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SOLVATION FORCES AND THE ELECTRICAL DOUBLE LAYER

G. RICKAYZEN

Physics Laboratory
The University of Canterbury
Kent CT2 7NR
UK

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Solvation Forces and the Electrical Double Layer

G. Rickayzen

The Physics Laboratory, The University, Canterbury, Kent, England

In these lectures, I am going to survey some aspects of the role of liquid structure in determining the forces between solids immersed in ~~the~~ liquids. This is a problem of particular importance for understanding the stability of colloids, especially sols. Sols comprise of solid particles dispersed through a liquid medium. Although the particles are large compared with the ~~size of the~~ liquid molecules they are still microscopic and their surfaces play an important part in their behaviour.

Seen from a distance these particles are usually neutral and the dominant long range force between them is ~~the long~~ the van der Waals attraction. This force arises from the polarisability of the particles and of the medium between. Because of this polarisability and of the long range of the interaction of the dipoles the ~~whole system~~ polarisation of the whole system has normal modes ~~which depend~~ whose frequencies depend on the separation of the particles. The zero point energies of these oscillations contribute to the total energy of the system and since the zero point energies are lower the closer the particles, this gives rise to an attraction between the particles. For separations, r, large compared with their size (but not so large that retardation effects become important), the potential energy of interaction is of the form

$$V = -\lambda/r^6 ,$$

where λ is a quantity which depends on the dynamic polarisabilities of the particles and of the liquid. On the other hand, for separations small compared with their size

the particles can be treated as thick flate plates (see below). In this case the interaction energy is

$$V = -\frac{A}{12\pi r^2}$$

where A depends on the polarisablities and is known as Hamaker's constant for the system. There is an extensive theory of Hamaker constants which we do not have time to explore.

Since this force is attractive, it will tend to bring the suspended particles together into a coagulate. However, many sols have very long lives and appear to be stable. Thus this attractive force must be opposed by a shorter ranged repulsive force which prevents coagulation. In electrolytes this force is believed to be an electrostatic force due to electrical double layers surrounding the colloidal particles. In electrolytes, the solid particles acquire a net charge which the surrounding ions in the liquid will tend to neutralise. However because of their finite size and kinetic energy there will be some separation of ~~charge between~~ the net charge on the particle from the net charge in the fluid. This is the electrical double layer. When two such layers approach each other, like charges ~~will~~ in the liquid will come closest together and this will cause a repulsion which opposes co-agulation. These lectures are concerned with the calculation of this repulsion according to the classical DLVO theory and to recent modifications of this work.

Throughout these lectures we shall for simplicity ~~assume~~ consider only the forces between two deformable flat plates separated by a distance h. As Derjaguin has shown the force between two large spherical particles of radius R and separation $h (\ll R)$ can be obtained from that between two plates. In fact if $V(h)$ is the potential between the plates, the forces between the spheres is

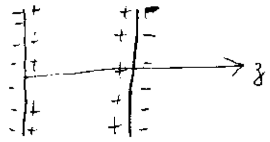
$$F(h) = \pi R V(h) .$$

Thus the problem of flat plates is of practical importance. One important consequence of the classical theory (below) is the existence of a critical concentration of electrolyte, ρ_c, below which the colloid is stable. In the theory ρ_{0c} satisfies the Schulze - Hardy rule

$$\rho_{0c} \propto T^5/Z^6$$

where T is the temperature and Z the valency of the ions. This rule appears to be in reasonable agreement with experiment although it has not been very severely tested.

Gouy – Chapman Theory of The Electrical Double Layer



For simplicity we consider the case of equally charged surfaces. In the theory of Gouy and Chapman (GC) one treats the solution as a medium of dielectric constant ε_r in which the ions sit. If there are different kinds of ion of charge e_i and number density $\rho_i(z)$ at position z, there is an electrostatic potential $V(z)$ which satisfies the Poisson-Equation

$$\nabla^2 V = - \sum_i e_i\rho_i(z)/\varepsilon_0\varepsilon_r \qquad (1)$$

Now at low density the ions can be treated as independent and in a potential $V(z)$ each ion has an energy $e_i V(z)$. The number of ions at a particular point is then given by the Boltzmann distribution

$$\rho_i(z) = \rho_{0i} \exp[-\beta e_i V(z)] \qquad (2)$$

~~The total charge of ions i per unit area of each kind of ion between the plates is then~~

~~$Q_i = e_i\int dz\, \rho_i(z) = e_i\rho_{0i}\int \exp[-\beta e_i V(z)]\, dz$.~~ (3)

~~The ratio of the Q_i's is determined by the valencies of the ions and dissociation rates of many salts, the absolute values of the Q_i is determined by overall charge neutrality~~

~~$\sum_i Q_i = 2Q$~~ (4)

~~where Q is the charge / unit area on one plate. Equations (1) to (4) determine the problem completely. For example for~~

where ρ_{0i} is the number density in the bulk ($V(z)=0$) of the species i.

For a given surface charge density, Q, on each plate the potential is fixed by the condition of overall charge neutrality

$$\sum_i e_i \int \rho_i(z)\,dz = -2\Phi \qquad (3)$$

Given the densities ρ_{0i}, equations (1) to (3) are sufficient to determine $V(z)$ completely. Since the bulk is neutral these densities satisfy

$$\sum e_i \rho_{0i} = 0. \qquad (4)$$

We consider two special cases

Case I $\quad \beta e_i V(z) \ll 1$, all i.

This is the dilute limit and leads to Debye-Huckel theory. If equation (2) is used in (1) we have

$$\frac{d^2V(z)}{dz^2} = -\sum e_i \rho_{0i} \exp[-\beta e_i V(z)]/\varepsilon_0\varepsilon_r \qquad (5)$$

Because of the assumption of a weak potential, the exponents can be expanded and we keep only the first order terms in $V(z)$. The zeroth order terms vanish because of equation (4). Thus

$$\frac{d^2V(z)}{dz^2} = \frac{\sum e_i^2 \rho_{0i} \beta V(z)}{\varepsilon_0\varepsilon_r} = \frac{V(z)}{\lambda^2} \qquad (6)$$

where λ is the Debye length defined by

$$\lambda^{-2} = \kappa^2 = \beta \sum e_i^2 \rho_{0i}/\varepsilon_0\varepsilon_r, \quad \lambda > 0 \qquad (7)$$

If the plates are placed at $z = \pm h/2$ so that their separation is h we require the solution of (6) which is symmetrical about the origin. This is

$$V(z) = A \cosh z/\lambda \qquad (8)$$

The field at any point in the fluid is

$$E(z) = -\frac{\partial V}{\partial z} = -\frac{A}{\lambda} \sinh z/\lambda \qquad (9)$$

But just outside the lefthand plate the field is

$$E(h/2) = \frac{\Phi}{\varepsilon_0\varepsilon_r} = \frac{A}{\lambda} \sinh h/2\lambda, \qquad (10)$$

whence

$$A = \lambda\Phi/\varepsilon_0\varepsilon_r \sinh h/2\lambda \qquad (11)$$

$$V(z) = \lambda\Phi \cosh z/\lambda \,/\, \varepsilon_0\varepsilon_r \sinh h/2\lambda \qquad (12)$$

This solution automatically conserves charge. The Debye length is the parameter which characterises the distance over which the potential (and hence the ion densities) tend to vary.

The energy in the system, Ω is the energy required to charge the plates to charge Φ from zero. This is

$$\Omega[\Phi] = 2\int_0^{\Phi} V(\Phi')\,d\Phi' \qquad (13)$$

where $V(\Phi')$ is the potential of a plate when the charge is Φ'. Since $V(\Phi)$ is proportional to Φ this becomes

$$\Omega[\Phi] = V(\Phi)\Phi$$

$$= (\lambda\Phi^2/\varepsilon_0\varepsilon_r)\coth(h/2\lambda)$$

This is the potential energy from which the force can be obtained at constant charge on the plates. For the more common case of constant potential on the plates one must use the function $\mathcal{F}[V]$ related to $\Omega[\Phi]$ by ~~the~~ a Legendre transformation [Grimson & Rickayzen, 1981],

$$\mathcal{F}[V] = \Omega[\Phi] - 2V_0\Phi$$

$$= -\frac{\varepsilon_0\varepsilon_r V_0^2}{\lambda} \tanh(h/2\lambda) \qquad \cancel{(14)}$$

where V_0 is the potential on a plate,

$$V_0 = (\lambda\Phi/\varepsilon_0\varepsilon_r)\coth(h/2\lambda). \qquad (14)$$

Measured relative to the potential energy when the separation is infinite,

$$\mathcal{F}[V] = \frac{\varepsilon_0\varepsilon_r V_0^2}{\lambda}\left[1 - \tanh(h/2\lambda)\right]. \qquad (15)$$

This is positive so the plates tend to repel each other — not surprising as we are trying to bring like charges close together. The force of repulsion when V_0 is held fixed is

$$f_V(h) = -\frac{\partial\mathcal{F}}{\partial h} = \frac{\varepsilon_0\varepsilon_r V_0^2}{2\lambda^2}\operatorname{sech}^2 h/2\lambda. \qquad (16)$$

As $R \to \infty$ this becomes $(2\varepsilon_0\varepsilon_r V_0^2/\lambda^2)\exp(-R/\lambda)$ and decays exponentially with decay length λ.

A useful estimate of the size of λ is that at $T = 298\,K$, $\varepsilon_r = 78$ and a 1-1 electrolyte of 0.5M $\lambda = 4\,Å$. Note that $\lambda \propto \rho_0^{-1/2}$. For $\lambda \sim 4\,Å$ one would certainly expect to take account of solvent structure. We discuss this case further after considering the Gouy-Chapman theory.

Case II z-z electrolyte

In this case there are two ions with $e_1 = -e_2 = ze$, e the charge on an electron and $\rho_{01} = \rho_{02} = \rho_0/2$. Equations (1) and (2) then yield

$$\frac{d^2V}{dz^2} = -\frac{ze\rho_0}{2\varepsilon_0\varepsilon_r}\left\{\exp(-\beta zeV) - \exp(\beta zeV)\right\}$$

$$= \frac{ze\rho_0}{\varepsilon_0\varepsilon_r}\sinh(\beta zeV) \qquad (17)$$

Hence

$$\frac{1}{2}\frac{d}{dV}\left(\frac{dV}{dx}\right)^2 = \frac{ze\rho_0}{\varepsilon_0\varepsilon_r}\sinh[\beta zeV]$$

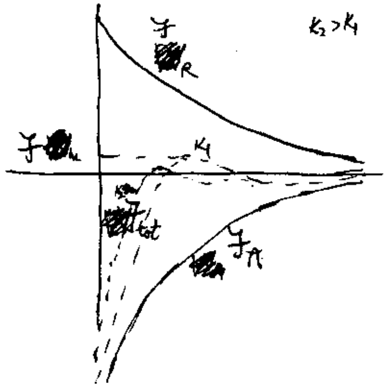
which can be integrated to

$$\left(\frac{dV}{dx}\right)^2 = \frac{2\rho_0}{\beta\varepsilon_0\varepsilon_r}[\cosh\beta zeV - \cosh\beta zeV_0] \qquad (18)$$

where $V = V_0$ when $\frac{dV}{dx} = 0$, at the mid point between the plates. Equation (18) can be integrated further in terms of elliptic integrals. This is useful for computational purposes but it does not alter the qualitative results. [redacted] We have no time to develop this analysis further here. We note that for infinite separation of the plates $V_0 = 0$ and (18) can be integrated in terms of elementary functions. When [redacted] $\beta zeV \ll 1$, the cosh functions can be expanded to second order in V and this leads to the Debye-Huckel theory. (cf Tozi's lectures)

Conditions for coagulation

The interaction between two plates is now made up of two parts, a repulsion, arising from the Coulomb interaction of the charges which decays exponentially at large separations and tends to a finite limit as the plates approach, and an van der Waals attraction which depends on separation according to an inverse power [redacted] law. The different contributions to the potential energy of the plates is shown schematically in the figure. At both large and very close separations the van der Waals forces are dominant. Between them the repulsion is comparable and the total potential rises to a maximum $\mathcal{F}_m$. If $\mathcal{F}_m < 0$, [redacted] there is no impediment to the plates coming together and coagulation will take place rapidly.



barrier to be overcome and co-agulation will be slowed down. Thus a rough criterion for stability is $\mathcal{F}_m > 0$. Thus there is a critical ion concentration, ρ_c, given by

$$\frac{\partial \mathcal{F}(h)}{\partial h} = 0 \quad , \quad \mathcal{F}_t(h) = 0 \qquad (19)$$

at which the colloid becomes unstable. For $\rho_0 < \rho_c$ the colloid is stable while for $\rho_0 > \rho_c$ it is unstable.

The total potential energy between the walls including the van der Waals contribution is

$$\mathcal{F}_t(h) = \frac{\varepsilon_0 \varepsilon_r V_0^2}{\lambda}\left[1 - \tanh h/2\lambda\right] - \frac{A}{12\pi h^2} \qquad (20)$$

where A is Hamaker's constant. For $\exp(h/\lambda) \gg 1$ this has the form

$$\mathcal{F}_t(h) = \frac{2\varepsilon_0 \varepsilon_r V_0^2}{\lambda} e^{-h/\lambda} - \frac{A}{12\pi h^2} \qquad (21)$$

From equations (19) this leads to the conditions

$$h/\lambda = 2 \qquad (22)$$

and

$$4\pi \varepsilon_0 \varepsilon_r V_0^2 e^{-2}/\lambda = A/24\lambda^2 \qquad (23)$$

Since λ depends on ρ_0, this is an equation for the critical concentration ρ_{0c}. It has been derived assuming that $e^{h/\lambda} \gg 1$ and $z\beta e V_0/2 \ll 1$ (i.e. $V_0 \ll 100/z$ mV). Neither of these approximations is entirely satisfactory. Improving on the first changes the value of h/λ slightly and changes the number in equation (23) but it makes little qualitative difference. However, it seems that in most practical cases $z\beta e V_0/2 \gg 1$ and the second approximation must be improved. In turn this means that the Gouy-Chapman equation (18), must be solved.

this means that $(z\beta e V_0/2)$ is replaced by $\tanh(z\beta e V_0/2) \sim 1$.

The new condition becomes for a z-z electrolyte

$$\rho_c = \frac{32\pi^2 (4\pi\varepsilon_0\varepsilon_r)^3 (k_B T)^5}{Z^6 e^6 A^2} \exp(-4)$$

For water at 25°C, this is

$$\rho_c = 8.65 \times 10^{-39} / Z^6 A^2 \qquad (24)$$

This is known as the Schulze-Hardy Rule and is shown in the slide. Agreement with experiment here is good but the value of A is overestimated.

Slide A = Table 1 of Hunter.

Criticisms

Four unjustified assumptions of the theory are

(i) additivity of electrostatic & van der Waals forces

(ii) the potential in which an ion sits is assumed to be the average potential

(iii) uniform solvent, unperturbed by colloid, with a uniform dielectric constant

(iv) point charges.

One would expect (iii) & (iv) to be unsatisfactory when $\lambda \sim \sigma$, a molecular diameter. For water with $\sigma \sim 4$ Å, this happens at a concentration of 0.5 M which is high for a colloid, but not for all applications of the double layer. Further the theory leads to unrealistic values for the concentration of ions near the surface when $V_0 \gtrsim 100$ mV which is the surface potential assumed in deriving the Schultze-Hardy rule. Results are sensitive w.r.t. to potential at these positions. Finally the rule and the law of force have not yet been subject to very stringent tests. For all these reasons attempts have been made to take some account of liquid structure. There are also reasons connected with dynamic properties of the system which also require some extension of the theory.

Stern-Layer

This is a phenomenological attempt to introduce liquid structure especially to improve our understanding of a single double layer. It is simply assumed that the ions can only approach up to some distance σ_s of the wall known as the Outer Helmholtz Plane. Then one has to solve the electrostatic problem separately in the inner region and the outer one which is again treated as a diffuse layer. The two solutions are then joined. Models of the inner layer can be quite sophisticated & have led to a greater understanding of double layer properties. They are often expressed in terms of the capacity C of the double layer, defined by

$$C = dQ/dV_0 . \qquad (25)$$

Then for a simple model with the diffuse layer treated by D-H theory (ie. dilute ~~[illegible]~~ electrolyte) ~~and~~ a charge free inner layer with dielectric constant ε_s

$$C^{-1} = \frac{\lambda}{\varepsilon_0 \varepsilon_r} + \frac{\sigma_s}{\varepsilon_0 \varepsilon_s}, \qquad (26)$$

a sum of capacitors in series. The theory involves the new constant σ_s/ε_s.

However, the split of a liquid into two regions is completely artificial and modern understanding of bulk liquid structure has led to attempts to apply that knowledge to the behaviour of liquids near walls and most recently to the double layer. The main methods used are computer simulation and integral equation methods. Given sufficient time and money the former will presumably be able to solve all problems. However we are a long way from doing this for ~~the~~ the double layer because of the enormous number of particles one would have to include in the simulation to get reasonable statistics. In fact, present computer simulations cope with about 1024 particles. However, in even a concentrated electrolyte of about 0.5M only about 1 in 30 molecules is an ion. Thus to get a reasonable statistics for the electric potential one would need many more particles. For dilute electrolytes the situation is worse although this is the area where analytic theories are probably best. Thus analytic approaches are useful although the approximations that are made are usually uncontrolled. They can usefully be monitored by computer simulation for cases where both are applicable. This is then a subject where computer simulation and analytic techniques supplement each other.

Several different techniques have been applied to these problems most notably the BYG equations, generalisations of the Boltzmann equation and density functional or equivalent methods. All have strengths and weaknesses. I have time for one only so I shall choose that which I have used which is the last. The first developments have been made for neutral fluids & since some of the effects are important in charged fluids & it is in any case useful pedagogically I shall describe the case of neutral fluids first.

Density-Functional Approach to Neutral Fluids

These start from the fact that if a fluid has an average local density $\rho(\mathbf{r})$ imposed upon it, there exists a thermodynamic potential $\Omega[\rho]$ which depends on $\rho(\mathbf{r})$ and which is a minimum in the equilibrium state. This was a result proved mathematically by Mermin but it makes good physical sense. In general Ω for a fluid in an external potential $U(\mathbf{r})$ is defined by

$$\exp[-\beta\Omega] = \sum_N \frac{z^N}{N!}\int \exp\Big[-\beta V(\mathbf{r}_1,\mathbf{r}_2\ldots\mathbf{r}_N) - \beta\sum_i U(\mathbf{r}_i)\Big]\, d^3r_1\ldots d^3r_N \qquad (27)$$

where $V(\mathbf{r})$ is the interparticle potential and z depends the chemical potential & comes from the kinetic degrees of freedom. The average local density is

$$\rho(\mathbf{r}) = \exp(\beta\Omega) \sum_N \frac{z^N}{N!}\int \exp\Big[-\beta V - \beta\sum U\Big] \sum_i \delta(\mathbf{r}_i - \mathbf{r})\, d^3r_1 \ldots d^3r_N \qquad (28)$$

But if we change $U(\mathbf{r})$ by a small amount $\delta U(\mathbf{r})$, Ω will change by a small amount $\delta\Omega$ where

$$-\beta\,\delta\Omega = -\beta \sum_N \frac{z^N}{N!}\int \exp\Big[-\beta F \quad\Big] \sum_i \delta U(\mathbf{r}_i)\, d^3r_1 \ldots d^3r_N$$
$$= -\beta \sum_N \frac{z^N}{N!}\int \exp\Big[-\beta F \quad\Big] \sum_i \delta(\mathbf{r} - \mathbf{r}_i)\, d^3r_1 \ldots d^3r_N\, \delta U(\mathbf{r})\, d^3r$$
$$= -\beta \int \rho(\mathbf{r})\, \delta U(\mathbf{r})\, d^3r . \qquad (29)$$

Hence $\Omega(\rho)$ will have the form

$$\Omega[\rho] = \Omega_0[\rho] + \int d^3r\, \rho(\underline{r})\, U(\underline{r}) \qquad (30)$$

where Ω_0 is independent of $U(\underline{r})$. Ω + Ω_0 depend on $\rho(\underline{r})$ at all points of the fluid and are called functionals of ρ.

If we know $\Omega_0[\rho]$ we have a well defined problem for a given potential $U(\underline{r})$ such as that due to walls and $\rho(\underline{r})$ is then to be obtained by minimising (30), a problem in the calculus of variations. However, we do not know $\Omega_0[\rho]$ and a first step in the application of the method is to make an educated guess for $\Omega_0[\rho]$.

In some circumstances, one can make reliable guesses as to the form of $\Omega_0[\rho]$. For example, this is the case when ~~δ~~ρ is believed to be varying slowly in space. Then $\Omega_0[\rho]$ can be expanded in powers of the spatial derivatives of ρ. This approach has been used successfully in studies of the liquid vapour interface. However, near walls one expects short range order ~~and a~~ with ~~density~~ layers of atoms nearby and a corresponding oscillation in $\rho(\underline{r})$ with period equal to a molecular diameter, a behaviour similar to $g(r)$ for a bulk liquid. Thus a gradient expansion does not seem to be appropriate.

(a) Linear theory If the potential is weak then a perturbation theory is applicable. In fact the discontinuous effect of a wall is not weak. Nevertheless this approach is helpful qualitatively and not bad quantitatively. Let us suppose that when U is zero the ~~de~~ equilibrium density is uniformly ρ_0. A weak potential $U(\underline{r})$ will change this to $\rho_0 + \delta\rho(\underline{r})$. Since ρ_0 minimises $\Omega_0[\rho]$ an expansion of Ω_0 in powers of $\delta\rho(\underline{r})$ will contain no linear terms. To second order we have

$$\begin{aligned}\Omega[\rho] - \Omega_0[\rho_0] = {} & A\int d^3r\, \delta\rho^2(\underline{r}) \\ & + \tfrac{1}{2}\int d^3r\, d^3r'\, K(\underline{r},\underline{r}')\, \delta\rho(\underline{r})\,\delta\rho(\underline{r}') \\ & + \int d^3r\, [\rho_0 + \delta\rho(\underline{r})]\, U(\underline{r}). \qquad (31)\end{aligned}$$

If we minimise with respect to $\delta\rho(\underline{r})$ we obtain the equation

$$A\,\delta\rho(\underline{r}) + \int d^3r'\, K(\underline{r},\underline{r}')\, \delta\rho(\underline{r}') + U(\underline{r}) = 0 \qquad (32)$$

Now A and $K(\underline{r},\underline{r}')$ depend on ρ_0 and so are properties of

the bulk fluid. In fact, it is shown in standard fluid theory (eg Hansen and MacDonald p 98) from equation ~~(28)~~ that

$$\delta\rho(\underline{r}) = -\beta\rho_0 U(\underline{r}) - \beta\rho_0^2 \int h(\underline{r},\underline{r}')\, U(\underline{r}')\, dr' \qquad (33)$$

where $h(\underline{r},\underline{r}')$ is [redacted] the indirect correlation function related to the pair distribution $g(\underline{r},\underline{r}')$ by

$$g(\underline{r},\underline{r}') = 1 + h(\underline{r},\underline{r}') \qquad (34)$$

To compare (33) with (32) we need to invert it and this can be done using the Ornstein – Zernike (OZ) equation

$$h(\underline{r},\underline{r}') = c(\underline{r},\underline{r}') + \int d^3r''\, c(\underline{r},\underline{r}'')\,\rho_0\, h(\underline{r}'',\underline{r}') \qquad (35)$$

where this equation provides one definition of the direct correlation function $c(\underline{r},\underline{r}')$. With this function equation (33) can be rewritten

$$\frac{\delta\rho(\underline{r})}{\beta\rho_0} - \frac{1}{\beta}\int c(\underline{r},\underline{r}')\, d^3r'\, \delta\rho(\underline{r}') + U = 0 \qquad (36)$$

Comparing equations (32) and (36) we see that

$$A = \frac{1}{\beta\rho_0}, \quad K(\underline{r},\underline{r}') = -\frac{1}{\beta}\, c(\underline{r},\underline{r}'). \qquad (37)$$

Hence the approximate form of Ω is

$$\begin{aligned}\Omega[\rho] - \Omega[\rho_0] = {} & \frac{1}{2\beta\rho_0}\int d^3r\, \delta\rho^2(\underline{r}) - \frac{1}{2\beta}\int d^3r\, d^3r'\, \delta\rho(\underline{r})\, c(\underline{r},\underline{r}')\, \delta\rho(\underline{r}') \\ & + \int d^3r\, [\rho_0 + \delta\rho(\underline{r})]\, U(\underline{r}). \qquad (38)\end{aligned}$$

If then the direct [redacted] correlation function for the bulk liquid is known exactly or approximately this functional can be used to determine $\delta\rho$ in an inhomogeneous fluid. For a fluid trapped between two walls ~~we~~ at $x = 0$ and $x = h$, we take $\rho(\underline{r}) = 0$ for $x<0, x>h$. Hence

$$\delta\rho(\underline{r}) = -\rho_0, \quad x<0,\ x>h \qquad (39)$$

For the density between the walls, we write

$$\frac{\rho(x) - \rho_0}{\beta\rho_0} - \frac{1}{\beta}\int_0^h dx' \int c(\underline{r},\underline{r}')\, dy'\, dz'\, \rho(x') + \frac{\rho_0}{\beta}\int dv\, c(\underline{r},\underline{r}') + U(x) = 0 \qquad (40)$$

where $U(x)$ is the potential, which may be zero, acting on the liquid between the walls [redacted]. In some special cases, this equation can be solved analytically but generally it has to be solved by computer.

Equation (40) is a linear theory for $\rho(x)$ and is in that sense analogous to Debye-Hückel theory. In fact, as we shall see when ions are introduced and their sizes allowed to tend to zero it reduces to Debye–Hückel theory. It is the equation obtained when one applies the Percus-Yevick approximation to a bulk liquid comprising two species of different radii and density. If one allows the radius of the second species to tend to infinity while letting its density tend to zero, ~~[illegible]~~ the pair distribution function of the first liquid becomes $\delta\rho(\mathbf{r})$ and it satisfies equation (40) for the case of a single wall. Thus this approach is also called the P-Y approximation.

The force on the plates at separation h is given by

$$f(h) = -\frac{\partial\Omega}{\partial h} \qquad (41).$$

From equations (38) and (40) one finds that (if U=0) this is

$$f(h) = \rho_S^2(h)/2\rho_0\beta \qquad (42)$$

where $\rho_S(h)$ is the liquid density at one plate when the separation is h. This, however, gives the force due to the liquid between the plates. There is also a force due to the liquid on the other side of the plates. Since there is no plate facing this side this corresponds to infinite separation. Hence the net force is

$$F(h) = \frac{\rho_S(h)^2 - \rho_S(\infty)^2}{2\rho_0\beta} \qquad (43)$$

We discuss the results obtained from this theory after we look at a second approximate density functional.

(b) Non-linear theory

One obvious defect of the previous approximation for the density functional is that if the fluid comprises independent particles it does not lead to the Boltzmann factor for the dependence of density on $U(\mathbf{r})$

$$\rho(\mathbf{r}) = \rho_0\, e^{-\beta U(\mathbf{r})} \qquad (44)$$

Let us see what form of Ω_0 does lead to this result.

To make $\Omega[\rho]$ stationary we note that if

$\rho(\mathbf{r})$ increases by $\delta\rho$, Ω increases by $\delta\Omega$, Ω_0 by $\delta\Omega_0$ where $\delta\Omega_0$ depends linearly on $\delta\rho(\mathbf{r})$ & can be written

$$\delta\Omega_0 = \int d^3r\, \frac{\delta\Omega_0}{\delta\rho(\mathbf{r})}\,\delta\rho(\mathbf{r}) \qquad (45)$$

where $\delta\Omega/\delta\rho(\mathbf{r})$ is defined by this equation and written in this suggestive form by analogy with the ~~theorem~~ behaviour of functions of several variable. Thus for Ω to be a minimum, $\rho(\mathbf{r})$ must satisfy

$$\int d^3r \left[\frac{\delta\Omega_0}{\delta\rho(\mathbf{r})} + U(\mathbf{r})\right]\delta\rho(\mathbf{r}) = 0$$

for all functions $\delta\rho(\mathbf{r})$. This requires

$$\frac{\delta\Omega_0}{\delta\rho(\mathbf{r})} + U(\mathbf{r}) = 0 \qquad (46)$$

However, for the solution (44),

$$\frac{1}{\beta}\ln\frac{\rho(\mathbf{r})}{\rho_0} + U(\mathbf{r}) = 0, \qquad (47)$$

and for the density functional to give rise to this we must have

$$\frac{\delta\Omega_0}{\delta\rho(\mathbf{r})} = \frac{1}{\beta}\ln\left[\frac{\rho(\mathbf{r})}{\rho_0}\right]. \qquad (48)$$

As ρ at only one point is involved ~~Hence~~ this equation can be integrated to yield for independent particles

$$\Omega_{I0}[\rho] = \int \frac{1}{\beta}\,\rho(\mathbf{r})\left[\ln\frac{\rho(\mathbf{r})}{\rho_0} - 1\right] d^3r. \qquad (49)$$

This can also be obtained directly from equations (27) and (28). In the absence of interaction we want $\Omega_0[\rho]$ to reduce to $\Omega_{I0}[\rho]$.

We can relate the difference to the inhomogeneous direct correlation function as follows. Suppose that we change $U(\mathbf{r})$ by a small amount. Then $\delta\rho(\mathbf{r})$ changes by a small amount and the two changes are connected by the change in equation (46). Thus

$$\int \frac{\delta}{\delta\rho(\mathbf{r}')}\left[\frac{\delta\Omega_0}{\delta\rho(\mathbf{r})}\right]\delta\rho(\mathbf{r}')\,d^3r' + \delta U(\mathbf{r}) = 0 \qquad (50)$$

But from the general theory we have

$$\delta\rho(\mathbf{r}) = -\beta\rho(\mathbf{r})\,\delta U(\mathbf{r}) - \beta\rho(\mathbf{r})\int h(\mathbf{r},\mathbf{r}')\,\rho(\mathbf{r}')\,\delta U(\mathbf{r}')\,dr' \qquad (51)$$

This differs from equation (33) because we are now dealing with a small change in an inhomogeneous fluid. Nevertheless, we have a generalised OZ equation

$$h(\underline{r},\underline{r}') = c(\underline{r},\underline{r}') + \int d^3r''\, c(\underline{r},\underline{r}'';\rho)\,\rho(\underline{r}'')\,h(\underline{r}'',\underline{r}') \qquad (52)$$

and this can be used to invert equation (51) to yield

$$\frac{\delta\rho(\underline{r})}{\beta\rho(\underline{r})} - \frac{1}{\beta}\int d^3r'\, c(\underline{r},\underline{r}';\rho)\, d^3r'\delta\rho(\underline{r}') + \delta U(\underline{r}) = 0 \qquad (53)$$

where $c(\underline{r},\underline{r}';\rho)$ now depends on ρ at all points. Comparison of equations (50) and (53) shows that

$$\frac{\delta^2\Omega_0}{\delta\rho(\underline{r}')\,\delta\rho(\underline{r})} = \frac{\delta(\underline{r}-\underline{r}')}{\beta\rho(\underline{r})} - \frac{1}{\beta}\, c(\underline{r},\underline{r}';\rho)\,. \qquad (54)$$

The first term comes from Ω_{I0}, the second term is the effect of interactions between the particles.

To find Ω_0 we now have to 'integrate' with respect to ρ. Unfortunately c is a completely unknown function for a general ρ and this cannot be done. Formally we have not advanced at all. However, the direct correlation function is a short range function and it seems that comparatively simple approximations for it yield reasonable results. In the remainder of these lectures I shall make the drastic approximation that we can use for this function the direct correlation function of the homogeneous fluid. By comparison with machine calculations where possible we shall be able to judge how well it works. Thus we use

$$c(\underline{r},\underline{r}';\rho) \approx c(\underline{r},\underline{r}';\rho_0) \equiv c(\underline{r},\underline{r}') \qquad (55)$$

In this case ~~equation~~ equation (54) can be integrated to yield

$$\frac{\delta\Omega_0}{\delta\rho(\underline{r})} = \frac{1}{\beta}\ln\frac{\rho(\underline{r})}{\rho_0} - \frac{1}{\beta}\int d^3r'\, c(\underline{r},\underline{r}')\,[\rho(\underline{r}')-\rho_0], \qquad (56)$$

and

$$\Omega_0 = \frac{1}{\beta}\int d^3r\, \ln\left[\frac{\rho(\underline{r})}{\rho_0}\right] - \frac{1}{2\beta}\int d^3r\, d^3r'\,[\rho(\underline{r})-\rho_0]\,c(\underline{r},\underline{r}')\,[\rho(\underline{r}')-\rho_0] \qquad (57)$$

Equation (56) is connected with the HNC approximation in the same way as the linear theory is connected with the PY approximation. The approximation (55) is not the only one to have been used. However, the others are much more complex and have not yet shown themselves to be sufficiently ~~super~~ superior to justify the complexity. From equations (41), (56) and (57) we find that, in this approximation, the force between two plates immersed in a hard sphere fluid is

$$F(h) = [\rho_s(h) - \rho_s(\infty)]/\beta\,. \qquad (58)$$

This can be shown to be the exact result if $\rho_s(h)$ is exact. For weak perturbations, where $\rho_s(h)-\rho_0$ is small, equations (43) and (58) agree.

Results

Slides 1-6

Neutral systems.
Note problem of pressure at the wall.

Add results for sticky sphere fluid.

$$c_{hs}(r) = -\lambda_1 - 6\eta\,\lambda_2\left(\frac{r}{\sigma}\right) - \tfrac{1}{2}\eta\,\lambda_1\left(\frac{r}{\sigma}\right)^3 \quad , \; r<\sigma,\ \text{diameter.} \tag{59}$$

$$= 0 \quad , \; r>\sigma$$

$$\lambda_1 = \frac{(1+2\eta)^2}{(1-\eta)^4} \quad , \; \lambda_2 = \frac{-(1+\frac{1}{2}\eta)^2}{(1-\eta)^4} \quad , \; \eta = \frac{\pi\rho_0\sigma^3}{6},\ \text{packing fraction} \tag{60}$$

These are obtained from the PY approximation for the bulk fluid. This assumes $c_{hs}(r) = 0$, $r>\sigma$. With the exact result for hard spheres $g(r) = 0$, $h(r) = -1$ for $r<\sigma$, it is possible to solve the OZ eqn to obtain the result above.

The Electrical Double Layer

In this case we have to include at least 3 kinds of molecule – the two kinds of ion and the solvent molecules which either carry dipoles or are polarisable or both.
We discuss in some detail the simplest case which is the primitive model (PM) electrolyte. This ~~[illegible]~~ is ~~[illegible]~~ a fluid of two kinds of hard spheres with equal diameters which carry equal and opposite charges at their centres. The solvent ~~medium~~ is still taken to be a structureless medium of dielectric constant ε_r. The potentials between the molecules are then

$$V_{\lambda\nu}(r) = \begin{cases} 0 & \text{for } r<\sigma \\ \dfrac{e_\lambda e_\nu}{4\pi\varepsilon_0\varepsilon_r r} & \text{for } r>\sigma \end{cases} \quad , \; e_1 = -e_2 \tag{61}$$

In this case to specify the state of the fluid we have to give the average densities of the two components $\rho_1(r), \rho_2(r)$, and Ω will be a function of both of these. Perturbation theory and the non-linear approach lead, respectively, to the ~~potentials~~ thermodynamic potentials

$$\Omega(\rho) = \Omega_0(\rho_0) + \frac{1}{2\beta}\sum_{\lambda\nu}\int d^3r\,d^3r'\,\delta\rho_\lambda(r)\left[\frac{\delta_{\lambda\nu}\,\delta(r-r')}{\rho_{0\lambda}} - c_{\lambda\nu}(r-r')\right]\delta\rho_\nu(r') \tag{62}$$

and

$$\Omega(\rho) = \Omega_0(\rho_0) + \frac{1}{\beta}\int d^3r \sum_\lambda \left\{\rho_\lambda(r)\ln\left[\frac{\rho_\lambda(r)}{\rho_{0\lambda}}\right] - [\rho_\lambda(r) - \rho_{0\lambda}]\right\}$$

$$- \frac{1}{2\beta}\sum_{\lambda\nu}\int d^3r\,d^3r'\,[\rho_\lambda(r) - \rho_{0\lambda}]\,c_{\lambda\nu}(r-r')\,[\rho_\nu(r') - \rho_{0\nu}] . \tag{63}$$

There now exist four direct correlation functions $c_{\lambda\nu}(r-r')$ which we need to know before we can apply the functional. These are not known exactly & so they have been obtained using the Mean Spherical Approximation in the bulk liquid. This approximates

$$c_{\lambda\nu}(r) = -\beta V_{\lambda\nu}(r) \quad , \; r>\sigma, \tag{64}$$

which is correct only as $r\to\infty$,

and uses the exact result

$$g_{\lambda\nu}(\underline{r}) = 1 + h_{\lambda\nu}(\underline{r}) = 0 \quad , \quad r<\sigma. \tag{65}$$

Then in the region $r<\sigma$, the d.c.f. can be found by solving the OZ equation which is valid in this case

$$h_{\lambda\nu}(\underline{r}) = c_{\lambda\nu}(\underline{r}) + \sum_\mu \int d^3\underline{r}'\, c_{\lambda\mu}(\underline{r}')\rho_\mu h_{\mu\nu}(\underline{r}'-\underline{r}). \tag{66}$$

This leads to

$$c_{\lambda\nu}(r) = c_0(r) - \frac{\beta e_\lambda e_\nu}{4\pi\varepsilon_0\varepsilon_r\sigma}\left(2B - \frac{B^2 r}{\sigma}\right) \; ; \; r<\sigma \tag{67}$$

where $c_0(r)$ is the dcf. for the hard sphere liquid given in equation (59),

$$B = (\lambda/\sigma)\left[1 + \frac{\sigma}{\lambda} - (1+2\sigma/\lambda)^{1/2}\right] \tag{68}$$

and λ is the Debye length for this electrolyte. A measure of the strength of the Coulomb interaction is given by the dimensionless parameter

$$\beta^* = \frac{\beta e_\lambda^2}{4\pi\varepsilon_0\varepsilon_r\sigma}. \tag{69}$$

For $\varepsilon_r = 78.54$, $T = 298$, $\sigma = 4.25$ Å, and mono-valent ions $\beta^* = 1.68$ and it increases in size as the square of the valency.

The total free energy includes the interaction of the walls with the charges and, if we are to get the total force, we should include the interaction of the walls with each other. If we confine our attention to the linear case the total ~~free~~ thermodynamic potential becomes

$$\Omega[\rho] = \Omega_0[\rho] + \sum_\lambda \int d^3r\,\rho_\lambda(\underline{r})\,\frac{e_\lambda\,\sigma(\underline{r}')}{4\pi\varepsilon_0\varepsilon_r|\underline{r}-\underline{r}'|} + \frac{1}{2}\int d^3r\,d^3r'\,\frac{\sigma(\underline{r})\sigma(\underline{r}')}{4\pi\varepsilon_0\varepsilon_r|\underline{r}-\underline{r}'|}, \tag{70}$$

where $\sigma(\underline{r})$ is the charge density on the walls. Minimisation of $\Omega[\rho]$ with respect to $\rho_1(\underline{r})$, $\rho_2(\underline{r})$ leads to equations for these densities in terms of the charge on the walls.

For the PM electrolyte the simple form (67) for $c_{\lambda\nu}(\underline{r})$ ~~contains~~ allows a useful division of the thermodynamic potential into two mutually independent parts, one which depends on the total density and one which depends on the charge density. To make this explicit we replace ρ_1, ρ_2 by

$$\rho(\underline{r}) = \rho_1(\underline{r}) + \rho_2(\underline{r}) \tag{71}$$

and

$$q(\underline{r}) = \sum e_\lambda \rho_\lambda(\underline{r}) = e_1\left[\rho_1(\underline{r}) - \rho_2(\underline{r})\right]. \tag{72}$$

Then

$$\Omega[\rho_\lambda] = \Omega_\rho[\rho] + \Omega_q[\rho] \tag{73}$$

where Ω_ρ is the thermodynamic potential (38) and

$$\Omega_q(\;) = \frac{1}{2\beta\rho_0 e^2}\int d^3r\,q^2(\underline{r}) + \frac{1}{8\pi\varepsilon_0\varepsilon_r}\int d^3r\int d^3r'\,q(\underline{r})\,c^e(\underline{r}-\underline{r}')\,q(\underline{r}')$$

$$+ \int \frac{q(\underline{r})\,\sigma(\underline{r}')}{4\pi\varepsilon_0\varepsilon_r|\underline{r}-\underline{r}'|}\,dr\,dr' + \frac{1}{2}\int d^3r\,d^3r'\,\frac{\sigma(\underline{r})\sigma(\underline{r}')}{4\pi\varepsilon_0\varepsilon_r|\underline{r}-\underline{r}'|}. \tag{74}$$

[redacted]

where

$$c^e(\underline{r}-\underline{r}') = \begin{cases} -\dfrac{1}{\sigma}\left(2B - \dfrac{B^2 r}{\sigma}\right) & , r<\sigma \\ -\dfrac{1}{r} & , r>\sigma. \end{cases} \tag{75}$$

Thus $\rho(\underline{r})$ is the same as for the corresponding neutral fluid and gives rise to the same force, while the charge density is to be determined by minimising (74). [redacted]

[redacted]

[redacted]

Thus the charge satisfies the integral equation

$$\frac{q(\underline{r})}{\beta\rho_0 e^2} + \frac{1}{4\pi\varepsilon_0\varepsilon_r}\int d^3r'\,c^e(\underline{r}-\underline{r}')\left[q(\underline{r}') + \sigma(\underline{r}')\right] = 0 \tag{76}$$

In the limit that the spheres tend to point charges $c^e(\underline{r})$ becomes $(-1/r)$ and the equation becomes,

$$\frac{q(\underline{r})}{\beta\rho_0 e^2} - \frac{1}{4\pi\varepsilon_0\varepsilon_r}\int d^3r'\,\frac{1}{|\underline{r}-\underline{r}'|}\left[q(\underline{r}') + \sigma(\underline{r}')\right] = 0. \tag{77}$$

This is the integrated form of the Debye-Hückel equation for this problem as can be seen by operating with ∇^2 on the equation. This yields

$$\nabla^2 \frac{q(\underline{r})}{\beta\rho_0 e^2} = \frac{q(\underline{r}) + \sigma(\underline{r})}{\varepsilon_0\varepsilon_r} \tag{78}$$

But equation (77) can also be written

$$\frac{q(\underline{r})}{\beta\rho_0 e^2} - V(\underline{r}) = 0 \qquad (79)$$

where $V(\underline{r})$ is the electric potential. Hence inside the fluid where $\sigma(\underline{r}) = 0$,

$$\nabla^2 V(\underline{r}) = \frac{\beta\rho_0 e^2}{\varepsilon_0\varepsilon_r} V(\underline{r}) = \frac{V(\underline{r})}{\lambda^2}. \qquad (80)$$

Hence as the diameter of the molecules tends to zero we obtain Debye-Huckel theory. Equation (76) is a generalisation which takes into account the finite size of the molecules. In the same way the non-linear theory reduces to the Gouy-Chapman theory as $\sigma \to 0$.

If the equations are specialised to the case of electrolyte between 2 parallel plates, there are a couple of points which must be noted. The first is that because the plates extend to infinity $\underline{E} \not\to 0$ necessarily at infinity. Hence, charge is not necessarily conserved. This we have to take care of explicitly by introducing a Lagrange multiplier and adding a term to Ω,

$$\lambda\int[q(\underline{r}) + \sigma(\underline{r})]\,d^3r \qquad (81)$$

where λ is to be chosen to impose

$$\int[q(\underline{r}) + \sigma(\underline{r})]\,d^3r = 0.$$

Further ρ and σ become functions of x, the coordinate normal to the plates and the correlation function required is

$$C'(x) = \int C(\underline{r})\,dy\,dz \qquad (82)$$

Now because of the Coulombic dependence of C for large r (see equations (64) and (61)), this integral diverges. However, if the system is overall neutral this divergence makes no contribution to the total energy & $C'(x)$ is the solution of the one-dimensional Poisson equation

$$\frac{d^2C'(x)}{dx} = \frac{\beta}{\varepsilon_0}\delta(x), \qquad (83)$$

$$C'(x) = -\frac{2\pi\beta}{\varepsilon_0}|x| \qquad (84)$$

[redacted] The force depends on whether the surface charge

or surface potential is being held fixed. In the latter case and the one-dimensional geometry [redacted] for a PM electrolyte between hard plates the force is

$$F_V(h) = \frac{1}{2\beta\rho_0 e^2}\left[q_s^2(h) - q_s^2(\infty)\right] - \frac{1}{2\varepsilon_0\varepsilon_r}\left[\Phi^2(h) - \Phi^2(\infty)\right] \qquad (85)$$

where $\Phi(h)$ is the charge on the plate required to keep the potential at V_0 at separation h and $q_s(h)$ is the surface charge on the fluid at the same separation. If the charge is held fixed $\Phi(h) = \Phi(\infty)$ and

$$F_\Phi(h) = \frac{1}{2\beta\rho_0 e^2}\left[q_s(h)^2 - q_s(\infty)^2\right] \qquad (86).$$

Results

Slides 7 —