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CONSEIL DE PHYSIQUE SOLVAY
BRUXELLES 1911

Centennial of the 1st Solvay Congress
Nanoshells
Nanowires

CONTENT

BΦ - Belgian Physical Society Magazine
Issue 3-2011

Nanoshells (p. 6 & p. 17)

Pt Nanowires on a Ge(001) surface (p. 11)

EDITORIAL

Dear member,

This autumn, the physics community in Belgium celebrates the 100th anniversary of the Solvay conferences. Physics has come a long way since that 1911 gathering, a time when (as we note from the cover photo) you needed a suit and a moustache to be a distinguished physicist (the latter requirement doesn't apply to madame Curie). One hundred years later, once again many Noble laureates and other leading physicists will meet at the Hôtel Métropole to discuss the future of quantum mechanics. Several public activities are planned in the wake of the Solvay centenary, such as physics debates and theatre plays, and you can find more information about those in this BPhy issue.

One of the many ways in which quantum mechanics becomes ever more prominent in everyday applications, is the rise of nanotechnology. In this issue we also have a rich harvest of nanophysics-related articles from our prize winning young physicists. There is an exposé on the density functional Monte Carlo technique to find the work function of nanoparticles, followed by reports on platinum nanowires and gold nanoshells. For these applications, the non-relativistic quantum physics on which the first Solvay conference participants were brooding is satisfactory. But for relativistic particles, quantum field theory is essential, and this is the framework of the featured article on high-spin fermion fields.

Not only quantum mechanics itself has naturally changed since the first Solvay meeting, but also the way in which we perform research on it. Whereas many of the physicists on the cover photo were essentially working in small (even one-person) research groups (with the notable exception of Kamerlingh Onnes), now there is a drive to create every bigger research groups. For big science experiments, such as the elementary particle physics experiments Atlas or CMS, this is natural, necessary and beneficial.

But sometimes university administrations –maybe driven by a need to simplify research evaluation– advocate the formation of bigger entities where it actually might be detrimental. This is known in economics as the "law of diminishing marginal utility" or "Gossen's law": an added unit of resource tends to be less useful as the collection to which it is added gets bigger. It's rarely a good idea to apply such ideas to researchers, but anyway there was a recent study [E.Spruyt and T.Engels, *"Dient massaliteit excellentie in onderzoek?"*, TheMa **15**, 39 (2008)] that did just this, and its results can be summarized in this table:

Group size:	Average #publications per researcher	Average # citations per researcher	average # Ph.D.'s per researchers
Small (1-4 researchers)	13	75	0.55
Medium (5-11)	8.3	55	0.37
Large (12 and more)	5.7	27	0.32

This study is based on a set of 108 research groups in exact sciences and biomedical sciences. It would of course be nonsense to profess that small groups should be the thing to strive for, since the optical collaboration size differs from case to case and from subfield to subfield. But what one can infer from these results is that it is equally nonsense to assume that forming larger research groups always leads to higher average output. Collaborations –and their size– optimally evolve naturally, in a way driven by the researchers themselves rather than by

EDITORIAL

science administrators. Whereas researchers realize that output numbers are highly debatable anyway, these numbers matter to science administrators that at the same time contradictorily seem to prefer mergers of smaller research units.

With this coffee-break discussion topic, I leave you to enjoy your current issue of BPhy and wish you a very good academic year 2011-2012.

Jacques Tempere , BPS President

Centennial celebration of the 1ˢᵗ Solvay Congress

One hundred years ago, the celebrated first *Conseil de Physique Solvay* took place in Brussels, with the participation of the leading physicists of the time. It marked a profound rupture between the old *classical physics* and the new *quantum physics* that describes the strange behaviour of Nature at the microscopic level. The Conference was one of the most important events in the advent of the quantum revolution. No other physics conference has acquired the same legendary status

To celebrate this unique conference, the International Solvay Institutes will organize a series of exceptional events that will make Brussels the world's capital of physics for ten days in October 2011. Some of these events are open to all. Chronologically one has (please consult the website www.solvayinstitutes.be for more information):

Thursday October 13: Opening of the exhibition *Brainstorming in Brussels - One Hundred Years of Solvay Conferences* in the building of the Belgian Academy. The exhibition will stay in Brussels until the end of 2011 and will then travel within Belgium. The exhibition itself is open to all but the opening can be attended by invitation only.

Friday October 14: Workshop *The Early Solvay Councils and the Advent of the Quantum Era*. Open to all but registration mandatory.

NEWS

Monday October 17: (evening): Reading of the theatre play *Copenhagen* with Nobel Laureates Alan Heeger and David Gross in the respective roles of Nobel Laureate Niels Bohr and Werner Heisenberg, and Actress Fiona Shaw in the role of Margrethe Bohr. Playwright: Michael Frayn. Play director: Nancy Kawalek (University of California at Santa Barbara) - free and open to all but registration mandatory.

Sunday 23 October: Solvay Public Event *The Future of Physics* with two popular lectures by Nobel Laureates William Phillips and Franck Wilczek followed by a panel discussion chaired by Nobel Laureate David Gross - free and open to all but registration is mandatory.

All details can be found on our website www.solvayinstitutes.be.

NEWS FROM THE DEPARTMENTS

UA

Dr. Jo Verbeeck, postdoc at the EMAT laboratory, has received the Ernst Ruska Prize 2011 from the "Deutsche Gesellschaft für Elektronenmikroskopie". This is considered the most prestigious prize for electron microscopy worldwide, and is awarded once every two years. The prize goes to a young researcher who during the preceding five years has made a considerable impact on electron microscopy research. Dr Verbeeck receives this distinction for developing the Electron Energy Loss Spectroscopy (EELS) model.
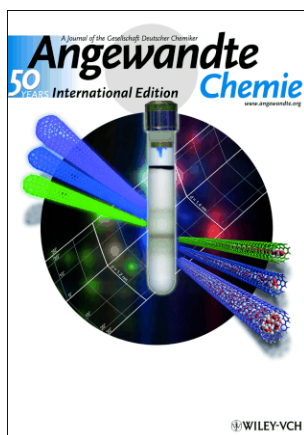
Wim Wenseleers and Sofie Cambre from the laboratory of experimental condensed matter physics have demonstrated that empty and water filled carbon nanotubes can be separated by ultracentrifuge methods. In this way, they obtained isolated empty nanotubes that exhibit improved optical, electronic and thermal properties. Moreover, their method allows separation of distinct types of nanotubes (with distinct diameters, chirality, ...), and that is of importance since each type has its own characteristic optical and electronic properties. Their work has appeared in the prominent journal *Angewandte Chemie*.

FEATURED ARTICLE

Density-Functional Monte-Carlo for calculating properties of nanosystems

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The pieces…

The method we propose, Density-Functional Monte-Carlo, consists of two pieces: "Density Functional Theory" and "Monte-Carlo simulation".

The first piece of the proposed method is "Density Functional Theory". This theory is based on two theorems formulated by Hohenberg and Kohn [1] which can be used to find the ground state density of a system.

The first theorem states that to each possible particle density distribution in a system there corresponds a certain value of the energy of the system. One says that the energy of a system is a unique functional ('function of a function') of the particle density. You can compare this with the more well-known concept of 'function': if you have a function f of a variable x, then with every x-value there corresponds only one function value f(x).
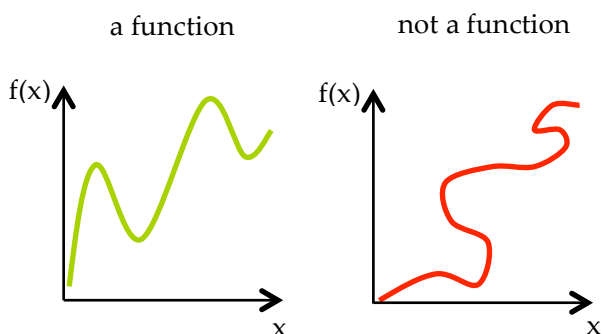
In the second theorem it is stated that, if the number of particles in the system is conserved, the energy functional reaches its minimum in the correct ground state density. So of all possible density distributions one can imagine in the system, only one results in the lowest energy and this distribution is the ground state density distribution.

The second piece of the method is "Monte-Carlo simulation". A simplified and short description for this kind of numerical simulation could be something like 'calculating something by using random numbers many times'. And that is what we do in the method that will be explained in the next section.

a function   not a function
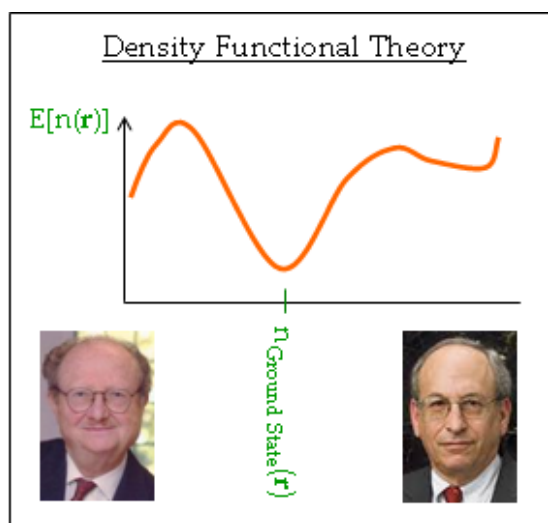
Graphical interpretation of Hogenberg and Kohn and the Hohenberg-Kohn theorems which form the basis of Density Functional Theory.

… combined …

Use is made of the Monte-Carlo principle to construct and change the particle density in a nanosystem in order to find the ground state density distribution. In what follows, the general procedure of the proposed Monte-Carlo simulation is explained and linked to the Hohenberg-Kohn theorems. In the next section an example is given with some possible concrete details.

One starts with constructing a _mesh_ in the nanosystem.
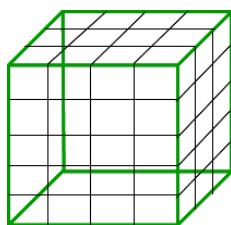
Random numbers are used to mimic the electron density on the mesh: the number of generated points that is put on a mesh point reflects the local density. One can generate as many points as there are particles in the system but one can also generate less points to speed up the calculations. In the latter case there will be a one-to-one correspondence between the number of points and the number of particles: to every point corresponds a certain number of particles. In this way the particle density can be calculated from the number of generated points in the mesh points.
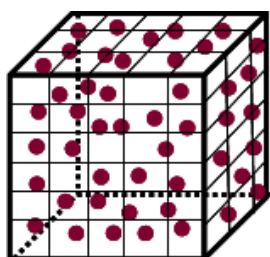
Random numbers are used in two different ways to construct a certain density distribution.

In the beginning of the calculations random numbers are used to generate a _starting density_ according to a given distribution.

During the calculations random numbers are used to change the number of generated points per mesh point, i.e. to _change the particle density_. A generated point is allowed to move to another mesh point with a certain probability. It looks as if the generated points walk around during the calculations. Therefore the generated points are called "_walkers_".

After every walker move the _energy functional_ corresponding to the actual density is calculated. This energy functional typically consists of a kinetic term, a Hartree (direct Coulomb) term and a term describing the exchange-correlation energy. There exist several approximations for the kinetic energy and exchange-correlation term which can be found in literature.

$$E[n(\mathbf{r})] = T[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{XC}[n(\mathbf{r})]$$

After every walker move the energy functional is compared with the energy functional of the previous density in order to find the minimum value of the energy and so also the ground state density. This comparison leads to a _choice_ of the distribution with which the next iteration is started.

If the actual energy is smaller than the previous one, one discards the previous distribution (remember one wants to find the lowest energy value) and takes the actual distribution to the next iteration for changing the number of walkers of another mesh point.

If the actual energy is higher than the previous one, one accepts the actual distribution with a certain probability. At first sight it can seem illogical to sometimes accept a distribution

which leads to a higher value of the energy in looking for the lowest energy value. The reason for doing the calculations like this is that we want to be sure that we find the *global* minimum of the problem and not any *local* minimum.


During the calculations the lowest energy value that has been found so far is stored, together with the corresponding density distribution. The energy value can be considered to be the ground state energy if moving walkers 'never' results in a lower value of the energy.

Off course one cannot let the calculations run forever to be really sure that no other density can be found which corresponds to an even lower minimum. One has to consider a 'reasonable number' of iterations and perform the entire calculation a 'reasonable number' of times to have some certainty about the results.

… for application to nanosystems…

To check whether the proposed method can indeed be used to calculate properties of nanosystems, we have used it to calculate the radial dependence of the electron density and potential energy profile in a nanoshell. A nanoshell is a spherical symmetric nanosize particle with a dielectric core and a metallic shell which has applications in biomedicine, opto–electronics, … [2] We have considered a particle with a SiO_2 core and a golden shell that has a core radius of 60 nm and a shell

radius of 75 nm and is placed in vacuum; this kind of particle is commercially available.

Considered nanoshell
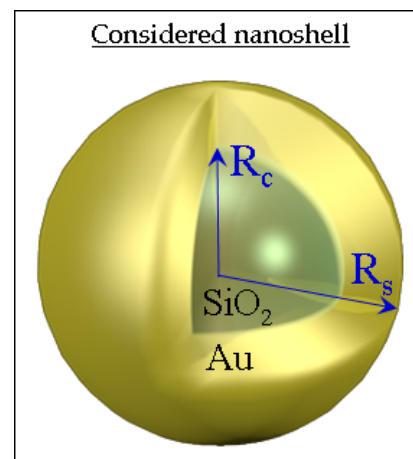
The technical details of the calculations are the following.

We have chosen a uniform _mesh_ with 20 mesh point per nm, so approximately a mesh point per Bohr radius.

We've considered 100000 _walkers_ to mimic the density of the (approximately) 5.1 million conduction electrons of the metallic shell. We started with a random uniform distribution in the shell. For the walks we have considered nearest neighbour moves where the direction of a move is determined by a uniform random number between 0 and 1: if the number is smaller than 0.5 there is a move to lower radius, otherwise the move is made to higher radius.

The _energy functional_ we have used consists of the kinetic energy of a uniform electron gas, the Hartree energy calculated in closed form from the radial Poisson equation in which we have assumed a uniform neutralizing background (Jellium model), and an exchange term calculated in the random phase approximation.

For the _choice_ of the accepted distribution we have used a 0.2 threshold acceptance. This means that a higher energy is accepted if a uniform random number between 0 and 1 is smaller than 0.2. One can also use e.g. the method of simulated annealing but the

described simple evaluation already gives quick and good results. The described method leads to the following results.

The ground state density that results from the calculations looks like what can be expected: nearly uniform in the centre of the shell with a small charge spill-out into the core and the medium.
The work function, i.e. the energy that is needed for an electron to leave the shell, is also in good agreement with the expected value: of the same order of magnitude as the bulk work function (Au to vacuum: 5.1 eV) but somewhat larger due to confinement.

If we have a look at the minimum energy that has been reached for a given number of iterations (where in an iteration a move in every mesh point has been proposed) we see that the ground state properties are found in about 500 iterations. For the described nanoshell this takes about 1'30'' on a 32 bit laptop.

To conclude we can say that in a quite simple way we get good results very quickly. The method thus looks very promising.

## … without 1-electron calculations!

When people hear or talk about 'Density Functional Theory' they mostly think of another way to construct and change the electron density of a system. That's because a there is another method to implement the Hohenberg-Kohn theorems which is known for a longer time. In these so called Kohn-Sham calculations [3] the electron density is constructed from the single-electron wave functions of all the electrons in the system. These wave functions are the solutions of single-particle Schrödinger equations in which the interaction between the electrons is taken
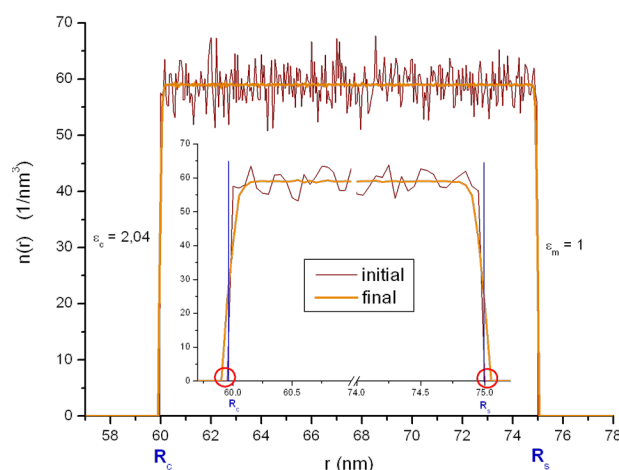
Electron density distribution in a nanoshell as a function of the distance from the centre. In the inset the spill-out into the core and the medium is shown.
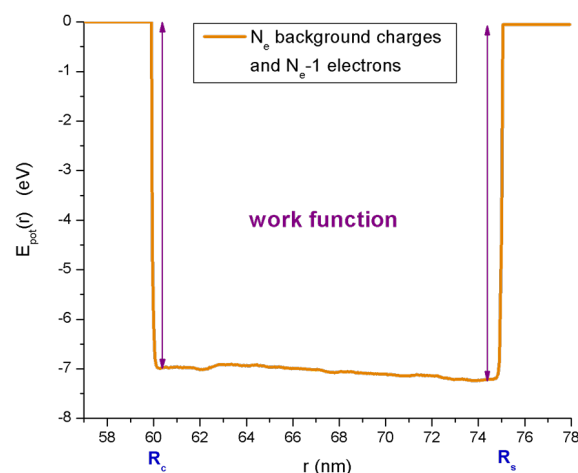
Potential energy profile in a nanoshell due to a number of background charges and one electron less.
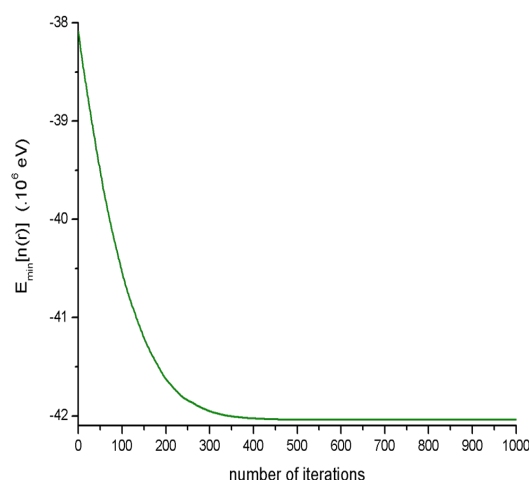
Minimum value of the energy functional found after a number of iterations as a function of the number of iterations.

into account via a mean-field potential. The constraint that the number of particles is conserved is included by using Lagrange multipliers.

To solve self-consistently the Kohn-Sham equations for 25592 electrons in a nanoshell takes about 1400', or about 23 hours on a single processor IBM RS6000/43P workstation [4]. If one wants to handle a number of electrons in a nanoshell that can be fabricated, about tens of millions of electrons, this kind of calculations takes a considerable amount of one's lifetime: the times scales much worse than linear with the number of electrons in the system… Using Lagrange multipliers is also somewhat more complicated than just not changing the number of walkers.

In conlusion one can say that the Density-Functional Monte-Carlo method is an appropriate method to calculate the charge and potential distribution in nanosystems, even when there are a considerable number of particles in the system.

References

[1] Hohenberg P., Kohn W., _Inhomogeneous electron gas_, PR, vol. 136, nr. 3B, p. B864-B871 (1964)

[2] Halas N., _Optical properties of nanoshells_, Optics & Photonics news, p. 26-30 (August 2002)

[3] Kohn W., Sham L.J., _Self-Consistent Equations Including Exchange and Correlation Effects_, Phys. Rev., 140, A1133-1138 (1965)

[4] Prodan E., Nordlander P., _Electronic structure and polarizability of metallic nanoshells_, Chem. Phys. Lett., p. 140-146 (2002)

Pt Nanowires on Ge(001):
Sheep in Wolf's Clothing?

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The deposition of small amounts of platinum on a germanium (001) surface gives rise to the formation of monatomic nanowires. These nanowires are defect- and kink-free and their length is only limited by the underlying terrace, to which they are uniquely connected. Using **ab initio** *calculations and simulated scanning tunneling microscopy (STM) images we model these nanowires, and show them to consist of germanium atoms, in contrast to earlier proposed models.*

Small, Smaller, Nano

Everybody knows Moore's Law, or at least has a rough idea of its consequence: "Next year's computer will be faster." In 1965, Gordon Moore observed that the number of components per integrated circuit, which could be produced at the lowest cost, doubled roughly every year. This primarily economical law has meanwhile become a self-fulfilling prophecy, driving the micro-electronics industry forward. The exponential growth in processing power is mainly due to ever further miniaturization. However, this miniaturization cannot be maintained indefinitely: modern lithographical techniques are expected to meet their limits in the coming decade. Moreover, miniaturization is steadily approaching its ultimate and final limit: atomic size devices connected by atomic wires. To build these ultimate devices, chips makers are looking toward self-assembly of surface nanostructures and nanowires.

In 2003, the group of Zandvliet (UTwente, The Netherlands) observed the formation of one atom thick nanowires, which could be hundreds of nanometers long [1] (Fig. 1); this appeared to be any chip designer's dream come true. The nanowires formed after the
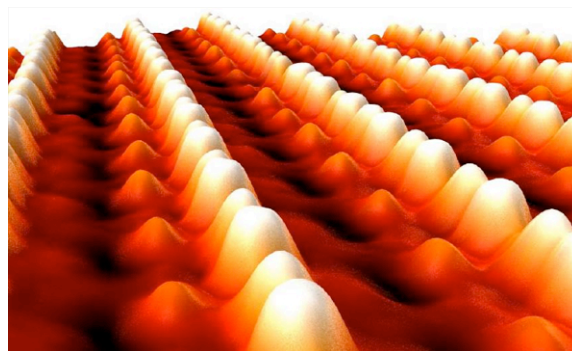

Fig. 1: STM image of an array of "platinum" nanowires on a Ge(001) surface. The spacing between the nanowires is 1.6 nm. The bulges on the left of each nanowire are also present symmetrically on the right side. The nanowires themselves show clear dimerization. (Source: [2])

deposition of about one quarter of a monolayer of platinum (Pt) on a reconstructed germanium (Ge) 001 surface, and successive annealing at more than 1000 Kelvin. These nanowires are always located between the dimer rows of the Ge surface (Fig. 2), resulting in the formation of equally spaced arrays of nanowires. Despite their length which seems only limited by the underlying terrace, the nanowires are defect- and kink-free.

The experimental story, however, does not end here. In 2005, the same group presented the observation of quantum confinement between these nanowires [2]. The one-dimensional states, for which the nanowires act as barriers,
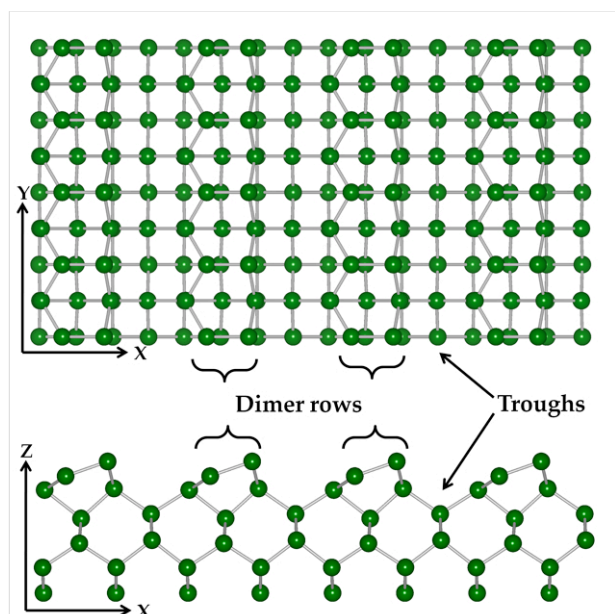
Fig. 2: Ball-and-stick representations of the reconstructed Ge(001) surface, showing dimer rows and troughs between the dimer rows. Top: top view. Bottom: side view.

show the almost textbook behavior of a particle in a box.

This was a somewhat surprising result: considering the assumption that the wires consist of 'metal' (*i.e.* Pt) atoms, one would expect the wires to act as conductors rather than barriers for these states. One would expect barrier behavior from an insulator or semiconductor, such as Ge, which makes up the substrate. This observation makes the nature of the nanowires a bit of a conundrum.

Zandvliet's group also did experiments on the adsorption of carbon monoxide (CO) on the nanowires and surface [3]. Because CO sticks well to Pt and poorly to Ge, it provides an indirect way of identifying the nature of the nanowires. The CO molecules are found to stick to the nanowires but not to the surface. Therefore, the nanowires are thought to consist of Pt, and the surface of Ge, by the authors of [3].

What you see is what you get

Seeing–and more specifically the recognition of shapes and patterns–is an important aspect of human information processing. This is the case not only in everyday life, but in research as well. We build telescopes to peer into the furthest reaches of the universe and we build microscopes to look at the smallest structures of nature. Although conventional microscopes can be very powerful, atoms remain too small to be seen with any of them. To investigate a surface at atomic resolution, one can make use of scanning tunnelling microscopy or STM. The basic principle underlying this technique is quite different from that of a light microscope. In STM, an atomically sharp needle is being traced over the sample surface, resulting in a height map of that surface. In the resulting image, the positions where atoms are present or missing are visible as the hills or valleys of the imaged surface. As such, it is an extremely powerful research tool, but it does come with one major shortcoming: it is chemically insensitive. STM can tell us *where* an atom is located, but *not which type* of atom it is.

This observation is relevant here because STM is the main technique deployed for investigating nanowires. So, although STM images clearly show the nanowires and their position, it does not reveal their composition.

However, based on knowledge of the system as well as chemical and physical intuition, one could try to make an educated guess regarding the composition of the nanowires. In our case, we know that the substrate is pure Ge and that Pt is deposited. Observations at room temperature show that the Pt atoms do not remain on the surface when they are deposited: they move into the substrate. It is only when the sample is annealed at a temperature above 1000 Kelvin that atoms pop out of the substrate again, in an amount which

is comparable to the amount of Pt deposited. This makes it very compelling to conclude that the nanowires consist of Pt atoms.
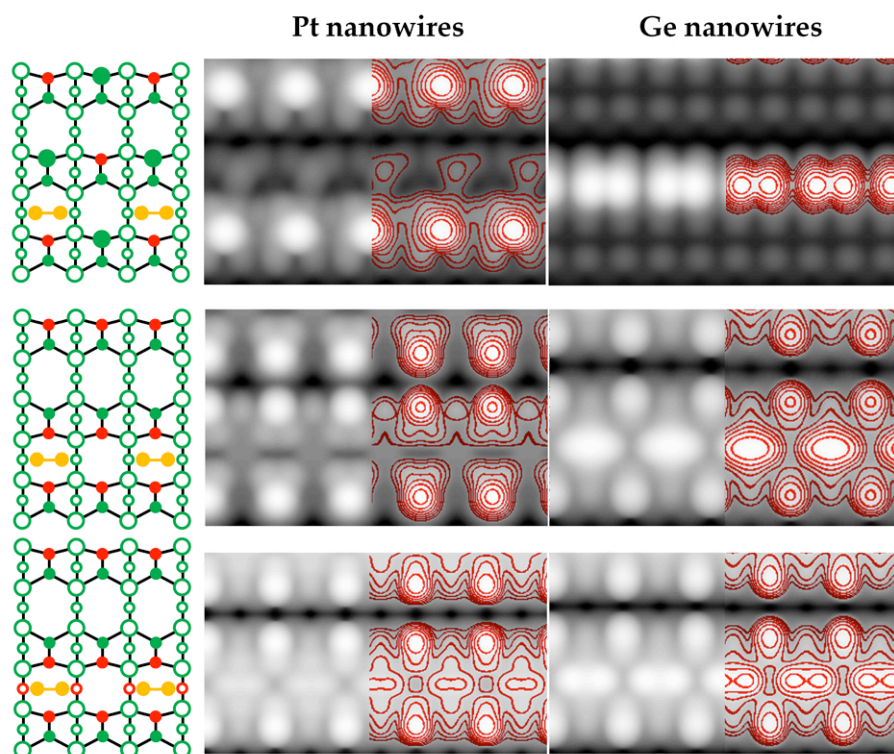

Fig. 3: Models and simulated STM images for different nanowires. The left column shows surface models for the Pt modified Ge surface (top), the model with only Pt-Ge heterodimers (middle), and the surface model with Pt at the bottom of the trough (bottom). The yellow dimers show the position of the nanowire dimers. The right column shows simulated STM images of the Ge nanowire, showing increasing similarity to the experimental STM images, when going from top to bottom. (Source: [5])

In Theory…

Indeed, in the tentative model proposed by the group of Zandvliet the nanowires consist of Pt atoms. This tentative model, however, leads to some puzzling follow-up questions:

1. Why are regions between the nanowires conducting whereas the nanowires are not?
2. Why do the nanowires appear in every second trough of the Ge surface, instead of in every trough?

To answer these questions, a theoretical model is required. This model turns out to be more complex than one might have expected initially. The modeling task starts with the substrate, which is not an entirely pure Ge surface, but a Pt-modified Ge surface, called the 'beta-terrace' [4]. It consists of a checkerboard pattern of Ge dimers and Pt-Ge heterodimers. Because this type of substrate contains exactly a quarter monolayer of Pt, and because we know that during high temperature annealing atoms are ejected from the substrate, we can imagine the following two scenarios for nanowire formation.

In the first scenario, there is more Pt present locally (not the entire surface is transformed into beta-terraces) and the excess Pt gets ejected and then forms dimers, which in turn form a nanowire. In the second scenario, the Pt of the beta-terrace is ejected and replaced by Ge from the bulk of the system. This Pt again forms dimers which in turn form the nanowires.

To test these scenarios, we build an atomistic model for a reconstructed Ge surface and a modified Ge surface, and stick Pt dimers at likely adsorption positions. Then, all these structures are run through the VASP computer program, which relaxes the atoms into their actual equilibrium positions and calculates the ground state energy of the structures [7]. After a few weeks of calculations, the resulting energies are supposed to tell us which structures are most stable, and thus should represent the experimental structure. However, in this case, all structures come back showing them to be unstable, with the single exception of a structure in which the surface was entirely demolished, certainly not corresponding to the experimental data (Fig. 3 top row, middle). Because the only experimental reference points for this system are STM images, we also simulate STM images [8]. Combined with what we see in the relaxations, we learn three important things. Firstly, none of the systems we tried was even close to representing the real system. Secondly, the Pt dimers 'want' to move into the substrate, *i.e.* we can put more Pt in the substrate. Thirdly, it might be Ge dimers which are observed as the nanowire (see Fig. 3 top row, right).

Second Attempt

Based on the knowledge acquired in the first modelling attempt, we build a second surface model, containing only Pt-Ge heterodimers. By alternately lining a trough with Pt and Ge atoms, we also introduce a reason why the nanowires should only be present in every second trough, solving already one of the mysteries of the Pt nanowires. In this case, we also use Ge dimers as possible nanowires.

The two nanowire systems are stable for this surface model, with the Pt nanowire being the most stable. The simulated STM images of the Ge nanowires also look promising: the symmetric bulges are present and a dimerized nanowire is visible. Only the nanowire dimers do not show the experimentally observed double peak (see Fig. 3 second row, right). Unfortunately, the Pt nanowire does not solve this small difference. Even worse, the Pt nanowire is entirely invisible, and the surface dimer images have changed strongly. For every two dimers, there is now only one big 'blob' to be seen (Fig. 3 second row, middle).

Looking at the geometries, we also learn that this Pt nanowire sinks into the trough. Could it sink further and take the position of the Ge atoms at the bottom of the trough?

Third time is the charm

In our third surface model, also the Ge atoms of the Pt–lined trough are replaced with Pt atoms, bringing the Pt concentration in the substrate up to three quarters of a monolayer. Again, both Pt and Ge dimers are used as nanowires, and this time only the Ge nanowires are stable. The simulated STM images are even better than before; now, almost every experimental feature is accounted for (see Fig. 3 third row, right). The nanowire is dimerized, with each dimer image doubly peaked, and the symmetric bulges are clearly present. We have a winner: *a **Ge nanowire** on a Pt modified Ge surface* [5]. Now that we know that the nanowires are Ge, it is clear why the nanowires are not conducting, while the regions in between them (which contain most of the Pt) are conducting. It also shows that intuition can be wrong, even if it is based on solid arguments.

Peierls instability

In experiment, the nanowires have a 4×1 periodicity along the wire: up-down-down-up. This was originally ascribed to the presence of Peierls instability. Since our simulated cell is only half the size of such a unit cell (to reduce the computational cost), it is impossible to

observe such a periodicity. Now that we have a model for the nanowires, it can be used with a cell of larger size to investigate this periodicity. We use (a) a doubled cell, and (b) a doubled cell in which we buckle the nanowire dimers to have the correct 4×1 periodicity.
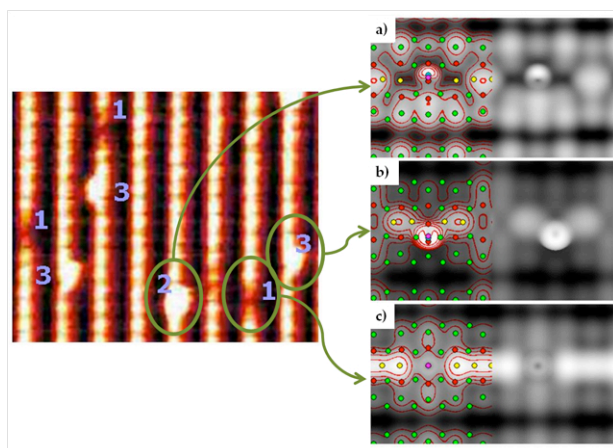

Fig. 4: Comparison of experimental STM image (left) to simulated STM images (right) of different CO adsorption sites. (Sources: [3] and [6])

However, in both cases, we do not find the 4×1 periodicity. Even in case (b), which starts out with buckled dimers, the dimers flatten out again.

When we add yet another extra Pt atom in the trough, this Pt atom binds to two Ge nanowire dimers, pulling them towards this Pt atom, both pinning the dimers in their position (increasing their stability) and buckling them physically, resulting in the experimentally observed 4×1 periodicity.

CO adsorption?

Now that we have a good theoretical model for the "Pt nanowires made of Ge atoms", we can also compare with the experimental test on the nature of the nanowires using CO molecules. Because CO binds very well to Pt and very poorly to Ge, it can be applied as a tool to discover which part of the surface contains Pt and which Ge. Remembering that the experiments show the CO molecules are adsorbed on the nanowires, this seems to

contradict our model. Or is there something else going on? Further computational analysis proves–again–that this conclusion is drawn to quickly.

In the experiments, the CO molecules appear to perform a random walk along the nanowires at room temperature. This means that there should be a path along the nanowire which the CO-molecule can follow. At 77 K, the mobility is frozen and three adsorption sites are found [3]: one centred on the nanowire, showing a depression in the nanowire image, another one also centred on the nanowire, but this time showing a large protrusion, and a third one asymmetrically to either the left or the right side of the nanowire, also showing a protrusion.

Modelling the adsorption behaviour can be done by placing CO molecules at or near probable adsorption sites, and running the solid state computer program to optimize the geometry. From these calculations, we also learn the adsorption energy of the molecules at the given site, and we find that CO preferably adsorbs at Pt atoms, as one would expect from experiments. This, however, means that there is no viable adsorption site "on" the nanowire. Checking the simulated STM images for all adsorption sites, we find three adsorption sites which nicely match the experimental images. Because the CO molecules bound to the Pt atoms bend strongly toward the nanowire, this gives the impression that the CO molecules are located "on" the nanowire [6].

Also the extra Pt atom that was introduced to provide the 4×1 periodicity is very important here, because it gives the only anchoring point "on" the nanowire for a CO molecule. As a result, it gives rise to the first adsorption site with the depression on the nanowire. When a CO molecule is bound in a bridging configuration between this extra Pt atom and

one of the Pt atoms in the substrate, we find the asymmetric adsorption site.

So, we can conclude that the presented model for the nanowires is in full agreement with the CO adsorption experiments.

Chemically sensitive STM

In addition to the obvious presentation of a model for Pt induced nanowires on a Ge surface, this work also shows how STM can be made chemically sensitive, which is achieved through the comparison of experimental and theoretical STM images. Energies from *ab initio* calculations can change dramatically depending on the conditions used, resulting in changing stabilities and stability orders. In contrast, the simulated STM images barely change. This robustness of STM images, in the sense that changes in the starting conditions do not radically change the features, makes them an easy and safe tool to compare theoretical modelling results and experimental data.

In conclusion, we have shown that the Pt nanowires on Ge(001) consist of Ge atoms on a Pt modified substrate[†]. In this model, CO molecules bind to the Pt atoms in the substrate and bend toward the nanowire, giving the impression of CO adsorption sites on the nanowire. By comparing simulated STM images to experimental STM images, chemical sensitivity is added to this experimental technique, alleviating its major shortcoming.

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[3] D. Kockmann *et al.*, "*Remarkably long-ranged repulsive interaction between adsorbed CO molecules on Pt modified Ge(001)*", Phys. Rev. **B** 78, 245421 (2008).
[4] D. E. P. Vanpoucke and G. Brocks, "*Density functional theory study of Pt-induced Ge(001) reconstructions*", Phys. Rev. **B** 81, 035333 (2010)
[5] D. E. P. Vanpoucke and G. Brocks, "*Formation of Pt-induced Ge atomic nanowires on Pt/Ge(001): A density functional theory study*", Phys. Rev. **B** 77, 241308(R) (2008).; Phys. Rev. **B** 81, 085410 (2010).
[6] D. E. P. Vanpoucke and G. Brocks, "CO adsorption on Pt-induced Ge nanowires", Phys. Rev. **B** 81, 235434 (2010).

Programs and codes:
[7] VASP-code,
http://cmp.univie.ac.at/vasp/
[8] HIVE-STM,
http://users.ugent.be/~devpouck/hive.shtml

Moral:
[†] The moral of our story: The Pt atoms intermingle with the top layer Ge atoms, acting as wolves in sheep's clothing. This enables some of the Ge atoms to leave the flock. As sheep in wolf's clothing they appear as nanowires in STM, which cannot directly check their identity.

FEATURED ARTICLE

Metallic nanoshells on a solar cell

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The rise of the solar cell

In 2009 almost 44% of the energy consumption in Belgium came from fossil fuel. Another 50% was provided by nuclear power plants, leaving only about 6% for renewable energy resources. No wonder that in our modern society, where the predictions for the fossil fuel stock are pessimistic and the long-term dangers of radioactive waste are well known, a lot of people are putting their money on (and using it for) sustainable and renewable energy resources. And mankind has proven to be very resourceful in finding ways to gain energy from wind, water and even from the sun.

Located almost 150million km from here, the sun provides nearly all of the earth's energy. Without it we would surely perish. Still we struggle to convert this huge amount of energy into the electricity that our devices yearn so much.

Our first hopes of harvesting the power of the sun arose in 1839 when Becquerel discovered the photovoltaic effect. It took almost 50 years before this effect was used to create the first solar cell, with an efficiency of only 1%. And it took another 25 years before Einstein explained to the world how the solar cell actually works.

Today's solar cells are a significant improvement in comparison to the first solar cells, since the current record stands at 43.5% efficiency. However, it is unfortunate that these high-efficiency solar cells are very specialized, experimental and above all expensive setups, hardly ready to be mounted on every roof. In the consumer market the cheaper, easy to use solar cells remain on top. The current ruling champions are mono- and polycrystalline silicon solar cells. These have an average efficiency of 15% while the laboratory versions are capable of reaching up to 25%.

So, where is the super-high-efficiency-almost-free solar cell? To be honest: we are still far from this goal, but we are getting there step by step. A lot of small steps are being taken: adding anti-reflection layers, combining different materials and different band gaps, putting concentrators on the solar cells and so on. And now "small steps" is to be taken rather literally since the introduction of nanotechnology into the solar cell research.
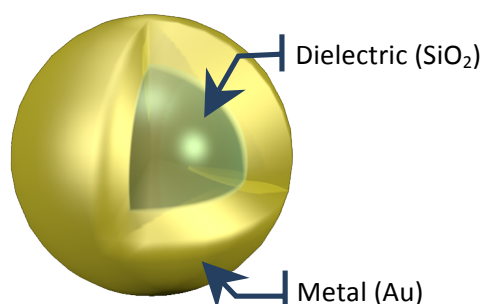
Figure 1: drawing of a nanoshell: The center consists of a SiO₂ core and the outside is a metallic shell (e.g. gold, silver or copper). Real life size is only about 50-400 nm diameter.

Nanoshells: golden speed bumps

In nanoscience the surface rules over the bulk and the properties of materials can change drastically in comparison to our everyday-life intuition. This is certainly true in nanoshells. Consisting of a silicon dioxide core and a thin metallic shell, their properties are dominated by the surface Plasmon polaritons residing on their surfaces. These surface Plasmon polaritons can be seen as a collective oscillation of the electron sea in resonance with the frequency of an incoming light wave. The light itself seems to be trapped along the surface for a while, resulting in a very high electric field around the particles. To some extent one can compare it to a speed bump, temporarily slowing the light down and capturing it as it passes by the nanoshell.

A very useful feature is that the resonance frequency of these Plasmon polaritons can be changed by changing the radii of the nanoparticle and the shell, or by a change in the optical response of the materials.

Due to these tunable surface Plasmon polaritons the nanoshells have pronounced and useful optical features. This results in a huge amount of applications. Most of these are biosensors, where finding and curing cancer is

one of the most mind-blowing, but there are applications in solid state physics as well, for example in solar cells.

In biophysics nanoshells are used instead of chemical labels or isotopes by combining them with antibodies. Antibodies are molecules which are always searching for their partner. We can use them to find specific molecules and capture these. If a nanoshell is attached to the end of such an antibody, it will be dragged along while the antibody seeks its partner molecule. The nanoshells can be easily detected because of their excellent optical response, making it easy to find the target molecule. But what is even better is that the optical response can be adjusted by changing the size of either the nanoshell or its core. This allows us to fabricate the nanoshells in such a way that they are easily visible in absorption spectra.

What is also special is that these nanoshells are quite sensitive to changes in their environment. For example: when the antibody couples to its partner, the nanoshell will sense this and its optical response will change. Thus, we can see which nanoshells are coupled to the
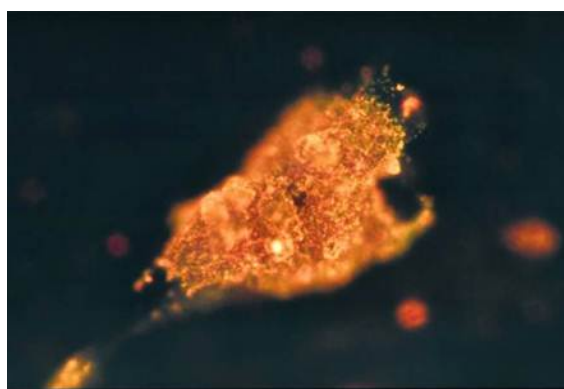

Figure 2: a false-color picture of a cancer cell visualized by nanorods. Image courtesy of Mostafa El-Sayed, Georgia Tech.

target molecule and which are not because they respond to a different frequency. In this way, we can track down all kinds of molecules, even *in vivo.*

This technique is being used in studies to cure cancer. First the cancer is found and even visualized using the nanoshells. But the usefulness of the nanoshells does not stop there. Once the cancer is found one can illuminate the nanoshells for some time with a laser of the right frequency. This will make the electrons in the metallic shell vibrate. The vibration heats up the nanoshell, heating up the environment and literally cooking the cancer cells. This technique has been tested on white mice with very positive results.

Other applications can be found in plasmonics. As Moore's law dictates computers are getting smaller and smaller. However, we would also like them to go faster and faster. Light would be ideal when talking about speed, but it would be bad for size. To control and redirect light the components have to be larger than the wavelength, meaning that computers would once again become 20 times as big as they are now. That is why electrons are used because they have a very small wavelength. But they are not as fast as light.

Plasmon polaritons, such as the ones that exist in nanoshells, are a combination of light and electrons. The idea is to use the electron side for steering, while using the light side to pass the information. A chain of nanoshells could be used as a channel to transport these plasmons.

A pinch of nanoshells

It is not hard to imagine that before long more and more applications of nanoshells surfaced. One of these new ideas was the application to solar cells with as ultimate goal a better efficiency.

In 2005 Schaadt *et. al.* published an article in which they studied nanospheres on top of a solar cell experimentally. Nanospheres are similar to nanoshells, except that they have no core, but are completely filled golden orbs. These nanospheres had a remarkable effect on the solar cell since they made the photocurrent increase in certain parts of the spectrum. This photocurrent is important since it is the main goal of a solar cell: getting current out of the light from the sun. At that moment, the idea of nanoshells on top of a solar cell was born.

Once, a professor asked me: *"How could you possibly hope to increase the efficiency of a solar cell by coating them with reflecting nanoparticles?"* Indeed a good question. Yet the experiment by Schaadt *et. al.* clearly shows an increase in the photocurrent. The honest answer is that so far were still not quite sure about which effect is responsible for this counter-intuitive behavior. But we do have a bunch of ideas and indications.

Off the straight path

At a first glance two ideas come to mind: scattering of light and surface Plasmon polaritons. Ever since Rayleigh and his experiments explained why the sky is blue, we know that light will scatter at particles smaller than its wavelength. Scattering means that a part of the light will be absorbed by the particle, a part will bounce of it and change direction and the rest will continue without ever seeing the particle. The interesting part is

the one that changes direction. To understand why one must first know something about the inner workings of a solar cell.

A solar cell consists of two doped semiconductors placed together forming a pn-junction. The main goal of the cell is to turn photons into usable electrons. The catch is in the "usable" part. Whenever a photon is absorbed it will create a free electron and a free hole. Both will travel through the material, but if they ever come close to each other, they will recombine and the energy will be lost. To prevent this we must find a way to permanently separate the electron and the hole. This is the task of the pn-junction. This junction creates a barrier which will only allow electrons to pass in one way and not the other, while treating holes in the opposite way. Obviously the farther away from this barrier the electron is created, the smaller the chance that it will pass over it. Therefore much of the current research focuses on increasing these chances.
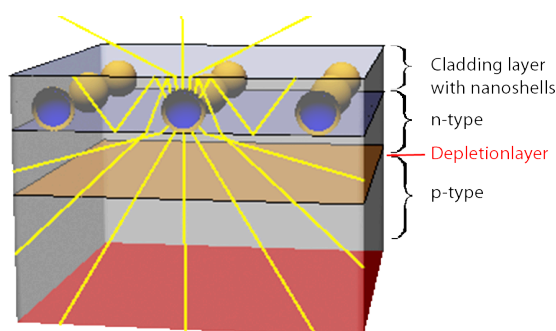

Figure 3: schematic view of the far-field scattered photon paths in a solar cell. It is clear that the slope of the paths change which could have a positive effect on the efficiency.

One way to increase the chance of getting a usable electron from a photon is to make sure the photon is absorbed as closely to the barrier as possible. And here our nanoshells come into play. Picture yourself a rectangular tank of water. Your goal is to get a large rod (considerably larger than the tank) as wet as possible without touching the tank. If you would stick the rod vertically in the tank a big part would become wet. But to get the bar as wet as possible you would have to place it diagonally in the tank, from one corner to the opposite. This is similar to a solar cell. The rod is the path of the photons in the solar cell, while the water represents the barrier. The larger the path inside or nearby the barrier, the greater the amount of electrons that are created in and near the barrier. Placing the rod vertically can be compared to the standard working of a solar cell where the light from the sun falls in perpendicular to the cell. But if we could somehow change this path to imitate the diagonal position of the rod, then we could increase the chance that the created electrons are useful. This is where nanoshells come in, since they can scatter the incoming light in all directions. But this is only one of the possibilities why nanoshells could have a positive effect on solar cells.

Close encounter

Another candidate is the near-field effect. Favored by many researchers, the near-field effect has proven to be an important contribution in many simulations performed by many groups in many different ways. Contrary to the far-field, which is actually responsible for the scattering, the near-field is restricted to the proximity of the nanoshell.

This near-field effect is the result of the surface plasmon polaritons. Due to the electron oscillations in the shell and the temporary trapping of the light on the surface, the electromagnetic field around the nanoshell will be very strong, an effect that is already being used in Surface Enhanced Raman

Spectroscopy. This high concentration will increase the number of electrons and holes created near the nanoshell. But is this a good thing? Yes, remember that the goal was to increase the number of creations around the barrier, which is actually called the depletion layer or the charge separation region. Current solar cells are constructed with a thin, 300 nm n-type semiconductor connected to a 150 μm thick p-type. The barrier is in between these two, meaning that it is located very close to the top of our solar cell, well within the reach of the near-field effects.

Although this is a popular idea, theoretical calculations and predictions remain scarce due to the difficulty of the calculations. Most studies of these effects are currently done using numerical simulations e.g. with finite element methods.

Some theory

When facing problems regarding electromagnetic waves and scattering the Maxwell equations are always a safe bet. Solving them for the geometry under consideration is usually challenging, but will generally result in an exact solution for your problem. This method has been used to study the electromagnetic fields around the nanoshells. A nanoshell can be described as two concentric spheres and the solution in this spherically symmetric case is usually referred to as Mie-theory.

The big question is what the influence of an absorbing solar cell is. Now the problem becomes less obvious since the nanoshell is best described in spherical coordinates in contradiction to the flat solar cell. There are ways to work around this by making some

assumptions but you have to be careful in doing so. It is surprising how easily you can get a 140% efficiency solar cell because you accidentally added extra photons to your system.

The scattering problem is far easier to tackle using some assumptions. By calculating the scattering cross section far away from the nanoparticle we know how much photons are scattered in each direction. Then, by simply assuming that these photons travel in a straight line from the core of the nanoshell in each direction, we can calculate the difference between normal incident photons and scattered photons. In this way we do not have to solve the sphere-on-a-flat-surface problem. What we actually do is replacing the nanoshell with a light bulb, shining out the scattered photons in all directions.

And some results

One of the first steps in doing this kind of research is determining the goal. Taking into account all assumptions, what is the efficiency of the solar cell without any kind of nanoparticles? In the considered case the efficiency was 35.82%, which is quite close to experimental results given the assumptions and simplifications. More than a year later I had implemented the far-field effects of the nanoshell and recalculated the efficiency: 32.9%. But that did not worry me, since it was only calculated with an example nanoshell and the system was not yet optimized. Thus the next question was set: what is the best nanoshell to put on such a solar cell? So one weekend I infiltrated our university and seized as many computers as I could to study a fair amount of well-chosen nanoshells. As you can imagine, I was deeply disheartened when my

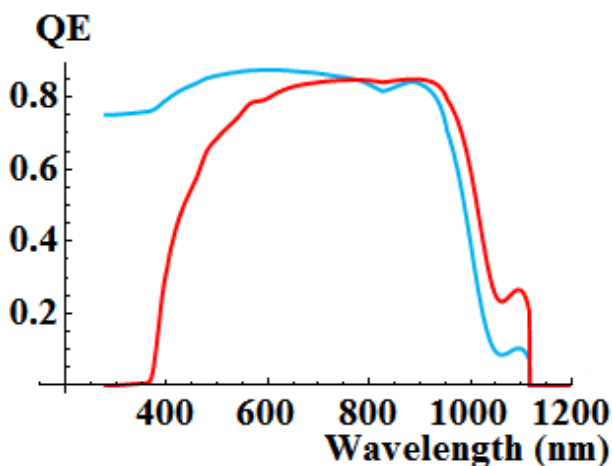top configuration only reached 35.81% efficiency.

Figure 4: the quantum efficiency (QE) for normal incident light (blue) and for light radiated from a point source, resembling the nanoshell (red). Notice that above 800 nm the red curve is higher (= better) than the blue curve.

So, what went wrong? Well, part of the idea was right as you can see in Figure 4. For larger wavelengths it was indeed better to scatter the light. The downfall was that half of the scattered light was scattered back and thus became useless. This required the remaining half of the scattered light to more than double their chances, which was just too much to ask for. Also, putting the nanoshells in front of the solar cell is a bit similar to closing the curtains. You gain less light because the nanoshells not only scatter backwards, but will also absorb some photons.

Light at the end of the tunnel

Even though this result was a disappointment, it still teaches us a valuable lesson. The experimental result still claims a higher photocurrent. Therefore the simple conclusion of this part of the research is that there must be another effect that is responsible for the experimental result. Luckily we have not yet

run out of ideas. The near-field effects are still to be incorporated. And since the current research included much of the counteracting effects, while still reaching almost the same efficiency, the hopes are high that this effect might indeed explain the experiments.

Some reading material

- A general introduction and all the calculations mentioned can be found in the author's thesis: Nick Van den Broeck: *Metallische nanoschillen op een zonnecel*, Universiteit Antwerpen, 2010 (in Dutch).
- A good book about solar cells: J. Nelson: *The physics of solar cells*, Imperial College Press, UK 2003.
- For more information about the Maxwell equations and Mie-theory:
  - ➢ J.A. Stratton: *Electromagnetic theory*, McGraw-Hill Book Company, USA, 1941.
  - ➢ C.F. Bohren and D.R. Huffman: *Absorption and scattering of light by small particles*, Wiley, 1983.
- There are many articles about nanoshells in literature. Some good starters are:
  - ➢ N. Halas: *The optical properties of nanoshells*, Optics & photonics news, pp. 26-30, 2002.
  - ➢ L.R. Hirsch *et. al.*: *Metal Nanoshells*, Annals of Biomedical engineering 34, pp. 15-22 2006.

BOOK REVIEWS

BPS408 Turning Dust to Gold. Building a Future on the Moon and Mars.

H. Benaroya.

Recently, we heard on the BBC that "fiction is good for you." Then fiction on the Moon or Mars must be even better for you. Why? Because the reader of fiction broadens his or her views of the world and life on Earth. Then, if the fiction takes place on the Moon or Mars, the fiction reader will further broaden his or her views and better exercise his or her ability to create or at least dream. This is certainly the goal of this book, a book that is not a science or physics book but, rather, a science fantasy book or, at best, a science fiction book.

The author's goal is to convince the reader of the value of space exploration for humankind, an exploration that creates "new opportunities for freedom and limitless growth." The book is disconcerting, at first, for any reader who has not read the foreword. Indeed, as indicated in the foreword, this book is written "from the perspective of a future observer, more than 150 years into the future." It is based both on a fictitious and incomplete repertory of documents dating back to the last half of the twenty-first century and on real and original interviews with several scientists, engineers, and politicians involved in space exploration in the late twentieth century.

The book bares a 2010 copyright, i.e., it was written and copyrighted after President George W. Bush's "visionary speech" of 14 January 2004 placing the U.S. on track to return to the Moon. In 2011 with a different American administration and the end of the shuttle program, this return is far from certain but, of course, the author and the reader are free to dream. Indeed, the author does dream of a settlement on the Moon, of extraterrestrial tourism, of a scientific lunar laboratory, of lunar sports, and, why not, of lunar sex. The materials scientist will be happy to dream about low gravity casting processes, or about the preparation of thin films by chemical vapor deposition, or by molecular beam epitaxy, without their having to worry about vacuum pumps by taking advantage of the hard vacuum readily available on the Moon. The avid reader of the sports section of a newspaper will be surprised to read about pole-vaulting records of more than 30 m. Surely, the readers of the *Physicalia Magazine* will be comforted to know that the original *Joy of Sex* by Alex Comfort has been updated into *The Joy of Low g Sex* which claims that "sex in space may be the ideal exercise to prevent muscle atrophy."

We think that by now, the readers of the *Physicalia Magazine* are convinced that this book is not a physics book. It is however a well illustrated book with many diagrams, artistic views, and photographs. We really wonder why 21 color plates were necessary but they are nice. Unfortunately, the text contains a large number of typos. Further, it is very difficult to delineate the readership for this book. We see it best used in a creative writing class either as an example of science fiction or as a basis for discussion between students of science and literature.

Gary J. Long

Fernande Grandjean