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FOCUSING ON PARTICLES, CONTACT ANGLE AND SURFACE THERMODYNAMICS

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TENTH INTERNATIONAL SYMPOSIUM ON PARTICLES ON SURFACES: DETECTION, ADHESION AND REMOVAL, to be held in Toronto Canada, June 19-21, 2006.

FIFTH INTERNATIONAL SYMPOSIUM ON CONTACT ANGLE, WETTABILITY AND ADHESION; to be held in Toronto Canada, June 21-23, 2006.

EDITORIAL NOTES

During the week of June 19, 2006 MST CONFERENCES will be holding the 10th in its series of symposia on Particles on Surfaces along with the 5th International Symposium on Contact Angle, Wettability and Adhesion in Toronto, Canada. At first blush these two symposia seem to bear little or no relation to one another. After all what do people interested in detecting and removing dust from surfaces have in common with those who watch how liquids bead up and spread? The answer lies in the common unifying concepts of surface thermodynamics and intermolecular forces which control both types of behavior. Small particles have a very high fraction of their mass located either at or close to the particle surface. Thus the surface free energy constitutes a very significant fraction of the total free energy of the particle. In addition, the surface free energy dominates the particles interactions with any foreign surfaces to which it may come in contact with. Anyone interested in removing a particular type of particle contaminant from a surface should have a keen interest in knowing the nature of the interactions which are binding the particle to the surface. Likewise, those who want to spread a liquid over a surface in order to form a uniform coating also need to know the nature of the interactions between the spreading liquid and the substrate.

The importance of surface thermodynamics goes well beyond the fairly obvious examples given above. Consider for example the common use of solvents in surface cleaning applications. In this case we now have three different materials each with its own surface free energy. The person interested in removing the particle from a surface would like to use a solvent that interacts more strongly with the particle than the particle interacts with the surface. In this manner the solvent can effectively wet the particle and hold it in solution so that it can be carried away during the rinse step. Clearly removing a particular type of particle contaminant requires knowledge of how well solvents interact with the particles in question. The topic of contact angle behavior of liquids on particles has clear relevance for particle

cleaning applications.

Finally, we would be remiss not to mention the biomedical ramifications of particle solvent and particle surface interactions. Fine particles have found very important applications in the realm of stabilization and controlled release of a variety of medications. Nearly all drugs require that they be absorbed by the body in the correct concentration over some appropriate time span. Too low a concentration is ineffectual and too high a concentration can act as a poison with serious side effects. In addition many medications need to be maintained at some effective concentration over a long time span. It has been found that particles can serve as carriers for a variety of drugs and have the capability of releasing the medication into the blood stream in a systematic way which is controlled by the balance of the surface and bulk chemical potentials governing attachment and release of the active molecule from the particle surface. Needless to say the surface thermodynamics of the interactions of the medication with the particle surface and the ambient in vivo environment are critical in determining how this process of controlled release progresses.

With the above comments in mind, the topic of this issue's essay deals with a review of the unifying aspects of surface thermodynamics and molecular interactions which bind the concepts of contact angle measurement and particle adhesion as seemingly different aspects of common underlying phenomena. As usual we invite the comments and constructive criticisms of our readers on all aspects of this newsletter.

THE CURIOUS WORLD OF CONTACT ANGLES AND PARTICLE ADHESION:

Surface Free Energy: The Common Denominator Between Contact Angle Behavior and Particle Adhesion

In my earlier career in the microelectronics industry there was a critical need to know the surface wetting behavior of silicon and ceramic

surfaces by photoresist materials and electrically insulating polymers such as the polyimides. The key goal was to be able to fabricate uniform coatings with the proper level of adhesion. The photoresist materials, for instance, had to have sufficient adhesion to endure patterning and deposition processes but should not adhere too strongly so as not to be removable in the final stripping step. The polyimide insulator coatings on the other hand could never adhere strongly enough since they formed an integral part of the final product which had to last indefinitely. The most favored surface analytical techniques at the time were the various surface spectroscopies such as X-ray Photoelectron Spectroscopy (XPS, alias ESCA), Secondary Ion Mass Spectroscopy (SIMS), Electron Energy Loss Spectroscopy (EELS), ... (the list is nearly endless). All these methods were quite powerful and important in elucidating our understanding of the chemical nature of the surfaces of interest, but they had the distinct drawback of being tied to very complex and expensive equipment which required dedicated expert handling. In many cases our main interest was whether a coating material was going to wet properly, and of course always being in a hurry, the use of relatively simple contact angle measurements seemed to offer a solution that was both effective and ready to hand.

At the crudest level one simply applies a drop of the liquid of interest to the relevant surface and notices how the drop tends to bead up. A near spherical drop that forms a steep angle with the substrate at the drop edge would be indicative of poor wetting and thus apparently weak attraction to the surface. A nearly flat drop on the other hand indicates good wetting and therefore a fairly strong interaction with the substrate. A truly quick and dirty method of assessing the interaction of the drop with a given surface consisted of placing a drop of the liquid in question on a flat strip of the substrate material and then raising one end of the strip relative to the supporting table to form an inclined plane at some angle θ . By progressively increasing θ until the drop just starts to roll down the slope one can come up with an ersatz contact angle which is indicative of how well the drop wets the surface. However, whereas such "hook or by crook" methods may have been good enough for

the practical types, those of us in the research laboratory required something more controlled and accurate and thus resorted to the use of a contact angle goniometer.

With the contact angle goniometer one measures the angle the drop makes with the surface directly using a telescopic microscope while the drop and substrate are in an enclosed environmental chamber. Thus one should be able to analyze the data in terms of some physical theory based on thermodynamic principles.

Classical Theories of Contact Angle Behavior

Etzler¹ has given an overview of several of the more popular theories of contact angle behavior. Without going into details, what one finds is that all theories are an amalgam of the following ingredients:

- ▶ Classical thermodynamics
- ▶ Mechanics of elastic bodies (continuum theory)
- ▶ Empirical phenomenology

Treating the above items one at a time we first need to understand what is meant by "Classical Thermodynamics". Consulting nearly any text on the topic we find that Classical Thermodynamics is neatly encapsulated in the following basic principles:

- ▶ First Law: Conservation of Energy
- ▶ Second Law: Existence of the Entropy functional S with the property that for all physical processes in an isolated system the change in S is positive semi-definite ie. $\Delta S \geq 0$.

¹"Characterization of Surface Free Energies and Surface Chemistry of Solids", F. Etzler, in Contact Angle, Wettability and Adhesion, Vol. 3, Ed. K. L. Mittal (VSP, Utrecht The Netherlands, 2003) p 222.

- ▶ Zeroth Law: Material bodies at equilibrium can be characterized by a quantity known as the temperature T with the transitive property that any two bodies in equilibrium with a third body at temperature T will also be at this temperature. This law essentially allows for the practical measurement of temperature.

The precise formulation of classical thermodynamics is more involved than the above terse summary but it suffices for current purposes.

A definitive formulation can be found in the excellent text by Callen.² Though the above axioms form the crux of the classical theory, one final notion is required to complete the picture and that is the concept of a thermodynamic model of a system at equilibrium. Not all references are clear or specific about the concept of a thermodynamic model but I can highly recommend the text by Callen which gives the best treatment I am aware of. What it comes down to is this: for a material body or collection of material bodies at equilibrium one postulates the existence of a collection of thermodynamic variables and the existence of a functional expression which relates them. The simplest example would be a gas or liquid in some sort of container that is characterized by the volume V, the entropy S, and the number of each of the different types of particles present N₁, N₂, ...etc. The functional in question would be the total energy U defined as U=U(S, V, N₁, N₂, ...). Unfortunately the classical theory has little to say about the details of U except that it must be a first order homogeneous function of all the extensive variables. One is left to one's own devices to come up with a specific form for U which might be arrived at through some kind of guess based on intuition, experiment or possibly divine revelation. More likely one derives U using the methods of Statistical Mechanics on the basis of some atomic or molecular model. However one goes about it, once U is established then the following equations of state follow directly:

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, N_1, N_2, \dots etc}$$

$$P = \left(\frac{\partial U}{\partial V} \right)_{S, N_1, N_2, \dots etc}$$

$$\mu_1 = \left(\frac{\partial U}{\partial N_1} \right)_{S, V, N_2, \dots etc}$$

$$\mu_2 = \left(\frac{\partial U}{\partial N_2} \right)_{S, V, N_1, \dots etc}$$

[1]

With the equations of state in hand all relevant properties of the system are now prescribed. For instance the second relation gives the pressure, volume, temperature equation of state of which the ideal gas law is the simplest example. The first relation is less well known but from it one can get such useful quantities as the specific heat of the system. The bottom two relations are the chemical potentials which govern all manner of phase equilibria, diffusion processes and chemical reactions. Callen refers to U=U(S, V, N₁, N₂, ...) as the fundamental relation of the system. The importance of knowing U is summarized in Callen's inimitable wording:

"...if the fundamental relation of a particular system is known all conceivable thermodynamic information about the system is ascertainable therefrom. The importance of the foregoing statement cannot be overemphasized. The information contained in a fundamental relation is all-inclusive – it is equivalent to all conceivable numerical data, to all charts, and to all imaginable types of descriptions of thermodynamic properties. If the fundamental relation of a system is known, there remains not a single thermodynamic attribute that is not completely and precisely determined."

Needless to say we are rarely in possession of the fundamental relation for the system we are most interested in, and that is certainly the case for

² "Thermodynamics", by Herbert B. Callen (John Wiley & Sons, 1960), Chapter 1.

contact angle problems. The contribution of classical thermodynamics to contact angle theory comes in the form of the Dupre equation which is essentially equivalent to the first postulate or conservation of energy given by:

$$W_{ad} = \gamma_s + \gamma_l - \gamma_{sl} \quad [2]$$

Where:

- W_{ad} = Work of adhesion (J/m²)
- γ_s = Surface tension of solid (J/m²)
- γ_l = Surface tension of liquid (J/m²)
- γ_{sl} = Surface tension of liquid-solid interface (J/m²)

This relationship states that if you remove a unit area of liquid from the solid surface you gain the surface energy of the solid plus the surface energy of the liquid but simultaneously lose the interaction energy between the two. The difference between what is gained and what is lost then amounts to the net work that must be done to remove the drop which is defined as the work of adhesion W_{ad} . Equation (2) has 4 variables of interest the main one being the work of adhesion. Of the remaining three the surface tension of the liquid γ_l is most readily available from tables of thermodynamic data. This leaves 3 undetermined quantities to deal with (W_{ad} , γ_s , γ_{sl}). At this point one has to leave the realm of classical thermodynamics and invokes a basic principle of mechanics which states that the sum of all the tensions acting at the edge of the drop must balance to zero for equilibrium to hold. This then leads directly to the well known relationship of Thomas Young:

$$\gamma_l \cos(\theta) = \gamma_s - \gamma_{sl} \quad [3]$$

Where θ is the contact angle the drop makes with the solid surface and all the other quantities are as defined in Eq.(2). Figure 1 illustrates the standard geometrical picture.

Equations (2) and (3) contain a total of 5 quantities of interest four of which are listed above plus the contact angle θ . In practice θ is measured using a goniometer and γ_l is readily measured using independent methods such as the

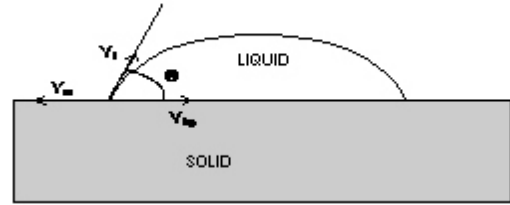


Figure 1 Liquid drop on solid surface exhibiting relevant surface tensions and resulting contact angle.

Wilhelmy plate experiment which relies on the capillarity behavior of the liquid caused by the surface tension. Three quantities now remain to be determined which are: W_{ad} , γ_s and γ_{sl} . Since we have only two equations relating these quantities the problem remains indeterminate. However, we note that the quantities γ_{sl} and γ_s appear in both equations as the combination $u = \gamma_s - \gamma_{sl}$. Substituting u into Eqs.(2) and (3) gives:

$$\begin{aligned} W_{ad} &= \gamma_l + u \\ \gamma_l \cos(\theta) &= u \end{aligned} \quad [3]$$

We can readily eliminate u from Eqs. (3) to yield the famous Young-Duprey relation:

$$W_{ad} = \gamma_l(1 + \cos(\theta)) \quad [4]$$

In principle Eq.(4) allows us to determine the work of adhesion W_{ad} by measuring the contact angle of a drop of liquid with a known surface tension γ_l . This leaves γ_s and γ_{sl} still at large and both are difficult quantities to measure while being of great interest for reasons both academic and practical.

From the experimental point of view there are a number of alternate methods for getting at γ_s and γ_{sl} a short list of which includes:

1. Surface flow calorimetry
2. Inverse gas chromatography
3. Observation of solid-liquid melt boundary

A detailed description of these methods is well beyond the scope of this short essay. Needless to say each method comes with its own particular set

of advantages and disadvantages. The interested reader should consult the review article by Etzler¹ mentioned above or the edited volume by Neumann and Spelt.³

In order to make further progress in determining γ_s and γ_{sl} by theoretical methods we invoke the third item in our amalgam of ingredients listed above which is the use of empirical phenomenology. We have to somehow come up with another equation relating γ_s and γ_{sl} . At this point there are basically two schools of thought. The first approach goes under the heading of "equation of state theory" which is described in detail in the volume of Neumann and Spelt mentioned above. Going back to the thermodynamic modeling formalism of Callen², one posits the existence of a fundamental relation which describes the equilibrium properties of the contact angle system in Fig.(1). Having done this one can then claim the existence of three further equations of state similar to those in Eq.(1) which define each of the surface tensions γ_{lr} , γ_s and γ_{sl} in terms of the surface strains which must exist at each interface.

$$\begin{aligned} \gamma_s &= f_s(\epsilon_s, \epsilon_p, \epsilon_{sp}, \dots) \\ \gamma_l &= f_l(\epsilon_s, \epsilon_p, \epsilon_{sp}, \dots) \\ \gamma_{sl} &= f_{sl}(\epsilon_s, \epsilon_p, \epsilon_{sp}, \dots) \\ &\cdot \\ &\cdot \\ &\cdot \end{aligned} \quad [5]$$

In principle the first two relations can be solved for the strains ϵ_s and ϵ_l in terms of γ_s and γ_{sl} and then substituted into the third relation to give the following equation of state condition:⁴

³ "Applied Surface Thermodynamics", Ed. A. W. Neumann and Jan K. Spelt, (Surfactant Science Series, Vol. 63, Marcel Dekker, 1996). See in particular the article: "The Equation of State Approach to Interfacial Tensions" by Jan K. Spelt and Dongqing Li. chapter 5, page 239.

⁴ The reader should note that for the sake of clarity Eq.(5) lists only three of a much larger collection of equations of state which must exist for the model system in Fig.(1). In particular

$$\gamma_{sl} = f(\gamma_s, \gamma_p, \dots) \quad [6]$$

Spelt and Li (Ref. 3) have given alternate arguments based on both experimental and theoretical considerations that further support the existence of Eq.(6). It would appear then that the existence of the equation of state relationship is unassailable on the basis of fundamental thermodynamic principles. The problem, as explained above, is that in general we do not know the fundamental relation that is required in any sort of tractable form. Thus some sort of guess must be made which essentially comes down to empirical phenomenology. The interested reader can pursue this line of thought further in the reference by Neumann and Spelt³.

The second school of thought comes down to the use of empirical combining rules. This mode of reasoning attempts to take into account the fact that the surface tensions in question are a consequence of the ubiquitous molecular interactions which are responsible for holding the liquid and solid phases of our materials together. Though such forces are not recognized explicitly by classical thermodynamics per se., they do figure prominently in any attempt to construct the fundamental relation on the basis of a statistical mechanical model. The simplest example would be to estimate γ_{sl} from γ_{lr} and γ_s by some sort of mean approximation such as $\gamma_{sl} = (\gamma_{lr} \gamma_s)^{1/2}$. This approach has a fairly long history apparently going back to an idea proposed by Berthelot⁵ in the 19th century and is commonly referred to as the geometric mean approximation. Assuming that γ_{lr} and γ_s are derived from dispersion forces and are reasonably close to each other, the geometric mean formula can give reasonably good results. As might be expected, there are many systems that do not yield to the simple geometric mean rule. In general one can have strong polar

there will be the temperature, the pressure, the mole numbers and the bulk strains each of which has its own equation of state.

⁵ D. Berthelot, *Compt. Rend.*, 126, 1857 (1898).

interactions, hydrogen bonding and acid-base interactions that require special consideration. The response is to go to more refined types of combining rules which posit the existence of specific contributions from each of the different interactions present. This method has been referred to as the surface tension components approach and a fairly detailed critique has been given by Etzler¹ mentioned above.

Road to Particle Adhesion Through Interaction of Solid Surfaces

All the while one group of investigators were trying to probe the mysteries of the surface tension of solids, yet another group was keenly interested in the interaction of solid particles with solid substrates from the point of view of removing those particles. By and large neither group was particularly aware of the activities of the other but as I hope to point out in what follows they should have been. In my own experience in the microelectronic industry, particle removal was rather more of a nuisance that had to be addressed than a topic of scientific inquiry. The short sightedness of this attitude will become manifestly apparent in what follows.

Anyone with experience coating thin films onto smooth surfaces such as silicon wafers knows that particle contamination is the kiss of death for the coating. Imbedded particles with a diameter of roughly the coating thickness (typically a micron or so) form a material discontinuity in the coating and thereby act as centers of stress concentration creating a local stress field some 3 times larger than the normal biaxial stress that tends to exist in all coatings. This can easily give rise to radial and hoop cracks emanating from the particle with possible associated delamination near the crack edges.

The first line of defense against particle contamination is to work in an ultra clean environment. This implies special clean rooms which are quite expensive to operate not to mention inconvenient to work in and typically do not achieve total particle exclusion. At the next level, given that some amount of contamination will be present regardless of how clean the

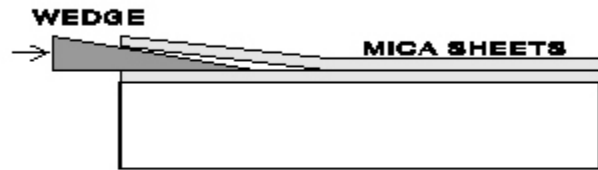


Figure 2 Schematic of Obreimoff experiment. A wedge is gently tapped between two mica sheets. The deformation of the top sheet can be monitored by interferometric methods.

environment is, one tries various methods of particle removal. It is at this stage that one begins to realize that particles can be strongly attracted to surfaces even though no one has applied any glue to them and they quite likely simply fell out of the air. It is the nature of this attraction that we need to focus on now because we strongly suspect that the same intermolecular forces that give rise to solid surface tension are also implicated in the particle adhesion problem.

Early Work of Obreimoff

Under ordinary circumstances, one does not get the immediate impression that solid bodies can interact simply by bringing the two together. The reasons for this are readily understandable since for any solid large enough to hold in your fingers, or even with tweezers, the forces involved are very small. In addition, most surfaces tend to be quite rough and contaminated with all manner of foreign substances. All of these conditions tend to suppress strong interactions. However, there are exceptions to be found and one of them is thin mica sheets. Obreimoff,⁶ who was working in Russia early in the 20th century where an exceptional type of Muscovite mica was available, noticed that relatively large sheets of perfectly clean, smooth and flat mica could attract each other quite strongly. Curious to investigate this phenomenon more closely he set up a simple

⁶ J. W. Obreimoff, Proc. Royal Society, **A 127**, 290 (1930).

experiment whereby a wedge could be used to separate two sheets in a controlled manner as shown schematically in figure (2). By gently taping a wedge between the two mica sheets they could be separated in a controlled manner. The deformation of the top sheet could also be monitored by interferometric methods, essentially Newton ring type phenomena which one readily sees by bringing a curved lens into contact with a flat reflecting surface. By this method Obreimoff demonstrated that the sheet being lifted of was behaving like an elastic beam just as one would expect if it were a peice of sheet metal being lifted off the floor by one edge. What is of interest though is that upon removing the wedge the sheets were observed to rejoin quite readily and that the energy recovered was not always equal to the energy spent in splitting the sheets. Further it made a difference whether the experiment was performed in air or under vacuum conditions. These earliest experiments on separating mica sheets were giving the world one of the earliest glimpses into the nature of the atomic and molecular forces which bind all matter.

Improved Observations of Tabor and Winterton

The work of Obreimoff was a good start but there were a number of problems with the method. First, using a wedge to split the mica introduced drag forces associated with driving the wedge. In addition during the splitting process a significant amount of charge separation between the sheets could occur giving rise to electrostatic forces which made themselves known through electrical discharges. However, the use of nice flat clean mica sheets was definitely a good idea and Tabor and Winterton⁷ took up on it while making a number of substantial improvements.

The first improvement was to avoid the use of a wedge for separating the sheets. To get around this problem they came up with the idea of bending the sheets into the form of cylindrical

sections by gluing them to cylindrically shaped substrates. By bringing the two cylindrical sections together at a right angle to each other they could get a carefully controlled circular contact area.

The second improvement involved bringing the two cylindrical sections together in a precisely controlled way by using a piezoelectric actuator and measuring the force acting between the two surfaces by mounting one of the cylinders on a carefully fabricated cantilever beam with precisely known bending behavior.

Finally, by applying a thin reflecting metal coating to the back of each sheet they could observe the interference behavior of multiple reflections between the two surfaces instead of the standard Newton's rings as was done in the Obreimoff experiment. With the Newton ring method one has a measurement sensitivity down to a few tenths of a micron whereas the multiple reflection method gets one down to a few nanometers.

Hamaker Theory or at Atomic Distances the World Follows the Rules of Quantum Mechanics

Tabor and Winterton were able to fit their force separation data very nicely to a disarmingly simple formula due to Hamaker.⁸ This relation states that, if dispersion forces are all that are present, then the attractive force between two surfaces carefully brought together to within 10 nanometers or so should vary as the inverse square of the separation distance as follows:

$$F = \frac{A(\text{area})}{12\pi d^2} \quad [6]$$

Where:

F = Attractive force (N)
 area = effective area of sheets (m²)
 d = separation distance between sheets (m)
 A = Hamaker constant (roughly 10⁻¹⁹ J)

⁷ D. Tabor and R. H. S. Winterton, Proc. Royal Society, **A 312**, 435 (1969).

⁸ H. C. Hamaker, Physica, **4**, 1058 (1937).

Though Eq.(6) is quite simple its derivation is decidedly not. However, we can get some insight into the problem by making a few elementary observations. By the time the 20th century was half over it was well established that the properties of all common matter were fundamentally governed by electromagnetic interactions. Classical electromagnetism was well explained by Maxwell's equations and quantum theory explained how the electromagnetic interactions between the fundamental particles such as the proton and the electron served to bind atomic matter together. What was happening within the atomic nucleus was still problematic since an entirely different set of forces were operating but these forces held the typical nucleus together so strongly and within such a small volume that for the purposes of understanding the chemical nature of matter the nucleus could be assumed to be a point mass and a source of positive charge which attracted and bound the electrons. To get some idea of the sizes and distances involved consider that a typical atomic nucleus is on the order of $3.4 \times 10^{-15} \text{m}$, the electromagnetic radius of the electron comes to $2.8 \times 10^{-15} \text{m}$ and within a typical atom electrons and protons are separated on average by roughly a Bohr radius which is close to $5.3 \times 10^{-11} \text{m}$. From these numbers one readily perceives that atomic matter amounts to relatively small point masses separated by huge distances. To put the matter in better perspective simply scale the numbers up by a factor of 10^{13} . The nucleus then would have a radius of 3.4 cm, which is roughly a small orange, and the electron would come to 2.8 cm, or a crab apple, and they would be separated on average by a distance of 530 meters or roughly half a kilometer! Thus the world at the atomic level is mostly empty space. Or is it? What is it that fills all that space and gives the impression that atomic matter is something sturdy and substantive? The answer in a word is the electromagnetic field. Technically according to Maxwell's equations when charges are present and moving around then both electric and magnetic fields have to be present. However, the electric field tends to be substantially stronger than the magnetic so for purposes of illustration we can focus on the electric field only. Going back to our lessons from Physics 101 we know that the fundamental relation governing the force of attraction or repulsion between two

charged particles is given by:

$$F = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{R^2} \quad [7]$$

Where:

- F = Attractive/repulsive force (N)
- q_1, q_2 = Particle charges (coulomb)
- R = Radial separation between particles (m)
- ϵ_0 = Permittivity of free space ($\text{coul}^2/\text{N m}^2$)

To get some idea of the implications of Eq.(7) we can put in a few numbers and see what comes out. The prefactor $(1/4 \pi \epsilon_0)$ is roughly 9×10^9 . Thus if we had two particles each with opposite charges of 1 coulomb and separate by a distance of 1 meter the force attracting them would be 9 billion newtons! One had better step back rather quickly because the resulting collision would be rather spectacular amounting to a small nuclear explosion. This explains why in the natural world most matter is approximately neutral since the forces due to charge separation mount up rather rapidly. For another example consider a simple capacitor consisting of two conducting plates each 1 cm^2 in area and separated by a gap of 1 millimeter. If we were to put opposite charges of roughly 9×10^{-9} coulombs (9 nano coulombs) on each plate then the voltage between the plates would rise to 10,000 volts or more than the breakdown voltage of air.

The force in equation (7) is moderated by the electric field between the charges. Each charge is the source of an electric field given by:

$$E = \frac{1}{4\pi\epsilon_0} \frac{q}{R^2} \quad [8]$$

This field is indeed a quite palpable quantity and is what fills all that apparently empty space in atomic matter. In fact the energy density associated with a general electric field **E** is:

$$U = \frac{1}{2} \epsilon_0 \mathbf{E} \cdot \mathbf{E} \quad [9]$$

U is an energy density with units of Joules per cubic meter (J/m^3). Now the solidness of a typical slab of matter is generally gaged by its elastic modulus Y which normally has the units Gpa

(N/m²) but also has the units of an energy density (J/m³ since N/m² is equivalent to N-m/m³ which is J/m³). The basic unit of charge floating around in any solid is the charge on the electron which is 1.6x10⁻¹⁹ coul. We can get some idea about the electromagnetic energy density close to a typical electron by combining Eqs.(8) and (9) and using the electron charge for q. Condensed down to essentials the following formula emerges:

$$U = \frac{2300}{\pi} \frac{1}{r^4} \quad [10]$$

Where r is in angstrom units and U in units of giga Pascals (GPa) where a giga Pascal is the same as 10⁹ J/m³ and is the more common label for an elastic modulus. Table 1 summarizes the electromagnetic energy density at a few representative atomic distances.

| TABLE 1: Electromagnetic energy density in a neighborhood of an electron at representative atomic distances estimated from Eq.(10) | | |
|--|--|--|
| DISTANCE FROM ELECTRON (angstrom) | ENERGY DENSITY/ELECTROMAGNETIC MODULUS (GPa) | COMMENTS |
| 4.0 | 2.8 | Roughly the modulus of a thermoplastic i.e. polystyrene |
| 1.37 | 208.0 | Modulus of metal such as steel |
| 1.0 | 732.0 | Modulus of refractory material like silicon carbide or diamond |

Table 1 clearly shows that the electromagnetic energy density associated with the electron's electric field can account, at least in a heuristic fashion, for the elastic properties of all forms of common matter. Thus, knowing the electron charge density in a solid should also allow us to estimate the attractive fields responsible for the Hamaker force. The problem is how to go about it?

From our force estimates based on Eq.(7) we understand why matter is basically neutral with few or no free charges floating around. Thus the direct use of Eq.(7) is of no help in explaining the Hamaker force. However, even though the typical solid has no free electrons, i.e. no electrons not simultaneously coupled to an opposite proton, there is still an enormous amount of electronic charge present and at any point in time it is not necessarily uniformly distributed. That is, a certain amount of charge separation can be present giving rise to non uniform charge distributions which can exert their own local electromagnetic influence. One way to sneak up on this problem is through what is known as the multipole expansion formula for the potential field due to a general charge distribution:⁹

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left[\frac{q}{r} + \frac{\mathbf{p}\cdot\mathbf{r}}{r^3} + \frac{1}{2} \sum_{ij} Q_{ij} \frac{r_i r_j}{r^5} + \dots \right] \quad [11]$$

Where:

- $\Phi(\mathbf{r})$ = Electrostatic field potential (volt)
- q = Free charge in coulombs (coul)
- \mathbf{p} = Dipole moment of charge distribution (coul m)
- \mathbf{r} = Radius vector from origin with magnitude $r = (\mathbf{r}\cdot\mathbf{r})^{1/2}$ (m)
- Q_{ij} = Quadrupole moment of charge distribution (coul m²)
- r_i, r_j = Cartesian components of radius vector \mathbf{r} (m)

Equation (11) neatly dissects any general charge distribution into components of ever decreasing strength. If an amount of free charge q is present this is accounted for by the first term which is the potential responsible for the classic coulomb force and electric field given by Eqs.(7) and (8). If no free charge is present the next term dominates which is due to a simple dipole charge separation. Higher order terms are also present such as the

⁹ This is a standard formula from classical electromagnetic field theory worked out in a number of texts. My favorite from graduate school is "Classical Electrodynamics", by John David Jackson (John Wiley & Sons, NY, 1962).

quadrupole contribution but these terms are substantially weaker than the first two and generally neglected unless circumstances dictate otherwise. Nuclear physicists in particular have to grapple with these terms in order to sort out the charge distribution of atomic nuclei. For our purposes, since we are assuming that essentially no free charge is present, we have to deal with the second dipole term. It is well known that many molecules have dipole moments due to asymmetric electronegativities of their component atoms. A carbon atom bonded to any of the halogens is a typical example. Thus we have good reason to believe that dipole fields will be present in otherwise neutral matter and these fields will interact with the general charge distribution present. In particular, and again from classical electromagnetic theory, we know that an electric field can give rise to a local polarization charge density given by:

$$\rho_{pol} = -\nabla \cdot \mathbf{P} \quad [12]$$

Where:

- ρ_{pol} = Polarization charge density (coul/m³)
- $\mathbf{P} = N\alpha\epsilon_0\mathbf{E}$
- N = Number of charges/unit volume (m⁻³)
- α = Polarizability (m³)
- \mathbf{E} = Electric field (volt/m)

The components of the electric field \mathbf{E} in Eq.(12) arising from the dipole moment p are given by:¹⁰

$$\begin{aligned} E_r &= \frac{2p\cos\theta}{r^3} \quad (\text{radial component}) \\ E_\theta &= \frac{psin\theta}{r^3} \quad (\text{theta component}) \\ E_\phi &= 0 \quad (\text{azimuthal component}) \end{aligned} \quad [13]$$

Eqs (12) and (13) come from the standard theory of electro statics and define what is called the

¹⁰ Note that spherical coordinates are assumed here where the basic variables are the radius distance r , the declination from the z axis θ , and the azimuthal angle ϕ which measures the angular displacement of the projection of the radius vector r on the x,y plane from the x axis.

polarization field due to a dipole charge distribution. Thus we have a dipole moment in an electrically neutral molecule giving rise to an electric field which in turn can induce another polarization charge density in the local neighborhood. Now the local energy density associated with the polarization charge interacting with the induced field is given by another standard formula:

$$U = \Phi(\mathbf{r}) \rho_{pol}(\mathbf{r}) \quad [14]$$

In Eq.(14) U is the energy density (J/m³) generated by the potential Φ interacting with the charge density ρ_{pol} . The potential Φ and polarization charge ρ_{pol} can be substituted from Eqs.(11) and (12) with the help of Eq.(13) (we leave the chore of taking the divergence of \mathbf{E} to the reader) to give the following formula for the dipole-induced dipole energy density:

$$U = -\frac{N\alpha p^2 \cos^2 \theta}{16\pi\epsilon_0 r^6} \quad [15]$$

Equation (15) represents the dipole - induced dipole contribution to what commonly are called van der Waals interactions between elements of neutral matter. The dipole - induce dipole is also referred to as the Debye interaction in honor of Peter Debye who did pioneering work on dipole interactions. The main feature of Eq.(15) is the $1/r^6$ spacial dependence of the interaction which makes it a short range effect.

Though Eq.(15) gets us somewhat closer to understanding the nature of electromagnetic interactions in charge neutral materials the story of the interactions between elements of neutral matter does not end here. It is well known that the attractive force exists even when no permanent dipoles are anywhere present. What now enters the picture are the so called London dispersion forces where one imagines that due to fluctuations in one region a net dipole moment is momentarily created which then induces further charge separation and thus another dipole in the local neighborhood which gives rise to yet another

net interaction. At this stage classical electromagnetic theory alone can carry us no further in trying to sort out what is going on. We really have to understand in more detail the dynamics of charges under the influence of electromagnetic interactions which means we must now go into the realm of quantum mechanics.

Down the Rabbit Hole into the Wonderland of Quantum Mechanics

In his classic childrens story "Alice in Wonderland" Lewis Carrrol¹¹ tells of the adventures of Alice who one day happens to follow an unusual rabbit down a hole into a very strange fantasy land. We are about to follow Alice in a sense but the world we will now enter is far stranger than Wonderland in that it is also very real in the sense that it is confirmed by all the best experimental data available.

No sooner had the mysteries of the electromagnetic field been sorted out by Maxwell's theory than another serious problem arose in trying to understand the structure and stability of atoms. With the work of Rutherford and others it became clear that atomic structure amounted to negatively charged electrons orbiting around a positively charged proton nucleus. The binding force between the two is easily understood on the basis of the standard coulomb interaction given by Eq.(7) but on the basis of classical mechanics the arrangement could not be stable since while orbiting the proton the electron would be in a constant state of angular acceleration and Maxwell's equations were positively unequivocal in predicting that under these conditions the electron would have to radiate away its energy and thus

¹¹ From ALICE'S ADVENTURES IN WONDERLAND by Lewis Carroll (1865). Lewis Carroll is the pseudonym of the English writer and mathematician Charles Lutwidge Dodgson, b. Jan. 27, 1832, d. Jan. 14, 1898, known especially for children's books that are also distinguished as satire and as examples of verbal wit. Carroll invented his pen name by translating his first two names into the Latin "Carolus Lodovicus" and then anglicizing it into "Lewis Carroll."

eventually fall into the nucleus which was in total disagreement with all experimental observations.

The quantum world is a strange place indeed. Whereas in classical theory we understand the dynamics of a point mass by specifying its position and momentum which can be calculated through Newton's second law, in the quantum world these quantities cannot be specified simultaneously. Instead, for a particle such as an electron, we must specify its amplitude function ψ which is in general a complex number. Already things are getting weird. In classical mechanics one always dealt with real numbers whereas in quantum mechanics complex numbers¹² are the norm. If the position of the electron is given by some radius vector \mathbf{r} then its amplitude for being at \mathbf{r} is given by $\psi(\mathbf{r})$. What makes $\psi(\mathbf{r})$ useful is the fact that its magnitude squared $\psi(\mathbf{r})^*\psi(\mathbf{r})$ is interpreted as the probability of finding the electron at \mathbf{r} . Thus $\psi(\mathbf{r})^*\psi(\mathbf{r})$ specifies where the electron spends most of its time and can therefore be thought of as a charge density, so knowing $\psi(\mathbf{r})$ gives us a good start on the problem. The question is how to go about determining $\psi(\mathbf{r})$.

As mentioned above, from the point of view of classical thermodynamics everything we wanted to know about a system could be derived from the fundamental relation $U=U(S,V,N_1,N_2,\dots)$ where U is essentially the total energy of the system. In quantum theory things are a little different. instead of U one deals with the quantity H called the hamiltonian. H again represents the total energy of the system with the little twist that it is an operator as opposed to a function. Operators are entities that act on functions and turn them into other functions. The common derivative is a simple example of an operator. Thus in the elementary calculus of a single variable the derivative operator d/dx can operate on a function such as $f(x) = x^2$ to give a different function

¹² Just to remind everyone a general complex number z is defined in terms of real numbers x and y as $z = x + iy$ where $i=(-1)^{1/2}$. The complex conjugate of z is $z^* = x - iy$ and the magnitude of z squared is given by $zz^* = (x + iy)(x - iy) = x^2 + y^2$.

$g(x) = df/dx = 2x$. Operators can also involve integrals so we see that we are dealing with an altogether higher order entity when confronting the hamiltonian H . For our current purposes we need only deal with the time independent theory where all states are considered to be stationary and thus not changing in time. This is roughly the equivalent of the notion of equilibrium from classical thermodynamics. Thus the problem comes down to this. If we know the hamiltonian for our system then the amplitude function or more commonly the wave function ψ is a solution of the following equation:

$$\bar{H}\psi = E\psi \quad [16]$$

Thus, amazingly, the correct wave function is the one that when operated on by the hamiltonian is turned into itself multiplied by a constant E which turns out to be the energy of the system when in the state specified by ψ . It turns out further that in general there is a whole collection of solutions ψ_n $n = 1, 2 \dots N$ which satisfy Eq.(16) each corresponding to a different energy level E_n . In the mathematics literature Eq.(16) is called an eigenvalue problem and the solutions ψ_n are called eigenstates (also eigenvectors) of the operator H corresponding to the eigenvalues E_n . It should be noted that there is an enormous literature on this type of problem since it crops in in a wide variety of applications including the vibrations of a drum head, the principle axes of rotation of a solid body, the resonance frequencies of microwave cavities, the vibrations of beams, determination of the partition function of interacting spin systems and the chemical kinetics of interacting molecules derivable from a master equation. In my own experience many years were spent struggling with an eigenvalue problem resulting from the dynamic behavior of polymer chains. Thus we know quite a bit about the mathematics involved in dealing with problems like Eq.(16).

To get back to solving the problem of electromagnetic interactions in solid materials the general solution of Eq.(16) is hopelessly complex notwithstanding all that we know about this type of problem. The basic obstacle which stands in the

way is that for even a small volume of common matter the number of interacting particles is astronomical and even writing down the appropriate hamiltonian operator can be nearly impossible much less solving the associated eigenvalue problem. However, we can still gain some insight by looking at simple systems and making approximating assumptions. The simplest nontrivial system one can conjure up is the hydrogen atom where we have one electron interacting with one proton. This problem has been truly beaten to death mainly because it is one of a very small number of problems that can be treated exactly in a mathematical sense. Many treatments have been given but my favorite is that of Feynman from his classic Lectures on Physics.¹³ In this case the hamiltonian operator is:

$$H = -\frac{\hbar^2}{8\pi^2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0r} \quad [17]$$

Where:

- e = Electron charge (coul)
- m = Electron mass (kg)
- ϵ_0 = Permittivity of free space (coul²/N m²)
- h = Plank's constant = 6.63×10^{-34} (J s)
- r = radial distance between electron and proton at any given time
- ∇^2 = Laplacian operator most conveniently expressed in spherical coordinates

The eigenvalues of H are the allowed energy levels which the atom can occupy and are give by:

$$E_n = -\frac{2\pi^2me^4}{h^2}\left(\frac{1}{n^2}\right) \quad n = 1, 2, 3 \dots \infty \quad [18]$$

According to Eq.(18) the electron can occupy any one of an infinite number of energy levels but the one of most interest to us is the ground state which is obtained when $n=1$. This is the state of lowest energy and therefore the one most likely to be occupied under normal circumstances. The

¹³ See in particular "The Feynman Lectures on Physics - Vol III", by R. P. Feynman, R. B. Leighton and M. Sands, (Addison-Wesley Publishing Company, 1963) chapter 19.

corresponding wave function ψ_1 yields a charge distribution $\psi_1^*\psi_1$ which is spherically symmetric and contained within a sphere of radius roughly $\frac{1}{2}$ angstrom or 5×10^{-11} m. This is given by what is called the Bohr radius $r_B = h^2/(4\pi^2 me^2)$.

Technically, since the charge density falls off exponentially with increasing radial distance, the electron can spend some time outside the Bohr radius but not much. The exponential tail of the charge distribution can be important however in explaining another strange quantum phenomenon known as electron tunneling whereby an electron manages to tunnel its way through an energy barrier that would be strictly forbidden from the point of view of classical mechanics.

As seen from a distance the hydrogen atom is an electrically neutral spherically symmetric object with no net dipole or quadrupole moment whatever. It should therefore be electromagnetically invisible to any other hydrogen atom which is suitably far away. This would certainly be the case for the hydrogen atoms held in a container at room temperature and pressure where the mean spacing between the atoms is something like 10^{-7} m or more than 10,000 Bohr radii distant. The case we are interested in is when the atoms get much closer together as they can at very high pressure or in the liquid but not too close. Thus consider two hydrogen atoms separated by a distance R much larger than the Bohr radius but much smaller than the spacing in the ideal gas state as shown in Fig.(3).

For the configuration shown in Fig.(3) the electrons are close enough to perceive that there is definite structure present but not so close that we have to worry about the fact that the electron has an internal spin degree of freedom which gives rise to a magnetic moment and further makes it a Fermi particle which must obey the Pauli exclusion principle. In this simpler case the interaction energy of the system is given by Eq.(19)

Even though Eq.(19) looks reasonably simple putting it into the hamiltonian operator would still give a rather difficult problem. Therefore, at this point we take advantage of the fact that R is much larger than r_1 and r_2 and expand Eq.(19) in powers of $1/R$. We find that the first nonvanishing

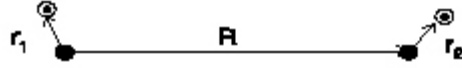


Figure 3 Schematic diagram of two hydrogen atoms separated by a distance large compared to the Bohr radius but close compared to the mean spacing in an ideal gas.

$$\Phi = -\frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{R} + \frac{1}{|R + r_2 - r_1|} \right] + \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|R + r_2|} + \frac{1}{|R - r_1|} \right] \quad [19]$$

term occurs at second order giving rise to the following simplified version of the interaction energy:

$$\Phi = -\frac{e^2}{4\pi\epsilon_0} \left[\frac{r_1 \cdot r_2}{R^3} - \frac{3(r_1 \cdot R)(r_2 \cdot R)}{R^5} \right] \quad [20]$$

Eq.(20) may not look much simpler than Eq.(19) but it has the definite advantage of being small since it is on the order of $1/R^3$. Also note that Eq.(20) is precisely the interaction energy we would expect for two interacting dipoles. Thus the two hydrogen atoms in Fig.(3) appear to be interacting through a weak dipole-dipole mechanism. What this will do is cause the energy levels of each atom to shift slightly and since the interaction is relatively weak we do not have to solve the whole problem again from scratch but we can make use of the well known results for the isolated atom to calculate the energy shift using

perturbation theory.¹⁴ Essentially what the perturbation approach comes down to is this. We have some hamiltonian H for which we know all the amplitude functions ψ_n^0 and energy levels E_n^0 and we want to solve the problem where H is perturbed by some small interaction ΔH . Since ΔH is small we expect the changes in ψ_n^0 and E_n^0 to be small also so we write the wave function and energy levels for the perturbed system as:

$$\begin{aligned}\psi_n &= \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots \\ E_n &= E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots\end{aligned}\quad [21]$$

In Eq.(21) ψ_n^0 and E_n^0 are the known wave functions and energy levels of the unperturbed system. ψ_n and E_n are the wave functions and energies of the new system which we seek. The $\psi_n^1, \psi_n^2, \dots$ and E_n^1, E_n^2, \dots are the first, second and higher order corrections which must be determined. The parameter λ is a number less than 1 used to serve as an expansion marker to keep track of the order of the terms in the expansion. One usually hopes that the first order corrections will be good enough and if that doesn't work out then the second order corrections must be calculated. You are in for a very bad day if you have to go higher than second order which fortunately does not occur very often. It turns out that for the interaction energy given by Eq.(20) the first order corrections turn out to be zero due to the symmetry of the hydrogen ground state. Going to second order fortunately gives a finite result which turns out to be:

$$\Delta E = -\frac{e^2}{4\pi\epsilon_0 r_B} \left(\frac{r_B}{R}\right)^6 \zeta \quad [22]$$

Where:

$$\begin{aligned}r_B &= h^2/(4\pi^2 me^2) \text{ the Bohr radius} \\ \zeta &= \text{Dimension less constant } \sim 6.5\end{aligned}$$

Again we note the ubiquitous $(1/R^6)$ spacial dependence of the interaction energy just as was found in the dipole induced dipole case though in this case it arises under circumstances where there are no permanent dipoles. It was this type of result that apparently led Hamaker¹⁵ to conclude that if two neutral bodies are brought close enough together then these van der Waals London dispersion forces would kick in and give a net attraction. All one had to do was divide each of the approaching solids up into small segments and assume a pair wise interaction of the segments according to the $(1/R^6)$ behavior and add them all up to get the net attraction. Though there are some problems with these assumptions they were good enough for the time and allowed Hamaker to come up with his interesting little formula given by Eq.(6). Details of Hamaker type calculations for various solid shapes have been worked out in the text by Rimai and Quesnel.¹⁶ For two parallel half spaces we get the following formula for the interaction energy per unit area W:

$$W = -\frac{A}{12\pi d^2} \quad \text{Two parallel surfaces} \quad [23]$$

¹⁴ What we present here is intended to give a brief overview of the methodology of perturbation theory. To go into details would get us in very deep water very fast and would not be all that illuminating to the topic at hand. Perturbation theory is covered in a number of standard texts such as "Introduction to Quantum Theory" by David Park, (McGraw Hill, New York, 1964). At a more advanced level one can consult "Quantum Mechanics Volume I: Fundamentals", by Kurt Gottfried, (W. A. Benjamin, Inc., New York, 1966).

In the above d the separation distance and A the Hamaker constant which is of order 10^{-19} J depending on the specific materials and geometry.

At this point we see that the attractive forces between solid surfaces that were explored by

¹⁵ H. C. Hamaker, *Physica*, **4**, 1058 (1937)

¹⁶ "Fundamentals of Particle Adhesion", by Donald S. Rimai and David J. Quesnel (Global Press, 2001).

Obreimoff and later by Tabor and Winterton and several others, can be explained by electromagnetic interactions arising either from the presence of dipoles or from the quantum mechanical effect of fluctuating charge distributions giving rise to transient dipole moments which can interact on average to give the same $1/R^6$ behavior which arises when permanent dipoles are present. These so called dispersion forces can then be used to derive the Hamaker interaction in Eq.(23). This was all very nice but was only the beginning of the story. As pointed out previously, there are conceptual problems with the Hamaker approach to adding up all the pair wise interactions since if there is an intervening medium between the two bodies it will materially complicate matters by introducing various types of many body effects. Enter Lifshitz and co-workers into the fray with another approach to working out the problem of how the short range molecular and atomic interactions give rise to the macroscopic attraction between bulk material objects. At this point the story starts to become not only more interesting but stranger as well. From Lifshitz point of view the real actor was the electromagnetic field which moderates the interactions between atoms and molecules and, as demonstrated for the case of simple hydrogen atoms above, could also be shown to give rise to the London van der Waals dispersion forces.

To really understand what the electromagnetic field is doing one has to go beyond classical electrodynamics and Schrödinger equation style quantum theory to the then emerging concepts of Quantum Electrodynamics (QED). What one has to realize is that even after the development of classical electrodynamics and the quantum theory of the early 20th century there was still a big hole in our understanding of electromagnetism which essentially arose from the neglect of relativistic effects. Classical electrodynamics as worked out by Maxwell was relativistically correct from the outset. In fact the best approach to understanding Einstein's famous theory is through electrodynamics. However, the early quantum theory was not relativistically correct. In particular, the Schrödinger style hamiltonian in Eq.(17) does not account for relativistic effects. Though this was not a major problem early on it

was a conceptual difficulty that had to be worked out. This was all eventually taken care of by roughly mid century. P. A. M. Dirac formulated his now famous Dirac equation¹⁷ which gave the relativistically correct hamiltonian for the electron and, as a clever bonus, also predicted the existence of the positron ahead of the experimentalists. Dyson, Feynman, Schwinger and Tomonaga later followed up by formulating the complete and relativistically correct theory of electromagnetic radiation.¹⁸ In QED the source of the electromagnetic field is the photon which can be considered as a sort of quasi particle. The typical photon can be in 1 of two possible polarization states and always travels at the speed of light from its creation to its eventual destruction. Although a single photon is a rather feeble entity they have the capacity of adding up under the superposition principle thereby creating an electromagnetic field of nearly any magnitude. Now Lifshitz took the approach that all the interactions were through the exchange of photons (i.e. electromagnetic radiation) between the the bodies in question. Thus using the principles of QED he was able to work out the formula for the Hamaker force by an entirely different approach than the original work of Hamaker described above. The result for two material planes separated by a third medium as shown in Fig.(4) came to the following:¹⁹

¹⁷ P. A. M. Dirac, Proc. Roy. Soc. (London), Ser A., 117, 610 (1928).

¹⁸ The interested reader can follow up on the details of the development of Quantum Electrodynamics (QED) in the following review article: "QED and the men who Made it: Dyson, Feynman, Schwinger and Tomonaga", S. S. Schweber, (Princeton Series in Physics. Princeton University Press, Princeton, NJ, 1994).

¹⁹ A fairly concise and informative discussion of the Lifshitz theory can be found in "Theoretical Approaches for Estimating Solid-Liquid Interfacial Tensions" by E. Moy and A. W. Neumann, in Applied Surface Thermodynamics, A. W. Neumann and Jan K. Spelt Eds. (Surfactant Science Series, Marcel Dekker, Inc., New York,

$$\begin{aligned}
A_{132} &= \frac{3kT}{2} \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{[\Delta_{13}(m)\Delta_{23}(m)]^m}{m^3} \\
\Delta_{13}(m) &= \frac{\epsilon_1(i\zeta_m) - \epsilon_3(i\zeta_m)}{\epsilon_1(i\zeta_m) + \epsilon_3(i\zeta_m)} \\
\Delta_{23}(m) &= \frac{\epsilon_2(i\zeta_m) - \epsilon_3(i\zeta_m)}{\epsilon_2(i\zeta_m) + \epsilon_3(i\zeta_m)} \\
\zeta_m &= \frac{4\pi^2 kT}{h} m
\end{aligned}
\tag{24}$$

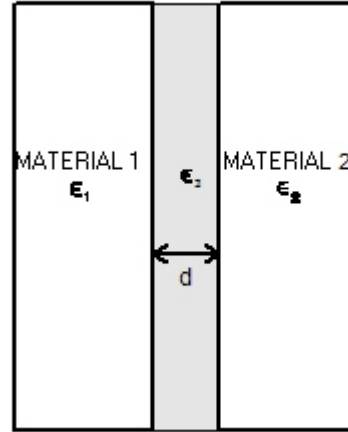


Figure 4 Material configuration corresponding to the Hamaker constant calculation in Eq.(24).

Where:

- A_{123} = Hamaker constant for the interaction of materials 1 and 2 separated by material 3
- k = Boltzman constant (1.38×10^{-23} J/ molecule K)
- h = Planks constant 6.63×10^{-34} (J s)
- T = Temperature (K)
- $\epsilon_1, \epsilon_2, \epsilon_3$ = Complex dielectric constants for materials 1,2 and 3 respectively
- i = $(-1)^{1/2}$ imaginary unit from complex variable theory
- ζ_m = m^{th} response frequency

What is interesting about Eq.(24) is that all material properties are now represented by the complex dielectric constant which is a measure of the material's response to an applied electromagnetic field. The dielectric constant is a function of frequency and the frequency range we are interested in is that in which a typical electron lives.

1996). A far more detailed review has been given in "Origins and Applications of London Dispersion Forces and Hamaker Constants in Ceramics", Roger H. French, *J. Am. Ceram Soc.*, **83** [9], 2117 (2000).

The energy of a photon is given by $E = h\nu$ (h = Plank's constant and ν is the frequency) and it will interact with electrons of roughly the same energy. Going back to our hydrogen atom the energy of the ground state is given by Eq.(18) with $n=1$ which works out to 2.17×10^{-18} J (or -13.6 electron volts (eV) which are the more common units). Equating electron and photon energies we see that the hydrogen electron will interact with radiation near the frequency $\nu = ((2.17 \times 10^{-18} \text{ J}) / (h = 6.63 \times 10^{-34} \text{ J s})) = 3.27 \times 10^{15} \text{ Hz}$. This puts us in the range of ultra violet radiation. In general most materials have energy levels which interact with radiation ranging from the infrared through the visible to the ultraviolet with the visible to ultraviolet range being the most common. The implication is that measuring the absorption and refractive index behavior of materials in the visible to ultraviolet range will allow us to make predictions about the short range attractions. Very interesting indeed. Stay tuned the story is about to get more interesting yet.

Equation (23) tells us that the interaction energy between the two solid slabs in Fig.(4) is proportional to the Hamaker constant given by Eq.(24) divided by the separation gap squared. Now if we let the gap d shrink to zero an infinite interaction energy is predicted. However, we know this is impossible since as the surfaces start to get

too close very strong repulsive forces kick in and prevent any further approach. What happens is an equilibrium separation d_0 is reached where the attractive and repulsive forces just balance one another. A moments reflection reveals that at this separation the interaction energy predicted by Eq.(23) must amount to exactly twice the surface energy γ_1 assuming that both material slabs are made of material 1. This clearly must be the case since performing the inverse operation of separating the surfaces to infinity will yield two free surfaces each of surface energy γ_1 . Thus at the separation d_0 Eq.(23) can be written as:²⁰

$$\gamma_1 = -\frac{A_{11}}{24\pi d_0^2} \quad \text{Surface energy of material 1} \quad [25]$$

The precise value of d_0 is a matter of some controversy but it cannot be too far from the atomic spacing in crystalline solids or the mean intermolecular spacing in bulk amorphous materials. A commonly assumed value is $d_0 = 1.65 \times 10^{-10} \text{m}$.

Now if we go back to our contact angle experiment in Fig.(1) and assume that the materials are such that the surface energies (surface tensions) are determined predominantly by dispersion forces, then for this system we can write:

$$\begin{aligned} \gamma_l &= -\frac{A_{ll}}{24\pi d_0^2} \quad \text{Surface energy of liquid} \\ \gamma_s &= -\frac{A_{ss}}{24\pi d_0^2} \quad \text{Surface energy of solid} \end{aligned} \quad [26]$$

$$\gamma_{sl} = -\frac{A_{sl}}{12\pi d_0^2} \quad \text{Energy of solid liquid interface}$$

²⁰ Here we use the convention that if the material in the gap is either air or vacuum then the middle subscript in the Hamaker constant is suppressed.

Going back to Young's equation for the contact angle and assuming a fixed value for d_0 we get:

$$A_{ll} \cos\theta = A_{ss} - 2A_{sl} \quad [27]$$

This readily implies that the contact angle is given by:

$$\theta = \arccos\left(\frac{A_{ss} - 2A_{sl}}{A_{ll}}\right) \quad [28]$$

With Eq.(28) the whole argument now comes full circle. We started off investigating surface energies as the source of contact angle and wettability behavior. This lead us directly to peer into the realm of atomic and molecular London - van der Waals interactions as the source for the surface energies. A moments consideration made it clear that electromagnetic interactions were the root cause of the interactions and thus the surface energies. We then followed Hamaker back up to the macroscopic scale with his deceptively simple formula involving the constant named after him. The electromagnetic interactions then reassert themselves with the work of Lifshitz who demonstrated that the Hamaker constant is a consequence of quantum electrodynamic interactions between the solids involved which lead to Eq.(24) which determines the Hamaker constant in terms of the dielectric properties of the materials involved. Thus measuring the Hamaker constant involves making index of refraction and ultra violet absorption measurements. So the spectroscopists have something to say to the lab chemists measuring contact angles and presumably vice versa. To be sure there are a number of loose ends which can not be addressed in such a short essay but the overall picture makes for a self consistent and most curious story with rather profound consequences for a wide range of practical applications including:

1. Flocculation behavior of colloid suspensions
2. Cleaning of particles from surfaces
3. Surface wetting and application of coatings
4. Biomedical applications which depend critically on all of the above
5. Sintering of particle aggregates

In the upcoming June symposia on PARTICLES and CONTACT ANGLE behavior we hope that a number of the issue brought up here can be addressed in more detail and we invite all our readers to join us in Toronto at that time. Details of the symposia are given in the "Call for Papers" at the end of this newsletter.

Before leaving the realm of atomic and molecular behavior at the nanoscale, there remains one further topic which bears on this discussion which is by far the most curious aspect of surface interactions in the quantum world and that is the Casimir effect.

Through The Looking Glass into the Realm of the Casimir Effect or What has Quantum Electrodynamics to Do with it?

In 1948 the Dutch physicist Hendrik B. G. Casimir while working on problems of colloid suspensions for Philips Research Labs predicted that two uncharged parallel metal plates will be subject to a force pressing them together given by the following:²¹

$$\frac{F_c}{S} = \frac{\pi \hbar c}{480d^4} \quad [29]$$

Where:

- F_c = Attracting force
- h = Planck's constant
- c = Speed of light
- d = Distance between the two plates
- S = Surface area of plates

Although Eq.(29) bears a curious resemblance to Hamaker's equation the appearance is deceptive since in the Hamaker case the interaction results from the presence of atomic and molecular matter.

²¹ A short review of the literature on the Casimir Effect can be found in the following articles: "The Casimir Effect: a Force from Nothing" A. Lambrecht, Physics World, September 2002.; "Demonstration of the Casimir Force in the 0.6 to 6 μm Range", S. K. Lamoreaux, Phys. Rev. Lett. **78**, 5 (1997).

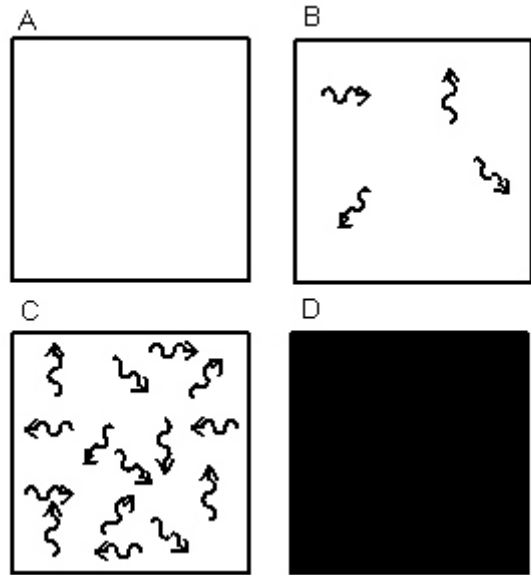


Figure 5 Box A: represents a vacuum. Box B: A weak radiation field. Box C: much stronger field. Box D: All possible radiation.

With the Casimir effect the interaction arises out of completely nothing being wholly independent of any material property as Eq.(29) clearly shows. How can this be?

To most of us nothing is precisely that a total lack of anything of interest. However, once one enters the realm of Quantum Electrodynamics nothing takes on an entirely different significance. A look at Fig.(5) gives a crude sort of analogy. In figure(5A) we have a representation of the vacuum, i.e. a perfectly empty box. In Fig.(5B) a small amount of radiation is added and Fig.(5C) adds still more radiation. Finally Fig.(5D) goes to the ultimate limit and adds all possible radiation and thus is a representation of absolutely everything. Or is it? If we change the color of the photons from black to white and the background from white to black, i.e. look at the negative photograph then the picture is precisely reversed and Fig.(5D) becomes the vacuum and (5A) everything? This is precisely the picture of the vacuum offered by Quantum Electrodynamics. The vacuum is nothing more than a seething sea of radiation of all magnitudes, phases and directions such that on average everything tends to cancel out but not quite perfectly. There are fluctuations

such that at any given moment a virtual photon is created for a brief interval and then immediately sucked back into the milieu. Since these virtual photons are exceedingly feeble they go completely unnoticed under ordinary circumstances. However, as we start making very small microelectromechanical systems (MEMS) such as tiny sensors and actuators, that are fabricated on silicon substrates we start to enter a new world. The Casimir effect can start to have a significant impact on this technology and thus is no longer simply some academic curiosity.

But just what is this mysterious effect. The easiest way to look at it is through a simple analogy. Say we have two small uncharged metal plates sitting in a vacuum at a macroscopic separation of a few centimeters. To within any degree of measurable accuracy there is no interaction between them. The virtual photons of the vacuum are popping up and vanishing like so many bubbles in a boiling kettle of water but they are so feeble that their existence is completely unnoticed. Now we start to bring the two plates together in a very careful way all the time monitoring for the presence of any net attraction between them. As we start to get into the range of 10 nanometers and less an interesting effect starts to take hold. The virtual photons that are being continually created and destroyed in the gap between the plates have distinct wavelengths and as the plates get closer and closer they start to act as a sort of microwave cavity which only allows certain wavelengths to exist. In effect then the creation of virtual photons in a certain range of wavelengths is being suppressed between the plates but not on the outside. Since the photons are electromagnetic waves they exert a pressure and since fewer can exist in the gap between the plates than outside there is a net pressure difference between the outside and inside which creates the Casimir attraction. Its not unlike the situation that would exist if the plates were in a chamber filled with some ideal gas and we were by some mechanism evacuating the space between the plates. The gas outside would generate a net pressure forcing the plates together. A better analogy comes from the era of sailing ships. Two ships sitting on the ocean with very little breeze blowing but very heavy swells present can

experience something close to the same phenomenon. When the ships are far apart the waves buffet them more or less randomly from all sides and on average they tend to hold their positions. However, if the ships are brought together side by side in a parallel fashion they tend to also create a wave cavity between them where certain wavelengths are preferred and others suppressed. Again the water waves exert a pressure on the hulls of the ships and since the wave action between the ships is being suppressed by the cavity effect there is more wave pressure occurring from the outside than from within the gap thus creating a net force which tends to draw the hulls together. This was apparently a serious problem in days of yore when sailing ships had extensive sails and rigging that could become entangled if they got too close.

So it seems that the closer we look at the interactions between material bodies the stranger it seems to get. One is again reminded of Alice's adventures in Wonderland. Among her many adventures was a curious encounter with a Cheshire cat who had the annoying habit of disappearing and reappearing at random moments all of which lead to the following conversation:

'...and I wish you wouldn't keep appearing and vanishing so suddenly: you make one quite giddy.'

'All right,' said the Cat; and this time it vanished quite slowly, beginning with the end of the tail, and ending with the grin, which remained some time after the rest of it had gone.

'Well! I've often seen a cat without a grin,' thought Alice; 'but a grin without a cat! It's the most curious thing I ever saw in my life!'

So there you have it. We look at the vacuum and expect to see nothing but yet we perceive its grin through the Casimir effect.

BOOK REVIEWS

"Applied Surface Thermodynamics", A. W. Neumann and Jan K. Spelt, Eds. (Surfactant Science Series Volume 63, Marcel Dekker, Inc., 1996) 646 pages.

The curious aspect of this volume is that the editors and several of the contributors hail from the department of Mechanical Engineering at the University of Toronto. One is more used to thinking that investigators in the realm of surface thermodynamics would come from chemistry or physics departments. However, on reflection one realizes that a significant amount of fluid dynamics and continuum theory get involved in investigating the details of the spreading of liquids on surfaces and this is definitely in the realm of mechanical engineering. Notwithstanding the somewhat unusual genesis, the book is an excellent volume covering many aspects of contact angle behavior and the behavior of particles in solution. The volume espouses what might be called the Toronto School of contact angle behavior which is based on the equation of state approach discussed in this issue's introductory essay. The book has chapters contributed by 7 different authors and is well organized with a useful index. Thus this book can serve as a supplementary text for courses in surface science or chemical engineering that deal with surface wetting behavior or the behavior of particles in a variety of circumstances. The chapters are organized as follows:

- Chapter 1: The Generalized Theory of Capillarity
- Chapter 2: Thermodynamics of Axisymmetric Capillarity Systems
- Chapter 3: Thermodynamic Status of Contact Angles
- Chapter 4: Line Tension in Multiphase Equilibrium Systems
- Chapter 5: The Equation of State Approach to Interfacial Tensions
- Chapter 6: The Theory of Surface Tension Components and the Equation of State Approach
- Chapter 7: Theoretical Approaches for Estimating Solid-Liquid Interfacial Tensions
- Chapter 8: Contact Angle and Liquid

- Surface Tension Measurements
- Chapter 9: Capillary Rise at a Vertical Plate as a Contact Angle Technique
- Chapter 10: Axisymmetric Drop Shape Analysis (ADSA)
- Chapter 11: Wettability and Surface Tension of Particles
- Chapter 12: Behavior of Particles at Solidification Fronts

As is apparent from the chapter listing the volume has quite an extensive scope. Since each of the chapters is written by experts in the respective fields the depth of the presentations matches the breadth of the coverage. The first two chapters give a strong hint of thermodynamic continuum theory as evidenced by the advanced treatment of curved surfaces and the generalized Laplace Equation. In particular it was amusing to note a reference to Clifford Truesdell's "Rational Thermodynamics" volume. Truesdell is as strong an exponent of 19th century continuum theory as you are likely to find anywhere as is clearly evidenced by his multi volume "Encyclopedia of Physics".

Chapters 3 through 10 cover nearly every aspect of contact angle behavior from theory to experiment. Chapter 8 in particular is a nice overview of the delicate art of making reliable contact angle measurements.

Of particular interest here is the theoretical treatment of solid and solid-liquid interfacial tensions given in chapter 7 by Moy and Neumann. Here one finds an introduction to the work of Hamaker on the attraction between solid surfaces due to the ever present van der Waals-London dispersion forces. The discussion extends to the pioneering work of Lifshitz who demonstrated that the Hamaker constant can be determined through the measurement of ultra violet absorption data. The relation to surface tension measurements and thus contact angle data is also discussed as reviewed in this issue's leading essay. This is quite an exciting area of investigation because one has in principle the rare opportunity to determine the surface tension of solids and solid liquid interfaces by two entirely different physical approaches. One through the direct observation of

liquid drops on surfaces and the other by spectroscopic measurements. The fact that one also has to confront the Quantum Electrodynamics aspects of interacting matter definitely puts this work at the very frontier of surface chemistry and physics.

Finally the last two chapters deal with contact angle behavior and particle wettability which is one of the motifs of the upcoming MST symposia in June 2006. Those interested in the biological aspects of particle wettability will be interested in the treatment given in chapter 11 which deals with problems of bacterial adhesion and methods of measuring it.

"Adhesion: Current Research and Applications", Ed. Wulff Possart (Wiley-VCH Verlag GmbH & Co. KGaA, 2005) 575 pages.

Anyone interested in the current state of research into problems of adhesion being carried out by the European community will have a definite interest in this volume. Presented are 34 research papers originally given at the 7th European conference on Adhesion (EURADH) held in Freiburg Germany in September 2004. The editor and contributors are to be congratulated on a well put out volume with a uniform format and a handy index to facilitate locating topics of interest. This volume is definitely a cut above the usual proceedings volumes one comes across which are typically no more than a bunch of papers hastily stapled together. It is one of the lamentable features of modern times that given heavy work loads and impossibly crowded schedules that many investigators have little time to spend on carefully editing their publications. We see this very often in our efforts to document the MST CONFERENCES symposia and can therefore appreciate the effort that has gone into this volume.

One of the main research avenues covered deals with advanced adhesives technology including the ever growing problem of recycling products put together with adhesives. In this regard the innovative paper by Nishiyama and Sato on "Behavior of Dismantlable Adhesives Including Thermally Expansive Microcapsules" will be of great interest to those in industry who are more

and more being faced with ever stricter environmental regulations aimed at the proper recycling of products that have outlived their usefulness.

The problems of testing and inspection of adhesive joints are addressed in the following papers;

- "Mapping epoxy Interphases" by M. Muntz, J. Chung and G. Kalinka
- "Mechanical Interphases in Epoxies as seen by Nondestructive High Performance Brillouin Microscopy" by J. K. Kruger, U. Müller, R. Bactavatchalou, D. Liebschner, M. Sander, W. Possart, C. Wehlack, J. Baller and D. Rouxel
- "Calibration and Evaluation of Nonlinear Ultrasonic Transmission Measurements of Thin Bonded Interfaces", by S. Hirsekorn, A. Koka, S. Kurzenhäuser and W. Arnold
- "Nondestructive Testing of Adhesive Curing in Glass-Metal Compounds by Unilateral NMR", by K. Kremer, B. Blümich, F. -P. Schmitz and J. Seitzer
- "Scanning Kelvin Probe Studies of Ion Transport and De-adhesion Processes at Polymer/Metal Interfaces" by K. Wapner and G. Grundmeier

The above papers alone would constitute a fairly comprehensive monograph on recent advances in nondestructive testing and inspection.

A second feature of the book is the number of papers dealing with the continually advancing field of bioadhesives. More and more we find ourselves in societies where people live longer and certain body parts fail or wear out while the remaining entity is still fully functional. This has given rise to the need for adhesive materials for healing fractures and the need to adhere special biocompatible coatings to various types of body implant replacements. In addition there is the ever growing need to confront the problem of bacterial films and the age old problem of barnacle adhesion. Several papers will be found dealing with problems in this arena including:

- "Structure Formation in Barnacle Adhesive", by M. Wiegemann

- "Adhesion Molecule-Modified Cardiovascular Prostheses: Characterization of Cellular Adhesion in a Cell Culture Model and by Cellular Force Microscopy", by U. Bakowsky, C. Erhardt, C. Loebach, P. Li, C. Kneuer, D. John, D. Hoekstra and C. -M. Lehr
- "Surface Engineering by Coating of Hydrophilic Layers: Bioadhesion and Biocontamination", by G. Legeay and F. Poncin-Epaillard

One will find many more papers in this volume dealing with a wide range of topics ranging from atomic force microscopy to positron annihilation experiments. The range covers many of the more conventional topics including advanced adhesive formulations, surface preparation methods, surface analysis, surface chemistry and the mechanics of adhesive joints. Any kind of comprehensive coverage is well beyond the scope of this brief review.

Finally, we would like to draw special attention to the paper by M. Aufray and Alain Roche "Properties of the Interphase Epoxy-amine/Metal: Influences from the Nature of the Amine and the Metal". Prof. Roche passed away in 2005 and this paper was quite likely his last contribution to the literature. Alain was a reliable contributor to the Journal of Adhesion Science and Technology and a regular participant in the MST CONFERENCES symposium series as well as a good friend of both Dr. Mittal and myself. His presence in the adhesion community will be missed.

"Particles on Surfaces 8: Detection, Adhesion and Removal", Ed. K. L. Mittal (VSP, Utrecht - Boston, 2003) 352 pages.

"Contact Angle Wettability and Adhesion, Volume 3", Ed. K. L. Mittal (VSP, Utrecht - Boston, 2003) 519 pages.

As we are holding the 10th International Symposium on Particles and the 5th International symposium on Contact Angle this coming June it is apropos at this time to review two volumes which document the 8th and 3rd symposia in the series which were held during the same week in Providence Rhode Island in June 2002. The 9th

and 4th volumes which document the 9th and 4th symposia held in Philadelphia in June 2004 are currently with the publisher and will hopefully be available for review in the next issue of the newsletter.

Particles on Surfaces 8: This volume will be of definite interest to those who have a practical interest in particle characterization, detection and removal. The book comprises 21 papers which are divided into two topical sections. Part I covers the general area of particle analysis and characterization. The tone of the section is encapsulated nicely in the overview paper of Kohli: "The Nature and Characterization of Small Particles". In this paper an introductory description of the nature of small particles is presented first. This is followed by a detailed description of a number of emerging techniques for characterizing particles such as scanning near-field optical microscopy (SNOM), hot electron microscopy, multiphonon microscopy and Raman chemical imaging. In addition a list of 128 up to date references is given which will allow the reader to come abreast with the latest technology in particle detection and characterization.

The second part of the volume treats the topics of particle adhesion and removal. The paper by Tomas: "Mechanics of Nanoparticle Adhesion - A Continuum Approach" stands out not only for its uniqueness but also for its near encyclopedic coverage of the mechanics of particle deformation and how it reflects on particle adhesion. Tomas basically takes up where the pioneering work of Johnson, Kendall and Roberts (the classic JKR theory) leaves off. In a single table Thomas gives an overview of some 16 different approaches to the particle adhesion and deformation problem. This paper is quite likely the most comprehensive review of this important topic available anywhere.

In addition to the rather unique paper by Tomas, a number of important papers on particle removal are also presented. Those in the microelectronics industry will have a definite interest in the paper by Vos et al on "Advanced Wet Cleaning of Sub-Micrometer Sized Particles" as well as the paper by Beaudry et al on "Modified SC-1 Solutions for Silicon wafer Cleaning". In addition to this, papers

are given on ultrasonic and megasonic cleaning along with presentations on laser surface cleaning. Unfortunately, limited space does not allow for a more detailed description of these innovative papers. The reader can get full details from the volume itself which will be available at the June 2006 symposium in Toronto discussed in detail in the "Call for Papers" at the end of this letter.

Contact Angle Wettability and Adhesion,

Volume 3: In tandem with the 8th international symposium on particles the 3rd international symposium on Contact Angle and Wettability was also held during the same week. Though not a particular focal point of this symposium, the interaction between contact angle behavior of fluids and the adhesion and behavior of particles was already starting to emerge as will be discussed later. The volume contains 25 papers divided into three separate sections. Part I deals with general papers on contact angle, adsorption, evaporation and fluid flow at the contact line. Part 2 gets into the meaty matter of contact angle measurements and the determination of solid surface free energy while part 3 covers fundamental and applied aspects of wetting and spreading behavior.

As mentioned above the relation of contact angle wetting behavior and particle surfaces emerges in the following papers:

- "Wetting of a Substrate by Nanocrystallites", By E. Ruckenstein
- "Wetting in Porous Media: some Theoretical and Practical Aspects", by A. Marmur
- "Dynamic Aspects of Wetting in Granular Matter" by D. Geromichalos, M. Kohonen, F. Mugele and S. Herminghaus
- "The Effect of Rock Surface Characteristics on Reservoir Wettability", by C. S. Vijapurapu and D. N. Rao

The last paper in the above list explores the highly practical topic of contact angle behavior and oil recovery from deep wells. As is all too apparent these days the world seems to be running out of

oil reserves with the consequent effect on price volatility at the gas pump which can see regular jump in price by as much as \$1.00/gallon in a weeks time! Though no one really knows how much recoverable oil is still in the Earth's crust it is certain that our ability to get at it is going to depend more and more on the interaction of oil, water and the rock/shale medium they are locked up in which definitely underscores the practical importance of this type of research. As pointed out in the related paper by Rao in this volume ("The Concept, Characterization, Concerns and Consequences of Contact Angles in Solid-Liquid-Liquid Systems") the environment at the bottom of an oil well presents some fairly extreme challenges for carrying out contact angle measurements. As pointed out by Rao one is interested in conditions of up to 200 C in temperature and 70 MPa pressure.²² In addition to this practical consideration, in the oil well one is interested in the solid-liquid-liquid system (S-L-L) as opposed to the more conventional solid-liquid-vapor (S-L-V) configuration which brings some unusual complications into the problem. Rao points out that the complications involved with the (S-L-L) system has given rise to considerable concern and skepticism in the oil industry at large concerning the applicability of contact angle techniques to this problem. In response to these problems the author goes on to describe the Dual-Drop Dual-Crystal (DDDC) contact angle technique for overcoming these criticisms.

Again limited space precludes any attempt to further discuss the many fine papers in this volume. However, a final mention of the overview article by Etzler ("Characterization of Surface Free Energies and Surface Chemistry of Solids") should be made as this paper gives an excellent and compact summary of contact angle measurement methods and their relevance to the determination of surface free energies. A nice feature of this paper is that it also covers competing techniques such as inverse gas chromatography, flow

²² To get some idea of the meaning of 70 MPa pressure one should note that in tension 70 MPa is roughly the ultimate tensile stress of common thermoplastic materials.

calorimetry, Scanning Probe Microscopy and Electron spectroscopy for Chemical Analysis (ESCA). The relationship among the methods is discussed as well as the major theories which are currently employed to analyze the experimental data.

As with the above mentioned volume on particles, the reader can get full details from the volume itself which will be available at the June 2006 symposium in Toronto discussed in detail in the "Call for Papers" at the end of this letter.

UPCOMING SYMPOSIA

MST CONFERENCES is organizing two follow on symposia in the Particle Adhesion and Contact Angle and Wettability series for the week of June 19, 2006 in Toronto Canada. All readers of this letter are cordially invited to join us at that time for what should be a most informative and exciting continuation of the topics discussed above.

Finally the conference Director Dr. Kash Mittal and I would like to extend our BEST WISHES FOR THE NEW YEAR to everyone and we hope you will be able to join us in Toronto this Summer.



CALL FOR PAPERS

TENTH INTERNATIONAL SYMPOSIUM ON PARTICLES ON SURFACES: DETECTION, ADHESION AND REMOVAL

Toronto, Canada, June 19 - 21, 2006

This will be the tenth event in the series of symposia on particles on surfaces initiated as part of the Fine Particle Society meeting in 1986. Particles are yield detractors in the manufacture of sophisticated and sensitive electronic components and are very undesirable in many other technologies. Contamination of optical surfaces and shorting of microelectronic circuits by conducting particles, among other concerns, underscore the importance of particle detection, adhesion and removal. On the other hand,

however, in certain instances particle adhesion to surfaces is necessary. The purpose of this symposium is to address the vast ramifications of particles on solid surfaces by bringing together specialists in many allied fields to discuss their latest findings and to identify areas for further investigation. Various types of substrates and particles --metals, oxides, glass, and polymers-- will be covered. The technical program will comprise both invited and contributed papers ranging from topical overviews to original research and industrial applications.

The symposium will emphasize the following topics:

- ▶ Sources and mechanisms of particle contamination
- ▶ Factors that influence particle adhesion: chemistry, topography, shape, size, relative humidity, medium, etc.
- ▶ Particle adhesion measurement techniques
- ▶ Detection, identification and characterization of particles on surfaces
- ▶ Techniques for particle removal
- ▶ Implications of particle contamination
- ▶ Thermodynamics of particle removal including interactions with fluids, electrolytes and solvents
- ▶ Removal of bacteria/viruses considered as particles

This symposium is being organized under the direction of Dr. K. L. Mittal, Editor, Journal of Adhesion Science and Technology by MST Conferences, LLC. A proceedings volume is planned for this symposium and further details will be provided in due course. Please notify the conference chairman of your intentions to present a paper as early as possible. An abstract of about 200 words should be sent by **March 15, 2006** to the conference chairman by any of the following methods:

E-mail: rhl@mstconf.com
 FAX: 212-656-1016
 Regular mail:

Dr. Robert H. Lacombe
 Conference Chairman
 3 Hammer Drive
 Hopewell Junction, NY 12533

Contact by phone: 845-897-1654; 845-227-7026
 Full conference details and registration via the Internet will be maintained on our web site:

<http://mstconf.com/particle10.htm>

Or mail response form below to conference chairman at address above

TENTH INTERNATIONAL SYMPOSIUM ON PARTICLES ON SURFACES: DETECTION, ADHESION AND REMOVAL

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- ATTEND
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CALL FOR PAPERS

FIFTH INTERNATIONAL SYMPOSIUM ON CONTACT ANGLE, WETTABILITY AND ADHESION Toronto, Canada, June 21 - 23, 2006

In his opening remarks at the first symposium in this series Professor Robert Good pointed out that Galileo in the 17th century was quite likely the first investigator to observe contact angle behavior with his experiment of floating a thin gold leaf on top of a water surface. Since that time contact angle measurements have found wide application as a method for determining the energetics of surfaces. This, in turn, has a profound effect on the wettability and adhesion of liquids and coatings to surfaces. This symposium will be concerned with both the fundamental and applied aspects of contact angle measurements. Issues such as the applicability and validity of various measurement techniques and the proper theoretical framework for the analysis of

contact angle data will be of prime concern. In addition, a host of applications of the contact angle technique will be explored including but not limited to: wettability of powders, fibers, wood products, papers, polymers and monolayers. Further focus will be on the use of contact angle data in evaluating surface modification procedures, determining relevance of wettability to adhesion, the role of wettability in bioadhesion, ophthalmology, prosthesis and in the control of dust in mining and milling applications. The primary focus of this symposium will be to provide a forum for the discussion of cutting edge advancements in the field and to review and consolidate the accomplishments which have been achieved thus far.

SYMPOSIUM TOPICS:

Factors Influencing Contact Angle Measurements:

- ◆ Static and dynamic contact angles, effect of surface flaws and surface roughness on wetting.
- ◆ Effect of pore size distribution
- ◆ Effects of velocity and viscosity of liquid on solid-liquid interfacial behavior.
- ◆ Interaction forces including: van der Waals, Acid-Base, Hydrogen bonding, ...etc

Wettability Behavior and Surface Characterization of Various Materials:

- ◆ Contact angle interpretation and hysteresis.
- ◆ Wettability of various material surfaces including but not limited to: wood, elastomers, silicon wafers, pharmaceutical powders, metals, polymers, paper, particles, fibers... etc.
- ◆ Surface treatments to modify wettability behavior.

Wettability, Adhesion and Applied Aspects of Contact Angle Measurements:

- ◆ Effect of surface energetics on adhesion.
- ◆ Biological applications including protein and bacterial adhesion.
- ◆ Fine particle adhesion and control of dust.
- ◆ Other technological applications including: printing, agriculture, pharmaceuticals, textiles and paper.

This symposium is being organized under the direction of Dr. K. L. Mittal, Editor, Journal of Adhesion Science and Technology by MST Conferences, LLC. A proceedings volume is planned for this symposium and further details will be provided in due course. Please notify the conference chairman of your intentions to present a paper as early as possible. An abstract of about 200 words should be sent by

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