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# Charge renormalization, osmotic pressure, and bulk modulus of colloidal crystals: Theory

S. Alexander,<sup>a)</sup> P. M. Chaikin, P. Grant, G. J. Morales, and P. Pincus<sup>b)</sup>

*Department of Physics,<sup>c)</sup> University of California, Los Angeles, California 90024*

D. Hone<sup>d)</sup>

*Department of Physics, University of California, Santa Barbara, California 93106*

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The interactions between charged colloidal particles with sufficient strength to cause crystallization are shown to be describable in terms of the usual Debye-Huckel approximation, but with a renormalized charge. The effective charge in general is smaller than the actual charge. We calculate the relationship between the actual charge and the renormalized charge by solving the Boltzmann-Poisson equation numerically in a spherical Wigner-Seitz cell. We then relate the numerical solutions and the effective charge to the osmotic pressure and the bulk modulus of the crystal. Our calculations also reveal that the renormalization of the added electrolyte concentration is negligible, so that the effective charge computations are useful even in the presence of salts.

## I. INTRODUCTION

During the last few years ordered monodisperse suspensions of latex particles have received increased attention because (1) they constitute an interesting model system for the study of solid state structural phenomena and (2) the coupling between the elastic rigidity of the ordered latex with the suspending fluid leads to unusual viscoelastic phenomena. More specifically the systems are often polystyrene spheres<sup>1,2</sup> or rod-like viruses<sup>3,4</sup> which are suspended in a solvent (usually, but not necessarily, water). The particles have typical dimensions in the range  $10^{-6}$ – $10^{-3}$  cm and have of the order of  $10^2$ – $10^4$  surface ionizable groups.

In low ionic strength solvents, the electrostatic repulsions between the macroions are sufficient to stabilize an ordered structure for interparticle separations of the order of  $1\ \mu$ . Such lattices are conveniently studied by Bragg scattering of visible light.<sup>5–8</sup> Optical techniques allow one to investigate melting as functions of temperature<sup>8</sup> and ionic strength<sup>2</sup>; structural (fcc–bcc) phase transition,<sup>8</sup> and defects such as dislocations and grain boundaries.<sup>9</sup> The shear modulus of the colloidal crystal has been investigated by high frequency torsional oscillation experiments<sup>10,11</sup> and propagating shear mode resonance methods<sup>12–14</sup> at low frequencies. The osmotic bulk modulus is measured directly by osmotic pressure. More recently colloidal glasses have been prepared<sup>14</sup> as well as two dimensional ordered lattices.<sup>15</sup>

The utility of colloids as a model system for solid state structural studies is based on the assumption that, at sufficiently low densities  $\phi \ll 1$  ( $\phi$  is the volume fraction of the sample occupied by macroions), the physics is dominated by electrostatic interactions. At low ionic strength, the colloidal suspension is a three component system: latex spheres (radi-

us  $a$ ,  $Z$  ionizable sites), small counterions (charge  $e$ ), and solvent (dielectric constant  $\epsilon$ ). At higher ionic strengths, additional Debye screening is provided by at least one further ion species. It is tempting to consider the interactions between particles separated by a distance  $r$  to be of the Yukawa form<sup>10</sup>:

$$V(r) = [(Ze)^2/\epsilon r]e^{-Kr}, \quad (\text{I.1})$$

where  $K$  is the inverse Debye screening length associated with the small ions (assumed monovalent for simplicity)

$$K^2 = 4\pi n e^2/\epsilon k_B T, \quad (\text{I.2})$$

where  $n$  is the concentration of the small screening ions. It is convenient to introduce the Bjerrum length  $\lambda$ :

$$\lambda = e^2/\epsilon k_B T \sim 7\ \text{\AA} \quad (\text{I.3})$$

which is the characteristic distance over which the Coulomb interaction for singly charged ions is comparable to the thermal energy.

We suggest that at low densities an effective interaction between macroions of the Yukawa form may be retained if the bare charge per particle  $Ze$  is replaced by a renormalized effective charge  $Z^*e$ . A simple argument for this charge renormalization may be obtained by considering a dilute suspension (concentration  $c$ ) of macroions. Each spherical macroion has  $Z$  surface ionizable groups. For simplicity we neglect any specific interactions arising from hydration effects, etc., and only treat explicit Coulombic forces, where the solvent is approximated by a medium of dielectric constant  $\epsilon$ . We assume that at large distances from the sphere the electrostatic potential has the Yukawa form [Eq. (I.1)] with  $Z$  replaced by  $Z^*$  and with the screening length  $K^{*-1}$  given by the corresponding counterions,

$$K^{*2} = 4\pi Z^* e^2 c/\epsilon k_B T. \quad (\text{I.4})$$

We now estimate the renormalized charge  $Z^*$ .

In the interstitial regions distant from any macroion surface, the electrostatic forces are weak and the counterion chemical potential is mainly associated with configurational

<sup>a)</sup> Permanent address: Department of Physics, Hebrew University, Jerusalem.

<sup>b)</sup> Permanent address: Exxon Research and Engineering Co., P.O. Box 45, Linden, N.J. 07036.

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entropy,

$$\mu_i \sim k_B T \ln(f), \quad (\text{I.5})$$

where  $f$  is the volume fraction occupied by counterions of volume  $v$ ,  $f \sim Z^* c v \ll 1$ . On the other hand, on the surface of a macroion sphere, the electrochemical potential  $\mu_s$ , principally arises from the electrostatic interaction between a counterion and the spherical surface charge,

$$\mu_s^* \sim -Z^* e^2 / \epsilon a = -k_B T (Z^* \lambda / a). \quad (\text{I.6})$$

Since exponential (or stronger) screening quickly reduces the potential from a large surface charge, we expect the maximum effective surface potential to be of the order of the potential  $\mu_1$ . Thus, equating Eqs. (I.6) and (I.5) we find

$$Z^* \lambda / a \sim -\ln(f). \quad (\text{I.7})$$

In the range of experimental parameters the logarithmic term is slowly varying and has a value of order 10, which yields a maximum effective charge of about 500 for 500 Å spheres. More physically, one may argue that if the electrostatic potential energy gained by a counterion in reassociating on the surface of a macroion exceeds thermal energies, it will bind and therefore renormalize downward the effective energy for subsequent counterions. This process will continue until the chemical equilibrium described by Eq. (I.7) obtains.

Experiment should be able to span the range from the bare charge regime ( $Z^*/Z \sim 1$ ) to the significant charge renormalization ( $Z^*/Z \ll 1$ ). Indeed Schaefer's conductometric titration experiments<sup>17</sup> provide some evidence for an incomplete ionization of the spheres and his numbers are consistent with our findings. Some justification for our approach is given by numerical solutions to the Boltzmann–Poisson equation which assume that the counterion distribution is determined by the average potential arising from the macroions and the other counterions; the Debye–Hückel (DH) approximation is a linearization of the Boltzmann–Poisson (BP) equation. Indeed Ohtsuki *et al.*<sup>11</sup> have numerically solved the BP equation in a Wigner–Seitz cell of the lattice and then calculated the shear modulus, which was compared to experiment.<sup>10,11</sup> Our point of view is that experimental determinations of the elastic moduli and osmotic pressure sufficiently fix the interactions (i.e., they determine  $Z^*$ ) so as to allow predictions for melting and structural transitions. Therefore, in order to test the adequacy of the BP or DH approximation, we calculate the osmotic pressure and bulk modulus of the ordered state, which may then be compared with experiment.

In Sec. II, we calculate the counterion distribution in a Wigner–Seitz cell as carried out by Ohtsuki *et al.*<sup>11</sup> for different ionic strengths. Within this model we show that the DH approximation can be used with a renormalized charge and we calculate  $Z^*$  as a function of  $Z$ . In Sec. III we use these results to determine the osmotic pressure and the bulk modulus. Some concluding remarks are made in Sec. IV.

## II. BOLTZMANN–POISSON IN A SPHERICAL WIGNER–SEITZ CELL

We consider the ordered state where the latex spheres are organized on a regular lattice, usually either bcc or fcc.<sup>8</sup>

For the fixed lattice of macroions the distribution of small counterions may be approximately determined by the mean field Boltzmann–Poisson (BP) equations.<sup>17</sup> For simplicity, at this point, we restrict our attention to zero salt concentration and monovalent small counterions. Then the BP equations are (in CGS units)

$$\begin{aligned} \operatorname{div} \mathbf{E}(r) &= (4\pi/\epsilon) \rho(r) = (4\pi/\epsilon) [\rho_m(r) + \rho_c(r)], \\ \mathbf{E}(r) &= -\operatorname{grad} \phi(r), \\ \rho_c(r) &= \rho_0 \exp[-e\phi\beta], \end{aligned} \quad (\text{II.1})$$

where  $\mathbf{E}(r)$  is the electric field at the position  $r$ ;  $\epsilon$  is the solvent dielectric constant;  $\phi(r)$  is the electrostatic potential;  $\beta = (k_B T)^{-1}$ ;  $e$  is the charge on a proton;  $\rho_m(r)$  is the macroion contribution associated with fixed lattice sites and  $\rho_c(r)$  is the counterion charge density which is determined by a Boltzmann distribution in the self-consistent potential  $\phi(r)$ . Combining Eqs. (II.1) yields the nonlinear BP equation

$$-\nabla^2 \phi(r) = \frac{4\pi}{\epsilon} \{ \rho_m(r) + \rho_0 \exp[-\beta e \phi(r)] \}, \quad (\text{II.2})$$

where  $\rho_0$  is a normalization constant which is determined by global charge neutrality. Because the solution of Eq. (II.2) must have the full lattice periodicity, it is only necessary to solve it in the appropriate Wigner–Seitz cell.<sup>18</sup> That is, we divide the volume of the crystal into cells surrounding each macroion (constructed by finding the smallest volume enclosed by planes which are the perpendicular bisectors of the vectors to all neighboring macroions). Since each cell is related to all others by translation by a linear combination of lattice vectors, a solution in one cell is sufficient to define the electrostatic potential and charge density for the entire lattice. As in lattice band theory, it is computationally an enormous simplification to replace the Wigner–Seitz polyhedron by a sphere of equal volume which, for example, for a bcc lattice has a radius  $R$  equal to about one-half the basic cube edge.

Once we have adopted a spherical Wigner–Seitz cell the idea of DH with a renormalized charge becomes clear. Due to the global neutrality of the system, the charge within the cell (macroion plus counterions and any additional electrolyte) must be zero. From Gauss's law the electric field at the surface of the sphere must be zero. We define the adjustable additive constant in the potential so that the potential is zero at the surface as well. Then integrating the electric field in from the surface we see that the potential increases slowly and remains small for some distance inward. As long as the potential remains smaller than the thermal energy, the linear expansion of the BP equation must be valid.

Although this proves that near the surface of the Wigner–Seitz sphere a DH solution is appropriate, it does not allow a determination of the coefficients which appear in the screened Coulomb potential. These must be calculated from the actual densities present. We suggest that since a renormalized DH is appropriate near the surface of the Wigner–Seitz cell, it is also the appropriate description for all interactions which occur outside the unit cell.

Fixing a latex particle carrying a surface charge  $Z$  at the center of the Wigner–Seitz sphere, the neutralizing counter-

ion distribution in the spherical cell is given by

$$\nabla^2 \phi(r) = (4\pi Ze/\epsilon) \exp[-\beta e \phi(r)] / \left\{ \int_a^R \exp[-\beta e \phi(r)] 4\pi r'^2 dr' \right\}. \quad (\text{II.3})$$

Taking advantage of the spherical symmetry, we may readily transform Eq. (II.3) by Gauss' Law to an integral equation in terms of dimensionless variables,

$$\frac{-x^2 \mathcal{E}'(x)}{Z} = \frac{\int_{a/\lambda}^x x'^2 \exp\left[\int_{a/\lambda}^{x'} \mathcal{E}(x'') dx''\right] dx'}{\int_{a/\lambda}^{R/\lambda} x' \exp\left[\int_{a/\lambda}^{x'} \mathcal{E}(x'') dx''\right] dx'} - 1, \quad (\text{II.4})$$

where  $x = r/\lambda$  and  $\mathcal{E}(x) = e\beta\lambda E(x)$  and  $\lambda$  is again the Bjerrum length. The counterion distribution is given from Eqs. (II.1) by

$$\rho_c(r) = (Z/4\pi\lambda^3) \frac{\exp\left[\int_{a/\lambda}^{r/\lambda} \mathcal{E}(x) dx\right]}{\int_{a/\lambda}^{R/\lambda} x^2 \exp\left[\int_{a/\lambda}^x \mathcal{E}(x') dx'\right] dx}. \quad (\text{II.5})$$

The electric field and counterion distributions are easily determined by numerically iterating Eq. (II.4). Note (i) that symmetry and charge neutrality require  $E(R) = 0$ ; (ii)  $E(a) = -Ze/ea^2$ . In Fig. 1 the counterion charge density calculated from Eqs. (II.4) and (II.5) is compared with a solution of the linearized Boltzmann–Poisson equation with the same charge on the macroion in the Wigner–Seitz sphere. The two sets of curves are quite similar, largely due to conditions (i) and (ii) above.

However, there is a significant quantitative difference in the value of the charge density at the WS cell boundary, which becomes considerably more substantial as the total charge in the cell increases. Since this density is what determines the range of the interaction [the DH screening length from Eq. (II.1)] as well as physically observable quantities such as the osmotic pressure and the bulk modulus (which depend on derivatives of the potential and hence on the char-

acteristic range of the potential), we suggest that a better representation of the interaction in terms of a DH approximation is one in which the correct density at the cell surface is used. As discussed above, it is only in the region of this surface that the DH solution is necessarily valid.

The potential which solves the DH equation in spherical geometry is

$$\phi = [A \exp(-Kr) + B \exp(Kr)]/r + D. \quad (\text{II.6})$$

As the best approximation for the potential at large distances we choose the coefficients so that the potential and the electric field are zero at the cell surface, and the density which is calculated from the BP equation is equal to the density from Eq. (II.6) at the surface. The effective charge ( $Z^*$ ) which characterizes our solution is then determined by integrating the charge density in Eq. (II.6) from  $R$  to  $a$ , or equivalently, by evaluating the electric field at  $a$  and multiplying by  $a^2/e$ . The actual charge density at the surface is always less than what would be obtained in the usual DH (as the screening is more effective in BP) so that the charge in our solution ( $Z^*$ ) is always less than the actual charge  $Z$ .

In Fig. 2 we show the charge distribution for the exact solution to the BP equations, the DH approximation using the total charge as equal to the actual charge and the DH approximation using the recipe above to obtain the renormalized charge. The latter method gives a potential which matches the actual potential at the surface up to its third derivative [since  $\nabla(\nabla^2 \phi) = \nabla(\rho) = -\rho_0 \beta \phi$  for both DH and BP]. The usual DH only matches to the first derivative.

The exact solution to the BP equation can be numerically obtained for any geometry by setting boundary conditions, assuming an initial charge distribution, calculating the potential, recalculating the distribution using Boltzmann statistics, and iterating the process until it converges. For the case of the spherical WS well the calculation is considerably easier requiring a single numerical integral.  $E$  and  $\phi$  and the total integrated charge are 0 at  $R$ . A density at the surface is chosen and this determines the total charge inside a sphere an incremental radius smaller. From this one has the electric field and the potential and hence the charge density at the

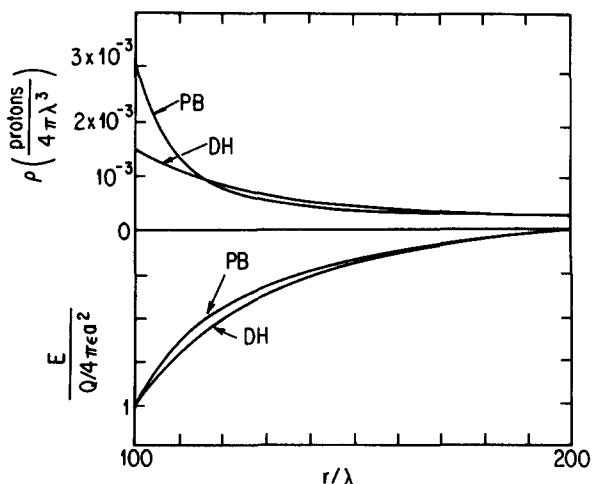


FIG. 1. Debye–Hückel and Boltzmann–Poisson solutions for the charge distribution and electric field in a sphere.

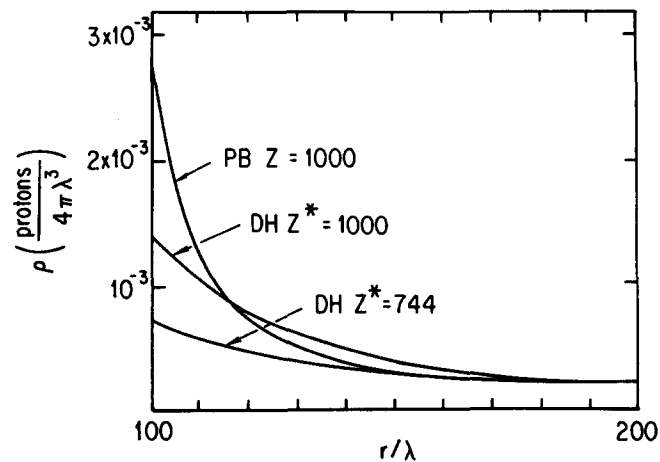


FIG. 2. BP and DH solutions for the charge distribution in a sphere. The bottom curve is the best DH approximation to the BP solution and serves to define the effective charge.

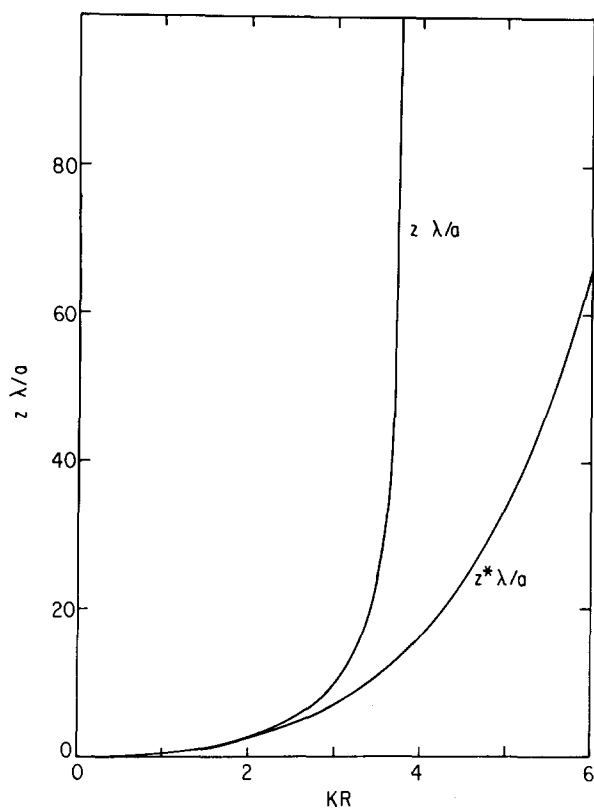


FIG. 3. Actual charge and effective charge as a function of the counterion density at the surface of the Wigner-Seitz cell. Note that there is a maximum surface density possible with a finite actual charge.

smaller radius. The process is repeated as follows:

$$Q(r) = Q(r + dr) + 4\pi r^2 dr \rho(r),$$

$$E(r) = Q(r)/4\pi r^2,$$

$$\phi(r) = E(r)dr + \phi(r + dr),$$

$$\rho(r) = \rho_0 \exp(-e\phi/k_b T).$$

Here  $Q(r)$  is the total charge up to radius  $r$ . In practice this latter method leads to no convergence problems and more rapid computer calculations, although both methods were used.

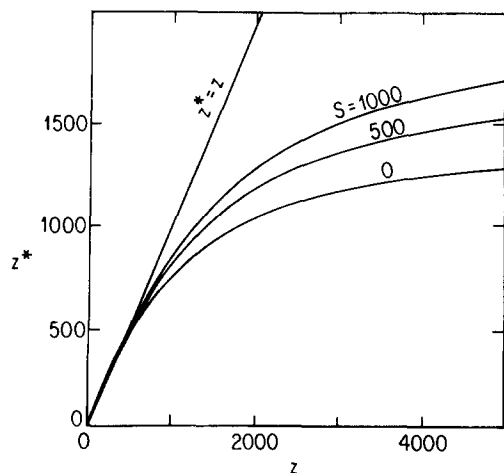


FIG. 4. Effective charge as a function of actual charge for several values of added electrolyte.  $S$  is the number of ion pairs per macroion.

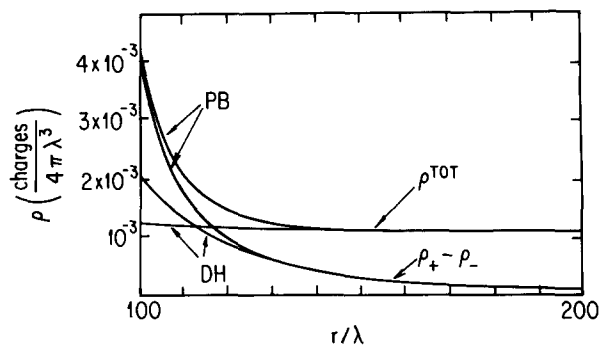


FIG. 5. Distribution of charge ( $\rho_+ - \rho_-$ ) and number of ions ( $\rho_+ + \rho_-$ ) for the DH and BP solutions.

The charge density at the cell boundary, which is of primary importance in our calculations, is a very weak function of the macroion charge due to the strong screening. Conversely, the effective charge and the actual charge are very strong functions of the density at the cell boundary. This is illustrated in Fig. 3 which shows  $Z$  and  $Z^*$  as a function of  $KR$ . For low densities both  $Z$  and  $Z^*$  are smooth functions of  $\rho(R)$  and are approximately equal. The usual DH is reasonable. At larger densities  $Z$  diverges, indicating that for a real system there is a maximum for  $\rho(R)$ . Increasing  $Z$  has negligible effect on  $\rho(R)$ . The excess counterion charge is contained in the highly nonlinear region at radii near that of the macroion. This is the origin of the saturation of  $Z^*$ .

In Fig. 4 we show the effective charge  $Z^*$  vs the actual charge  $Z$  for a macroion of radius  $a = 100\lambda$  in a WS cell of radius  $R = 200\lambda$  (corresponding to a volume fraction of 12.5% macroion). At low charge  $Z$  and  $Z^*$  agree very well, as the DH approximation is good throughout the cell. For actual charge  $\sim 1000e$ , the renormalization is substantial, while for larger values of  $Z$  the effective charge shows saturation toward a value of  $\sim 1500e$ . As previously suggested, this maximum effective charge is about  $15a/\lambda$  [see Eq. (I.7)].

We now consider the situation in which electrolyte is added. The iterative or integral solutions for the BP equation are still readily obtained, and we continue to match the DH solution to the "exact" BP solution to third derivative at the WS cell boundary. In Fig. 5 we show the charge distribution

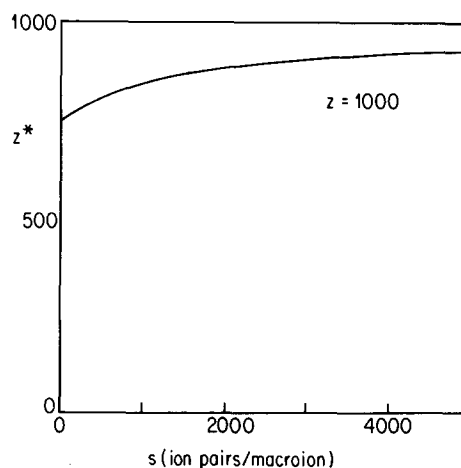


FIG. 6. Dependence of  $Z^*$  on added electrolyte for a fixed actual charge.

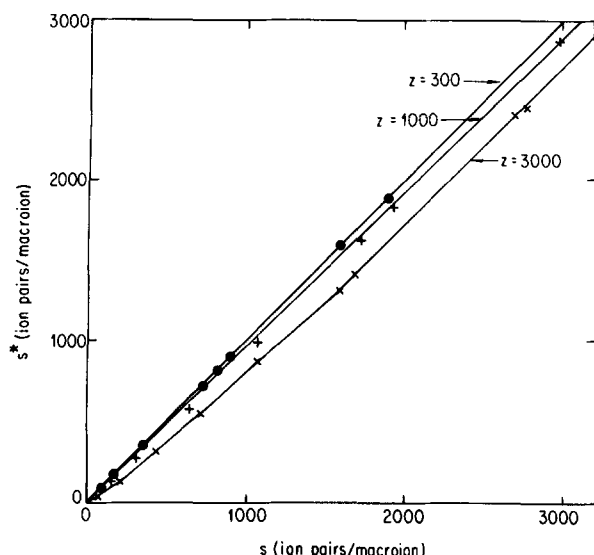


FIG. 7. Effective salt concentration vs actual salt concentration for typical values of the actual charge.

( $\rho = \rho_+ - \rho_-$ ) and the “total” ion density ( $\rho_t = \rho_+ + \rho_-$ ) from the BP solution and from the DH solution. Note that the two forms are virtually identical over most of the cell.

With additional electrolyte there are two parameters which are needed to characterize the DH solution, an effective charge and an effective electrolyte concentration. In the first instance we are interested in whether the curve in Fig. 4 for  $Z^*$  as a function of  $Z$  is significantly changed in the presence of electrolyte. The additional curves in Fig. 4 show that  $Z^*$  is only slightly changed as a substantial amount of electrolyte is added. This is more readily observed in Fig. 6, where the actual charge  $Z$  is fixed and  $Z^*$  is calculated as a function of the electrolyte concentration. For ionic strength up to five times that of the counterions,  $Z^*$  changes by approximately 10%.

The problem with naively using this result for calculating the interaction potential is that the effective salt concentration also changes as the actual salt concentration is changed. Our calculations, as illustrated in Fig. 7, indicate that in the range of interest the renormalization of the salt concentration is a minor effect and for all but the most accurate computations it seems reasonable to use the bare salt concentration. The largest corrections to the effective salt concentration come when the number of counterion charges in solution is several times the added electrolyte concentration. In this case the screening is largely due to counterions and the salt concentration renormalization has little effect on the final interaction.

### III. OSMOTIC PRESSURE AND BULK MODULUS

The osmotic pressure  $\pi$  may be calculated from the free energy  $F$  by the thermodynamic relation

$$\pi = - \left( \frac{\partial F}{\partial V} \right)_N, \quad (\text{III.1})$$

i.e., the change in free energy with volume at fixed number of macroions. In any macroscopic volume Donnan equilibrium<sup>19</sup> assures global charge neutrality and therefore, by sym-

metry, charge neutrality of each Wigner-Seitz cell. Thus the cellular solutions of the last section may be used to yield

$$\pi = - (4\pi R^2)^{-1} \left( \frac{\partial f}{\partial R} \right)_N, \quad (\text{III.2})$$

where  $f$  is the free energy of a Wigner-Seitz sphere. The partition function for the  $Z$  counterions is  $z^Z$  in the canonical ensemble where

$$z = 4\pi \int_a^R \exp[-\beta e\phi] r^2 dr. \quad (\text{III.3})$$

The entropy  $S$  associated with the translational disorder of the counterions is then

$$S + \frac{\partial}{\partial T} (Z k_B T \ln z) \quad (\text{III.4})$$

which using Eq. (II.1) becomes

$$S = k_B Z \ln z + \frac{e}{T} \int \rho(r) \phi(r) dr. \quad (\text{III.5})$$

Then, constructing the free energy of the Wigner-Seitz sphere, we find

$$f = (2\pi e) \int_0^R \phi [\rho_c - (Z/4\pi a^2) \delta(r-a)] r^2 dr - TS, \quad (\text{III.6})$$

where the first term is the Coulomb interaction energy and the entropic contribution  $-TS$  is obtained from Eq. (III.5). Combining Eqs. (III.5) and (III.6), the free energy becomes

$$f = k_B T Z \ln z - (e/2) \int \rho_c \phi dr - (Ze/2) \phi(a). \quad (\text{III.7})$$

Using this expression in Eq. (III.2), we immediately derive a simple expression for the osmotic pressure

$$\pi = k_B T \rho_c(R), \quad (\text{III.8})$$

i.e., because the electric field is zero on the surface of the Wigner-Seitz sphere, only the kinetic terms contribute. Of course, the counterion density  $\rho_c(R)$  involves the self-consistent screening of the macroions by the counterions and is obtained from the BP calculations of Sec. II.

The bulk osmotic modulus  $B$  (the inverse of the osmotic compressibility) is given by

$$B = - V \left( \frac{\partial \pi}{\partial V} \right)_N \quad (\text{III.9})$$

or using Eq. (III.8),

$$B = - \frac{1}{3} k_B T R \frac{\partial \rho_c(R)}{\partial R}. \quad (\text{III.10})$$

### IV. CONCLUSIONS

The main purpose of this paper is to demonstrate that the interaction between charged colloidal particles retains a Yukawa form even when the charge on the particle produces a surface potential which is considerably larger than thermal energies. The exponential screening inherent in the Boltzmann distribution implies that strong potentials are strongly screened by a buildup of counterion charge at small radii. Coupled with the requirement of global charge neutrality, we demonstrated that the Boltzmann-Poisson equation

must have a Debye–Huckel like solution in the region near the Wigner–Seitz cell boundary (as long as a spherical Wigner–Seitz cell is a good approximation to the actual cell—usually an excellent approximation). The effective charge which characterizes the DH solution differs from the actual charge on the colloidal particle. We calculated the relationship between  $Z^*$  and  $Z$  by numerically solving the BP equation and found that  $Z^*$  tended to saturate at a value such that the surface potential at the particle was  $\sim 10k_B T$ , as had previously been suggested. Our calculations also show that any added salt concentration is not strongly renormalized.

We therefore feel that the interactions between colloidal particles and thus most of the physical properties of colloidal crystals can be characterized by knowing the effective charge on an individual particle (which depends somewhat on the size of a unit cell). The particle effective charge can be obtained from the curves such as those shown in Fig. 4 if the actual charge is known, or it may be experimentally determined from a single measurement such as osmotic pressure or bulk or shear modulus. Such measurements will determine a  $Z^*$  similar to what would be determined by conductivity or electrophoresis only for low  $Z$  or  $Z^*$ . As the difference between  $Z$  and  $Z^*$  increases the latter two measurements will differ from elastic constant measurements. The DH approximation with this renormalized charge describes the actual potential up to its third derivative in the neighborhood of the cell boundary and thus should suffice for most of the interesting properties.

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- <sup>17</sup>D. W. Schaefer, *J. Chem. Phys.* **66**, 3980 (1977).
- <sup>18</sup>See for example C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963), Chap. 13.
- <sup>19</sup>C. Tanford, *Physical Chemistry of Macromolecules* (Wiley, New York, 1961), p. 225.