

Water, Nanotechnology and Biotechnology

Energy Dissipation due to Capillary Interactions: Hydrophobicity Maps in Force Microscopy

Hydrated Ions as Nano-Ball-Bearings

The Puzzling Behavior of Liquid Water: Some Clues from the Nanoscale

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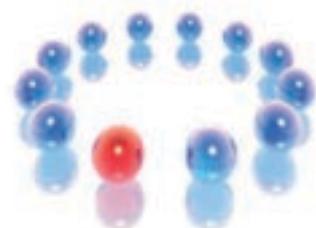
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Dear Readers:

This E-Nano Newsletter issue is mainly dedicated to provide insights in a field devoted to study nano-interactions mediated by water ("water at the nanoscale") with huge expectatives for possible applications in the nanotechnology and biotechnology world.

In addition, an overview of the outstanding scientific activity in the Department of Fundamental Research on Condensed Matter at CEA-Grenoble (France) is given in a few key figures.

We would like to thank all the authors who contributed to this issue as well as the European Union (FET/NanoICT) for their close collaboration.

Dr. Antonio Correia

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Water, Nanotechnology and Biotechnology

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Water has been always considered just as a solvent with no special role in mediating molecular interactions at the nanoscale. However, recently, this vision is changing.

For example, recent studies suggest that water promotes protein folding and unfolding. Active proteins in living cells adopt a single folded structure called the native structure. However, when the protein is first synthesized it is just a chain of aminoacids with no particular shape. How does the protein find its way to the native structure from the unfolded state? This is an old problem in biophysics. The usual approach is to consider the interaction energy among the different components of the protein without taking into account any water effect. However, this situation is changing nowadays and recent numerical studies seem to point towards the possibility of water mediating between the aminoacids in order to promote folding to the native state. Also a change in water structure could be the responsible for the cold denaturation found in some proteins and for the changes on shape found in some proteins such as collagen.

Another example of an interaction at the nanoscale promoted by water is the pumping up of protons inside the cell. Cells are charged by transporting protons across biological membranes using proton-pumps proteins. This energy gain in the cell is transformed into ATP by the ATP synthase. These proteins are basically channels of nanometric size placed across and along the membrane. Structural studies have shown that, actually, these channels are normally filled with a chain of hydrogen bonded water molecules. Some recent proposals are based on the idea that protons are jump conducted along chains of interfacial water molecules aligned along the membranes surfaces.

Water is also expected to control the concentration of potassium and sodium atoms inside the cell. Recent theories propose that potassium atoms fit in low density structured water while more hydrophilic (smaller) sodium atoms have a tendency to fit in more dense water structures. The change in water structure inside the cell, from high density liquid (HDL) to low density liquid (LDL) could balance this equilibrium towards an increment in potassium inside the cell and an increment of sodium outside the cell with no need of using ATP activated ion-pumps placed at the membrane. This balance is fundamental in order to get a functional cell. If the balance is broken, for example because of a failure of the sodium-potassium pump, there is no regulation in the amount of water inside the cell and the cell dies.

The field devoted to study nano-interactions mediated by water is hatching right now and there are huge expectations for possible applications in the Nanotechnology and Biotechnology world. Controlling the role of water at the nanoscale may allow us to control, at some extent, the basic mechanisms of proteins, cells and surfaces with

specifically tailored bio-interactions. Potential applications in the world of medicine are enormous. However, many important questions need to be answered. For example, how is really the behaviour of water at the nanoscale? How does it behave when embedded inside nanometric reservoirs? How does water behave close to biomolecules and bio-surfaces? How does it behave when close to ions in biological environments?

Next "Trends in Nanotechnology" conference (TNT2007 – <http://www.tnt2007.org>) to be held in San Sebastian (Spain) this coming September has focused a new session devoted to deal with these questions. World renowned scientists will discuss these problems and present their main results on "water at the nanoscale" during the conference. This article summarizes some of their contributions.

Energy Dissipation due to Capillary Interactions: Hydrophobicity Maps in Force Microscopy

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Atomic Force Microscopy (AFM) has made possible the manipulation and acquisition of images with nanometer resolution. Recent improvements have allowed the study of not only hard inorganic substrates but also soft organic and biological samples and even living systems. In order to minimize sample deformations due to the tip interaction, AFM images are usually taken by using different dynamic operation modes [1]. Phase contrast images, obtained by recording the phase lag of the cantilever oscillation relative to the driving signal, often provides significantly more contrast than the topographic image. At fixed feedback amplitude, phase shift variations are directly related to energy dissipation processes [2]. However, most of the phase and energy dissipation images are purely qualitative, mainly due to the absence of simple relationships linking phase changes and energy dissipation with surface properties.

The amplitude of the cantilever and particularly the phase contrast is strongly influenced by capillary forces [3] in air ambient condition. As a matter of fact, environment humidity has always represented a handicap for the correct observation of tip-sample interactions. When the tip approaches the sample, water in air can condensate inducing the formation of a nanometer-sized water bridge. The relevance of liquid bridges have driven numerous experimental [4] and theoretical [5] efforts to understand systems involving capillaries. Understanding capillary contrast in AFM maps would be particularly interesting for biological applications [6], where the recognition of different species is often based on their hydrophilic or hydrophobic nature [3, 5].

In a recent work [7], we have performed a theoretical

analysis of the energy dissipation involved in the formation and rupture of capillary-condensed water bridges. Using a simple model for capillary forces, we predicted a quantitative relation between the energy dissipated U_{dis} and tip and sample contact angles and relative humidity (RH). One could naively argue that the averaged power dissipated by capillary forces in amplitude modulated AFM (AM-AFM) would simply be given by $P_{dis} \approx U_{dis}\omega/2\pi$, i.e. the energy dissipated per oscillation times the number of oscillations per unit time. However, as we recently showed [7], this is, in general, not true. The dissipation contrast is a result of a non-trivial interplay between the energy dissipated in each rupture process and the bi-stable motion of the cantilever [8].

AM-AFM presents two regimes of operation: the attractive (AR) and the repulsive (RR) regimes [1,9] (also known as low and high amplitude regimes). As we will see, only in the RR one can be sure that the tip hits the surface in each oscillation in presence of dissipative forces (capillary forces). The dissipated power is then a function of the tip and sample contact angles being independent of the elastic properties of the system. If dissipation is dominated by capillary processes, only when working in the RR, energy dissipation images can be regarded as surface hydrophobicity maps.

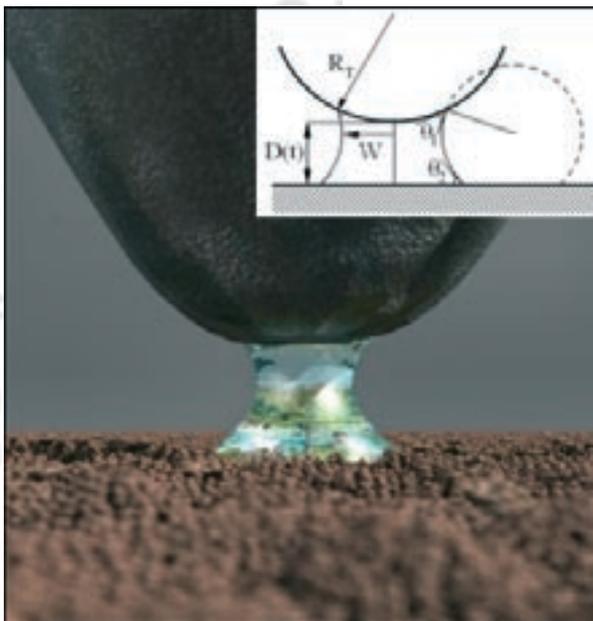


Figure 1: Artistic representation of a tip linked to a substrate through a water bridge. Inset: Schematic representation of the tip-neck-substrate system.

Let us consider the simplified model of the tip-neck-sample system sketched in **Figure 1**. The homogeneous liquid meniscus is assumed to have a constant curvature radius. For a given tip radius R_T and a tip-sample distance D , the pendular ring geometry of the bridge (see Fig 1) is characterized by the tip and sample contact angles θ_1 and θ_2 and the bridge width W . The hysteresis associated to the formation and rupture of a liquid bridge is sketched in

Figure 2. The “excess” grand potential [10], $\Delta\Omega_{tot}$ to condense the water bridge is given by the sum of surface and volume contributions as discussed in Refs. [7,10]. Figure 2c shows typical $\Delta\Omega_{tot}$ vs W for different tip-sample distances. For D smaller than a critical distance D_c , the grand potential presents a maximum corresponding to the nucleation free energy barrier and a minimum $\Delta\Omega_0(D)$ corresponding to a liquid bridge in mechanical equilibrium.

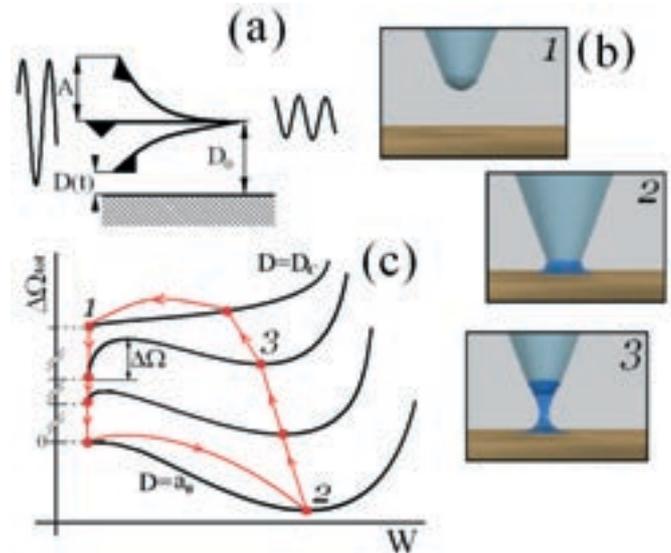


Figure 2: (a) Tip-cantilever-driver system. (b) Graphic representation of water neck formation/rupture. (c) Schematic representation of the formation/rupture process in tapping mode. (Based on Sahagún et al. [7]).

As the tip approaches the sample, the nucleation free energy barrier decreases and capillary condensation can take place. When the tip retracts, the condensed water bridge elongates and breaks at a critical distance $D \approx D_c \approx r_k X$, where r_k is the absolute value of the Kelvin radius over the logarithm of H^{-1} ($r_k = 0.54 \ln(1/H)$ nm for water at 20°C) and $X = (\cos\theta_1 + \cos\theta_2)$. Since the tip-sample contact corresponds to $D = a_0$ (being a_0 an intermolecular distance [11]), the total energy dissipated by the tip-cantilever system in each condensation-rupture cycle would be

$$U_{dis} \approx \Delta\Omega_0(D_c) - \Delta\Omega_0(a_0) \quad (1)$$

One important thing is that U_{dis} depends on θ_1 and θ_2 because so does the volume and surface of the bridge. Then U_{dis} is hydrophobicity sensitive.

Let us now discuss the dynamic response of the AFM in the presence of capillary phenomena. The usual theoretical approach [1,7,12] describes the system as a driven anharmonic oscillator (Fig.2a) including the cantilever elastic response, the hydrodynamic damping with the medium and the tip-sample interaction forces F_{ts} . For F_{ts} , we include both van der Waals and Dejarguin-Muller-Toporov (DMT) [13], plus the contribution of capillary forces, F_{cap} , obtained from the numerical minimization of

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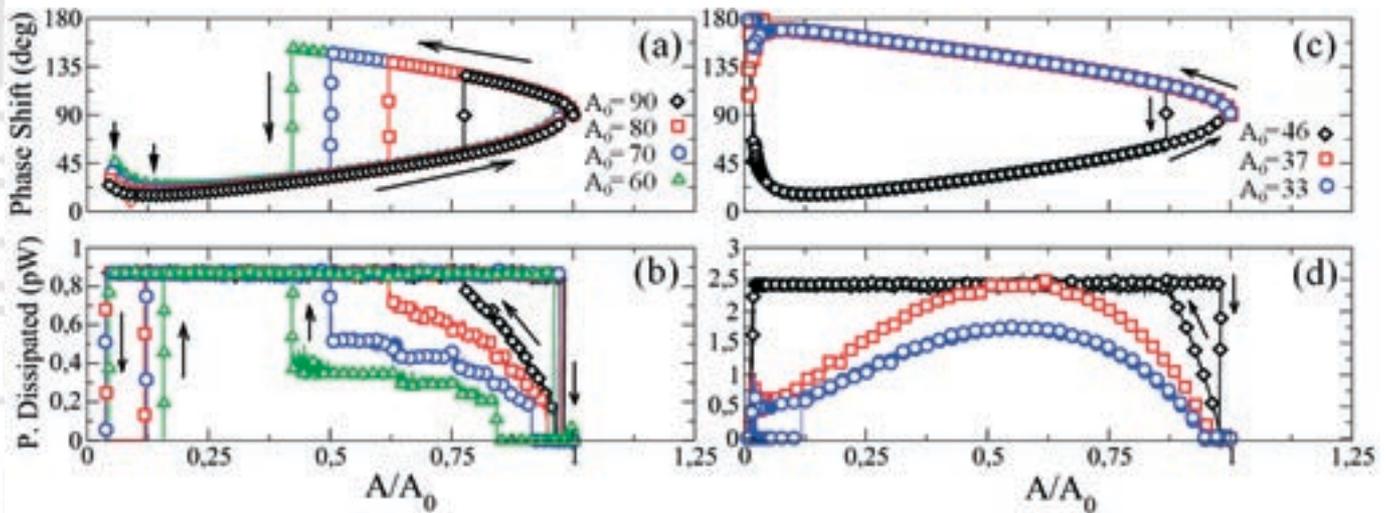


Figure 3: Phase (a) and power dissipated (b) vs normalized amplitude. The cantilever parameters are $k=2N/m$, $Q=100$, $v=w_0 / (2\pi)=100kHz$. (c,d) are the same as (a,b) but for lower amplitudes (and different cantilever constants: $k=27.5N/m$, $Q=400$, $v=280kHz$). In the RR ($\phi < 90^\circ$), the energy dissipated per oscillation is simply given by U_{dis} . The rest of simulation parameters can be found in reference [16]. (Based on Sahagún et al. [5]).

$\Delta\Omega_{tot}$ (assuming that the neck evolves in thermodynamic equilibrium, the capillary force is simply given by $F_{cap}(D) = -\delta\Delta\Omega_0/\delta D$. While the amplitude, A , and phase, ϕ , of the cantilever can be acquired directly from the experiment, P_{dis} must be calculated indirectly. The numerical results are in full agreement with the well known expression derived by Cleveland et al [2].

The results of the simulations are summarized in **Figure**

3, where we plot the typical behaviour of the phase shift and dissipated power vs the normalized amplitude A/A_0 (being A_0 the free oscillation amplitude). By looking at the phase curves (Fig. 3a and c) it is possible to identify the AFM working regime. At large averaged tip sample distance (D_0), where $A/A_0=1$, and working at resonance, the initial phase lag is 90° . As D_0 decreases the amplitude decreases and there is a continuous growth of the phase

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ϕ . This region, where $\phi > 90^\circ$, corresponds to the AR. The corresponding dissipated power, P_{dis} (shown in Fig. 3b and d), presents a maximum with respect to the amplitude ratio in full agreement with recent experimental results [17]. The maximum in the dissipated power has been associated to the existence of hysteresis in the long range interaction forces [17] or to viscoelastic interactions. As shown in Fig. 3d capillary interactions (in general, any contact interaction leading to surface energy hysteresis) may also lead to a maximum in the AR: Dissipation takes place once the closest tip-surface distance goes below a critical distance ($D_{min} \leq a_0$ in our model). Since the energy lost in each contact breaking process is constant, changes in the dissipated power arise as a consequence of a beating phenomenon [3]. After the breaking process, the cantilever has less energy than before and will not reach the same amplitude as before the impact. Then the tip may not hit the sample surface during the next swings. As D_0 decreases, the time delay between two contacts decreases and, as a consequence, dissipation increases. The maximum in the dissipated power correlates with a minimum in the averaged value of D_{min} with respect to the amplitude ratio. In the AR, the maximum dissipated power depends not only on the capillary interactions but also on the elastic properties of both cantilever and sample. It will then be difficult to interpret power dissipation contrast in heterogeneous samples.

Abrupt changes in the phase from values above to below 90° correspond to the transition from AR to RR. These jumps, and the associated hysteresis [13], arise as a consequence of the bi-stable motion of the cantilever [11]. The transition is usually marked by a discontinuous jump in the dissipated power. Although the oscillation is chaotic in the high amplitude regime, the tip, at the closest distance, is always in (repulsive) contact with the sample and there is a condensation-rupture cycle for each oscillation. This is a very important result since, once the system is in the RR, P_{dis} does not depend on the amplitude and saturates to the theoretical limit. In this regime, the energy dissipated per oscillation coincides with U_{dis} and is independent on the amplitude and elastic properties of the system. This is a general result that does not depend on the details of the liquid bridge model. The dependence of U_{dis} on RH and θ_1 and θ_2 could be experimentally checked by measuring the energy dissipated per oscillation in the RR. In summary, we have shown that capillary dissipation contrast in AM-AFM strongly depends on the operation regime. Only in the RR the energy dissipated per oscillation is independent on the amplitude and elastic properties of the system. For a given tip and RH, the dissipated power is just a function of the sample contact angle. As a consequence, only when working in the repulsive regime, energy dissipation images of biological samples in air can be regarded as surface hydrophobicity maps.

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Hydrated Ions as Nano-Ball-Bearings

Jacob Klein, University of Oxford (UK) and Weizmann Institute (Israel)

The combination of strong attachment of hydration layers to ions in aqueous salt solutions, together with the possible lability of these layers (covering some 14 orders of magnitude in exchange/relaxation rates) leads to interesting nanomechanical properties, including the long-known hydration repulsion. In recent years the central role of such hydrated ions in lubrication phenomena in both synthetic and especially biological systems has been pointed out [1-3]. The main element providing the lubrication appears to be the hydration layers which resist removal under pressure but are very fluid under shear [1], as indicated in Figure 1.

v_x up to 1200 nm/sec, γ up to 1500 sec⁻¹

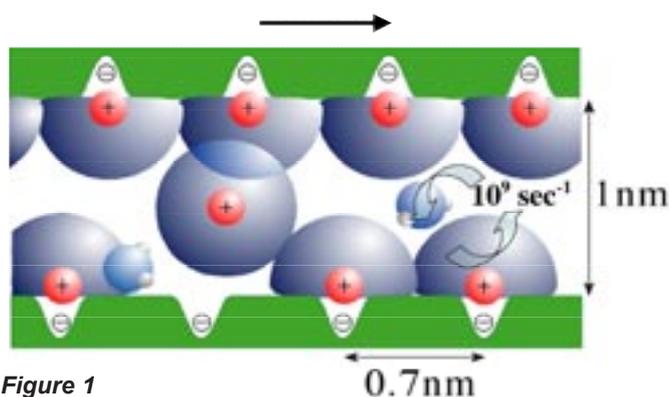


Figure 1

Research

This shows two charged surfaces under substantial compressive load, between which are hydrated ions. The ions are trapped between the surfaces by the need for overall electroneutrality, while the pressure between them is supported by the repulsion arising from the hydration layers tenaciously attached to the ionic charges. The hydration layers may readily shear, however, due to the rapid exchange (for alkali and many transition metal ions) of the hydration water with surrounding water molecules, as indicated schematically in Fig. 1, and this enables the very efficient lubrication.

This concept of lubrication by hydration layers transfers also to lubrication by charged or hydrated polymer brushes [2]. In this case, in addition to the well-known entropic effects that lead to polymer brushes being excellent friction-reduction coatings, the ultimate lubricants at the high-est pressures – where configurational entropy effects are negligible – are again the hydration layers about the charged segments, as shown in **Figure 2**.

Very recently we discovered [3] that boundary lubrication by surfactant layers, which classically takes place in an air or oil environment through shear at the interface between the layers, behaves in a very different manner when the surfactant-coated surfaces are immersed under water. In this case the polar headgroups become hydrated, and again it is the resulting hydration layers which act to lubricate the motion: in this case the slip plane shifts from the midplane to that between the hydrated head-groups and the solid substrates, as illustrated in **Figure 3 page 11**.

The demonstrations that hydration layers can act as nano-

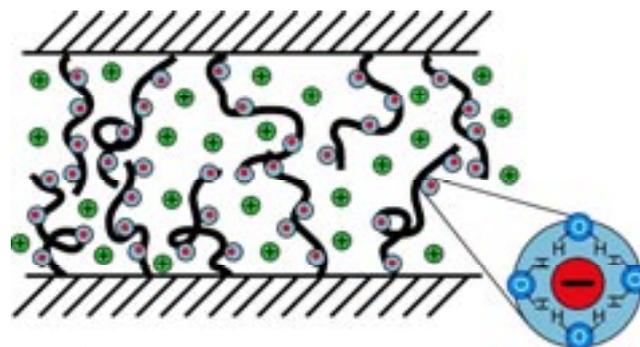


Figure 2

ball-bearings have implications not only for possible used in nanotechnology, but also in biolubrication [5] and implemented in biomedical devices such as implants, and this is being actively pursued.

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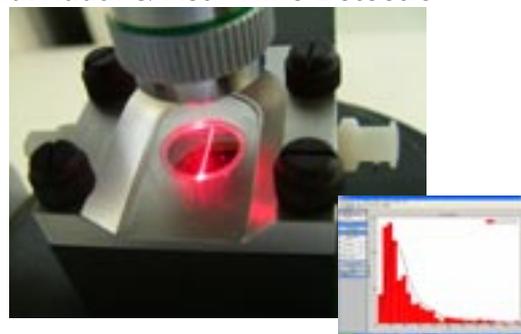
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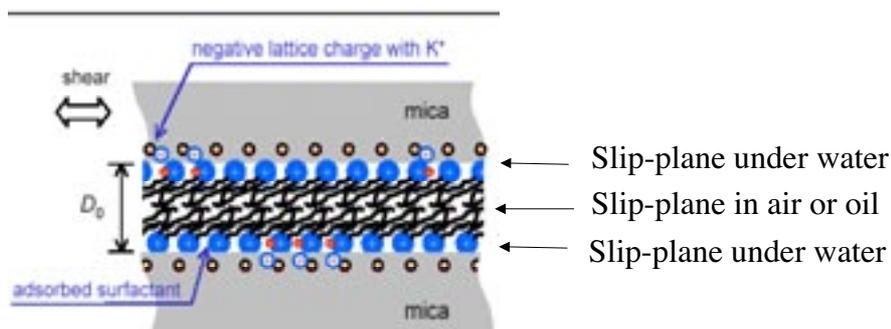


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Figure 3

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The Puzzling Behavior of Liquid Water: Some Clues from the Nanoscale

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Abstract

Despite decades of research water's puzzling properties are not understood and 63 anomalies that distinguish water from other liquids remain unsolved. We introduce some of these unsolved mysteries, and demonstrate recent progress in solving them. We present recent evidence from experiments and computer simulations on bulk and on nanoconfined water supporting the hypothesis that water displays a special transition point (which is not unlike the "tipping point" immortalized by Malcolm Gladwell). The general idea is that when the liquid is near this "tipping point," it suddenly separates into two distinct liquid phases. This concept of a new critical point is finding application to other liquids as well as water, such as silicon and silica. We also discuss related puzzles, such as the mysterious behavior of water near a protein.

Introduction

Water is perhaps the most ubiquitous, and the most essential, of any molecule on earth. Indeed, H₂O challenges the imagination of even the most creative science fiction writers (such as K. Vonnegut) to picture what life would be like without water, and one often hears the adage "biology cannot be understood until water is understood". Despite 300 years of research, however, the 63 anomalies (<http://www.lsbu.ac.uk/water/anmlies.html>) that distinguish water from other liquids lack a coherent explanation so sometimes water is called the prototype "complex fluid".

We will introduce some of the 63 anomalies of water, and will demonstrate some recent progress in solving them using concepts borrowed from various disciplines including chemistry and physics. In particular, we will present evidence from experiments designed to test the hypothesis that water displays a special transition point (which is not unlike the "tipping point" immortalized in Malcolm Gladwell's book of the same title). The general idea that when water is near this tipping point, it can separate into two distinct liquid

phases distinguished by their density. This new concept of a critical point is also proving useful in understanding some of the anomalies of other liquids, such as silicon, silica, and carbon.

We will also discuss two other water mysteries, such as the puzzling behavior of water near a protein, and the breakdown of the Stokes-Einstein relation in supercooled water.

What is the phenomenon?

We start with three thermodynamic functions. The first is the compressibility - the response of the volume to an infinitesimal change in pressure. In a typical liquid, this response function decreases when we lower the temperature. I understand this decrease via statistical physics. This thermodynamic response function is proportional to the thermal average of all the fluctuations in specific volume in the system. As we lower the temperature, we imagine that fluctuations of necessity decrease, thus the compressibility decreases.

Water is unusual in three respects. First, the average compressibility of water is twice as large as what one would expect were water a typical fluid and were one to plug all the prefactors into the formulas that give compressibility in terms of volume fluctuations. Second, the magnitude of that factor of two actually increases as one lowers the temperature. That being the case, there is ultimately a minimum - which occurs at 46°C. Below that temperature, the compressibility increases dramatically. At the lowest attainable temperature (-40°C) the compressibility takes on a value that is twice of that at the minimum. This is not a tiny effect; it is huge (**Figure 1 page 12**).

The second thermodynamic function is the specific heat, and we observe three similar anomalies: it is twice as large as that of a typical liquid, the discrepancy gets bigger as the temperature is lowered, and a minimum occurs at 35°C.

The third thermodynamic function is the coefficient of thermal expansion, the response of the volume to an infinitesimal change in temperature. This quantity we assume to always be positive because if there is a local region of the liquid in which the specific volume is larger than the average, then there will be more arrangements of the molecules and hence the entropy will be larger than the average. This is true of almost all liquids, but the magnitude of

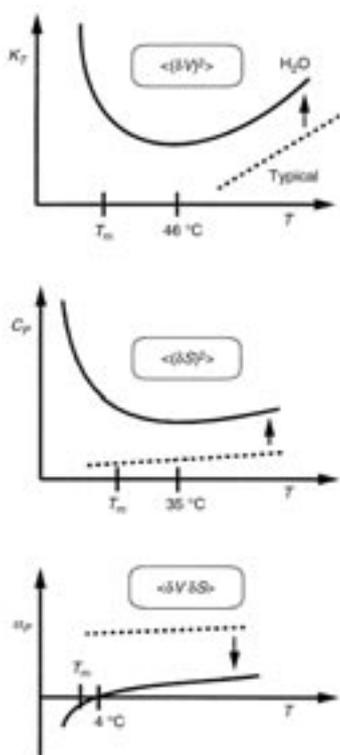


Figure 1: Schematic dependence on temperature of (a) the isothermal compressibility K_T , (b) the constant-pressure specific heat C_p , and (c) the thermal expansivity α_p . The behavior of a typical liquid is indicated by the dashed line, which, very roughly, is an extrapolation of the high-temperature behavior of liquid water. Note that while the anomalies displayed by liquid water are apparent above the melting temperature T_m , they become more striking as one supercools below T_m .

this cross-fluctuation of volume and entropy in water is approximately three times smaller than we would expect, and at 4°C the coefficient of thermal expansion passes through zero and actually becomes negative.

Why do we care about this anomalous behavior?

To begin with, if we do not understand water we will never understand biology. That is a major reason to care. Scientifically, water is the prototype complex fluid. It is not a simple, “bag-of-marbles” liquid, but a “bag of tetrahedra.” These tetrahedra are not only irregularly shaped, but are charged. Two of the arms are positively-charged, corresponding to the protons on each water molecule, and two are negatively-charged, corresponding to the lone pairs. In addition to short-range forces, these “charged tetrahedra” interact with long-range Coulomb forces.

What do we do?

Our approach is based on the fact that water has a tetrahedral local geometry. In this sense water shares features with other liquids such as silicon. Because water is both tetrahedral and charged means that a simple Lennard-Jones potential is not sufficient to describe its complexity. One way to modify the Lennard-Jones potential to provide at least a simplified description is to bifurcate the single minimum into two minima [3-6]. The first minimum, at a closer distance, corresponds to two pentamers (a water molecule and its four neighbors) of water interacting with

each other in a rotated configuration. The second minimum, at a greater distance, occurs in the unrotated position. This second position is a deeper minimum because although the pentamers are farther apart there is the potential for hydrogen bonding between the molecules and we can see the beginnings of an ice-like hexagonal structure (Figure 2).

The important point is that there are two minima with the

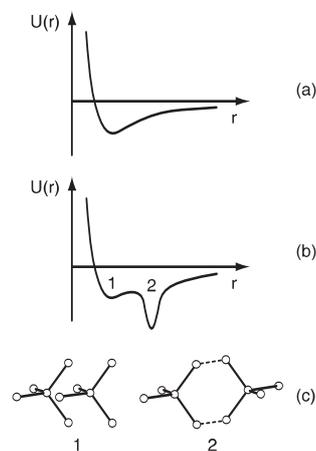


Figure 2: Physical arguments relating to the plausibility of the existence of the known liquid-gas critical point C and the hypothesized LDL-HDL critical point C'. (a) Idealized system characterized by a pair interaction potential with a single attractive well. At low enough T ($T < T_c$) and high enough P ($P < P_c$), the system condenses into the “liquid” well shown. (b) Idealized system characterized by a pair interaction potential whose attractive well has two sub-wells, the outer of which is deeper and narrower. For low enough T ($T < T_c'$) and low enough P ($P < P_c'$), the one-phase liquid can “condense” into the narrow outer “LDL” subwell, thereby giving rise to a LDL phase, and leaving behind the high-density liquid phase occupying predominantly the inner subwell. (c) Two idealized interaction clusters of water molecules (“Walrafen pentamers”) in configurations that may correspond to the two sub-wells of (b). This figure is courtesy of Dr. O. Mishima.

outer one corresponding to a larger specific volume - because the distance is larger - and a lower entropy. The possibility is that liquid water could at low temperatures condense not into a single phase - as we anticipate when a gas with a simple interaction like a Lennard-Jones potential condenses into a fluid - but into two different phases. This possibility was first raised by Takahashi 60 years ago and various elaborations of this model have been made by a number of people since then, including seminal work of Per Hemmer and George Stell in 1971 [7-9]. The implications of this is the possibility of two different liquid phases contributing to an increase in these fluctuations in specific volume and a negative contribution to the cross-fluctuations, negative because the deeper well has a larger volume and a lower entropy. The consequences of this fact qualitatively explain the phenomenon we were describing at the beginning - volume fluctuations are increased, entropy fluctuations are increased, and cross-fluctuations of volume and entropy are decreased. This picture further predicts the possibility that at low temperatures there will be a genuine phase transition in which the

single component liquid separates into two different phases. The implications of this when applied to real water molecules produce a phase diagram of liquid water (Figure 3). This was first uncovered by Poole, Sciortino, and Essmann [10]. At one atmosphere (the left axis) we see the melting temperature and the limit of supercooling around -40°C . At a very low temperature we see the presence of the glassy phase, not unlike that of any other liquid except that at high pressure this glassy phase shifts from a low-density form to a high-density form. In typical liquids we do not find two different glassy phases. These two forms correspond to the two different local arrangements characteristic of water tetrahedra. The order parameter jump between these two phases is not a trivial amount, but on the order of 30 percent [11].

Between the liquid and glassy phases of water we have a

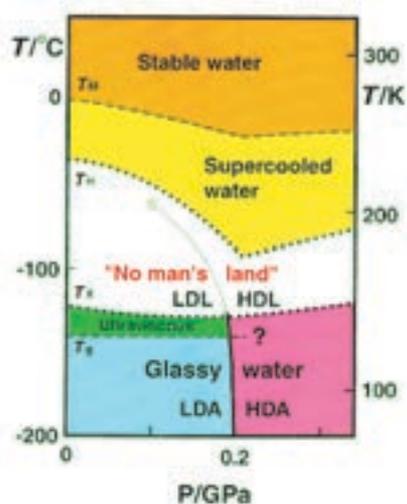


Figure 3: Schematic illustration indicating the various phases of liquid water (color-coded).

This figure is courtesy of Dr. O. Mishima.

region in which water does not exist as a liquid. I like to call this a No Man's Land." The hypothesis that follows from the reasoning we have just described is that this first order phase transition line known to separate the two amorphous forms of solid water extends into this No Man's Land and ultimately terminates at a critical point. Just as the glassy water first-order transition line separates a low-density amorphous from a high-density amorphous phase of water, so also this extension of the line into the liquid region separates a low-density liquid from a high-density liquid. The power-law behavior uncovered over the years by Angell, Anisimov and collaborators corresponds to the fact that the extension of this first-order line beyond the critical point - the "Widom line" - has the effect where any experiment approaching that line looks as though it is going to diverge with critical exponents but does not.

This phase diagram is hypothesized, but it has not been proved. What has been proved is that computer simulations using tried and tested models of liquid water confirm the broad features of this phase diagram (see Ref. [12] and refs. therein). But computer models of water (like computer models of anything) are subject to the charge

"garbage-in, garbage-out" - you get out what you put in. All computer models of complex systems such as liquid water are of necessity simplifications.

Current experiments on this problem are of two sorts. The first is a set of experiments inspired by Mishima that involves probing the No Man's Land by studying the metastable extensions of the melting lines of the various high-pressure polymorphs of ice: ice III, ice V, ice IV, and ice XII [13, 14]. Two of these lines clearly display "kinks." Since the slope of any melting line is the difference of the volume change divided by the entropy change of the two phases that coexist at that line, if there is a change in slope there must be a change in these quantities. Since there is no change in the crystal part, there must be a change in the liquid part. This means the liquid must undergo a jump in either its volume or its entropy or both. That is the definition of a first-order phase transition. A second set of experiments is being carried out in the MIT group of Chen and the Messina group of Mallamace, which have stimulated much of our recent work.

Recent Work on Bulk and Nanoconfined Water

Next we describe, for two water models displaying a liquid-liquid critical point, the relation between changes in dynamic and thermodynamic anomalies arising from the presence of the liquid-liquid critical point. We find a correlation between the dynamic fragility transition and the locus of specific heat maxima C^{\max}_P ("Widom line") emanating from the critical point. Our findings are consistent with a possible relation between the previously hypothesized liquid-liquid phase transition and the transition in the dynamics recently observed in neutron scattering experiments on confined water. More generally, we argue that this connection between C^{\max}_P and dynamic crossover is not limited to the case of water, a hydrogen bonded network liquid, but is a more general feature of crossing the Widom line. Specifically, we also study the Jagla potential, a spherically symmetric two-scale potential known to possess a liquid-liquid critical point, in which the competition between two liquid structures is generated by repulsive and attractive ramp interactions. Using molecular dynamics simulations, we also investigate the relation between the dynamic transitions of biomolecules (lysozyme and DNA) and the dynamic and thermodynamic properties of hydration water. We find that the dynamic transition of the macromolecules, sometimes called a "protein glass transition", occurs at the temperature of dynamic crossover in the diffusivity of hydration water, and also coincides with the maxima of the isobaric specific heat C_P and the temperature derivative of the orientational order parameter. We relate these findings to the hypothesis of a liquid-liquid critical point in water. Our simulations are consistent with the possibility that the protein glass transition results from a change in the behavior of hydration water, specifically from crossing the Widom line.

The Widom Line

By definition, in a first order phase transitions, thermodynamic state functions such as density ρ and enthalpy H discontinuously change as we cool the system along a

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path crossing the equilibrium coexistence line [Figure 4(a), path β page 15]. In a real experiment, this discontinuous change may not occur at the coexistence line since a substance can remain in a supercooled metastable phase until a limit of stability (a spinodal) is reached [15] [Figure 4(b), path β]. If the system is cooled isobarically along a path above the liquid-gas critical pressure P_c [Figure 4(b), path α], the state functions continuously change from the values characteristic of a high temperature phase (gas) to those characteristic of a low temperature phase (liquid). The thermodynamic response functions which are the derivatives of the state functions with respect to temperature [e.g., isobaric heat capacity $C_P \equiv \delta H / \delta T)_P$] have maxima at temperatures denoted by $T_{\max}(P)$. Remarkably these maxima are still prominent far above the critical pressure [17-21], and the values of the response functions at $T_{\max}(P)$ (e.g., $C_P^{\max}(P)$) diverge as the critical point is approached. The lines of the maxima for different response functions asymptotically approach one another as the critical point is approached, since all response functions become expressible in terms of the correlation length. This asymptotic line is sometimes called the Widom line, and is often regarded as an extension of the coexistence line into the "one-phase regime." Water's anomalies have been hypothesized to be related to the existence of a line of a first order liquid-liquid phase transition terminating at a liquid-liquid critical point [10, 13, 15, 16], located below the homogeneous nucleation line in the deep supercooled region of the phase diagram - sometimes called the "no-man's land" because it is difficult to make direct measurements on the bulk liquid phase [13]. In supercooled water, the liquid-liquid coexistence line and the Widom line have negative slopes. Thus, if the

system is cooled at constant pressure P_0 , computer simulations suggest that for $P_0 < P_c$ [Figure 4(c), path α] experimentally-measured quantities will change dramatically but continuously in the vicinity of the Widom line (with huge fluctuations as measured by, e.g., C_P) from those resembling the high density liquid HDL to those resembling the low density liquid (LDL). For $P_0 > P_c$ [Figure 4(d), path β], experimentally-measured quantities will change discontinuously if the coexistence line is actually seen. However, the coexistence line can be difficult to detect in a pure system due to metastability, and changes will occur only when the spinodal is approached where the HDL phase is no longer stable. The changes in behavior may include not only static quantities like response functions [17-21] but also dynamic quantities like diffusivity. In the case of water, a significant change in dynamical properties has been suggested to take place in deeply supercooled states [16, 22-25]. Unlike other network forming materials [26], water behaves as a non-Arrhenius liquid in the experimentally accessible window [16, 27, 28]. Based on analogies with other network forming liquids and with the thermodynamic properties of the amorphous forms of water, it has been suggested that, at ambient pressure, liquid water should show a dynamic crossover from non-Arrhenius behavior at high T to Arrhenius behavior at low T [24, 29-33]. Using Adam-Gibbs theory [34], the dynamic crossover in water was related to the $C_P^{\max}(P)$ line [22, 35]. Also, a dynamic crossover has been associated with the liquid-liquid phase transition in simulations of silicon and silica [36, 37]. Recently a dynamic crossover in confined water was studied experimentally [38-40, 42] since nucleation can be avoided in *confined* geometries. In this work, we interpret

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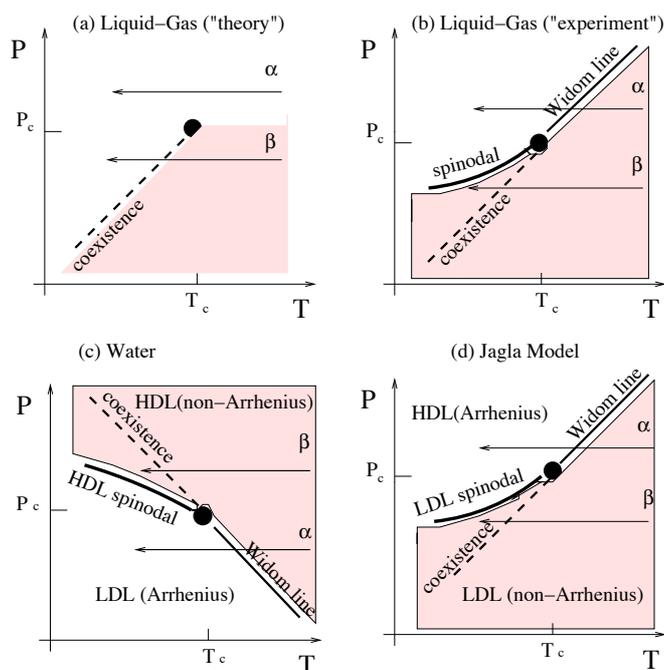


Figure 4: (a) Schematic phase diagram for the critical region associated with a liquid-gas critical point. Shown are the two features displaying mathematical singularities, the critical point (closed circles) and the liquid-gas coexistence (bold dashed curve). (b) Same as (a) with the addition of the gas-liquid spinodal and the Widom line. Along the Widom line, thermodynamic response functions have extrema in their T dependence. The path α denotes a path along which the Widom line is crossed. Path β denotes a path meeting the coexistence line. (c) A hypothetical phase diagram for water of possible relevance to the recent neutron scattering experiments by Chen et al. [39, 40] on confined water. The liquid-liquid coexistence, which has a negative sloped coexistence line, generates a Widom line which extends below the critical point, suggesting that water may exhibit a dynamic crossover (non-Arrhenius-to-Arrhenius) transition for $P < P_c$ (path α), while no dynamic changes will occur above the critical point (path β). (d) A sketch of the P - T phase diagram for the two-scale Jagla potential, as well as for the double-step potential [41], the liquid-liquid phase transition line has a positive slope. Upon cooling at constant pressure above the critical point (path α), the liquid changes from a low density state (characterized by a non-glassy Arrhenius dynamics) to a high density state (characterized by glassy Arrhenius dynamics with much larger activation energy) as the path crosses the Widom line. Upon cooling at constant pressure below the critical point (path β), the liquid remains in the LDL phase as long as path β does not cross the LDL spinodal line. Thus one does not expect any change in the dynamic behavior along the path β , except upon approaching to glass transition where one can expect the non-Arrhenius behavior characterized by the Vogel-recent experiments on water [39, 40, 42] as arising from the presence of the hypothesized liquid-liquid critical point, which gives rise to a Widom line and an associated fragility transition [Figure 4(c), path α].

Results for Bulk Water

Using molecular dynamics (MD) simulations [43], Xu et al. [44] studied three models, each of which has a liquid-liquid critical point. Two of the models (the TIP5P [45] and the ST2 [46]) treat water as a multiple site rigid body, inte-

acting via electrostatic site-site interactions complemented by a Lennard-Jones potential. The third model is the spherical "two-scale" Jagla potential with attractive and repulsive ramps which has been studied in the context of liquid-liquid phase transitions and liquid anomalies [21, 30-32, 47, 48]. For all three models, Xu et al. evaluated the loci of maxima of the relevant response functions, compressibility and specific heat, which coincide close to the critical point and give rise to the Widom line. They found evidence that, for all three potentials, the dynamic crossover occurs just when the Widom line is crossed (Figure 5 page 16).

These findings are consistent with the possibility that the observed dynamic crossover along path α is related to the behavior of C_P , suggesting that enthalpy or entropy fluctuations may have a strong influence on the dynamic properties [21, 22, 37]. Indeed, as the thermodynamic properties change from the high-temperature side of the Widom line to the low-temperature side, $(\delta S/\delta T)_P = C_P/T > 0$ implies that the entropy must decrease. The entropy decrease is most pronounced at the Widom line when $C_P = C_P^{\max}$. Since the configurational part of the entropy, S_{conf} , makes the major contribution to S , we expect that S_{conf} also decreases sharply on crossing the Widom line. According to Adam-Gibbs theory [34], $D \sim \exp(-A/TS_{\text{conf}})$. Hence, we expect that D sharply decreases upon cooling at the Widom line. If S_{conf} does not change appreciably with T , then the Adam-Gibbs equation predicts an Arrhenius behavior of D . For both water and the Jagla model, crossing the Widom line is associated with the change in the behavior of the diffusivity. (i) In the case of water, D changes from non-Arrhenius to Arrhenius behavior, while the structural and thermodynamic properties change from those resembling HDL to those resembling LDL, due to the negative slope of the Widom line. (ii) For the Jagla potential, D changes from Arrhenius to non-Arrhenius while the structural and thermodynamic properties change from those resembling LDL to those resembling HDL, due to the positive slope of the Widom line. Thus these results for bulk water are consistent with the experimental observation in confined water of (i) a fragility transition for $P < P_c$ [39, 40], and (ii) a peak in C_P upon cooling water at atmospheric pressure [49], so this work offers a plausible interpretation of the results of Ref. [40] as supporting the existence of a hypothesized liquid-liquid critical point.

Glass Transition in Biomolecules

Next we explore the hypothesis [50] that the observed glass transition in biomolecules [12, 51-63] is related to the liquid-liquid phase transition using molecular dynamics (MD) simulations. Specifically, Kumar et al. [50] studied the dynamic and thermodynamic behavior of lysozyme and DNA in hydration TIP5P water, by means of the software package GROMACS [64] for (i) an orthorhombic form of hen egg-white lysozyme [65] and (ii) a Dickerson dodecamer DNA [66] at constant pressure $P=1$ atm, several constant temperatures T , and constant number of water molecules N (NPT ensemble). The simulation results for the mean square fluctuations

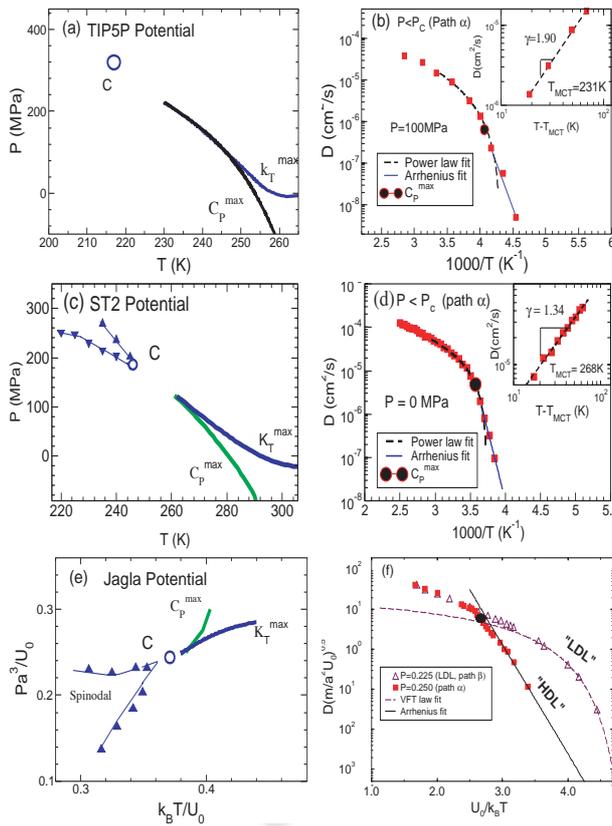


Figure 5: (a) Relevant part of the phase diagram for the TIP5P potential, showing the liquid-liquid critical point C at $P_c=320$ MPa and $T_c=217$ K, the line of maximum of isobaric specific heat C_p^{\max} and the line of maximum of isothermal compressibility K_T^{\max} . (b) D as a function of T for $P=100$ MPa (path α). At high temperatures, D behaves like that of a non-Arrhenius liquid and can be fit by $D \sim (T - T_{MCT})^{-\gamma}$ (also shown in the inset) where $T_{MCT}=220$ K and $\gamma=1.942$, while at low temperatures the dynamic behavior changes to that of a liquid where D is Arrhenius. (c) The same for the ST2 potential. The liquid-liquid critical point C is located at $P_c=246$ MPa and $T_c=146$ K. (d) D as a function of T for $P=100$ MPa (path α). At high temperatures, D behaves like that of a non-Arrhenius liquid and can be fit by $D \sim (T - T_{MCT})^{-\gamma}$ (also shown in the inset) where $T_{MCT}=239$ K and $\gamma=1.57$, while at low temperatures the dynamic behavior changes to that of a liquid where D is Arrhenius. (e) Phase diagram for the Jagla potential in the vicinity of the liquid-liquid phase transition. Shown are the liquid-liquid critical point C located at $P_c=0.24$ and $T_c=0.37$, the line of isobaric specific heat maximum C_p^{\max} , the line of isothermal compressibility K_T^{\max} , and spinodal lines. (f) D as a function of T for $P=0.250$ (squares, path α) and $P=0.225$ (triangles, path β). Along path α , one can see a sharp crossover from the high temperature Arrhenius behavior $D \sim \exp(-1.53/T)$ with lower activation energy to a low temperature Arrhenius behavior $D \sim \exp(-6.3/T)$ with high activation energy, which is a characteristic of the HDL. Along path β , there is no sharp changes near the critical point, because the liquid remains in the LDL phase. However, near the glass transition, LDL exhibits a non-Arrhenius behavior characterized by the VFT fit at very low temperature.

$\langle x^2 \rangle$ of both protein and DNA are shown in **Figure 6(a)**. Kumar et al. calculated the mean square fluctuations $\langle x^2 \rangle$ of the biomolecules from the equilibrated configurations, first for each atom over 1 ns, and then averaged over the total number of atoms in the biomolecule. They find that $\langle x^2 \rangle$ changes its functional form below $T_p \approx 245$ K, for both

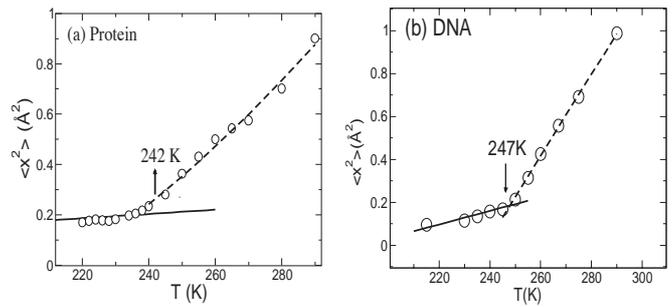


Figure 6: Mean square fluctuation of (a) lysozyme, and (b) DNA showing that there is a transition around $T_p \approx 242 \pm 10$ K for lysozyme and around $T_p \approx 247 \pm 10$ K for DNA. For very low T one would expect a linear increase of $\langle x^2 \rangle$ with T , as a consequence of harmonic approximation for the motion of residues. At high T , the motion becomes non-harmonic and we fit the data by a polynomial. We determine the dynamic crossover temperature T_p from the crossing of the linear fit for low T and the polynomial fit for high T . We determine the error bars by changing the number of data points in the two fitting ranges.

lysozyme [Fig. 6(a)] and DNA [Fig. 6(b)]. Kumar et al. calculated C_p by numerical differentiation of the total enthalpy of the system (protein and water) by fitting the simulation data for enthalpy with a fifth order polynomial, and then taking the derivative with respect to T . Figures 4(a) and 4(b) display maxima of $C_p(T)$ at $T_w \approx 250 \pm 10$ K for both biomolecules.

Further, to describe the quantitative changes in structure of hydration water, Kumar et al. calculated the local tetrahedral order parameter Q [67-70] for hydration water surrounding lysozyme and DNA. Figures 4(c) and 4(d) show that the rate of increase of Q has a maximum at 245 ± 10 K for lysozyme and DNA hydration water respectively; the same temperatures of the crossover in the behavior of mean square fluctuations.

Upon cooling, the diffusivity of hydration water exhibits a dynamic crossover from non-Arrhenius to Arrhenius behavior at the crossover temperature $T_x \approx 245 \pm 10$ K [Figure 7(e) page 17]. The coincidence of T_x with T_p within the error bars indicates that the behavior of the protein is strongly coupled with the behavior of the surrounding solvent, in agreement with recent experiments [51]. Note that T_x is much higher than the glass transition temperature, estimated for TIP5P as $T_g \approx 215$ K [72]. Thus this crossover is not likely to be related to the glass transition in water.

The fact that $T_p \approx T_x \approx T_w$ is evidence of the correlation between the changes in protein fluctuations [Figure 6(a)] and the hydration water thermodynamics [Figure 7(a)]. Thus these results are consistent with the possibility that the protein glass transition is related to the Widom line (and hence to the hypothesized liquid-liquid critical point). Crossing the Widom line corresponds to a continuous but rapid transition of the properties of water from those resembling the properties of a local HDL structure for $T > T_w(P)$ to those resembling the properties of a local LDL structure for $T < T_w(P)$ [44, 40]. A consequence is the expectation that the fluctuations of the protein residues in predominantly LDL-like water (more ordered and more

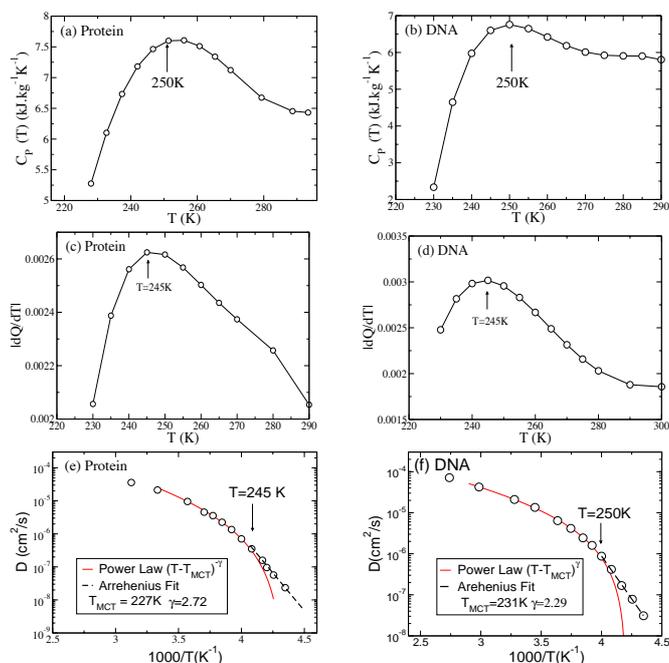


Figure 7: The specific heat of the combined system (a) lysozyme and water, and (b) DNA and water, display maxima at 250 ± 10 K and 250 ± 12 K respectively, which are coincident within the error bars with the temperature T_p where the crossover in the behavior of $\langle x^2 \rangle$ is observed in Figure 4. Derivative with respect to temperature of the local tetrahedral order parameter Q for (c) lysozyme and (d) DNA hydration water. A maximum in $|dQ/dT|$ at Widom line temperature suggests that the rate of change of local tetrahedrality of hydration water has a maximum at the Widom line. Diffusion constant of hydration water surrounding (e) lysozyme, and (f) DNA shows a dynamic transition from a power law behavior to an Arrhenius behavior at $T_x \approx 245 \pm 10$ K for lysozyme and $T_x \approx 250 \pm 10$ K for DNA, around the same temperatures where the behavior of $\langle x^2 \rangle$ has a crossover, and C_p and $|dQ/dT|$ have maxima.

rigid) just below the Widom line should be smaller than the fluctuations in predominantly HDL-like water (less ordered and less rigid) just above the Widom line.

The quantitative agreement of the results for both DNA and lysozyme [Figures 3 and 4] suggests that it is indeed the changes in the properties of hydration water that are responsible for the changes in dynamics of the protein and DNA biomolecules. Our results are in qualitative agreement with recent experiments on hydrated protein and DNA [73] which found the crossover in side-chain fluctuations at $T_p \approx 225$ K.

Outlook

It is possible that other phenomena that appear to occur on crossing the Widom line are in fact not coincidences, but are related to the changes in local structure that occur when the system changes from the “HDL-like” side to the “LDL-like” side. In this work we concentrated on reviewing the evidence for changes in dynamic transport properties, such as diffusion constant and relaxation time. Additional examples include: (1) a breakdown of the Stokes-Einstein relation for $T < T_w(P)$ [74–79], (2) systematic changes in the static structure factor $S(q)$ and the corresponding pair correlation function $g(r)$ revealing that for $T < T_w(P)$ the system more resembles the structure of LDL than HDL, (3)

appearance for $T < T_w(P)$ of a shoulder in the dynamic structure factor $S(q, \omega)$ at a frequency $\omega \approx 60$ $\text{cm}^{-1} \approx 2$ THz [51], (4) rapid increase in hydrogen bonding degree for $T < T_w(P)$ [80, 81], (5) a minimum in the density at low temperature [82], and (6) a scaled equation of state near the critical point [83]. It is important to know how general a given phenomenon is, such as crossing the Widom line which by definition is present whenever there is a critical point. Using data on other liquids which have local tetrahedral symmetry, such as silicon and silica, which appear to also display a liquid-liquid critical point and hence must possess a Widom line emanating from this point into the one-phase region. For example, after this work was completed, we learned of interesting new work on silicon, which also interprets structural changes as arising from crossing the Widom line of silicon [84]. It might be interesting to test the effect of the Widom line on simple model systems that display a liquid-liquid critical point, such as two-scale symmetric potentials of the sort recently studied by Xu and collaborators [21].

Acknowledgments

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The deadline for submitting applications is October 1, 2007

For further details concerning the research project, please contact: davide.ricci@iit.it

✦ Postdoctoral Research position (Centro de investigación Nanociencia y Nanotecnología (CIN2) (CSIC-ICN), Spain): *"Atomic Manipulation and Spectroscopy Group"*

Applications are invited for a postdoctoral position in experimental condensed matter physics and synchrotron radiation spectroscopy. Research topics include the investigation of the magnetic properties of molecular and metallic clusters at surfaces, dilute metal impurities in bulk oxides, and the combination of magnetic resonance techniques with x-ray magnetic dichroism.

Interested candidates should send a CV, a short description of interests/experience, and at least two references with contact information to Pietro Gambardella at pietro.gambardella.icn@uab.es

✦ PhD Position (Centro de investigación Nanociencia y Nanotecnología (CIN2) (CSIC-ICN), Spain): *"Atomic Manipulation and Spectroscopy Group"*

A Ph.D fellowship is available in the Atomic Manipulation and Spectroscopy Group of the Centre d'Investigacions en Nanociència i Nanotecnologia in Barcelona to qualified students who are interested in pursuing experimental physics research on the properties of nanostructured magnetic materials. A successful applicant will work on the synthesis/investigation of molecular and metallic magnetic films and clusters on surfaces using scanning tunneling microscopy and polarized x-ray absorption spectroscopy.

Interested students and researchers are invited to send a CV, a short description of interests/experience, and at least one reference with contact information to Pietro Gambardella at pietro.gambardella.icn@uab.es

✦ PostDoctoral Position (CEA/DRFMC, France): *"Theory & modelling of charge transport in semiconducting nanowires-based devices"*

A postdoctoral position (2 years) is opened at CEA/DRFMC (Grenoble, France) starting from January 2008 to work on the theory and simulation of charge transport in semiconducting nanowires (SC-NWs) based materials and devices (field effect transistors).

The candidate should send her/his CV to Yann-Michel Niquet (yniquet@cea.fr) and Stephan Roche (stephan.roche@cea.fr), with a list of publications, and contact details of two persons for references.

The deadline for submitting applications is October 1, 2007

✦ PostDoctoral Positions (3) (University of Santiago de Compostela, Spain): *"Nanocarriers for the targeted delivery of anticancer drugs; New synthetic vectors for interfering RNA delivery; Needle-free vaccination strategies based*

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1. Nanocarriers for the targeted delivery of anticancer drugs (project in collaboration with industry)
2. New synthetic vectors for interfering RNA delivery (project in collaboration with several research groups in Spain)
3. Needle-free vaccination strategies based on nanotechnologies (project in collaboration with US research groups and financed by the Bill and Melinda Gates Foundation).

Applications should be in the form of curriculum vitae accompanied by a cover letter describing the qualification of the candidate for the position. Applications should be mailed to:

Mrs. Purificación Domínguez (Departamento de Farmacia y Tecnología Farmacéutica) Facultad de Farmacia, Campus Sur s/n 15782 Santiago de Compostela, Spain e-mail: purido@usc.es

PostDoctoral Position (CEMES-CNRS, France): "Graphene-based nanoelectronics"

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The candidate should send her/his CV to Erik Dujardin (dujardin@cemes.fr)

PhD Position (Universitat Autònoma de Barcelona, Spain): "Advanced characterization and innovative applications based on nanomechanical testing"

The aim of the project is two-fold: 1) Characterize the mechanical behavior of various materials at the nanometer scale (metallic glasses, thin films, lithographed elements, nano-composites, etc.) 2) Use nanomechanical testing to locally modify the physical properties of some materials, aiming at novel applications (such as new types of magnetic recording systems).

Contact Person: Jordi Sort / Jordi.Sort@uab.es

PhD Position (Leibniz Institute, Germany) : "RT9: Imaging CNT: micro-MRI and NMR studies"

PhD Position (Leibniz Institute, Germany): "RT8: Imaging ferromagnetic CNT: spatially resolved SQUID studies"

The CARBIO partners apply a multidisciplinary approach to exploit the potential of multi-functional carbon nanotubes (CNT) for biomedical applications, in particular to act as magnetic nano-heaters, drug-carrier systems and sensors which allow a diagnostic and therapeutic usage on a cellular level.

Website: <http://www.carbio.eu/carbio>

Contact Person: Bennie ten Haken (Leibniz Institute, Germany) / B.tenHaken@tnw.utwente.nl

PhD Students (CIC nanoGUNE Consolider, Spain): "Nanoelectronics and Nanophotonics"

The Nanoscience Cooperative Research Center CIC nanoGUNE Consolider invites applications for two positions as PhD Students.

Contact Person: director (CIC nanoGUNE Consolider, Spain) / director@nanogune.eu

PhD Positions (Centro de investigación Nanociencia y Nanotecnología (CIN2) (CSIC-ICN), Spain): "2 PhD positions in Thin Film Nanostructures for a new generation"

Future generations of portable devices (laptop computers, palm PC, mobilePhones, etc...) require higher power consumption, lighter weight, and longer lasting battery refill. Solid Oxide Fuel cell technology devices have two distinct advantages over present Li batteries: higher energy density per weight unit and rapid refuelling.

Applicants (Postgraduate students with a Physics, Chemistry or Materials Engineering degree) are requested to send their CV and the contact details of two referees by email to santiso@icmab.es (Ref.: PhD Nanoionics)

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October 10-12, 2007. Paris (France)

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NanoMaterials

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Nanoelectronics, Nanotechnology Business

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<http://wzar.unizar.es/actos/nanolitho/default.html>

NanoMaterials, NanoLithography, Nanotechnologies

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http://gesprecons.aidico.es:8084/EurekaBuild/faces/workshop_venue.jsp

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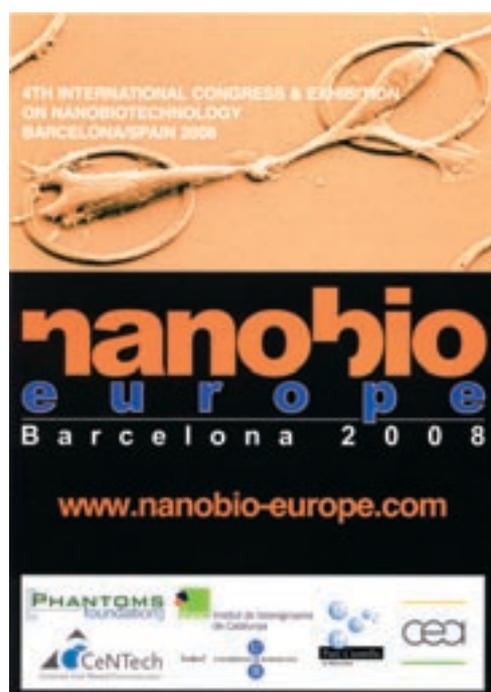
Theory & Modeling, NanoFabrication, Nanotechnologies

■ NanoTRANSFER 2007.

December 03-04, 2007. Novotel Charenton-Paris (France)

http://www.nanosprint.com/events/nano_transfer_2007/

Energy, Nanotechnologies



NANO News - <http://www.phantomsnet.net/Resources/news.php>

⚡ Nanoscale blasting adjusts resistance in magnetic sensors (17-08-2007)

<http://www.physorg.com/news106505783.html>

A new process for adjusting the resistance of semiconductor devices by carpeting a small area of the device with tiny pits may be the key to a new class of magnetic sensors, enabling new, ultra-dense data storage devices.

Nanomagnetism, Nanosensors & Nanodevices

⚡ Actuators get tuned on the nanoscale (16-08-2007)

<http://nanotechweb.org/articles/news/6/8/15/1>

A nanomechanical resonator that converts electrical energy into mechanical strain using a highly efficient, tuneable actuation mechanism based on the piezoelectric effect has been developed by researchers in the US.

NEMS & MEMS, Nanosensors & Nanodevices

⚡ Nanotubes can act as phonon waveguides (14-08-2007)

<http://nanotechweb.org/articles/news/6/8/12/1>

Nanotubes made of carbon or boron nitride can act as phonon waveguides and retain their excellent heat transmission properties even when they are severely distorted, report physicists in the US.

Nanotubes

⚡ From microscopy to nanoscopy (10-08-2007)

<http://www.physorg.com/news105966261.html>

Layer-by-layer light microscopic nanoscale images of cells and without having to prepare thin sections? A team led by S. Hell and M. Bossi is now leading the way with a technique called optical 3D far-field microscopy - with nanoscale resolution

Nanophotonics & Nano-Optoelectronics

⚡ Nanotechnology Australia capability report (07-08-2007)

<http://investaustralia.hyperlink.net.au/media/NANOREPORT07.pdf>

This 96-page report is a snapshot of the current state of nanoscience and nanotechnology in Australia.

Nanoelectronics, Nanomaterials, Scientific Policy

⚡ Nanowires face THz probe (19-07-2007)

<http://nanotechweb.org/articles/news/6/7/15/1>

Single-photon detectors or nanoscale transistors have all been named as promising applications for semiconductor nanowires. In each case, understanding the dynamics of the charge carriers is critical.

Nanomaterials, Nanosensors & Nanodevices

⚡ Discussion Paper on a Policy Framework for Nanotechnology (09-07-2007)

<http://cielap.org/pdf/NanoFramework.pdf>

The policy challenges for nanotechnology are enormous, and currently are dominated by a lack both of scientific information and also of basic policy tools; and structures and resources for public engagement.

Keywords: Scientific Policy

⚡ Molecular machines and switches (06-07-2007)

<http://www3.interscience.wiley.com/cgi-bin/jissue/114186589>

A recent theme issue of *Advanced Functional Materials* 2007, 17, Issue 5 "Molecular machines and switches" is dedicated entirely to Molecular Electronics and mechanics.

Keywords: Molecular Electronics

⚡ Reviews in organic and molecular electronics (06-07-2007)

<http://pubs3.acs.org/acs/journals/toc.page?incoden=chreay&indecade=0&involume=107&inissue=4>

A theme issue of *Chemical Reviews*, 2007, 107, 4 "Organic electronics and optoelectronics" contains 12 review articles from leading scientific groups that provide up-to date information and cover various aspects of chemistry, physics, and application of organic electronic materials.

Keywords: Molecular Electronics

Phase Shift of Electrons Across A Quantum Dot

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Recent advances in mesoscopic physics have led to dramatically renewed interest in the Kondo effect. Coupling a quantum dot to a source and a drain, an experimental device is obtained which simulates an artificial isolated Kondo impurity. Recent experiments at the Weizmann Institute of Science (Israel) using quantum interferometry have given access to a key ingredient of the Kondo effect the phase shift after transmission through an impurity. We present here our interpretation of these results in the framework of the scattering theory.

The experiments which consist in inserting a quantum dot into one arm of an Aharonov Bohm interferometer have enabled the evolution monitoring of the phase shift δ in the electronic wave function when the gate voltage V_G is changed. V_G controls the number of electrons in the dot.

Figure 1 shows the intensity of the source-drain current as a function of magnetic field B and V_G . The shift in the magneto-conductance oscillations as a function of V_G corresponds to the phase shift δ . When these results came out five years ago, it was a great surprise among the scientific community. In the Kondo regime, i.e. when the dot electron population is close to 1, the measurements (**Figure 2**) show a monotonous increase of δ as a function of V_G with a plateau at value π . This value is twice as large as the theoretical prediction $\pi/2$ predicted for metals more than 30 years ago. When V_G still increases well above the plateau value, δ shows a phase lapse of value π .

We have proposed an interpretation of these results on the basis of a one-dimensional scattering theory developed for an Anderson model. The quantum dot acts as a scattering center for the electron. Relying on theorems known in nuclear physics, we have shown that the phase shift an electron undergoes when it crosses the quantum dot is equal to π times the total number of electrons inside the dot.

Moreover, we have shown that the conductance varies as $\sin^2\delta_\sigma$ where δ_σ is the phase shift per spin channel. In the absence of magnetic field, δ_σ is equal to half the total phase δ . This explains the factor of 2 difference observed between the experimental value π at the plateau and value $\pi/2$. Using the exact solution of the Anderson model, we then computed the average number of electrons in the dot as a function of the parameters of the model and henceforth deduced the phase shift as a function of V_G at zero temperature (Fig. 2). Our prediction shows a quantitative agreement with the experimental results, including the phase lapse.

Kondo effect

The Kondo effect is observed when the spin of a magnetic impurity is antiferromagnetically coupled to the spin of the conduction electrons of a metal. It corresponds to an impurity spin flip after each collision with a conduction electron. The spin flip frequency is related to a character-

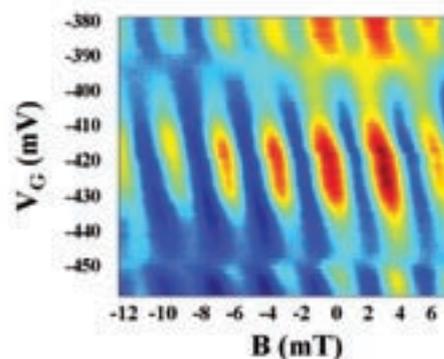


Figure 1: Interference pattern of the source-drain current in the ABI as a function of magnetic field B and gate voltage V_G . The red (blue) color corresponds to a maximum (minimum) intensity, i.e. to constructive (destructive) interferences between the electrons flowing in each of the ABI arms.

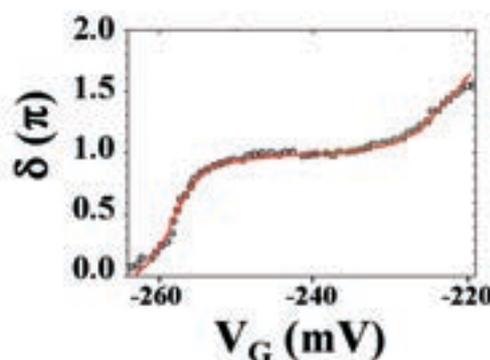


Figure 2: Comparison of theoretical and experimental results for the gate voltage (V_G) dependence of the phase shift in the Kondo regime.

istic temperature scale, the so-called Kondo temperature T_K . Above T_K , the impurity spin is more or less free and below T_K while it forms a spin singlet with the conduction electron. Each collision leads to a phase shift of the wave function. While its direct measurement was out of scope in bulk materials, its value could be evaluated theoretically and the predicted value was found to be equal to $\pi/2$.

Quantum interferometry

An Aharonov Bohm quantum interferometer (ABI) is a device composed of two conducting arms which merge at two points called source and drain (**Figure 3 page 26**). The obtained ring is submitted to a magnetic field B . The interferometer is thus the quantum equivalent of Young slits in optics. If the ring is small enough, the electrons flowing through each of the arms interfere coherently, which leads to periodical oscillations of the source-drain current as a function of B . This is the Aharonov Bohm effect. Quantum interferometry consists in inserting an object, typically a quantum dot, in one of the arms of the ring, the other acting as reference arm. The oscillations which remain periodical are shifted by the presence of the dot. The measurement of the shift in the magneto-conductance as a function of V_G determines the phase shift associated with the quantum dot.

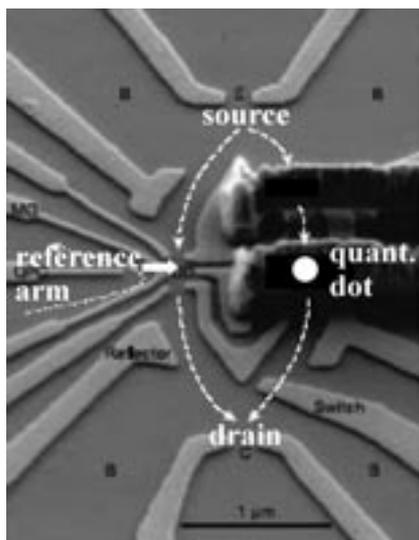


Figure 3: SEM picture of an Aharonov Bohm quantum interferometer. The two arms are depicted in white.

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M. Lavagna, P. Vitushinsky, and A. Jerez, *Phys. Rev. Lett.* **96**, 189706 (2006)

Improved Prediction of Chemical Reactions

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Walter Kohn first demonstrated that all the properties of an electronic system could be determined through the electronic density, thereby providing the bases for the density functional theory (DFT). DFT should make possible the description of chemical reactivity by substituting the concept of electronic density for that molecular orbital, provided that new theoretical tools are developed. Our group has recently proposed an improvement of the DFT prediction of the selectivity of chemical reactions by using a parameter derived from the electronic density.

Don't lose the phase

Intuitively, it is convenient to consider molecules as assemblies of atoms linked together by chemical bonds, electrons being described by mathematical functions named orbitals. Unfortunately, atoms in molecules, chemical bonds and orbitals are not observable. They are products of the mind, non empirical objects that can be considered as noumena. In contrast, in the functional theory of electronic density, molecules are described as electronic densities stabilized and shaped by the electrostatic potential created by the nuclei (**Figure 1**). Chemical reactions are described through topological modifications of the electronic and nuclear density. Chemical reactivity is thus studied with observable and quantifiable parameters. Substitution of the wave function by the electronic density (electronic density is the square of the wave function) ne-

vertheless leads to a loss of information on the phase of the electronic wave. Indeed, molecular orbitals exhibit lobes of opposite signs. During a chemical reaction, interactions between molecular orbitals in phase opposition are destabilizing. Unfortunately, they are not taken into account by classical DFT-based descriptors. The dual descriptor (DD) we propose, defined as the second derivative of the electronic density with respect to the number of electrons, enables partial recovery of the missing information.



Figure 1: Classical and DFT-based representations of the benzene molecule.

The best line of attack

This new function describes the differential response of the electronic density of loss or gain of electrons. The topological regions where DD exhibits a positive value tend to gain rather than to lose an electron. Conversely, a negative DD value means that a site will quite easily lose an electron. With this in mind, a convenient way to determine the best approach between two molecules during a reaction is to optimize the overlap between sites associated with opposite DD values. For example, in the reaction shown in **Figure 2**, optimization of the interactions between the DD of each reactant led to the best addition angle. No preliminary hypothesis on the relative orientation of the molecules was required. During this optimization, destabilizing interactions between regions with DD of the same sign led to opening of the angle defined by the three atoms involved in the reaction.

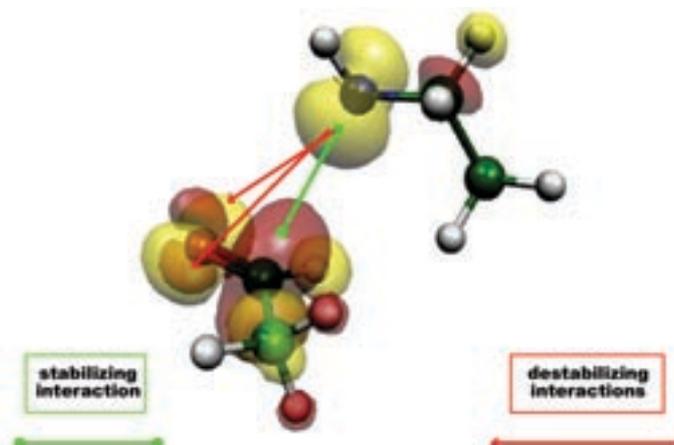


Figure 2: Interaction between two molecules during an addition reaction. The yellow and red lobes associated with the atoms respectively represent the negative and positive values of the dual descriptor.

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A matter of gentleness

The DD describes the response of the hardness of a molecule (see inset) when it undergoes a variation of electrical potential, for instance when another molecule comes closer. During a chemical reaction, application of the Pearson principle to the two interacting fragments shows that they will adopt a relative orientation in order to be as hard as possible. This condition is better fulfilled when regions of opposite DD overlap. Use of this criterion for numerous chemical organic reactions (cycloadditions, reductions, substitutions, etc.) allowed us to successfully rationalize their selectivity. Evaluation of this maximal hardness criterion only requires limited computer power since most of the calculations were performed on personal computers. The dual descriptor is thus a powerful and cheap tool for qualitative prediction of the reactivity and selectivity of molecules imagined by chemists before they actually synthesize them.

Hardness and softness

The Fermi level and the energy gap defined in solid semiconductors have equivalents at molecular level. These are respectively the chemical potential (μ) and the hardness (η) (see **Figure 3**). These concepts have the same physical meanings. In particular hardness, which can be roughly calculated by the energy difference between the HOMO (Highest Occupied Molecular Orbital) and the LUMO (Lowest Unoccupied Molecular Orbital), describes the resistance of a molecule to charge transfer similar to electrical resistance.

Chemical reactions always involve transfer of electrons between the reactants. Molecules of low hardness, referred to as soft molecules, are sensitive to charge transfer in contrast to hard molecules. The chemical stability is thus associated to hard molecules whereas soft ones are more reactive. Based on these physical considerations, the Pearson principle shows that molecules rearrange in order to be as hard as possible and thereby the least reactive.

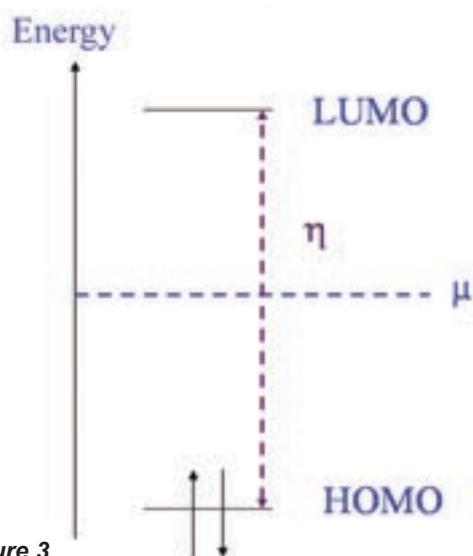


Figure 3

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A Hard Disk Drive of Terabyte Capacity

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At present magnetic recording presents the most economical means of storing large amounts of data with fast access time for a period of at least 10 years. This technology is based on a magnetic medium optimized for maximum recording bit density, allowing for fast read/write access times and guaranteeing retention of the stored information for at least 10 years. The polycrystalline nature of the magnetic medium sets a limit for the maximum storage density of the written information. Indeed, at very high densities (>300 Gigabits per square inch), under the effect of thermal agitation, the small dimension of the grains (around 10nm) is not sufficient to stabilize the magnetization direction over a long time period. The consequence is a loss of the stored information and progressive erasure of the data. To overcome this problem, known as the superparamagnetic limit, each magnetic bit has to be physically separated in a two-dimensional patterned magnetic medium.

SPINTEC is currently working on development and characterization of patterned media. The media are fabricated in two steps. The first step consists in fabricating a grid of silicon (Si) pillars on a Si wafer using a nanoimprint technique. The second step is to deposit a magnetic layer on these nano-pillar structures. The read and write testing is carried out using an experimental setup developed in the laboratory. This setup enables the performance of the discrete media to be determined under real working conditions (**Figure 1**). It uses a real magnetoresistive head and is also an effective magnetic microscopy tool which complements conventional near-field microscopy techniques.

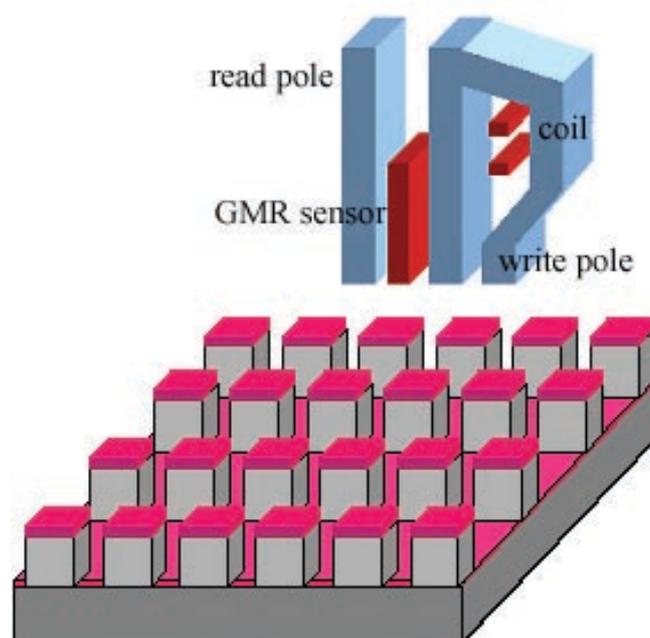


Figure 1: Layout of the magnetic read/write head and the discrete medium

Patterned media: a new way towards ultra high densities

In patterned media systems, the value of 0 and 1 bits is stored directly in the magnetization direction of each magnetic dot. The medium is usually patterned by standard lithography techniques on a Si substrate or directly in the magnetic layer. The preferred choice at SPINTEC was to decouple nanofabrication from magnetic material deposition. This allows all the existing expertise in deep Si etching to be used. The pattern is first transferred to the Si wafer by nano-imprinting. Co/Pt multilayers with magnetization perpendicular to the plane are then deposited on the patterned substrate. The medium is currently patterned to square pillars each with a 50nm side. Pillars of 25nm side length have already been fabricated, which corresponds to a storage density of 1 terabyte per square inch.

Bit writing and reading

In order to write the information bit, the magnetization direction of an individual bit has to be reversed in a time that is close to 1ns. The only way to perform such an experiment is to use write heads, which have micron-size electromagnets capable of generating very large magnetic fields on a small and localized area. The characteristic dimension of the generated magnetic field is 100nm. The field can be turned on and off at frequencies of 1 GHz with amplitudes in the Tesla range. A dedicated new test platform was developed using read/write heads in collaboration with two industrial companies: Seagate and Headway. This setup enables precise magnetic configurations to be written with the electromagnet. The magnetic configuration is then imaged using the integrated magnetoresistive read head shown in Fig. 1. The head sweeps the sample surface actuated by an XY piezoelectric actuator. This test platform is capable of sending pulse currents to the electromagnet, setting the magnetization direction of the pillars in predetermined configurations as shown in **Figure 2**. In this image, two types of magnetic dots (black and white) correspond to the two possible magnetization directions of the dots.

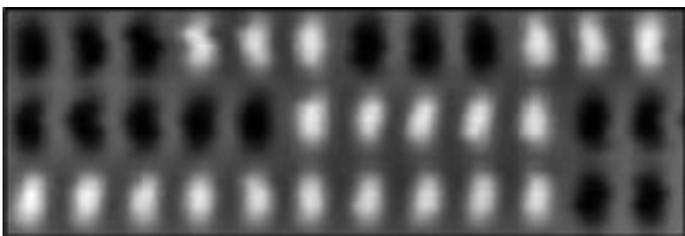


Figure 2: Magnetic imaging using the read head signal of a partially written area (white dots). The length of each information bit is 200 nm.

A new magnetic microscopy

This setup using read/write heads is complementary to the classical Kerr and near-field magnetization microscopy techniques. The main advantage is the possibility to generate very localized magnetic fields to set the direction of the magnetization before imaging the pattern. This advantage is fundamental in studies concerning discrete media, where each dot must be addressed individually. It can also

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be used in other types of studies, looking for example at the magnetization dynamics of individual dots in the picosecond range. This gives valuable insight into the magnetization reversal process influenced by precession, damping and dot-to-dot interactions. Usually these processes can only be measured in large macroscopic arrays.

Further reading:

Asbahi M., Moritz J., Nozières J. P., Dieny B., et al., **Proceedings of the IEEE International Magnetism Conference 2006**

GeMn: A Room Temperature Ferromagnetic Semiconductor

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Spintronics, which consists in manipulating both spins and charge carriers in microelectronics devices, is experiencing an unprecedented boom. Indeed, it enables memory and logic functions to be combined. One difficulty is to inject a spin-polarized carrier population into a semiconductor. Direct injection of polarized spins from a metal to a semiconductor is not possible: a tunnel barrier has to be inserted. Ferromagnetic metal / tunnel barrier / semiconductor diodes remain rather difficult to achieve.

Recently we discovered a new ferromagnetic alloy with a Curie temperature exceeding 400 K. It consists of a thin film of GeMn (with 6% manganese) grown by molecular beam epitaxy on (001) oriented germanium.

Our GeMn is made of self-assembled nanopillars with 3 nm diameter and 80 nm height (the thickness of the deposited layer) that are Mn-rich and spaced an average of 10 nm apart (see **Figure 1**). Magneto-transport measurements in the plane of the sample on a nanopillar assembly enabled a pronounced extraordinary Hall effect (linked to the magnetization of the columns) to be demonstrated. This observation is proof that the charge carriers (here the holes) are spin-polarized.

Further reading:

M. Jamet, A. Barski, T. Devillers, et al., *Nature Materials* **5** (2006) 653

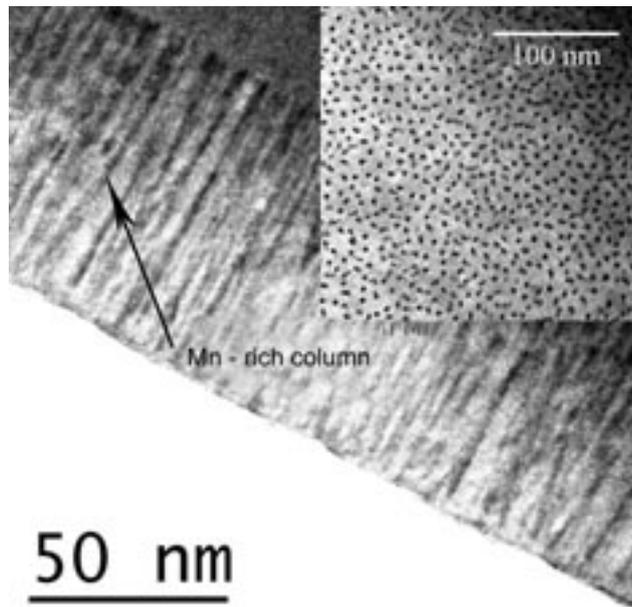


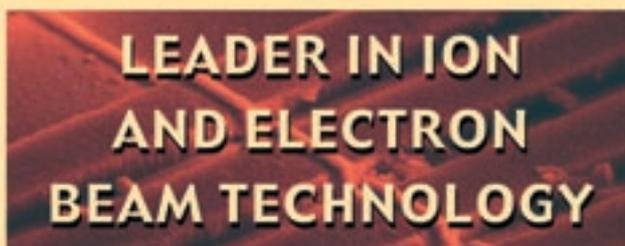
Figure 1: Plane view (inset) and cross-section in transmission electron microscopy of a GeMn layer. In the middle of the matrix, the self-assembled manganese-rich columns can be observed.

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Moving Walls...

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A ferromagnetic material (iron...) is microscopically magnetized, but does not always have a macroscopic magnetization. This paradox was solved by Weiss: in a solid divided into magnetic domains, the magnetization direction varies between domains so that the resulting magnetization can vanish.

When a magnetic field is applied, the magnetic domains

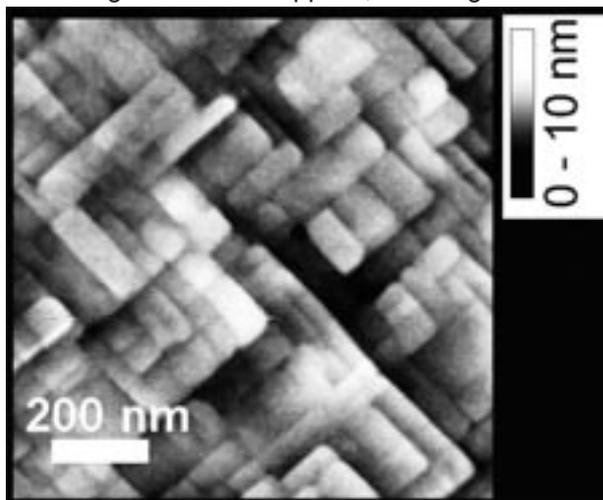


Figure 1: Surface of the FePt film (top): the microtwins can be seen (AFM image). These defects are organized in a quasi-periodic lattice that delimits the terraces. The color code indicates the relative height of the terraces (see vertical scale). TEM section of a microtwin (bottom).

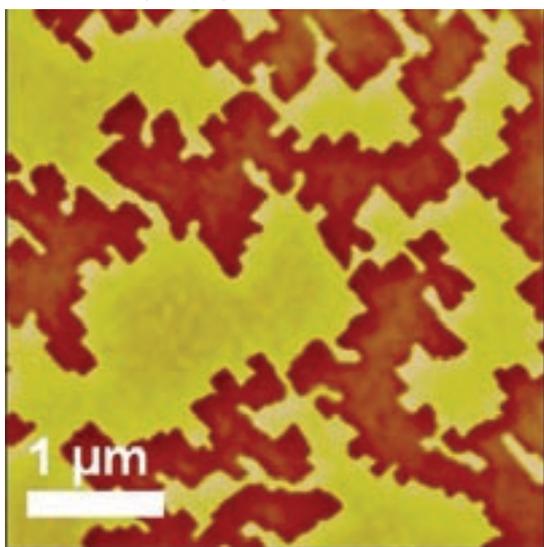


Figure 2: MFM image of the sample: two magnetic domains are observed (brown and yellow). The domain walls are trapped on microtwins.

that follow the external field grow, at the expense of the others. Magnetization reversal is a nucleation-growth process. In most ferromagnetic materials, this happens through propagation of the domain boundaries, called magnetic domain walls. These can be trapped by defects, hence the magnetic hysteresis effects. We have observed for the first time detrapping of an isolated domain wall on a defect by measuring the electronic transport in a nanostructure.

Domain wall propagation

When the external field remains close to the magnetic inversion field, the inversion dynamics are controlled by trapping of the domain walls by crystal defects. A wall thus propagates discontinuously, jumping from defect to defect. In a simple one-dimensional model, the wall can be seen as a particle jumping from one potential well to another under the influence of the field and the thermal activation. This trapping is the cause of the hysteresis: in a permanent magnet the domain walls are fixed; the solid cannot return to the demagnetized equilibrium state. Although the study of domain wall jumps goes back a long time (Barkhausen, 1919), the study of domain wall pinning on defects only started in the 80's with the development of thin films that facilitate observation of domain walls, and then of lithographed structures that enable a single domain wall to be isolated.

A random propagation time

In collaboration with Orsay University, we made nanostructures by lithographing alloy thin films: FePt(40nm)/Pt/MgO. During growth, a defect array called "microtwins" appears, these microtwins being trapping sites for the domain walls (**Figures 1 and 2**).

The nanostructure consists of two magnetic Hall crosses linked by a central wire (**Figure 3**). By electronic transport measurements, we measure the time needed by a domain wall to propagate from one cross to the other under the influence of the magnetic field. The result is surprising: for a given structure, in exactly the same conditions (fixed field and temperature), the propagation time of a domain wall is not identical from one measurement to the other. However, in experiments performed on other systems by other teams, the propagation time depends only on the temperature and on the field, and two consecutive mea-

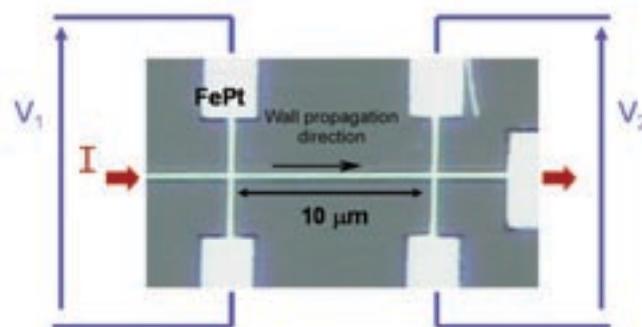
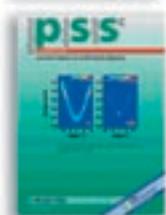
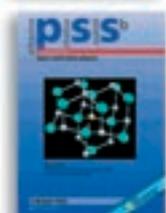


Figure 3: Overview of the nanostructure (optical microscopy). A current is injected in the central wire. By measuring the Hall voltage V_1 and V_2 , propagation of the domain wall through the first and the second cross is detected.

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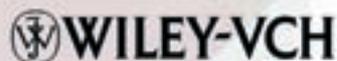
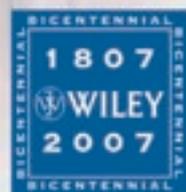
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surements thus give the same results. In our case, the propagation time is random and varies from less than one second to more than one hour for identical conditions. How can we explain this phenomenon?

A domain wall trapped on a single defect

Let us assume that a domain wall is pinned on a defect, i.e. is trapped inside a potential well and tries to escape through thermal activation. The escape probability per unit time being constant, the trapping time is uncertain and follows an exponential law. In most systems, there are lots of defects along the propagation path. The unknown escape times due to the various defects compensate so that the propagation time ends up always being the same: the uncertainty of the microscopic events is erased at macroscopic level.

In our system, the trapping strength of the microtwins varies a lot. It's like hurdling with hurdles that have very different heights. If one hurdle is much higher than the others, it takes much more time to climb this single hurdle than to jump over all the others. Similarly, the most trapping microtwin controls the inversion of the entire structure, the other defects being cleared much faster. Hence the uncertainty in the propagation time that we observe is the signature of pinning of the domain wall on this single microtwin defect.

This propagation time should therefore follow an exponential law. This happens for certain temperature and field conditions, but for other conditions some discrepancies are observed. We propose a model that explains these deviations from the exponential law and extracts the characteristics of the potential well associated with the single defect. This study is one milestone in the understanding and mastering of magnetization reversal at nanometer scale.

Further reading:

J.-P. Attané, et al., *Phys. Rev. Lett.* **96** (2006) 147204

Chemistry for Nanoelectronics at CEA: "ChimTronique" Program

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Abstract

The "ChimTronique" program has been launched in 2006 to boost chemistry for microelectronics at the French Atomic Energy Commission (CEA). The aim of this program is to develop strong coupling between research efforts in nanosciences and in microelectronics, and to foster collaborations in molecular and nano-electronics between the Physical Sciences Division (DSM) in Grenoble and Saclay and the Technological Research Division (DRT) in Grenoble.

Keywords: nanoelectronics, molecular electronics, nanotubes, nanowires, polymers, electronic devices.

Introduction

"ChimTronique", a program on Chemistry & Nanoelectronics recently launched by CEA (<http://www.cea.fr>), has been set up to stimulate within a single institution the coupling between upstream and downstream approaches to microelectronics. It involves an increasing number of scientists (about 160 today) working in basic and applied nanosciences (chemistry, physics and electronics) in Saclay (Paris) and Grenoble. The main research topics include (1) the chemistry and physics of carbon nanotubes and their potential applications (fuel cells, displays, molecular electronics); (2) the physics of nanowires (IV-IV and III-V); (3) molecular chemistry (functional molecules for molecular memories, polymers for nanoFETs) and self-assembly; (4) simulation of electron transport in 1D devices (carbon nanotubes, organic and silicon nanowires); (5) novel circuit architectures; and (6) hybridization of molecular devices to CMOS integrated circuits. Naturally, this program is strongly correlated to MINATEC, the largest center for micro & nanotechnologies in Europe, opened in June 2006 (<http://www.minatec.com>), to the activities of Leti in nanoelectronics, MEMS, NEMS, biochips, etc. (<http://www.leti.fr>), and to basic research in the fields of chemistry and nanoelectronics, as the Marie-Curie PhD fellowships (<http://www-drfmc.cea.fr/chemtronics>) funded by the EU. This program is evolutionary in nature, and it takes into account the various generations of devices and structures, which are foreseen within the frame of "More Moore", "Beyond CMOS" or "More than Moore" approaches. Before commercialization of such products, basic and R&D challenges are also raised in collaboration with industrial partners within bi or multipartner programs.

Global Architecture

A. Context

"ChimTronique" has been first implemented in the CEA laboratories of Saclay and Grenoble, which are established among strong scientific and academic (Orsay) communities. Such a situation guarantees easy access to large instrument facilities such as the European Synchrotron Radiation Facility, Soleil or the ILL neutron source, and to the technological infrastructures of MINATEC. It also facilitates collaboration with highly skilled CNRS and academic laboratories and we are now setting up various partnerships on the national or international scenes.

B. Architecture

The global architecture of the program is presented as a matrix in **Figure 1 page 34**. Upstream/downstream research is integrated vertically on three main types of nanocomponents, and fields of competence are described horizontally. Anticipated applications in devices are shown in yellow, and significant fields to be explored in the future are highlighted at the bottom.

Vertical integration is organized along the following issues:

- Topic 1: Carbon nanotubes for applications in electronics.

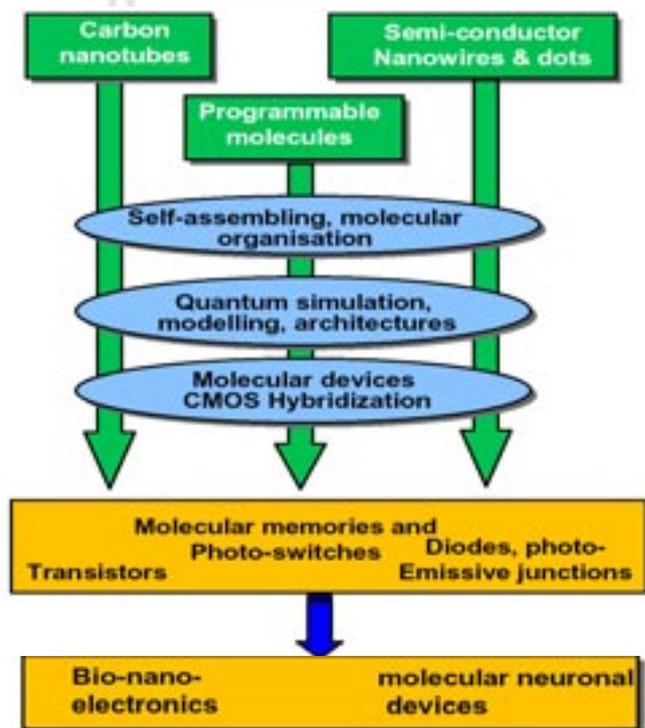


Figure 1: Architecture of "ChimTronique".

- Topic 2 : Bistable, redox, photosensitive conjugated molecules and polymers for memories, switches, and general electronics and photonics active devices.
 - Topic 3: Optics and electronics with semiconductor nanowires and nanocrystals.
- Horizontal organization is described along the following themes and skills:
- Theme 1: Research on self-assembly of nano-objects is expected to lead to the creation of architectures at low cost, with new functions useful in electronics and other fields. In this platform the use of miniaturized objects and their functionalization will lead to more complex systems
 - Theme 2: Simulation of quantum devices (organic, inorganic and molecular) and modelling of new architectures for the accompanying technology.
 - Theme 3: Hybridization of CMOS electronics with molecular objects and devices, and later to emerging functions.

On Figure 1 the arrows go from basic to applied research. Basic fields are shown on top, while at the bottom are the various applications (transistors, molecular memories, sensors), and those which are presently under discussion in the scientific advisory board of the program.

Concerning topics 1-3, long and short-term research programs already exist and they extend from synthesis to development of functional devices, as shown on **Figure 2**. Topic 2 is related to the supramolecular chemistry approach, it includes research on functional molecules ("obedient" porphyrins, 4f metal complexes, chromophores) and nano-structured polymers and on their applications to (opto)-electronics. The "ChimTronique" program mainly deals with conjugated polymers, or oligomers including metal complexes, in which nanostructure is obtained by controlling π -stacking and hydrogen bonds, and/or in the form of nanocomposites including nano-objects such as carbon nanotubes or semicon-

ducting particles (quantum dots). This field promises to be an exciting field for basic and applied research, in particular when it will merge both conventional nanoelectronics (Moore's law) and organic electronics.

The synthesis of functional molecules and nano-structured polymers (at the chain scale), their controlled deposition or grafting at fairly well defined positions on defined substrates (silicon, glass, plastic) using self-assembly and self-repair, fabrication of nanomolecular devices (molecular memories, transistors, photo-switches, etc) have been demonstrated only in few examples. Therefore the three platforms described above entail the understanding of physical properties, the ability to characterize and manipulate materials at the nanometer scale (using neutrons and synchrotron radiation, nearfield, optical, electron microscopies, nanotooling), the prediction of basic or novel properties (theory, quantum simulation, design of architectures) and a strong effort towards conditions of applications (putting reliability and system-ability in fabrication of all these device elements for applications in electronics, optoelectronics, nanotechnology, and in other fields)

Acknowledgment

All colleagues at CEA and CNRS are acknowledged for their enthusiastic participation in the project.

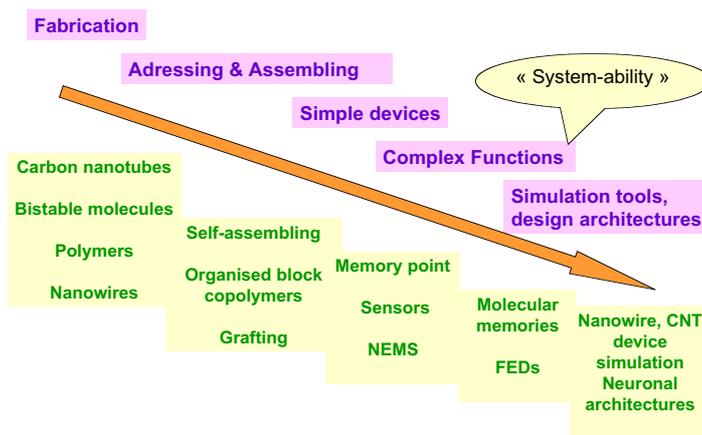


Figure 2: Description of general tasks for each topic with examples.



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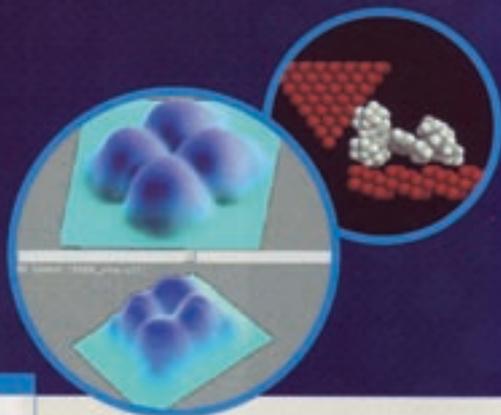


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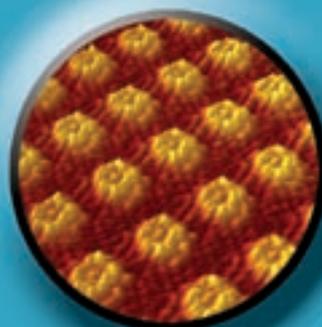
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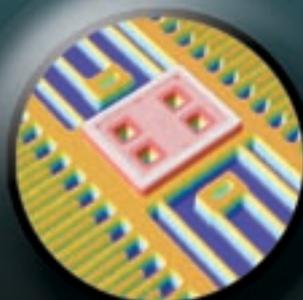
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