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Self-Consistent-Field Theory for Confined Polyelectrolyte Chains

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The Poisson-Boltzmann theory of the forces between two charged macroscopic surfaces has been generalized to a case where the intervening space contains a uni-univalent electrolyte as well as long polyelectrolyte chains. The polyelectrolyte chains bear charges of opposite sign with respect to the fixed charges on the confining surfaces. The approach is based on the self-consistent-field (SCF) theory widely used in the context of the polymer excluded volume interactions. Numerical as well as approximate analytical solutions of the SCF equations have been obtained in the limit of ground-state dominance and the connection between the polyelectrolyte conformation and the intersurface forces has been investigated for different values of the parameters describing the system. The most important characteristic of the interaction forces is a region of intersurface separations characterized by net attractive forces between bounding surfaces, stemming from the bridging of polyelectrolyte chains between the two charged surfaces. These attractive forces are of different nature than the Lifshitz-van der Waals interactions. They appear to decrease approximately exponentially with separation but can be much stronger in the overall magnitude.

I. Introduction

Electrostatic interactions between macroscopic surfaces with fixed charges immersed in an aqueous electrolyte with mobile charge carriers are essential in assessing the stability of charged (bio)colloids that play an important role in numerous chemical and biochemical systems. Their study has been extensive and the understanding reached on the theoretical level is usually summed under the heading of the DLVO theory.¹ In this framework the electrostatic interactions between macroscopic bodies are broken into two disjointed contributions. First of all there is a contribution that has its origin in the creation of double layers close to the charged surfaces. Their existence is due to the interplay of entropic effects that favor homogeneous distribution of mobile charges, and electrostatic attraction between the charges on the surfaces and their counterions in the aqueous environment, described on the level of the Poisson-Boltzmann (PB) equation. This contribution to the total force between the surfaces is repulsive if the surfaces bear charges of the same sign. The second contribution is attractive, irrespective of the charges on the surfaces, and has its origin in the fluctuations (thermodynamic as well as quantum mechanical) of the local electrostatic fields in the dielectric media involved. It is usually referred to as the van der Waals-Lifshitz interaction.

The original DLVO point of view on the electrostatic interactions between macroscopic surfaces based on the Poisson-Boltzmann equation has proved to be inadequate in several respects, but the introduction of some effective parameters (e.g., Stern layer, effective surface charge) can usually save the theory and make it conform to the experiment.^{1,2} There are cases, however, where mere fitting of the parameters is not enough to make the DLVO theory agree with experiments.² In fact it does not even predict correctly the sign of the electrostatic interaction.³ For example, in a divalent electrolyte the forces between equally charged surfaces can become attractive for quite reasonable values of the model system parameters as shown by advanced statistical mechanical calculations and as can be inferred also from experimental studies.² Cases like this one made us all aware that the mean-field ansatz implicit in the PB theory can be completely off the mark if the electrostatic coupling in the system is large enough. A quite substantial upgrading of the Poisson-Boltzmann theory is needed to go beyond the mean-field approximation and into the regime where local fluctuations in the mobile charge

density distribution begin to dominate the free energy.⁴ Such an upgrading has been recently worked out on an accuracy level equal to the one achieved by the bulk-liquid-state theories.²

The present study will be concerned with a modification in the composition of the model system standardly taken as a starting point of the DLVO theory. To the aqueous electrolyte, described in the primitive model framework and spanning the intersurface space, we shall add flexible polyelectrolyte chains of charge opposite to the one fixed on the bounding surfaces and study the changes in the interaction between charged, bounding surfaces effected by this addition. This modification can be viewed from two different directions. It is either an upgrading of the model system that lies in the basis of the DLVO theory or a generalization of the conditions imposed upon polyelectrolyte chains in an ionic environment. The latter case too has a substantial history. Polyelectrolytes are a subject by themselves⁵ and the statistical mechanics of a single polyelectrolyte chain in the bulk has been worked out on different levels of approximations starting from the seminal work of Richmond.⁶ On the other side, the problem of a confined (neutral) polymer, first addressed by Dolan and Edwards⁸ and independently by Richmond and Lal,⁹ is also well worked out and the forces between confining surfaces have been studied in detail.^{10,27} The present problem lies somewhere between these two and has been, to our knowledge, first approached by Wiegel¹¹ who studied the conformational properties of a single polyelectrolyte chain in contact with a charged wall. His work has been generalized by van Opheusden³⁶ to include two charged surfaces with charged polymers in between. More recently Miklavic and Marčelja¹² have made an attempt to assess the forces between charged walls in a different system, where the polyelectrolytes are grafted to the charged bounding surfaces and immersed in an electrolyte solution. A further step was taken by Åkesson, Woodward, and Jönsson¹³ who addressed the problem

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(2) Kjellander, R.; Marčelja, S. *J. Phys.* 1988, 49, 1009. Kjellander, R.; Marčelja, S.; Pashley, R. M.; Quirk, J. P. *J. Phys. Chem.* 1988, 92, 6489.

(3) Gulbrand, L.; Jönsson, B.; Wennerström, H.; Linse, P. *J. Chem. Phys.* 1984, 82, 2221.

of confined polyelectrolyte chains between two charged walls without any intervening electrolyte. In their case it is only the connectivity of the polyelectrolyte chain that separates their model system from the counterion—only case where the intersurface space contains only mobile counterions. In spite of this similarity the intersurface forces bear almost no resemblance to the latter case.^{13,20}

In our treatment of the problem of confined polyelectrolyte chains immersed in an electrolyte solution we shall try to remain as close to the Poisson–Boltzmann approach to a confined electrolyte as possible. We shall formulate the appropriate partition function in a form of a field theory quite similar to the one used in the case of a confined Coulomb fluid.⁴ We showed for this case that the stationary point configuration of the local electrostatic fields corresponds to the solution of the Poisson–Boltzmann equation. Using the stationary point ansatz in the presence of additional polyelectrolyte chains will naturally lead to a generalization of the Poisson–Boltzmann equation where the statistical averages over the polymeric degrees of freedom will be included in a self-consistent manner. The equations derived by this procedure will be similar to those used in the self-consistent-field (SCF) treatment of the polymer excluded volume and indeed represent a variation on the SCF equations for the electrostatic excluded-volume problem derived by Kholodenko and Beyerlein.¹⁴ This new set of coupled self-consistent equations, which in turn lead to a modified PB equation, will be solved numerically and the nature of the solutions for different parameters characterizing the state of the system will be investigated. Also some conclusions will be drawn on the connection between the polyelectrolyte conformation and the intersurface forces; specifically, we shall demonstrate that the bridging mechanism, just as in the simpler model system investigated by Åkesson, Woodward and Jönsson,^{13,20} has a pronounced effect on the interaction forces present in this system.

The outline of the paper is as follows. In section II we shall define our model system and derive the general form of the partition function in the guise of a field theory similar to the one used in the context of nonhomogeneous electrolyte. A second-order perturbation expansion effected in section III will lead to an approximate form of the interaction free energy that will serve as an introduction to the self-consistent-field method, derived at the end of this section. Section IV will start with the explicit form of the SCF equations in the form of a modified Poisson–Boltzmann equation for the local mean electrostatic potential and an equation for the polyelectrolyte charge density distribution. Sections IV–VII are self-contained and the reader not interested in formal details can just skip the introductory sections II and III and start his reading at the beginning of section IV, where the SCF equations are derived from purely physical arguments. The SCF equations will be solved numerically in section V for different values of the characteristic parameters determining the state of the confined system. Two approximate analytical solutions of the SCF equations will be derived in the next section for a very constrained set of characteristic parameters. The final section will be devoted to the critical discussion of the results obtained in the light of the previous work relevant to the problem.

II. Model Description and Formalization

A combined model is utilized to specify the system under study. The uni-univalent electrolyte is described in the frame of the primitive model with ionic charge e_0 , dielectric constant ϵ , and activity z_0 . For the level of subsequent approximations the hard core radius is not important. The polyelectrolyte chains are described in the frame of a modified continuum version of the Baumgärtner model³⁶ with the proper inclusion of the polyelectrolyte–ion interactions. In this framework the polyelectrolyte chains are described as freely jointed links of charge τ per bead of length l , with a total contour length equal to Nl . The total number of polymer chains is N . The electrolyte as well as the

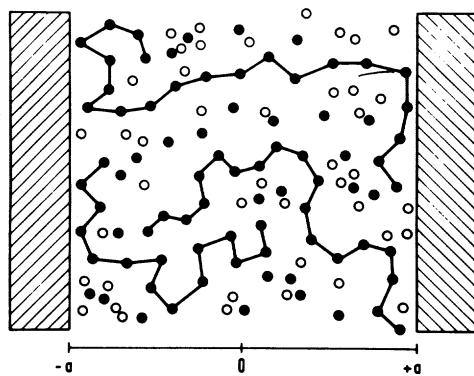


Figure 1. The model system. Two charged surfaces (surface charge density σ) at a separation $2a$ with a uni-univalent electrolyte and charged polyelectrolyte chains (charge per bead τ) in between. Positive charges are represented by filled circles and negative ones by open circles. The dielectric constant ϵ is supposed to be the same in all regions of the space. Surfaces are impenetrable to ions as well as to the polyelectrolyte. Ions are allowed to exchange with the bulk reservoir while polymers are in a restricted equilibrium. The sign of the charges residing on the polymer beads is opposite to the sign of the fixed charges on the bounding surfaces.

polyelectrolyte chains are confined between two impenetrable surfaces separated by $2a$ and each carrying a surface charge density σ (presumed negative), Figure 1, of sign opposite to τ . All the electrostatic interactions are mediated by a Coulomb potential of the form $u(\mathbf{r}, \mathbf{r}') = 1/4\pi\epsilon_0|\mathbf{r} - \mathbf{r}'|$, being a solution of the Poisson equation $-\epsilon\epsilon_0\nabla^2 u(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$. The configurational part of the Hamiltonian for this model system can be written in a discretized form

$$H = \frac{3kT}{2l^2} \sum_{\alpha} \sum_p (\mathbf{r}_{p+1}^{\alpha} - \mathbf{r}_p^{\alpha})^2 + \frac{1}{2} \sum_{ij} e_i e_j u(\mathbf{r}_i, \mathbf{r}_j) - \frac{1}{2} \sum_k N_k e_k^2 u(\mathbf{r}, \mathbf{r}) + \sum_i e_i \phi_e(\mathbf{r}_i) \quad (\text{II.1})$$

In the above equation index p runs over all the polymer beads in α th chain. Indices i and j run over all polymer beads of all the chains ($e_i = \tau$), all anions ($e_i = -e_0$) and all cations ($e_i = e_0$) while index k can designate the polymer ($N_k e_k^2 = N\tau^2$), the cations ($N_k e_k^2 = N_c e_0^2$) or the anions ($N_k e_k^2 = N_a e_0^2$). The third term in the above expression merely removes the self-energy terms ($i = j$) from the Hamiltonian. $\phi_e(\mathbf{r})$ is the external electrostatic potential due to the charges on the surfaces. In what follows we shall strictly use a continuum representation of the Gaussian chain that amounts to the following formal replacement $\sum_{\alpha} \sum_p (\mathbf{r}_{p+1}^{\alpha} - \mathbf{r}_p^{\alpha})^2 \rightarrow \sum_{\alpha} \int_{0}^{N_{\alpha}} (dR^{\alpha}(n)/dn)^2 dn$, where $R^{\alpha}(n)$ now stands for the continuous coordinate of the n th bead along the α th polymeric chain. In the above form of the Hamiltonian the possibility of discrete surface charges as well as the presence of dielectric discontinuities was disregarded since they rarely have any qualitative effects.²⁸

In constructing the partition function of the system characterized by the configurational Hamiltonian H we have to take into account the fact that the ions are allowed to exchange with the bulk reservoir as the separation between the surfaces varies.⁴ As for the polymeric chains, we assume that they are not in equilibrium with the bulk phase²⁷ since the transversal diffusion rate of a polymer trapped between two surfaces is quite small and the overall situation is the one of restricted equilibrium.³⁰ The appropriate partition function is therefore

$$\Xi = \prod_{\alpha} \prod_{s=a,c} \sum_{N_s=0}^{\infty} \frac{\zeta^{N_s}}{N_s!} \int_{[R^{\alpha}, r]} e^{-\beta H} \mathcal{D}R^{\alpha}(n) \mathcal{D}^{N_s} \mathbf{r} \quad (\text{II.2})$$

where a and c stand for anions and cations, α is the index of polymeric chains, ζ is the renormalized value of the absolute activity, $\zeta = z_0 e^{1/2\beta e_0^2 u(r, r)}$, and β is the inverse thermal energy, $\beta^{-1} = kT$. The integration measures in the above equation are defined as: $\mathcal{D}R^{\alpha}(n) = d^3 R^{\alpha}(1) d^3 R^{\alpha}(2) \dots d^3 R^{\alpha}(N_{\alpha})$ and $\mathcal{D}^{N_s} \mathbf{r} = d^3 \mathbf{r}(1) d^3 \mathbf{r}(2) \dots d^3 \mathbf{r}(N_s)$, where $\mathbf{r}(N_s)$ is the position vector of the N_s th anion or cation ($s = a, c$), respectively. Furthermore,

(14) Kholodenko, A. L.; Beyerlein, A. L. *Phys. Rev. A* 1986, 33, 2640.
(15) Muthukumar, M. *J. Chem. Phys.* 1987, 86, 7230.

we will disregard the possibility of polydispersity of polymeric chains, thus setting $N^* = N$.

We shall now proceed by introducing the Hubbard–Stratonovich transformation for the pair interactions, reducing them to effective one-particle interactions with auxiliary field ϕ (see ref 4 for details)

$$\exp[-1/2\beta \sum_{i,j} \xi^2 u(\mathbf{r}_i, \mathbf{r}_j)] = \Delta(\beta) \int_N \mathcal{D}\phi(\mathbf{r}) \exp[-1/2\beta \sum_{i,j} \phi(\mathbf{r}_i) u^{-1}(\mathbf{r}_i, \mathbf{r}_j) \phi(\mathbf{r}_j) + i\beta \sum_i \xi \phi(\mathbf{r}_i)] \quad (\text{II.3})$$

where $\Delta(\beta) = (2\pi)^{N/2} (\det \beta u^{-1}(\mathbf{r}, \mathbf{r}'))^{1/2}$ and $\mathcal{D}\phi(\mathbf{r}) = \lim_{n \rightarrow \infty} d\phi(\mathbf{r}_1) d\phi(\mathbf{r}_2) \dots d\phi(\mathbf{r}_n)$. Though the Hubbard–Stratonovich transformation has been written in a discretized form it is straightforward to get its continuum representation, amounting to a formal replacement $\sum_i \phi(\mathbf{r}_i) \rightarrow \int \phi(\mathbf{r}) d^3\mathbf{r}$. The inverse of the pair interaction potential has been defined in a standard manner as $\int u^{-1}(\mathbf{r}, \mathbf{r}') u(\mathbf{r}', \mathbf{r}'') d^3\mathbf{r}' = \delta(\mathbf{r} - \mathbf{r}'')$. Clearly for the Coulomb potential $u^{-1}(\mathbf{r}, \mathbf{r}') = -\epsilon\epsilon_0\delta(\mathbf{r} - \mathbf{r}')/\nabla^2$.

Since the Hubbard–Stratonovich transformation permits us to write the pair interactions in an effective one-particle form we can perform the summations in eq II.2 explicitly remaining with the following compact form of the partition function

$$\Xi = \Delta(\beta) e^{U_p(N)} \prod_\alpha \int \int \langle G_\phi(\mathbf{R}^\alpha, \mathbf{R}'^\alpha; N^\alpha) d^3\mathbf{R}^\alpha d^3\mathbf{R}'^\alpha \rangle_\phi \quad (\text{II.4})$$

where $U_p(N) = 1/2\beta\tau^2 \sum_\alpha N^\alpha u(\mathbf{R}^\alpha, \mathbf{R}^\alpha)$ is the electrostatic self-energy of the polyelectrolyte chain. $G_\phi(\mathbf{R}^\alpha, \mathbf{R}'^\alpha; N^\alpha)$ is obtained in the following form

$$G_\phi(\mathbf{R}^\alpha, \mathbf{R}'^\alpha; N^\alpha) = \int_{\mathbf{R}^\alpha(0)=\mathbf{R}'^\alpha}^{\mathbf{R}^\alpha(N)=\mathbf{R}^\alpha} \mathcal{D}\mathbf{R}^\alpha(n) \exp\left(-\frac{3}{2\beta^2} \times \int_0^{N^\alpha} \left(\frac{d\mathbf{R}^\alpha(n)}{dn}\right)^2 dn + i(\beta\tau) \int_0^{N^\alpha} \phi(\mathbf{R}^\alpha(n)) dn\right) \quad (\text{II.5})$$

and is clearly nothing but the Green's function of the α th polymeric chain in an external field.¹⁶ A representation of the polyelectrolyte partition function similar to eq II.4 has already been derived by Kholodenko and Beyerlein¹⁴ for a single polymeric chain. There is, however, an important difference in the meaning of the ϕ averages in our formulation and theirs that we elucidate in what follows. First of all, since the auxiliary field $\phi(\mathbf{r})$ acts as an effective external field we can make a transformation $\phi + i\phi_e \rightarrow \phi$ after the application of Hubbard–Stratonovich transform to eq II.2. Now, since $u(\mathbf{r}, \mathbf{r}')$ is a solution of the Poisson equation we can use its inverse in a continuous version of eq II.3 to obtain the following form for the ϕ average in eq II.4

$$\langle \dots \rangle_\phi = \int \mathcal{D}\phi(\mathbf{r}) \prod_{s=a,c} \sum_{N_s=0}^{\infty} \frac{\xi^{N_s} \left(\int e^{i\beta e_s \phi(\mathbf{r})} d^3\mathbf{r} \right)^{N_s}}{N_s!} (\dots) \times \exp\left[-1/2\beta\epsilon\epsilon_0 \int (\nabla\phi)^2 d^3\mathbf{r} - i\beta \int \phi \sigma d^2\mathbf{r}\right] = \int \mathcal{D}\phi(\mathbf{r}) (\dots) e^{-\beta H_\phi} \quad (\text{II.6})$$

where the action in the last line of the above equation is nothing but the Poisson–Boltzmann form of the free energy evaluated at imaginary values of local potentials or, what amounts to the same thing, at imaginary values of the charges, which we already encountered in the case of a confined Coulomb fluid.⁴

$$H_\phi = F_{PB}(ie) = \frac{1}{2\epsilon\epsilon_0} \int (\nabla\phi)^2 d^3\mathbf{r} - 2kT\xi \int \cos(\beta e_0 \phi) d^3\mathbf{r} + i \oint \phi \sigma d^2\mathbf{r} \quad (\text{II.7})$$

The form of the ϕ average used by Kholodenko and Beyerlein¹⁴ is somewhat different from the above (aside from the $i\phi$ term)

(16) Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley and Sons: New York, 1987. Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, U.K., 1986.

since it corresponds to the polymer intersegment potential of the screened Coulomb (Debye–Hückel) type in 3d, viz., $u_{KB}(\mathbf{r}, \mathbf{r}') \sim |\mathbf{r} - \mathbf{r}'|^{-1} \exp(-\kappa|\mathbf{r} - \mathbf{r}'|)$, set as a starting point for further analysis in ref 14. Since for the screened Coulomb type potential one has $u_{KB}^{-1}(\mathbf{r}, \mathbf{r}') \sim \delta(\mathbf{r} - \mathbf{r}')(\nabla^2 + \kappa^2)$, one can conclude that the ϕ average used by Kholodenko and Beyerlein would correspond exactly to our form eq II.7 developed up to the second order in ϕ .

We can now take into account all the above developments and derive the final expression for the partition function eq II.4

$$\Xi = \Delta(\beta) e^{U_p(N)} \prod_\alpha \int \mathcal{D}\phi(\mathbf{r}) e^{-\beta H_\phi} \times \left(\int \int G_\phi(\mathbf{R}^\alpha, \mathbf{R}'^\alpha; N^\alpha) d^3\mathbf{R}^\alpha d^3\mathbf{R}'^\alpha \right) = \Delta(\beta) e^{U_p(N)} \int \mathcal{D}\phi(\mathbf{r}) e^{-\beta S_\phi} \quad (\text{II.8})$$

where the action in the above equation can be put into the form $S_\phi = H_\phi - kT\mathcal{N} \ln \left(\int \int G_\phi(\mathbf{R}, \mathbf{R}'; N) d^3\mathbf{R} d^3\mathbf{R}' \right) = H_\phi - kT\mathcal{N} \ln Q(N) \quad (\text{II.9})$

since all the integrals over $G_\phi(\mathbf{R}^\alpha, \mathbf{R}'^\alpha; N^\alpha)$ are equal. A related representation of the partition function in the case of excluded volume interactions has been derived first by Edwards (see ref 16 for details).

In what follows we shall be mainly interested in the free energy and its properties therefore the above form is a right starting point. Should we want to approximate the Green's function itself or its moments, the $(\mathbf{R}, \mathbf{R}')$ integrations in eq II.9 would be spurious. This concludes our formal developments.

III. Perturbation Expansion and the Self-Consistent-Field Theory

Clearly the partition function eq II.8 cannot be evaluated explicitly since the action in the functional integral is highly non-Gaussian. However, if the local potential $\phi(\mathbf{r})$ is sufficiently small, corresponding to vanishing electrostatic coupling (i.e., charges), we can proceed by constructing a perturbation expansion of the action S_ϕ around a state characterized by the “bare” Green's function $G_0(\mathbf{R}, \mathbf{R}'; N) = G_{\phi=0}(\mathbf{R}, \mathbf{R}'; N)$ that is a solution of

$$\left[\frac{\partial}{\partial N} - \frac{P}{6} \nabla_R^2 \right] G_0(\mathbf{R}, \mathbf{R}'; N) = \delta(N) \delta(\mathbf{R} - \mathbf{R}') \quad (\text{III.1})$$

This was also the path taken by Edwards in his analysis of the excluded volume effect (see ref 16). We shall denote the statistical sum corresponding to the bare Green's function as

$$Q_0(N) = \int \int G_0(\mathbf{R}, \mathbf{R}'; N) d^3\mathbf{R} d^3\mathbf{R}' \quad (\text{III.2})$$

Taking now the first two terms in the perturbation expansion of $G_\phi(\mathbf{R}, \mathbf{R}'; N)$ with respect to $\phi(\mathbf{R})$ we can derive the following identity

$$Q(N) = Q_0(N) \left[1 + i\beta\tau \int d^3\mathbf{R} \rho_0(\mathbf{R}) \phi(\mathbf{R}) - (\beta\tau)^2 \int d^3\mathbf{R} d^3\mathbf{R}' \phi(\mathbf{R}) \Sigma_0(\mathbf{R}, \mathbf{R}') \phi(\mathbf{R}') + O(\phi^3) \right] \quad (\text{III.3})$$

where we introduced the local density of the polymeric segments

$$\rho_0(\mathbf{R}) = \frac{\int \int d^3\mathbf{R}' d^3\mathbf{R}'' \int_0^N dn G_0(\mathbf{R}', \mathbf{R}; N-n) G_0(\mathbf{R}, \mathbf{R}''; n)}{\int \int d^3\mathbf{R} d^3\mathbf{R}' G_0(\mathbf{R}, \mathbf{R}'; N)} \quad (\text{III.4})$$

It is clearly appropriately normalized since $\int d^3\mathbf{R} \rho_0(\mathbf{R}) = N$. Furthermore

$$\Sigma_0(\mathbf{R}, \mathbf{R}') = \left[\int \int d^3\mathbf{R}'' d^3\mathbf{R}''' \int_0^N dn \int_0^n dn' G_0(\mathbf{R}'', \mathbf{R}; N-n) \times G_0(\mathbf{R}, \mathbf{R}'; n-n') G_0(\mathbf{R}', \mathbf{R}'''; n') \right] / \int \int d^3\mathbf{R} d^3\mathbf{R}' G_0(\mathbf{R}, \mathbf{R}'; N) \quad (\text{III.5})$$

To this order in the perturbation expansion we therefore obtain for the action eq II.9 the following approximate form

$$\begin{aligned} S_\phi = -N \ln Q_0(N) + \frac{1}{2} \epsilon \epsilon_0 \int (\nabla \phi)^2 d^3r - \\ \zeta(\beta e_0)^2 \int \phi^2(r) d^3r + i \oint \phi \sigma d^2r - i N \beta \tau \int d^3r \rho_0(r) \phi(r) - \\ N(\beta \tau)^2 \int \int d^3r d^3r' \phi(r) [\Sigma_0(r, r') - \frac{1}{2} \rho_0(r) \rho_0(r')] \phi(r') \end{aligned} \quad (\text{III.6})$$

Since our problem has distinct plane-parallel geometry it is helpful to introduce the Fourier-Bessel transform of all the quantities depending on \mathbf{R} as, e.g., in the case of the Green's function that leads to

$$G_0(\mathbf{R}, \mathbf{R}'; N) = \int \frac{S d^2Q}{(2\pi)^2} G_Q(z, z'; N) e^{-iQ(\rho - \rho')} \quad (\text{III.7})$$

where $\rho = (x, y)$ is the two-dimensional radius vector perpendicular to the transverse coordinate. This representation, together with eq III.1, leads to the following expression for the zero-order Green's function

$$G_Q(z, z'; N) = \frac{1}{a} \sum_j \cos \left((2j+1) \frac{\pi z}{2a} \right) \cos \left((2j+1) \frac{\pi z'}{2a} \right) e^{-E_j(Q)N} \quad (\text{III.8})$$

where the eigenvalues are determined from the vanishing of the Green's function at the hard walls located at $z = \pm a$, thus $E_j(Q) = (l^2/6)[\pi^2/(2a)^2](2j+1)^2 + (l^2/6)Q^2$. The vanishing of the Green's function at the hard boundaries is a consequence of the fact that the polymeric chains cannot penetrate the bounding surfaces. Furthermore, in the subsequent discussion we shall limit ourselves to the thermodynamic limit defined by the following limiting procedure, $N \rightarrow \infty$, $S \rightarrow \infty$ (in this order) with $N/S = \text{constant}$, where S is the area of the bounding surfaces. The order of both limits is important since it prevents trapping of the polymeric chain in the vicinity of a single surface. This signifies that we shall consider only the $j = 0$ term in the expansion of eq III.4. Furthermore, the \mathbf{R} integrations involving the Green's function in the previous formulas are reduced, via the ansatz eq III.7 to z integrations of the $Q = 0$ term.

Since the action in the functional integral eq II.8 is now of a general quadratic form derived explicitly in eq III.6, we can perform all the ϕ integrations and remain with the following form of the surface free energy density

$$\begin{aligned} \mathcal{F} = -\frac{kT}{S} \ln Z \\ = -N \ln Q_0(N) + \frac{1}{2} \frac{\beta(N\tau)^2}{\epsilon \epsilon_0} \times \\ \int_{-a}^{+a} \int_{-a}^{+a} \rho_0(z') g_\kappa(z, z') \rho_0(z) dz dz' - \frac{\beta(N\tau\sigma)}{\epsilon \epsilon_0 \kappa} \times \\ \int_{-a}^{+a} \rho_0(z') \frac{\cosh(\kappa z')}{\sinh(\kappa a)} dz' + \frac{1}{2} \frac{\sigma^2}{\epsilon \epsilon_0 \kappa} \coth(\kappa a) \end{aligned} \quad (\text{III.9})$$

where we have introduced what turns out to be a Green's function of the linearized Debye-Hückel equation with appropriate boundary conditions

$$\begin{aligned} g_\kappa(z, z') &= \frac{\cosh \kappa(z-a) \cosh \kappa(z'+a)}{\kappa \sinh 2\kappa a}; \quad z > z' \\ &= \frac{\cosh \kappa(z+a) \cosh \kappa(z'-a)}{\kappa \sinh 2\kappa a}; \quad z < z' \end{aligned} \quad (\text{III.10})$$

κ is the standard inverse Debye screening length for a uni-univalent electrolyte. In order to get an explicit dependence of \mathcal{F} on the intersurface separation we have to evaluate the integrals in eq III.9 by taking into account the definition of the local polymer segment density eq III.4 in the thermodynamic limit where $G_0(z, z'; N)$ is approximated by the first term in the expansion eq III.8. This leads to the following form of the surface free energy density

$$\begin{aligned} \mathcal{F} = kT \frac{\pi^2}{6} P \left(N \frac{N}{S} \right) \frac{1}{(2a)^2} + \frac{1}{4} \frac{\tau^2}{\epsilon \epsilon_0} \left(N \frac{N}{S} \right)^2 f(\kappa a) - \\ \frac{\tau \sigma}{\epsilon \epsilon_0 \kappa} \left(N \frac{N}{S} \right) \frac{1}{\kappa a} \frac{(\pi/a)^2}{\kappa^2 + (\pi/a)^2} + \frac{1}{2} \frac{\sigma^2}{\epsilon \epsilon_0 \kappa} \coth(\kappa a) \end{aligned} \quad (\text{III.11})$$

where $f(\kappa a)$ is a slowly varying function of its argument assuming values on the interval $[3/2, 1]$ for $a = [\infty, 0]$. The structure of the free energy density eq III.11 is quite transparent since each term corresponds to a different interaction mechanism. The first term is the entropic repulsive contribution due to the exclusion of all configurations that would violate the impenetrability of the bounding surfaces to the polymeric chains. The last term, on the other hand, is the standard Debye-Hückel electrostatic free energy density for a confined uni-univalent salt of inverse Debye length κ . The other two terms represent different couplings between electrostatic and steric interactions for the polymeric chains. Thus the second term is the electrostatic interaction energy of the polymer self-interaction while the third term is the electrostatic polymer-wall interaction. The free energy eq III.11 gives the first, though very approximate, picture of the forces between charged surfaces in the presence of charged polymeric chains and intervening electrolyte.

What is already apparent at this approximation level is that the electrostatic polymer-wall interactions lead to an attractive component (third term in eq III.11) in the expression for total force (derivative of the surface free energy density with respect to the intersurface separation) between charged boundaries. Due to the limitations inherent in the derivation of eq III.11 its validity is restricted to the case of small σ , τ and it would be difficult at this point to assess which term of the free energy dominates at a specified separation.

However, a far better approximation can be obtained if changes in the local polymer density distribution, that are due to the electrostatic interactions between the beads and the surfaces are appropriately taken into account. In order to include the corrections in the density distribution of ions as well as in the local segment density of polyelectrolyte chains, we have to employ a variant of the self-consistent-field method amply used in the treatment of excluded volume interactions in polymers.¹⁶

There are several variants of the SCF method¹⁸ and we shall consistently use only one of them that will provide a good approximation for the free energy of the system that we want to analyze. This leads to the consideration of stationary points of the action eq II.9 (see ref 17 for details)

$$\delta S_\phi / \delta \phi(\mathbf{r}) = 0 \quad (\text{III.12})$$

We shall not write down this functional derivative explicitly at this stage. In order to evaluate it one needs the following identity that can be derived from a differential equation corresponding to eq II.5, viz.

$$\frac{\delta}{\delta \phi(\mathbf{r})} \ln \left(\int \int G_\phi(\mathbf{R}, \mathbf{R}'; N) d^3R d^3R' \right) = i \beta \tau \rho_\phi(\mathbf{r}) \quad (\text{III.13})$$

where $\rho_\phi(\mathbf{r})$ is the polymer segment density evaluated at point \mathbf{r} defined in analogy with eq III.4.

The functional derivative eq III.12 now decouples into two terms: a volume contribution that amounts to a modified Poisson-Boltzmann equation and a surface contribution in a form of a boundary condition, expressing the electroneutrality of the system. It is straightforward to see that the boundary condition demands that the stationary point ϕ be pure imaginary. Making thus the substitution $\phi \rightarrow i\phi$ one remains with the following stationary point equations

$$\begin{aligned} \epsilon \epsilon_0 \nabla^2 \phi(\mathbf{r}) &= 2 \zeta e_0 \sinh(\beta e_0 \phi(\mathbf{r})) - \tau N \rho_\phi(\mathbf{r}) \\ -\epsilon \epsilon_0 \frac{\partial \phi}{\partial n} &= \sigma \end{aligned} \quad (\text{III.14})$$

(17) Rivers, R. J. *Path Integral Methods in Quantum Field Theory*; Cambridge University Press: Cambridge, U.K., 1987, Chapter 5.

(18) Freed, K. F. *J. Chem. Phys.* 1971, 55, 3910.

where \mathbf{n} is the local normal of the boundary surfaces. Furthermore, the polymer segment density is obtained from eq III.4 with the Green's function satisfying

$$\left[\frac{\partial}{\partial N} - \frac{l^2}{6} \nabla^2 + (\beta\tau)\phi(\mathbf{R}) \right] G_\phi(\mathbf{R}, \mathbf{R}'; N) = \delta(\mathbf{R}-\mathbf{R}') \delta(N) \quad (\text{III.15})$$

Relations eqs III.14 to III.15 represent the self-consistent-field equations¹⁸ for a polyelectrolyte immersed in an electrolyte solution. They are a natural generalization of a set of SCF equations derived by Kholodenko and Beyerlein¹⁴ in the context of a single polyelectrolyte chain in the bulk. Setting aside the presence of additional electrolyte the SCF equations derived above relate also to the polyelectrolyte Poisson–Boltzmann approximation (PPB), set forth by Akesson, Woodward, and Jönsson.¹³ The major difference with respect to this work is in the treatment of the statistical average over the polyelectrolyte configurations, which is done explicitly in our case, eqs III.14 and III.15, in contrast to a seminumerical procedure exploited in ref 12. In order to avoid confusion we shall refer to our approximation scheme as the self-consistent-field Poisson–Boltzmann approximation for polyelectrolytes (SCF-PBP).

IV. The SCF Equations in the Form of a Modified Poisson–Boltzmann Equation

The main conclusions of the rather formal developments of the previous sections can be restated also on the basis of purely physical arguments that are standardly used in different derivations of the Poisson–Boltzmann equations.¹ Since the only mobile charged species in our model system are anions, cations, and charged polymeric chains, the local Poisson equation can be straightforwardly written as

$$\epsilon\epsilon_0\nabla^2\phi(\mathbf{r}) = -\rho(\mathbf{r}) = -\sum_i \rho_i(\mathbf{r}) \quad (\text{IV.1})$$

where $\phi(\mathbf{r})$ is the local mean electrostatic potential at point \mathbf{r} , while $\rho(\mathbf{r})$ is the local total charge density, composed of the local charge density of cations, anions, and polymeric chains (represented by index $i = \text{cations, anions, polymeric chains}$). With the Boltzmann ansatz one has for the salt ions $\rho_i(\mathbf{r}) = \pm\zeta e_0 e^{\pm\beta e_0\phi(\mathbf{r})}$, if we write the bulk charge density as ζe_0 . Introducing this form of the local charge density into the Poisson equation, eq IV.1, we remain with the standard form of the Poisson–Boltzmann equation. For polymers, however, the local charge density can be written as $\rho_i(\mathbf{r}) = \tau N \langle e^{-\beta\tau\phi(\mathbf{r})} \rangle$, if the charge per bead is τ and if there are N chains between the charged surfaces. The averaging $\langle \dots \rangle$ has to be done over all the internal degrees of freedom (corresponding to the coordinates of the polymer beads) of a single polymeric chain. Inserting now all the local charge densities (cationic, anionic, and polymeric) into the Poisson equation, we are led exactly to the first equation of eqs III.14, i.e.

$$\epsilon\epsilon_0\nabla^2\phi(\mathbf{r}) = \zeta e_0 e^{\beta e_0\phi(\mathbf{r})} - \zeta e_0 e^{-\beta e_0\phi(\mathbf{r})} - \tau N \rho_\phi(\mathbf{r}) \quad (\text{IV.2})$$

if we set

$$\rho_\phi(\mathbf{r}) = \langle e^{-\beta\tau\phi(\mathbf{r})} \rangle \quad (\text{IV.3})$$

The question now remains of how to represent $\rho_\phi(\mathbf{r})$ explicitly as a function of the local mean potential $\phi(\mathbf{r})$. It is a well-known result of the polymer theory²⁰ that the polymer density can be expressed with the help of the polymer Green's function $G(\mathbf{R}, \mathbf{R}'; N)$, see eq III.4, which gives the probability that a chain starting at \mathbf{R} has the last bead N at \mathbf{R}' . Since the mean potential acts as an external field on each bead of the polymer, the Green's function has to satisfy eq III.15. Therefore, the main difference between an ion and a charged polymeric chain is that the charge density of the latter cannot be written explicitly as a function of the mean (electrostatic) potential, but can be obtained only implicitly through the Green's function of the polymer in an external (mean) field.

The arguments given above are purely heuristic but are well substantiated by the detailed formal developments of the previous

two sections. The conclusion would therefore be that the modified Poisson–Boltzmann equation eq III.14 can also be derived by plausible physical arguments, leading to the same basic equations as a more thorough formal analysis.

As already stated, we shall limit ourselves to the consideration of the thermodynamic limit that is defined by letting the number of beads on each chain, N , and the total surface area of the boundary surfaces, S , go to infinity in such a way that no chain can remain trapped in the vicinity of only one surface. This can be accomplished by letting first $N \rightarrow \infty$, followed by $S \rightarrow \infty$, with $N/S = \text{constant}$. The ground-state dominance ansatz $N \rightarrow \infty$ thus guarantees that no antisymmetric solutions for the polymer segment distribution have to be taken into account (see ref 36).

In the ground-state dominance ansatz¹⁹ the polymer Green's function assumes the form

$$G_\phi(\mathbf{R}, \mathbf{R}'; N) = G_\phi(z, z'; N) \approx \psi(z) \psi(z') e^{-E_N N} \quad (\text{IV.4})$$

where $|E_N|$ is the lowest lying energy eigenvalue. Configurations with negative E_N correspond to a case where the polyelectrolyte chain has at least one surface-bound state. In this limit clearly we can eliminate the dependence of the Green's function on the transverse coordinates, thus obtaining

$$\rho_\phi(z) = (N/S)\psi^2(z) \quad \text{with} \quad \int_{-a}^{+a} \psi^2(z) dz = 1 \quad (\text{IV.5})$$

With these simplifications eqs III.14 and III.15 are reduced to the following set of two coupled nonlinear equations for the local average potential $\phi(z)$ and the polymer "density field" $\psi(z)$

$$\begin{aligned} \frac{l^2}{6} \frac{d^2\psi}{dz^2} + (E_N - \beta\tau\phi)\psi &= 0 \\ \epsilon\epsilon_0 \frac{d^2\phi}{dz^2} - 2\zeta e_0 \sinh(\beta e_0\phi) + \tau N \frac{N}{S} \psi^2 &= 0 \end{aligned} \quad (\text{IV.6})$$

The impenetrability of the surfaces to polymer beads is now reduced to the boundary condition $\psi(z=\pm a) = 0$, while the appropriate boundary condition for the electrostatic potential can be deduced from eq III.14. Clearly in the absence of polymeric chains the above two equations reduce to the standard Poisson–Boltzmann equation for a uni-univalent electrolyte. With the polymeric chains present, we can view eqs IV.6 as a modified Poisson–Boltzmann equation, where the dependence of the polymeric charge density on the mean electrostatic potential has to be determined self-consistently, via the dependence of the polymer "density field" $\psi(r)$ on the electrostatic potential.

We are now ready to evaluate the surface free energy density defined as eq III.9

$$\mathcal{F} = -\frac{kT}{S} \ln \Xi = kT N \frac{N}{S} E_N + \frac{F_{PB}}{S} \quad (\text{IV.7})$$

where F_{PB} is the standard Poisson–Boltzmann free energy of a nonhomogeneous electrolyte. Taking into account eqs IV.6 with the appropriate boundary conditions we are led to the following explicit form of the surface free energy density

$$\begin{aligned} \mathcal{F} = \int_{-a}^{+a} f(\psi(z), \phi(z)) dz &= kT N \frac{N}{S} \left[\frac{l^2}{6} \int_{-a}^{+a} \left(\frac{d\psi}{dz} \right)^2 dz + \right. \\ &\quad \left. \beta\tau \int_{-a}^{+a} \phi\psi^2 dz \right] - \frac{1}{2} \epsilon\epsilon_0 \int_{-a}^{+a} \left(\frac{d\phi}{dz} \right)^2 dz - \\ &\quad 2kT \zeta \int_{-a}^{+a} \cosh(\beta e_0\phi) dz - 2\phi(z=\pm a)\sigma \end{aligned} \quad (\text{IV.8})$$

where we introduced the local nonequilibrium free energy density f as a functional of $\psi(z)$ and $\phi(z)$. The form of the surface free energy density was written down in order to derive the variational principle for which eqs IV.6 are just the Euler–Lagrange equations. It clearly follows from the above developments that the quantity that has to be minimized is simply

(19) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

$$\mathcal{J}' = \mathcal{J} - \mu \int_{-a}^{+a} \psi^2 dz = \int_{-a}^{+a} dz (\mathcal{J}(\phi(z), \psi(z)) - \mu\psi^2) \quad (\text{IV.9})$$

where μ is a Lagrange multiplier that keeps the normalization of the polymer segment density fixed ($\mu = kT\mathcal{N}(N/S)E_N$). After deriving the free energy density that leads to correct SCF equations we can now apply the argument of de Gennes³⁰ and show that the pressure acting between the two bounding surfaces located at $z = \pm a$ can be reduced to

$$P = -(\mathcal{J}(\phi(z), \psi(z)) - kT\mathcal{N}(N/S)E_N\psi^2(z))_{z=0} \quad (\text{IV.10})$$

Inserting now the definition of $\mathcal{J}(\phi, \psi)$ eq IV.8 we obtain for the pressure

$$P = 2kT\zeta \cosh(\beta e_0\phi(z=0)) - kT\mathcal{N}\frac{N}{S}\frac{P}{6}\left(\frac{d^2\psi}{dz^2}\right)_{z=0} \quad (\text{IV.11})$$

There are different ways to express the identity eq IV.11, most notably by the application of the first integral of eqs IV.6 that can be derived straightforwardly in the form

$$\begin{aligned} \frac{1}{2}\epsilon\epsilon_0\left(\frac{d\phi}{dz}\right)^2 - 2kT\zeta \cosh(\beta e_0\phi) - \\ kT\left(\mathcal{N}\frac{N}{S}\right)\frac{P}{3}\left[\left(\frac{d\psi}{dz}\right)^2 - \frac{1}{4}\frac{d^2}{dz^2}\psi^2\right] = \text{const} \end{aligned} \quad (\text{IV.12})$$

and leads to the following equation for the pressure in the form of a "contact theorem"

$$P = 2kT\zeta \cosh(\beta e_0\phi(z=a)) - \frac{1}{2}\frac{\sigma^2}{\epsilon\epsilon_0} + kT\mathcal{N}\frac{N}{S}\frac{P}{6}\left(\frac{d\psi}{dz}\right)_{z=a}^2 \quad (\text{IV.13})$$

It represents an appropriate generalization of the "contact theorem" amply used in the Poisson-Boltzmann theory of interacting double layers³¹ to the case with added polyelectrolyte chains. The first two terms of the above equation are clearly identical with the standard Poisson-Boltzmann contact theorem, while the last term embodies the equilibrium of forces due to the presence of polymeric chains.

This concludes the formal developments as connected with the application of the SCF ansatz to the present problem.

V. Numerical Solution of the SCF Equations

In order to solve eqs IV.6 it is advantageous to introduce dimensionless quantities and then to assess on which parameters the final solution of the SCF equations depends. Without any loss in generality of the arguments we shall assume in what follows that $\tau = e_0$. Furthermore, we shall assume that the fixed surface charges are of negative sign. In this case it is straightforward to deduce that the solution of eqs IV.6 is governed by the value of dimensionless separation $w_0 = \kappa a$, where κ is the inverse Debye screening length for a one-one electrolyte, viz., $\kappa^2 = 2\zeta\beta e_0^2/\epsilon\epsilon_0$, the value of the dimensionless surface charge $\Gamma = \beta e_0\sigma/\epsilon\epsilon_0\kappa$, the value of the electrostatic coupling between the polyelectrolyte chain density and the mean total charge density $\lambda = (\beta e_0^2/\epsilon\epsilon_0\kappa)\mathcal{N}(N/S)$ and the product κl . The solution of the basic set of SCF equations is quite complicated in the space defined by these parameters and we can only provide some more interesting sections of this space defined by assuming constant values for most of these parameters. In dimensionless form the SCF equations eqs IV.6 can be written as

$$\begin{aligned} \frac{d^2u}{dw^2} - \sinh u + \lambda\psi^2 &= 0 \\ \frac{d^2\psi}{dw^2} + \frac{6}{(\kappa l)^2}(E_N - u)\psi &= 0 \\ \frac{du}{dw}(w = \pm w_0) &= \mp\Gamma \end{aligned} \quad (\text{V.1})$$

where $w = \kappa z$ and $u = \beta e_0\phi$.

In what follows we shall be mostly concerned with the eigen-energy E_N , the dimensionless pressure $P^* = ((\beta e_0)^2/\epsilon\epsilon_0\kappa^2)P$, and

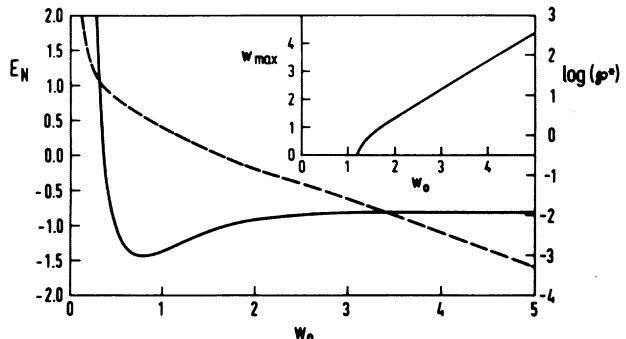


Figure 2. Energy eigenvalue, E_N (bold curve), obtained from the solution of eqs V.1 with logarithm of the dimensionless pressure, $\log P^*$ (dashed curve), obtained from eq IV.11, as functions of the dimensionless intersurface separation $w_0 = \kappa a$. The values of the dimensionless coupling constants are $\Gamma = 5.4$, $\lambda = 1.0$, $\kappa l = 1.0$. At these values of the parameters the energy eigenvalue clearly displays the transition of the polymers from a bulk state with positive E_N to a surface-bound configuration with negative E_N . At large w_0 the pressure displays an exponential dependence on the intersurface spacing just as in the case of no added polyelectrolytes. The slight kink (more clearly seen in Figure 6a) in the $\log P^*$ curve observed at $w_0 \approx 2.0$ is already due to the bridging attraction caused by the soft electrostatic adsorption of the polyelectrolyte chains to the charged surfaces. The inset represents the position of the maximum in the density distribution of the polymers as a function of w_0 . The displacement of the maximum from the middle of the intersurface region toward the boundaries measures the strength of the bridging.

different charge density profiles that we shall define later on. Though the two expressions derived for pressure eqs IV.11 and IV.13 are completely equivalent, their numerical accuracy is different, especially in the regime of large w_0 where eq IV.11 does yield far better accuracy than the latter one.

In order to get a definite reference frame for the values of the parameters specified above, we shall use a value $\Gamma \approx 5.4$ for specifying the magnitude of the dimensionless surface charge that corresponds to the surface charge density of one electron charge per 2 nm^2 and $\kappa^{-1} = 1.2 \text{ nm}$, obtained from a recent experiment.³⁴ Also by setting arbitrarily $\lambda = 1.0$ and $\kappa l = 1.0$ we get the energy eigenvalue E_N and the dimensionless pressure P^* as a function of dimensionless separation $w_0 = \kappa a$ in the form presented in Figure 2. It is evident that the profile of the energy eigenvalue is not monotonic and has a pronounced minimum at $w_0 \approx 0.7$, saturating for larger values of the dimensionless separation. For most of the intersurface separations E_N is negative amounting to the statement that the polymers are in a surface-bound state. The logarithm of dimensionless pressure shows exponential dependence at large intersurface separations with an effective value of the surface charge. There is a very slight kink (it is much more clearly discernible in Figure 6a) in the $\log P^*$ curve for separations $w_0 \approx 2.0$ that stems from the attraction between surfaces promoted by the bridging of the polymeric chains from one surface to the other one. This statement is derived from observation of the polymer density distribution between the two impenetrable, charged walls, Figure 3, defined as $\rho(w) \sim \psi^2(w)$. It shows how the polymers undergo a transition from configurations where the bulk of the polymeric chains is concentrated in the middle of the intersurface region to the one where most of the polymeric chains are confined to regions close to the bounding surfaces on increase of the dimensionless separation. In the latter situation those parts of the polymeric chains that are not "trapped" in the vicinity of the charged boundaries act as bridges, spanning the intersurface region and pulling them toward each other. It will become clear later on (section VI) that the bridging attraction is basically elastic in origin. The bridging promoted by electrostatic interactions in our model system is therefore of the same type as the one described by Åkesson et al. for a situation where polymers are the only charged species in the system.

The transition of the polymer density distribution from a unimodal to a bimodal (bridging) form is seen even more clearly if we plot the position of the density maximum as a function of intersurface separation (see inset Figure 2). The transition occurs

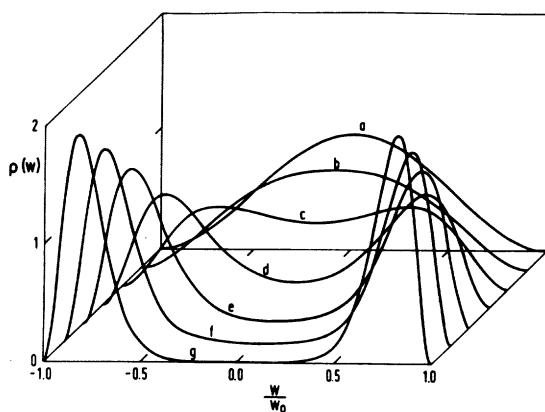


Figure 3. Polymer density profile $\rho_p(w) \sim \psi^2(w)$ as a function of reduced transverse coordinate w/w_0 for different values of w_0 . The values of the dimensionless coupling constants are the same as in Figure 2. Curve a corresponds to $w_0 = 0.5$ and curve g to $w_0 = 3.5$, the rest follow in steps of $\Delta w_0 = 0.5$. One can clearly distinguish the progressive strengthening of the bridging effect as the separation gets larger since more and more of the polymer segments are crowded in the vicinity of the boundary surfaces. The transition from the monomodal to the bimodal form of the density distribution is clearly seen on increase of the intersurface separation.

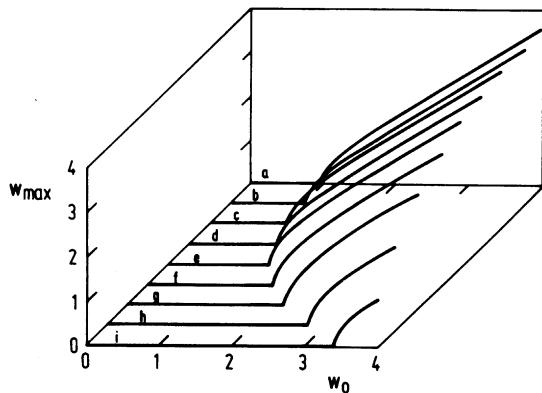


Figure 4. Changes in the position of the maximum of the density distribution curve, w_{\max} , as a function of the intersurface separation w_0 for different values of Γ . λ and κl are kept constant at 1.0. The values of Γ for different curves are (a) 55.0, (b) 22.0, (c) 11.0, (d) 5.4, (e) 2.7, (f) 1.3, (g) 0.6, (h) 0.3, (i) = 0.15. The progressive shift in the monomodal-bimodal transition to smaller values of w_0 observed on increase of Γ testifies to the electrostatic nature of this transition.

at a point determined by the value of Γ , λ , and κl with a clear tendency that for larger values of the electrostatic coupling the transition moves towards smaller value of intersurface spacings (Figure 4). The changes in the character of the polymer density distribution have pronounced effects on the profile of the total charge density in the system, Figure 5, promoting the accumulation of positive charge close to the surface if the polymers have a bimodal distribution, and conversely promoting negative charge accumulation if the distribution of the polymeric chains is monomodal. The monomodal-bimodal transition of the polymer segment density is closely related to the bound-free transition of the polymeric chain first analyzed by Wiegel¹¹ in the case of a single bounding surface.

Without the presence of charged polymers, the changes in Γ would basically only displace $\log P^*$ curve upwards or downwards. With the polymers added and λ kept at a constant value $\lambda = 1.0$, the changes are not only quantitative but also qualitative, Figure 6a. One observes that the slight kink at $w_0 \approx 2.0-3.0$ becomes more and more pronounced as dimensionless surface charge is changed from $\Gamma = 5.0$ to $\Gamma = 3.0$. This we can interpret as due to the shift in the equilibrium of two force mechanisms. The first one is the electrostatic repulsion between the two charged surfaces and the second one is an attraction due to the bridging of the polymeric chains between the surfaces. As Γ is diminished the

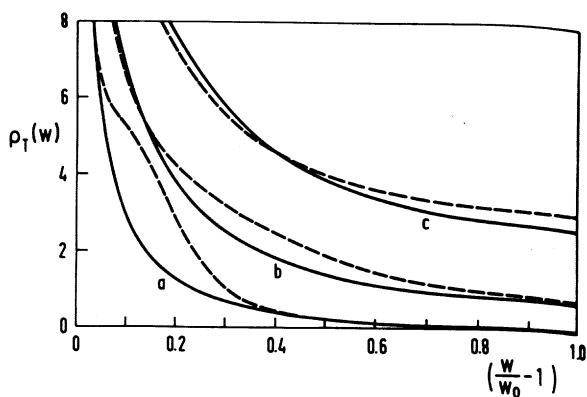


Figure 5. Dimensionless total space charge density $\rho_T = -\sinh u + \lambda \psi$ as a function of reduced transverse coordinate $((w/w_0) - 1)$ for different values of w_0 . Only half of the intersurface space is shown. Curve c corresponds to $w_0 = 1.0$, curve b to $w_0 = 2.0$, and curve a to $w_0 = 5.0$. The values of the dimensionless coupling constants are the same as in Figure 2. The buildup of positive charge density close to the wall is seen if the polymer density is bimodal in form. Otherwise the excess of positive (mostly polymeric) charges is observed to move toward the middle of the intersurface region.

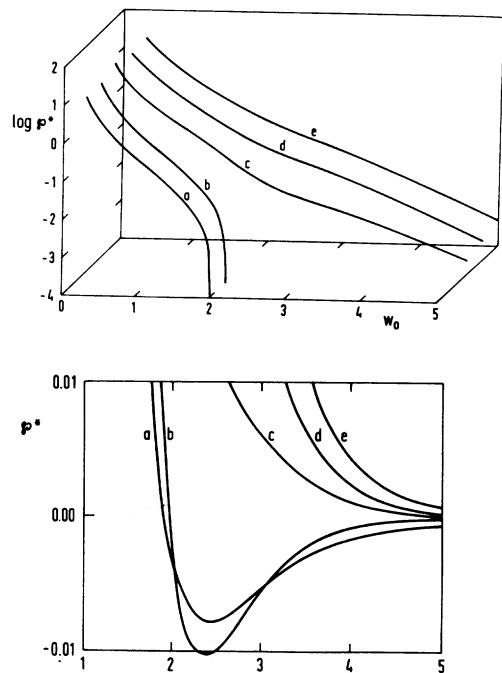


Figure 6. (a, top) Logarithm of the pressure, $\log P^*$, from eq IV.11 as a function of w_0 for different values of Γ . λ and κl are fixed at the same values as in Figure 2. Curve e corresponds to $\Gamma = 5.0$ and the rest follow in steps of 1.0 so that curve a corresponds to $\Gamma = 1.0$. As Γ is diminished the kink observed in Figure 2 at $w_0 \approx 2.0$ slowly develops into the beginning of an attractive region that is already fully developed for $\Gamma = 2.0$ and extends from $w_0 \approx 2.0$ onwards. (b, bottom) Same as Figure 6a except that P^* is plotted instead of the log. The attractive region, corresponding to negative pressures, is now more clearly seen. Curve a corresponds to smallest Γ . One should notice that the depth of the attractive minimum is not a monotonic function of Γ . At large w_0 , even if it is attractive, the pressure still decays approximately exponentially though with a different decay length.

electrostatic repulsion is reduced and the bridging effects tend to become dominant as is clearly seen from the fact that reducing Γ even further ($\Gamma < 3.0$) eventually leads to net attractive interactions at sufficiently large intersurface spacings. This effect can be observed even more directly if instead of $\log P^*$ we switch our attention to P^* itself (Figure 6b). The pressure switch not only signs on going from large to small Γ , but also develops a minimum at intermediate values of the intersurface spacings. For, even if the bridging effect is dominating at large intersurface spacings, the entropic repulsion, stemming from the exclusion of

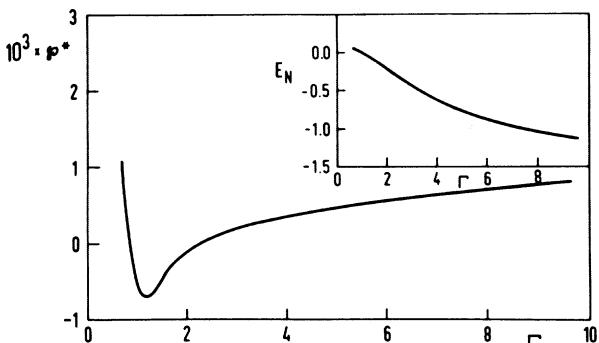


Figure 7. Variation of pressure ($10^3 P^*$) and energy eigenvalue E_N (inset) as functions of Γ for $w_0 = 5.0$. The other parameters are the same as in Figure 2. The pressure is clearly a nonmonotonic function of Γ . It develops a minimum for small values of Γ (see text) and then saturates. This saturation value in the limit of $w_0 \rightarrow \infty$ is the same as in the pure PB case since for very large Γ the presence of charged polymers is irrelevant. The eigenenergy conversely displays a monotonic dependence on Γ starting from positive and passing to negative values at a finite value of Γ .

polymeric configurations at the impenetrable surfaces, does lead to a dominant repulsion at small intersurface spacings that is decoupled from all the electrostatic effects that prevail at larger values of w_0 . These statements can be given additional support if we observe the continuous changes in the net pressure as Γ is varied while the separation is kept constant, Figure 7. At small values of Γ ($\lesssim 0.4$) the pressure is repulsive due to the fact that mobile ions alone have to effect an efficient screening of the polymer charges. At larger values of Γ the effects of bridging in turn become dominant leading to a net attraction between the charged surfaces. This trend, however, is reversed as soon as the charges on the surfaces become large enough for the direct electrostatic repulsion between the surfaces to become dominant. On increasing Γ even further, a saturation of the repulsive pressure is reached at a value close to the one obtained without the added polymers. This nonmonotonic variation of the pressure at a constant value of the intersurface separation can be contrasted to the concurrent variation of E_N . Apparently the changes in surface charge merely promote the unbound to surface-bound transition at a certain critical value of Γ (≈ 1.5). After that the eigenenergy remains negative but eventually saturates for large values of Γ . While the net pressure is therefore a result of opposing tendencies, the eigenvalue merely reflects the tendency of electrostatic attraction to softly bind the polymers to the surfaces.

The section of the parameter space considered next is defined by keeping Γ fixed while varying λ , Figure 8a. In this way the electrostatic coupling between the polymeric and other mobile charges is regulated. For small values of λ , $\log P^*$ approaches the standard Poisson-Boltzmann pressure profile with basically exponential dependence on the intersurface separation. In this regime the pressure is repulsive for all values of intersurface spacings. For larger values of λ ($1.0 < \lambda < 2.0$) a kink is again observed in the $\log P^*$ curve that eventually develops into a region of w_0 values, characterized by net attractive forces. Outside this region the forces turn again repulsive but for different reasons. For small separations the steric exclusion of polymer configurations generates an entropic repulsion between the surfaces. For large separations, however, the direct screened electrostatic repulsion between charges on the opposite surfaces outweighs the bridging attraction stemming from the soft absorption of the same polymeric chain to both surfaces. Increasing λ even further finally leads to a total domination of the bridging attraction for any regime of intersurface separations except in the limit $w_0 \rightarrow 0$ where entropically driven steric repulsion becomes once again the dominant source of the intersurface forces. The most interesting feature of the force curve revealed by the above examples is a restricted region of the parameter space where (on increasing w_0) the pressure goes through the sequence repulsive-attractive-repulsive (Figure 8b). This leads to a conclusion that a secondary minimum in the force curve exists for this system even if the van

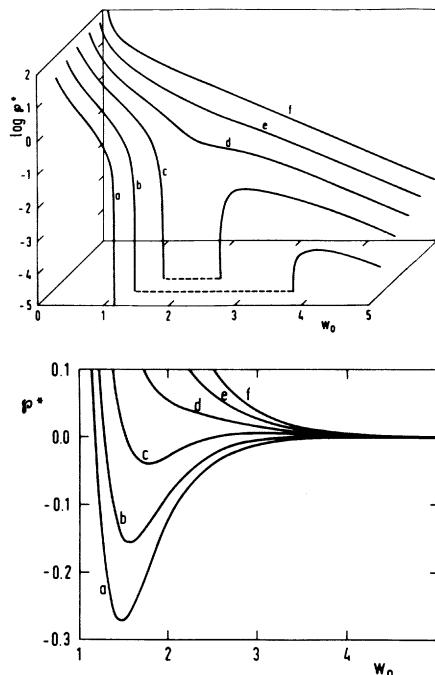


Figure 8. (a, top) Logarithm of the pressure, $\log P^*$, from eq IV.11 as a function of w_0 for different values of λ . Γ and kT are fixed at the same values as in Figure 2. Curve f corresponds to $\lambda = 0$ and the rest follow in steps of 1.0 so that curve a corresponds to $\lambda = 5.0$. The $\log P^*$ curve for $\lambda = 0$ shows the same exponential behavior as in the standard PB theory. As the electrostatic coupling of polymeric chains increases, a slight kink in the force curve slowly develops into an attractive region. There is, however, a window in λ values where the pressure after becoming attractive reverts again to repulsive for large values of w_0 . It shows the same exponential dependence in this regime as in the case $\lambda = 0$, but the preexponential factor is diminished. For $\lambda \geq 5.0$ the pressure remains attractive for all, except the very small values of the intersurface spacing. (b, bottom) Same as Figure 8a except that P^* is plotted instead of the log. The attractive region, corresponding to negative pressures, is now more clearly seen. Curve a corresponds to largest λ . The force curve c corresponding to $\lambda = 3.0$ now displays in the clearest fashion the sequence repulsion-attractive-repulsion as w_0 goes from small to large values.

der Waals-Lifshitz forces are not incorporated into the balance of forces. The behavior of the pressure as a function of λ at a particular value of w_0 , Figure 9, supports the notion that changes in the electrostatic coupling merely affect the magnitude of the electrostatic bridging that lies at the origin of the polymer-promoted attraction between two equally charged surfaces. The variation of the eigenenergy, however, is quite different in this case, inset to Figure 9. Apparently large λ does not only signify large electrostatic interactions between the polymer and the surfaces, promoting bridging, but also accumulation of the polymer material between the two surfaces, which should finally lead to desorption. The increase in λ with Γ kept fixed would therefore lead to a situation where for almost any w_0 the entropic exclusion of the polymers at the impenetrable boundaries would be the overwhelmingly largest contribution to the forces between the surfaces. This regime is, however, not reached by the values of λ included in Figure 9.

Finally the variation in kT , Figure 10, merely changes the range of electrostatic interactions and at complete screening ($kT \gg 1$), all the electrostatic effects, including the attraction promoted by electrostatic bridging, are simply wiped out. The system behaves as a solution of uncharged, sterically confined polymers. The other extreme of very small ionic screening of the electrostatic interactions would displace the whole system toward the case where the electrostatic interactions would effectively exist only between fixed surface charges and charged polymers. This system was analyzed before²⁰ and will be addressed again in the next section.

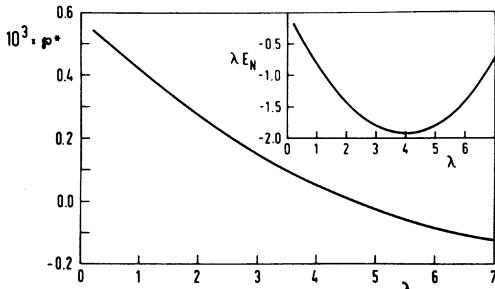


Figure 9. Variation of pressure ($10^3 P^*$) and scaled energy eigenvalue λE_N (inset) as functions of λ for $w_0 = 5.0$. The other parameters are the same as in Figure 2. Comparison with Figure 7 shows that the roles of P^* and E_N are now reversed, since pressure remains a monotonic function of λ , going from repulsion to attraction at $w_0 = 5.0$. The energy eigenvalue reaches a minimum with a negative value and then starts growing again.

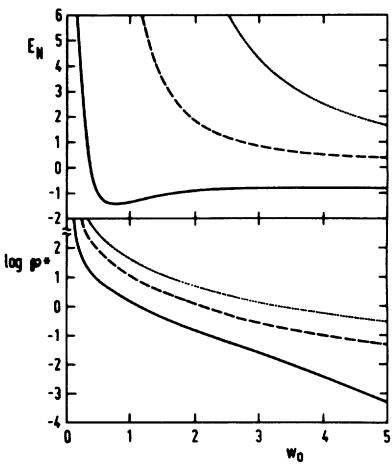


Figure 10. Energy eigenvalue, E_N (upper graph), and logarithm of the pressure, $\log P^*$ (lower graph), as functions of dimensionless separation for different values of κl . All the other parameters are the same as in Figure 2. The upper (dotted) curves on both graphs correspond $\kappa l = 10.0$, the medium (dashed) ones to $\kappa l = 5.0$, and the lower (full) ones to $\kappa l = 1.0$. The value of the product κl controls the overall range of the electrostatic interactions, and for $\kappa l \gg 1.0$ they are effectively screened so that the force curve as well as the eigenenergy approach the confined neutral polymers values.

VI. Approximate Analytical Solutions for Certain Limiting Cases

Numerical solutions of the previous section gave some revealing insights into the complexity of the problem. Though one could stop at that, we believe it is equally important to have some asymptotic formulas that would embody these insights in analytical terms. There are just two cases for which analytical computations are feasible and we shall dwell on them in some detail.

The first limiting case will be defined by demanding that $\lambda \ll 1$ while Γ should be small enough so that a linearization of eq V.1 is feasible. In this case we can make the approximation $\sinh u \approx u$ in eq V.1 and assume that the term $\lambda\psi^2$ gives a negligible contribution to the total charge density. This is an approximation originally proposed by Wiegeland¹¹ thus we referred to it as the Wiegeland approximation²⁶ and used it in the context of a polymer in contact with a single charged wall. Also, the same approximation has been exploited by van Opheusden³⁶ to analyze the same system but in the case of two confining charged surfaces. Though the equations derived below in the frame of the Wiegeland approximation are directly related to those derived by van Opheusden, there are several important differences in their subsequent treatment. First of all we use the Wiegeland approximation to generate certain approximative but analytical solutions. We do not solve the basic equations thus obtained numerically since this was already done for the complete set of the SCF equations that have a much larger range of validity. Also we do not analyze the finite size effects, as was done by van Opheusden, since our

primary aim is to obtain the interaction pressure and the polymer density distribution in the thermodynamic limit.

The basic equation that we have to solve in this particular case (provided that we use the Wiegeland approximation in the simplification of eqs V.1) reduces to

$$\frac{d^2\psi}{dw^2} + \left(\epsilon_N + \frac{\hbar^2}{2} \cosh 2w \right) \psi = 0 \quad \text{with } \psi(w=\pm w_0) = 0 \quad (\text{VI.1})$$

where we introduced several dimensionless variables: $\epsilon_N = [24/(\kappa l)^2]E_N$, $w = \kappa z/2$, $w_0 = \kappa a/2$, and

$$\frac{\hbar^2}{2} = \frac{24}{(\kappa l)^2} \frac{\Gamma}{\sinh \kappa a} = \frac{\hbar_0^2}{\sinh \kappa a}$$

Clearly eq VI.1 is nothing but the modified Mathieu equation, the solution of which appropriate for the case at hand can be written as^{21,23}

$$\psi(w) = J_{\epsilon_N}(h, w) \sim \sum_{n=-\infty}^{n=+\infty} (-1)^n a_n^{(s)} J_{s+2n}(h \cosh w) \quad (\text{VI.2})$$

where we basically follow the notation of Morse and Feshbach.²¹ (In what follows we shall address the general issues pertaining to the solutions of the modified Mathieu equation only inasmuch as they bear relevance to our discussion. We direct the reader to one of the standard references for further details.²²) $J_m(x)$ is the Bessel function of order m and $a_n^{(s)}$ are the coefficients entering the recursion relations when the solution eq VI.2 is inserted into eq VI.1. The order of the solution, s , is obtained by the application of the boundary condition. The solution of the boundary condition is indeed quite complex except in the limit of large separations where $h \ll 1$ and²¹

$$a_1^{(s)}/a_0^{(s)} = O(h^2)$$

$$E_N = -\frac{(\kappa l)^2}{24} s^2 + O(h^4) \quad (\text{VI.3})$$

The boundary condition $\psi(w_0) = 0$ in this case assumes the following simplified form valid to the order $O(h^2)$

$$J_s \left(\left[\frac{24}{(\kappa l)^2} \Gamma \coth \left(\frac{\kappa a}{2} \right) \right]^{1/2} \right) = 0 \quad (\text{VI.4})$$

The ground-state dominance ansatz now demands that among all the solutions of the above equation with $s \geq 0$ we should pick the one corresponding to the largest value of s , therefore, the first zero of a Bessel function with the largest value of s .

The first general statement we can now make is that solutions of the boundary condition eq VI.4 exist for real s only if $[24/(\kappa l)^2]\Gamma \coth(\kappa a/2)]^{1/2} \geq j_{0,1}$, where $j_{0,1}$ is the first zero of the zeroth Bessel function. If this is the case then by eq VI.3 the energy eigenvalue is negative, indicating the existence of a surface-bound state. By using an asymptotic form for the zeros of $J_s(x)$ valid for large values of s ,²³ we arrive at the following approximate relation

$$E_N \approx -\frac{(\kappa l)^2}{24} \left(\frac{2}{\pi} \right)^2 \left(\left[\frac{24}{(\kappa l)^2} \Gamma \coth \left(\frac{\kappa a}{2} \right) \right]^{1/2} - \frac{3\pi}{4} \right)^2 \quad (\text{VI.5})$$

valid for large values of $|E_N|$.

It is clear from the above analysis that, in the limit of $w_0 \rightarrow \infty$, which corresponds to the case analyzed by Wiegeland,¹¹ we also recover his results, viz., for $[24/(\kappa l)^2]\Gamma^{1/2} > j_{0,1}$ the polyelectrolyte

(21) Morse, P. M.; Feshbach, H. *Methods of Theoretical Physics*; McGraw-Hill: New York, 1953; p 556.

(22) McLachlan, N. W. *Theory and Application of Mathieu Functions*; Clarendon Press: Oxford, U.K., 1947. Campbell, R. *Theorie Generale de L'Equation de Mathieu*; Masson et Cie.: Paris, 1955. Erdelyi, A.; Magnus, M.; Oberhettinger, F.; Tricomi, F. G. *Higher Transcendental Functions*; McGraw-Hill: New York, 1955; Vol. III, p 91.

(23) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; Dover: New York, 1968.

chains are surface-bound due to the electrostatic attraction between the positive charges residing on the polymer beads and the negative fixed charges on the surfaces. Furthermore, since coth is a decreasing function of its argument, we can deduce that if we start with $[(24/\kappa l)^2] \Gamma^{1/2} > j_{0,1}$ for $w_0 \rightarrow \infty$ the energy eigenvalue will remain negative also for finite (κl) .

Though we obtained an explicit analytical solution in the limiting case $\Gamma, \lambda \ll 1$, its analysis does not seem to be of a lower complexity than the original numerical problem analyzed in the previous section. A clear analytical insight, however, is possible if we delimit ourselves to not too large separations. In this case the solution of eq VI.1 can be approached through the WKB approximation or equivalently the Horn-Jeffreys method, as it is called in the context of the modified Mathieu equation.²²

If we introduce an auxiliary function $\chi(w) = (\epsilon_N + (h^2/2) \cosh(2w))$, the WKB solution of the modified Mathieu equation can be written as

$$\psi(w) \sim \chi(w)^{-1/4} \exp(\pm i \int^w \chi^{1/2} dw); \quad \chi > 0$$

$$\psi(w) \sim (-\chi(w))^{-1/4} \exp(\pm \int^w (-\chi)^{1/2} dw); \quad \chi < 0 \quad (\text{VI.6})$$

The above two forms of the WKB solution represent two different branches that separate the whole space of the WKB solutions into two distinct regions characterized by the sign of $\chi(w)$. One should note here that the sign of $\chi(w)$ is not directly related to the sign of ϵ_N .

Starting with the branch corresponding to $\chi(w) > 0$, or equivalently $|\epsilon_N| < h^2/2$, a WKB solution displaying an even symmetry has the form²²

$$\psi(w) \sim \left(\epsilon_N + \frac{h^2}{2} \cosh(2w) \right)^{-1/4} \cos \left(\int_0^w \left[\epsilon_N + \frac{h^2}{2} \cosh(2w) \right]^{1/2} dw \right) \quad (\text{VI.7})$$

while the boundary condition eq VI.1 reduces to the following expression determining the lowest lying energy eigenvalue ϵ_N

$$\int_0^{w_0} \left[\epsilon_N + \frac{h^2}{2} \cosh(2w) \right]^{1/2} dw = \frac{\pi}{2} \quad (\text{VI.8})$$

The general solution of this equation is quite complicated but in the limit $h \gg 1$, that corresponds to $w_0 \rightarrow 0$, we remain with the following limiting form that can be easily deduced from eq VI.8 by setting $\chi(w) \approx \chi(w_0)$ on the interval $[0, w_0]$

$$\epsilon_N \approx \pi^2 \frac{1}{(2w_0)^2} - \frac{h^2}{2} \quad \text{for any } h_0 \text{ and } w_0 \ll 1 \quad (\text{VI.9})$$

This form of the eigenenergy has already been derived by a completely different route in a short exposition of the present work.²⁶ Evidently in the limit of very small intersurface separations the major contribution to ϵ_N comes from the steric interactions that are due to the impenetrability of the boundary surfaces to the polymer beads. Electrostatic interactions represent only a first-order correction to pure steric interactions.

The WKB solution can be in principle extended to the whole range of w_0 values. One has to be aware, however, that this solution is strictly valid only if ϵ_N and $h^2/2$ are two large equivalents,²² a statement that is strictly true only in the limit of $w_0 \rightarrow 0$. The solutions eq VI.6 are therefore exact for $w_0 \rightarrow 0$, approximative for intermediate values of w_0 , and highly unreliable for $w_0 \gg 1$. With this caveat in mind one can investigate the boundary condition eq VI.8 also for intermediate values of w_0 .

In the regime of intermediate to large w_0 , h is also quite (exponentially) small and can be safely ignored if compared with ϵ_N . This leads to the following form of the boundary condition eq VI.8

$$\epsilon_N^{1/2}(w_0 - \tanh(w_0)) + \tanh(w_0)[\epsilon_N + h_0^2 \coth(2w_0)]^{1/2} \approx \frac{\pi}{2} \quad (\text{VI.10})$$

which can be solved for ϵ_N only in the case that $h_0 < \pi/2$. The approximate solution of the above boundary condition for intermediate to large values of w_0 has the form

$$\epsilon_N \approx \left(\frac{\pi}{2} - h_0 \right)^2 \frac{1}{(w_0)^2} \quad \text{for } h_0 < \frac{\pi}{2} \text{ and } w_0 \gtrsim 1 \quad (\text{VI.11})$$

It is clear from the above discussion that the branching point $h_0 = \pi/2$ should be viewed upon as a WKB approximation to the exact condition $h_0 = j_{0,1}$ that can be derived from eq VI.4 in the limit of $w_0 \rightarrow \infty$.

A more complicated situation arises if $\chi(w) < 0$ or equivalently if $|\epsilon_N| > h^2/2$, corresponding to the regime above the branching point, $h_0 > \pi/2$. If we define w_z in this case as a "turning point" of $\chi(w)$

$$-|\epsilon_N| + \frac{h^2}{2} \cosh(2w_z) = 0 \quad (\text{VI.12})$$

than by properly extending the WKB solution beyond the turning point²² we remain with

$$\begin{aligned} \psi(w) &\sim \left(|\epsilon_N| - \frac{h^2}{2} \cosh(2w) \right)^{-1/4} \cosh \left(\int_0^w \left[|\epsilon_N| - \frac{h^2}{2} \cosh(2w) \right]^{1/2} dw \right); \quad 0 < w < w_z \\ \psi(w) &\sim \left(\frac{h^2}{2} \cosh(2w) - |\epsilon_N| \right)^{-1/4} \left[e^{M_0} \cos \left(\frac{\pi}{4} - \xi(w) \right) + e^{-M_0} \sin \left(\frac{\pi}{12} + \xi(w) \right) \right]; \quad w > w_z \end{aligned} \quad (\text{VI.13})$$

where the following definitions have been used

$$\begin{aligned} M_0 &= \int_0^{w_z} \left[|\epsilon_N| - \frac{h^2}{2} \cosh(2w) \right]^{1/2} dw \\ \xi(w) &= \int_{w_z}^w \left[\frac{h^2}{2} \cosh(2w) - |\epsilon_N| \right] dw \end{aligned} \quad (\text{VI.14})$$

According to the previous discussion, the solution branch eq VI.13 is applicable only if $h_0 > \pi/2$ and even then for not too small values of w_0 , since for $w_0 \rightarrow 0$ the representation in eq VI.7 is always the correct one. The boundary condition for this branch of the WKB solution that determines the values of the eigen-energy reduces to the form

$$\cos \left(\frac{\pi}{4} - \xi(w_0) \right) + e^{-2M_0} \sin \left(\frac{\pi}{12} + \xi(w_0) \right) = 0 \quad (\text{VI.15})$$

It is quite straightforward to establish that the solution of the above boundary condition, ξ , lies in the interval $3\pi/4 < \xi < 3\pi/4 + \pi/6$, no matter what the value of M_0 . It is therefore always close to $3\pi/4$ and we shall take this value as a starting point for the subsequent discussion.

We start by investigating the regime far away from the turning point, where $w_0 \gg w_z \gg 1$. In this case we can deduce the approximate form for $\xi(w_0)$

$$\xi \approx -(\pi/2)(|\epsilon_N|)^{1/2} + h_0 \coth(w_0) \quad (\text{VI.16})$$

that leads to the following expression for the energy eigenvalue $\epsilon_N \approx -(2/\pi)^2(h_0[\coth(w_0)]^{1/2} - \xi)^2$, for $h_0 > \pi/2$ and $w_0 \gg 1$ (VI.17)

Aside from the small difference between ξ and $3\pi/4$ we see that the above form of the energy eigenvalue is completely consistent with the one found through the analysis of the exact solution in the regime where it leads to negative eigenenergy, cf. eq VI.5. For negative eigenstates with sufficiently large energy eigenvalue, the asymptotic analysis of the exact solution and the WKB approximation both lead to basically identical dependence of the energy eigenvalue on the intersurface separation.

For the same branch of the WKBJ solution we can also obtain an approximative solution of the boundary condition eq VI.15 when $w_0 \lesssim 1$. In this case we assume the following ansatz

$$|\epsilon_N| = (h^2/2) \cosh(2w_0) - \Delta \quad (\text{VI.18})$$

with $\Delta \ll h^2/2$, which can be justified a posteriori by showing that in the limit $h_0 > \pi/2$, $w_0 \lesssim 1$, it leads to $\Delta \approx (\xi h_0^2/2)^{2/3}$, being indeed much smaller than $h^2/2$. In the limit of small to intermediate w_0 we therefore obtain the following approximation for the eigenenergy

$$\epsilon_N \approx -\frac{h^2}{2} \cosh(2w_0) + \left(\frac{\xi h_0^2}{2}\right)^{2/3} \approx -\frac{h^2}{2} \cosh 2w_0 \quad (\text{VI.19})$$

This form of the eigenenergy has also already been derived by a completely different route in a short presentation of this work.²⁶ It corresponds to the interaction of two charged surfaces with an intervening polyelectrolyte chain that is partially collapsed to the surfaces due to the electrostatic attraction between the surface charges and the oppositely charged polymer beads. If one approximates $\cosh 2w_0 \approx 1 + [(\kappa a)^2/2]$, the quadratic dependence on (κa) suggests that the most important contribution to the free energy in this limit is elastic in origin, with regions of the polyelectrolyte chain that are not trapped in the vicinity of both surfaces and extend from one surface to the other one acting as "entropic springs" drawing the surfaces together. The electrostatic interactions between polymer beads and oppositely charged surfaces thus act as an external field stretching the polymer. This stretching reduces the number of possible configurations of the polymeric chains, thus diminishing its entropy in proportion to the square of its average extension.¹⁹

We can now state the final forms of the intersurface pressure that follows from the above discussion. Taking into account the definition eq IV.7 we can write

$$\begin{aligned} \mathcal{P} = \frac{1}{2} \frac{\partial \mathcal{F}}{\partial a} \approx kT \frac{\pi^2}{3} l^2 \mathcal{N} \frac{N}{S} \frac{1}{(2a)^3} - \\ \left(\frac{\sigma \tau}{\epsilon \epsilon_0 \kappa^2} \left(\mathcal{N} \frac{N}{S} \right) - \frac{1}{2} \frac{\sigma^2}{\epsilon \epsilon_0 \kappa^2} \right) \frac{1}{a^2} \quad \text{for } (\kappa a) \rightarrow 0 \end{aligned} \quad (\text{VI.20})$$

which is a universal limiting form of the pressure for small separations, independent of the absolute magnitude of the electrostatic coupling in the system as long as it remains small. It is therefore obvious that for small separations the system acts as if it would be effectively discharged with electrostatic effects entering only as a first-order perturbation to the entropically driven repulsion. The above form of the pressure agrees with the perturbation result eq III.11 except for the term corresponding to the polymer electrostatic self-energy which is excluded from eq VI.20 in view of the condition $\lambda \ll 1$.

Next we state the forms of the pressure for intermediate to large separations that depend crucially on the electrostatic coupling in the system, quantified by the value of h_0

$$\begin{aligned} \mathcal{P} \approx kT \frac{4l^2}{3} \mathcal{N} \frac{N}{S} \left(\frac{\pi}{2} - h_0 \right)^2 \frac{1}{(2a)^3} + \\ \frac{1}{4} \frac{\sigma^2}{\epsilon \epsilon_0} \sinh^{-2}(\kappa a) \quad \text{for } h_0 < \frac{\pi}{2} \end{aligned} \quad (\text{VI.21})$$

or analogously

$$\begin{aligned} \mathcal{P} \approx -kT \frac{(\kappa l)^2}{24} \left(\frac{2}{\pi} \right)^2 \mathcal{N} \frac{N}{S} \left(\frac{h_0 \kappa}{4} \right) \left(h_0 - \frac{3\pi}{4} \right) \sinh^{-2} \left(\frac{\kappa a}{2} \right) + \\ \frac{1}{4} \frac{\sigma^2}{\epsilon \epsilon_0} \sinh^{-2}(\kappa a) \quad \text{for } h_0 > \frac{\pi}{2} \end{aligned} \quad (\text{VI.22})$$

(24) Chan, D.; Davies, B.; Richmond, P. J. Chem. Soc., Faraday Trans. 2 1976, 72, 1584.

(25) Mansfield, M. L. J. Chem. Phys. 1988, 88, 6570.

(26) Podgornik, R. Chem. Phys. Lett. 1990, 174, 191.

For smaller values of the intersurface spacing, $w_0 \lesssim 1$, the corresponding pressure can be obtained from eq VI.19 in the form

$$\mathcal{P} \approx \left(\frac{1}{4} \frac{\sigma^2}{\epsilon \epsilon_0} - \frac{\sigma \tau}{2 \epsilon \epsilon_0} \left(\mathcal{N} \frac{N}{S} \right) \right) \sinh^{-2}(\kappa a) \quad \text{for } h_0 > \frac{\pi}{2} \quad (\text{VI.23})$$

The above approximate forms of the pressure have a very limited range of validity especially in the regime of large intersurface spacings in agreement with the general caveat for the range of validity of the WKBJ approximation. Most notably eq VI.22 cannot remain valid in the strict limit of $w_0 \rightarrow \infty$ where the solutions of the boundary condition have to be derived from the more general eq VI.4.

This ends our discussion of the case $\Gamma, \lambda \ll 1$. The other limiting case that is amenable to a simple analytical treatment is conversely the case $\Gamma, \lambda \gg 1$. In this case the presence of mobile ions is irrelevant since their contribution to the local charge balance in the system is small. Therefore, eqs V.1 are reduced to the following form of a one-dimensional Hartree equation

$$\frac{d^2\psi}{dx^2} + \left(y + \int_{-x_0}^{+x_0} |x-x'| \psi^2(x') dx' \right) \psi = 0 \quad (\text{VI.24})$$

where we have introduced the following dimensionless variables

$$\lambda_B = \frac{6\beta\tau\sigma}{\epsilon \epsilon_0 l^2}; \quad x = \lambda_B^{1/3} z; \quad x_0 = \lambda_B^{1/3} a; \quad y = \frac{6}{l^2} \lambda_B^{-2/3} E_N \quad (\text{VI.25})$$

Furthermore, the electroneutrality condition in this specific case can be reduced to a simplified statement that $\sigma = \tau \mathcal{N}(N/S)$. The surface free energy density in this limit can be derived in the following form

$$\mathcal{F} = kT \mathcal{N} \frac{N}{S} \frac{l^2}{6} \lambda_B^{2/3} (y(x_0) + x_0) \quad (\text{VI.26})$$

The dependence of y on x_0 is obtained from the boundary condition at the impenetrable walls, stating that the solution of eq VI.24 should satisfy $\psi(x=\pm x_0) = 0$. We shall not proceed by solving eq VI.24 numerically but shall rather obtain an approximate analytical solution, which displays all the relevant features of the numerical solution. This approximate analytical solution can be arrived at by developing the last term in eq VI.24 into a Taylor series around $x = x_0$. The limitations of this approximation are discussed in ref 20. In this manner the following approximate equation of the general Airy type is obtained from eq VI.24

$$\frac{d^2\psi}{dx^2} + (y + x)\psi = 0 \quad \text{for } x \geq 0 \quad (\text{VI.27})$$

the unnormalized solution of which can be written as

$$\psi(x) \sim Bi'(-y) Ai(-y-x) - Ai'(-y) Bi(-y-x) \quad (\text{VI.28})$$

where $Ai(z)$ and $Bi(z)$ are the two independent solutions of the Airy's equation and the prime stands for the derivative with respect to the argument.

After the boundary condition $\psi(x_0) = 0$ is solved the explicit dependence of the dimensionless eigenenergy on x_0 is obtained that leads to the following asymptotic forms for the surface free energy density

$$\lim_{\lambda_B^{1/3} a \rightarrow 0} \mathcal{F} = kT \mathcal{N} \frac{N}{S} \frac{l^2}{6} \left(\left(\frac{\pi}{2} \right)^2 \frac{1}{a^2} + \frac{1}{2} \lambda_B a + \dots \right) \quad (\text{VI.29})$$

$$\lim_{\lambda_B^{1/3} a \rightarrow \infty} \mathcal{F} = kT \mathcal{N} \frac{N}{S} \frac{l^2}{6} \lambda_B^{2/3} \left(ai_0 - \frac{1}{2} C \exp[-\frac{4}{3} \lambda_B^{1/2} a^{3/2}] + \dots \right) \quad (\text{VI.30})$$

where ai_0 is the first zero of the Airy's function of the first kind, i.e., $Ai(-ai_0) = 0$, while $C = Bi(-ai_0)/Ai'(-ai_0)$. In the limit of small separations again the dominant contribution to the free energy comes from entropically generated repulsion while the

electrostatic interactions enter only as a first-order perturbation. In the opposite extreme of large separations eq VI.30 the dominant contribution to \mathcal{I} comes from the bridging attraction due to the soft, electrostatic absorption of the polymeric chains to the surfaces. It should be noted that the transition from repulsive to attractive forces is accompanied by a conformational transition of the polymer density distribution from monomodal to bimodal form (see ref 20 for details). It is only in this limit that the nature of the forces (attraction-repulsion) follows exactly the form of the polymer density profile.

The form of the free energy eq VI.30 does also provide some additional information on the magnitude of the forces when the net pressure is attractive. It follows from eq VI.30 that in the regime where attraction predominates one has

$$\mathcal{P} \approx -\frac{1}{2} \frac{\sigma^2}{\epsilon \epsilon_0} \lambda_B^{1/6} \mathcal{C} \sqrt{a} \exp[-\frac{1}{3} \lambda_B^{1/2} a^{3/2}] \quad (\text{VI.31})$$

Though the attractive pressure decays approximately exponentially it does follow from the above approximate form that its magnitude is not inherently bounded, as is the case with the Lifshitz-van der Waals interactions, which are bounded from above by the ideally polarizable half-spaces case. One can therefore reach quite high attractive pressures if the surface charge density is large enough and the ionic screening is negligible. There is therefore no need to invoke hydrophobic interactions to rationalize the existence of strong attractive interactions between charged surfaces in the presence of flexible polyelectrolytes,³⁴ since the bridging mechanism can lead to attractions of a magnitude well above the Lifshitz-van der Waals forces.

VII. Discussion

In the preceding sections we have developed a SCF method for obtaining the intersurface forces operating in a system composed of charged polymeric chains immersed into an electrolyte confined between two charged, impenetrable walls, where the charges on the polymers are of opposite sign to the charges fixed on the surfaces. In the outline the method is quite similar to the SCF approach¹⁸ widely used in the analysis of the excluded volume interactions of polymers in the bulk or in confined regions.²⁹ There are, however, two main differences. First of all the pair potential is Coulombic whereas it is approximated by a delta function in the excluded volume case. Furthermore, interactions between different segments of the polyelectrolyte chain as well as the interactions between the polyelectrolyte beads with charged walls are mediated by the presence of mobile ions.

The SCF-PBP approximation introduced in this work has direct ties with work on the single polyelectrolyte chain by Kholodenko and Beyerlein¹⁴ except that what we wish to approximate is the free energy rather than the Green's function or its moments. There exists also a direct connection between the Poisson-Boltzmann theory used in the case of a nonhomogeneous electrolyte. In the Poisson-Boltzmann treatment the local density of the mobile charge carriers is approximated by $\rho(r) \sim e^{-\beta e\phi(r)}$, if e is the magnitude of the charge residing on the charge carriers. In the case treated here, eqs III.14 and III.15 simply state that in the case of a charged polymer the local density of polymeric charge has the form $\rho_p(r) \sim \langle e^{-\beta r \phi(r)} \rangle$, where the averaging has to be done over internal polymeric degrees of freedom, i.e., positions of the beads along all the polymeric chains.

There are several drawbacks of the SCF method, and besides the standard ones²⁹ one should mention that at this level of sophistication one is unable to treat effects like electrostatic stiffening of the chain. Nevertheless, by making an analogy with the semi-infinite case,¹⁵ one can conjecture that inclusion of terms beyond the SCF approximation would lead to an effective step length that would probably among other things depend also on the value of intersurface spacing.

Though the SCF-PBP approximation scheme represents a natural extension of the usual Poisson-Boltzmann approximation to the case of added charged polymers, the results obtained in this work bear only a minor resemblance to the predictions that follow from the standard PB equation. In general there are three tendencies that govern the interactions between charged surfaces in the presence of confined polyelectrolyte chains. First of all, there is the entropic contribution of the sterically excluded configurations amounting to a repulsion between the surfaces. Second, the direct electrostatic interactions between the surfaces have the same origin as in the standard PB case and correspond to the changes in free energy due to the double-layer overlap on approach of the two charged boundaries. Third, the soft adsorption of the polymeric chains to the surfaces also stems from the electrostatic interactions between the polymeric charges and the charges fixed to the walls. However, in spite of the electrostatic nature of this effect, it promotes (bridging) attraction between the bounding surfaces that can in certain cases overwhelm the other two repulsive contributions. This effect has no counterpart in the standard PB theory or its modifications and has its root solely in the connectivity of the confined polymeric chains.

Thus the most important difference with respect to standard PB results is that the solutions of the SCF-PBP equations lead to a range of intersurface separation values where the interaction forces between the bounding surfaces can become attractive. As already argued by Åkesson, Woodward, and Jönsson¹³ in the case of two charged surfaces with intervening polyelectrolyte chains without any added electrolyte, the mechanism responsible for attractive forces is the bridging of polyelectrolyte chains between the surfaces. The same mechanism was established in section V to be the primary source of attraction also for the model system analyzed in this work. This bridging is quite different in character from the one promoted by short-range surface interactions trying to trap the chain that wanders into the vicinity of the surfaces. It corresponds to local minima in the polymer energy close to the surfaces that can be quite long ranged (on the order of κ^{-1}) with a depth depending on the intersurface separation. As such the attractive interactions also have an electrostatic background and are therefore dependent on the value of the electrostatic coupling in the system specified by the dimensionless coupling constants Γ and λ . Furthermore, as the separation is varied a window exists in the Γ, λ space where the pressure can go from repulsive to attractive and back to repulsive. This effect has some very interesting consequences in terms of the equilibrium of the system under an imposed external stress that will be investigated in a forthcoming publication.³² The notion of an electrostatically driven soft adsorption differs in content from the usual adsorption problems encountered in the context of confined polymers. Usually, as e.g. in the model system treated by Chan, Davies, and Richmond,²⁴ the adsorption energy is considered as a constant independent of system parameters. This leads to an important consequence, namely, that the interaction energy as a function of the intersurface separation, a , has no turning points, being of the same sign for all values of a . The sign of course depends on the value of the adsorption energy but it does not depend on a . In the case of electrostatically driven "soft adsorption", the adsorption energy, on the contrary, is not a constant but depends in a nontrivial way on the system parameters, most notably the electrostatic coupling and the intersurface spacing. The behavior of a confined polyelectrolyte chain could therefore be understood in the context of an intersurface separation dependent adsorption energy. Furthermore, the transition between monomodal and bimodal conformations of the polymeric chains bears a lot of resemblance to the coil-stretch transition of polymers in external fields. Mansfield²⁵ has recently shown how a transition between a unimodal and bimodal distribution of a polymer can be accomplished by varying the strength of an external field stretching the polymer. This external field would in our case correspond to the electrostatic mean potential created by the fixed charges on both surfaces, the strength of which varies with the separation.

It is interesting to compare our results with the studies of interactions between the surfaces in the presence of electrically

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neutral polymers. The situation there too is quite complicated since the interaction forces are not amenable to any general form, their behavior depending on the amount of the dissolved polymer, solvent quality and the nature of polymer-surface interactions. However, one can establish a close correspondence between the results derived in this contribution and the force profile in the case of strongly adsorbed polymers at partial coverage.²⁷ The interaction potential there remains repulsive at small separations but develops an attractive minimum at low coverages (corresponding to small Γ in our case) that gradually disappears as the coverage is increased. Bridging is claimed as the only cause of this attraction. Work of Muthukumar and Ho²⁹ which is methodologically quite close to our analysis also yields force curves that can be correlated with the behavior of our system. In their case the bridging of the polymeric chains is promoted by attractive van der Waals interactions between polymer beads and bounding surfaces. In fact our model system (electrostatic interactions between polymer beads are repulsive) would correspond closely to case 5 of their Conclusions-section, which describes polymers above Θ temperature at different magnitudes of the van der Waals attraction between polymer beads and the bounding surfaces.

Finally one should add a note on the experimental situation. At this point we were unable to find any systematic investigation

of forces between charged surfaces in the presence of polyelectrolytes that we could use for a direct comparison with our theoretical predictions. However, investigations of the short-range order of silica particles in the presence of cationic polymers³³ or the direct measurements of forces between mica surfaces in the presence of polypeptides³⁴ do suggest that strong attractions exist between charged particles in a solution of oppositely charged polyelectrolyte. Furthermore, a study of forces between mica surfaces in the presence of poly(2-vinylpyridine)³⁵ that is fully charged in acidic solutions gives strong support to the bridging origin of attractive interactions. The polyelectrolyte bridges were inferred from the force curves following surface adhesion and were seen to disappear for shorter polymer chain lengths. The conclusions reached in our work are in sound qualitative agreement (see, e.g., Figure 8a) with the results of the above work.

The problem of interactions between charged surfaces with intervening polyelectrolyte chains is of a far greater complexity than one would naively expect on the basis of our experience with the Poisson-Boltzmann equation. From the theoretical side it is indeed quite fascinating since it leads to a blending of different methods used profusely by the molecular force and the polymer community.

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Physicochemical Studies on Microemulsions: Test of the Theories of Percolation

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On the basis of percolation results of 32 water/oil microemulsion systems, a detailed analysis of the validity of the effective medium theory (EMT), EMT with dipole-dipole interaction (EMTDD), and Bernasconi-Weismann (BW) theory has been made. It has been found that most of the systems obey either the EMT or the EMTDD (chain) formalism whereas a slender few follow the EMTDD (cluster) and BW formalisms. The results suggest that the internal structure of microemulsions can be either isolated, randomly dispersed spheres or spheroidal aggregates formed by dipolar interaction.

Introduction

A conducting microheterogeneous dispersion in a very weakly conducting or nonconducting medium may show a rapid rise in conductance above a threshold concentration. This phenomenon is called percolation.¹⁻⁶ Water-in-oil (w/o) microemulsions stabilized by ionic surfactants or by an ionic surfactant and a cosurfactant are microheterogeneous dispersions of conducting water droplets. They often exhibit percolation in conductance after a threshold concentration of water.⁷⁻¹¹ Quantitative the-

oretical treatment on the percolation phenomenon in microemulsions has been attempted with the help of the effective medium theory (EMT).^{1,2,12} In a recent work, Fang and Venable¹³ have used the EMT theory of Böttcher¹² for quantitative accounting of the structural parameters of several microemulsion systems. The equation has been also used by Bisal et al.¹⁴ for quantitative description of a good number of w/o microemulsion systems with special reference to their structural properties. The results have been shown to be comparable with those obtained from other sophisticated methods, viz., light scattering, small-angle neutron scattering, fluorescence quenching, etc.

For microheterogeneous dispersions of metal and metal oxides in suitable media,¹⁵ the EMT theory has been shown to be often inadequate, and modifications of the equation have been put forward. The percolation threshold (one-third of the volume fraction of the dispersion) according to the EMT theory of Böttcher¹² is not always the practical limit. A number of authors^{3,15-17} have suggested that the percolation thresholds realized

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