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Surface Forces: Changing Concepts and Complexity with Dissolved Gas, Bubbles, Salt and Heat.

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Abstract.

A number of missing factors influence surface forces strongly; so much so that the classical theory is often irrelevant to the real world. Among these factors, dissolved atmospheric gas or other sparsely soluble solutes play a central role in long range hydrophobic forces. Bubble-bubble interactions exhibit unexplained non-Hofmeister ion specificity. Inhomogeneity in temperature between bubbles and solvent can be used to catalyse high temperature reactions at low temperatures.

Further, the additivity of electrostatic and dispersion forces assumed in DLVO theory is inadmissable. It also neglects ion specificity (Hofmeister effects) due to dispersion forces acting on ions.

An account is given of these complexities that are missing from classical theories of surface forces. It is shown how these phenomena can be exploited for a range of novel technologies.

Molecular and Surface Forces .

1. The Classical Picture: Limitations and Insights

The van der Waals interaction potential between two atoms behaves as $V(r) \sim r^{-6}$. This was known to Newton. The potential of interaction between two planar surfaces at separation L follows by pairwise addition. It varies as L^{-2}. Newton tried to measure this force, but gave up, with the comment (Art. 31 of the Principia) "surface combinations were owing".

Unlike gravity, surface forces decay rapidly over very short distances and depend critically on material properties. And, as for contamination, it will always be with us.

For the opposing electrical double layer forces between two charged surfaces in a continuum electrolyte, the repulsive forces decay exponentially with distance; asymptotically, $V(L) \sim \exp(-\kappa L)$ with κ^{-1} the electrolyte Debye length. The pre-factor depends on assumed boundary conditions, constant potential or constant charge. These conditions were relaxed with the extension to allow charge regulation [1]. This was a conceptual advance. The degree of ionisation of surface charges - and therefore surfaces forces - recognises, and changes in its response to the proximity of, and signalling from, another body.

These few lines, with a few decorations, underlie the DLVO theory of colloid particle interactions. The theory was a core belief to physical and electrochemists. It still is. It ranks with the book of Genesis as a credible account of creation, and is less useful.

The theory has severe limitations, acknowledged by both Deryaguin and Overbeek: because a liquid between interacting bodies is assumed to have bulk properties up to a molecular distance from an idealised surface. Further, apart from the contamination issue, the idea of a protein or DNA molecule presenting as a smooth homogeneous "surface" is clearly problematic. A real protein has to be flexible and capable of rearrangement on interactions with changing environment, (hence epigenetics) or with another molecule, or on adsorption at a surface or with interactions.

The DLVO ansatz supposes van der Waals and electrostatic forces are additive. They are not. [2,3]

2. First Steps Beyond DLVO theory

2 a. Complexities with Double Layer Forces

The standard Debye length for symmetric electrolytes is not valid for asymmetric electrolytes. It has a much more complex form . Direct force measurements for 12:1, 8:1 electrolytes (cytochrome C) and insulin 5:1 and 3:1 give precise agreement with theory [4,5].

2 b. Oscillatory Forces.

At small distances, of the order of several molecular sizes, the electrostatic forces are dominated by oscillations. These are sometimes called depletion forces. They act to stabilise emulsions. and other systems where e.g. proteins or micelles form part of a fluid that separates two interacting objects [6].

This "molecular granularity" shows up in any liquid, from van der Waals hard core fluids [7,8,9] to colloidal suspensions of micelles [6]. The oscillations decay with separation and merge into the continuum theories after about 6 oscillations.

2 c. Hydration: Surface Induced Liquid Structure

The assumption that a liquid adjoining a surface has bulk properties up to contact (a molecular distance) can break down for reasons other than molecular granularity. The profiles of surface induced liquid order (e.g., dipole or hydrogen bond ordering) can overlap to give rise to either repulsive or attractive hydration forces. These dominate at small separation distances. For surfaces rough at a molecular level, e.g. phospholipid head groups of a bilayer, the oscillations are smoothed out and decay with an exponential form with a range of the order of a molecular diameter (0.3nm). They dominate van der Waals interactions up to say 3nm separations. Correlated fluctuations in constituent surface dipoles of head groups can give rise to other forces They can appear in force measurements as a hidden contribution that changes effective hydration decay length. Thus, the smaller ethanolamine dipolar head group has a larger such contribution than does the bulkier phosphotidyl choline group . The apparent hydration range is smaller for the former [10].

Hydration forces were first calculated, correctly, by J Clerk Maxwell in a magnificent paper in 1876 and forgotten [11]. They were rediscovered exactly 100 years later by Marcelja [12].

3. Complexity in Van der Waals Forces

3 a. Lifshitz theory: Emerging Concepts of Recognition

D'Arcy Thompson , in *Growth and Form* CUP (1918), had reported the views of the early founders of the cell theory of biology and of the early physiologists of the 19th century, that progress in their new sciences would wait on, and depended on advances in molecular forces.

That plea had been articulated most eloquently in 1894 by the Russian physicist P.N. Lebedev, discoverer of light radiation pressure as follows :

" *…..of special interest and difficulty is the process which takes place in a physical body when many molecules interact simultaneously , the oscillations of the latter being interdependent owing to their proximity. If the solution of this problem ever becomes possible we shall be able to calculate in advance the values of the intermolecuar forces due to molecular inter-radiation, deduce the laws of their temperature dependence, solve the fundamental problem of molecular physics whether all the so-called 'molecular forces' are confined to the already known mechanical interaction of light radiation, to electromagnetic forces, or whether forces of hitherto unknown origin are involved . ….*". It is especially fitting that his speculations and grand vision on forces should have been confirmed by the Russians in the dramatic simultaneous advance in theory by Lifshitz in 1955, and in experiments by Abrikossova and Deryaguin in 1956. Deryaguin was Lebedev's son-in-law and Lebedev was a friend of J. Clerk Maxwell.

The vision was implemented by his step-son Deryaguin through Lifshitz. It was extended by Dzyaloshinski, Lifshitz and Pitaevski who developed a complete theory of interactions between planar dielectric bodies separated by a liquid. The liquid was assumed to have bulk properties (i.e., hydration was ignored).

Given that assumption, the theory invoked the full apparatus of quantum field theory to give what seemed to be a complete solution of the problem. It included temperature dependence of interactions, all many body interactions, so called retardation and contributions from all electromagnetic frequencies. Its genius lay in recognising that the measured dielectric susceptibilities of interacting materials as a function of frequency included implicitly all many body interactions [13].

A difficulty was that no one had any idea of how to use the theory, a problem solved by Ninham and Parsegian [14]. The theory underwent all sorts of further extensions to different shapes, layered, magnetic and conducting materials and electrolytes. [15]

The key insight from our point of view is this: The potential is a sum of contributions from all electromagnetic frequencies. Some can be positive, some repulsive depending on the interacting materials. Each frequency component $F(\omega)$ is damped exponentially

(for planar media)

$F(\omega,L) \sim [-A(\omega)/L^2] \exp\{-2\omega L/c\, E(i\omega)\}$

Where ω is the frequency, L distance of separation, c the velocity of light, and $E(i\omega)$ the dielectric susceptibility of the intervening medium at frequency ω in the imaginary axis. The pre-factor is complicated).

The conceptual picture that emerges is this: two objects sense and recognise temperature dependent zero frequencies first. As they come closer infra red frequencies kick in (~20-50 nm), followed by optical frequencies (~4nm) far ultraviolet (1nm) until atomic contact or hydration where chemistry takes over.

In other words, two objects feel each other's specific vibrations, and respond appropriately. Sometimes that specificity can be very strong and the forces very long ranged.

(An extreme example is that of parallel thin cylinders. If non-conducting, the interaction potential is $V(r) \sim r^{-4}$. If conducting, e.g DNA molecules, the interaction goes as $1/\{[r^3/2]\ln r\}$. This force is strictly non additive and essentially infinitely long ranged. For two dimensions, and for conducting planes, the potential (Casimir force) is by comparison short ranged [16].)

With electrolytes the situation become more complicated in that the temperature dependent contributions are modified to decay with another factor, depending on the Debye length, $\exp(-2\kappa L)$ [15].

3 b Semi Classical and Quantum Field Theory: a Digression

The in-principle notion of recognition, dependent on material properties and physico-chemical environment, was agreeable. But the claims for generality, even granted the bulk medium approximation, went too far. The theory turned out to include a hidden sleight of hand. (Technically, at a certain point in the development, a nonlinear coupling constant integration in a Dyson integral equation for the dielectric susceptibility was approximated by a linear integration). The mystique of quantum field theory was exposed. The whole theory collapsed to a semi-classical theory. That is; it was nothing more than Maxwell's equations for the electromagnetic field with boundary conditions plus the Planck hypothesis for quantisation of light [17].

This equivalence of QFT with semi-classical theory allowed much more difficult extensions of theory to be tackled. Much of the literature in physics on molecular interactions is derived at zero temperature, e.g, the Casimir Polder and Casimir interactions for "retarded" van der Waals interactions. "Retardation" refers to a weakening of the interactions attributed to the finite velocity of light. It turns out that this is quite wrong! [18].

Similarly the literature treatment of resonance or retarded Forster interactions involving excited state-ground state interactions on which mooted quantum computing is based are even more incorrect and unphysical [19]. The illusions, like the DLVO theory, persist and comfort the Boetians.

Another unnoticed development occurs if one allows a connection to be made between Casimir–Lifshitz forces at finite temperature in a vacuum and particle physics. Weak interactions (mesons) emerge naturally and quantitatively [20].

4. Complexity due to the Hofmeister Problem. Ion Specificity and the Failure of DLVO theory.

4a The Hofmeister Problem.

Theories of physical chemistry have been unable to accommodate ion specificity for over 200 years except by invoking arbitrary parameters like postulated ion size. The size is adjustable and different for every case and temperature. The problem exists for Born energies, interfacial tensions, activities, pH, pKas, buffers, ion binding and viscosities. The present state of affairs with Hofmeister effects is discussed in the preceeding volume of this Journal.

Two examples are illustrative of the problem.

For the measured pH of a sequence of 1:1 salts in buffered solutions: the "pH" change in phosphate buffer follows a Hofmeister sequence. But if the sodium salts are replaced by potassium salts the sequence reverses! In a cacodylate buffer at the same nominal pH the sequence reverses from the phosphate case also [3, 21]. This and many other standard measurements are inexplicable with classical theory, which does not accommodate specific ion effects.

4b Indirect forces

Another stark example of the failure of theory is that of the efficiency of linear DNA cutting by a restriction enzyme [22].

Again this is inexplicable in classical theory, which provides no source of energy to describe the activity. Hofmeister effects need to be are recognised and treated correctly.

The mechanism is indirect and involves hydrophobic cavitation and cooperative harnessing of all weak van der Waals forces [3, 22].

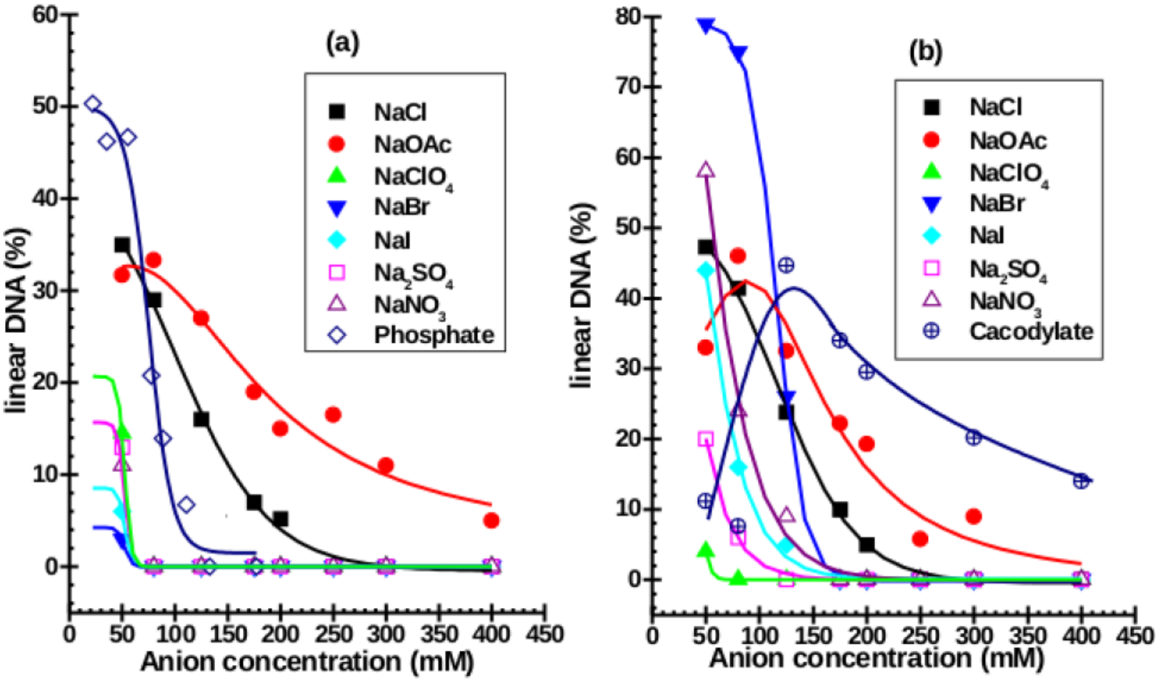

Fig 1. Illustration of a Hofmeister series in restriction enzyme cutting as a function of a series of 1:1 salts. The y axis measures cutting efficiency. The x-axis is salt concentration. The series reverses on changing from phosphate to cacodylate buffer at the same nominal pH [22].

4c More Complexity due to Hofmeister Effects: Disagreeable facts and agreeable consequences.

Specific ion effects show up dramatically in many other cases, e.g., in the self assembly of surfactants in micelles, vesicles and microemulsions. Forces with different counterions and coions and forces between interfaces can vary by orders of magnitude [3,23]. By contrast the DLVO theory can only try, but fails to accommodate such variability by importing extra non predictive parameters like ion size. These are often absurd. The resolution can be traced to the fact that the ansatz of DLVO theory that underpins the entire theoretical fabric of the discipline is flawed. Additivity of electrostatic forces, treated in *non-linear* theory, and van der Waals forces treated in a *linear* theory is not allowed in physics. The matter is not just one of approximation, and the entire theory has to be rewritten. The consequences are that most measurements like pH, Buffers, ion binding that rely on the classical theory are of dubious value. At one level this is disagreeable and is therefore almost universally ignored. On the other hand, an agreeable consequence is that those few who actually understand the situation are in a good position to exploit forces due to specific ion effects. Deryaguin and Overbeek both were well aware of the limitations of their theory of interactions of lyophobic not hydrophobic colloids, of specific ion effects and that it failed above 0.05M. The best advice of the IUPAC Committee on pH is to avoid electrolyte concentrations above at most 0.1M. And anything more complicated : Forget it . For a detailed account of the present state of affairs on Hofmeister effects see recent COCIS issues.

However, the challenge posed by the erroneous nature of the foundations of the theory and the neglect of Hofmeister effects is the least of our concerns.

5. Complexity due to Hydrophobic Forces and Dissolved Gas

Measurements of long ranged hydrophobic forces between interfaces have been the attention of numerous publications [24, 25]. They remain mysterious. On removal of atmospheric gas they disappear [26, 27]. (This fact provides a likely clue to mechanism: Surface induced water structure can extend only about 6 molecular diameters. Dissolved gas molecules perturb bulk water also and extend that range by percolating and carrying the fluctuations from one gas moelcule to another . Salt ions either oppose or enhance those complex density fluctuations.)

It is not necessary to use specialised equipment to demonstrate the operation of hydrophobic interaction forces. For example, if we take a small droplet of oil of density only slightly above that of water, we can visually observe the effects of surface forces in determining whether we observe the droplet to coalesce or float above an oil-water surface. DLVO theory predicts that the droplet should not coalesce because the repulsive force generated by the surface charge density at the oil-water interface should overcome the gravitational force acting on the droplet. See example in Fig 2. This is not just a thought experiment but has been carried out using droplets of the oil bromododecane (BDD) which has a density just slightly above that of water. Dynamic light scattering was used to determine the surface potential at the oil-water interface in 10mM NaCl. Using these values droplets of 1mm diameter or less should form a cream at the oil-water interface but they do not. They all coalesce. This appears to be one of the clearest demonstrations of the effects of a surface force apparently generated because of the presence of a two interacting hydrophobic surfaces [28].

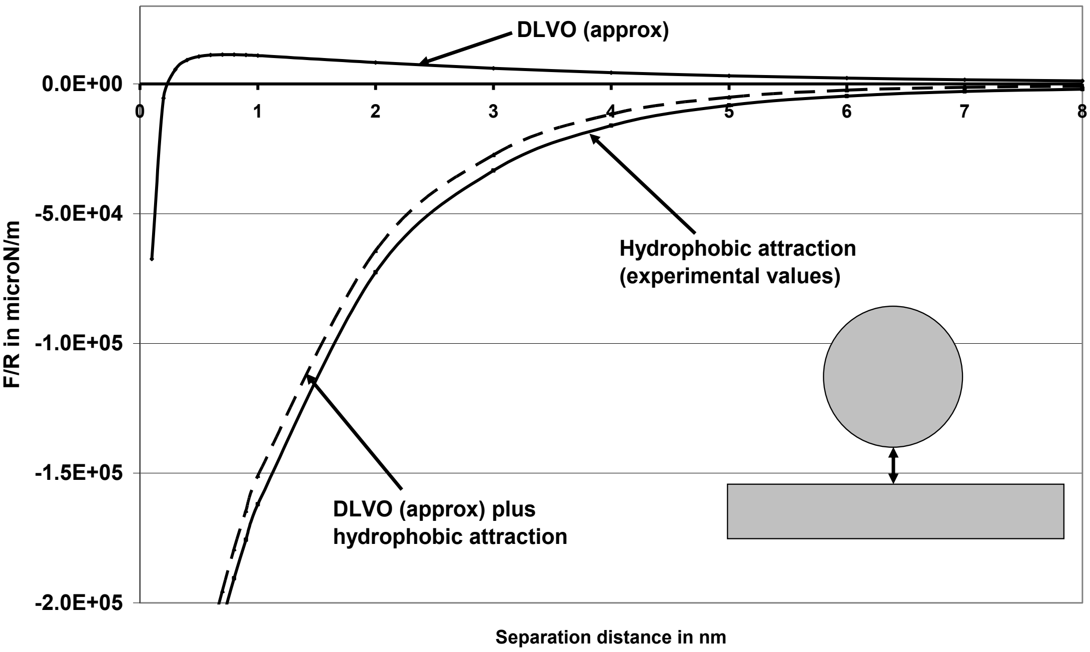

Fig 2. Calculated interaction forces (F) between a spherical BDD droplet of radius R and a flat surface of BDD immersed in 10mM NaCl solution. The surfaces were assumed to have a surface potential of -75mV and a Hamaker constant of $5E^{-21}$J.

Another very visual demonstration of the effects of surface forces arises when oil and water mixtures are almost completely de-gassed. Some years ago it was reported that cavitation occurred when two hydrophobic surfaces were pulled apart in water [24]. This led to the idea that removal of dissolved gases may facilitate 'oil mixing with water' because dissolved gases enable cavitation. This has now been well demonstrated [29,30]. A typical example is given in Fig 3.

Fig 3. 0.2ml of perfluorohexane oil dispersed in 25ml of water (degassed on right, gassed on left). Photograph taken 2-3 minutes after 10 seconds of vigorous shaking.

The de-gassed dispersions remain stable for many hours whereas the gassed mixtures phase separate very quickly. It was even proposed that this offers a new process for cleaner drug delivery since many anti-cancer drug are oily liquids [31].

If dissolved gases strongly affect the hydrophobic interaction then such effects should be observable from direct surface force measurements and these have been reported, although the area is fraught with confusing results [32]. It might be useful to observe the effect of dissolved gases on coalescing single oil droplets, as discussed before, but this has not yet been done.

The high interfacial tension between oil and water presumably causes local cavitation, perhaps via nano bubbles, and these effects extend the attractive force between two hydrophobic surfaces to a much longer range than could be expected from merely a solvent molecular ordering perturbation, which in water could only be expected to extend a few nms. By comparison, hydrophobic attractions have been reported out to about 90nm [33].

5. Non Hofmeister Ion Specificity: Bubble-bubble interactions

The effects of most salts on inhibiting bubble coalescence has been well studied [34,35] but there is still with no progress on understanding of the fundamental processes involved. In practice, producing a bubble column filled with suitable salt solutions is a simple task but understanding the reasons for the visible observation of an opaque column (i.e. produced with fine bubbles) compared with a clear column, say in water, with substantially larger bubbles, is hard to understand.

The problem is that fundamental physical chemistry predicts bubble coalescence enhancement with added high salt because (a) it should screen out any electrical double layer repulsion between negatively charged bubbles and (b) should increase the surface tension – favouring bubble coalescence. The situation is further, and greatly complicated, by the fact that some salts inhibit coalescence and some don't and their behaviour can be accurately described by a remarkable table, given below:

{ SHAPE * MERGEFORMAT }

Table 1. Experimental combining rules for added salts on inhibiting bubble coalescence.

The complexity of this behaviour is clearly hard to explain with any simple theory, although recently the classical DLVO explanation has once again been invoked to "explain" the phenomenon. The explanation is specious and wrong. It indictates the religious fervour in which the DLVO theory is clung to. Murmur [36] proposed the speciation of dissolved carbon dioxide and the associated surface adsorption onto bubbles as a possible mechanism. But experiments already published demonstrate very clearly that (a) the original bubble coalescence experiments were carried out specifically under conditions designed to exclude and carbon dioxide (b) recent experiments using air gave the same results and (c) any DLVO model cannot possibly work at the very high salt concentrations where the inhibition is observed (see Fig 4). That is, the presence or absence of dissolved carbon dioxide has little or no effect on bubble coalescence inhibition.

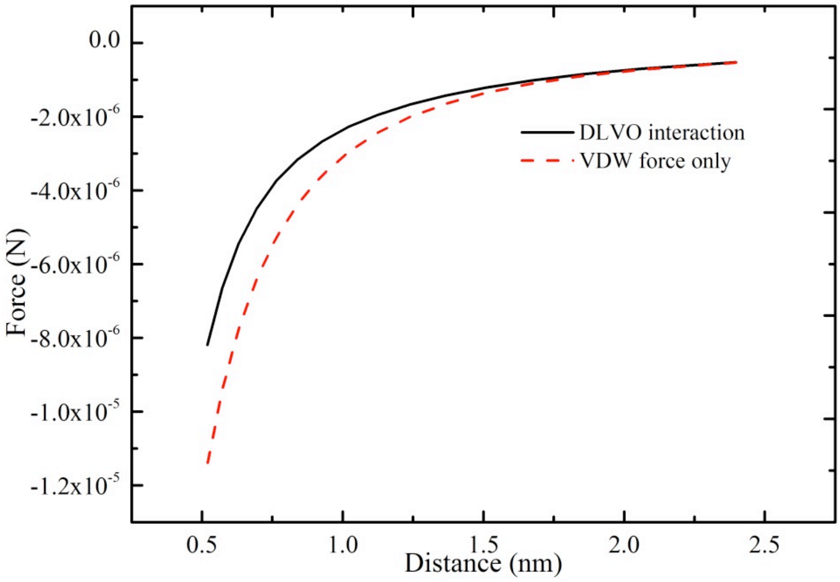

Figure 4. DLVO calculation using the non-linear Poisson-Boltzmann equation { ADDIN EN.CITE <EndNote><Cite><Author>Chan</Author><Year>1980</Year><RecNum>336</RecNum><DisplayText>(Chan, Pashley, & White, 1980)</DisplayText><record><rec-number>336</rec-number><foreign-keys><key app="EN" db-id="xra9tp5wz52f0redrsq505zyv5fx25pe2pp2" timestamp="1464654008">336</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>Chan, Derek YC</author><author>Pashley, Richard M</author><author>White, Lee R</author></authors></contributors><titles><title>A simple algorithm for the calculation of the electrostatic repulsion between identical charged surfaces in electrolyte</title><secondary-title>J. Colloid Interface Sci. </secondary-title></titles><periodical><full-title>J. Colloid Interface Sci.</full-title></periodical><pages>283-285</pages><volume>77</volume><number>1</number><dates><year>1980</year></dates><isbn>0021-9797</isbn><urls></urls></record></Cite></EndNote>} of the force between two bubbles, radius 1 mm, surface potential −40 mV and Debye length 0.3 nm, which corresponds to a concentration of 1M for a 1:1 electrolyte, and a non-retarded Hamaker constant of 37×10^{-21} J.

The effect does not follow any Hofmeister series and recent experimental studies aimed at elucidating the underlying mechanism have, if anything, made understanding the process even more intractable. An explanation was proposed based on the observation that nearly all bubble column studies used dry gases and since the bubbles formed must adsorb water vapour, a higher solute concentration should be transiently produced around the bubbles. When two bubbles collide an interlayer of higher osmotic pressure would be formed, which would act to force colliding bubbles apart.

This model has been thoroughly tested, however, by using an inlet gas 100% water vapour saturated – which would remove this evaporative effect. In these experiments the coalescence inhibition was found to be the same as that observed with dry inlet gas. Thus, water vapour evaporation was found not to be part of the explanation [38].

Other proposed explanations have been based on ion hydration and viscosity effects in the film draining between two colliding bubbles. Both these factors should be influenced by using very hot inlet gases, which must affect the coalescence behaviour, at least just above the sinter in a bubble column. Experimental studies have recently been carried out at gas inlet temperatures as high as 275^0C. Some typical results are given in photographic form in Fig 5.

Figure 5. Bubble column containing pure water (left-hand photo) and 0.5m NaCl solution (right-hand photo) with inlet gas dry air at 275°C. Adapted from ({ ADDIN EN.CITE <EndNote><Cite><Author>Shahid</Author><Year>2014</Year><RecNum>69</RecNum><DisplayText>(Shahid & Pashley, 2014b)</DisplayText><record><rec-number>69</rec-number><foreign-keys><key app="EN" db-id="xra9tp5wz52f0redrsq505zyv5fx25pe2pp2" timestamp="0">69</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>Shahid, Muhammad</author><author>Pashley, Richard Mark</author></authors></contributors><titles><title>A study of the bubble column evaporator method for thermal desalination</title><secondary-title>Desalination</secondary-title></titles><pages>236-242</pages><volume>351</volume><dates><year>2014</year></dates><isbn>0011-9164</isbn><urls></urls></record></Cite></EndNote>}.

Clearly there was no significant effect at this high temperature compared with room temperature, even though the air bubble-water interface must have been very different in the two extreme cases, at least in the first 5cm above the sinter. This appears to have no effect on the bubble sizes produced in a bubble column. Once again, these results present a problem for finding an explanation, since adsorbed ion hydration and film viscosity both appear not to influence the observation that it is the presence or absence of certain salts which control this phenomenon.

6 . Complexity due to Hot Bubbles and a New World of Forces

Although bubble column evaporators (BCE) are, in practice, easily set up, especially using aqueous solutions that prevent bubble coalescence and produce dense bubble columns, our theoretical understanding is still lagging behind. Bubbles in the 1-3 mm size range are easily produced in aqueous salt solutions and this range seems to be ideal for this process because these bubbles rise at the maximum possible rate for any size bubble and yet they are small enough to produce a reasonable air-water interfacial area (see Fig 6). They also pick up water vapour quite rapidly, becoming saturated within a few tenths of a second [40]. This occurs because of a combination of oscillating shape and shear forces at the rising bubble's surface between the air and the water.

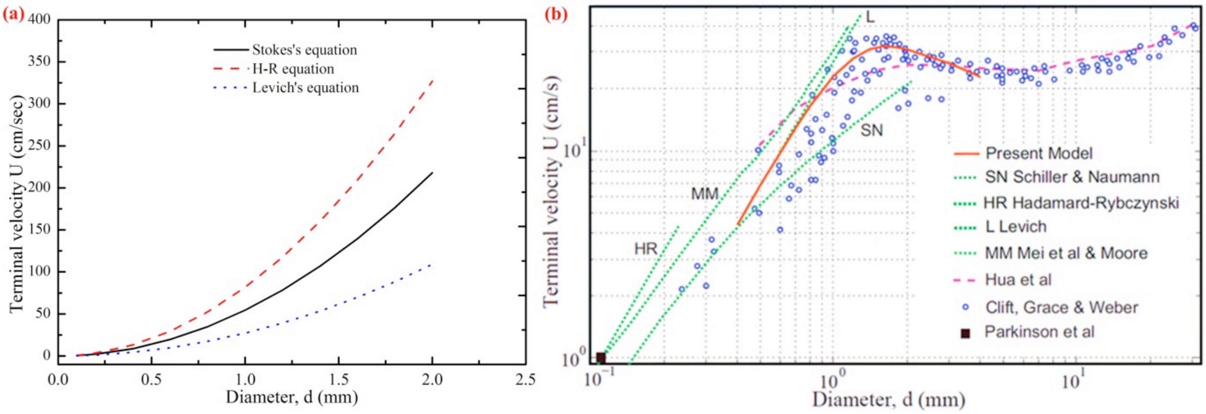

Figure 6. The relationship between the rise velocity of isolated bubbles and bubble diameter

from: (a) calculated values using Stokes' Law, and the Hadamard-Rybczynski and Levich equations; and (b) experimental data and several typical models, adapted from { ADDIN EN.CITE <EndNote><Cite><Author>Klaseboer</Author><Year>2011</Year><RecNum>111</RecNum><DisplayText>(Klaseboer et al., 2011)</DisplayText><record><rec-number>111</rec-number><foreign-keys><key app="EN" db-id="a9ra5sf2bzpfd7efvw4xxt5lrdtar0tp59vs" timestamp="1447117225">111</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>Klaseboer, Evert</author><author>Manica, Rogerio</author><author>Chan, Derek YC</author><author>Khoo, Boo Cheong</author></authors></contributors><titles><title>BEM simulations of potential flow with viscous effects as applied to a rising bubble</title><secondary-title>Eng. Anal. Bound. Elem.</secondary-title></titles><pages>489-494</pages><volume>35</volume><number>3</number><dates><year>2011</year></dates><isbn>0955-7997</isbn><urls></urls></record></Cite></EndNote>}.

Another remarkable property of the bubble column evaporator is that when aqueous solutions are used the inlet gases can be extremely hot but still, independent of flow rate, the column solution will not reach boiling point. A simple equation was derived in 2009 [42] which accurately describes the thermal energy balance in this situation:

$$[\Delta T \times C_p(T_e)] + \Delta P = \rho_v(T_e) \times \Delta H_{vap}(T_e) \quad \text{(in units of J}\cdot\text{m}^{-3}\text{)},$$

where $C_p(T_e)$ is the specific heat of the gas flowing into the bubble column at constant pressure in units of $J\cdot m^{-3}K^{-1}$; T_e is the steady-state temperature of the column in units of °K; ρ_v is the water vapour density at T_e, in units of $mol\cdot m^{-3}$; ΔT is the temperature difference between the gas entering and leaving the column in units of °K; and ΔP is the corresponding differential pressure in units of $J\cdot m^{-3}$, which represents the work done by the gas from when it flows into the base of the column until it is released at the top of the solution.

The equation can be easily explained because it is based on the assumption that when the bubble column reaches a steady state temperature, each new bubble, on average, must impart to the column precisely that amount of heat equal to that needed to evaporate water to saturate the bubble. Note that evaporative cooling means that the column will always equilibrate at a temperature much lower than the inlet gas temperature, as illustrated in Fig 7.

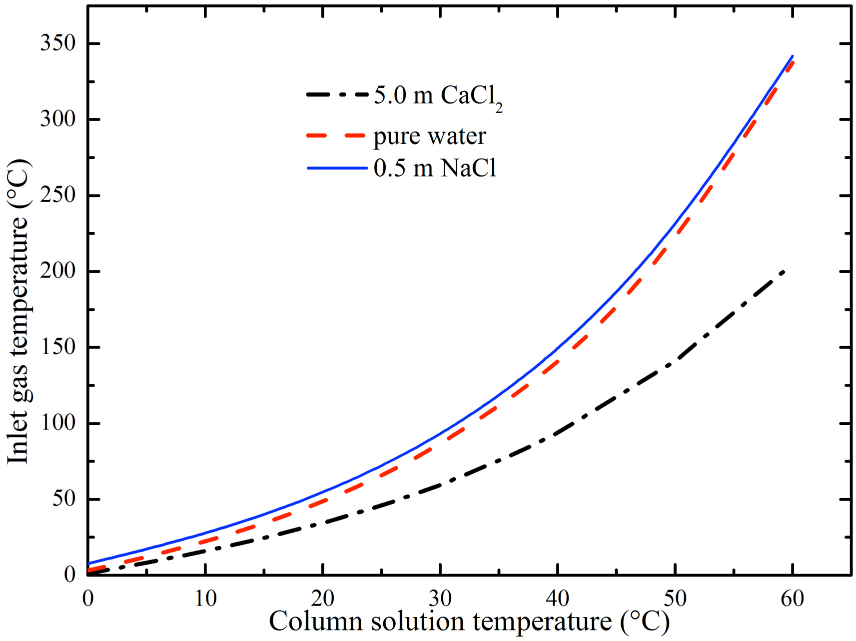

Fig 7. Calculated steady state temperatures for a bubble column containing pure water, 0.5 m NaCl and 5.0 m $CaCl_2$ solutions as a function of inlet (dry) gas (air) temperature under atmospheric pressure.

These predictions have been accurately tested, so far, up to inlet gas temperatures of 275^0C. This has already meant that hot gas BCE systems have been used to inactivate coliforms at column solution temperatures of only 50^0C or less. Recently, these systems have been used to decompose solutes at much lower temperatures than through normal heating bath methods. If the equation continues to work at even higher temperatures, then hot gas BCEs could be used for many more applications in water treatment processes.

The efficiency of the process for inactivating coliforms has recently been enhanced by controlling the surface forces between hot bubbles and the coliforms. Both have negatively charged surfaces and it has been demonstrated that addition of 0.01M $CaCl_2$, which substantially reduces the double layer repulsion, has a dramatic effect [43]. These results also strongly support the collision model (i.e. between bubble and cell) for this low temperature sterilization process.

Future applications of this novel technique will no doubt be focussed on the use of very hot gases and these systems will have wide applicability to many aqueous based solutes and particles, especially in waste water treatment. And to a wide range of high temperature reactions, now possible at low solution temperatures.

7. Complex Forces in the Real World

Our survey has shown that much of what we held sacred on forces is often irrelevant. And certainly impotent in application to biology and energetics.

We have identified substantial deficiencies in theory, and in consequence, in measurements that depend on those theories. Suppose those difficulties are resolved - the matter is more complex still. Dissolved gas, cavitation and bubbles, specific ion effects, and temperature, are all components of the ancient Greek view of the elements: earth, air, water and fire. We have been missing air and fire and light, which we have hardly touched on.

The effects these omissions can have on our intuition can be seen in the work of McCollom on the formation of meteorite hydrocarbons from thermal decomposition of siderite ($FeCO_3$).

Thermal decomposition of siderite had been proposed as a source of magnetite in martian meteorites. Laboratory experiments were conducted to evaluate the possibility that this process might also result in abiotic synthesis of organic compounds. Siderite decomposition in the presence of water vapor at 300°C generated a variety of organic products dominated by alkylated and hydroxylated aromatic compounds. The results suggest that formation of magnetite by thermal decomposition of siderite on the precursor rock of the martian meteorite ALH84001 would have been accompanied by formation of organic compounds and may represent a source of extraterrestrial organic matter in the meteorite and on Mars. The results also suggest that thermal decomposition of siderite during metamorphism could account for some of the reduced carbon observed in metasedimentary rocks from the early Earth [44].

The important point hardly noticed is that the addition of water to the inorganic iron carbonate rock produced a huge range of complex organic products that occur in oil reservoirs. It had been thought that such “life” product molecules in oil reservoirs had to be the consequence of bacterial activity. It had been postulated by T. Gold in the 1990’s and other model experiments done in 2004 confirmed that such processes can indeed be the source of semi-infinite, as yet untapped sources of natural gas and inorganic oil [45] . The matter is completely open and of extreme interest. It is connected also to the present interest in “climate change”.

forces COCIS

Another problem to ponder is that of Greek fire. A closely guarded secret, it preserved the Byzantine Empire for a thousand years by keeping the Turks at bay. Secret recipe for Greek Fire: (due to Marcus Graecus, 10th century, quoted by John Julius Norwich, Byzantium, the Early Centuries, Penguin Press, 1990) “Take pure sulphur, tartar, sarcocolla (Persian gum), pitch, dissolved nitre, petroleum, (obtainable from surface deposits in Mesopotamia and the Caucasus) and pure resin; boil these together, then saturate tow with the result and set fire to it. The conflagration will spread, and can be extinguished only by wine, vinegar or sand.”

Let us finish now on a less strident note, and borrow from wiser predecessors:

From Morris Kline in his peroration on the plight of Mathematics (Mathematics the Loss of Certainty Oxford (1960))
It behooves us therefore to learn why, despite its uncertain foundations and despite the conflicting theories of mathematics, mathematics has proved to be so incredibly successful. So too for science.

And from his translation of some aphorisms of Xenophanes that seem to be apposite:
The Gods have not revealed all things from the beginning, But men seek and so find out better in time.
Let us suppose these things are like the truth. But surely no man knows or will ever know The truth about the gods and all I speak of. For even if he happens to tell the perfect truth, He does not know it, but appearance is
fashioned over everything.
There are rapid strides being made to improve and remedy present theories. And what is encouraging is that when the chemistry is done correctly, when the conceptual locks are removed, more often than not the emerging theories do actually work, predictively.

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