



## Consequences of shifted ion adsorption equilibria due to nonelectrostatic interaction potentials in electrical double layers



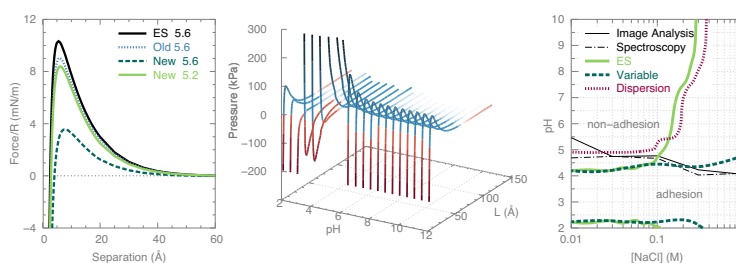
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### HIGHLIGHTS

- Consistent incorporation of ionic dispersion potentials promote their significance.
- Force fitting procedures become boundary condition dependent.
- Chemisorption interaction component can exceed the entropic in significance.
- Pressure peak profiles versus pH exhibit a non-monotonic behaviour.
- Ionic dispersion potentials improve oil–glass adhesion predictions.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Consistent incorporation of nonelectrostatic interactions in the chemical potential for electrical double layers at interfaces interacting across electrolytes under the constant potential or charge regulation boundary conditions has recently been presented for the case of ionic dispersion potentials. This gives rise to shifted adsorption equilibria, and thereby a shift in the predicted surface electrostatic potential. It also results in an additional component previously unaccounted for in the total double layer interaction force. The new force component due to ionic dispersion can be repulsive or attractive and can in some cases exceed entropic repulsion in magnitude. The altered force leads to the need to recalibrate electrostatic surface potentials and equilibrium constants when fitting to experimental force data. We explore the implications and consequences for model systems of mica surfaces, to illustrate the effect of salt concentration, and cellulose surfaces to illustrate the effect of pH. The final example is the more complex, asymmetric system of crude oil and glass interacting across salt solutions of varying concentration and pH. The DLVO theory augmented by ionic dispersion potentials is used to fit measured data for  $\zeta$ -potentials of oil and glass, from which the calculated disjoining pressure isotherms are compared to measured macroscopic oil–glass adhesion data.

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## 1. Introduction

Colloidal stability is typically modelled using classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [1,2]. Part of its appeal is due to the simple ansatz of completely separating the

direct van der Waals interaction between the colloidal surfaces from interactions attributed to electrostatic charge present in the double layer, bound on the surface of the colloidal particles or as dissolved ionic species in solution.

Essential to proper understanding of colloids is therefore appropriate theoretical descriptions of the double layers [3–5]. A handy approach for gaining information about the relationship between the bound surface charge, the dissolved charge distribution and electrostatic potential profile thus generated is the

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Gouy–Chapman [6,7] model, based on the Poisson–Boltzmann (PB) formalism.

Despite the limitations inherent to the PB approach, its relative simplicity of theoretical formulation and ease of computation offers a quick and transparent way of probing and understanding general trends and tendencies in colloidal systems. The model can be extended by imposing additional constraints to capture effects such as surface and ion hydration [8,9] or excluded volume [10]. Most notably, however, is the extension to capture ion specificity, ubiquitous in electro- and biochemistry [11]. The DLVO ansatz of separating forces of nonelectrostatic origin from those of electrostatic origin ignores van der Waals interactions between solutes and the interfaces [12]. In part this omission can be rectified by assuming a more general chemical potential for the solute ion–surface interaction that includes nonelectrostatic potentials alongside the Coulombic electrostatic potential in the Boltzmann factor of the PB equation. This extension also renders the double layer free energy and force sensitive to nonelectrostatic contributions, thus permitting modelling of ion specificity. The approach has met with varying degrees of success in predicting ion-specific effects [11,13]. However, in the context of interfacial phenomena, the incorporation of the ionic nonelectrostatic interaction potentials was consistently developed [14] only for interfaces under the condition of constant surface charge density [15–19]. The application of this extended model to interfaces under the condition of constant potential or charge regulation [20–26] is therefore inconsistent. A model that resolves this inconsistency was only recently developed [27]. While the new treatment is general to any additional interaction potential, ionic dispersion potentials were used to illustrate principles and generate preliminary results.

In this article we briefly summarise the theoretical framework in Section 2, details of which can be found elsewhere [27,28]. Section 3 presents numerical results of model systems to further explore the implications of this new consistent treatment, again in the context of ionic dispersion potentials. In particular, symmetric model systems of mica surfaces or cellulose surfaces interacting across a 1:1 electrolyte are analyzed as a function of salt concentration or pH, respectively. Section 4 addresses the asymmetric system of crude oil and glass surfaces interacting across 1:1 electrolyte of varying concentration and pH, and demonstrates the application of the augmented DLVO theory to the fitting and prediction of experimental data. Concluding remarks are provided in Section 5.

## 2. Theoretical background

### 2.1. Chemical Potential

The central argument on which the theoretical framework rests is that of the adsorption equilibrium of the potential determining ions (pdi) in their physisorbed (ps) and chemisorbed (cs) states. The difference in chemical potential of the pdi in the bulk reference state to that of their bound state at the surface drives the build-up of surface charge [29]. We envisage the process that the ion undergoes as two separate, consecutive steps; the ion is first pulled out of bulk (B) to a physisorbed state at the interface (I) and then bound into a chemisorbed state at a surface site (S). The total change in chemical potential of species  $j$  can thus be expressed as

$$\Delta\mu_{\text{tot},j} = (\mu_j^I - \mu_j^B) + (\mu_j^S - \mu_j^I) \equiv \Delta\mu_{\text{ps},j} + \Delta\mu_{\text{cs},j}, \quad (1)$$

which at equilibrium is zero, or equivalently

$$\Delta\mu_{\text{cs},j} = -\Delta\mu_{\text{ps},j}. \quad (2)$$

This enables the unknown  $\Delta\mu_{\text{cs}}$  to be replaced with the, by postulation, known  $\Delta\mu_{\text{ps}}$ .

### 2.2. Double layer free energy

The Gibbs free energy of transfer of the electrical double layer (DL), gives the total free energy change per unit area as

$$F_{\text{DL}} = - \int_0^{\sigma_0} (\Delta\tilde{\mu}_{\text{ps}} + \Delta\tilde{\mu}_{\text{cs}}) d\sigma \equiv F_{\text{ps}} + F_{\text{cs}}, \quad (3)$$

where  $\sigma_0$  is the equilibrium surface charge density and  $d\sigma$  is the amount of charge transferred per unit surface area. An acidic surface has been assumed with  $\text{H}^+$  as the sole pdi. The tilde symbol denotes nonequilibrium states.

*Physisorption.* Permitting the ions in solution, including the pdi, to interact both electrostatically as well as nonelectrostatically (NES) with the interface, the physisorption chemical potential can be expressed as

$$\Delta\tilde{\mu}_{\text{ps},j} = qz_j\tilde{\psi}_0 + \Delta\tilde{\mu}_{\text{ps},j}^{\text{NES}} \quad (4)$$

where  $\tilde{\psi}_0$  is the electrostatic surface potential,  $q$  is the elementary charge,  $z_j$  the valency of ion species  $j$  and  $\mu_{\text{ps},j}^{\text{NES}}$  the nonelectrostatic chemical potential, which may include ionic dispersion energy, cavity energy, image force, steric hindrance, etc. In the classical electrostatics-only treatment  $\Delta\tilde{\mu}_{\text{ps},j}^{\text{NES}}$  naturally is set to zero.

In the general treatment, the physisorption free energy change comprises the following parts

$$F_{\text{ps}} = F_{\text{el,ps}} + F_{\text{NES,ps}} + F_{\text{ent}}, \quad (5)$$

where the first two terms of the right hand side constitute the internal energy and the final term is the entropic energy.

*Chemisorption.* The overall change to the free energy will also include a contribution from the chemisorption process. Depending on the boundary condition imposed to describe the reactions, some adsorption isotherm must be invoked. For a charge regulated (CR) surface, a common choice is the Langmuir model, which for a monoacidic surface gives the following relationship

$$\Delta\tilde{\mu}_{\text{ps}} = k_B T \ln \frac{H_B}{K_-} - k_B T \ln \left( \frac{\sigma_{\text{max}} - \sigma}{\sigma} \right). \quad (6)$$

Here  $\sigma_{\text{max}} = -qN$  with  $N$  the total number of adsorption sites per unit area, such that the ratio  $\sigma/\sigma_{\text{max}}$  represents the fraction of charged surface sites. The bulk concentration of  $\text{H}^+$  is  $H_B$ ,  $K_-$  is the acid equilibrium constant, and  $k_B$  the Boltzmann constant and  $T$  the temperature.

Recalling the relationship given by Eq. (4), it is evident that, in the CR case for a given  $K_-$ , the magnitude of  $\tilde{\psi}_0$  in relation to the magnitude of  $\sigma$  becomes offset by the nonelectrostatic component when it is included. The same considerations apply to the case of the constant potential (CP) boundary condition, for which the right hand side of Eq. (4) is constant with respect to  $\sigma$  (and separation in the case of interacting interfaces).

From Eq. (3), the chemisorption free energy change of the double layer can thus be evaluated as

$$F_{\text{cs}} = - \frac{\sigma_0}{q} (q\tilde{\psi}_0 + \Delta\mu_{\text{ps}}^{\text{NES}}) + k_B T N \ln \left( 1 - \frac{\sigma_0}{\sigma_{\text{max}}} \right), \quad (7)$$

in the CR case, while for CP it yields

$$F_{\text{cs}} = - \frac{\sigma_0}{q} (q\tilde{\psi}_0 + \Delta\mu_{\text{ps}}^{\text{NES}}). \quad (8)$$

In both cases the additional contribution from the nonelectrostatic interaction potential is explicitly marked out.

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