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ADHESION SCIENCE AND CONTACT ANGLE FROM A DIFFERENT ANGLE

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EDITORIAL COMMENTS

At the 9<sup>th</sup> in the symposium series on CONTACT ANGLE, WETTABILITY AND ADHESION there was a most interesting paper presented by Prof. Herbert Jennissen on "Advances in Hyperhydrophilic Surfaces, Their Characterization by Imaginary Contact Angles and First Preclinical Studies". A quick look at the classic Young's equation shows that when dealing with high surface tension substrates such as metals the surface interaction energy of the solid becomes so large that the cosine of the contact angle is predicted to be greater than 1. This would seem to present a problem as standard tables of the cosine function do not list any numbers greater than 1 and if you try to compute the inverse cosine of a number greater than 1 on your calculator you will most likely get an error. So what is happening? This leads to the topic of our editorial essay.

In addition this issue of the NEWSLETTER announces the upcoming 10<sup>th</sup> in the symposium series on CONTACT ANGLE, WETTABILITY AND ADHESION which will be held July 13-15, 2016 at the Stevens Institute of Technology in Hoboken, New Jersey.

Finally we would like to bring every ones attention to the next session of the short course on:

THE CHEMISTRY, PHYSICS AND MECHANICS OF ADHESION SCIENCE

The course will be given again this coming November 4-6, 2015 at the Marriott Inn in Newburgh, NY and all readers of the NEWSLETTER are invited to join us this November in Newburgh or simply to pass the word along to colleagues or associates who might be interested.

CONTACT ANGLE FROM A DIFFERENT ANGLE

For a drop of some liquid sitting on a solid substrate as shown in Fig.(1), the cosine of the angle the drop makes with the supporting surface is given by the classic Young's equation:

$$\gamma_{lv} \cos(\theta) = \gamma_{sv} - \gamma_{ls} \quad [1]$$

Where:

- $\gamma_{sv}$  = Surface tension of solid (J/m<sup>2</sup>)
- $\gamma_{lv}$  = Surface tension of liquid (J/m<sup>2</sup>)
- $\gamma_{sl}$  = Surface tension of liquid-solid interface (J/m<sup>2</sup>)

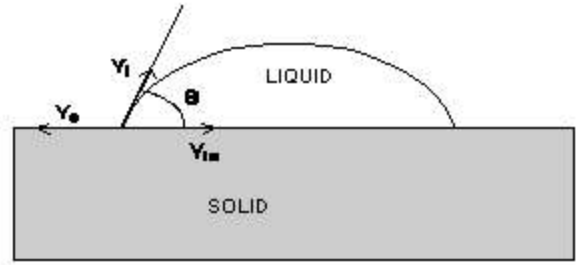


Figure 1 Liquid drop on solid surface exhibiting relevant surface tensions and resulting contact angle.

As pointed out above if the surface tension of the solid-vapor interface  $\gamma_{sl}$  becomes large Eq.(1) can predict that the cosine of the contact angle will be a number greater than 1 which presents a significant problem for most experimentalists who do contact angle measurements. However, if you talk to any mathematician familiar with complex variable theory he will tell you there is no problem here since the cosine is a perfectly analytical function defined over the entire complex plane. Thus, in this case, the contact angle must be an imaginary number. So simple. Well this is fine for the mathematician who does not have to make sense of this situation in physical terms but what is the practical experimentalist to make of this?

COMPLEX NUMBERS ARE COMMONPLACE IN THE PHYSICAL SCIENCES

First we should point out that complex numbers are commonly used in the physical sciences in a variety of situations. A few examples should suffice to make the point:

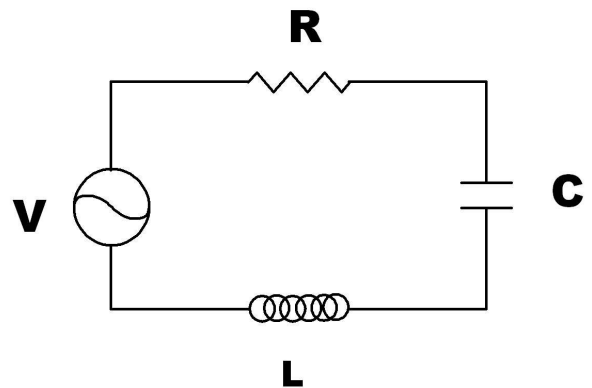


Figure 2: Standard alternating current circuit

**EXAMPLE 1: Electromagnetic Fields Propagating Through Conductive Media**

In vacuum or air the electric field of a plane electromagnetic wave such as that transmitted by your local radio station is given by the simple formula:

$$E = E_0 \sin(kx - \omega t) \quad (2)$$

Where:

$k$  = Wave vector  
 $\omega$  = Frequency

In non conductive media the wave vector  $k$  is a simple real number inversely proportional to the wavelength of the radiation. However, in a conductive medium such as copper the field is strongly attenuated and the wave vector becomes a complex number as follows:

$$\begin{aligned} k &= \alpha + i\beta \\ \alpha &= \frac{\omega}{c} (\mu\epsilon)^{1/2} \\ \beta &= \frac{2\pi}{c} \sigma (\mu/\epsilon)^{1/2} \end{aligned} \quad (3)$$

Where:

$\mu$  = Magnetic permeability  
 $\epsilon$  = Dielectric constant  
 $c$  = Speed of light  
 $\sigma$  = Electrical conductivity

The conductivity of the metal gives rise to dissipative currents which attenuate the electric field and thus prevent the radiation from propagating very far into the metal. This is the basis for using metal enclosures as shielding from electromagnetic waves.

**EXAMPLE 2: Alternating Current Circuits**

Figure (2) exhibits a common alternating current circuit. The differential equation relating the current  $I$  in the circuit to the applied voltage  $V$  is given by:

$$\begin{aligned} L \frac{dI}{dt} + RI + \frac{1}{C} \int I(t) dt &= V(t) \\ V(t) &= V_0 \exp(i\omega t) \end{aligned} \quad (4)$$

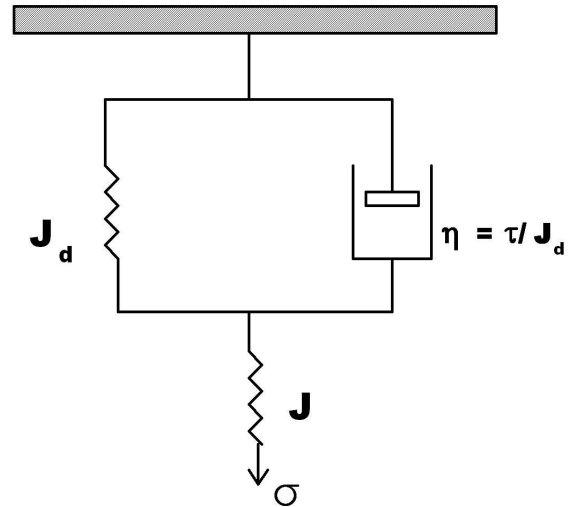
Where:

$C$  = Capacitance  
 $L$  = Inductance  
 $R$  = Resistance

Invoking a solution for the induced current of the form  $I = I_0 \exp(i\omega t)$  gives the following relationship between the current and voltage amplitudes  $I_0$  and  $V_0$

$$\begin{aligned} V_0 &= I_0 Z \\ Z &= R + i\omega L + \frac{1}{i\omega C} \end{aligned} \quad (5)$$

In the case of a circuit with just a simple resistor carrying a direct current the voltage current relationship is simply the standard Ohm's law  $V=IR$ . We see that in the case of a time varying alternating voltage applied to a circuit with both a finite capacitance and inductance as well as a simple resistance Ohm's law generalizes to  $V=IZ$  where  $Z$  is the complex impedance required to take into account the reactance of the inductor ( $i\omega L$ ) and the reactance of the capacitor ( $1/i\omega C$ ). These relations are wholly commonplace and are routinely used by electricians and electrical designers everywhere.



**Figure 3** Basic model for the viscoelastic response of a material commonly called the Kelvin or Voigt model

### EXAMPLE 3: Dynamic Mechanical Response of Viscoelastic Materials

Figure (3) exhibits one of the simplest models known which can describe the viscoelastic behavior of a material. The elastic behavior is captured in the compliance coefficients  $J$  and  $J_d$ . In the case of a constant applied load  $\sigma$  the resulting strain deformation  $\epsilon$  will be given by:

$$\epsilon = (J + J_d)\sigma \quad (6)$$

This is just a variation on the well known Hook's law since the compliance  $J$  is simply the inverse of the Young's modulus  $E$ . In the case of a more general time varying load  $\sigma(t)$  it can be readily shown that the time varying behavior of this model is governed by the following differential equation:<sup>1</sup>

$$(J_d + J)\sigma + \tau J \frac{d\sigma}{dt} = \epsilon + \tau \frac{d\epsilon}{dt} \quad (7)$$

If we apply an oscillating load to the model then  $\sigma(t)$  has the form:

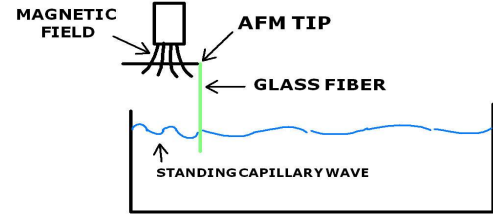
$$\sigma(t) = \sigma_0 \exp(i\omega t) \quad (8)$$

With this form of the applied load the strain response of the model is easily calculated as:

$$\begin{aligned} \epsilon(t) &= (\epsilon_1 + i\epsilon_2)\exp(i\omega t) \\ \epsilon_1 &= \sigma_0 J_1 ; \epsilon_2 = \sigma_0 J_2 \\ J_1 &= J + \frac{J_d}{1 + (\omega\tau)^2} \\ J_2 &= \frac{J_d \omega\tau}{1 + (\omega\tau)^2} \end{aligned} \quad (9)$$

<sup>1</sup> These results are well known. Complete derivations are given in a number of texts including: "Anelastic Relaxation in Crystalline Solids", A. S. Nowick and B. S. Berry (Academic Press, 1972); "Mechanical Properties of Solid Polymers" 2nd Ed., I. M. Ward (John Wiley & Sons, 1983); "Thermal-Mechanical Behavior of Polymer Resins: an Introduction and Overview", R. H. Lacombe (1983). This report is available online at <http://www.mstconf.com/DynamicMechV2.pdf>

### SCHEMATIC OF MICRORHEOMETER



**Figure 4:** Highly simplified diagram of the microrheometer experiment for measuring dynamic mechanical response of liquid surfaces.

Thus we see that the overall response of the model to an oscillating load has two components, an elastic response  $\epsilon_1$  and a viscous response  $\epsilon_2$ .

In all of the above examples we see that complex numbers come in handy in describing time varying behavior. Much the same should be possible for describing the time varying behavior of liquid drops on solid surfaces since all liquids exhibit both elastic and viscous behavior.

### DYNAMIC BEHAVIOR OF SURFACE CAPILLARY WAVES OF LIQUIDS

Recent work by Jennissen<sup>2</sup> has shown that the contact angle of a liquid on a surface can be treated as a complex number. The concept of treating the surface tension of a liquid as a complex number has further been persuasively demonstrated in papers by Xiaomin Xiong and coworkers<sup>3</sup>. Using the novel microrheometer apparatus depicted in Fig.(4) the authors are able to monitor the dynamic mechanical response of the

<sup>2</sup> Jennissen, H. P. Hyperhydrophilic Rough Surfaces and Imaginary Contact Angles. *Materialwiss. Werkstofftech. (Mater. Sci. Eng. Technol)*, 43, 743-750 (2012); Jennissen, H. P. On the Origin of the Imaginary Part of Complex Contact Angles. *Materialwiss. Werkstofftech. (Mat. Sci. Engineer. Technol)*, 46, 786-795 (2015)

<sup>3</sup> "Role of Complex Surface Tension in the Dispersion Relation of a Capillary Wave", Lan Chen, ... and Xiaomin Xiong, in *Journal of Physical Chemistry C* 2014, 118, pp26877-26881. See also "Imaginary Part of the Surface Tension of Water", Xiao-Min Xiong, ... and Jin-Xiu Zhang, in *Chin. Phys. Lett.* 2014, 31, 076801.

liquid surface in the following manner: A thin glass fiber attached to the tip of an Atomic Force Microscope (AFM) is dipped a short length into the surface of the liquid fairly close to the edge of the liquid container. The AFM tip can be brought into forced vibration by an applied oscillating magnetic field. The resulting dynamic mechanical response of the system is sensitively measured by the AFM apparatus by the method of Apparent Dissipation Factor Frequency Spectroscopy (ADFFS)<sup>4</sup>. The system behaves in a manner closely analogous to that shown in Fig.(3), described mathematically by Eqs.(6-9) where in this case  $\sigma$  is interpreted as the surface tension of the liquid. For the case of water the authors report a value of  $\sigma$  as  $(0.73+i0.017)$  N/m.

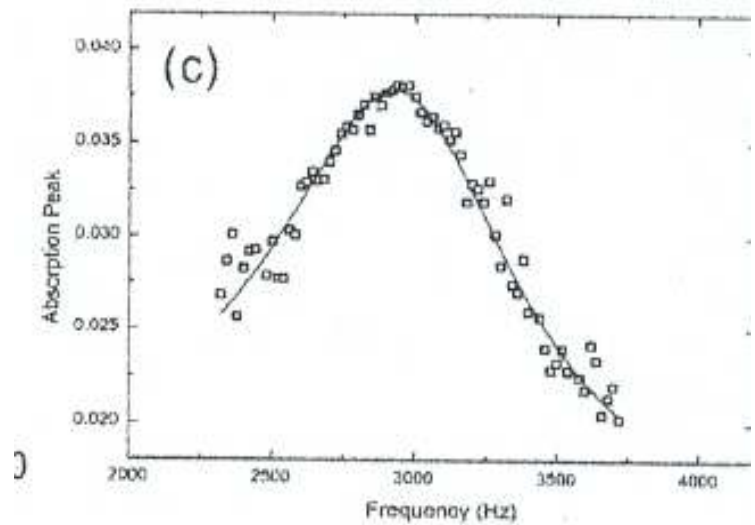
At first glance it would seem that the dissipative component of the complex surface tension would arise from the viscosity of the liquid. However this is apparently not the case and Xiong and coworkers demonstrate rather convincingly that the imaginary component of the surface tension arises from the anelastic behavior of the liquid surface involving mechanisms not present in the bulk of the fluid. Figure (5) from Xiong et. al exhibits a relaxation spectrum of water derived from their microreohometer apparatus. This is substantial proof that the dissipative component of the complex surface tension arises from an anelastic mechanism occurring at the water surface very similar to the ones that occur in crystalline solids<sup>5</sup>.

### CONSEQUENCES FOR CONTACT ANGLE BEHAVIOR

Currently the overwhelming number of contact angle measurements carried out in academic and industrial labs are done under static or quasi-static conditions or in other terms at zero or very low frequency. In the case of the elastic properties of bulk solids this is equivalent to performing a simple tensile test the results of which are adequately described by the classic Hooke's law involving Young's modulus which is always a real number. However, going by the results of Xiong and coworkers, at high frequencies the liquid surface

<sup>4</sup> "Resonant Frequency and Damping of a coupled Resonant System measured by Apparent Dissipation Factor Frequency Spectra", W. L. Zuo et al, in Rev. Sci. Instrum., 2013, 84, p. 085110.

<sup>5</sup> A comprehensive discussion of the anelastic behavior of crystalline solids arising from grain boundaries, dislocations and point defects can be found in the volume by Nowick and Berry mentioned in footnote 1.

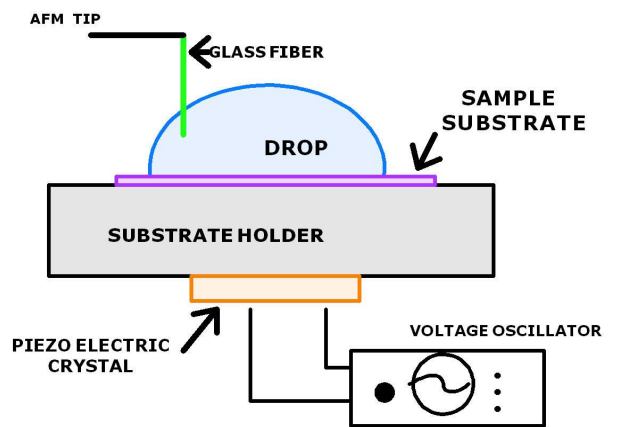


**Figure 5** Relaxation spectrum for surface tension of water after Xiong et. al (ref. 2)

tension is a complex number and from Eq.(1) above  $\cos(\theta)$  must also be complex implying the contact angle  $\theta$  must be complex as well.

The above comments may be perfectly correct but what are the "practical" consequences for anyone making contact angle measurements? Figure(6) illustrates a hypothetical contact angle measurement experiment where the complex nature of the contact angle will come into play.

The liquid drop/substrate system under investigation is mounted securely onto a substrate holder. Attached to the holder is a piezoelectric crystal which can be driven into a wide range of frequency oscillations by a suitable drive oscillator as depicted in the figure.



**Figure 6** Hypothetical experiment for measuring the consequences of the high frequency response of contact angle behavior.

With this apparatus the surface of the drop can be driven into small oscillations at a fixed frequency and the value of the contact angle  $\theta_0$  will vary by some small amount  $\Delta\theta(t)$ . Following the example of the microreometer experiment mentioned above, the induced elastic strain in the surface of the drop is monitored by a thin glass fiber attached to an AFM tip.

At small amplitudes  $\Delta\theta(t)$  will follow the following equation describing the anelastic response of the system:

$$m \frac{d^2 \Delta\theta}{dt^2} + \gamma_{lv} \cos(\theta_0 + \Delta\theta) \quad (10)$$

$$+ \gamma_{ls} - \gamma_{sv} = \sigma_0 e^{i\omega t}$$

Where:

- m = Mass of drop
- $\theta_0$  = Classic static contact angle
- $\gamma_{lv}$ ,  $\gamma_{ls}$ , and  $\gamma_{sv}$  as given in Eq(1)
- $\omega$  = Frequency of applied dynamic load
- $\sigma_0$  = Amplitude of applied surface tension
- t = Elapsed time

Using the apparatus described in Fig.(6) one can expect to observe the type of relaxation behavior observed in the microreometer due to the presence of the  $\gamma_{lv}$  term in Eq(10). However, and more interesting, the  $\gamma_{ls}$  term can potentially give rise to anelastic relaxation behavior occurring at the liquid/solid interface. In particular, for the case of a polymer substrate one can expect to observe molecular relaxation behavior arising from chain backbone motions as well as diffusion of surface contaminant species showing up in the dynamic mechanical spectrum. Such relaxations are commonly observed in dynamic mechanical measurements on bulk polymers and it would be interesting to see how these common relaxations are modified at the surface due to the highly asymmetric environment. Additionally, entirely new phenomena might be observed due to the close interaction of the liquid drop with the polymer surface.

CALL FOR PAPERS: TENTH INTERNATIONAL SYMPOSIUM ON CONTACT ANGLE, WETTABILITY AND ADHESION ;Stevens Institute of Technology, Hoboken, New Jersey, July 13-15, 2016

## SYMPOSIUM HISTORY AND MOTIVIATION

In his opening remarks at the first symposium in this series Professor Robert Good pointed out that Galileo in the 17<sup>th</sup> 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 not only as a method for determining the energetics of surfaces but also for investigating the consequences of ultrahydrophobic and oleophobic 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, paper, 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.

## SUBMITTING A PAPER

This symposium is being organized under the direction of Dr. K. L. Mittal, Editor, Reviews of Adhesion and Adhesives and by MST Conferences. 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 February 15, 2016 to the conference chairman by any of the following methods:

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Full conference details and registration via the Internet will be maintained on our web site:

[www.mstconf.com/Contact10.htm](http://www.mstconf.com/Contact10.htm)

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### 3- Day Impact Course The Chemistry, Physics & Mechanics of Adhesion Science

November 4-6, 2015

Courtyard by Marriott, Stewart-Newburgh New York

Quite likely the most comprehensive course on adhesion science, it is directed toward engineers, technical staff, technically oriented sales representatives and management personnel who need to have a basic understanding of the multifarious aspects of adhesion phenomena and how they affect a wide range of practical and applied situations. This course is of particular interest to those in the coatings industry who have to deal with the adhesion of paints, thin films and problems of surface preparation.

Adhesion science has the unique property of dealing both with sticky phenomena while at the same time giving rise to numerous slippery problems. The sticky aspects of adhesion are apparent to even the most casual observer whereas the slippery aspects become apparent only to those who try to control the adhesion behavior of the various, coatings, structures and devices they are trying to develop. Our aim is to allow the student to get a firm grip on the slippery aspects of adhesion by learning the fundamental principles behind all adhesion behavior and also by gaining an overview of the many methods and tools that have been developed to uncover and elucidate these principles.

The course is being taught by Drs. Kash Mittal and Robert Lacombe who have had more than 20 years experience each in this field in both academic and industrial settings. Dr. Mittal, in particular, Editor of Reviews of Adhesion and Adhesives, has edited over 100 books dealing with all aspects of adhesion science and related topics. Dr. Lacombe brings 30 years of experience dealing with adhesion issues in the microelectronics industry and will cover such

key topics as the fracture mechanics aspects of coating delamination and adhesive joint failure, the atomic and molecular aspects of the fundamental interactions which give rise to adhesion forces and the universal problem of measuring adhesion. He has written a comprehensive handbook and reference work entitled "Adhesion Measurement Methods: Theory and Practice" (CRC Press, 2006) which will be part of the course handouts. Expanded details are available on the MST CONFERENCES website at:

[www.mstconf.com/AdhesionCourse.htm](http://www.mstconf.com/AdhesionCourse.htm)

We hope you or members of your staff will be able to join the course this coming November as we delve into the inner workings of the subtle material interactions that hold the world together and also cause it to fall apart and the basic principles that determine which outcome will prevail.

#### Topics to be Covered

- I. Surface Contamination and Cleaning
- II. Theories or Mechanisms of Adhesion
- III. Contact Angle, Wettability and Adhesion
- IV. Investigation of Interfacial Interactions
- V. Surface Modification Techniques including Plasma
- VI. Ways to improve Adhesion of Organic Coatings
- VII. Silanes and Other Adhesion Promoters
- VIII. Adhesion Aspects of Thin Films
- IX. Adhesion Measurement of Films and Coatings
- X. Basics of Adhesion Measurement
- XI. Residual Stress and Material Mechanical Properties
- XII. Setting Adhesion Requirements for Coating Applications
- XIII. Adhesion Measurement at Atomic and Molecular Level
- XIV. Fundamental Adhesion Applications

Audience: Scientists, management and professional staff in R&D, manufacturing, processing, quality control/reliability involved with adhesion aspects of coatings and adhesion sensitive applications.

Level: Beginner- Intermediate;  
introduction/overview

Prerequisites: Elementary background In chemistry, physics or materials science.

Duration: 3 days

Course fee and materials: \$1,295, includes break refreshments, complete set of lecture notes and copy of handbook and reference guide ADHESION MEASUREMENT METHODS: THEORY AND PRACTICE, (CRC PRESS, 2006)

#### INSTRUCTORS AND CONTACT INFORMATION

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For detailed information and registration:

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