

Exactly Solvable Model for the Interaction of Two Parallel Charged Plates in an Ionic Medium

L. Blum*

Department of Physics, POB AT, Faculty of Natural Sciences, University of Puerto Rico,
Rio Piedras, Puerto Rico 00931

and B. Jancovici

Laboratoire de Physique Théorique et Hautes Energies, Université de Paris-Sud, 91405 Orsay, France[†]
(Received: September 7, 1983)

A model for the interaction of two charged plates in an electrolyte is solved exactly. In this model the two plates are two charged lines immersed in a two-dimensional, one-component plasma at the reduced inverse temperature 2. When the plates are brought together, the pressure tends to the limit $p = [(d-1)\pi/\epsilon]\bar{\sigma}^2$, which is a result valid for the $d = 2, 3$ dimensional case of any ionic system ($-\bar{\sigma}$ is the charge density on each plate, and ϵ is the dielectric constant of the electrolyte solvent). Furthermore, we conjecture that the charge between plates must be less than the charge on each plate. On the basis of this conjecture it is argued that simple superposition approximations will lead to unphysical results because the correlations are calculated by using only one plate. This is illustrated by using the exactly solvable model.

I. Introduction

The diffuse double layer is responsible for the stability of colloidal suspensions. Although, quite generally, colloidal particles are spheroidal or spherocylindrical, the early treatments¹⁻³ have used, as a starting point of the theory, the interaction between parallel plates immersed in an electrolyte.

This simple geometry is mathematically tractable, and in some cases (Gouy-Chapman (GC) theory) amenable to analytic solutions. Parsegian and collaborators⁴ have solved the weak-coupling limit for the case in which the ionic medium is confined by the two plates. Because of electroneutrality requirements, in this theory the amount of charge confined by the plates is constant as the plates approach each other; therefore, the pressure between the plates remains constant. This is unsatisfactory, because intuition tells us that we must squeeze out the solution as the plates approach each other. At zero separation, the correct limit for the pressure p between the plates is

$$p = (2\pi/\epsilon)\bar{\sigma}^2 \quad (1.1)$$

where $-\bar{\sigma}$ is the surface charge density on each plate and ϵ is the dielectric constant of the electrolyte solvent. Equation 1.1 is the Maxwell stress tensor result and is an exact asymptotic result for the plane geometry.

Clearly, eq 1.1 and the electroneutrality requirements are satisfied if the solution surrounds the plates. This case was discussed by Ohshima,⁵ who solved the Poisson-Boltzmann equation for noninteracting ions (GC theory). It corresponds also more closely to the recent experiments of Israelachvili,⁶ who measured the force between mica plates in various electrolytes.

The purpose of the present investigation is to present a non-trivial, exactly solvable model of this case, which could serve as a benchmark to determine the accuracy of the approximations used in the theory of colloid stability. In particular, according to the recent work of Patey,⁷ the electrostatic interactions may lead to attractive forces; this interesting possibility has been challenged by other workers.⁸⁻¹⁰ In our present work the charge profiles are always monotonic, and since the attractions are caused by charge oscillations, we cannot discuss this fact in the context of this simple model. Thick plates will, presumably, show oscillations¹² and will be discussed in future work.

Our model is the two-dimensional, one-component plasma (OCP) in a uniform neutralizing background. At coupling parameter $\Gamma = 2$, where

$$\Gamma = (1/kT)e^2/\epsilon \quad (1.2)$$

this system is analytically solvable, both in the bulk¹³ and at charged interfaces.¹² In eq 1.2, k is Boltzmann's constant, T the absolute temperature, e the particle charge, and ϵ the dielectric constant.

The strip geometry, in which the electrolyte is confined between the plates, was recently solved by Forrester and Smith.¹⁴ Our method of solution is similar to this work.

In section II we discuss very briefly the method of solution. Readers interested in technical details are referred to ref 12-14 and 21. In section III we give a discussion of the main results

-
- (1) B. V. Derjaguin, *Kolloid-Z.*, **69**, 155 (1934).
 - (2) B. V. Derjaguin and L. Landau, *Acta Physicochim. (URSS)*, **14**, 633 (1941).
 - (3) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids", Amsterdam, 1948.
 - (4) V. A. Parsegian and D. Gingell, *Biophys. J.*, **12**, 1192 (1972).
 - (5) H. Ohshima, *J. Colloid Polym. Sci.*, **252**, 257 (1974).
 - (6) J. N. Israelachvili, *Faraday Symp. Chem. Soc.*, **13**, 20 (1978).
 - (7) G. N. Patey, *J. Chem. Phys.*, **72**, 5763 (1980).
 - (8) M. Medina Noyola and D. A. McQuarrie, *J. Chem. Phys.*, **73**, 6279 (1980).
 - (9) H. Wennestrom, B. Jonsson, and P. Linse, *J. Chem. Phys.*, **76**, 4665 (1982).
 - (10) L. Blum, J. Hernando, and J. L. Lebowitz, *J. Phys. Chem.*, **87**, 2825 (1983), and references contained therein.
 - (11) M. Teubner, *J. Chem. Phys.*, **75**, 1907 (1981).
 - (12) B. Jancovici *J. Phys. Lett.*, (Orsay, Fr.), **42**, 223 (1981).
 - (13) B. Jancovici, *Phys. Rev. Lett.*, **46**, 386 (1981).
 - (14) P. J. Forrester and E. R. Smith, *J. Phys. A: Math. Gen.*, **15**, 3861 (1982).
 - (15) A. Erdelyi, "Higher Transcendental Functions", Vol. 2, McGraw-Hill, New York, 1953.
 - (16) Ch. Gruber, J. L. Lebowitz, and Ph. A. Martin, *J. Chem. Phys.*, **75**, 944 (1981).
 - (17) L. Blum, Ch. Gruber, J. L. Lebowitz, and Ph. A. Martin, *Phys. Rev. Lett.*, **48**, 1769 (1982).
 - (18) L. Blum, D. Henderson, Ch. Gruber, J. L. Lebowitz, and Ph. A. Martin, *J. Chem. Phys.*, **75**, 5974 (1981).
 - (19) L. Blum, Ch. Gruber, D. Henderson, J. L. Lebowitz, and Ph. A. Martin, *J. Chem. Phys.*, **78**, 3195 (1983).
 - (20) D. Henderson, L. Blum, and J. L. Lebowitz, *J. Electroanal. Chem.*, **102**, 305 (1979).

[†]Laboratoire Associé au C.N.R.S.

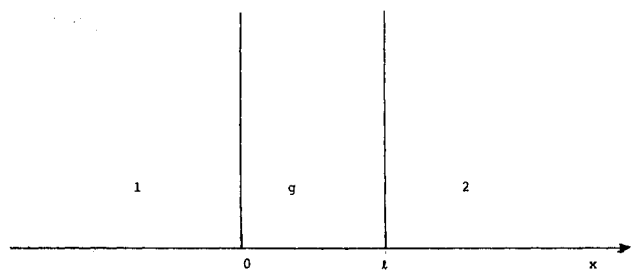


Figure 1. System geometry.

and compare them to a simple superposition approximation.

II. Method of Solution

Our system consists of two parallel plates charged with charge densities $-e\sigma_1/\pi$, $-e\sigma_2/\pi$, and separated by a distance l (see Figure 1). The uniform background charge density is $-e\alpha/\pi$. For simplicity in the equations we will take $\alpha = 1$ (i.e., the average interparticle distance is taken as the unit of length).

Following Jancovici^{12,13} we consider initially our system to be confined to a disk of radius R . The plates are two rings of radii R_1 , R_2 , with

$$R_2 = R_1 + l \quad (2.1)$$

The total number of ions N must satisfy the electroneutrality relation

$$N = 2(\sigma_1 R_1 + \sigma_2 R_2) + R^2 \quad (2.2)$$

We take the origin at the center of the disk. The Hamiltonian of this model is

$$\mathcal{H} = (1/2)e^2 \sum_{N \geq k > j \geq 1} \ln |\mathbf{r}_k - \mathbf{r}_j|^2 + \sum_{k=1}^N [2\sigma_1 R_1 \ln (r_k/R_1)^2 \theta(r_k - R_1) + 2\sigma_2 R_2 \ln (r_k/R_2)^2 \theta(r_k - R_2) + r_k^2] + B_N \quad (2.3)$$

where \mathbf{r}_k is the position of ion k , of charge e , and $\theta(x)$ is the Heaviside function of x . B_N is a background term that is irrelevant to our present calculation.

We compute the canonical partition function

$$Z_N = (1/N!) \int d\mathbf{r}^N e^{-\beta H} \quad (2.4)$$

One finds

$$Z_N = e^{-\beta B_N} (2\pi)^N \times \prod_{n=0}^{N-1} \left\{ \int_0^{R_1} dr r^{2n+1} e^{-r^2} + (1/R_1^{2(n_g-n)}) \int_{R_1}^{R_2} dr r^{2n_g+1} e^{-r^2} + (1/R_1^{2(n_g-n)}) (1/R_2^{2(n_g-n)}) \int_{R_2}^R dr r^{2n_g+1} e^{-r^2} \right\} \quad (2.5)$$

where

$$n_g = n - 2\sigma_1 R_1 \quad (2.6)$$

$$n_2 = n - 2\sigma_1 R_1 - 2\sigma_2 R_2 \quad (2.7)$$

and $\beta = 1/kT$ is the Boltzmann factor. Introducing the incomplete γ function

$$\gamma(a, b) = \int_0^b dt t^{a-1} e^{-t} \quad (2.8)$$

we get

$$Z_N = e^{-\beta B_N} \pi^N \prod_{n=0}^{N-1} \{ \gamma(n+1, R_1^2) + (1/R_1^{2(n_g-n)}) [\gamma(n_g+1, R_2^2) - \gamma(n_g+1, R_1^2)] + (1/R_1^{2(n_g-n)}) (1/R_2^{2(n_g-n)}) [\gamma(n_2+1, R^2) - \gamma(n_2+1, R_2^2)] \} \quad (2.9)$$

The single particle density is found to be

$$\rho(r) = (1/\pi) \exp(R_1^2 - r^2) \sum_{n=0}^{N-1} (1/D_n) \{ (r/R_1)^{2n} \theta(R_1 - r) + (r/R_1)^{2n_g} [\theta(r - R_1) - \theta(r - R_2)] + (r/R_2)^{2n_g} (R_2/R_1)^{2n_g} \theta(r - R_2) \} \quad (2.10)$$

with

$$D_N = \exp(R_1^2) \{ (1/R_1^{2n}) \gamma(n+1, R_1^2) + (1/R_1^{2n_g}) \times [\gamma(n_g+1, R_2^2) - \gamma(n_g+1, R_1^2)] + (1/R_1^{2n_g}) (1/R_2^{2(n_g-n)}) [\gamma(n_2+1, R^2) - \gamma(n_2+1, R_2^2)] \} \quad (2.11)$$

Similarly, the pair density distribution function is

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \rho(r_1) \rho(r_2) - \sum_{m_1, m_2} Z_1^{m_1} Z_1^{*m_2} Z_2^{*m_1} Z_2^{m_2} (1/R_1^{2(m_1+m_2)}) G(r_1) G(r_2) / D_{m_1} D_{m_2} \quad (2.12)$$

where D_m is defined in eq 2.11, Z_i is the complex number which represents the two-dimensional vector \mathbf{r}_i , and

$$G(r) = \exp(R_1^2 - r^2) \{ \theta(R_1 - r) + (r/R_1)^{2\Delta_g} [\theta(r - R_1) - \theta(r - R_2)] + (r/R_2)^{2\Delta_g} (R_2/R_1)^{2\Delta_g} \theta(r - R_2) \} \quad (2.13)$$

with

$$\Delta_g = -2\sigma_1 R_1$$

$$\Delta_2 = -2\sigma_1 R_1 - 2\sigma_2 R_2$$

We now choose a new origin on the ring of radius R_1 , with the x axis directed outward along a radius. We take the limit $R, R_1, R_2 \rightarrow \infty, R_2 - R_1 = l$. The plate of radius R_1 becomes the y axis. Using

$$\gamma(n+1, N) \sim (\pi n/2)^{1/2} \exp(-n + n \ln n) \{ 1 + \Phi[(N-n)/(2n)^{1/2}] \} \quad (2.14)$$

with

$$\Phi(x) = (2/\pi^{1/2}) \int_0^x dt e^{-t^2} \quad (2.15)$$

and replacing sums by integrals, we obtain for the density profile

$$\pi \rho(x) = (2/\pi^{1/2}) \int_{-\infty}^{\infty} dt \exp(-2x^2 - 2xt(2^{1/2})) (1/D_t) \{ \theta(-x) + \exp(-4\sigma_1 x) [\theta(x) - \theta(x-l)] + \exp[-4\sigma_1 x - 4\sigma_2(x-l)] \theta(x-l) \} \quad (2.16)$$

with

$$D_t = \exp(t^2) [1 + \Phi(t)] + \exp[(t + 2^{1/2}\sigma_1)^2] \{ \Phi(t + 2^{1/2}\sigma_1 + 2^{1/2}l) - \Phi(t + 2^{1/2}\sigma_1) \} + \exp[4\sigma_2 l + [t + 2^{1/2}(\sigma_1 + \sigma_2)]^2] \{ 1 - \Phi[t + 2^{1/2}(\sigma_1 + \sigma_2) + 2^{1/2}l] \} \quad (2.17)$$

and for the pair density

$$\rho(z_1, z_2) = \rho(x_1) \rho(x_2) - (4/\pi^3) G(x_1) G(x_2) \int_{-\infty}^{\infty} dt \exp[-(z_1 + z_2^*) 2^{1/2} t] / D_t^2 \quad (2.18)$$

where $z_i = x_i + iy_i$; we have defined

$$G(x) = \exp(-2x^2) \{ \theta(-x) + \exp(-4\sigma_1 x) \times [\theta(x) - \theta(x-l)] + \exp[-4\sigma_1 x - 4\sigma_2(x-l)] \theta(x-l) \} \quad (2.19)$$

III. Discussion

For the simple geometry that we have considered, there are few surprises: the density profiles are monotonic near the charged plates, there are no charge oscillations, and, since the correlations have the exponential clustering property, the pair correlation function has no dipole and higher multipole moments.^{16,17} There will be no long-range correlations along the surface of the plates. We remark that this situation may change in the case of plates of finite width.^{18,19}

The interesting features of this model come from the analysis of $\rho(x)$ and its integrals. This function is shown in Figures 2-4

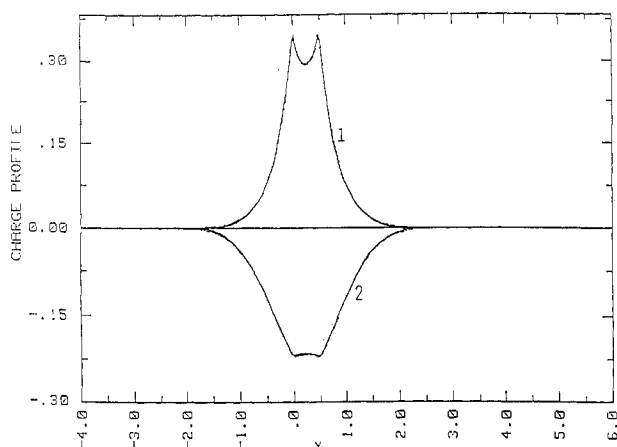


Figure 2. Charge density profile for $l = 0.5$. Here $\sigma_1 = \sigma_2 = \sigma$. Curve 1: $\sigma = 0.6$. Curve 2: $\sigma = -0.6$.

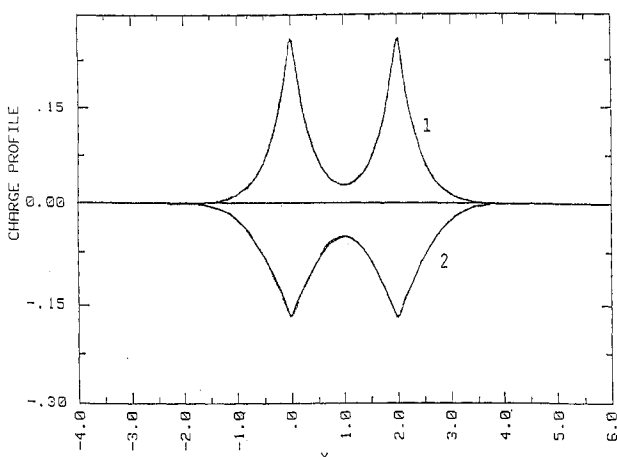


Figure 3. Same as Figure 2 but with $l = 2$.

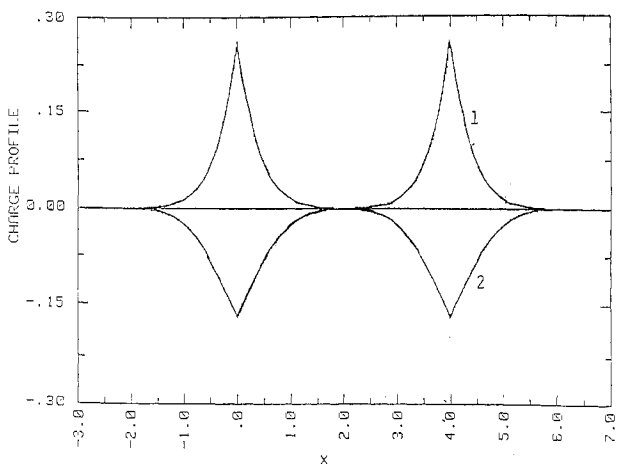


Figure 4. Same as Figure 2 but with $l = 4$.

for various plate separations and surface charges ($\sigma_1 = \sigma_2 = \sigma$). Because of the fact that the plates are of zero width, the density profile comes out to be continuous everywhere. The contact density is

$$\rho(0) = \rho(l) = (2/\pi^{3/2}) \int_{-\infty}^{\infty} dt (1/D_t) \quad (3.1)$$

As we mentioned earlier, the pressure between the plates plays a central role in the theory of colloid stability. The electrostatic pressure between the plates is

$$p = -E(l)(e\sigma/\pi) \quad (3.2)$$

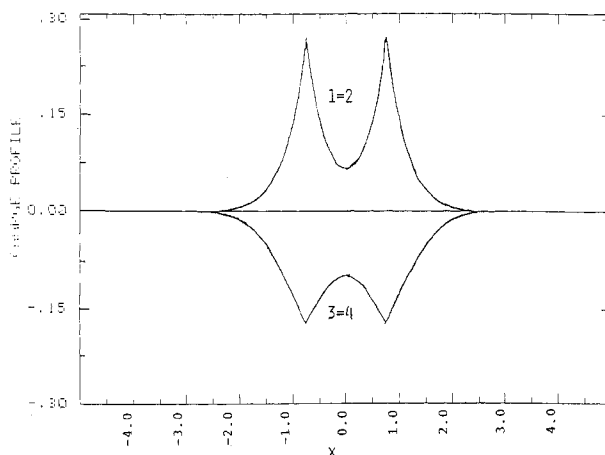


Figure 5. Superposition approximation. Curve 1: $\sigma = 0.6$, exact. Curve 2: $\sigma = 0.6$, superposition. Curve 3: $\sigma = -0.6$, exact. Curve 4: $\sigma = -0.6$ superposition. All of these are for the distance $l = 1.5$.

where $E(l)$ is the electrostatic field at $x = l$ (not including the field of the second plate). Clearly

$$E(l) = (e/\epsilon)(a - \sigma) \quad (3.3)$$

where ea/π is the charge (per unit length) enclosed between the plates

$$a = \pi \int_0^l dx [\rho(x) - (1/\pi)] \\ = (1/2^{1/2}) \int_{-\infty}^{\infty} dt (1/D_t) \exp[(t+2^{1/2}\sigma)^2] \times \\ [\Phi(t+2^{1/2}\sigma+2^{1/2}l) - \Phi(t+2^{1/2}\sigma)] - l \quad (3.4)$$

Thus, the pressure is given by

$$p/kT = (2/\pi)\sigma(\sigma - a) \quad (3.5)$$

Clearly, in the three-dimensional case this equation generalizes to

$$p = (2\pi/\epsilon)\bar{\sigma}(\bar{\sigma} - \bar{a}) \quad (3.6)$$

where $-\bar{\sigma}$ is now the charge density on the plates and \bar{a} the charge (per unit area) between the plates.

Because of the electroneutrality requirements, this equation will have the correct asymptotic behavior in the limit $l = 0$. We remark that the value of \bar{a} will depend on the details of the interactions between the ions in the system, so that no general theorem can be established, neither for \bar{a} nor for the pressure p . However, if we assume that there are only repulsive and Coulomb interactions, then we conjecture that

$$|\bar{a}| < |\bar{\sigma}| \quad (3.7)$$

It is clear that the Landau-DeGrujauin relation, which is also derived from Maxwell's stress tensor, is always correct, and in fact equivalent to eq 3.5 or 3.6

$$p = (1/\omega_d)[(E_+)^2 - (E_-)^2] \quad (3.8)$$

where

$$\omega_d = 8\pi/\epsilon \quad (\text{three dimensions}) \quad (3.9)$$

$$\omega_d = 4\pi/\epsilon \quad (\text{two dimensions}) \quad (3.10)$$

and E_+ and E_- are the fields on both sides of a plate (E_+ outside, E_- inside).

In the general case of two plates immersed in a primitive electrolyte there is no contact theorem²⁰ which is independent of the pair interactions of the ions in the bulk. In three dimensions, the general relation is

$$P = kT \sum \rho_i(0) - (2\pi/\epsilon)(\bar{\sigma} - \bar{a}/2)^2 \quad (3.11)$$

where P is the bulk pressure. This relation involves not only the

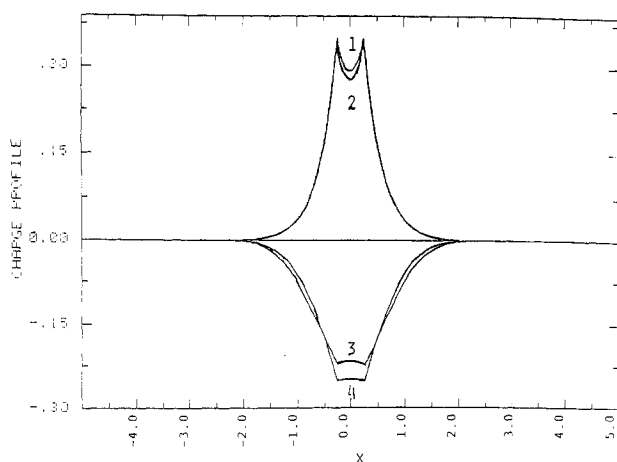


Figure 6. Same as Figure 5 but for the distance $l = 0.5$.

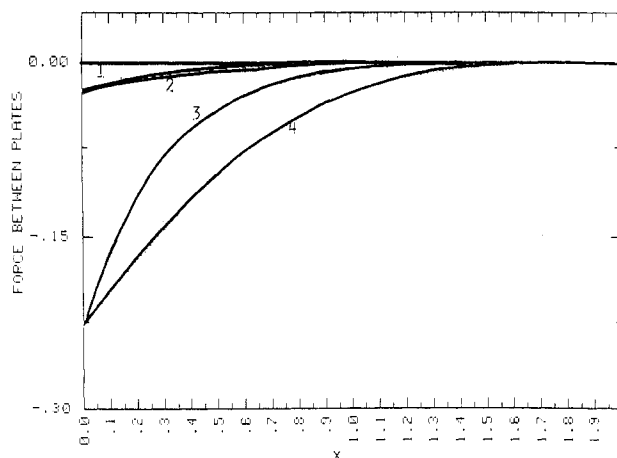


Figure 7. Pressure between plates. Curve 1: $\sigma = 0.2$. Curve 2: $\sigma = -0.2$. Curve 3: $\sigma = 0.6$. Curve 4: $\sigma = -0.6$.

contact densities $\rho_i(0)$ but also \bar{a} , which is not a priori known.

It is particularly important that, when $l \rightarrow 0$, we must have $\bar{a} \rightarrow 0$. In any approximation where this is not satisfied, we will not get the correct limit (eq 1.1).

In a superposition type approximation, a will not have its correct value, and the pressure between the plates will not be correct. To illustrate this point we compared the exact result to a simple-minded approximation in which the total charge density is just the sum of the distributions of the two plates taken independently. As can be seen in Figures 5 and 6 this approximation works fairly well for separations larger than the average interparticle distance ($=1$). For smaller distances, as can be seen in Figure 6, the superposition ansatz leads to rather severe overestimation of a . In simple terms, we cannot squeeze out the solution if we do not have the two walls present simultaneously.

Consider finally the case of weakly charged lines: the pressure between the lines can then be computed from a wavenumber-dependent dielectric constant $\epsilon(k)$. Here we take the solvent dielectric constant $\epsilon = 1$. The line at $x = 0$ has charge density

$$-(e\sigma/\pi)\delta(x) = -(e\sigma/\pi) \int_{-\infty}^{\infty} dk \exp(ikx)/2\pi \quad (3.12)$$

and creates the potential

$$\phi(x) = -(e\sigma/\pi) \int_{-\infty}^{\infty} dk \exp(ikx)/[k^2\epsilon(k)] \quad (3.13)$$

where the dielectric function is related to the bulk structure function $S(k)$ by

$$1/\epsilon(k) = 1 - 4S(k)/k^2 \quad (3.14)$$

But

$$S(k) = 1 - \exp(-k^2/4) \quad (3.15)$$

(see ref 13). Then, from eq 3.13 we can compute the field at $x = l$, from where the electrostatic pressure (eq 3.2; see Figure 7) is given by

$$p/kT = (2\sigma^2/\pi)\{(2l^2 + 1)[1 - \Phi(l)] - 2l \exp(-l^2)/\pi^{1/2}\} \quad (3.16)$$

which agrees with the expansion of the exact expression 3.5 for $|\sigma| \ll 1$.

Acknowledgment. L.B. is grateful to Drs. D. Henderson, M. Lozada-Cassou, and M. Medina Noyola for very useful discussions. L.B. was supported by NSF Grant CHE 80-01969.

Photophysics and Photochemistry of Xanthene Dyes in Polymer Solutions and Films

Prashant V. Kamat and Marye Anne Fox*

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712 (Received: April 21, 1983; In Final Form: October 28, 1983)

The singlet and triplet lifetimes of erythrosin B and rose bengal, two representative xanthene dyes, are significantly increased by enclosing the dye in a cage of poly(4-vinylpyridine) (PVP). The fluorescence yield, controlled by the rate of intersystem crossing, is also increased by such encapsulation. Parallel effects are observed upon adding the polymer to an ethanolic solution of the xanthene or upon loading the dye into a polymer matrix dispersed on a metal oxide surface. The effect of the polymer on static quenching of the excited dye and the implications of dye-loaded polymer films in solar energy conversion are discussed.

Introduction

Dyes incorporated within a polymer host are of great interest to photochemists and electrochemists.^{1,2} For example, the observation that electrodes modified with dye-containing polymer

films exhibit excellent catalytic² and photoelectrochemical³ properties has stimulated much recent activity in characterizing sensitized redox reactions in nonhomogeneous media. The importance of dyes in the direct conversion of light energy into electrical energy or chemical energy⁴ thus demands an investigation

(1) Farid, S.; Martic, P. A.; Daly, R. C.; Thompson, D. R.; Specht, D. P.; Hartman, S. E.; Williams, J. L. R. *Pure Appl. Chem.* **1979**, *51*, 241 and references cited therein.

(2) Kamat, P. V.; Fox, M. A. *J. Electroanal. Chem.*, **1983**, *159*, 49.

(3) Kamat, P. V.; Fox, M. A. *J. Am. Chem. Soc.*, **1984**, *106*, 1191.

(4) Gerischer, H.; Willig, F. In "Topics in Current Chemistry"; Springer-Verlag: West Berlin, 1976; Vol. 61, p 31.