Phoenix-Moriarty debate: Part II
E-mails and letters Dec. 12th – Dec. 31st '04

In the following, lines and passages from e-mails sent by 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**.

Letter to Chris Phoenix from Philip Moriarty, Dec. 12th 2004

Chris,

My sincere apologies that it has taken rather longer to respond to your recent e-mails than I had first anticipated – it tends to get a little more hectic for me towards the end of each term. Let me first return to the questions related to Freitas' tip tool strategy. I'd like to address some of Freitas' comments directly (please feel free to forward this letter to him if you feel that he and/or Merkle might be interested in commenting on the issues below).

From your e-mail of 01/12/04 which contained Freitas' response:

"It is possible that the aspect ratio of this tool could be extremely poor…would at worst be flat, hence even at minimum can serve as a primitive tool to experimentally demonstrate positionally controlled diamond mechanosynthesis (DMS)"

I must admit that I can't see how a *flat* tool could be used for the DMS reactions described in Freitas' proposal (or those in his previous papers with Merkle et al.). First, the additional carbon atoms surrounding the weakly bonded C dimer (which originally protrudes from the base of the triadamantane dimer placement tool) will make the dimer-by-dimer synthesis of layers of diamond impossible due to steric hindrance arising from the width of the tool. (I think that Freitas tacitly accepts this when he states later in his message that a flat tool could be used *"for building limited subsets of* ***vertical*** *structures"* [emphasis in bold type is mine] but please forgive me if I've misinterpreted his comment). It's worth noting that this is an alternative take on the 'fat fingers' argument.

Second, I'd be extremely interested in an ab initio calculation which accounts for the flat tip tool geometry. For the ideal case (i.e. with a tip-tool+handle having a perfect 'tetrahedral' geometry) Mann et al. [J. Comp.Th. Nanosci. **1** 79 (2004)] find a success rate for Ge triadamantane-based dimer deposition of ~ 20%. With one large flat slab of diamond approaching another, the total van der Waals (vdW) interaction energy (which can roughly be calculated using an Hamaker/ Lifshitz theory approach such as that described in Chapter 3 of Nanosystems and references therein [particularly Israelachvili]) scales directly with area. I would expect that this additional vdW interaction (and its overall dependence on plane-plane separation) would rather strongly affect the overall potential energy landscape. I do realise, however, that an ab initio calculation for the flat tool geometry will be rather computationally expensive.

Third, I'm not at all convinced that I know what Freitas means by "*limited subsets of vertical structures*". This sounds as if he is arguing that one could grow a small (one dimensional?) 'pillar' of dimers from an initial de-hydrogenated site on the diamond surface. Before I pursue this further, however, I'd appreciate it if Freitas could clarify just what he means by 'vertical structures'.

Addressing a number of comments in your e-mail of 03/12/04:

"But then I'd think that raising the temperature of the tooltip surface would increase boiloff at least as fast as diffusion"

"Boil-off" (with its associated phase transition connotations) is not a good term to use here – "evaporation" is much more appropriate. The evaporation and diffusion rates are both described by a very simple Arrhenius expression of the form:

$$\nu = \nu_0 \exp(-\Delta E / kT)$$

where ΔE is either the desorption energy or the diffusion barrier. The energy barrier associated with diffusion is smaller than that for desorption and thus "boil-off" (i.e. evaporation) can't increase "at least as fast as diffusion".

"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 the adsorbing species just 'stick in place' then we're in the ballistic deposition limit briefly discussed by Richard Jones in his e-mail to you on this topic. If the temperature is high enough for the adsorbant to, as you put it, "boil off", it's certainly high enough for diffusion to occur.

"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.)"

I have extreme difficulties trying to picure what you mean here. If we ignore for now the - let's say, non-trivial - practical problems of engineering the thermal properties of the system so that you can produce the 'sweet spot', I'm still in the dark as to the physics underlying your proposed scenario. By "bonded" and "non-bonded" do you mean "chemisorbed" and "physisorbed" respectively? Why would some of the radicals physisorb and others chemisorb? A sketch would perhaps be useful here. I think, however, that we might be going down a blind alley. I hope that I've done enough to convince you at this point that the tool handle growth proposed by Freitas is flawed.

Let me now turn to your carefully considered letter of 30th November '04 (i.e. the Moriarty 1.pdf document). You first ask that we defer a discussion of perception. This is fine with me and we can certainly address this issue in future correspondence. To progress, however, and before I address the technical issues raised in your letter, I first need to return to what remains for me an extremely important element of the molecular manufacturing debate: *the requirement for clear and careful definitions/ delineations of the underlying principles and processes*. [*Quote from Drexler removed - PJM*]. So, in the following, please bear with me while I reiterate my arguments on the significance of 'nailing down' – to borrow a phrase from *Engines of Creation* – some definitions. I apologise if I appear somewhat pedantic in doing this but, as I know from collaborative work with colleagues in the life sciences and, more recently, computer science, it's easy to get very confused (very quickly) if a common vocabulary is not adopted.

A Question of Defintion

"New fields often need new terms to describe their characteristic features, and so it may be excusable to begin with a few definitions". So writes Drexler on p.1 of *Nanosystems*. Similarly, we find a dictionary definition of 'machine' on p.3 of *Engines of Creation*. Moreover, the CRN website features a helpful glossary of some of the key terms in nanotechnology. For example:

"Molecular manufacturing: *The building of complex structures by mechanochemical processes."*

As you know, "mechanochemical" in the definition above is associated with a hyperlink to the following entry:

"Mechanochemistry: *Chemistry accomplished by mechanical systems directly controlling the reactant molecules; the formation or breaking of chemical bonds under direct mechanical control. [See "How does 'mechanochemistry' work?]"*

Turning to *Nanosystems*, we find the following:

*"**Mechanosynthesis**: chemical synthesis controlled by mechanical systems operating with atomic-scale precision, enabling direct positional selection of reaction sites"*

"Molecular manufacturing: *The production of complex structures via nonbiological mechanosynthesis"*.

If I now re-read your letter and consider the definitions above, I am immediately confused by the following passage:

"The third distinction is between molecular manufacturing and mechanosynthesis…Although we are talking about mechanosynthesis in this conversation, other forms of molecular manufacturing may be important in bootstrapping".

How does this passage 'tally' with the CRN or *Nanosystems* definition of molecular manufacturing? According to both Drexler and the CRN website, molecular manufacturing is fundamentally based on mechanosynthesis and mechanochemistry. You seem to deviate from this definition but then state that a possible bootstrapping pathway might involve "*mechanical* protection or deprotection of depolymerisation points" or "*mechanical* selection of the sequence of monomers" – but are each of these processes not mechanosynthesis? So, if 'gram scale manufacturing' is derived from 'molecular manufacturing' which in turn is derived from 'mechanosynthesis', I stick with my assertions in previous e-mails. That is, if mechanosynthesis is defined, as you suggest, in terms of "*whether the proposed manipulation/reaction can be carried out by a nanoscale robot in an integrated gram-scale manufacturing system*", then this 'definition' is (a) void of information content, and (b) circular.

Remaining with the question of definitions, you [*sentence edited to remove reference to Drexler – PJM*] seem to think that it is worthless "quibbling" over whether or not mechanosynthesis involves the manipulation of single atoms or reactive molecules[†]. I could not disagree more. Drexler himself states the following in his open letter to Smalley:

"My proposal is, and always has been, to guide the chemical synthesis of complex structures by mechanically positioning reactive molecules, ***not by manipulating individual atoms****."*

[†] I realise that you have stated that you are not attempting to validate "Nanosystems". However, your letter is very much couched in terms of the "Drexlarian" concept of molecular manufacturing.

Although the emphasis in bold type is mine, it is very clear that Drexler feels there is a critical distinction to be made between single atom manipulation and the mechanosynthesis concept he has expounded in his work (and which is detailed on the CRN website)[‡]. This distinction is crucial. You state towards the end of your letter that I have conflated topics and am guilty of *"an unwarranted blurring of distinctions"* - an accusation with which I actually have some sympathy (see below). To suggest, however, that definitions of the processes underlying MNT are not required represents a comparable unwarranted blurring of distinctions. Any attempt to develop molecular manufacturing necessitates a clear and consistent picture of just what is required at the atomic/ molecular level (regardless of whether demonstration of the mechanosynthesis steps is the first or last step in the supposed 'implementation pathway' – again, see below). The manipulation of individual atoms is radically different from the atomic scale positioning of reactive molecules and to state that drawing a distinction between these is 'quibbling' or, worse, is unimportant betrays a startling lack of appreciation of the underlying physics and chemistry *and* the associated experimental complexities.

(On a somewhat - but not entirely - frivolous point with regard to definitions, you suggest *"I'm not sure that it's useful to attempt to define it* [mechanosynthesis] *precisely because the important question is not what method is used in an MNT fabricator but whether one can be made to work"*. This statement puts me in mind of Richard Dawkins' impassioned plea for a *"usable or even faintly coherent"* definition of 'postmodernism'. [*A Devil's Chaplain*, R. Dawkins, Weidenfeld & Nicholson (2003)]. I have yet to meet a philosophy student who has provided any semblance of a satisfactory definition of postmodernism – they also tend to argue that it's not 'useful' to attempt to define it. It would be rather a shame if the term "mechanosynthesis" were relegated to a similar status!)

Exploratory Engineering and Drexler's approach

A large section of your letter focuses on exploratory engineering and bootstrapping. To my mind, your arguments largely distil a considerable amount of Chapter 16 of *Nanosystems (*and Appendix A of that volume) into a few clearly written paragraphs. This, in itself, is extremely helpful because it facilitates an insight into the differences in 'mindset'/perspective between those working in the physical sciences as compared to the viewpoints of engineers and computer scientists. When I have previously broached the topic of strategy Drexler has continually pointed me to Part III of *Nanosystems*. Let me state, once again, that I've read *Nanosystems* (my copy is now rather dog-eared) and, as your arguments on exploratory engineering are extremely supportive of Drexler's approach, I hope that you'll forgive me if I again refer to *Nanosystems* in the following discussion.

Your comments on bootstrapping, exploratory engineering, and 'proof-of-principle' experiments seem to parallel Drexler's 'backward chaining' argument in Section 16.2 of *Nanosystems*. Is this a fair comparison? If so, we agree that the goal – in Drexler's approach - is to plan backwards towards situations that are 'immediately accessible'. In section 16.2.3 of Nanosystems, a four-stage route towards molecular manufacturing is suggested with AFM-based molecular manipulation of polymers forming the first stage. Note that the alternative vacuum-based mechanosynthesis route described by Merkle et al. **is cited as an alternative Stage 1** (and it is this strategy for Stage 1 that we have debated in our correspondence to date). At this point, let us consider what is required for Stage 4 (which, in fact, is the low level 'machine language' process at the heart of molecular manufacturing: *"advanced nanomachines will themselves be products of advanced mechanosynthesis"* [Section 8.1, Nanosystems]). Can we agree that the *fundamental low-level processing steps/ criteria/ design constraints* [note that I have not described a particular *reaction* as *fundamental*] are the following:

1. The ability to manipulate individual molecules with atomic precision [let's ignore for now Drexler's confusing and misleading references to 'atom by atom' construction and take the definition used in his open letter to Smalley];

[‡] Nevertheless, there are numerous instances in Drexler's writings where mechanosynthesis is described in terms of "atom by atom" processing.

2. The ability to control via (internal or external) computer-actuated transducers the trajectories of large numbers of atoms (either sequentially or in parallel) with a precision that is comparable to an atomic diameter;

3. The ability to form covalent bonds between reactive molecules on a bond-by-bond basis by selecting individual reaction sites with atomic scale precision.

4. ...and, if robotic grippers are to be used to pick up workpieces constructed by mechanosynthesis or to construct nanomachines from their component parts [see Part II of *Nanosystems*] (that is, to successfully integrate Stage 4 with "higher level modules"): *the ability to arbitrarily passivate and depassivate multiatom surface regions yet retain molecular/atomic level control of the surface structure*. (One could argue that this is simply an alternative statement of criterion 1 but it's so important in terms of 'bootstrapping' and 'backward chaining' that I've decided to state it as a separate point).

Can we agree on this list of low level processes? If so, then SPM technology represents an "immediately accessible" solution to at least one of the criteria above. It is clear from the introductions to Merkle and Frietas' papers that they believe that SPM is an extremely important route towards 'proof-of-principle' experiments. I'm now willing to believe that Drexler also accepts this and that, as you state, I was most likely blurring the distinctions between "*preliminary research, bootstrapping, and high-throughput production*" in earlier correspondence. Nevertheless, both you and Drexler have quite specifically stated that SPM-type technology will not ultimately be used in the implementation of molecular manufacturing due to throughput issues.

This now raises the question of blueprints and milestones. You state that Drexler does not supply blueprints and that therefore he shouldn't be expected to formulate or detail the alternative technology that will be used instead of SPM. Let's consult *Nanosystems* again: have a look at Fig. 13.11 or Fig. 13.14 or Fig. 10.32 or Fig. ….etc..etc.. If those are not blueprints (in *any* sense of the word) then what are they? (We're even told how many atoms are required for each structure!). So, while Drexler is more than keen to provide blueprints at one "level of abstraction" he is not willing to suggest a plausible non-SPM strategy to satisfy the "design criteria" listed as 1- 4 above. Yet, turn to the back cover of *Nanosystems* and the reader is informed that Drexler has "*written a detailed, top-to-bottom analysis of molecular machinery – how to design it, how to analyze it, and how to build it*" (emphasis in underlined text is mine). I, of course, fully agree that there is more than one path to a possible milestone but Drexler, while *arguably* presenting an alternative milestone, does not produce any type of alternative strategy to reach this milestone. That Drexler is willing to produce detailed blueprints for molecular machinery while, at the very best, glossing over the low level assembly routines at the core of the machinery speaks volumes.

Drexler has suggested that by requesting 'proof-of-principle' SPM experiments (and thus 'bypassing' Stages 1 to 3 and jumping directly to Stage 4 in his "strategy" outlined in Chapter 16 of *Nanosystems*) I am asking for a result that is simply not possible with today's technology. The analogy he repeatedly uses is that of the Apollo programme (see quote in my previous letter). However, if the goal of the "back-chaining" approach is to track back from the final molecular manufacturing 'vision' to an 'immediately accessible' technology, then the obvious 'immediately accessible' technology is SPM (as is used in Stage 1 of Drexler's strategy). My argument has always been: why not apply that technology directly to the implementation of basic mechanosynthesis steps? Indeed, this is the strategy that Frietas and Merkle have adopted (see their published work and their proposal for the next logical step in molecular manufacturing R& D at http://www.foresight.org/stage2/project1A.html). Why is this any less valid than starting off with polymer manipulation and "building up" to mechanosynthesis? [I'm pretty certain that I know the answer to this one but I'd first like to hear your comments…]

My apologies for such a long and rather convoluted reply to your comments on bootstrapping but I felt that it was important to point out (again) that I've read (in detail) Drexler's back chaining approach outlined in Chapter 16 of Nanosystems (although, admittedly, that may not have been apparent from my previous 'conflation' of the various topics).

Technical Issues

Moving back to questions of physics and chemistry, I'll work through the issues you raise one-by-one:

"But if we have a conductive pathway, what's wrong with hooking it to an external current source?"

To have a current one needs a potential difference. A potential difference between a tip tool and a substrate in extremely close (~ nm) proximity in vacuum[†] will produce a very strong electric field (regardless of whether that substrate is an 'infinitely' extended solid or a molecular cluster). Electric fields are non-local and are problematic in terms of inducing diffusion over >> atomic distances (particularly if we're working with hydrogenated diamond substrates). This runs counter to design criterion 2 above. One can, of course, make the argument that we'll simply choose low enough bias voltages and an appropriate system so that electric field effects are negligible. (For example, with passivated semiconductor surfaces one could argue that it might be possible to drop a substantial fraction of the bias voltage in the bulk of the semiconductor. Then, however, we get into substantial difficulties because we need to consider the role of tip-induced band-bending in the near-surface region). Regardless of the detailed physics, however, yet again we're narrowing down the range of materials systems that could possibly be exploited for molecular manufacturing. [Note also that we need to dope the diamondoid structures if a current is going to flow – that's going to involve some rather tricky mechanosynthesis steps.]

[It's worthwhile noting that Drexler raises the question of E fields and electrochemistry in mechanosynthesis (Nanosystems, Section 8.3.3 d) but decides not to consider them in his analysis. (Perhaps this is what you meant by "that creates a slippery slope?" – I didn't quite get your meaning).]

"So when you discuss the difficulties of a "fundamental" reaction, I must disagree. No single reaction is fundamental in the sense that the project collapse if it doesn't work. In addition to diamond,….."

You, Drexler, and I are most definitely "talking past" each other, as you put it so well. I do not mean that a particular sequence of reactions is fundamental, I mean that the low-level operations listed as 1- 4 a few pages back are the basic steps required to perform mechanosynthesis. (Drexler's inability to explain how one would carry out specific reactions described in Nanosystems (or elsewhere) is a separate matter and relates to my discussion of blueprints/milestones above.)

Of the non-diamond materials you list, I'll choose one for now (silicon) and get back to you with detailed considerations on the others when I get some time. Silicon is already problematic for mechanosynthesis because we need to consider, as one key example, the complex Si(111)-(7x7) reconstruction. I'll quote from a letter I've previously sent to Drexler:

"Merkle[1] argues that "when there are serious questions about how to apply existing natural law to a particular structure, we avoid using that structure". The key example given is the (7x7) reconstruction of Si(111) mentioned above – this … unit cell is deemed 'too complex'[1] for molecular manufacturing purposes!" [[1] www.foresight.org/SciAmDebate/]

There are "serious questions" associated with silicon not only in terms of the (7x7) structure but also because hydrogenation of the (7x7) surface produces a significant amount of Si cluster formation as the

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[†] I'm adopting the same strategy as Merkle and Frietas and will focus on vacuum mechanosynthesis.

original reconstruction is disrupted by H-bond formation. Criterion/ design constraint #4 then becomes an issue…

"It is 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".

Right, I'm interpreting this to mean that van der Waals-bonded systems are an option? (That is, you're considering the fullerene molecule or graphene sheet as the fundamental molecular unit rather than the internal structure of the covalently bound molecules?) Now, I can immediately see two key problems:

(a) the diffusion barrier for hopping on a C_{60} (111) plane is ~ 0.17 eV (it's extremely easy to do a back-of-an-envelope calculation to derive this – see the list of problems at my Atoms & Molecules at Surfaces website (http://www.nottingham.ac.uk/~ppzpjm/probs.htm)). This means that there's an appreciable rate of diffusion at room temperature and so molecules won't remain fixed in place (so Criteria #1 and #2 not fulfilled). STM images clearly show that fullerenes form highly ordered close-packed islands and films when adsorbed on a fullerene plane. Of course, you might be arguing that you'll somehow compress the molecules with an AFM tip so that they covalently bond to the underlying layer but, then, why won't they also bond to the tip?

(b) Criterion 4 – a key aspect of Part II of Nanosystems – is not fulfilled. Van der Waals bonding will always produce extremely weak bonding interactions (as compared to covalent bonds) and thus rather limit the complement of nanomachines that can be constructed. [Yes, I realise that, in Drexlarian parlance, this is a design constraint rather than a fundamental "show stopper" but the parameter space keeps getting smaller and smaller.]

"For example, incorporate half of a chromophore pair in each of the tips and measure the light emitted as they approach"

Which particular chromophore? How is it incorporated in the tip? Before I comment on this, I need to be certain I'm clear on what you're proposing. Do you envisage some type of fluorescence resonance energy transfer (FRET) process? Given that the "tips" are structures that grow continually during the mechanosynthesis process, unless the chromophores are continually replenished won't they be buried in the bulk of the growing diamondoid structure very quickly? Am I thinking of this correctly? A sketch would be very helpful here.

"Characterise the position of each tip while scanning…move the tips into free space and let them approach each other from opposite directions".

So what we need is closed-loop control of a dual tip AFM system with at least 5 degrees of freedom per tip (6 DOF per tip would be better to ensure that we can accurately align the tips). Moreover, we need a subnanometre precision coordinate system spanning at least tens of microns. This isn't impossible, it's just far beyond what is currently technologically achievable. (The quote on page 2 of my letter to you dated 30th November 2004 is relevant here).

"It would not surprise me if someone developed a polymer-based molecular manufacturing system before 2010"

Let's be completely clear here. By "molecular manufacturing" in this context do you really mean the following: the synthesis of "*gram quantities of atomically precise, functional product that is heterogeneous and engineered at all scales [requiring] computer-controlled nanoscale machines building nanoscale machines*" as you state in the fourth paragraph of your letter? This will be with us in 5 years or less? Where are the publications describing work towards this goal (e.g. computer-controlled

mechanosynthesis resulting in the production of a functional nanomachine)? I'd be extremely grateful if you could provide me with a list of references to this work. Which groups are attempting this? How can you be so confident that polymer-based molecular manufacturing will be with us on such a short time scale? On what recent developments do you base your prediction? [You have also referred to some silicon-polystyrene work which I have been unable to trace in the literature. Could you please send me the citation for that work?]
[See: http://crnano.typepad.com/crnblog/2004/05/what_is_nanotec.html#comments for further discussion related to the 'timeline' for molecular manufacturing].

"But they only explored two tips…"

Yes, my apologies for the incorrect citation with regard to the scope of 'tool space' that was explored. Although only two tips are explored in the Mann et al. paper, I was thinking of the earlier (complementary) Merkle and Freitas paper where a range of tip tools are explored [J. Nanosci. Nanotech. **3** 319 (2003)].

"Instead of trying to control the force during the "insert-bind" phase, I would control the position. I'd detect the tool in 'tapping mode'….".

Errmm, how does "not controlling the force but controlling the position" work in tapping mode? How do you (or, indeed, why would you want to) disentangle force- and distance control in a tapping mode AFM experiment (assuming we're agreed on what "tapping mode" actually means: the tip is on a cantilever oscillating close to its resonant frequency?) That you're using tapping mode AFM now also means that there's a cantilever to consider (with an associated relatively large volume). Let's assume that we're using a Giessibl-type tuning fork system and we're measuring the (high Q) tuning fork resonance (see, for example, http://www.foresight.org/Conferences/MNT11/Abstracts/Giessibl/ and associated cited references). The shift of the resonance as a function of position is fundamentally related to the force gradient. So, just as the control variable in STM (i.e. current in 'constant current' mode) directly controls the z position of the tip, the force gradient (from the shift in resonant frequency) in AFM provides a 'measure' of the tip position.

…unless, of course you mean that you neglect feedback completely and approach the surface using some type of sensor control only. Then we really have a technological challenge because you're asking for "closed-loop" control with ~pm resolution. Actually, no, it's not even as "straight-forward" (!) as that – you need to determine some type of 'origin' for your coordinate system *and* you need to monitor the position of the end of the cantilever (i.e. where the tip is mounted) which will not be related in a simple fashion to the x-y-z-ϕ–θ coordinates of the manipulating transducer (whatever that may be – let's assume that we've got a 5 degree of freedom (per tip) dual tip AFM-type set-up). I can't see why, under any circumstances, you would *not* want to measure the force so I really can't understand your "instead of trying to control the force" statement above.

"I could tell whether and how the molecule was fastened to the tip by imaging a very sharp point…"

First, this approach – as I'm sure you're aware – is extremely laborious and time-consuming. *If* you measured the force it would probably be relatively clear from the force-distance curves when a "molecule capture" event occurred. Second, "a very sharp point" in this case means atomically sharp and a single atom height step-edge would probably do – but then what happens if the molecule decides to bind to the step edge? (Choose a different material for the step edge? Oh, of course!). Deconvolution of the image to produce an image of the molecule will be extremely difficult (the convolution process is highly non-linear) but of course not impossible as long as we have a very good idea of the overall tip structure. [By the way, have you ever carried out an AFM or STM experiment?]

While we're on the subject of molecular manipulation in the Frietas model, I must be missing something very fundamental (apologies), because I can't see why in one case (Slide 100 of Frietas' presentation) the dimer is removed from the surface when the tip-tool is retracted whereas in Slide 40 the dimer is placed on the surface. What is it about the mechanism in Slide 100 that means the dimer is taken off the surface along with the tip-tool? [I thought that after deposition of a dimer, the tool tip was recharged via gas phase acetylene 'cracking'? Indeed, this raises another technological question re. just where the acetylene recharging will be carried out, but I'll come back to that one…]

I look forward to hearing your response to the comments above and, once again, please accept my apologies for the delay in responding to your e-mail messages.

Best wishes,

Philip

Subject: Addendum to second letter
Creation Date 28/12/2004 14:41:14
From: Philip Moriarty
To: Chris Phoenix

Chris,

Re. comments on Si(111)-(7x7) in my second letter to you...

If we assume that everything operates at room temperature (i.e. we're not considering any type of gas phase growth at elevated temperatures, along the lines of Freitas et al.'s proposal) then the Si(111)-(2x1) structure is much more relevant than the (7x7) reconstruction (there's quite a high barrier to the formation of the (7x7) reconstruction from the Si(111)-(2x1) phase). So, my discussion of the (7x7) structure, important though it is, is arguably somewhat of a "red herring" for room temperature-based mechanosynthesis operations (which raises the question as to why Merkle brought it up in the first place...).

Nevertheless, there remain important questions re. the alternative materials systems you list in your letter. For example, Si(nnn) and C(nnn) surfaces, while having some similarities (e.g. Pandey pi-bonded chains on (111) and dimerisation on (100)) also have key chemical differences - I'll return to a comparison of the detailed surface physics and chemistry in later letters and e-mails. In addition, hydrogenation and dereconstruction for sp3-bonded crystal surfaces are issues only briefly addressed by Drexler in "Nanosystems" and in a rather unconvincing fashion (see Section 8.6.3a - the line "whatever the true situation..." doesn't inspire confidence!). (To be fair, however, Drexler's (laudable) caution here was due to our rather less detailed knowledge of the surface physics of these systems at the beginning of the 90's).

On a closely related theme, I don't know if you're aware of the following rather neat paper on STM-stimulated conversion of H:Si(111)-(1x1) to Si(111)-(2x1) by Becker et al. (Phys. Rev. Lett. 65 1917 (1990) - note that it's electron mediated). Finally, regarding your discussion with Richard re. sliding surfaces, I am currently digging out some (mid-nineties) literature on Si wafer bonding via H-passivated surfaces by Francois Grey et al. which I feel is rather relevant. More on this later...

Best wishes,

Philip

*[Note that a number of e-mails involving topics discussed at the "Soft Machines" blog (*http://www.softmachines.org/wordpress/index.php?p=50*) have been omitted. This discussion involved topics which are largely (though not entirely) covered in later correspondence. – PJM]*

Letter from Phoenix to Moriarty
December 31st 2004

Philip –

No need to apologize for taking time to reply; it seems I'm at least as bad. I'm still quite busy/distracted, so will have to spend less attention on some sub-threads than I would like.

For example, Freitas's CVD growth proposal appears now to be a non-issue. I wish I had time to go into the physics of surface diffusion, because it's an interesting topic. I'll tie off a loose end by agreeing that by "bonded " and "non-bonded " I did mean chemisorbed and physisorbed. I just wish I had time to get into the question of whether there can be a mix of physisorbed and chemisorbed molecules on the surface; I was surprised at your surprise at this suggestion; surely impact angle would have some effect. And on a related topic, I'll provisionally accept that the term "self-assembly " can be used for molecules wiggling on a surface, but I think my point about drag applies in that case as well.

On definitions, I'm not much of a philosopher, but I know that there are several ways to define things; for example: by how they're made, how they function, what they accomplish, or what they're good for. Drexler's definition was a how-they-function definition. My definition is a what-they-accomplish definition. The fact that either definition can be derived from the other (more or less, and if all goes well) does not make them circular.

For example, suppose that a method was developed which would grab self-assembling (non-bonding) blocks out of solution, pull off physisorbed protective caps, and push them together to make a shape. Then, when this was finished, the fabricated shapes would be flashed with photons to crosslink them and make them stiffer and stronger. This involves no mechanochemistry. But if it were capable of building self-manufacturing systems with nanoscale features, programmable properties, digital operations, and low error rates, I would expect it to be very useful at least for building massively parallel computers, probably a range of sensor types, useful actuators, etc. I would be surprised if it was difficult to scale up a manufacturing system based on this technology to make integrated gram-scale products. And if such a technology were developed, I would think it was silly to say that because it didn't fit Drexler's or CRN's definition of molecular manufacturing, then Drexler's work was wrong or irrelevant.

I think when I wrote the line about the distinction between molecular manufacturing and mechanosynthesis, I misspoke on the second term; I should have said machine-phase chemistry rather than mechanosynthesis. In machine-phase chemistry, the position of every molecule is mechanically constrained. In solution-phase mechanosynthesis, the position of every reaction is mechanically constrained, but some molecules (e.g.solvent) are unconstrained.

The atom-vs-molecule question was made much more complicated than it needs to be by the "fingers" strawman: the completely false and ridiculous idea that Drexler was proposing to pick up individual, unbonded atoms with "fingers" somehow smaller than the atoms. (Smalley, Whitesides, and Ratner, among others, are guilty of spreading this confusion. Do they think Drexler doesn't know grade school science, or do they simply go in for character assassination?) Every atom would be bonded to a molecule; thus Drexler's proposal involves manipulating molecules,not atoms, which he should never have needed to clarify. But a reaction might involve the transfer of a single atom from one molecule to another; this in my opinion qualifies as building "atom by atom." I don't think we need to waste any more time on this topic.

I wrote the exploratory engineering and boots rapping section of my previous letter without looking at Nanosystems Chapter 16. I'm glad that I managed to give a clear summary of it.

Your list of low-level requirements for stage-4 mechanosynthesis is slightly too restrictive. For example, it may not be necessary to depassivate surfaces, if a complete part can be built unpassivated and then passivated just before it is handled. But we should not expect to develop a perfect characterization without testing how well it applies, so let's see where this list takes us.

The first thing I notice is that your list is not complete; it does not require high throughput. Its conditions are necessary, but certainly not sufficient. It appears you're trying to use the list as an element of a logical argument that SPMs should be considered as a stage-4 component. But this doesn't make sense. You say you are *"requesting 'proof-of-principle' SPM experiments ((and thus 'bypassing ' Stages 1 to 3 and jumping directly to stage 4 in his "strategy " outlined in Chapter 16 of Nanosystems)"*. But if it doesn't have high throughput, it isn't stage 4. If you were arguing that SPMs are sufficient for stage 4, then I'm not surprised Drexler disagreed with you! If you were arguing that they might be useful for earlier stages, then I don't think anyone disagrees with you. Drexler has his favorite method, and it may be the best. I go back and forth on whether I favor Drexler's polymer bootstrapping or Freitas's SPM bootstrapping. But that does not mean that either of them is wrong.

My discussion of electric fields and currents was prompted by what I read as your claim that they wouldn't scale from singular systems to nanofactories. If they don't work, we don't have to use them. If they work in singular systems, then they should also work in nanofactories. Considering all they reasons why they might fail in singular systems is "beyond the scope."

As to Drexler's providing or not providing blueprints: I do not consider the pictures of a robot arm to be blueprints. They do not show dimensions; they do not show atomic components, even where the placement of individual atoms is crucial to the correct working of the system. The pictures are architectural concepts. An architect may produce a drawing of a house to show how it will look and where the rooms will go, but the house cannot be built from that drawing —whether or not the drawing indicates the approximate floor space of the house. Your desire to see these drawings as blueprints seems closely connected to your desire to prove that Drexler is wrong about something. I am not interested in that game. I am interested in whether nanoscale machines can be used for nanoscale construction in a way that makes it relatively easy for engineerable manufacturing systems to build copies of themselves rapidly and reliably. As an architectural concept, the robot arm is a general-purpose positioning system, intended to be useful for whatever reactions are eventually discovered. I do not think it is premature to demonstrate that a rotating-sliced-tube structure can be a stiff and useful manipulator concept. To call this work "detailed blueprints " and then castigate Drexler for providing too much detail speaks volumes about your mindset and intentions —not about Drexler.

Would the hydrogenation of the (7x7) silicon surface still produce unwanted clusters if we could select the sequence to add the atoms in?

By graphene/fullerene, I did not mean vdW-bonded systems. I meant that it appears possible to deposit atoms on the growing edges of graphene and fullerene structures, making desired shapes out of covalent sheets. So your objections don't apply.

Yes, by chromophore pairs I did mean FRET. I was proposing this for early research, so your objection that the chromophores will be buried does not apply. If you can add enough structure to bury a chromophore (which can work over multi-nm distances) then your basic research has succeeded!

In a two-tip scenario,you do not need 5 DOF in each tip. You need 5 DOF total. And you might get by with only 3 nanoscale DOF if you can pre-rotate the tips to be aligned correctly.

There is a vast difference between "It would not surprise me" and "will be." Your entire paragraph appears to be an attempt to blame me for something I didn't say. Quit that and let's get back to the science. [See also http://crnano.typepad.com/crnblog/2004/05/what_is_nanotec.html#comments for further discussion related to the 'timeline' for molecular manufacturing]

The polystyrene work was done a Northwestern. Cover article of September 27,2004 issue of Applied Physics Letters .Full reference:R. Basu,N.P.Guisinger,M.E.Greene,and M.C.Hersam,"*Room temperature nanofabrication of atomically registered heteromolecular organosilicon nanostructures using multistep feedback controlled lithography*," Appl.Phys.Lett.,85 ,2619 (2004).
http://www.hersam-group.northwestern.edu/news.html
http://www.northwestern.edu/univ-relations/media_relations/releases/2004/09/molecular.html

By "not controlling the force but controlling the position," I meant that when actually trying for the reaction, you would apply a "blind" motion. Immediately before that, of course, you would detect your position relative to the substrate very carefully, using tapping mode, which of course senses force.

Yes, I have carried out an STM experiment. Several years ago I was sat in front of an STM for the first time, handed a paper on depositing gold nanodots via voltage pulses, and told to replicate it. Within one day I was working without supervision, including cutting and installing my own tips. Within two days I had replicated the dot deposition. Within three days or so, I had learned the software interface to the microscope and written a program that would write dot-matrix letters a few tens of nm high. The word "ZYVEX" spelled out this way was displayed on their web site for several years. By the end of the week, I had learned to make "towers" of multiple gold dots, but they wouldn't stick together so I couldn't get the towers more than a few nm high. I asked to set up a nitrogen box to reduce surface contamination, but they didn't want to spend the extra time.

I don't know all the details of Freitas's calculations and proposals, and the plan for recharging the tool tip depends on the stage of research. In the initial efforts, of course, the tip would be built pre-loaded and discarded after one use. In the final nanofactory-class system, it would be recharged from physisorbed/bound molecules, not gas. In intermediate stages (or first stage if it proves easier to build a discharged tip than a loaded tip), gas-phase acetylene sounds like a proposal worth investigating.

I don't have time to learn Freitas's model well enough to defend it in detail. I'll have to skip your question about deposition vs. liftoff of dimers, though it may (or may not) be relevant that one set of conditions in his simulations showed the dimer being deposited probabilistically. You may want to write him directly.

I'm not sure whether these answers have moved the discussion forward, or just gotten stuck on trivialities. I'll also include in my email, a rough draft of my latest science essay for our newsletter. I think the topics in my essay are more interesting, and discussion of them will be more useful, than spending more time on whether Drexler's pictures are too detailed or whether we all know the difference between atoms and molecules. The first section is on friction and superlubricity. Other sections of the essay discuss other techniques that molecular manufacturing can use but biology has not. It's written informally, for non-scientists, but if you (or Richard) see any thing that's incorrect please let me know.

Chris

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