtained from the definition (5.16) and formula (5.30). It follows that

$$f(0) = \frac{1}{(2\pi)^d} \frac{2\pi^{(d-1)/2}}{\Gamma((d-1)/2)} \int_0^\pi d\theta (\sin\theta)^{d-2} = \frac{1}{(2\pi)^d} \frac{2\pi^{(d-1)/2}}{\Gamma((d-2)/2)} \times \frac{\pi}{2^{d-3}(d-2)B(d/2,(d-2)/2)} , \tag{5.35}$$

$$B(d/2,(d-2)/2) = \frac{\Gamma(d/2)\Gamma((d-2)/2)}{\Gamma(d-1)} . \tag{5.36}$$

Results are particularly transparent in $d=2$ and 3. In the first case, we obtain $f(0) = 1/2\pi$ and in the second $f(0) = 1/2\pi^2$. Consideration of the general case is left for the reader. Using above results we can rewrite Eq. (5.34) for $x = 0$ as follows:

$$A(0) = 1 - \frac{\beta^2}{2} \frac{1}{2\pi} \frac{d\Lambda}{\Lambda} , \quad \text{for } d=2 \tag{5.37}$$

$$A(0) = 1 - \frac{\beta^2}{2} \frac{1}{2\pi^2} d\Lambda , \quad \text{for } d=3 . \tag{5.38}$$

By combining Eqs. (5.26), (5.37), and (5.38), we can write

$$\delta\lambda = \lambda - \lambda' = -\lambda[A(0)-1] = \lambda \frac{\beta^2}{4\pi} \frac{d\Lambda}{\Lambda} , \quad \text{for } d=2 \tag{5.39}$$

$$\delta\lambda = \lambda - \lambda' = \lambda \frac{\beta^2}{(2\pi)^2} d\Lambda , \quad \text{for } d=3 . \tag{5.40}$$

Analogously, we also obtain ($d=2,3$)

$$\delta(\beta^2) = \beta^2 - \beta'^2 = -\beta^2 \left[\frac{1}{1 + 2\lambda^2\beta^2 a_2 A^2(0)} - 1 \right] \approx 2\beta^6 \lambda^2 \frac{d\Lambda}{\Lambda^5} \alpha_2 . \tag{5.41}$$

Instead of a momentum cutoff Λ it is convenient now to introduce the real-space cutoff $\sigma_i = \Lambda^{-1} = a$ which was defined in Sec. II. In terms of this cutoff, Eqs. (5.39), (5.40), and (5.41) can be rewritten as follows:

$$\delta\lambda = -\lambda \frac{\beta^2}{4\pi} \frac{da}{a} , \quad \text{for } d=2 \tag{5.42}$$

$$\delta\lambda = -\lambda \frac{\beta^2}{(2\pi)^2} \frac{da}{a^2} , \quad \text{for } d=3 \tag{5.43}$$

$$\delta(\beta^2) = -2\lambda^2\beta^6 \alpha_2 a^3 da . \tag{5.44}$$

At this point it is convenient to recall that $\beta^2 = 4\pi\alpha^2$ [see Eq. (3.6)] and $\alpha^2 = e^2/\epsilon kT = \lambda_B$ [see Eq. (2.1)]. Also in the regime at which the given renormalization-group treatment is valid, we can identify λ with n_0, according to Eq. (3.17b). Using all these facts we can rewrite Eqs. (5.42)–(5.44) in somewhat more suggestive form,

$$\delta n_0 = -n_0 \lambda_B \frac{da}{a} , \quad \text{for } d=2 \tag{5.45}$$

$$\delta n_0 = -n_0 \frac{\lambda_B}{\pi} \frac{da}{a^2} , \quad \text{for } d=3 \tag{5.46}$$

$$\delta(\lambda_B) = -2(4\pi n_0)^2 \alpha_2 \lambda_B^3 a^3 da . \tag{5.47}$$

By recalling the definition of the nonideality parameter η defined in Eq. (2.6), we obtain that combination $n_0\lambda_B^3 = \eta^3$. We define now a new variable $y = n_0 a^2$ in two dimensions so that

$$dy = a^2 dn_0 + n_0 da^2 . \tag{5.48}$$

Using here results of Eqs. (5.45)–(5.47), we obtain

$$dy=-an_0\lambda_B da+2n_0 a\,da$$
$$=n_0 a(2-\lambda_B)da, \quad \text{for } d=2 . \tag{5.49}$$

Similarly, in three dimensions we define $y=n_0a^3$, then

$$dy=-n_0 a\frac{\lambda_B}{\pi}da+3n_0a^2da$$
$$=n_0a^2\left[3-\frac{\lambda_B}{\pi a}\right]da, \quad \text{for } d=3 . \tag{5.50}$$

The reason for introduction of the new variable y becomes more apparent if we notice that the condition

$$2-\lambda_B=0, \quad \text{for } d=2 \tag{5.51}$$

provides the estimate of the temperature of the phase transition.[8] The existence of the phase transition requires not only the existence of the fixed point (line) relevant to this transition but also the investigation of the stability of the above fixed point (line). However, since our main purpose is to apply the renormalization procedure to the three-dimensional case, we will not investigate the stability of the fixed point (line) for the two-dimensional case. For the latter case, we are only interested in illustrating that our renormalization procedure reproduces the earlier results of Kosterlitz.[10]

For the $d=2$ case, we define a new variable $x=\lambda_B-2$. Then Eq. (5.49) can be rewritten as follows:

$$\frac{dy}{dt}=-xy, \tag{5.52}$$

where $t=\ln a$. Similarly, we can obtain the equation for x using Eq. (5.47),

$$\frac{dx}{dt}=-32\pi^2\alpha_2(x+2)^3y^2\cong-256\pi^2\alpha_2y^2 . \tag{5.53}$$

The last line assumes that $x\ll1$ [see Eq. (5.51) and the definition of x]. Multiply Eq. (5.52) by $2y$ and Eq. (5.53) by $2x$ so that we obtain

$$\frac{dy^2}{dt}=-2xy^2 , \tag{5.52'}$$

$$\frac{dx^2}{dt}=-512\pi^2\alpha_2xy^2 . \tag{5.53'}$$

The above equations may be combined to give

$$\frac{dx^2}{dt}=c\frac{dy^2}{dt} , \tag{5.54}$$

where $c=256\pi^2\alpha_2$. This then gives

$$x^2-cy^2=\text{const} . \tag{5.55a}$$

Finally, we can redefine the cutoff a in order to absorb the constant c, i.e., $a\to(c)^{1/4}a$ (recall that $y=n_0a^2$). After these manipulations Eq. (5.55) can be rewritten in its final form,

$$x^2-y^2=\text{const} . \tag{5.55b}$$

This is just the equation for hyperbolas in the (x,y) plane. The constant on the right-hand side of Eq. (5.55) is evidently different for each hyperbola. The (x,y) plane is separated onto two domains by the equation

$$x^2-y^2=0 . \tag{5.55c}$$

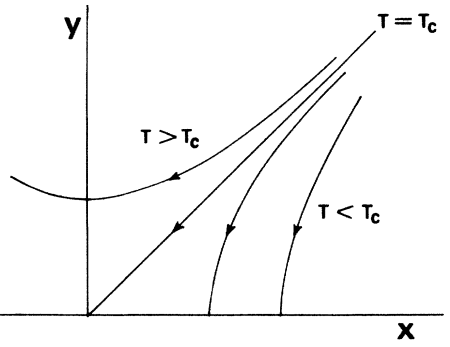

FIG. 5. Renormalization-group trajectories given by Eq. (5.55b). The arrows indicate the direction of the flow described by the equations of motion (5.52') and (5.53') when the successive renormalization-group iterations are performed.

This is graphically depicted in Fig. 5. Unlike the naive estimate, Eq. (5.51), the critical temperature is now determined by Eq. (5.55c) which in the usual system of units can be rewritten as follows:

$$(2-\lambda_B)^2=n_0^2a^4 , \tag{5.56}$$

where $a\sim\sigma_i$ as it was already mentioned.

Consider now the case of three dimensions. Then Eq. (5.50) can be rewritten as follows:

$$\frac{dy}{dt}=-xy , \tag{5.57a}$$

where we have defined a new variable x via $x=\lambda\beta/(\pi a)-3$. For this variable we obtain

$$dx=\frac{d\lambda_B}{\pi^a}-\frac{\lambda_B}{\pi a^2}da=-cy^2(x+3)^3dt-(x+3)dt , \tag{5.57b}$$

or

$$\frac{dx}{dt}\approx-3[\hat{c}y^2(6x+9)+1] , \tag{5.58}$$

where $\hat{c}>0$ is some unimportant constant and it was assumed that $x\ll1$. Equations (5.57) and (5.58) should be compared with Eqs. (5.52) and (5.53). The presence of the extra term in Eq. (5.58) compared to Eq. (5.53) complicates matters considerably. Even if we ignore this term, which is proportional to x, on the right-hand side of Eq. (5.58), we still will be unable to perform the same kind of integration as in the two-dimensional case. Moreover, the assumption $x\ll1$ is also, in fact, incorrect. Indeed, let $x=0$ and consider the steady-state solution of Eqs. (5.57) and (5.58). We see that Eq. (5.57) admits any value of y but Eq. (5.58) gives for y the following result:

$$9\hat{c}y^2=-1 . \tag{5.59}$$

This relation can never be satisfied because $y=n_0a^3\geqq0$. Hence we see that the system of equations [(5.57) and

(5.58)], or more generally,

$$\frac{dx}{dt} = -3(x+3)[\hat{c}y^2(x+3)^2+1] , \tag{5.58'}$$

do not have any *physically acceptable* fixed point. Consequently, there is no equilibrium phase transition for the restricted primitive model of the three-dimensional symmetric electrolyte solution in the domain of $\eta < 1$.

VI. DISCUSSION

In spite of the rather extensive analysis of the electrolyte problem, many questions still remain to be investigated. First the given methods do not permit us, in their present form, to study the problem of phase transitions for the case of asymmetric electrolytes. Second, we have studied only the equilibrium phase transitions. Meantime it is known[6] that even for the primitive model nonequilibrium phase transitions can take place. Third, we completely ignored boundary effects in our work. They might be of crucial importance for the above problem. Fourth, the nonperturbative analysis of Sec. IV also involves renormalization effects which would lead to a renormalization-group analysis very different from that presented in Sec. V. Future, more systematic, treatments are necessary to provide more definitive answers to above posed questions. Also, the conclusive answers could be obtained only by comparing the theoretical results with thorough experimental measurements. Some available experimental data indicate that for electrolytes prepared from solvents with low dielectric constants, such as benzene or diethyl ether, there are some miscibility gaps which could be interpreted as "liquid-vapor-type" phase transitions involving the ions of the electrolyte.[2,37] A similar conclusion was reached by the authors of Ref. 38, who observed the miscibility gap in sodium-liquid ammonia solutions with Na^+ and solvated electrons representing the ionic solute. Experimentally the above gaps were characterized by noticeable changes in the electric conductivity, as it was explained in the Introduction. Above experiments show that the complexity of the problem of phase transitions in electrolytes is only indirectly related to the RPM presented in our article because of a number of reasons. First, within the framework of the RPM model we considered only the symmetric electrolyte. Second, the highly polarizable groups in the macroions of the electrolytes studied experimentally may provide a significant non-Coulomb contribution to the interion potential. Third, one of the most recent model calculations for the case of square well fluid[39] indicates that the improved Percus-Yevick (PY) computational procedure produces the standard mean-field results[29] for the exponents γ and δ, and the question of phase transition in the Yukawa fluid, directly related to our problem, remains open within the PY approach although, as authors indicate, some nonclassical behavior in this case is expected. These and other factors already mentioned will be considered in future publications.

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