# THE EFFECT OF ADSORPTION ON THE INTERACTION BETWEEN SOLID PARTICLES

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**Abstract**—A unifying thermodynamic framework is developed within which the effects of adsorption on the interaction between solid particles can be discussed. The proposed treatment embraces interactions between solids immersed in a gaseous, pure liquid or solution environment, and is applicable to both electrolyte and non-electrolyte systems. In doing so it leads to several earlier results (especially in the case of electrolytes) but shows clearly the wide applicability of general thermodynamic principles. It also focusses attention on the shortcomings of a number of theoretical models and indicates some of the experimental approaches which should be explored.

One main conclusion from this study is that much has yet to be done, both theoretically and experimentally, to establish quantitatively the way in which adsorption by solid bodies is dependent upon their separation and orientation.

## INTRODUCTION

The most important theme in the evolution of colloid science has been the steady development of our understanding of the factors which determine the forces between small particles in a fluid medium. The first semi-quantitative generalisations concerning colloid stability emerged from experimental work on dispersions in aqueous electrolyte solutions. It was natural, therefore, that the first quantitative theories[1] should have dealt with the way in which electrostatic forces, arising from the interaction between ions in the solution and the electrically charged surface of colloid particles, combine with London–van der Waals dispersion forces to determine the thermodynamically stable (or metastable) state of the system.

More recently, attention has turned to non-aqueous colloidal systems which are found to be stabilised by adsorbed macromolecules. The mechanism of this stabilisation (which may not be the same in all systems) is rather loosely described as "steric stabilisation". Attempts to develop theories of steric stabilisation, mainly on the basis of statistical mechanical considerations, have made a good deal of progress in recent years.[2]

Other aspects of interparticle forces which have not yet received adequate attention are concerned with the adhesion between particles in powders, which determines various important practical properties such as bulk density, dispersability and free flow; and with interaction between emulsion droplets.

That adsorption processes play a decisive role in colloidal phenomena has of course been recognised for a long time, although the true nature of their influence has only recently been enunciated.[3] In one approach an additional contribution to the interaction potential, calculated by a Hamaker-type summation, is supposed to arise from a coating of adsorbed material of given thickness and density on each particle, and this is modified further by terms attributed to the interaction between the adsorbed molecules and solvent, and to the reduction in entropy of the absorbed macromolecular chains when the adsorption regions of the two approaching particles overlap.[4] Treatment of the problem in this piecemeal fashion is not aesthetically satisfying and a unified formulation is desirable.

The work summarised in this paper arose from an investigation of the possiblity of developing a formal thermodynamic treatment of adsorption and interparticle forces. Early preliminary work in collaboration with Ash was concerned with solid/gas systems,[5] and indicated that attention should be directed to the influence of particle separation on the adsorption isotherm. Further study suggested that the conclusions reached for solid/gas systems could be extended to solid/liquid systems in the following way:[6]

"When two surfaces are brought together in a solution, one of whose components is preferentially adsorbed, two effects may be distinguished. The force fields of the two surfaces will overlap and tend to increase the adsorption potential in the region between the particles; but at the same time the volume within which adsorption can occur is decreased. If the former effect predominates, then movement of the particles together will increase the adsorption and the surfaces will experience an attractive force, while if the volume exclusion effect is greater the adsorption will decrease and there will be a repulsive contribution to the interparticle force. An additional factor arises if the adsorbed species are chain molecules: the interpenetration of polymer chains adsorbed on opposite surfaces decreases the number of accessible configurations. The associated decrease in entropy also leads to a decrease in adsorption and a further contribution to the repulsion."

Subsequently Ash and Radke's work provided a firmer and more complete basis for these generalisations[7] and showed that they could with only very slight modification, be extended to interactions in electrolyte solutions.[8]

A somewhat similar analysis, though expressed in rather different terms, was carried out simultaneously and independently by Hall[9] and leads to broadly similar conclusions. Moreover, as Barker has shown,[10] the problem can be expressed in general statistical mechanical terms: his analysis confirms the correctness of the thermodynamic arguments. An alternative statistical mechanical treatment in which the forces are calculated through the stress tensor in the fluid has also been given by Kuni, Rusanov and Brodskaya,[11] although the effects of adsorption do not appear in the same explicit form as in the present work.

That these problems could be handled thermodynamically has, of course, been known for a long time and essentially thermodynamic attitude towards them is revealed in the early work of Langmuir,[12] in Overbeek's

presentation of the DLVO theory,[13] in Derjaguin's approach through the concept of disjoining pressure[14] and in the work of Mackor and van der Waals[15] and others. But so far there seems to have been no formal development in which systems, as widely different as gas/solid dispersions and electrolyte/charged solid dispersions, are brought together in a general thermodynamic framework.

Before outlining the present theory it is important to stress that colloidal phenomena are controlled both by thermodynamic and by kinetic factors. Since different processes, such as the approach of two particles in Brownian motion, and the establishment of adsorption equilibrium at the particle surface, may occur on widely different time scales, the observed phenomena may correspond in different circumstances to their evolution along different paths. In the case of electrolyte solutions, Verwey and Overbeek[16] justified the use of equilibrium theory on the basis that "the Brownian motion of the comparatively heavy colloid particles is much slower than the thermal diffusion of ions"; however, in the case of polymer adsorption, the attainment of adsorption/desorption equilibrium can be a very slow process, so that in many instances it will be necessary to discuss non-equilibrium states.[3b]

In the present paper, however, consideration is limited to cases in which adsorption equilibrium is maintained during the approach, encounter and subsequent aggregation or separation of the particles. We outline the theory as applied to the interaction between parallel plates, and then indicate later how it may be generalised to particles of arbitrary shape.

## GAS/SOLID SYSTEMS

The basic principles underlying this work are most conveniently explained by treating the special, and simplest, case of the effect of gas adsorption on the force between interacting plates. We consider, from an operational point of view, the system shown in Fig. 1. Mechanical work can be done on this system in two ways, by compression of the gas phase, or by movement of the plates relative to one another. To enable a measure of adsorption to be defined the system is compared with a reference system of the same volume, at the same temperature and pressure, but containing no adsorbing plates.‡ Because of the absence of adsorption, the reference system contains a smaller amount of gas $(n^\oplus)$ than that in the system being studied $(n)$. The difference $n - n^\oplus = n^\sigma$, and defines the Gibbs adsorption.

It can now be shown that the differential of the Gibbs energy $(\mathcal{G} = U - TS + pV)$, relative to the reference system, is given by

$$d(\mathcal{G} - \mathcal{G}^\oplus) = -(S - S^\oplus)dT + \mu dn^\sigma + 2\sigma dA + Af dh, \tag{1}$$

where $\mu$ is the chemical potential of the gas (the same in both systems) and $\sigma$ is the "surface tension" (differential surface excess free energy) of the solid surface. Integration of this equation at constant $T$, $\mu$, $\sigma$ and $h$, with subsequent differentiation and subtraction from the

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‡Alternatively, following Gibbs, we could take as a reference system one in which the gas concentration remains constant up to the surface of the plates which in this reference state have the same surface tension as in a vacuum; the argument will then differ slightly from that given, but leads to the same results.
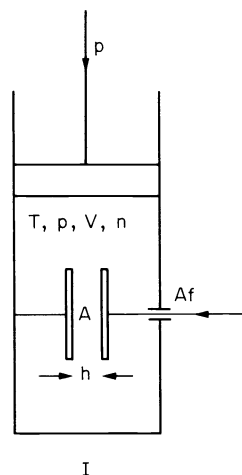


Fig. 1. System of volume $V$ containing amount $n$ of adsorptive gas, at pressure $p$, temperature $T$, incorporating two parallel adsorbent plates of area $A$ separated by a distance $h$ and repelling one another with a force $F = Af$.

original equation (following the standard procedure for obtaining a Gibbs–Duhem type equation) gives the modified Gibbs adsorption isotherm:

$$-2d\sigma = f dh + 2\Gamma d\mu, \quad (\text{const } T), \tag{2}$$

where $\Gamma = n^\sigma/2A$ is the surface excess concentration of adsorbate, i.e. one half the excess of adsorbate in a column of unit area between the surfaces.

In the limit of zero pressure $f \to f^\circ$, the force between plates in a vacuum, and $\Gamma \to 0$ so that

$$-2d\sigma^\circ = f^\circ dh, \tag{3}$$

where $\sigma^\circ$ is the "surface tension" of the clean solid surface at the separation $h$. Subtraction of (3) from (2) gives, at constant $\mu$,

$$\Delta f(h, \mu) = f(h, \mu) - f^\circ(h, \mu = -\infty) = -2\left[\frac{\partial(\sigma - \sigma^\circ)}{\partial h}\right]_{T,\mu}. \tag{4}$$

An equation of this form (applied to solutions) has been used previously.[15]

Alternatively, by cross-differentiation followed by integration, and assuming the gas to be perfect:

$$\Delta f(h, p) = 2RT \int_{p=0}^{p} \left(\frac{\partial\Gamma}{\partial h}\right)_{T,p} d\ln(p/p\dagger) \quad (\text{const } T), \tag{5}$$

where $p\dagger$ is a standard pressure (conveniently taken as the unit of pressure).

Since $f^\circ$ is the force arising solely from dispersion forces between the plates, $\Delta f$ is that part of the total force which arises from adsorption, or from the concomitant change in "surface tension" of the surfaces.

The change in potential energy caused by bringing the plates together from infinity to a separation $h$ is defined by

$$v_p(h) = \int_h^\infty f \, dh, \tag{6}$$

so that the effect of adsorption on the potential energy of

interaction is

$$\Delta v_p(h, p) = v_p(h, p) - v_p^{\circ}(h, p = 0) = \int_h^{\infty} (f - f^{\circ}) \, dh$$

$$= 2[(\sigma - \sigma^{\circ})_h - (\sigma - \sigma^{\circ})_{\infty}] \tag{7}$$

$$= 2RT \int_0^p [\Gamma(\infty) - \Gamma(h)] \, d \ln (p/p\dagger), \tag{8}$$

and can again be expressed in terms either of "surface tensions" or of adsorptions.

Equation (8) is particularly revealing as it shows clearly how the potential energy is affected by the change in the adsorption isotherm brought about by changing the plate separation.

When the two plates approach, the intermolecular potential fields emanating from them overlap causing an increase in adsorption: if this occurs at all pressures, $\Delta v_p$ is negative and an additional attraction is experienced by the plates. However, as the separation decreases so does the volume within which adsorption can occur. If this more than balances the increasing adsorption per unit volume of adsorption space, then $\Gamma$ will decrease with decreased separation: $\Delta v_p$ will be positive and adsorption will contribute a repulsive term to the interaction force.

In very crude qualitative terms we may say that an attractive contribution to the force results if movement of the plates together causes molecules to be *drawn into* the space between the plates, while a repulsive contribution results if in this process molecules are *expelled from* between the plates.

To calculate the total potential energy curve one has to know $v_p^{\circ}$, which can be evaluated either by the classical Hamaker method,[17] or using Lifshitz theory.[18]

Numerical calculations in the Henry's law (linear isotherm) region show (Fig. 2) that as the plates approach,
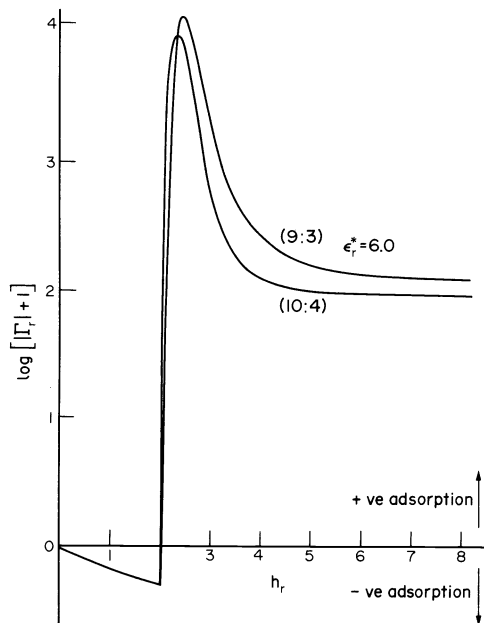
adsorption first contributes an attractive term and then a repulsive term to the interaction. When added to the dispersion energy curve the resulting curve shows a minimum at 0.8–0.9 nm separation (measured from the nuclei of the surface atoms), the depth of which increases with increasing gas pressure (Fig. 3). For the adsorption of argon by mica at room temperature it is estimated that plates are held in the equilibrium position by an excess force which rises to a maximum of about $10^3 p$; thus at 100 torr the force opposing compression or separation of the plates is of the order of 100 atm which is offset by a dispersion force attraction of about 15 atm. This suggests that while in a vacuum two mica sheets will adhere at an equilibrium distance of ~0.35 nm, at 100 torr they will adhere at an equilibrium separation of about 0.8 nm.

No experimental data are available to test the validity of this order-of-magnitude calculation.
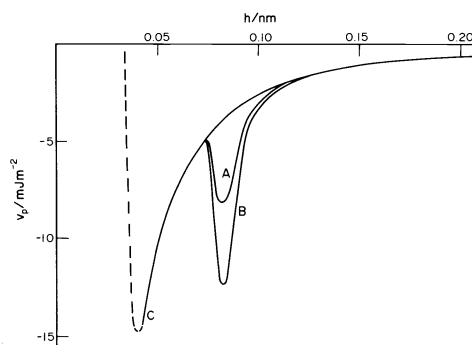


Fig. 3. Total potential energy of interaction, $v_p/\text{mJm}^{-2}$, as a function of $h/\text{nm}$ for flat parallel plates interacting with adsorptive molecules at a pressure of $10 \, \text{nm}^{-2}$ (or 0.076 torr), according to, curve A, a (9:3) potential; curve B, a (10:4) potential. Curve C is the vacuum dispersion-force potential and the dotted line represents schematically the short range repulsion between the plates.

The Hamaker constant for interaction between the plates is taken as $10^{-19}$ J; and for both potentials $\epsilon_r^* = 8.0$ (corresponding roughly to an adsorption potential of about $20 \, \text{kJmol}^{-1}$) and $\sigma = 0.34$ nm. (Reproduced by permission of the American Chemical Society.)

As the vapour pressure increases and multilayer formation sets in, the picture changes. We may expect, qualitatively, that the effect of plate separation on the adsorption isotherm may have the form shown in Fig. 4, which would then lead to the adsorption contributions to the excess force shown in Fig. 5. When thick multilayers are formed, adsorbate molecules furthest away from the solid surface will not be strongly influenced by the adsorption fields of the plates. These outermost layers on the two plates will thus begin to interact with one another before the adsorption fields overlap. The resulting reduction of the available adsorption space will decrease $\Gamma$ and hence lead to a long-range repulsive contribution to the total potential energy (Fig. 5, curves C, D). Another phenomenon may, however, intervene when the adsorbed layers on the two plates approach one another: intermolecular forces between the molecules in the two layers may, when the pressure approaches the saturation vapour pressure, lead to capillary condensation. It turns out, however, that the force between two particles connected by a bridge of condensed liquid can be treated thermodynamically in just the same way as the adsorption case already discussed.[19]

Unfortunately there is no satisfactory theory for multilayer adsorption between plates: the BET-$n$-layer theory is not very satisfactory since it considers only the



Fig. 2. Reduced adsorption $(\Gamma_r = RTn^{\sigma}/2Ap\sigma)$, expressed as $\log[|\Gamma_r| + 1]$ as a function of reduced separation $(h_r = h/\sigma)$ for adsorption on flat plates according to A: (9:3) potential; B: (10:4) potential with $e_r^*(= \epsilon^*/kT) = 6$. $\epsilon^*$ and $\sigma$ are respectively the depth of the energy minimum and the collision diameter $(\epsilon = 0)$ for interaction of adsorptive molecule with a single plate. (Reproduced by permission of the Chemical Society.)
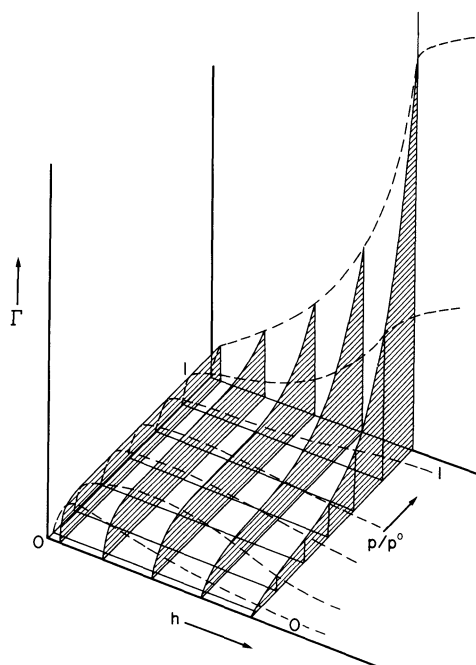
Fig. 4. Schematic representation of the effect of plate separation on the adsorption isotherm over whole relative pressure range. (Reproduced by permission of the Chemical Society.)
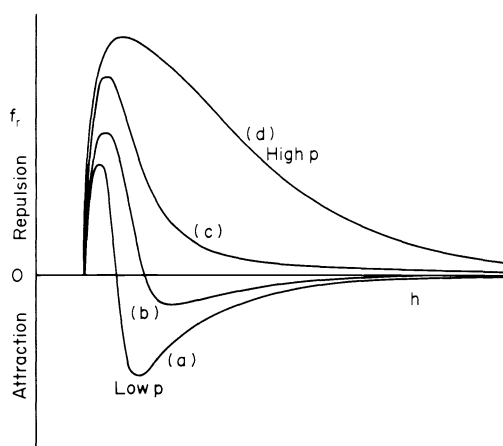


Fig. 5. Schematic representation of excess force between plates caused by adsorption as a function of plate separation at various total gas pressures: a→d increasing gas pressures. (Reproduced by permission of the Chemical Society.)

limitation on the volume of adsorption space and, because changes in the adsorption energy are confined to the layer of molecules in contact with the surface, it cannot deal with the effect of overlapping force fields. Nor are there any direct experimental data available, although Wittman has shown that water adsorption on quartz can influence the interaction.[20]

The modification of interparticle forces by gas adsorption may, however, affect many other properties such as the settling volume and flow characteristics of powders, the precipitation of aerosols of solid particles, the swelling and shrinking of porous solids, and the strength of compressed pellets. In some cases there is limited experimental evidence for such effects, but much of it is either qualitative, or not amenable to quantitative comparison with the theory.

## LIQUID/SOLID SYSTEMS: NON-ELECTROLYTES

The thermodynamic analysis in the case of solid plates immersed in a $c$-component liquid mixture follows the same lines as that for the gas/solid situation. The expressions for the force and potential energy turn out to have forms analogous to those derived previously:

$$f_c(h, \mu_i) - f_1(h, \mu_1^\circ) = 2\sum_{i=2}^{i=c} \int_{-\infty}^{\mu_1} \left(\frac{\partial \Gamma_{i,1}}{\partial h}\right)_{t,p,\mu \neq 1} d\mu_i; \quad (9)$$

$$v_{p,c}(h, \mu_i) - v_{p,1}(h, \mu_1^\circ) = 2\sum_{i=2}^{i=c} \int_{-\infty}^{\mu_i} [\Gamma_{i,1}(\infty) - \Gamma_{i,1}(h)] d\mu_i. \quad (10)$$

Here $f_c$ and $v_{p,c}$ refer to the force and potential energy in the $c$-component system; $f_1$ and $v_{p,1}$ in pure component 1; $\Gamma_{i,1}$ is the relative adsorption of component $i$ with respect to component 1. Except for the case of perfect solutions the prescription for determining experimentally the adsorption isotherms required to evaluate the integrals in eqns (9) and (10), i.e. keeping $\mu_2, \ldots \mu_{i-1}, \mu_{i+1} \ldots \mu_c$ constant while varying $\mu_i$, will be complex. In perfect solutions, however, this route can be achieved by replacing $i$ by 1 keeping the mole fractions of the other components constant. For a binary solution, the problem is simple in principle, since it is then only necessary to know the relative adsorption of component 2 as a function of plate separation and solution mole fraction.

We make the important observation that eqns (9) and (10) give the adsorption contributions to the force or potential energy relative to that in one of the pure components. If this reference value is to be calculated theoretically, then strictly speaking this should take account of adsorption in the one-component system, by employing a Hamaker constant (or, in the Lifshitz approach, a dielectric susceptibility) which varies with distance from the solid surfaces. Only preliminary attempts have so far been made to attack this problem.[21] Alternatively, one may consider the possibility of obtaining $\Delta f_1$ or $\Delta v_{p,1}$ by integrating of eqns (7) or (8) for the pure component, and combining the values obtained with the contribution from the dispersion force in a vacuum. Provided that the adsorption is reversible, then vapour adsorption measurements at various plate separations and from zero to saturated vapour pressure can in principle be used to find $f_1$ or $v_{p,1}$. It follows that, in principle, the difference between the forces in two pure liquids can be calculated in two ways: either from the vapour adsorption isotherms of the two pure vapours, or from solution adsorption measurements by determining $\Gamma_{2,1}$ as a function of $h$ and $x_2$ and integrating eqn (9) (with $c = 2$) over the whole concentration range from $\mu_i = -\infty$ to $\mu_i = \mu_i^\circ$.

Once again, in facing the problem of particle interaction in non-electrolyte solutions, we lack both adequate theories for adsorption from solution in the presence of two neighbouring surfaces and practicable experimental techniques for the measurement of adsorption isotherms under such conditions.

## LIQUID/SOLID SYSTEMS: ELECTROLYTES

The case of electrolyte adsorption poses some additional rather subtle problems, but, when these are taken into account, the formulation used earlier can be extended to provide rigorous thermodynamic expressions from which, on the basis of a simple model, the DLVO theory is recovered. Since some of the earlier work, notably that of Overbeek,[13] was also based on a thermodynamic analysis, several of the equations given below are closely similar to

those previously known. However, our analysis is, we believe, more rigorous and reveals some implicit assumptions in earlier discussions. It provides both a basis for further developments and completes the general account of the forces between colloidal particles immersed either in electrolyte or non-electrolyte solutions.

The thermodynamic formulation is presented in terms of the interaction between two parallel plate electrodes whose electrical state can be varied through an external potential source. Two cases arise, namely those of perfectly polarisable and perfectly non-polarisable electrodes.

The system under consideration is shown in Fig. 6. It is now possible to perform work on the system by electrical means. We consider first, as an example of a completely polarisable electrode, platinum plates in a dilute potassium chloride solution connected to an internal calomel electrode with respect to which the plates can be held at a potential $E$. This potential can also be measured relative to an external standard calomel electrode, giving a value $E^{\ominus}$. The thermodynamic derivation follows standard procedures taking account of the electroneutrality condition. A number of alternative expressions may be derived for the interplate potential energy; two of the potentially most useful are the following, calculated for positively charged plates,

$$
v_p(E, h, \mu_{KCl}) - v_p(E_{pzc}, h, \mu_{KCl})
$$
$$
= 2[(\sigma - \sigma_{pzc})_h - (\sigma - \sigma_{pzc})_\infty]
$$
$$
= 2 \int_{E_{pzc}}^{E} [q(\infty) - q(h)] \, dE, \tag{11}
$$

and

$$
v_p(E, h, \mu_{KCl}) - v_p(E, h, \mu_{KCl}^{pzc}) = 2 \int_{\mu_{KCl}^{pzc}}^{\mu_{KCl}} [\Gamma_{K^+, H_2O}(h)
$$
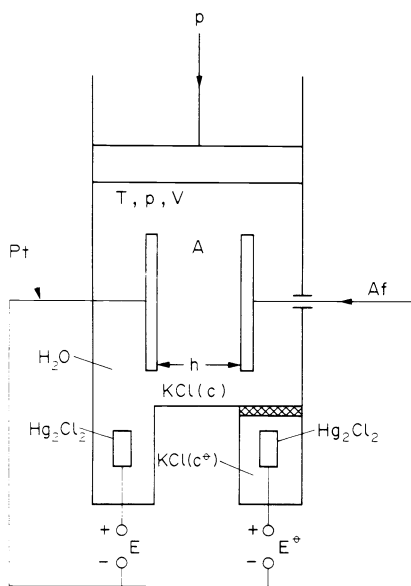$$
- \Gamma_{K^+, H_2O}(\infty)] d\mu_{KCl}. \tag{12}
$$



Fig. 6. Electrochemical system in which electrodes immersed in KCl at concentration $c$ are held at a separation $h$ by a force $F = Af$, and at a potential $E$ with respect to an internal calomel reference electrode. The potential $E^{\ominus}$ is that relative to an external calomel reference electrode containing KCl at concentration $c^{\ominus}$. (Reproduced by permission of the American Chemical Society.)

In the first of these, the potential energy at an electrical potential $E$ and distance $h$, in a solution of fixed salt activity, is given relative to that for the electrodes held at the same distance in the same solution but at the potential of zero charge ($E_{pzc}$). If it is now assumed that in the latter case electrostatic forces play no part, then $v_p(E_{pzc}, h, \mu_{KCl})$ can be attributed solely to London–van der Waals dispersion forces. We note incidentally that these should be calculated across a medium consisting of the salt solution. In this equation the potential energy is calculated from the change in the surface charge when the plates, initially at infinity, are brought together at constant potential.

In considering the second equation, we note that when the salt concentration is changed, keeping $E$ constant, then the potential of the internal reference electrode changes and consequently the potential of the plates relative to the external standard electrode is changed. It is therefore possible, at constant $E$, to vary $\mu_{KCl}$ until $E^{\ominus} = E^{\ominus}_{pzc}$: the potential energy calculated from this equation is now relative to electrodes carrying zero charge but in a solution of different salt concentration. The right-hand-sides of eqns (11) and (12) will be equal only if the dispersion forces between the plates are independent of electrolyte concentration. The potential energy is here calculated from the change in the relative adsorption of $K^+$ ions with respect to $H_2O$ when the electrodes held at constant $E$ are brought from infinity to $h$. Equation (12) is analogous to eqns (7) and (9) and reflects the effect of the distance dependence of the adsorption isotherm (here of the co-ions). Since for positively charged plates $\Gamma_{K^+, H_2O}$ is negative while $\Gamma_{Cl^-, H_2O}$ is positive, the adsorption of the neutral combination $K^+ + Cl^-$ is equal to $\Gamma_{K^+, H_2O}$. The general principle enunciated earlier applies therefore, provided that we consider the effect of plate separation, at constant $E$, on the adsorption of the co-ion or of the neutral salt species. The approach of positively charged plates expels positive ions from between them and the electrical contribution is always a repulsion.

A third equation gives the potential energy of the plates at a given surface charge, $q$:

$$
v_p(q, h, \mu_{KCl}) - v_p(0, h, \mu_{KCl}) = 2 \int_0^q [E(h) - E(\infty)] \, dq, \tag{13}
$$

and is calculated from the change in potential when the plates are brought from infinity to $h$ at constant $q$. Again the energy is relative to that between uncharged plates in the same electrolyte solution.

One important feature of the derivation of these equations is that it is necessary to assume that $E_{pzc}$ is independent of plate separation: this will be true in the purely electrostatic case but will not be valid if there is specific ion adsorption: an extension of the theory is needed to take account of this possibility.

The validity of the equations derived above may be checked by applying them to the simple point-charge double-layer model, when, using the linear approximation of the Poisson–Boltzmann equation, the classical results of the DLVO theory are retrieved. From equations (11) or (12) we obtain the 'constant potential' result:

$$
\frac{v_p(E, _{KCl}) - v_p(E_{pzc}, \mu_{KCl})}{2cRT/\kappa} = \xi_0^2 \left[ 1 - \tanh\left(\frac{h_r}{2}\right) \right], \tag{14}
$$

where $\kappa$ is the reciprocal Debye length, $c$ the salt

concentration, $\xi_0$ the reduced electrical potential, $F\psi_0/RT$, of the surface ($\psi_0$ is the surface potential) and $h_r$ the reduced plate separation $h$; while from (12) we obtain

$$\frac{v_p(q, \mu_{KCl}) - v_p(0, \mu_{KCl})}{2cRT/\kappa} = \xi_0{}^2(\infty)\left[\coth\left(\frac{h_r}{2}\right) - 1\right],$$
(15)

where $\xi_0(\infty)$ is the reduced potential at infinite separation. This is the form of the equation given by Usui.[22]

As an example of non-polarisable (reversible) electrodes, we choose silver/silver chloride electrodes. Since silver and chloride ions are present in solution at concentrations satisfying the solubility product, $K_S$, of silver chloride, they both serve as potential determining ions. The cell potential $E$ is thus determined by the potassium chloride concentration and ceases to be an independent variable. Consequently in the thermodynamic treatment we have one fewer variables and arrive at the equation

$$v_p(h, \mu_{KCl}) - v_p(h, \mu_{KCl}^{pzc}) = 2\int_{\mu_{KCl}^{pzc}}^{\mu_{KCl}} [\Gamma_{K^+, H_2O}(\infty) - \Gamma_{K^+, H_2O}(h)]\, d\mu_{KCl}$$
(16)

which is the analogue of eqn (12) except for the omission of $E$ as a variable. This again illustrates the role of electrolyte adsorption in determining the electrostatic part of the total potential energy curve for interacting reversible electrodes.

Application of the point charge model to eqn (16) leads to a result similar to, but significantly different from the DLVO result. The difference arises from the link between $\mu_{KCl}$ and $K_S$ and leads to a rather complicated algebraic result which can be approximated to (cf. eqn 14),

$$\frac{v_p(h, \mu_{KCl}) - v_p(h, \mu_{KCl}^{pzc})}{2cRT/\kappa}$$

$$= \xi_0{}^2\left[1 - \tanh\left(\frac{h_r}{2}\right)\right]\left[1 + \frac{K_S}{c^2} + 0\left(\frac{1}{c^4}\right)\right].$$
(17)

The correction term which multiplies the DLVO result involves the solubility product of the reversible electrode. For substances such as silver chloride with a very low solubility product $[K_S \sim 10^{-10}(\text{mol dm}^{-3})^2]$ the correction is unimportant except in very dilute solutions, i.e. it becomes more than 1% only when $C < 10^{-4}$ mol dm$^{-3}$. At lower concentrations the repulsion will be greater than that derived for the classical result. For more soluble substances, e.g. MgCO$_3$, $K_S = 2.6 \times 10^{-5}(\text{mol dm}^{-3})^2$, the effect will be appreciable for concentrations of added salt, having a common ion, of less than $5 \times 10^{-2}$ mol dm$^{-3}$.

We have used the point-charge/linear Poisson–Boltzmann approximate model to illustrate the simple application of our formulae: in simple cases these methods have no great advantage over the classical procedures. However, it seems possible that in the development of more sophisticated models it may well be more straightforward to direct attention immediately to the problem of calculating the appropriate adsorption isotherms, rather than working through calculations of the electrical potential profile between the plates.

## SOME FURTHER EXTENSIONS

### (i) Unlike surfaces, particles of arbitrary shape

The theory is readily generalised to surfaces having different adsorption isotherms. For parallel plates of different materials the surface tension $\sigma$ must be taken as the mean value for the two plates. For particles of arbitrary shape $\sigma$ will vary from point to point depending on the distance from the element of surface considered to all other surfaces. This in turn will depend not only on the distance between the particles but also on their relative orientations. For a given orientation, we suppose the surfaces can be divided into elements $\delta A_k$ having surface tensions $\sigma_k$; the appropriate 'surface tension' which appears in the thermodynamic equations is the mean value defined by

$$\bar{\sigma} = \frac{\Sigma\sigma_k\delta A_k}{\Sigma\delta A_k}.$$
(18)

Moreover, instead of defining a force per unit area of particle, we consider the total force ($\mathscr{F}$), and in place of the adsorption $\Gamma$, the total surface excess ($n^\sigma$). The various equations now take on more general forms:

$$\mathscr{F}(D) - \mathscr{F}^\circ(D) = \int_{-\infty}^{\mu} \left(\frac{\partial n^\sigma}{\partial D}\right)_{T, \mu, \text{ shape, orientation}} d\mu,$$
(19)

where $D$ is a conveniently defined distance of separation (e.g. between the centres of gravity of the particles), and

$$V_p(D) - V_p^\circ(D) = \int_{-\infty}^{\mu} [n^\sigma(\infty) - n^\sigma(D)]\, d\mu.$$
(20)

Since $n^\sigma(D)$ will depend on the relative orientation ($\theta, \phi$) of the particles, $V_p$ will in general depend on $D$, $\theta$ and $\phi$. We can thus calculate the adsorption contribution to the torque tending to rotate the particles into the mutual orientation corresponding to the minimum potential energy (which will also depend on the orientation dependence of the dispersion energy).

The different nature of the particles may also arise from different surface potentials; in this case the system studied will involve two external controlling potentials, one for each plate. The treatment of this case should again be straightforward and will again direct attention to the influence of adsorption, and allow studies not only of approach at constant potential of each plate and constant charge on each plate, but of other possibilities such as constant potential difference, but changing potential relative to the external reference, and constant total charge but varying individual charges.

### (ii) Specific adsorption of ions or neutral molecules

The methods employed in the present paper can be extended to the case of the simultaneous adsorption of neutral molecules and the specific adsorption of ions by the two surfaces, and indeed they seem to be the only route for the study of more complicated situations.

### (iii) Surface ionising groups

A particular example of a non-polarisable electrode is one possessing surface groups which ionise in response to changes in the ionic concentrations in the solution. The treatment in this case will again follow the general procedures outlined above, and we shall obtain equations such as (16) in which the correction term will involve the ionisation constants of the surface groupings. These corrections may be quite large in the case, for example, of some amphoteric oxides.

### (iv) Emulsions, membrane systems

In principle, the discussion presented in this paper is not limited to solid particles, but should be applicable with

little change to the forces between emulsion droplets, and between liquid enclosed in membranes (vesicles or cells). Two new features appear. In the first place the particles may not interact at constant surface area, and secondly they will change their shape as they approach. Thus if the pressure difference across the surface is constant, a change of interfacial tension resulting from changing adsorption as the particles approach will result in a change of surface curvature, probably concentrated in the regions of surface closest together. If close approach leads to increased adsorption, and hence decreased interfacial tension and increased local attraction, the curvature of the surfaces will increase. Conversely, decreased adsorption, and increase in interfacial tension will lead to repulsion between neighbouring surfaces and a flattening of the surfaces as they approach. An understanding of many processes (e.g. droplet coalescence, phagocytosis) may well depend on further study of this problem.

## CONCLUSIONS

The main outcome of this study has been to direct attention to the important thermodynamic links between adsorption and interparticle forces, and to stress the inadequacy of our knowledge, both theoretical and experimental, of the way in which adsorption isotherms depend upon the proximity to more than one surface. The problems involved in developing more sophisticated theories, or of designing experiments, to study the influence of separation on adsorption isotherms are considerable, but these approaches represent one way in which our understanding of interparticle forces may be advanced.

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