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A Review of Colloidal Interactions in Mambrane Separation

[1]*Akram Dakheel, [2]Naif A. Darwish and [3]Nidal Hilal*

[1]Department of Chemical Engineering, Al Baath university, Homs P.O. Box 77, Syria
[2]Department of Chemical Engineering, American University of Sharjah,
College of Engineering, Sharjah, P.O. Box 26666, United Arab Emirates
[3]Centre for Clean Water Technologies, The University of Nottingham, Nottingham NG7 2RD, UK

Abstract: Membrane separation processes are of great and increasing importance in a number of industrial sectors, most notably the production of clean drinking water, treatment of wastewater, the food and dairy industries and the pharmaceutical and biotechnology sectors. Understanding of interactions between dissolved solute molecules and suspended colloidal particles with membranes used industrially is fundamental for developing strategies for the reduction of fouling of separation membranes. Fouling of membranes by forming a cake or thin film over the membranes results in a time dependant reduction in the operating efficiency of such membranes and can incur a number of economic costs, due to reduced transport, the requirement for pre-treatment and downtime to clean membranes. In this review we will outline the interaction forces which may occur in solution between suspended colloids and membrane surfaces.

Key words: Membranes % Colloids % Separation % Fouling % Interactive forces % Atomic force microscopy

INTRODUCTION

Separation processes using filtration membranes are of increasing importance in a number of industrial sectors including water treatment, pharmaceuticals, food and dairy and biotechnology. However, due to the nature of the process, where solutions containing a wide variety of dissolved solutes and suspended particulates necessarily come into contact with the membranes surface, fouling of the membranes routinely occurs. As a result it is of key importance to understand interactions which may occur between solutes and colloids and membranes. In this review the interaction forces which may be experienced between colloids and colloids and membrane surfaces will be examined.

Membrane fouling and concentration polarisation are two aspects of the same problem which is the build-up of retained species in the boundary layer in the immediate vicinity of a membrane surface. These phenomena lead to a gradual reduction in the permeation flux through the membrane and change of the selectivity of the process [1]. Foulants comprise the materials which have left the liquid phase to form a deposit onto the membrane surface, or within the porous structure. The consequence of fouling is a modification of the transport properties of the membrane (change in permeability and cut-off). Fouling may be permanent or irreversible as mechanical or chemical cleaning is required to restore the membrane properties. Fouling may also in part be non-permanent or reversible as the deposited materials may be swept away by the cross-flow as the pressure gradient is released.

This section presents discussion about the different types of colloidal foulants and their physical and chemical properties, which are encountered during the processing of different fluids from the chemical, biological, food or water industries. Moreover, colloidal interaction forces under the frame work of DLVO (Derjaguin-Landau-Verwey-Overbeek) theory and those non-DLVO forces acting between the colloids built-up at membrane-solution interface as a result of the concentration polarisation and between the colloid and the membrane material will be described.

Physical and Chemical Properties of Foulants: Most fluids processed in a range of membrane separation processes are aqueous solutions or suspensions. The solutes or colloids are retained and deposited on the membrane due to concentration polarisation and

Corresponding Author: Dr. Nidal Hilal, Centre for Clean Water Technologies, The University of Nottingham,
Nottingham NG7 2RD, UK. E-mail: pandeyak64@hotmail.com

colloid-membrane interactions. All the fluids are complex in nature, but their components, potentially membrane foulants, can be classified in two different groups: small organic molecules and ions; colloidal particles and macromolecules.

The first group includes salts as well as simple molecules such as sugars, amino acids, humic acids and small peptides. Small organics play an important role in fouling which they may cause in several ways. Organics may adsorb onto membranes resulting in a modification of the surface characteristics (e.g. flux and fouling). They also are a nutrient source for microorganisms and as a result facilitate biofouling of membrane surfaces. Thirdly, organics may adsorb onto colloids, improve the stability of small colloids and hence make it more difficult for those colloids to be removed in pre-treatment. For example, in the natural environment colloids commonly have a negative surface charge due to an adsorbed layer of natural organic matter (NOM), which lead to stabilisation of the colloids [2, 3]. The degree of stability depends on the amount of organics adsorbed. Lastly, the organics themselves may also be regarded as "colloids" and therefore organic and colloidal fouling overlap. In water and wastewater treatment, natural and effluent organic matter are frequently seen and mainly made up of humic substances [4]. Effluent organic matter (EfOM) is the wastewater equivalent of NOM and contributes to membrane fouling by adsorption, surface accumulation or pore blocking, mostly by the humic fractions and polysaccharides [5]. There are four NOM categories identified as strong foulant [6] such as proteins, aminosugars, polysaccharides and polyhydroxyaromatics, one of which was found relevant to fouling in the wastewater treatment [7]. EfOM has been further fractionated and characterised and four fractions with both hydrophilic and hydrophobic characters were separated [8]. Both the hydrophilic and the hydrophobic fractions can adsorb significantly to UF membranes [9].

Salts can cause a serious problem in RO and nanofiltration (NF) systems resulting from the increased concentration of one or more species in the polarized layer beyond their solubility limits leading to their crystallisation and precipitation onto the membrane surfaces [6]. These inorganic foulants include carbonate, sulphate and phosphate salts of divalent ions and metal hydroxides.

The diffusion coefficient of small dissolved organic and inorganic ions is very large due to their small size according to the Stokes-Einstein law:

$$D_0 = \frac{k\,T}{6\,p\,m\,a_{\text{hyd}}} \qquad (1)$$

Where k is the Boltzmann constant, T the absolute temperature, μ the viscosity of the solvent and a_{hyd} the hydrodynamic radius. Because of their small size, solutions of these species have high osmotic pressure which is given by the law of van't Hoff, even at moderate concentrations [6].

Both the diffusion coefficient and the osmotic pressure are the two most influential parameters controlling the performance of membrane filtration of colloidal dispersions. Its theoretical prediction is essential for solving the governing partial differential equations and ultimately predicting the rate of cross-flow membrane filtration. These parameters have been investigated theoretically via a variety of approaches and also have been verified by experimental data obtained through different techniques [10, 11].

Properties of dissolved macromolecular foulants, such as solubility, charge and diffusivity generally depend on solution pH, ionic strength and on the nature of the dissolved electrolyte. These molecules have a moderate osmotic pressure, even at high concentration up to 300 g/l. However the osmotic pressure can be high enough to become significant compared to pressures typically experienced during ultrafiltration (typically 0.1 to 0.5 Mpa). Some of the larger molecules are flexible (e.g. PEG and polysaccharides) and their apparent size may change with concentration or local shear rate. Proteins generally are more rigid than other polymers, exhibiting more complex and diverse structural arrangements. One of the particularities of such complex molecules is that they can show different functional groups on their surface at the same time, including amino acid side chains which are polar, hydrophobic or able to display positive or negative charges. Conformational changes in the proteins due to changes in the local environment may alter which of these are displayed at the surface. As a result protein molecules may interact with most surfaces with which they may come into contact.

A major contributor to fouling is the presence of colloidal particles suspended in the solutions to be filtered. Colloidal particles are ubiquitous in natural waters, as well as many industrial, process and waste waters [12]. Examples of common colloidal foulants include inorganic clays, silica, salt precipitates, metal-oxides, aggregated natural and synthetic organics, bacteria, microorganisms, viruses and other biological matter.

Colloidal particles in aqueous electrolyte solutions usually possess a surface charge. The surface charge on colloids arises from a variety of mechanisms including: differential ion solubility (e.g. silver salts), direct ionisation of surface groups (e.g. -COOH, -NH$_3$, -SO$_3$H), isomorphous substitution of surface ions from solution (e.g., clays, minerals, oxides), anisotropic crystal lattice structures (especially in clays) and specific ion adsorption [12-16]. The surface charges contribute to electrostatic interactions, which typically determine colloid aggregation and deposition phenomena [17-19]. This in turn results in the formation of an electrical double layer comprising a charged particle surface and a diffuse layer of counter ions in the solution. The specific property of colloids that is used to quantify the relative magnitude of electrostatic interactions is the zeta potential, which is usually determined by measuring the electrophoretic mobility of colloids in a suspension and computing it using an appropriate theory [15, 20]. It is well known that solution pH and ionic strength directly influence the zeta potential and thus greatly influence colloidal interactions. It has been shown that the surface charge properties of colloids can dramatically influence colloid cake layer structure (porosity) and hydraulic resistance [21-24]. The osmotic pressures of particles in this group would decrease with increasing size and these particles have a low Brownian diffusivity. During membrane processing, not only the concentration of the species from each class happens to change, but new species can appear either by reaction or by colloidal aggregation, protein denaturation, salt crystallisation, particle attrition or cell breakage. Such phenomena are often unexpected and therefore are not accounted for when analysing the origins of fouling.

The importance of colloid-membrane and colloid-colloid interactions during colloidal fouling are evident when considering the influence of salt retention and concentration polarisation on the solution chemistry in the vicinity of the membrane surface. Electrokinetic properties of colloids and membranes are strongly dependent on pH, ionic strength and the presence of multi-valent ions [17]. Therefore, distinguishing the interaction forces of colloid-colloid and colloid-membrane interactions is critical to understanding the mechanisms of colloidal fouling.

Colloidal Interaction Forces - Theory:
Van Der Waals Forces: In the nineteenth century J.D. van der Waals derived an equation of state to account for deviations in the observed behaviour of gases from the ideal gas law, pV=nRT:

$$\left(p + \frac{n^2 a}{V^2} \right)(V - nb) = nRT \qquad (2)$$

Where p is the pressure, V is the volume of the container, n is the number of gas molecules in moles, R is the gas constant and T is the temperature. This equation contained two new terms to account for deviations from ideal behaviour which can be determined experimentally and which vary between different types of molecule; a which accounts for attractive forces between the molecules and b which accounts for the volume of space occupied by the gas molecules and from which other molecules are excluded. This exclusion leads to repulsive forces at short ranges, due to Born repulsion. Whilst there is a wide range of interactions which may occur between atoms, molecules and materials made from them, the term van der Waals forces has been applied to a set of attractive forces which have their origin in interactions between dipoles, both permanent and temporarily induced, present in atoms and molecules. They can be divided up into three types depending upon the precise nature of the interaction: dipole-dipole interactions (Keesom forces); dipole-induced dipole interactions (Debye forces) and interactions between dipoles induced on opposing atoms or molecules (London or dispersive forces) and are thus all of an electrostatic origin. The Keesom and Debye forces act between polar molecules. However, the London dispersive forces may arise between neutral atoms and are thus potentially present in all interactions between materials [17,18]. All of these forces have interaction potentials of the form:

$$w_{(r)} = -\frac{C}{r^6} = \frac{(C_K + C_D + C_L)}{r^6} \qquad (3)$$

Where $w_{(r)}$ is the interaction potential, C is the constant of the interaction and r is the closest separation distance between molecules - subscripts K, D and L denote Keesom, Debye and London interactions respectively. When reading the literature it is important to bear in mind which forces are being referred to by van der Waals forces. Some authors include all three of the types of dipole interactions mentioned here as van der Waals forces, whilst other authors specifically only mean the dispersion component of the interaction.

All van der Waals interaction decrease to the inverse sixth power of the separation distance. In effect this means that these forces are not significant at ranges greater than of the order of 100 nm and are unable to
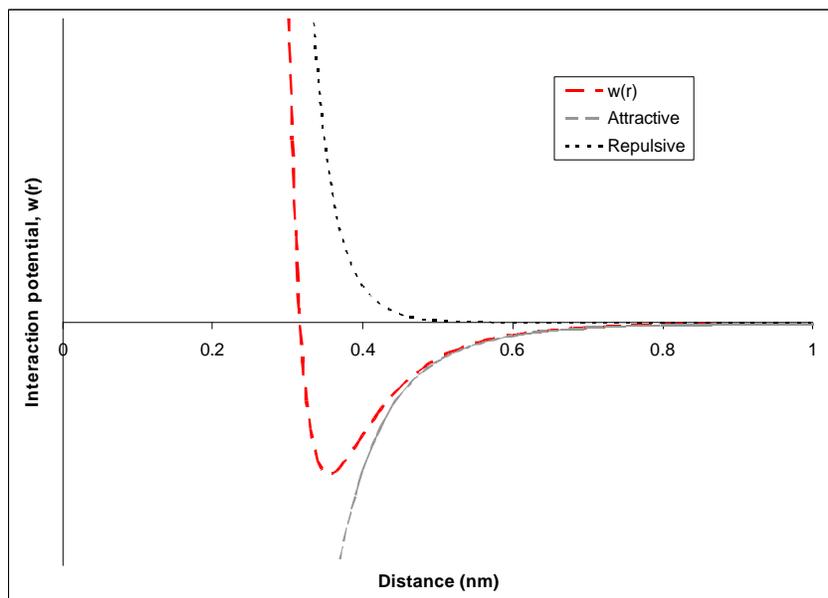
Fig. 1: Lennard-Jones potential for an interacting molecular pair. Also shown are the individual attractive and repulsive components

produce alignment effects in liquids at long ranges [18]. One simple approximation of the combined attractive van der Waals forces combined with the short range electron shell repulsion is the Lennard-Jones potential [18, 25]:

$$w_{(r)} = 4 \in \left[\left(\frac{s}{r} \right)^{12} - \left(\frac{s}{r} \right)^{6} \right] = -\frac{A}{r^6} + \frac{B}{r^{12}} \qquad (4)$$

Where , is the depth of the potential energy well, F is the distance at which the potential energy is zero. In the simpler form on the right $A = 4$, F^6, $B = 4$, F^{12} which are the attractive and repulsive components of the Lennard-Jones potential respectively. Whilst the attractive component declines to the sixth power, the repulsive short range forces decline to the twelfth power. This leads to a change in interaction potential with distance as illustrated in Figure 1. At large distances interaction forces are insignificant. On close approach between the molecules attractive (negative sign) forces begin to dominate, with the potential reaching a minimum before repulsive forces from repulsion of opposing electron shells dominates.

Keesom or orientational forces arise from the angle averaged interactions between permanent dipoles on opposing molecules. This gives rise to the following interaction free energy, $w_{(r)}$:

$$w_{(r)} = -\frac{u_1^2 u_2^2}{3 \left(4 \boldsymbol{p} \boldsymbol{e}_0 \boldsymbol{e} \right)^2 k_B T r^6} = -\frac{C_K}{r^6} \qquad (5)$$

for

$$k_B T > \frac{u_1 u_2}{4 \boldsymbol{p} \boldsymbol{e}_0 \boldsymbol{e} r^3}$$

Where u_1 and u_2 are the dipole moments of the two molecules or atoms, $\boldsymbol{g}_0$ is the permittivity of free space ($8.854 \times 10G^{12}$ C^2 JG^1 mG^1), $\boldsymbol{g}$ is the dielectric constant of the intervening medium, k_B is the Boltzmann constant ($1.380 \times 10G^{23}$ J KG^1) and T is the absolute temperature. The interaction between the dipoles increases the probability of an orientation between the dipoles which leads to mutual attraction.

The Debye, or induction, interaction is a result of permanent dipoles inducing temporary dipoles in opposing molecules and is the angle averaged interaction between such dipoles. The resulting free energy from such an interaction is:

$$w_{(r)} = -\frac{\left[u_1^2 \boldsymbol{a}_{02} + u_2^2 \boldsymbol{a}_{01} \right]}{\left(4 \boldsymbol{p} \boldsymbol{e}_0 \boldsymbol{e} \right)^2 r^6} = -\frac{C_D}{r^6} \qquad (6)$$

Where $''_{01}$ and $''_{02}$ are the electronic polarizabilities of the two molecules.

Both the Keesom and the Debye interactions involve polar molecules and are thus not always present, depending upon the molecules present. However the dispersive, or London, component of the interaction described by Fritz London during the nineteen thirties is always present. As two molecules come into close proximity the repulsion between the negative charges in the electron shells causes the induction of temporary dipoles. As the molecules do not have to be polar and can be electrically neutral this interaction can and does occur between any molecules within sufficient range of each other. The interaction free energy for the dispersion interaction between two molecules can be described as follows [26, 27]:

$$w_{(r)} = -\frac{3}{2}\frac{\alpha_{01}\alpha_{02}}{(4\pi\varepsilon_0)^2 r^6}\frac{h\nu_1\nu_2}{(\nu_1+\nu_2)} = -\frac{C_L}{r^6} \tag{7}$$

Where ν_1 and ν_2 are the orbiting frequencies of electrons and h is the Planck constant (6.626×10^{-34} m^2 kg s^{-1}).

Van Der Waals Forces Between Bulk Materials: For the useful estimation or measurement of van der Waals interaction forces between colloidal particles and/or surfaces then the theory outlined in the previous section needs to be extrapolated to describe behaviour between materials rather than purely between individual atoms or molecules. For a molecule at the surface of a particle in close proximity to another it will interact with its neighbouring molecules, with molecules on the opposing particle as well as with the constituent molecules of the intervening medium. The summation of all the pair potentials interacting between macroscopic bodies results in forces which decay much more slowly with distance than is the case for single molecular interactions [18].

The effect of the dispersion force was investigated theoretically by Hamaker [28] and de Boer [29]. For interactions between spherical particles they used a pairwise summation of the interatomic dispersion energies and demonstrated that although the range of the atomic forces was of the range of atomic dimensions, the sum of all of the dispersion energies resulted in an interaction range for colloidal bodies of the order of their dimensions. In other words when scaled up to particles containing a great number of atoms then the range of the forces no longer decreases by the sixth power of the distance when separation is small compared to the size of the particles [30]. The coefficient of interaction used by Hamaker is now referred to as the Hamaker constant (A_H). However,

pairwise additivity does not hold, especially if the interaction is occurring in a condensed medium, such as a liquid. This is because nearby molecules affect the forces acting between any interacting pair of molecules within a close vicinity [18].

Lifshitz later described a macroscopic approach which completely avoided the problems associated with additivity, neglecting atomic structure, treating large bodies as continuous media with forces being derived in terms of bulk properties such as the dielectric constants and refractive indices [31]. Here the force is the negative differential of the potential with respect to the minimum separation:

$$F = -\frac{dW}{dD} \tag{8}$$

The Hamaker constant contains elements describing all the material properties of the systems of interest. It can be summarised by the following formula:

$$A_H = \pi^2 C \rho_1 \rho_2 \tag{9}$$

Where ρ_1 and ρ_2 are the number of atoms per unit volume in the two interacting materials.

There are some general properties of van der Waals interactions between macroscopic bodies which are worthy of note. Firstly, interactions between two bodies across vacuum are always attractive, as are all interactions between two bodies of identical composition across a medium. However, for two bodies of dissimilar materials the net interaction may be either attractive or repulsive, depending upon the particular set-up. Whilst all van der Waals interactions *per se* are attractive, if one of the bodies has a greater attraction for the intervening medium than for the opposing body then this will result in a net repulsion between the two bodies [32]. Whether such an interaction is likely to be attractive or repulsive can be assessed by comparison of the dielectric constants of the materials involved. If the dielectric constant of the intervening medium is between that of the materials of the two bodies then the net forces between the two bodies will be repulsive. If it matches the dielectric constant of either of the interacting bodies then the van der Waals force will effectively vanish [33].

Retardation of Van Der Waals Forces: As the distance between interacting atoms increases the time for the electric field of one atom to interact increases and for a large enough distance will become comparable with the

time over which the dipole itself fluctuates leading to fluctuations in the interacting dipoles becoming out of step. This can lead to the interaction becoming less favourable, causing the strength of the interaction to decrease with the inverse seventh power of the separation distance rather than to the inverse sixth power [18, 34]. Because of this mechanism it is only the London dispersion interactions which are affected by these retardation affects and not the Debye or Keesom interactions.

Electrical Double Layer Forces: As stated above, van der Waals interactions between identical particles are always attractive. If this was the only force present between colloidal particles in solution then dispersions would be unstable due to aggregation leading to the formation of a precipitate. Fortunately this is not the case as particles in water or any liquid of high dielectric constant usually possess charges on their surfaces. Repulsion between identically charged particles is long range in character and is often sufficient to overcome the aggregating effects of attractive van der Waals interactions.

The Electrical Double Layer: From observations of colloidal systems it can be concluded that particles dispersed in water or any liquid with a high dielectric constant will usually develop a surface charge. The charging of a surface in a liquid can be brought about by one of two charging mechanisms [18]:

C   By the ionization or dissociation of surface groups, which leaves behind a charged surface (e.g., the dissociation of protons from carboxylic acid groups, which leave behind a negatively charged surface) and.

C   By the adsorption (binding) of ions from solution onto a previously uncharged surface. The adsorption of ions from solution can also occur onto oppositely charged sites, also known as ion exchange.

Since the system as a whole is electrically neutral, the dispersing medium must contain an equivalent charge of the opposite sign. These charges are carried by ions, i.e., by an excess of ions of one sign on the particle surface and an excess of ions of the opposite sign in the solution. Hence, if we consider an individual particle immersed in the liquid, it is surrounded by an electric double layer. One part of this double layer is formed by the charge of the surface of the particles. Another part of the electrical double layer is formed by the excess of oppositely

charged ions in the solution. As a result of the thermal motion of the ions the electrical charge carried by this layer extends over a certain distance from the particle surface and dies out gradually with increasing distance (diffuse layer) into the bulk liquid phase.

Distribution of Electrical Charge and Potential in the Double Layer: The first approximate theory for the electrical double layer was given by Gouy, Chapman, Debye and Hückel [19]. In this theory the average charge distribution and the corresponding electrical potential function have been related on the basis of the Poisson-Boltzmann equation (PBE) [35]:

$$\nabla^2 y = \frac{-1}{\varepsilon_0 \varepsilon} \sum_i n_i^0 z_i e \exp\left(\frac{-z_i e y}{k_B T}\right) \tag{10}$$

Where R is the electrical potential and n_i^0 the number density of ions of valency z_i and k_B the Boltzmann constant and T the absolute temperature and ε_0 the permittivity of vacuum and ε the dielectric constant of component i and e the elementary charge.

The above PBE has been deduced using a number of simplifying assumptions: that the electrolyte is an ideal solution with uniform dielectric properties, the ions are point charges and the potential of mean force and the average electrostatic potential are identical. Besides, the PBE is only applicable to the system with a symmetrical electrolyte or a mixture of electrolytes of the same valency type. According to this theory, the average charge density at a given point can be calculated from the average value of the electrical potential at the same point with Boltzmann's theorem. The electrical potential distribution can be related to the charge density with the aid of Poisson's equation. As a matter of fact, the Gouy-Chapman theory has a rather serious defect, which is mainly a consequence of the neglect of the finite dimensions of the ions. In dilute solutions, where the extension of the diffuse layer is considerable, this neglect is to some degree permissible; but in more concentrated electrolyte solutions the picture in terms of the Gouy-Chapman model becomes incorrect in some essential details.

Stern [36] modified the Gouy-Chapman model by taking into consideration the finite size of real ions, underlying the double layer theory for a solid wall by dividing the charges in liquid into two parts. One part is considered as a layer of ions adsorbed to the wall and is represented in the theory by a surface charge concentrated in a plane at a small distance * from
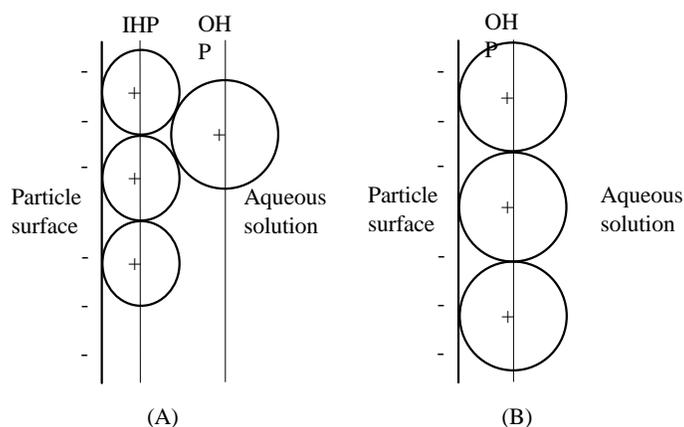
Fig. 2: Models for compact part of the double layer, (A) Gouy-Chapman-Grahame-Stern (triple layer) model and (B) Modified Gouy-Chapman model

the surface charge on the wall, also known as the outer Helmholtz plane (OHP), as shown in Figure 2. The second part of the liquid charge is then taken to be a diffuse space charge, as in the old theory, extending from the OHP at $x = {}^{\star}$ to infinity where the PBE can apply.

The method with which the distance to the OHP is calculated depends on the type of model used for describing the compact region. For an oxide surface, such as typically found on the surface of silica, a triple layer model such as the Gouy-Chapman-Grahame-Stern model [37] is often used to describe the compact region, see Figure 2(A). This model allows for a plane of adsorbed ions (partially dehydrated) on the particle surface (the centres of which form the locus for the inner Helmholtz plane (IHP)) followed by a plane occurring at the distance of closest approach of the hydrated counterions (the OHP). This is the mechanism by which the high surface charge on the oxide is reconciled with the quite low diffuse double layer potentials (zeta potentials). For other types of surfaces such as proteins, where there are few or no adsorbed ions at all, the modified Gouy-Chapman model [37], where the OHP is located at the plane of closest approach of the hydrated counterions is probably more appropriate, see Figure 2 (B). The distance to the OHP can be calculated from knowledge of the ionic crystal and hydrated ionic radii.

The non-linear PBE is used to calculate the potential distribution inside the diffusive part of the electric double layer between two surfaces [35, 37]. According to the non-linear PBE the aqueous solution is defined by its static dielectric constant only. The surface charge is usually taken as averaged over the surface and the discrete nature of ions is not considered.

In order to calculate the potential distribution around a particle, not only is the PBE needed but the boundary conditions have to be specified. A choice of boundary conditions are available at the particle surface. It is important to choose physically meaningful conditions, which depend on the colloidal material being considered. For metal sols in a solution, a constant surface potential boundary condition is appropriate; whereas a constant surface charge boundary condition may be appropriate when the surface charge is caused by crystal lattice defects, such as are found in clay minerals. In the case of biomaterials and oxide surfaces, the charge can be generated by a surface dissociation reaction that is influenced by the solution conditions. This can be described by a boundary condition known as charge regulation [18].

Interaction Forces Between Double Layers: When two like charged particles approach each other, their electrical double layers will begin to overlap, resulting in a repulsive force that will oppose further approach. For very dilute systems where just two particles can be considered in the interaction, it is possible to obtain analytical expressions for the calculation of the repulsive interaction energy between two spherical particles on the basis of the interaction energy equations derived for infinite flat plates of the same material with either the Derjaguin approximation [38] or the linear superposition approximation (LSA) [39] as shown below:

$$V_R = \frac{128 \boldsymbol{p} a_1 a_2 n_\infty k_B T}{(a_1 + a_2)\boldsymbol{k}^2} \boldsymbol{g}_1 \boldsymbol{g}_2 \exp(-\boldsymbol{k}h) \qquad (11)$$

Where h is the surface-surface separation between the particles; a_1 and a_2 denote the radii of particles 1 and 2; θ the Debye-Hückel reciprocal length; n_4 the bulk density of ions and ζ the reduced surface potential, which can be expressed as:

$$g = \tanh(\frac{ze\psi}{4kT}) \qquad (12)$$

The above equation is only valid when both the conditions $\theta a > 5$ and $h << a$ are satisfied. There are many other expressions available based on various assumptions for the sphere-sphere double layer interaction energy. For further information readers are referred to the literature [39-44]. In general, the LSA method yields the correct interaction at large separations for all surface potentials and particle sizes; Derjaguin's integration gives accurate results for large particles at short distances; and the McCartney and Levine formulation [45] is a good approximation at all separations except for small potentials. It should be noted that although the first two methods themselves place no restriction on the potentials, the resulting expressions often do because of the difficulty in solving the PBE. Therefore, care must be taken in choosing the correct expression.

DLVO Theory: The DLVO theory is named after Derjaguin and Landau [46], Verwey and Overbeek [19] who were responsible for its development during the 1940s. This theory describes the forces present between charged surfaces interacting through a liquid medium. It combines the effects of the London dispersion van der Waals attraction and the electrostatic repulsion due to the overlap of the double-layer of counterions. The central concept of the DLVO theory is that the total interaction energy of two surfaces or particles is given by the summation of the attractive and repulsive contributions. This can be written as:

$$V_T = V_A + V_R \qquad (13)$$

Where the total interaction energy V_T is expressed in terms of the repulsive double layer interaction energy, V_R and the attractive London-van der Waals energy, V_A. For a measurement made between a spherical colloid probe and a plane surface this can be adapted to give the relationship for a normalised force:

$$\frac{F}{R} = 2\pi (V_A + V_R) \qquad (14)$$

Contrary to the double-layer interaction, the van der Waals interaction energy is mostly insensitive to variations in electrolyte strength and pH. Additionally, the van der Waals attraction must always be greater than the double-layer repulsion at extremely small distances since the interaction energy satisfies a power-law (i.e., $V \% -D^n$), whereas the double-layer interaction energy remains finite or increases far more slowly within the same small separation range.

The DLVO theory was challenged by the existence of long-range attractive electrostatic forces between particles of like charge. The established theory of colloidal interactions predicts that an isolated pair of like-charged colloidal spheres in an electrolyte should experience a purely repulsive screened electrostatic (Coulombic) interaction. The experimental evidence, however, indicates that the effective interparticle potential can have a long-range attractive component in more concentrated suspensions [47, 48] and for particles confined by charged glass walls [49, 50]. The explanations for the observation are divided and debatable. One of the arguments [51] demonstrated that the attractive interaction measured between like-charged colloidal spheres near a wall can be accounted for by a nonequilibrium hydrodynamic effect, which was proved by both analytical results and Brownian dynamics simulations. Therefore, both DLVO and non-DLVO theories alone are not adequate for describing colloidal systems and the hydrodynamic effects play a vital role in determining the properties of the dispersions.

Solvation Forces: The DLVO theory successfully explains the long-range interaction forces observed in a large number of systems (colloids, surfactant solutions and lipid bilayers etc.) in terms of the electrical double layer and London-van der Waals forces. However, when two surfaces or particles approach closer than a few nanometres, the interactions between two solid surfaces in a liquid medium fail to be accounted for by DLVO theory. This is because the theories of van der Waals and double layer forces discussed in the previous sections are both continuum theories, described on the basis of the bulk properties of the intervening solvent such as its refractive index, dielectric constant and density, whereas the individual nature of the molecules involved, such as

their discrete size, shape and chemistry was not taken into consideration by DLVO theory. Another explanation for this is that other non-DLVO forces come into existence although the physical origin of the forces is still somewhat obscure [52, 53]. These additional forces can be monotonically repulsive, monotonically attractive, or even oscillatory in some cases. And these forces can be much stronger than either of the two DLVO forces at small separations [18, 54].

To understand how the additional forces arise between two surfaces a few nanometers apart we need to start with the simplest but most general case of inert spherical molecules between two smooth surfaces, first considering the way solvent molecules order themselves at a solid-liquid interface, then considering how this structure corresponds to the presence of a neighbouring surface and how this in turn brings about the short-range interaction between two surfaces in the liquid. Usually the liquid structure close to an interface is different from that in the bulk. For many liquids the density profile normal to a solid surface oscillates around the bulk density with a periodicity of molecular diameter in a narrow region near the interface. This region typically extends over several molecular diameters. Within this range the molecules are ordered in layers according to some theoretical work and particularly computer simulations [55, 56] as well as experimental observations [57, 58]. When two such surfaces approach each other, one layer of molecules after another is squeezed out of the closing gap. The geometric constraining effect of the approaching wall on these molecules and attractive interactions between the surface and liquid molecules hence create the solvation force between the two surfaces. For simple spherical molecules between two hard, smooth surfaces the solvation force is usually a decaying oscillatory function of distance. For molecules with asymmetric shapes or whose interaction potentials are anisotropic or not pairwise additive, the resulting solvation force may also have a monotonically repulsive or attractive component. When the solvent is water they are referred to as hydration forces. Solvation forces depend both on the chemical and physical properties of the surfaces being considered, such as the wettability, crystal structure, surface morphology and rigidity and on the properties of the intervening medium.

The hydration force is one of the most widely studied and controversial non-DLVO forces, a strong short-range force that decays exponentially with the distance, D, between the surfaces [59, 60]:

$$F_{SOL}(D) = Ke^{-D/l} \tag{15}$$

Where $K > 0$ relates to the hydrophilic repulsion forces and $K < 0$ to the hydrophobic attraction forces and l is the correlation length of the orientational ordering of water molecules.

The concept of a hydration force emerged to explain measurements of forces between neutral lipid bilayer membranes [60]. Its presence in charged systems is controversial, but there is experimental evidence of non-DLVO forces in systems as diverse as dihexadecyldimethyl ammonium acetate surfactant bilayers [61], DNA polyelectrolyte solutions [62] and charged polysaccharides [63]. In these experiments, the hydration forces show little sensitivity to ionic strength.

Many theoretical studies and computer simulations of various confined liquids, including water, have led to a solvation force described by an exponentially decaying cos-function of the form [64-67].

$$F_{SOL}(D) = f_0 \cos(\frac{2pD}{s})e^{-D/D_0} \tag{16}$$

Where F_{SOL} is the force per unit area; f_0 is the force extrapolated to separation distance, $D = 0$; F is the molecular diameter and D_0 is the characteristic decay length.

A repulsive force dominant at short ranges between silica surfaces in aqueous solutions of NaCl has been reported by Grabbe and Horn [68], which was also found to be independent of electrolyte concentration over the range investigated. They attributed this force to a hydration repulsion resulting from hydrogen bonding of water to silica surface and fitted the additional component to a sum of two exponentials to derive a formula for the hydration forces in the system.

The physical mechanisms underlying the hydration force are still a matter for debate. One possible mechanism is the anomalous polarisation of water near the interfaces, which completely alters its dielectric response [69-71]. These theories imply an electrostatic origin of the hydration force. However, other authors report [72] that there is no evidence for a significant structuring of water layers near interfaces, or a perturbation of its dielectric response, as envisaged by previous theories. Instead, they suggest that the repulsive forces are due to entropic (osmotic) repulsion of thermally excited molecular groups that protrude from the surfaces [73]. This theory explains many experimental observations in neutral

systems [74], but its validity in charged systems is not certain. Given the available evidence from experiments and simulations, it is not possible to reach a definitive conclusion on the precise role of these mechanisms in determining the hydration forces. Computer simulations of water films coated with ionic surfactants showed that protrusions are not significant in these systems [75]. On the other hand, computer simulations show that water has an anomalous dielectric behaviour near charged interfaces [76], but the observed electrostatic fields obviously differ from the predictions of electrostatic theories on hydration forces [70, 77]. The effect of this anomalous dielectric behaviour of water on the electrostatic force between surfaces or interfaces is still unknown.

Steric Interaction Forces: For molecules attached to a solid surface in a liquid environment, chains with a degree of freedom to move will tend to dangle out into the solution where they remain thermally mobile. On approach of two polymer-covered surfaces the force overlapping between the polymer layers results in a repulsive entropic force which, for overlapping polymer molecules, is known as the steric or overlap repulsion. However, steric repulsion does not necessarily have to be due to polymeric molecules; layers of small molecules can have the same effect, albeit at a much shorter range.

Steric stabilisation of dispersions is very important in many industrial processes. This is because colloidal particles that normally coagulate in a solvent can often be stabilised by adding a small amount of polymer to the dispersing medium. Such polymer additives are known as protectives against coagulation and they lead to the steric stabilisation of a colloid. Both synthetic polymers and biopolymers (e.g., protein, gelatine) are widely used in both non-polar and polar solvents (e.g., in paints, toners, emulsions, cosmetics, pharmaceuticals, processed food, soils, lubricants).

Theories of steric interactions are not well developed. There is no simple, comprehensive theory available as steric forces are complicated and difficult to describe [78-80]. The magnitude of the force between surfaces coated with polymers depends on the quantity or coverage of polymer on each surface, on whether the polymer is simply adsorbed from solution (a reversible process) or irreversibly grafted onto the surfaces and finally on the quality of the solvent [78, 81]. Different components contribute to the force and which component dominates the total force is situation specific.

Hydrophobic Interaction Forces: A hydrophobic surface usually has no polar or ionic groups or hydrogen-bonding sites so that there is no affinity for water and the surface to bond together. Ordinary water in bulk is significantly structured because of hydrogen bonding between the water molecules. The cooperative nature of this bonding [82] means that quite large clusters of hydrogen-bonded water molecules can form although they may continually form and break down in response to thermal energy fluctuations. The orientation of water molecules in contact with a hydrophobic molecule is entropically unfavourable, therefore two such molecules tend to come together simply by attracting each other. As a result the entropically unfavoured water molecules are expelled into the bulk and the total free energy of the system is reduced accordingly. The presence of a hydrophobic surface could restrict the natural structuring tendency of water by imposing a barrier that prevents the growth of clusters in a given direction. Similar effects occur between two hydrophobic surfaces in water. Water molecules confined in a gap between two such surfaces would thus be unable to form clusters larger than a certain size. For an extremely narrow gap, this could be a serious limitation and result in an increased free energy of the water in comparison with that in bulk. In other words this would give rise to an apparent attractive force between hydrophobic surfaces as a consequence of water molecules migrating from the gap to the bulk water where there are unrestricted hydrogen-bonding opportunities and a lower free energy.

Attraction between hydrophobic surfaces has been measured directly [83] and can be of surprisingly long range, up to about 80nm [84]. The attraction was much stronger than the van der Waals force and of much greater range. The interaction of filaments of hydrophobized silica was measured by Rabinovich and Derjaguin [85]. They found an attractive force at large separation distances, one to two orders of magnitude greater than van der Waals attraction.

It is now well established that a long-range (>10 nm) attractive force operates between hydrophobic surfaces immersed in water and aqueous solutions [86]. Unfortunately, so far no generally accepted theory has been developed for these forces, but the hydrophobic force is thought to arise from overlapping solvation zones as two hydrophobic species come together [18]. In fact, Eriksson, *et al.* [87] have used a square-gradient variational approach to show that the mean field theory of repulsive hydration forces can be modified to account for some aspects of hydrophobic

attraction. Conversely, Ruckenstein and Churaev suggest a completely different origin that attributes the attraction to the coalescence of vacuum gaps at the hydrophobic surfaces [88].

In recent years a number of studies have been undertaken to study the effect of nanoscale bubbles found on hydrophobic surfaces to explain the hydrophobic forces reported in many surface force measurements. These bubbles may be present on the hydrophobic surfaces when first immersed in aqueous solutions, or may form from dissolved gasses after immersion. Considine, *et al.* [89] when undertaking measurements between two latex spheres noted a large attractive force with a range much in excess of that expected from van der Waals attraction and independent of electrolyte concentration. They observed that degassing of solutions reduced the range of this attractive force significantly. Re-gassing of the solution restored the original range of this force, showing the influence of dissolved gas on the measurement of hydrophobic forces. The presence of such bubbles has been confirmed by the use of tapping mode AFM on hydrophobized silicon wafers [90, 91]. Bubble like features observed on these surfaces show a high phase contrast with the rest of the surface suggesting very different mechanical properties to the silicon surface. Force curves taken at the sites of these putative nanobubbles show much greater attractive and adhesive forces with a hydrophobic AFM probe than when taken from a bare area of the surface. Zhang and colleagues examined the effects of degassing and liquid temperature on the number and density on the surface of the nanobubbles [92]. Degassing of water and ethanol under vacuum reduced the surface density of nanobubbles to a very significant extent. Increasing the temperature of the fluid also increased the number and size of the nanobubbles on the surface, a phenomena witnessed by another group who also observed the spontaneous appearance of nanobubbles as the liquid temperature was increased [93]. For measurements where the hydrophobic force being measured is a result of the interaction of bubbles on the opposing surfaces, the forces measured are actually capillary forces rather than true hydrophobic forces, albeit capillary forces present as a result of the hydrophobicity of the surfaces. For those who wish to read further into the origins of forces measured between hydrophobic surfaces in aqueous solutions the authors would like to draw attention to a number of reviews in the literature [94-96].

Atomic Force Microzcopy Measurement of Adhesion of Colloidal Particles and Cells to Membrane Surfaces: The AFM has been used to measure adhesive forces between particles and a variety of process surfaces. One important example is adhesion between particles, including both inorganic colloidal particles and bacterial cells and filtration membranes. This interaction is of great importance when considering the fouling and biofouling of such surfaces. Particles adhere to the process membranes and reduce flow through the membrane greatly reducing the filtration efficiency and working lifetime of the membranes. The process testing of new membranes is potentially expensive and time consuming. The quantification of adhesion forces between colloids and membranes can provide an important contribution to developing the theoretical prediction and optimisation and control of many engineering separation processes. As a result the development of AFM methods to quantify the adhesion of different materials to membranes of different compositions can potentially be very useful for membrane manufacturers and engineers [97]. When particle sizes are greater than the pore size in the absence of repulsive double layer interactions, such particles may plug the pores very effectively leading to a catastrophic loss in filtration flux. Of the many established membrane characterisation techniques only the colloid probe method can measure the adhesive forces between particles and membrane surfaces and hence allow prediction of the membrane fouling properties of the particles. In addition the ability to make measurements in liquid allow the matching of observation conditions to those which occur in practice. The first demonstrations of the potential of the colloid probe technique to differentiate different membranes based upon the different adhesion properties was carried out by Bowen and colleagues [97-101]. Two commercially available membranes with polymer molecular weights of 4 kDa were investigated. The first, ES 404 was made from a single polymer, polyethersulphone. The second, XP 117, was made from a blend off different polymers created to hopefully have a low rate of membrane fouling. Measurements were made between polystyrene microspheres and these membranes in aqueous NaCl solutions at a $10G^2$ M concentration and at a pH of 8.0. In Figure 3 plots of force normalised by the microsphere radius versus the displacement of the piezo in the direction normal to the membrane surface recorded whilst retracting the colloid probe away from the membrane surfaces are shown. At points A to A' the probe is in the region of constant
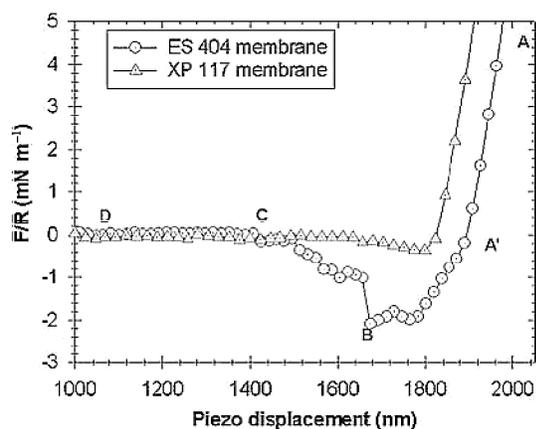
Fig. 3: Normalised retraction force versus displacement for a polystyrene colloid probe and two filtration membrane at pH 8.0, $10G^2$ M NaCl.

compliance with the surface. For the region of the plot A' to B for the ES 404 membrane a stretching of the probe and/or membrane occurs, due to the adhesive forces; the stretching continues at B to C, with adhesion force reducing as probe and membrane slowly separate, with final separation occurring at C. At C to D no net forces are acting between the probe and surface and this is taken as the point of zero force. The minimum force value (B) is taken as observed pull off force, F_{OFF} and is a direct measure of the adhesive force. For the measurements presented in Figure 1 the values are 1.98 mN mG^1 and 0.38 mNmG^1 for the ES 404 and XP 117 membranes respectively, an approximately fivefold reduction. This demonstrates quantitatively that the membrane manufacturer has produced a membrane to which the test colloid attaches only weakly compared with a more conventional membrane. In other words the membrane is potentially low fouling for actual process applications.

It is also worth noting that the adhesive interaction between the probe and the ES 404 membrane took place over a distance of approximately 400 nm, most likely due to the stretching of the probe and/or the membrane surface. When the adhesion of a 'cell probe' (Figure 2) created with a single yeast cell to a silica surface was undertaken the adhesive interaction also took place over a large distance [101] again most likely representing the stretching of the probe. Conversely, studying the adhesion between systems of hard inorganic surfaces, adhesive interactions take place over very short distances of the order of no more than a few nanometers [102-104]. This is a consideration for manufacturers of membranes when studying a heterogeneous range of materials.

This behaviour is also of note for general colloid probe interactions. The deformation of soft surfaces in close proximity due to long range forces and due to mechanical force when in contact make the determination of the actual surface separation and assignment of the point of zero distance problematic. For this reason many researchers only plot the displacement of the piezo, rather than the actual surface separation.

Protein coated colloid probes were used to compare the adhesive forces between silica colloids and BSA coated silica spheres with the same membranes as described above [99]. BSA coated silica probes demonstrated significant adhesion with both types of membrane, compared to silica probes which had no measurable adhesion. The development of the colloid probe technique for the AFM as a sensor for quantifying the adhesive forces at membrane surfaces provides a relatively fast procedure for assessing the potential fouling of membrane surfaces by particles of different materials. In addition only small pieces of membrane are necessary for experiments to be undertaken. Ultimately the direct measurements of the AFM will help to assist in the development of new membranes with more fouling resistant properties.

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