ELECTRICAL ENERGY OF TWO CYLINDRICAL CHARGED PARTICLES

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ABSTRACT. Using the approximate Debye-Hückel theory, an expression for the electrical energy of two cylindrical charged particles has been worked out. This energy is found to exhibit a minimum for a certain value of the interparticle distance and may be of importance in explaining thixotropic properties.

It is well known that colloidal systems, exhibiting thixotropic phenomena, generally consist of non-spherical particles. They are rod-shaped in the thixotropic sols of vanadium pentoxide, disc-like in the sols of iron-oxide and paste of clay. A general mathematical theory of the mutual interaction energy between two spherical colloidal particles and its applications to general problems of stability of colloidal sols has been developed by the author (Dube, 1940) and has proved to be quite successful in explaining several phenomena. The same procedure has been adopted in finding out the electrical energy of two cylindrical charged particles immersed in water containing a known electrolyte.

Let us consider two parallel cylindrical particles of circular cross-section, radius a, with distance R apart and having surface charge density σ. They are immersed in water containing a known electrolyte. We are required first to find out the electrical potential at any point in the dispersion medium. The electrical potential ψ is assumed to be given by the approximate Debye-Hückel equation in the theory of strong electrolytes,

$$\nabla^2\psi = k^2\psi \qquad \dots \quad (1)$$

where ∇^2 is the Laplacian operator and k is the characteristic quantity occurring in Debye-Hückel theory. $1/k$ is called Debye distance and is expressed in terms of the ionic strength J by the relation

$$\frac{1}{k} = 2.81 \times 10^{-10}\left(\frac{DT}{2J}\right)^{\frac{1}{2}} \text{ cms.} \qquad \dots \quad (2)$$

It is extremely difficult to solve this equation in the two-particle case considered here. Hence to get the qualitative features of the result, we suppose a linear superposition of the two potentials, which is equivalent to the supposition that if the two particles approach one another, the distribution of charge on their surfaces and in their ionic atmospheres remains undistorted.

N.B.—On the suggestion of Prof. J. D. Bernal, F.R.S., a similar problem was being tackled by Mr. S. Levine of Toronto, but due to communication difficulties, his result could not be ascertained.

Let ψ_1, ρ_1 be the potential and charge density in the ionic atmosphere of one of the particles and ψ_2, ρ_2 be the corresponding quantities for the second particle. The energy required to bring one of the particles along with its ionic atmosphere into the electrical field of the other is now

$$F=\frac{1}{2}\int_V \rho_1\psi_2 dv+\int_{S_1}\sigma\psi_2 dS_1 \qquad \ldots \quad (3)$$

where S_1 is the surface area of the first particle and V is the total volume of the medium excluding the volume occupied by the two particles.

Solution for a single particle.—The potentials ψ_1, ψ_2 separately satisfy the equation (1) which in cylindrical co-ordinates becomes

$$\frac{\partial^2\psi}{\partial r^2}+\frac{1}{r}\frac{\partial\psi}{\partial r}+\frac{1}{r^2}\frac{\partial^2\psi}{\partial\theta^2}+\frac{\partial^2\psi}{\partial z^2}-k^2\psi=0.$$

Let us assume axial symmetry and confine ourselves to the plane $z=0$. Then this becomes

$$\frac{\partial^2\psi}{\partial r^2}+\frac{1}{r}\frac{\partial\psi}{\partial r}-k^2\psi=0.$$

The solution* of this will be

$$\psi=A'J_0(ikr)+B'Y_0(ikr)$$

where J_0 and Y_0 are Bessel functions of order zero (Watson, 1922). Since ψ must vanish when r tends to infinity, we have

$$\psi=AK_0(kr) \qquad \ldots \quad (4)$$

where A is a constant quantity to be determined by the boundary conditions

$$-\frac{D}{4\pi}\left(\frac{\partial\psi}{\partial r}\right)_{r=a}=\sigma, \qquad \ldots \quad (5)$$

D being the dielectric constant of the dispersion medium. Thus

$$-\frac{D}{4\pi}A\frac{\partial}{\partial r}\left\{K_0(kr)\right\}=\sigma, \quad \text{or} \quad \frac{D}{4\pi}Ak.K_1(ka)=\sigma, \quad \text{or} \quad A=\frac{4\pi\sigma}{Dk.K_1(\tau)} \qquad \ldots \quad (6)$$

where $\tau=ka$ is a dimensionless quantity. Thus the required solution becomes

$$\psi=\frac{4\pi\sigma}{Dk.K_1(\tau)}.K_0(kr). \qquad \ldots \quad (7)$$

The zeta or electrokinetic potential is then given by

$$\zeta=\frac{4\pi\sigma}{Dk}.\frac{K_0(\tau)}{K_1(\tau)}. \qquad \ldots \quad (8)$$

Evaluation of the integrals in (3).—Considering unit length of the particle

$$I'=\int_{S_1}\sigma\psi_2 dS_1=\frac{4\pi\sigma^2 a}{Dk.K_1(\tau)}.\int_0^{2\pi}K_0(kr_2)\,d\theta_1.$$

* In the case $k=0$, the solution is $\psi=c_1+c_2\ln r$.

Now $$K_0(kr_2)=\sum_{m=-\infty}^{\infty} K_m(kR).I_m(kr_1).\cos m\theta_1 \quad \text{for } r_1 < R$$

$$=\sum_{m=-\infty}^{\infty} K_m(kr_1).I_m(kR) \cos m\theta_1 \quad \text{for } r_1 > R.$$

Hence $$\int_0^{2\pi} K_0(kr_2)\,d\theta_1=\int_0^{2\pi}\sum_{m=\infty}^{+\infty} K_m(kR).\ I_m(ka).\ \cos m\theta_1 d\theta_1$$

which is different from zero only when $m=0$ and then its value is

$$2\pi K_0(kR) I_0(\tau).$$

Therefore we have

$$P=\frac{8\pi^2\sigma^2 a}{Dk}.\ \frac{I_0(\tau)}{K_1(\tau)}.\ K_0(s\tau) \qquad \ldots (9)$$

where $$R=sa.$$

The other integral is

$$Q=\tfrac{1}{2}\int_v \rho_1\psi_2 dv=-\frac{Dk^2}{8\pi}\int_v \psi_1\psi_2 dv=-\frac{2\pi\sigma^2}{DK_1^2(\tau)}\int_v K_0(kr_1)K_0(kr_2)dv.$$

The integrand can be expressed as a function of (r_1,θ_1) only and then using $Kr_1=u$ and simplifying, the integral can be shown to be

$$-\frac{4\pi^2\sigma^2}{Dk^2K_1^2(\tau)}\left[\left(\int_0^{s\tau}-2\int_0^{\tau}\right)K_0(s\tau)K_0(u).I_0(u)u.du+\int_{s\tau}^{\infty} I_0(s\tau).K_0^2(u).udu\right]$$

Therefore,

$$Q=-\frac{4\pi^2\sigma^2}{Dk^2K_1^2(\tau)}\left[K_0(s\tau)\{L(s\tau)+L(0)-2L(\tau)\}+I_0(s\tau)\{J(\infty)-J(s\tau)\}\right]$$

where $$J(u)=\int uK_0^2(u)du=\frac{u^2}{2}[K_0^2(u)-K_1^2(u)]$$

$$L(u)=\int K_0(u)I_0(u)udu=\frac{u^2}{2}[I_0(u)K_0(u)+I_1(u)K_1(u)].$$

For small values of u,

$$K_0(u)\simeq ln\frac{2}{\gamma u}\ ;\ K_1(u)\simeq\frac{1}{u};\ I_0(u)=1,\ I_1(u)\simeq\frac{u}{2}$$

where γ= Euler's constant.

Hence it is easy to verify that

$$L(0)=0\ ;\ J(\infty)=0.$$

Therefore,

$$Q=-\frac{4\pi^2\sigma^2}{Dk^2K_1^2(\tau)}\{K_0(s\tau)L(s\tau)-I_0(s\tau)J(s\tau-2K_0(s\tau)L(\tau)\}.$$

Now $K_0(s\tau)L(s\tau)-I_0(s\tau)J(s\tau)=\frac{s^2\tau^2}{2}K_1(s\tau)\{K_0(s\tau)I_1(s\tau)+I_0(s\tau)K_1(s\tau)\}$

$$=\frac{s\tau}{2}K_1(s\tau).$$

Thus

$$Q=-\frac{2\pi^2\sigma^2\tau}{Dk^2K_1^2(\tau)}[s.K_1(s\tau)-2\tau K_0(s\tau)\{I_0(\tau)K_0(\tau)+I_1(\tau)K_1(\tau)\}]. \quad \dots \quad (10)$$

Combining (9) and (10) and defining

$$\phi(\tau)=2\tau^2\{I_0(\tau)K_2(\tau)+I_1(\tau)K_1(\tau)\} \quad \dots \quad (11)$$

we have

$$F=\frac{2\pi^2\sigma^2}{Dk^2K_1^2(\tau)}\cdot[K_0(s\tau)\phi(\tau)-s\tau K_1(s\tau)]$$

$$=\frac{D\zeta^2}{8}\cdot\frac{1}{K_0^2(\tau)}[K_0(s\tau)\phi(\tau)-s\tau K_1(s\tau)]. \quad \dots \quad (12)$$

This has a minimum value at a certain value of s, which is given by

$$\frac{\delta F}{\delta s}=0$$

or

$$\phi(\tau)=\frac{s\tau K_0(s\tau)}{K_1(s\tau)}. \quad \dots \quad (13)$$

This equation can be solved by numerical methods and the results are

τ = 0.1	0.5	1.0	1.5	2.0	2.5	3.0
s_m = 44.26	9.35	5.35	4.00	3.43	3.11	2.91

Then taking $\zeta=10^{-4}$ e.s.u, D=80, length of the particle $=10^{-4}$ cm. and $kT=4\times10^{-14}$, the values of F_{min}/kT are found to be 0.26, 1.4, 3.2, 7.3, 9.0, 11.3, 13.5 respectively.

The existence of an electrical energy minimum as a function of interparticle distance may be of considerable importance in explaining the thixotropic properties of non-spherical particles. The van der Waals energy must also be considered in a more rigorous treatment of the problem. Unfortunately, due to integration difficulties (Dube and Dasgupta, 1939), it has not yet been possible fo find an expression for the van der Waals energy between two cylindrical particles.

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