

MATERIALS SCIENCE AND TECHNOLOGY NEWSLETTER

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SURFACE SCIENCE ASPECTS OF PARTICLE REMOVAL

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EDITORIAL COMMENTS

In advance of the upcoming TWELVETH INTERNATIONAL SYMPOSIUM ON PARTICLES ON SURFACES: DETECTION, ADHESION AND REMOVAL, to be held May 4-6, 2010, Louisville, Kentucky USA, this issue of the MST newsletter will have a look at some of the fundamental surface science aspects of particle removal and how they can have a critical influence on the very practical problem of removing unwanted particles from surfaces. Removing unwanted particle contaminants from a surface can be a tricky business due to the number of different interactions that can be involved including:

1. Electrostatic attraction
2. Capillary forces
3. Chemical bonding
4. Weak bonding interactions, i.e. acid-base interactions, hydrogen bonding
5. van der Waals dispersion forces

Of the above interactions the first 4 occur only under specific circumstances. For instance electrostatic interactions will be active only when free charges are present in insulator contaminants. Capillary forces require the presence of a liquid layer such as water or oil. The van der Waals interactions, however, are always present under all conditions and for this reason we will deal exclusively with this case.

A copy of the program announcement for the above mentioned particle symposium is reprinted at the end of the newsletter. We are happy to announce that this meeting will be held in conjunction with the PCx exposition being held in the same location. The primary intent of the symposium is to compliment the exposition by providing a forum for presentation and discussion of fundamental and applied topics which are critical to all aspects of contamination removal. The conference Director Dr. Mittal and I cordially invite all readers of the newsletter to join us in Louisville this May for this joint event.

SURFACE SCIENCE ASPECTS OF PARTICLE REMOVAL

Overview of van der Waals Interactions

Since the van der Waals force is the basic interaction which we will be dealing with a brief overview of the nature of this topic will be given

here. A more detailed discussion has been presented in a previous issue of the newsletter.¹ The fundamental fact governing all interactions at the atomic and molecular level is that they are all electromagnetic in nature. The strongest interactions arise from the presence of free charges and they give rise to the electrostatic interactions. Ironically the electrostatic interaction is so strong that it in effect suppresses itself. For example if we had two particles each with opposite charges of 1 coulomb and separated by a distance of 1 meter the electrostatic 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 cm² 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.

Next in line are the dipole-dipole interactions. 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. Though molecules with dipole moments are overall electrically neutral the charge separation associated with the dipole gives rise to a weak electric field which can polarize the surrounding medium giving rise to a net interaction. Curiously enough the dipole interaction will also tend to neutralize itself if the molecules in a given dipolar material happen to be randomly oriented, as will be the case in amorphous materials, then the fields generated by neighboring dipoles will tend to cancel each other thus effectively erasing the net effect of the interaction.

Finally we get to the van der Waals interaction which occurs between molecules that are both electrically neutral and have no internal charge separation or dipole moment. The nature of the interaction in this case is quite subtle and requires a quantum mechanical calculation to understand in a rigorous fashion as is explained in more detail in reference (1). The basic nature of the interaction can be understood however by reference to figure 1 which gives a stylized depiction of two neutral hydrogen atoms in relatively close proximity. At

¹ "Hamaker Theory or at Atomic Distances the World Follows the Rules of Quantum Mechanics", available online at www.mstconf.com/Vol2No3-2005.

large separations the two atoms appear to be wholly neutral to one another and thus there is no interaction between them. However, at closer distances, on the order of 10-100 atomic radii or so, each atom begins to discern that each has some instantaneous charge separation between the electron and proton and thus looks like a dipole of sorts. Though this is rather loose reasoning the detailed calculation shows that the two molecules behave as though they were two dipoles and give rise to an interaction energy that falls off as the inverse sixth power of the radial separation between them similar to the behavior of two actual dipoles.



The Hamaker Coefficient or Adding it All up to Get a Net Interaction

Knowing the nature of the fundamental interaction between two molecules is fine but just what are the consequences for macroscopic bodies such as particle contaminants that consist of a colossal number of such molecules all mutually interacting under the influence of the fundamental forces. Sorting this problem out requires a bit more work.

It was apparently H. C. Hamaker² who concluded that if two macroscopic neutral bodies are brought close enough together then the van der Waals London dispersion forces would kick in and give a net attraction. His approach to computing what the net effect should be was to 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 the following remarkably simple result for a sphere next to a plane:

$$F = \frac{H D}{12z^2} \quad (1)$$

Where:

- F = force of attraction
- D = Sphere diameter
- H = Hamaker constant
- z = Separation between sphere and surface

Though there are a number of technical difficulties with Hamaker's calculation Eq.(1) does fit experimental results quite well for this simple case as can be seen from the Atomic Force Microscope (AFM) data in figure 2. Notwithstanding the

Figure 1 Schematic of two hydrogen atoms separated by a distance R large compared to their atomic size but close enough that each recognized the atomic structure of the other.

relative success of the simple Hamaker approach to computing the attraction of particles to surfaces a number of problems were outstanding such as the effect that an intervening material might have on the overall interaction. This led Lifshitz and coworkers³ to redo Hamaker's calculation on the basis of more fundamental principles of physics. At this point the theory leaves the ground and takes off to truly celestial heights. Lifshitz concluded that to do the problem correctly one had to consider the full effect of the electromagnetic fields which moderate the interactions at the atomic level. This meant using full blown quantum electrodynamics and the calculations lead rather rapidly to some very heavy sledding indeed. Instead of the nice compact result given by Eq.(1) the Lifshitz calculation leads to

³ The original work of Lifshitz and collaborators can be found in the following: "The Theory of Attractive Forces between Solids", E. M. Lifshitz, Sov. Phys. JETP, 2, 73 (1956); "van der Waals Forces in Liquid Films", I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Piatevskii, Sov. Phys. JETP, 37,[10] 161 (1960); "General Theory of van der Waals Forces", I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Piatevskii, Adv Phys., 10,[38] 165 (1961)

² H. C. Hamaker, Physica, 4, 1058 (1937)

$$A_{132} = \frac{3kT}{2} \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{[\Delta_{13}(m)\Delta_{23}(m)]^m}{m^3} \quad (2)$$

$$\Delta_{13}(m) = \frac{\epsilon_1(i\zeta_m) - \epsilon_3(i\zeta_m)}{\epsilon_1(i\zeta_m) + \epsilon_3(i\zeta_m)}$$

$$\Delta_{23}(m) = \frac{\epsilon_2(i\zeta_m) - \epsilon_3(i\zeta_m)}{\epsilon_2(i\zeta_m) + \epsilon_3(i\zeta_m)}$$

$$\zeta_m = \frac{4\pi^2 kT}{h} m$$

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

If Eq.(2) is not scary enough consider that each of the sub equations which go into defining the Hamaker coefficient A_{123} themselves involve integrations over the full electromagnetic spectrum which interacts between the materials using the Kramers Kronig relation from complex variable theory. Interestingly enough though, the theory implies that the Hamaker coefficient and thus the net force of attraction due to the van der Waals interactions can be deduced from optical absorption measurements on the materials involved. This is a quite remarkable result in that it implies that one can compute how strongly a particle of some given material will interact with a given surface by carrying out only optical absorption measurements on the materials involved. Needless to say that most experimentalists when faced with Eq.(2) choose a different route to answering this question. What is even more remarkable however, is that at least one investigator has taken up this challenge and has published his results in the open literature.⁴ The upshot for the practicing

⁴ "Calculation of Hamaker coefficients for Metallic Aerosols from Extensive Optical Data", I. W. Osborne-Lee, in Particles on Surfaces, Vol.1, Ed. K. L. Mittal (Plenum Press, New York, 1988).

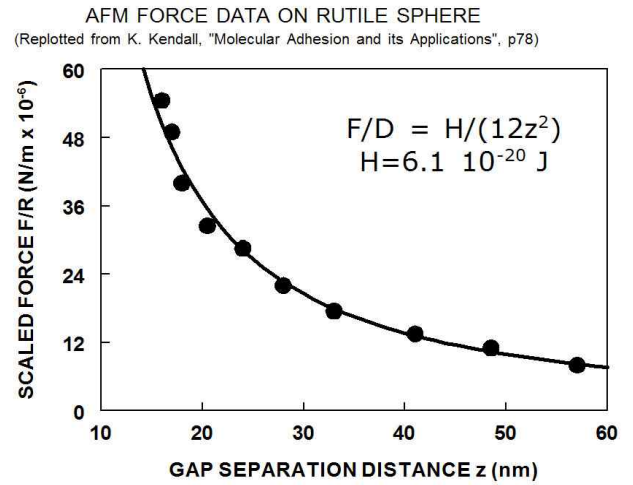


Figure 2 Atomic Force Microscope data for a titania sphere confirming Hamaker attraction force.

contamination removal engineer is that he does not have to wrestle with Eq.(2) since someone else has done all the heavy lifting.

Removing Aluminum Particles or Hamaker Theory in Action

Having the relevant Hamaker coefficients available is certainly nice but what can you do with them in terms of the practical problem of particle removal? To answer this question we consider a specific applied problem. Say we are in the business of machining precision aluminum parts and our customer demands that the finished product be ultra clean. We know that the machining process leaves behind aluminum particle debris ranging from gross contaminants the size of human hair down to micron size particles. Furthermore it would be convenient to remove this debris using a fluid jet. Rather than go out and invest in some capital equipment and then by trial and error see how well it works in removing the debris, can we make use of Hamaker theory to give us some idea as to how effective an impinging fluid jet will be in removing particles in the size range of interest and what sort of flow rates would be required and other important engineering specs. Having the Hamaker coefficient in hand we can calculate the adhesion force holding the particles to the surface but then we need to know also how much shear force can be applied by the fluid jet and whether it will be sufficient to remove particles in the size range of interest. Finally we would like to get this information in an hour or so using no more than a hand calculator to do the math. As luck would have it this problem has also been worked out in the

literature by Gim et. al.⁵ Figure 3 shows a schematic diagram of the simplified model of an impinging jet which the authors studied. Since the model is axi-symmetric the diagram depicts just half of a planar slice through the jet. Using their results and a little elementary algebra one can deduce the following handy expressing relating the required flow rate for particle removal in terms of particle size, fluid properties, jet geometry, the Hamaker coefficient and other relevant properties:

$$\begin{aligned}
 Q &= c_0(\tau)^{5/11}[r/r_j]^{1/11} \\
 Q &= \frac{Q}{Q_0} \quad (\text{Reduced jet flow rate}) \\
 \tau &= \frac{\tau}{\tau_0} \quad (\text{Reduced shear stress})
 \end{aligned}
 \tag{3}$$

Eq.(3) expresses the dimensionless jet flow rate Q in terms of τ the dimensionless shear stress required to remove a particle. Since τ itself depends on the particle size and the local Hamaker constant Eq.(3) can also be thought of as a relation defining the jet flow rate required to remove particles of a given size which are adhered to the surface by van der Waals forces which are described by the local Hamaker constant. The following parameters are required to fully describe Eq.(3):

- Q = jet flow rate (m^3/sec)
- $Q_0 = \pi r_j v$ = fluid characteristic flow rate (m^3/sec)
- r_j = impinging jet radius (m)
- v = kinematic viscosity of impinging fluid (m^2/sec)
- $\tau = A/(192h^2d)$ = net shear stress required to remove particle (N/m^2)
- d = particle radius (m)
- A = Hamaker coefficient describing net van der Waals attraction (Joule)
- h = mean particle separation from surface approximated by $1.65 \times 10^{-10}m$
- $\tau_0 = (\rho v^2)/r_j^2$ = characteristic shear stress imposed by fluid flow (N/m^2)
- ρ = fluid density (kg/m^3)
- r = radial coordinate measured from center of jet (m)
- c_0 = dimensionless constant = 4.6138

All we need to do now is round up all the relevant

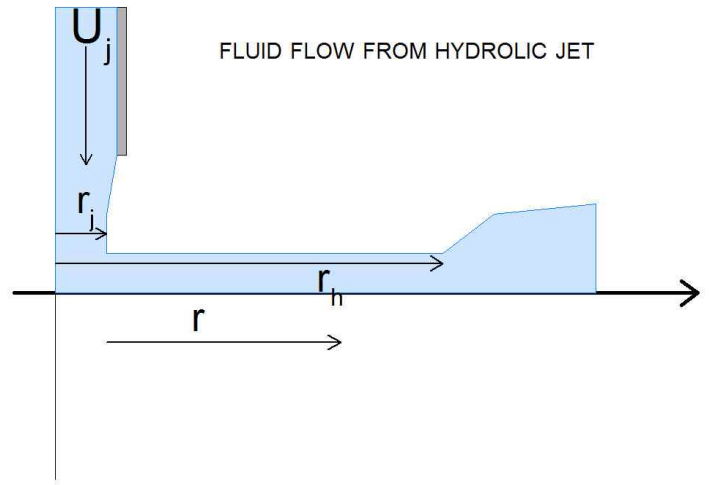


Figure 3 Schematic of impinging water jet after Gim et. al. Ref. (5).

parameters and plug them into Eq.(3) to get some idea as to what sort of flow rates will be required to remove the debris from our precision aluminum parts. As an example we can use a simple case given by Gim et al. where they use water as the fluid and a jet radius of 0.08 cm. Conveniently enough since Eq.(3) is cast entirely in terms of dimensionless variables we can use any consistent set of units for our calculation. The authors assume that the flow rate will be effective out to 6 times the impinging jet radius so the ratio r/r_j can be set to 6. collecting the relevant data we have for the case of aluminum particles and a water jet:

- $r/r_j = 6$
- $\rho = 1$ (water) gm/cm^3
- $v = 0.01$ (water) cm^2/sec
- $A = 33 \times 10^{-20}$ erg (aluminum)

Lastly we need to know how much shear stress the flow field must apply in order to remove a given particle. Again referring to the paper by Gim et. al. they give the following expression for the tangential force F_x which a flow field will apply to a particle of radius "d" in terms of the flow shear stress τ :

$$F_x = 32d^2\tau \tag{4}$$

In addition we know from Hamaker theory that the adhesion force holding the particle to the surface is given by:

$$F_{ad} = \frac{Ad}{6h^2} \tag{5}$$

Where all parameters are as given in Eq.(3). the particle will start sliding when the tangential force

⁵ "Fluid Dynamics of Liquid Jets Used for Particle Removal from Surfaces", Ronald Gim, Thomas Lesniewski and Stanley Middleman, in Particles on Surfaces: Detection, Adhesion and Removal, Ed. K. L. Mittal (Marcel Dekker, New York, 1995) p. 379

overcomes the force of adhesion which happens when $F_x = F_{ad}$ or⁶:

$$32d^2\tau = \frac{Ad}{6h^2} \rightarrow \tau = \frac{A}{192dh^2} \quad (7)$$

Eqs.(3) and (7) can now be combined using the material and geometry data listed above to give the following simple formula relating the applied flow rate Q of the impinging water jet to the shear stress required for particle removal and thus the particle size d :

$$Q = 0.0136 (4.04/d)^{0.4545} \quad (8)$$

Eq.(8) now lets us make some rough estimate of the flow rates required to remove aluminum particles in a given size range from our carefully machined parts. Table I gives a short summary:

TABLE I: SUMMARY OF FLOW RATES REQUIRED FOR A WATER JET TO REMOVE ALUMINUM PARTICLES FROM A SMOOTH ALUMINUM SURFACE AS A FUNCTION OF PARTICLE SIZE.(all parameters as given in refs. 4 and 5)		
PARTICLE SIZE (cm)	FLOW RATE (cm³/sec)	COMMENTS
10 ⁻²	4.5	HUMAN HAIR
10 ⁻³	13.7	COLLOIDAL DUST
10 ⁻⁴	39.0	MICRON SIZE
10 ⁻⁵	111.0	SUB MICRON SIZE

The data in Table I are what the practicing contamination engineer would be interested in as they give an important specification for any equipment that would have to be set up to clean the machined parts. Thus depending on what particle is deemed critical the required flow rate for removal can be estimated in advance. Thus we see that if we need to remove particles down to the one micron size then our equipment has to be able to deliver a flow rate of at least 39 cm³/sec. Furthermore, if the requirement is to remove sub micron particles also then the minimum flow rate more than doubles and perhaps an impinging jet approach may not be suitable for this application.

⁶ Note this condition assumes a maximal value of the local coefficient of friction of 1 which is a reasonable approximation for smooth surfaces.

PARTICLE REMOVAL SYMPOSIUM

In the spirit of the above discussion we would like to cordially all readers of the newsletter to join us in Louisville for the 12th in the PARTICLE ON SURFACES symposium series. Again we encourage papers from a wide range of expertise ranging from theoretical studies to commercial applications in the hope that fruitful common ground can be found. Details of the symposium are as follows:

TWELVETH INTERNATIONAL SYMPOSIUM ON PARTICLES ON SURFACES: DETECTION, ADHESION AND REMOVAL LOUISVILLE, KENTUCKY USA, May 4-6, 2010

This will be the 12th 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.

We are happy to announce that this symposium will be held in conjunction with the Process Cleaning Expo 2010 (**PCx 2010**) which will be held at the Kentucky International Convention Center in Louisville. The two events will be held in the same location in order to foster mutually beneficial interactions between those attending the exposition, whose primary interests are the practical removal of contaminants from commercial products, and those participating in the symposium who are more focused on understanding the fundamental physicochemical interactions and processes which are critical to successful particle contaminant removal. Thus we hope to promote a synergy between the two interests which both sides will find useful and informative. 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 ITEMS AND RELATED TOPICS:

- ▶ **Sources and mechanisms of particle contamination**
 - ▶ Intrinsic and extrinsic
 - ▶ Nanometer to micrometer scale
- ▶ **Factors that influence particle adhesion:** Chemistry, topography, shape, size, relative humidity, medium, etc.
- ▶ **Particle adhesion measurement techniques**
 - ▶ Forces affecting adhesion: JKR theory, Hamaker theory
- ▶ **Detection, identification and characterization of particles on surfaces**
 - ▶ Micrometer scale
 - ▶ Nanometer scale
- ▶ **Techniques for particle removal**
 - ▶ Challenge of nanoscale removal
 - ▶ Fluid dynamics of particle removal
- ▶ **Implications of particle contamination**
 - ▶ Microelectronic applications
 - ▶ Biomedical applications
 - ▶ Optics and precision tool applications
- ▶ **Thermodynamics of particle removal**
Including interactions with fluids, electrolytes and solvents
- ▶ **Detection/Removal of bacteria/viruses considered as particles**

This symposium is being organized under the direction of Dr. K. L. Mittal, Editor-in-Chief, Journal of Adhesion Science and Technology in concert with the organizing committee of **PCx 2010**. 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, 2010** 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 details will be maintained on the MST CONFERENCES web site:

<http://mstconf.com/particle12.htm>