Phoenix-Moriarty debate: Part I

E-mails and letters 24th Nov. '04 – 3rd Dec. '04

[Note that related correspondence between
Richard Jones and Chris Phoenix is also included]

Subject: Scanning probe chemistry
Creation Date 24/11/2004 18:09:38
From: Chris Phoenix
To: Philip Moriarty

Richard Jones recently gave you a recommendation in his blog as someone who's read Nanosystems closely and is very skeptical. "*he's from the 'hard' end of nanotechnology and is very familiar with the practical problems of moving atoms around in a scanning tunnelling microscope, so his critique is based on what he sees as a huge practical gaps in Drexler's implementation path.*"

I need to learn more about scanning probe chemistry as it relates to Drexler's proposals. If Drexler is wrong about mechanosynthesis, then CRN needs to change part of its message. Also, if it's theoretically workable but practically near-impossible, then it may take a long time to develop--and again, CRN would need to modify its message.

On the other hand, I see work like Aono, Oyabu, Lee and Ho, and Hla, and proposals like Freitas's recent Foresight talk, and it looks like it's "just" a matter of finding the right reactions and making them reliable or repairable. Far from trival, but doable with engineering R&D.
Bibliography:http://foresight.org/stage2/mechsynthbib.html.
Freitas:http://www.molecularassembler.com/Papers/PathDiamMolMfg.htm

So, can you give me an overview your objection to Drexler's proposals (or point me at a web page)? Have you looked at Freitas's proposal for building carbon-dimer tool tips, and have you spotted any problems with it?

Thanks,
Chris

Subject: Re: Scanning probe chemistry
Creation Date: 25/11/2004 08:55:56
From: Philip Moriarty
To: Chris Phoenix

Chris,
Thanks for your very interesting e-mail. I'm currently 'neck-deep' in teaching and admininstration and have meetings later today and most of tomorrow. Would it be OK if I got back to you either over the weekend or early next week with a document outlining my objections to Drexler's mechanosynthesis 'vision'? In addition, although I was aware of Freitas' J. Nanosci. Nanotech. paper (published last year), I have not yet read over the website you mentioned which details his "Pathway to Diamond-Based Molecular Manufacturing" invited lecture. I'd like to see if there's anything radically different in what he's suggesting (as compared to the 2003 paper).

Best wishes,

Philip

Subject: Re: Scanning probe chemistry
Creation Date 25/11/2004 15:12:54
From: Chris Phoenix
To: Philip Moriarty

No hurry. Thanks for taking the time.

Freitas's J.N.N. paper is only the first part of his "pathway" lecture. The rest of it suggests ways to build and manipulate tool tips in the lab. One possible pathway: Synthesize the small tip (capped with iodine), deposit it on a well-chosen surface that doesn't support CVD diamond, do CVD and it'll deposit only on the tool tip (something similar has been demonstrated, making sparse 2-micron crystals), then pick up the tip with MEMS.

Chris

Subject: Re: Scanning probe chemistry
Creation Date Tue, Nov 30, 2004 10:44 am
From: Philip Moriarty
To: Chris Phoenix

Hi Chris,

Apologies for the delay - please find attached a document outlining my thoughts on Freitas' (and others') mechanosynthesis work. I look forward to hearing from you. (Note that I have cc-ed the document to Richard Jones and Eric Drexler.)

Best wishes,

Philip

The document mentioned in the e-mail message above is reproduced on the following pages. [PJM 21st January 2005]

Letter from Moriarty to Phoenix
November 30th 2004

In the following, lines and passages from e-mails sent by K. Eric Drexler to Moriarty (PJM) and quoted in the original letter are suppressed because permission to include these quotes was not given. Areas where quotes have been removed are identified in blue type. Note that the loss of Drexler's comments from the letters, while disappointing, generally does not impact very heavily on the flow of the debate. Links to follow-up discussions related to the debate (on both Richard Jones' *"Soft Machines"* blog and the Center for Responsible Nanotechnolgy (CRN) blog) are included in **bold blue type**. In particular, this letter prompted discussion via the "Soft Machines" blog: see http://www.softmachines.org/wordpress/index.php?p=50

Dear Chris,

Thanks for your e-mail of 25/11/04 requesting a clarification of the difficulties I have with the mechanosynthesis concept expounded by Drexler and co-workers. You mentioned that CRN were particularly interested in Freitas' work and I'm grateful to you for sending me the URL for a very recent presentation by Freitas (of which I was not aware). Over the weekend I have spent quite some time reading (and, indeed in some cases, re-reading) Freitas' and Merkle's computational chemistry research on mechanosynthesis. Their most recent papers (published in *J. Nanosci. Nanotech.* and *J. Comp. Nanosci.*) represent an important advance in theoretical/computational analysis of reactive molecule positioning and the calculations are based on sound, peer-reviewed, and careful quantum chemistry. (As described below, however, I take issue with quite a number of the synthetic strategies put forward by Freitas both in his Oct. '04 presentation and in the Mann et al. paper ('04)). Notwithstanding these issues, however, I am very pleased to see that in both their peer-reviewed work and in other documents available from the Foresight Institute's website (as outlined below), Freitas and Merkle suggest that their analyses provide a foundation on which to base 'proof-of-principle' experiments of the most fundamental steps in mechanosynthesis. This is certainly a very different approach from that which has been described to me by Dr. Drexler in the past and I return to this important point on a number of occasions below. (As an experimental physicist, for me the theory-experiment 'feedback loop' is of primary significance).

Before I outline my views on mechanosynthesis, it is worth noting two points. First, during May '03 (and following the publication of my comments in *The Guardian* which broadly supported Richard Smalley's 'sticky atoms' argument), I had a rather extended e-mail discussion/ argument with Dr. Drexler on implementation pathways for mechanosynthesis (and other matters). I think that Dr. Drexler would wholly agree that he and I did not reach any type of consensus. Nevertheless, I found the exchange of e-mails extremely useful as, for me, it facilitated a more in-depth appreciation of Dr. Drexler's systems engineering stance. In the following discussion of mechanosynthesis, I quote extensively from my e-mail correspondence with Dr. Drexler. *(See comment at the head of this letter - PJM).* I sincerely hope that this is acceptable to Dr. Drexler and would welcome any comments/criticisms he might have. (Note that I have cc-ed him on the e-mail to which this document is attached).

It is also important to note that, while I do not accept the concept of a 'universal assembler' which will be able to build 'virtually anything' (as repeatedly espoused by Dr. Drexler and others at the Foresight Institute) **[see http://www.softmachines.org/wordpress/index.php?p=50 for further discussion on this theme - PJM]**, I have a *genuine interest* in the fundamental mechanosynthesis ideas outlined by Freitas and Merkle and believe that their willingness to at least accept the key significance of proof-of-principle experiments is a big step forward. I also wholeheartedly endorse the following statement in your e-mail: *"Also, if it's theoretically workable but practically near-impossible, then it may take a long time to develop--and again, CRN would need to modify its message."* While I am open to the idea of attempting to consider routes towards the development of an implementation pathway for Mann et al.'s Si/Ge-triadamantane dimer placement reaction, even this most basic reaction in mechanochemistry is practically near-impossible. For example, how does one locate one tool with the other to carry out the dehydrogenation step which is so fundamental to Mann et al.'s reaction sequence? In my correspondence with Dr. Drexler, I have put forward similar arguments re. reaction sequences previously described by Merkle and co-workers:

> *"… I (and, I'm certain, the Nanoscience community as a whole) would be exceptionally interested in learning how you will position the two Sn moieties in the manner shown in Reaction 18 (or indeed the Si atoms in Reaction 7 or those in Reaction 21) in Ref. 15 [RC Merkle, Nanotechnology* **8** *149 (1997)]. Many groups are working on dual probe scanning probe systems and have encountered fundamental limits on how close together two probes may be placed. Scanning probe tips have a finite radius of curvature. If exceptionally high aspect-ratio tips will be used (e.g. dual carbon nanotubes) or an alternative positioning system is envisaged (robotic arms etc…) then where is the proof-of-principle demonstration of this technology? The devil is in the detail and the clock is ticking – you and your colleagues envisage that molecular manufacturing will be with us 'early in the 21st century'. "*

Similar arguments apply to, for example, Fig. 8.14 in *Nanosystems*. Note that this is just an alternative formulation of Smalley's "fat fingers" argument. While I am more than aware that the term 'fingers' is not the most appropriate description of the molecular machinery, the same type of steric hindrance arguments raised by Smalley are going to appear for any type of mount on which the tool-tip is supported (see, for example, Fig. 4 in Mann et al.). For example, while reading Mann et al.'s paper, I continually tried to envisage just how one would set up an *experiment* whereby C dimers could be added one by one to the underlying diamond surface. To carry out the tool dehydrogenation, even an extremely small mismatch in the alignment of the tip-tools will result in unwanted bond formation. (...and just how will the tip tools be aligned?)

[Reference to e-mail correspondence between Moriarty and Drexler removed – PJM]. My question remains: to implement computer-controlled atomic precision positioners, if SPM technology is not to be used then what's the alternative? As I discuss in more detail in the following sections, arguments and analogies based on the Apollo Moon landings simply don't address this question. *[Quote to which preceding sentence refers has been removed but Drexler has put forward similar arguments in an interview printed in 'New Scientist 'in April 2003 – PJM].* If CRN and the Foresight Institute want to succeed in attracting public funding for the development of MNT then:

(i) a coherent strategy/ pathway to assembler development must be outlined. ['Stick' diagrams such as those shown in Fig. 8.14 of *Nanosystems* convince no-one. At least Freitas et al. are attempting to address the key technical issues rather than "stonewalling" on the precise details of the assembler and tip technology].

(ii) 'proof-of-principle' experiments must be attempted – this has been tactitly accepted by researchers at the Foresight Institute (see http://www.foresight.org/stage2/project1A.html).

In the following I consider Freitas' work in depth and revisit a number of issues related to assembler technology. In particular, I believe that there are fundamental flaws in the tip-tool + support fabrication strategy put forward by Freitas in his recent presentation

What is mechanosynthesis?

I would first like to provide a short definition of Dr. Drexler's mechanosynthesis concept. This is based on various sources (including personal correspondence with Dr. Dexler) and I hope that it correctly defines the core idea.

Mechanosynthesis: the synthesis of molecular assemblies - and ultimately bulk materials - from the mechanical positioning of reactive molecules with atomic precision.

Is this a correct and appropriate definition? If so, then I would ask the *proponents* of molecular manufacturing (including Freitas, Merkle et al.) not to misrepresent this concept. For example, single molecule manipulation experiments using STM and AFM are frequently cited as providing an 'existence proof' of mechanosynthesis. Indeed, Freitas' website features a 'technical bibliography' of supposed experimental demonstrations of mechanosynthesis. Given the definition above, *none* of the experiments Freitas cites are examples of mechanosynthesis for the reasons detailed in (i) – (iv) below. Please note that I provide the following list not to attempt to rule out (on physical rather than technological grounds) the 'prototypical' mechanosynthesis reaction described by Freitas and Merkle in their recent papers but rather to show that if we are to attempt to move the debate forward, we need to be extremely careful to define precisely what type of manipulation process is involved in an experiment.

(i) The beautiful STM work of Lyding et al. on atomic hydrogen desorption involves either E field- or tunnel current (vibrational heating)-induced removal of adsorbed H atoms from Si(100). This is not *mechanical* positioning. If E fields are to be employed within Drexlerian assemblers then this obviously opens up a broad new parameter space.

(ii) The work of Becker et al. [1987], Avouris et al. [173], and Aono et al. [1993] on STM-induced atomic manipulation does not involve reactive (and re-chargeable) molecular tools. Furthermore, as all of this work involved STM on semiconductors, electric fields of order 10^9 Vm^{-1} were again present. (It is worthwhile referring to TT Tsong's papers on electric field-assisted atomic manipulation when considering STM-based manipulation). Whitman et al. have also published some extremely nice work on field-induced diffusion of Cs atoms on GaAs(110). Ho and Lee's breathtaking work in 1999 *explicitly* involves tunnelling electrons and is thus outside the realm of mechanosynthesis.

(iii) While Oyabu et al.'s exciting experiment (PRL 90 176102) is AFM-based and therefore involves purely mechanical forces, it still doesn't fall within the scope of the definition above. There is no placement of a reactive *molecule* to drive the 'abstraction' process – rather, an atom from the AFM tip forms a bond with the surface. One might argue that this is simply "splitting hairs", i.e. that the experiment is clearly an example of mechanical interactions driving a surface modification and thus this exemplifies the 'essence' of mechanosynthesis. I cannot accept this argument. Mechanosynthesis necessitates the manipulation of *pre-chosen* reactive molecules and, moreover, will require the application of *rechargeable* tools.

(iv) Freitas' bibliography cites the molecular manipulation work of Karl Heinz Reider's group in Berlin (carried out in collaboration with Gerhard Meyer, now at IBM Zurich) as another example of molecular manipulation for mechanosynthesis. This work (along with that of Jim Gimzewski's group (previously at IBM Zurich) and the Nottingham Nanoscience group) involves STM tip-induced displacement of molecules from site to site across a metal or semiconductor surface. As for the experiments listed in (i) – (iii) there is no reactive molecular 'tool' involved in the experiments – the molecular motion involves STM driven diffusion on the *substrate*. Our C_{60} manipulation experiments in Nottingham, for example, utilise a reactive bulk *substrate* to provide atomic-level control of the molecular positions. This runs counter to the 'reactive tool' idea which is at the core of mechanosynthesis.

Why have I spent so much time discussing scanning probe technology? As Merkle and Freitas note (J. Nanosci. Nanotech. **3** 319 (2003)), SPM is currently a well-established method for achieving atomic level positioning of molecules. In addition - and as you specifically asked me to comment on Freitas' work - note that he includes 3 slides in his talk for the Molecular Machine Systems symposium illustrating various aspects of the experimental STM and AFM work outlined in (i) – (iv) above. I find it surprising that Freitas – whose papers with Merkle clearly show that he has carefully considered the fundamental chemistry underlying the proposed mechanosynthesis reactions – describes Oyabu et al's work as the 'first example of mechanosynthesis'. As stressed above, the experiment does not involve the positioning of a pre-chosen reactive molecule and thus cannot be described as mechanosynthesis (c.f. slide 34 of Freitas' talk, where he illustrates the operation of the carbene tool). Do you agree?

Implementation pathways and "sticky fingers"

A particularly laudable aspect of Mann et al.'s paper (corresponding author: Freitas) on Si/Ge-triadamantane dimer placement tools is the relatively large number of possible tools they explore. I quote directly from their conclusions:

"The overall deposition reactions are endothermic and, therefore, thermodynamically unfavorable for both Si and Ge tools. Retraction of the tool from the diamond substrate will retain the carbon dimer to the placement tool the vast majority of the time, so the proposed tools are inefficient at their designated task. However, depositing a C2 dimer onto the diamond surface may occur a finite percentage of the time, which might be an adequate performance for early experimental proof-of-concept demonstrations. "

So, even this most fundamental of mechanosynthesis steps on the only remotely viable materials system (i.e. diamond and 'diamondoid' structures) proposed to date is fraught with difficulties. (And this neglects the problems I have with Freitas' implementation strategy, outlined previously and below). During our correspondence last year, Dr. Drexler's response on issues such as these was that there is nothing fundamental about the reactions – we can just choose another set of reactions and/or materials systems. However, the same issues crop up time and time again. I wholeheartedly concur with Smalley's statement:

> *"But in all of your writings, I have never seen a convincing argument that this list of conditions and synthetic targets that will actually work reliably with mechanosynthesis can be anything but a very, very short list."*

The rather similar argument I made to Dr. Drexler last year was as follows:

> *"So, far from delivering the ability to synthesise 'most arrangements of atoms that are consistent with physical law' or to manufacture "almost any… product ….that is consistent with physical and chemical law", an extremely judicious choice of materials system, possible intermediate/ transition states, diffusion barriers, and symmetry is required to attempt even the initial, most basic and faltering steps in molecular manufacturing. "*

This is precisely what Merkle, Freitas, and Mann et al. find in their work and, if we're honest, at the most fundamental level this represents an alternative statement of Smalley's "sticky fingers" argument. That is, the detailed chemistry of each system provides a fundamental obstacle to the construction of a universal assembler that can handle all the technologically important elements in the periodic table. (See http://www.softmachines.org/wordpress/index.php?p=50 for a discussion of universal assemblers).

SPM and alternative (?) technologies

Slide 49 of Freitas' presentation clearly suggests that he believes SPM is a key contender for the development of a mechanosynthesis technology. The dimer placement tool in Slide 51 is also clearly an SPM tip-type structure. Furthermore, in Slides 66 – 103, Freitas outlines a sequence of steps whereby a DMS tool could be built. I have some problems with this strategy: let me specifically focus on Step 3. (Steps 1 and 2 as described in the presentation involve a number of statements along the lines of "we're currently working on this" and I'd like to have the opportunity to discuss these with Dr. Freitas before I criticise the ideas). I simply can't see why a nanocrystal will grow out from the tool tip as shown in Slides 83 – 87? That is, why will it have the shape shown in the slides, rather than minimise its surface area by 'filling out' at the bottom? (Did Giraud et al. observe this type of nanocrystal growth?!) That the substrate is passivated does not mean that the sticking coefficient of the impinging molecules is 0! Any molecule physisorbed on the surface will likely diffuse a considerable distance before desorbing. In particular, those molecules adsorbing from the vapour phase close to the tool-tip molecule will be able to diffuse to the base of the growing handle structure and surround the tool-tip. The growth process will also be complicated by surface reconstruction of the various facets of the handle structure. I'd appreciate it if you could let me know what I'm missing – i.e. why will the nanocrystal grow in a fashion whereby the tool tip remains "isolated" at the bottom of the grown structure?

The alternative strategy (outlined on Slide 100) also appears flawed. Why does the dehydrogenated 'diamond shard' not reconstruct to reduce the dangling bond density? Has a detailed DFT study been carried out on the combined tool-tip:"shard" structure? Why would the 'tool-tip' retain its structure when it binds to the diamond shard? And of particular significance for the arguments outlined below, just how does one measure and control/tune the force during the "insert-bind" phase (or indeed during any of the mechanosynthesis steps)? (Is it via SPM technology – interferometry, tuning forks, etc..?) [Please do not point me towards Section 11.2.2 (or similar 'force measurement-related' sections) of *Nanosystems* – that is not a strategy for force measurement, it's a "back of the envelope" calculation].

While I can seemingly identify flaws in Freitas' proposed methods, at least he (and Merkle) are attempting to outline a strategy (based around technology that to me looks as if it's fundamentally based on current SPM methods).

(A two sentence section which included a quote from Drexler has been removed at this point - PJM).

My question to Dr. Drexler – raised time and time again during our correspondence last year - remains: if not scanning probe technology then what? Why are Frietas and co-workers devoting so much time to a consideration of SPM methods if these are not ultimately relevant to mechanosynthesis? The 'Drexlarian' vision of mechanosynthesis necessitates computer-controlled actuation and positioning – *just how will these operations be carried out if SPM-type positioning and SPM-type tips are not to be used*? [I plead that you don't refer me to Chapter 16 of *Nanosystems* – I've read this and there is no coherent workable strategy capable of producing a prototype device described there].

The question of outlining workable strategies and formulating 'proof-of-principle' experiments was at the core of my argument with Dr. Drexler last year. In the final section of this letter/document, I outline why I feel that 'proof-of-principle' experiments are essential to illustrate that even the most basic steps in mechanosynthesis are possible.

(A sentence which described my interpretation of Drexler's position based on our e-mail correspondence has been removed at this point - PJM).

… it seems that Freitas and Merkle appreciate the relevance of defining appropriate strategies that might be tested by experiment.

Proof-of-principle experiments

I reproduce here what I feel is an important section from my correspondence with Dr. Drexler last year. It highlights the gulf between his approach to science and that of the vast majority of scientists I have met or with whom I've collaborated. I have highlighted a number of key phrases in bold type.

"Why then is so much effort devoted to density functional calculations of simple organic molecules while there is (apparently) no complementary experimental programme related to demonstrating an 'existence proof' of even the ***most basic operational step*** *of a molecular assembler****? I would argue that the performance of Reactions 16 – 21 in Reference 15 would provide an excellent 'proof of principle' experimental demonstration of reactive molecule manipulation****. (Although this is still only a small component of your overall molecular manufacturing concept which will also require assembler programming and self-replication). Are you or any of your colleagues working towards an experimental demonstration of this type?"*

Dr. Drexler's response to this was as follows:

(A four line quote from Drexler has been removed - PJM).

Dr. Drexler bemoans the lack of US government investment in molecular nanotechnology, yet on the basis of the statement above, is this absence of funding surprising? Why on earth would one expect to be awarded $Ms of public funding if there is not even an attempt to put forward a coherent strategy (…and, again, I plead that you don't cite *Nanosystems* in response), methodology, or 'proof-of-principle' experiment. If I was refereeing an NSF grant proposal that requested $5M dollars for the development of a novel **technology** and yet did not establish some type of experimental methodology to "support" the theoretical work, it would not be rated particularly highly. It appears that there are those at the Foresight Institute who agree with the significance of supporting 'proof-of-principle' experimental work:

"The purpose of this research is to influence further research, particularly experimental research. ***That is, a theoretical study, regardless of how penetrating or insightful, will not let us build molecularly precise products****."*

Moreover:

"The most important next step in achieving MNT is to provide clear and accurate descriptions of the fundamental chemical reaction…the purpose of this research is to influence further research, particularly experimental research. A significant reason for this… ***is the lack of a clear well-defined target whose feasibility has been well established by appropriate research****"*

[See: http://crnano.typepad.com/crnblog/2004/05/what_is_nanotec.html#comments
for further discussion related to the 'timeline' for molecular manufacturing].

My apologies for such a long response to your e-mail but I am keen that you (and Dr. Drexler and others at CRN and the Foresight Institute) do not assume that I am rejecting Freitas et al.'s work 'out of hand' without first carefully considering their ideas and reading their publications. I look forward to your responses to the issues raised above.

Best wishes,
Philip

Letter from Phoenix to Moriarty
November 30th 2004

I've read your letter, and by the time I finish writing this I will have read it twice. You raise some good points. Before I begin addressing them, I think it's important to distinguish several topics. In a field this speculative, it's all too easy for people to talk past each other, and arguments that would be decisive in one context may be irrelevant in another.

For example, the first distinction is between perception and physical possibility. You addressed perception at several points in your letter, as with your reaction to a hypothetical $5M pure-theory proposal. Although I agree that perception is crucially important in actually getting things done, I'd like to defer discussion of it until we've hashed out some issues of possibility.

The second distinction is between bootstrapping and mature technology. If a mature kinematic technology can do mechanosynthesis, and the first machine can be built with different methods, then mechanosynthesis is possible. This distinction gives us rather more flexibility in early-stage work. I'll return to this point.

The third distinction is between molecular manufacturing and mechanosynthesis. Molecular manufacturing is considerably broader. Although we are talking about mechanosynthesis in this conversation, other forms of molecular manufacturing may be important in bootstrapping. To me, molecular manufacturing encompasses any approach that can build gram quantities of atomically precise, functional product that is heterogeneous and engineered at all scales. As far as I can see, this requires computer- controlled nanoscale machines building nanoscale machines, where "machine" is taken broadly to include the ribosome--but not the cell, nor purely computational systems. Mechanical protection or deprotection of polymerization points, or mechanical selection of the sequence of monomers or deposition points,can be used to build engineered chemicals--and if the right monomers are chosen, engineered structures. This is one possible bootstrapping pathway.

With that distinction, we can make another, between limited MNT (LMNT)and near-universal MNT. LMNT requires only enough mechanosynthesis to support molecular manufacturing: that is, engineering closure for a manufacturing system to build and assemble all its parts. Smalley may have been talking about near-universal MNT when he said, "*The resultant technology of our 20th century is fantastic, but it pales when compared to what will be possible when we learn to build things at the ultimate level of control, one atom at a time.....It's amazing what one can do just by putting atoms where you want them to go*." http://www.house.gov/science/ smalley_062299.htm

Though both Smalley and Drexler recognize the ultimate desirability of near-universal MNT, I think the present conversation is about LMNT. Once we can build computer-controlled nanomachine fabricators in quantity, then we can start working (with the help of cheap petaflop computers and sub-molar quantities of parallel-testing robotics)to extend the chemistry. How close we can get to universal is unknowable at this point, and I'd argue that it's unimportant.

You raised the question of what exactly is meant by mechanosynthesis. In the context of the above distinctions, I would argue that the important distinction is whether the proposed manipulation/reaction can be carried out by a nanoscale robot in an integrated gram-scale manufacturing system. I hope we can agree that it's legitimate to engineer the electron distribution in the tool tip molecule to create static fields. But that creates a slippery slope.

Can we create a conductive pathway and move charges at one end to affect the field at the other? I'd be surprised if enzymes didn't use that trick. As long as we can show how to build it, I think we should be able to use it. But if we have a conductive pathway, what's wrong with hooking it to an external current source? This is not quite unlimited license, since an operation that required a picojoule of current per operation would not scale to the desired levels.I would argue that the use of electrostatics in mechanosynthesis appears quite legitimate, and I think it would be premature to rule out the use of electric currents. The importance of the mechanics is that it lets you choose the reaction site —not that it is a magically pure way of doing chemistry.

Finally, I want to touch on the difference between “exploratory engineering” and conventional engineering or scientific proposals. Much of what Drexler does is exploratory engineering. It works like this: First, assume the existence of an advanced but plausible technology. Second, figure out its implications: how well it can perform, and what else can be done with it. I suspect that the reaction to this approach depends heavily on one's personality. Most people, seeing a conclusion they don't like, will look for reasons why it might not be valid. And indeed, it's not difficult to argue that a diamondoid mechanosynthetic fabricator *might* not be valid. But a more cautious approach is to ask whether there's a possibility that it might in fact be valid, and if so, to incorporate the projected consequences into one's planning. I have found that if I assume that a problem in MNT has some solution, it is usually not hard to find a solution. In fact, the solution is usually simpler than I expected it to be.

To return to my point about bootstrapping: A milestone in MNT will be the first digitally controlled nanoscale robot capable of controlling molecular configuration with atomic precision to fabricate a copy of itself and its power/ control system under automated control. That covers a wide range of architectures. Unless one is prepared to argue that each architecture contains no designs within its design space, or that each design, though workable, cannot be built (bootstrapped) by any process whatsoever, one must accept that such a fabrication robot is possible. That opens the door to exploratory engineering. In such an exercise, it is no flaw to project the consequences of a technology for which one does not have the blueprints. And it is not “stonewalling” to refuse to supply blueprints which one does not have.

The ultimate utility of exploratory engineering is perhaps a matter of philosophy. One can reject the entire exercise, though as I said, I think that would be incautious. But it can't be judged by the completeness of its blueprints; that would be like criticizing inductive logic on the grounds that it is not purely deductive.

My point here is that Drexler has not tried to produce “proof of principle ” experiments, and thus should not be criticized for not doing so. Instead, Drexler has provided milestones, each of which he believes to be plausible. If someone argues that a certain milestone is implausible, he presents another milestone halfway between that and a previously established milestone, arguing implicitly that shorter and better-defined paths are more likely to be achievable —*but not ruling out the possibility of a different path to the disputed milestone*. (Eric, if I've misrepresented your approach, please correct me.) Again, this approach is different from engineering, and requires philosophical, not methodological disagreement.

I italicized the phrase in the previous paragraph because I think it answers some of your objections. Our discussion is taking place in the context of Drexler's projections of astonishingly high product performance on page 1 of Nanosystems. Can those be achieved? The necessary milestone is stiff, mechanical systems capable of building more of the same. All previous milestones are optional.

So when you discuss the difficulties of a “fundamental” reaction, I must disagree. No single reaction is fundamental, in the sense that the project collapses if it doesn't work. In addition to diamond, covalent mineral crystals include alumina, boron nitride, silicon carbide, silica, and silicon.

It is not probably not necessary that the system be built of covalent mineral crystal, or even using vacuum mechanosynthesis. A graphene/fullerene system would probably work just fine. “Buckybowls ” and 200-atom engineered graphene sheets have already been built via solution chemistry.

I'm not sure whether your argument about locating one tool with another applies to the bootstrapping phase of the project, or whether you're arguing that there's no physical way to build a system which can do that. In the latter case, I think you'd be on very shaky ground. In the bootstrapping phase, you're right that we don't know a way to do it yet, though I can think of several. For example, incorporate half of a chromophore pair in each of the tips, and measure the light emitted as they approach. Multiple pairs at different frequencies can be used for three-dimensional positioning. Or, characterize the position of each tip while scanning a known surface/feature, with respect to a larger feature attached to the tip (capacitive sensor, diffraction grid) that will allow precise positional measurement. Then move the tips into free space and le them approach each other from opposite directions.

You are right that the clock is ticking. However, since I began estimating the date when we would see molecular manufacturing, my estimate has moved steadily earlier even as time advances. It would not surprise me at all if someone developed a polymer-based molecular manufacturing system before 2010, and with the help of that, produced a high-performance diamondoid or graphene system before 2015.

With regard to your discussion with Drexler referenced on page 2 of your letter, you must have been talking past each other. It's clear that today's SPM's cannot be used for molecular manufacturing; they couldn't achieve the required throughput — they'd take far too long to process their own mass. It's equally clear that near-term deposition reaction experiments must use SPM's.

You ask about dehydrogenation. Freitas proposed to synthesize iodine-capped tools and deposit them on a surface, freeing the iodine. Doesn't that deal with the problem? Granted, that doesn't allow regeneration of the tool tip from acetylene. But it should allow a few depositions to be done for research purposes, using a fresh tool tip for each one.

I should make clear that research can be valuable even if it doesn't directly lead to a bootstrapping method. The more we know about dimer deposition —the more we can validate our models —the faster and more confidently we will be able to design bootstrapping recipes and MM architectures.(I should also clarify that I'm using “bootstrapping ” in the computer science sense of creating capabilities from more primitive capabilities.)

I'll ignore, for the duration of this letter, the question of how to attract public funding that you raise at the bottom of page 2.

On page 3, you raise the question of the definition of mechanosynthesis. As I implied above, I'm not sure it's useful to attempt to define it precisely, because the important question is not what method is used in an MNT fabricator, but whether one can be made to work. If I present you with a working kilogram-scale nanofactory that forms chemical bonds in vacuum to duplicate itself, I don't expect you to complain that it is not doing mechanosynthesis because it requires electricity to help the chemistry along. I don't think such considerations are more valuable now than they would be in such a case. Of course, there is value in simplifying the method, because simpler methods are more likely to be practical in the context of an eventual nanofactory.

Another reason why electrochemical demonstrations are relevant is that until recently, it was widely claimed that positional uncertainty would fundamentally prevent mechanosynthesis from working.

Electrochemical, atomically-precise SPM demonstrations — especially the recent Si/polystyrene one that worked at room temperature —serve to dismiss that objection.

And finally, precision electrochemical work gives us hints about what may be possible with mechanochemical work. If an atom is removed from a surface by any means, what the surface does afterward is surely of interest. In the polystyrene experiment, the dehydrogenated spot apparently did not migrate around the surface. This provides some indication that intuitions of surface migration based on metals may not be reliable guides.

You ask whether I agree that Oyabu's work is not an example of mechanosynthesis because it did not involve a pre-chosen reactive molecule. I find the question less important than you appear to. I would say that the work involves a pre- chosen molecular *family*, i.e. the family of silicon AFM tip structures. That's close enough for me.

Now, on to the experimental questions. You wrote, *"A particularly laudable aspect of Mann et al.'s paper (corresponding author: Freitas) on Si/Ge-triadamantane dimer placement tools is the relatively large number of possible tools they explore."* But they only explored two tips, and section 3.3 ends with, *"Further work should examine the impact of lower operating temperatures, the possible utility of Sn-and Pb-triadamantane molecules and other adamantane-based tool configurations proposed by Merkle and Freitas,2 and other dimer placement tool variants that might provide a purely exothermic dimer deposition reaction."* The fact that both of the reactions examined are endothermic is a bit surprising,but certainly doesn't cast doubt on the whole enterprise. After all, these are reactions with only one degree of mechanical freedom.To take just one example,they didn't look at what happens if the tip is twisted. Deformation of the tip may also be useful, as may the addition to the tip of electronegative atoms to modify the electron distribution of the dimer.

In the upper half of page 5, you raise the question of whether mechanosynthesis can encompass more than Smalley's "very, very short list" of reactions. Well, it's a good question, and you're right that there's no conclusive proof. But we must be careful to distinguish between "the initial, most basic and faltering steps" which are limited by our ability to build tools, and the capabilities that will be available once an initial set of tools has been built. If we once gain the ability to build tips that can move in four or six degrees of freedom instead of one or three, a much broader reaction space will be open to us.

You ask whether Giraud's method will "minimise its surface area by 'filling out' at the bottom." Is minimization of surface area a relevant mechanism in a covalent crystal at relatively low temperature? I would have thought that vapor-deposited moieties would bond rather quickly to the crystal where they landed and then not move further. A second mechanism of concern is whether molecules physisorbed on the substrate surface would migrate to the tool tip and bond there. My best answer is that this would appear likely to form a two-dimensional "collar" which would spread rather more rapidly than the three--dimensional crystal growing above it. Since no such collar was observed, this does not appear to be an operative mechanism. But asking Freitas and/or Giraud will give a better answer than either of us can come up with.I've written to Freitas with this question. You say, "The growth process will also be complicated by surface reconstruction of the various facets of the handle structure." But Giraud found that it made high--quality diamond. I guess the surfaces were H-terminated and didn't reconstruct, or the reconstruction re-reconstructed into diamond as more atoms were deposited on it. *"The resulting diamond layers presented a good cristallinity and the Raman spectra showed a single very sharp peak at 1331 cm(-1), indicating high-quality diamonds."* http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?cmd=Retrieve&db=PubMed&list_uids=11456874&dopt=Abstract

About the logistics of binding a small tool tip to a broken diamond shard:The binding is not intended to be precise. There may indeed be sparse binding between the shard and the molecule, due to partial reconstruction of the shard surface. It remains to be seen whether this is a substantial problem for experimental work, where even one or two successful depositions would be well worth doing.

Instead of trying to control the force during the “insert-bind ” phase, I would control the position. I'd detect the tool molecule in “tapping mode”, then lower the cantilever until it dropped into place due to surface forces, then lower it a bit more to provide a calculable force, then retract and see what I had. (I could tell whether and how the molecule was fastened to the tip by imaging a very sharp point; that will show the shape of the tip.) If I didn't pick up the molecule at all, I'd drop the cantilever lower next time.

Your statement, “*Dr.Drexler, however, does not agree with Freitas and Merkle ’s suggestion that SPM might be used to achieve positional control*,” is quite surprising. I suspect Drexler would see significant value in using an SPM to achieve positional control for preliminary research. That makes SPM's very relevant to mechanosynthesis. Again, we must distinguish between molecular manufacturing (the industrial activity) and mechanosynthesis (the method), and must distinguish further between preliminary research, bootstrapping, and high-throughput production. Your statements in that paragraph betray an unwarranted blurring of these distinctions. It's no wonder you have not been satisfied with what you've heard, if this is your understanding of the arguments!

From here, your letter goes deeper into conflation of topics and blurring of distinctions. I find your statement that Drexler is “fundamentally opposed ” to “proof-of-principle ” experiments to be more than surprising. There is a basic difference between planning for a future capability, and developing that capability. If Drexler is opposed to anything, I would guess that what he's opposed to is refusing to plan until conclusive experiments have been done. There,I agree with him. As long as it's uncertain whether molecular manufacturing can work, it would be extremely irresponsible to refuse to consider the possibility.

The discussion of funding is a sub-topic of perception, and this response is already too long, so I'll continue my deferral of perception-related topics to a future letter.

Chris

E-mail messages associated with preceding letters:

Subject: Do nucleated CVD crystals form a pyramid?
Creation Date 30/11/2004 20:07:56
From: Chris Phoenix
To: Rob Freitas

I'm discussing your proposal with Philip Moriarty. He's skeptical, but seems willing to look seriously. He asks how we can know that the CVD crystals will form the configuration shown in your slides 83-87. He suggests two mechanisms that could deform the pyramid:

1) the crystal will try to minimize its surface area. I didn't think that was operative for covalent crystals at low temperature.

2) molecules adsorbed on the substrate will migrate to the base of the seed and attach there. I'd think this would form a 2D collar that grew faster than the crystal, and this was not observed.

Can you give a better answer?

Chris

Subject: Re: Do nucleated CVD crystals form a pyramid?
Creation Date 01/12/2004 04:10:58
From: Chris Phoenix
To: Philip Moriarty

Here is Freitas's response to my questions about crystal growth:

''''''''''

The perfect inverted pyramid shown in the slides is, of course, the idealized case, used to communicate the essential concept. In an actual experimental setup, it is possible that the aspect ratio of this tool could be extremely poor. It may even be that the deposited crystal is "quasi-hemispherical but faceted", though Giraud's SEM images seem to show a well-faceted cubic-diamond (crystal) structure. Nevertheless, geometry dictates that the detached tool cannot be concave, and would at worst be flat, hence even at minimum can serve as a primitive tool to experimentally demonstrate positionally controlled diamond mechanosynthesis (DMS).

Alternatively, the detached tool may be somewhat better. Note that the deposition surface upon which the tool is grown is specifically selected from among "carbide exclusion" materials. Such materials have little or no solubility or reaction with C, and form no carbide layer. CVD experiments on such surfaces typically show negligible surface adsorption or crystal growth in non-nucleated areas, hence competing growth up from the surface in locations near the seed molecule (where no other seeds are present) is unlikely. Giraud's work also confirms essentially no crystal growth in areas where the vertically-mounted 2,2-divinyladamantane (DVA) seed molecules are absent. No "2-D collar" growth or other extraneous material around the tethered-molecule nucleation site has been observed experimentally. Only clean isolated crystal growth is seen during CVD. Growth also preferentially follows the crystal faces, which in the case of the C(110) faces (which grow 4-5 times faster than the C(111) or C(100) faces during CVD) lie upward at 45 deg from the vertical (given the orientation of the tooltip seed molecule).

Further observations on Giraud's (DVA/CVD) experimental system, perhaps using TEM imaging of early nanocrystals as suggested, might help resolve the question of tool aspect ratio in the close vicinity of the dimer attachment region. But even if the tool proves to be flat in that region, it would still be experimentally useful for demonstrating DMS, and for building limited subsets of vertical structures. One of the purposes of my proposal is to motivate this important experimental work to go forward.

''''''''''

My comment: The pictures in slide 99 make it look like the crystal tips sideways, but not as far as in Freitas's illustration in 83-87. If a flat surface grows around the seed (tooltip) molecule, but the surface plane is tipped with respect to the seed, then the dimer will not be presented to the diamond surface in the same orientation as what was simulated. You might still get a deposition reaction in this case, but it wouldn't be as easy to compare with molecular models.

Rob, can you send a higher resolution version of the picture in slide 99 showing the 10-12 crystals? If different crystals are tipped by different amounts, that would indicate some probability that the pyramid sides are growing down to the substrate forming a plane with an unpredictable angle. But I can't quite see that from this picture.

Chris

Subject: Re: Do nucleated CVD crystals form a pyramid?
Creation Date 30/11/2004 22:16:26
From: Philip Moriarty
To: Chris Phoenix

Chris,

Apologies for the lack of clarity in my writing. "*The crystal will try to minimize its surface area*" is a rather off-hand way of saying that the total free energy of the crystal as I see it will be much higher for the crystal as sketched in Dr. Freitas' proposal than for a 'quasi-hemispherical' (but faceted) structure. (It's a little bit difficult to explain this structure without a diagram - if you need further clarification please let me know). The question of kinetics vs thermodynamics (i.e. Chris' point 1) is a very good one and certainly I have no problem with a certain structure being kinetically locked into a metastable phase. I think, however, that the '**inverted** pyramid' structure as shown in Dr. Freitas slides is extremely unlikely. As regards a 2D 'collar', it's not at all clear to me why this 2D layer would grow faster than the 3D crystal and thus be easily observable in SEM images. I think that the crucial experimental observation needed is cross-sectional TEM - do you know whether this type of measurement was possible/ carried out by Giraud et al.? *If* it turns out that the crystal indeed grows as described in Dr. Freitas' presentation (i.e. with no 'extraneous' material around the tool tip) then I will be extremely surprised (but rather impressed!).

As regards your letter, I'll try to respond before the end of the week but I am currently extremely busy with undergraduates and administration and am finding it difficult to find time. However, I'll briefly address two points that you raise:

(i) "On page 3, you raise the question of the definition of mechanosynthesis. As I implied above, I'm not sure it's useful to attempt to define it precisely, because the important question is not what method is used in an MNT fabricator, but whether one can be made to work."

My apologies, but I simply can't accept that a basic definition is not required - we may already have reached a critical impasse in this discussion. The problem is that if one doesn't precisely define what is meant by 'mechanosynthesis' then *any* type of atomic/molecular manipulation experiment can be classed as a verification of the Drexlerian 'vision'. Similarly, every single advance in nanometre scale materials processing could be claimed as a vindication of "Nanosystems". Perhaps you would argue that this is acceptable. I obviously can't agree. More on this in a later e-mail.

On a similar theme: "*You ask whether I agree that Oyabu's work is not an example of mechanosynthesis because it did not involve a pre-chosen reactive molecule. I find the question less important than you appear to. I would say that the work involves a pre- chosen molecular family ,i.e.the family of silicon AFM tip strucures. That's close enough for me.*"

I indeed find the question to which you refer extremely important - it lies at the heart of my difficulties with the 'mechanosynthesis' vision. If one can continually reinvent the definition of mechanosynthesis (e.g. so that 'reactive molecules' now also spans 'AFM tips') then I can't see how the debate can proceed in any useful manner. [Richard, I'd be extremely interested - if you can spare the time - in your views on this].

..and, remaining with this issue for one last point: "*You raised the question of what exactly is meant by mechanosynthesis. In the context of the above distinctions, I would argue that the important distinction is whether the proposed manipulation/reaction can be carried out by a nanoscale robot in an integrated gram-scale manufacturing system.*"

Sorry - but to a physicist this definition is completely useless (and rather 'circular' don't you think: mechanosynthesis is what a nanoscale robot carrying out mechanosynthesis does...?).

(ii) On another point of clarification: "I'm not sure whether your argument about locating one tool with another applies to the bootstrapping phase of the project..." - yes, absolutely - it would of course be difficult to rule out "tip-tip location" in terms of basic physical principles. More on AFM, tips and cantilevers later...

Best wishes,

Philip

Subject: Re: Do nucleated CVD crystals form a pyramid?
Creation Date 01/12/2004 03:24:12
From: Chris Phoenix
To: Philip Moriarty

[Quotes from my previous e-mail to Chris are in italics - PJM].

Apologies for the lack of clarity in my writing. "The crystal will try to minimize its surface area" is a rather off-hand way of saying that the total free energy of the crystal as I see it will be much higher for the crystal as sketched in Dr. Freitas' proposal than for a 'quasi-hemispherical' (but faceted) struture.

Ah. You and Richard Jones both react as though equilibrium states were important in stiff covalent systems. At least you seem more willing than Richard to acknowledge that "The question of kinetics vs thermodynamics (i.e. Chris' point 1 below) is a very good one and certainly I have no problem with a certain structure being kinetically locked into a metastable phase."

As regards a 2D 'collar', it's not at all clear to me why this 2D layer would grow faster than the 3D crystal and thus be easily observable in SEM images.

The collar could grow both by deposition from gas and by deposition from surface-adsorbed migrating molecules.

*I think that the crucial experimental observation needed is cross-sectional TEM - do you know whether this type of measurement was possible/ carried out by Giraud et al.? *If* it turns out that the crystal indeed grows as described in Dr. Freitas' presentation (i.e. with no 'extraneous' material around the tool tip) then I will be extremely surprised (but rather impressed!).*

Let's wait for Freitas to answer this; I'm sure he's studied Giraud's work in detail.

(i) "On page 3,you raise the question of the definition of mechanosynthesis. As I implied above, I'm not sure it's useful to attempt to define it precisely,because the important question is not what method is used in an MNT fabricator, but whether one can be made to work."

*My apologies, but I simply can't accept that a basic definition is not required - we may already have reached a critical impasse in this discussion. The problem is that if one doesn't precisely define what is meant by 'mechanosynthesis' then *any* type of atomic/molecular manipulation experiment can be classed as a verification of the Drexlerian 'vision'.*

This would only be a problem if I were trying to play the game of searching for evidence to "verify" the "Drexlerian 'vision'". I'm not, and I'm surprised you would think I am.

My goal is to evaluate the likelihood that a nanoscale machine can guide or induce chemistry with sufficient precision to build a copy of itself using only simple chemicals, information, and energy. If it's theoretically possible, I'm trying to develop at least a crude estimate of how much time and effort it would take to build the first such device, and whether it would require scientific breakthroughs or just R&D. And I'm also interested in a narrower version of the question, involving high-performance materials (probably covalent crystal or graphene).

You see, my goal can be stated without the words "mechanosynthesis" or "Drexler." We don't need either of those words to talk about practicalities.

Similarly, every single advance in nanometre scale materials processing could be claimed as a vindication of "Nanosystems". Perhaps you would argue that this is acceptable. I obviously can't agree. More on this in a later e-mail.

Again, I am not trying to vindicate Nanosystems, and certainly not by scraping together questionable bits of irrelevant evidence. I thought we were talking about mechanically constrained depositional chemistry, not Nanosystems. If you want to attack me for a tactic I don't practice and have no interest in defending, then yes, the conversation is over; but don't try to pretend that that's my fault.

On a similar theme: "You ask whether I agree that Oyabu's work is not an example of mechanosynthesis because it did not involve a pre-chosen reactive molecule.I find the question less important than you appear to. I would say that the work involves a pre- chosen molecular family i.e.the family of silicon AFM tip strucures. That's close enough for me."

I indeed find the question to which you refer extremely important - it lies at the heart of my difficulties with the 'mechanosynthesis' vision. If one can continually reinvent the definition of mechanosynthesis (e.g. so that 'reactive molecules' now also spans 'AFM tips') then I can't see how the debate can proceed in any useful manner.

Well, if the debate is over the precise definition of mechanosynthesis, then I would agree with you that it's not useful. In fact, I already said as much.

I would rather debate, for example, whether Oyabu's work implies that silicon can be moved around even more effectively with a better engineered tip, or whether it's likely that Oyabu's approach can be extended to carbon (diamond tip on diamond surface).

..and, remaining with this issue for one last point: "You raised the question of what exactly is meant by mechanosynthesis. In the context of the above distinctions,I would argue that the important distinction is whether the proposed manipulation/reaction can be carried out by a nanoscale robot in an integrated gram-scale manufacturing system."

Sorry - but to a physicist this definition is completely useless (and rather 'circular' don't you think: mechanosynthesis is what a nanoscale robot carrying out mechanosynthesis does...?).

Well, that's not what I said. I'm not sure how you got from "robot in an integrated gram-scale manufacturing system" to "robot carrying out mechanosynthesis." My point is that whether an operation can be used in gram-scale manufacturing is much more important than whether that operation is or isn't mechanosynthesis.

Chris

Subject: Re: Do nucleated CVD crystals form a pyramid?
Creation Date 02/12/2004 09:38:20
From: Richard Jones <r.a.l.jones@sheffield.ac.uk>
To: Chris Phoenix (cc PJM)

Dear Chris,
I'm mostly leaving this to you and Philip, but I can't let this go by:

> Philip Moriarty wrote:
>> Apologies for the lack of clarity in my writing. "The crystal will try
>> to minimize its surface area" is a rather off-hand way of saying that
>> the total free energy of the crystal as I see it will be much higher for
>> the crystal as sketched in Dr. Freitas' proposal than for a
>> 'quasi-hemispherical' (but faceted) struture.
>
> Ah. You and Richard Jones both react as though equilibrium states were
> important in stiff covalent systems. At least you seem more willing
> than Richard to acknowledge that "The question of kinetics vs
> thermodynamics (i.e. Chris' point 1 below) is a very good one and
> certainly I have no problem with a certain structure being kinetically
> locked into a metastable phase."
>

You must have misunderstood me if you think that I don't think kinetic trapping is important - there's an entire section in Soft Machines about it (Beyond simple self-assembly, pp 117 - 120). The point I've been trying to make to you, evidently not entirely successfully, is that even in systems which can't get to full equilibrium, it is still important to understand where equilibrium is, because that's the direction towards which the system will evolve. The system will always move in the direction of lowering its free energy; the only exceptions to this are when the kinetics is so slow that no evolution at all is possible. In deposition problems, for example, this is the limit known as ballistic deposition, where atoms simply lie where they fall. It's clear that this isn't the situation in the diamond CVD case; the carbon atoms have some freedom to move around, and free energy considerations determine where they are most likely to attach to the growing crystal. This is obvious from Freitas's response - he says that growth is fastest on the C(100) face. The very existence of faceted crystal habits tells you that surface energy considerations must be important in crystal growth even of the most strongly covalently bonded substances. Read, for example, "The science of crystallisation" by W.A. Tiller (CUP, 1991) for a detailed exposition of this rather classical materials science.

Best wishes,
Richard

Subject: Re: Do nucleated CVD crystals form a pyramid?
Creation Date 02/12/2004 16:43:50
From: Chris Phoenix <cphoenix@CRNano.org>
To: Richard Jones (cc PJM)

Richard Jones wrote:
> *You must have misunderstood me if you think that I don't think kinetic*
> *trapping is important - there's an entire section in Soft Machines about it*
> *(Beyond simple self-assembly, pp 117 - 120). The point I've been trying to*
> *make to you, evidently not entirely successfully, is that even in systems*
> *which can't get to full equilibrium, it is still important to understand*
> *where equilibrium is, because that's the direction towards which the system*
> *will evolve. The system will always move in the direction of lowering its*
> *free energy; the only exceptions to this are when the kinetics is so slow*
> *that no evolution at all is possible.*

I guess it's more of a difference in approach. You see slow kinetics as a rare exception, and your last sentence sounds like you assume that if the system is active at all, then it will be able to move toward its lowest free energy state.

I see the reconstruction of a covalent system as the exception. Kinetics is usually slow enough, at room temperature, with CHON, that rearrangement of bonds is extremely improbable. But that doesn't mean the system is inert! It can evolve in all sorts of molecular mechanics and kinematics directions. Sure, there will be some systems where an unexpected combination of forces or vibrations or electron density causes a bond to rearrange. But those should be rare, and not take much of the design space; we can learn what they are and avoid them.

Certainly, in a molecular machine system that doesn't have to metabolize, the molecules will experience condidtions far less random and varied than a biological system. So I'd expect them to be less likely to reconstruct. But even in biological systems, most of the damage is done by very reactive species; two random chemicals randomly bumping into each other almost never cause a bond rearrangement.

So your ever-present question about equilibrium seems to me to be only a distraction. In practice, if a molecular machine system has non-zero bond rearrangement kinematics, the appropriate thing to do is to re-engineer the system, not try to figure out exactly how it will break.

Whether it will break at all is a different question. And it is a very important question. But that question is not answered by looking at the minimum, but at the first barrier.

> *In deposition problems, for example, this is the limit known as ballistic deposition, where*
> *atoms simply lie where they fall. It's clear that this isn't the situation in the diamond*
> *CVD case; the carbon atoms have some freedom to move around, and free energy*
> *considerations determine where they are most likely to attach to the growing*
> *crystal. This is obvious from Freitas's response - he says that growth is*
> *fastest on the C(100) face. The very existence of faceted crystal habits*
> *tells you that surface energy considerations must be important in crystal*
> *growth even of the most strongly covalently bonded substances.*

There are five possibilities for an atom/molecule encountering a surface. It can bond in place--either from thermal noise, or with the help of its kinetic energy; it can diffuse across the surface; or it can leave the surface--again from thermal noise or from its unthermalized kinetic energy ("bouncing off").

So it's not immediately obvious to me that the preferential growth of crystal facets necessarily implies that surface diffusion is a relevant mechanism. If all atoms striking the surface stick to it, then yes, surface diffusion would appear to be the only mechanism that could explain facets, let alone preferential face growth. But we're talking about methane--I don't think we can expect a methane adsorbed on a surface to migrate around looking for the lowest energy configuration.

Another question is, is there a combination of parameters that'll keep methane from bonding to the lower sides of the pyramid near the tool tip? If the bonding is a result of adsorption plus thermal energy, then probably not; the gas will diffuse there, stick, and bond. But if the bonding results from kinetic energy, then it may be possible to minimize deposition under the overhang provided by the top of the crystal.

So I won't rule out completely yet the possibility of growing a pointy pyramid, but I agree it doesn't look good at this point (no pun intended). Just remember that CVD diamond was thought for years to be contrary to the laws of thermodynamics.

Chris

Subject: Freitas' inverted pyramids
Creation Date Fri, Dec 3, 2004 9:13 am
From: Philip Moriarty
To: Chris Phoenix

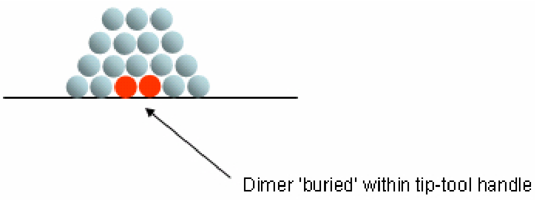
Chris,

Regarding the growth of inverted pyramids in Frietas' scheme, I obviously endorse the arguments outlined in Richard Jones' e-mail and would like to add the following:

I mentioned in a previous e-mail that I was going to draw some schematic diagrams of the growth process as I see it. As the diagrams I had in mind already exist in many places in the literature, I thought that I'd save myself some effort and simply refer you to the seminal work of John Venables on crystal growth. A particularly good recent reference is J. Vac. Sci. Tech. A **21** S96 (2004) – this is a detailed review/ overview of John's work on nucleation and kinetics in crystal growth. Fig.1 provides a nice synopsis of the various atomistic processes active in growth.

In my previous e-mail, I was using the adjective 'extraneous' in its broadest possible sense (admittedly somewhat unclearly – my apologies). What I meant was that the molecules adsorbing on the surface and subsequently diffusing to the nucleation site would 'surround' the primary tip tool molecule – i.e. the dimer (see simple diagram below). There is no reason why this process should result in lateral growth which is faster than the 'vertical' growth of the handle (see below). It's also important to note that obviously the methane is a precursor for diamond growth and a microwave plasma is used to create the free radicals necessary for growth. In terms of the diffusion processes, consider the 2D cluster shown on the right hand side of Fig.1 of Venable's JVST paper cited above. There needs to be 'overhang' of 2nd layer atoms at the edges of the cluster if this initial 2D structure is to grow as an inverted pyramid. Why would an atom bond by 'hanging off' the edge of the cluster where it has only two neighbours when there are more highly coordinated (i.e. lower energy) sites either in the 2nd layer or in the 1st layer? Moreover, to bond in this highly unstable manner, the atom has to surmount a rather hefty additional barrier (as compared to diffusion on a "flat" 2D plane) arising from the Schwoebel effect (see http://www.nottingham.ac.uk/~ppzpjm/sect4_4.htm for details) *and* then refuse to follow the potential energy surface in the "correct" direction. (There's "far from equilibrium" and then there's "*far* from equilibrium"!). I realise that the materials system in Freitas' proposal is much more complicated but the underlying concepts and reasoning are the same.

It's furthermore worthwhile noting that there is a very substantial body of literature on MBE, CVD, and MOCVD growth of quantum dots and nanoclusters where, in each case, the resulting structure is best described as a pyramid (i.e. a faceted island as sketched to the right) or, at worst, a 'quasi-hemispherical' (or 'lens') structure. Moreover, while one should bear in mind that *all* vapour phase growth processes occur out of equilibrium (one doesn't have detailed balance and hence the system can't be at equilibrium), in a considerable number of experiments we work in a limit where the system is relatively close to equilibrium and thermodynamic concepts that are strictly only valid at equilibrium are actually quite applicable (see discussion of Stranski-Krastanow-, Frank-van der Merwe-, and Volmer-Weber growth at http://www.nottingham.ac.uk/~ppzpjm/sect4_5.htm).



I'll also briefly address some pertinent comments in your second e-mail to Richard Jones today:

1. "But we're talking about methane--I don't think we can expect a methane adsorbed on a surface to migrate around looking for the lowest energy configuration."

The process in Giraud's experiments is microwave plasma CVD – so there's not a lot of methane involved in the growth. Rather, the chemistry is radical-based.

2. "Another question is, is there a combination of parameters that'll keep methane from bonding to the lower sides of the pyramid near the tool tip?"

Ditto – it's not methane that's the active species (plus see discussion above re. 'inverted pyramids').

I'll address your additional questions re. surface diffusion and thermalisation and return to a discussion of other aspects of Freitas' "How Do We Build The First DMS Tool" strategy in a letter either tomorrow or over the weekend. (Sorry for the abrupt end but I've just realised that it's 1:15 am here).

Best wishes,

Philip

Subject: Clarification
Creation Date Fri, Dec 3, 2004 10:38 am
From: Philip Moriarty
To: Chris Phoenix

Chris,

I've just read over what I wrote in the document of 03/12/04 and the following sentence is confusing and very poorly worded: "*There is no reason why this process should result in lateral growth which is faster than the 'vertical' growth of the handle (see below).*" What I mean is that your argument regarding the growth of a 2D "collar" is not sound: the diffusion kinetics on the substrate are much different to the diffusion kinetics along the tip tool "handle" so one can't just 'bundle' the rate constants together. That is, your argument is based on the incorrect assumption that surface diffusion + adsorption directly from the gas phase on the substrate will lead to a higher growth rate than along the handle of the tool because (in your model) only adsorption directly from the gas phase is important for the handle.

I am pleased that the discussion is focussing on sound physical ideas and strategies. You are most likely correct in stating that Drexler and I 'spoke past' each other. Nevertheless, it was exactly this type of discussion I wanted to pursue with Drexler. [I promise that I'll respond to your earlier, more general points on perception, bootstrapping etc.. within the next few days].

Subject: Facets and nanowires
Creation Date 03/12/2004 14:13:49
From: Philip Moriarty
To: Chris Phoenix

Chris,

When you get the time, have a look at J. Phys. Chem. B 108 18803 (2004) - it's a rather nice topical example of just how complex crystal growth can be. Note that while Fig. 3 might suggest that there's some mileage in Freitas' inverted pyramid idea, the 'seed' for the growth of the nanowires is an island similar to that sketched in the document I sent to you earlier today (and note just how much of the Zn_2TiO_4/TiN buffer layer the 'footprint' of the structure occupies) . Moreover, the angles at which the nanowires grow (with respect to the substrate surface normal) are directly related to the lowest free energy surfaces (i.e. the ZnO (0001) planes - but, as the authors discuss, there is a slight deviation due to strain). As Richard pointed out in his e-mail of 02/12/04: "the very existence of faceted crystal habits tells you that surface energy considerations must be important in crystal growth...". This is already clear from Freitas' response but I think that the paper cited above is a very nice complementary case.

Moreover, I really recommend that you study Venables' papers - I have learnt a heck of a lot about crystal growth from John's work. A few lines from his website are particularly useful in the context of the current discussion:

" *In particular, the nucleation barrier concept can be explored in both classical (macroscopic surface energy) or in atomistic terms..... It is rather artificial to think about surface energies of monolayers and very small clusters in terms of macroscopic concepts like surface energy. Numerically, the critical nucleus size, i, can be quite small, sometimes even one atom; this is the justification for developing an atomistic model, as discussed in the next section. **However, an atomistic model should be consistent with the macroscopic thermodynamic viewpoint in the large-i limit.*** "

Subject: Re: Clarification
Creation Date 03/12/2004 21:47:00
From: Chris Phoenix
To: Philip Moriarty

[Note that two paragraphs have been edited from this message as they were related to the logistics of posting the debate on an appropriate website and thus don't contribute to the overall debate - PJM].

Philip Moriarty wrote:
> *That is, your argument is based on the incorrect assumption that*
> *surface diffusion + adsorption directly from the gas phase on the*
> *substrate will lead to a higher growth rate than along the handle of the*
> *tool because (in your model) only adsoprtion directly from the gas phase*
> *is important for the handle.*

Yes, my argument is based on the assumption that a sub-methane radical will not stay unreacted on the tooltip surface long enough to diffuse very far. I was thinking it'd either react and then stick in place, or "boil off" due to its small size vs. the tooltip surface temperature. If that assumption is incorrect, then my argument falls apart; and in that case, I'd have to agree that energy considerations would be quite important.

But then I'd think that raising the temperature of the tooltip surface would increase boiloff at least as fast as diffusion, and would increase reaction speed a lot faster. If there was a "sweet spot" where it was too cold for bonded surface atoms to migrate, but too hot for non-bonded species to migrate, then I'd think minimum-energy considerations could take less importance. (This doesn't violate thermodynamics because the system can be kept far out of equilibrium by the bond-breaking energy supplied by the plasma.)

But based on what you've said, I'll agree that there's no particular reason to think we'd see a collar under random conditions.

> *I am pleased that the discussion is focussing on sound physical ideas*
> *and strategies. You are most likely correct in stating that Drexler and*
> *I 'spoke past' each other. Nevertheless, it was exactly this type of*
> *discussion I wanted to pursue with Drexler. [I promise that I'll respond*
> *to your earlier, more general points on perception, bootstrapping etc..*
> *within the next few days].*

I'm glad that this discussion is satisfying. I'm enjoying it too. I'm looking forward to seeing your response to what I wrote about bootstrapping. I didn't say anything about perception other than that it was a separate topic from technical feasibility, though of course the topics merge as soon as we consider the timeline of development.

Chris

Following this e-mail, a second letter was sent from Moriarty to Phoenix. For this letter , Phoenix's response, and the associated e-mail correspondence, see Part II of the debate.