

## Paralipomena of the Debye-Hückel Theory

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The relation of Debye-Hückel approximation for the internal energy of ionic solutions, to a general property of Coulomb forces and the principle of parameter invariance, has been reviewed.

As is well known, the theory of real gases (Mayer 1937) encounters a problem of divergence with the electric interactions because these have an 'infinite range'.

On the other hand, it is just this special feature of the Coulomb potential which sustains Debye and Hückel's theory – the old stand-by of Electrochemistry.

An important step forward was undoubtedly indicated by Mayer's identification<sup>1</sup> (and exact summation) of the ring-diagrams as the leading term of an ingeniously reordered cluster expansion. And most gratifying: The contribution of the ring-diagrams amounts precisely to the Debye-Hückel approximation. This certainly was a welcome substantiation of that clever theory – founded as it was on the somewhat problematic 'Poisson – Boltzmann Equation'.

Thus far, however, the complete system of successive corrections similar to Mayer's virial expansion, is not readily available. And even if it were, we cannot be certain of a corresponding progress with ionic solutions. Liquids, even non-ionic ones, are an unwieldy problem in Statistical Mechanics, and the equation of state for plasma may not be more useful to electrochemistry, than the (very perfect) theory of real gases could be for the theory of osmotic pressure. Witness to this is the 'kinetic interpretation' of van't Hoff's Law which, despite apparent simplicity, of course is not correct.

Under the circumstances, it may perhaps be worth-while to revisit some of the elementary conditions which the theory of electrolytes has to

comply with. This will also enable us to simplify some current derivations of the asymptotic formulae at high dilution.

1. *Electric stresses.* From Debye and Hückel's expression for the ionic part of internal energy, eqn. (1), where  $r_D = (ekTV/\sum N_i q_i^2)^{1/2}$  (the Debye-radius), it follows, by (usually long-winded) thermodynamical deductions, that the ionic correction to the pressure can be written as eqn. (2).

$$U^e = -\frac{1}{2} \sum_{\text{ions}} N_i q_i^2 / 4\pi\epsilon r_D \quad (q_i = ez_i) \quad (1)$$

$$P^e = \frac{1}{3} U^e / V \quad (2)$$

It is interesting to note that it has precisely the form of the Maxwell radiation pressure (albeit negative, that is, not a pressure but a suction – generally of the order  $\sim 10$  atm for 1-molar concentration of strong electrolyte).

In fact it has a similar origin *viz.* the Maxwell stresses due to the electric fields of the ions. Since eqn. (2) is much more general than the D. H. theory we shall pause to prove it without invoking eqn. (1).

At an arbitrary point ( $\mathbf{r}$ ) in the solution, the ions produce a field [see eqn. (3)], which is rapidly fluctuating as a consequence of the thermal motions.

$$\mathcal{E} = \sum (q_i / 4\pi\epsilon) (\mathbf{r} - \mathbf{r}_i) / |\mathbf{r} - \mathbf{r}_i|^3 \quad (3)$$

Writing their potential energy as volume integral over the energy density of this field [see appendix (1)], eqn. (4), we have in the canonical average (...), which of course involves also the repulsive forces tacitly implied here, eqn. (5).

$$E^e = \frac{1}{2} \epsilon \int dV (\mathcal{E}^2 - \text{self energies}) \quad (4)$$

$$U^e = \frac{1}{2} \epsilon V \overline{\mathcal{E}^2} - \text{s.e.} \quad (5)$$

The stress tensor of the fluctuating field is

$$\mathcal{F}_{ik} = \varepsilon (\mathcal{E}_i \mathcal{E}_k - \frac{1}{2} \mathcal{E}^2 \delta_{ik})$$

but because of isotropy its shear components:  $\mathcal{F}_{i \neq k} = 0$ , in the average, whereby it reduces to a scalar pressure, eqn. (6)

$$\begin{aligned} P^e &= -\overline{\mathcal{F}_{nn}} \\ &= \frac{1}{3} \varepsilon \overline{\mathcal{E}^2 - \text{s.e.}} \end{aligned} \quad (6)$$

Comparison of (5) and (6) shows that this is just the relation (2).

2. *The Thermodynamics.* Between excess functions  $U^e = U(e) - U(e=0), \dots$ , we have differential relations like eqn. (7), which together with the general eqn. (2) (see appendix (2)), implies two 'isentropic' relations, eqns. (8) and (9), showing that the excess entropy is a function:  $S^e(U^e/T)$ .

$$TdS^e = dU^e + P^e dV, \text{ et c.} \quad (7)$$

$$UV^{1/3} = \text{const.}(S^e \dots) \quad (8)$$

$$TV^{1/3} = \text{const.}(S^e \dots) \quad (9)$$

On the Debye Hückel theory this function is simply as eqn. (10) and consequently the excess free energy as eqn. (11).

$$S^e = \frac{1}{3} \frac{U^e}{T} = \frac{1}{24\pi} (V/r_D^3) k \quad (10)$$

$$F^e = \frac{2}{3} U^e \quad (11)$$

Neglecting compressibility of condensed phases under the pressures involved, the excess free energies  $F^e(V, \dots)$  and  $G^e(P, \dots)$  will be equal.

From this then follow activity coefficients *et c.* by the standard procedure:

$$\begin{aligned} \mu_i^e &= kT \log \gamma_i = \left( \frac{\partial G^e}{\partial N_i} \right)_{P, T, N(k \neq i)} \\ &= \frac{1}{24\pi} \frac{kT}{r_D^3} \left( \frac{\partial V}{\partial N_i} \right)_{P, \dots} - \frac{1}{2} \cdot \frac{q_i^2}{4\pi \varepsilon r_D} \end{aligned}$$

For ions, the first term  $\sim \partial V / \partial N_i$ , which may be negative as well as positive, should consistently be omitted in this approximation where compress-

ibility ( $G^e - F^e \sim (P^e)^2 \partial V / \partial P$ ) is neglected.

For the solvent ( $q_o = 0$ ) of a dilute electrolyte, on the other hand, G. N. Lewis' *partial* molecular volume will be  $v_o \approx V/N_o$ . Hence we have the familiar expressions,

$$\mu^e = \begin{cases} \frac{1}{24\pi} (v_o/r_D^3) \cdot kT & \text{for the solvent} \\ -\frac{1}{2} \cdot \frac{q_i^2}{4\pi \varepsilon r_D} & \text{for the ions} \end{cases}$$

respectively, whose asymptotic validity at high dilution seems to be generally agreed upon.

3. *Parameter invariance.* The isentropic constancy (10) of  $V/r_D^3$  is typical of the D.H.theory: A reversible change of the linear dimensions in the system, including the radius  $r_D$  of the 'ion atmosphere', will preserve the order imparted by the Coulomb forces and hence the negative contribution to entropy.

This invariance however, reflects a more general property of the Coulomb interaction. If by 'entropy' we mean  $S^e$ , one may say that the dimensionless ratio, eqn. (12), is 'adiabatically invariant'.

$$\xi = (e^2/\varepsilon kT)/V^{1/3} \quad (12)$$

It follows from the observation that the purely mechanical expression  $E^e/e^2$  is invariant under the parameter transformation:  $e \rightarrow e + \delta e$ . This transformation has, of course, been much used as a formal device in the D.H.theory. Its physical basis is that an invariance with respect to slow change of a mechanical parameter implies an isentropic relation in the thermodynamics of a system.

In this case the adiabatic invariance of  $U^e/e^2$  implies eqn. (13)

$$\left( \frac{\partial U^e}{\partial e} \right)_{S^e \dots} = -2 \frac{U^e}{e} \quad (13)$$

and hence

$$TdS^e = dU^e + P^e dV - \frac{2U^e}{e} de = U^e d \log \left( \frac{U^e V^{1/3}}{e^2} \right)$$

Accordingly we may specify the invariants in eqns. (8) and (9) as

$$\frac{U^e V^{1/3}}{e^2} (S^e, N_i \dots) \quad (8)$$

and

$$TV^{1/3}(S^e, e, N_i, \dots) \quad (9)$$

respectively.

These quantities may be multiplied by any function of the constraints and of the universal constants  $\varepsilon$  and  $k$  without impairing the invariance.

Thus we may write the relation (9) in the form

$$\frac{\varepsilon k T}{e^2} v^{1/3} = \phi\left(\frac{S^e}{Nk}, x_i = \frac{N_i}{N}, \dots\right) \quad (14)$$

where  $\phi$  must be homogeneous and dimensionless. From  $e, \varepsilon, k$ , alone no dimensionless combinations can be formed, hence they do not appear explicitly among the arguments of  $\phi$ . Inversion of (14) thus shows the adiabatic invariance of  $\xi$  as defined in (12).

Similarly we are allowed to multiply (8') with  $\varepsilon/N^{5/3}$  (but not with any function of  $e!$ ) to obtain eqn. (15),

$$U^e = N \frac{e^2}{\varepsilon v^{1/3}} f\left(\frac{S^e}{Nk}, \{x_i\}\right) \quad (15)$$

Hence in consequence of eqn. (14)

$$\begin{aligned} \frac{U^e}{kT} &= \frac{e^2}{kTv^{1/3}} f\left(\frac{e^2}{\varepsilon kTv^{1/3}}, \{x_i\}\right) \\ &= N \xi f(\xi, \{x_i\}) \end{aligned} \quad (16)$$

Since  $f$  must vanish at infinite dilution ( $x_i \rightarrow 0 \dots$ ) and also for  $e=0$ , power series in  $\xi$  seem conceivable. However, the attempts in this direction (Gosh 1918–21) are empirically ruled out by the success of the Debye-Hückel approximation:

$$f^{(1)}(\xi, \{x_i\}) = -\frac{1}{8\pi} (\sum z_i^2 x_i)^{3/2} \cdot \xi^{1/2}$$

So far, a big part of the whole problem is rather summarily disposed of by comprising the rôle of the neutral (though strongly polar!) solvent particles in a phenomenological dielectric constant  $\varepsilon$ .

For plasma, where cluster expansions are still to some extent feasible, Abe<sup>2</sup> was able to obtain a second approximation  $f - f^{(1)} \sim x \xi \log(x \xi)$ , indicating a more complicated singularity at infinite dilution.

Now, according to a hint from Lars Onsager (guest lectures in Oslo, 1968):  $U^e$  should be an entire function of  $e$ ! Whatever the reasoning behind this remark may be – it is honored in the first approximation of Debye and Hückel ( $U^e \sim e^3$ ), not, however, by the second approximation of Abe.

## REFERENCES

1. Mayer, J. E. *J. Chem. Phys.* 18 (1950) 1426.
2. Abe, R. *Prog. Theor. Phys.* 22 (1959) 213.

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## APPENDIX

(1) The proposition:

$$E^e = \frac{\varepsilon}{2} \int \mathcal{E}^2 dV - \text{self energies}$$

Proof:

$$E^e = \frac{\varepsilon}{2} \left(\frac{1}{4\pi\varepsilon}\right)^2 \sum_{m \neq n} q_m q_n I_{mn}$$

$$I_{mn} = \int r^2 dr d\Omega(\mathbf{r}) \frac{\cos\Theta}{r^2(r^2 + R^2 - 2rR\cos\theta)}$$

where

$$\mathbf{R} = \mathbf{r}_m - \mathbf{r}_n$$

$$\Theta = \angle(\mathbf{r} - \mathbf{r}_m, \mathbf{r} - \mathbf{r}_n)$$

$$\theta = \angle(\mathbf{r}, \mathbf{R})$$

Choosing polar axis along  $\mathbf{R}$ :

$$d\Omega = \sin\theta d\theta d\phi, \quad \sin\Theta = \frac{R}{|\mathbf{R} - \mathbf{r}|} \sin\theta$$

one sees that

$$\begin{aligned} I_{mn} &= \int_0^\infty dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \frac{r - R \cos\theta}{(r^2 + R^2 - 2rR \cos\theta)^{3/2}} \\ &= \int d\Omega \int dr \frac{-d}{dr} (r^2 + R^2 - 2rR \cos\theta)^{-1/2} \end{aligned}$$

$$= \frac{4\pi}{R}$$

*i.e.*

$$\frac{\epsilon}{2} \int \rho^2 dV - \text{s.e.} = \sum_{m < n} \frac{q_m q_n}{4\pi\epsilon r_{mn}},$$

*q.e.d.*

(2) The proposition (9):

$$TV^{1/3} = \text{const.} \quad (S^e \dots).$$

$$\begin{aligned} TdS^e &= \left(\frac{\partial U^e}{\partial T}\right)_V dT + \left[P^e + \left(\frac{\partial U^e}{\partial V}\right)_T\right] dV \\ &= \left(\frac{\partial U^e}{\partial T}\right)_V dT + \left[T\left(\frac{\partial P^e}{\partial T}\right)_V\right] dV \\ &= T\left(\frac{\partial U^e}{\partial T}\right)_V \left\{ \frac{dT}{T} + \frac{1}{3} \frac{dV}{V} \right\} \end{aligned}$$

whence the conclusion follows.