# Phoenix-Moriarty debate: Part III
# E-mails and letters Jan. 4th, 5th 2005

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 from Philip Moriarty to Chris Phoenix, January 4th 2005

Chris,

Thanks for your letter of Dec. 31st and I wish you and all at CRN the best for 2005. Before I respond to your comments in detail, I must admit at the outset to being very disappointed – although not particularly surprised - that you consider many of the issues I raised to be 'trivialities'. As I've stated time and time again, my primary issue with the molecular manufacturing "vision" is that the chemistry inherent in the lowest level mechanosynthesis steps is continually glossed over - and at worst, ignored – in favour of a detailed discussion of higher level machinery. (Freitas et al.'s work is a notable exception and I would be very surprised if Freitas were to consider the issues I've raised to be 'trivialities').

I had hoped that my detailed consideration of Freitas' proposal (on which you explicitly asked me to comment) might give you an insight into the complexity of the processes to be controlled at the molecular level and thus that distinctions between 'reactive molecule positioning' and 'atomic manipulation' are not mere trivialities. But, no, you apparently consider a number of my arguments to be at the level of "*whether we all know the difference between atoms and molecules*" and this strongly suggests that you find the physics and chemistry underlying the 'machine language' of mechanosynthesis to be of substantially lower importance than higher level systems engineering issues. Indeed, you've argued as much in a recent post on Richard's 'Soft Machines' blog[†]. Furthermore, you've explicitly stated in your "Design of a Primitive Nanofactory" paper that in the development of the factory "*diamondoid fabrication chemistry need not be completely understood*". It appears that, despite our recent discussions, you hold firm to this disappointingly naïve view and continue to imagine that the fundamental chemistry may simply be 'abstracted out' and contained within a low-level 'black box' module. (I wonder why your stance gives me such a sense of déjà vu…?).

Let's consider your arguments in detail (direct quotes from your letter are in red):

*"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 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."*

Interesting use of the term "non-issue" in the first line! By this, I guess that you mean you now agree that Freitas' proposal is flawed on the basis of the discussion of the underlying surface physics and chemistry

---

[†] *"For many applications, it's true, the chemistry used doesn't matter much. What's more important is the ability to do engineering design…."* http://www.softmachines.org/wordpress/index.php?p=60

we've had. This is certainly a step forward from your appraisal of Freitas' proposal on the CRN blog a few weeks ago (http://crnano.typepad.com/crnblog/2004/11/ diamondbuilding.html#comments):

*"The recipe is detailed enough that it's already hard to argue it can't work… The claim that diamond-building can't be used to build machine parts seems likely to lose most of its remaining credibility".*

I find it absolutely remarkable that you would publicly state: *"the claim that diamond-building can't be used to build machine parts seems likely to lose most of it's* [sic] *remaining credibility"* but yet now admit to "*not having time*" to fully understand the physics underlying Freitas' proposal. This lack of critical consideration of a proposal put forward by a leading proponent (some might argue *the* leading proponent) of molecular manufacturing, combined with the hyperbole with which you reviewed his work (e.g., "*radical nanotechnology has taken a big step closer to the lab*") is extremely worrying and not at all helpful in driving the molecular manufacturing debate forward. As you say in your letter, could I advise that you "*quit that and let's get back to the science*". (I make some comments on peer review at the end of this letter which are particularly pertinent to this issue.)

As I've mentioned elsewhere [http://nanobot.blogspot.com/2004/12/stop-worrying-and-learn-to-love.html], I have a great deal of respect for Freitas because he has at least attempted to put forward a strategy to implement the low level mechanosynthesis steps *to which a detailed critique could be applied*. This is rather more helpful than arguing that the precise details of the molecular manipulation steps are simply 'trivialities'. I will, as you suggest, contact Freitas directly.

On a final point with regard to Freitas' proposal, you note in your most recent e-mail to Richard Jones (dated 2nd January 2005):

*"I have agreed that one pathway for achieving one step appears to have serious potential difficulties. We haven't talked much about the alternate pathway--picking up the small synthesized tool tip molecule with an unterminated SPM tip."*

First, see Comment #3 under "http://www.softmachines.org/ wordpress/index.php?p=50#comments" where I have previously responded to a comment very similar to this. Second, I don't see a great deal of point in discussing the second (to my mind, similarly flawed) alternate pathway with you if, as you say, you "*don't have time to learn Freitas's model well enough to defend it in detail*". (I've certainly spent a lot of time considering it – as noted above it rather disturbs me that you only now admit that you haven't "*learnt*" Freitas' model "*well enough*".) We'd both be wasting our time, wouldn't we? I'll contact Freitas directly.

*"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."*

Fine, you're free to "provisionally" accept that self-assembly can occur in vacuum without the presence of a solvent. Just note that this directly contradicts your statement on the *Nanotechnology Now* website:

*"Another difference is that self-assembly has to take place in some solvent so that the molecules can float around randomly"*

Furthermore, as I've mentioned in a recent e-mail to you *[E-mail referred to here has not been included in the transcript of the debate - PJM]*, there's a vast body of literature supporting my assertion that self-assembly doesn't require a solvent and occurs on suitably passivated surfaces in ultrahigh vaccum. (In particular, there's a lot of recent exciting work exploiting hydrogen-bonding interactions on surfaces in UHV).

*"But I think that my point about drag applies in that case as well"*

Just why do you feel that drag is a useful concept to invoke when discussing UHV-based self-assembly? The speed of assembly is determined by the hopping rate of the molecules which is fundamentally related to the diffusion barriers (which may be anisotropic), the temperature, and the diffusion pre-factor[†]. While one *could* look for parallels between the motion of weakly bonded 2D assemblies on surfaces and classical hydrodynamic processes (indeed, this becomes an even more interesting question if we consider a binary or tertiary system comprising a number of different types of molecule), I'm pretty certain that this is not what you meant. In just what sense are you raising the issue of "drag" and could you clarify your assertion as to its relevance to UHV-based self-assembly?

*"On definitions, I'm not much of a philosopher... does not make them circular."*

*"For example, suppose that a method… 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."*

Chris, these paragraphs lazily evade the points I made. If molecular manufacturing doesn't necessarily involve molecule-by-molecule mechanochemistry – a distinction which, *as you state*, is contrary to Drexler's and CRN's current definitions - then don't you think that the CRN message re. molecular nanotechnology should be modified (so as not to mislead those of us who are actually attempting to critically consider just what is required to implement the process at the molecular and atomic levels)? The radical nanotechnology/molecular manufacturing 'vision' is fundamentally based on molecule-by-molecule control – if there are forms of molecular manufacturing that will not involve the construction of *"gram quantities of atomically precise, functional product that is heterogeneous and engineered* ***at all scales****"* [Phoenix, 2004] then please make the appropriate distinctions in your writing. After all, as noted previously, *[Quote from Drexler removed – PJM]*. What you describe is more akin to a development step on the way towards molecular manufacturing (e.g. something close to Stage 2 in Section 16.2.3 in *Nanosystems*).

,…and skipping back a bit: "*…grab self-assembling (non-bonding) blocks out of solution, pull off physisorbed protective caps, and push them together to make a shape"*. Do you mean an arbitrary *pre-defined* shape? Do you mean blocks whose internal structure involves covalent bonds? If you *"pull off"* physisorbed protective caps – is this molecule-by-molecule, or do you strip off the layer in a more conventional chemical fashion? - then the surfaces will be reactive and prone to reconstruction (see discussion below) so that the block will expose particular facets. The lowest free energy facets are directly related to particular crystallographic planes and so the shape/geometry of the block is constrained[‡]. In addition, why won't the solvent molecules adsorb on the reactive surfaces? (Or by '*grab…out of solution*' do you mean that you transfer the blocks to a UHV environment? The issue of surface reconstruction then still remains.) I realise, however, that I might be being a little unfair here. As you prefaced your scenario with the words "*…suppose a method was developed…*" and are using the discussion to attempt to support comments in your previous letter regarding the 'worthlessness' of carefully defining precisely what is meant by molecular manufacturing, please feel free to ignore my questions for now.

*"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*

---

[†] If you get a chance – and as you've stated you'd like to learn a little more about diffusion processes – you might wish to read about the relationship of this prefactor to entropy. Consult the surface science textbooks I list later in this letter.

[‡] Please read the e-mails from Richard and myself on crystal plane growth in the Freitas CVD proposal before citing kinetic limitations as a 'get out' here….

*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?)"*

I can't comment on what Smalley, Whitesides, and Ratner think. *I'm* certainly not interested in character assassination and have quite clearly expressed my opinions on the quality of Drexler's work on a number of occasions recently – I don't think that any of my posts on *Soft Machines* could in any sense be said to denigrate Drexler's character.

Second, I don't think that your appraisal of Smalley's arguments is entirely correct (although I have considerable sympathy with your position – see below). Smalley didn't suggest that the assemblers would have fingers "smaller than the atoms". He said that Drexler's assemblers *couldn't work* because of steric hindrance in the reaction region – this is subtly, though importantly, different from your position (i.e. you suggest Smalley's argument was that Drexler actually proposed assemblers with thinner-than-atom fingers). Smalley's exact quote is: *"There isn't enough room in the nanometer-size reaction region to accommodate all the fingers of all the manipulators necessary to have complete control of the chemistry…"*. Rebutting a straw man with a misinterpretation isn't helpful! (In addition, see my comments on the Soft Machines blog re. Drexler's use of the straw man tactic in another (unwarranted) context).

Nevertheless, *I actually agree with you in terms of the detail of Smalley's 'fat fingers' argument*. As he clearly pointed out in his Scientific American rebuttal, Drexler did not propose that a large number of fingers (certainly not 5 to 15) would be required to carry out the mechanochemistry. Thus, that element of Smalley's argument doesn't make sense to me. Richard Jones' post on this topic at Soft Machines (http://www.softmachines.org/ wordpress/ index.php?p=14) eloquently lays out the appropriate arguments.

But does this mean that we can simply neglect the issue of steric hindrance? Even if there are considerably fewer than the 5 to 15 fingers (or "actuators" or "tips" or "probes" or whatever term you wish to use) argued by Smalley, the "fat fingers" position (when used as a shorthand for "steric hindrance") is still an important issue. I've already pointed out to you that a flat tip tool for Freitas' model will rule out dimer-by-dimer synthesis of a diamond layer due to steric hindrance (see my e-mail of Dec. 27th 2004) – the tip will be "too fat". Moving beyond Freitas' proposal and consulting *Nanosystems,* we return to one of the figures in *Nanosystems* which consistently causes me great difficulty: Fig. 8.14. I've raised this point with Drexler and cited it in our previous correspondence and I've not had an appropriate response. *[Sentence modified (in a very minor sense) to remove reference to e-mail correspondence with Drexler- PJM]*. So I'll ask you one more time: just how is the reaction in Fig. 8.14 carried out using, for example, tetrahedral tips similar to those described by Freitas et al? Perhaps you might argue that we use a higher aspect ratio structure such as a carbon nanotube? Unfortunately, that also has a finite radius of curvature. How do you stop the tips 'clashing'? This is, as I've previously suggested, an alternative take on the fat fingers problem.

Are there other examples from Nanosystems of problems associated with steric hindrance? How about Fig. 8.20? In Step 2, how does one apply sufficient force *only* at the point indicated? Or how about Fig. 8.23? I *must* be missing something here because I can't believe that Drexler omitted in his analyses the steric constraints due to the finite size of the tip tool and its support in these reactions. (He even states in Section 8.6.1 of Nanosystems that *"diamond has the highest atom and covalent bond density of any well characterized material…maximizing problems of steric congestion"*.)

*"…. 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."*

Avoiding this type of confusing and difficult-to-follow writing is precisely why I continually plead for clear, accurate and self-consistent descriptions of what's required in the fundamental mechanosynthetic steps. How is transfer of an atom from molecule to molecule *not* atomic manipulation[†]? Just because an atom is transferred via a computer-driven molecular reaction pathway doesn't mean that an individual atom has not been manipulated: the fundamental, very simple, question to address is *whether the basic, discrete unit of change is an atom or a molecule*. You seemingly argue that the distinction between a reaction such at that shown in Fig. 8.14 of *Nanosystems* and the dimer placement chemistry described in Freitas et al.'s work is "trivial". There is an exceptionally "non-trivial" difference in the chemistry required! In Fig. 8.14 of *Nanosystems* an individual atom has been transferred via a chemical reaction. In Freitas' work, a dimer is transferred. Building "atom-by-atom" is a considerably different process from building "molecule-by-molecule". Ignore or trivialise this distinction if you will but I'd be surprised if Freitas, for one, did not agree that the distinction is extremely important.

*"I don't think we need to waste any more time on this topic"*

Fine, Chris, please continue to delude yourself that the details of the fundamental chemistry aren't an issue. Consider this: in the 15 years since Eigler et al.'s groundbreaking atomic manipulation work (on an extremely well-chosen materials system in UHV at 4K), with year-on-year advances in SPM technology since then, there has yet to be a **single** experimental demonstration of a mechanosynthetic reaction carried out by *positioning reactive molecules with atomic precision* **despite** the availability of a technology which in principle should enable these experiments to take place. (As detailed in my comments below, at the moment I couldn't care less about bandwidth – if the reactions are carried out at the rate of one a day or one a week that's good enough as a 'proof-of-principle' demonstration of a mechanosynthetic process for me. See the following page for an example of a simple reaction sequence I'd like to see. Can you propose a vaguely workable, detailed, step-by-step strategy to implement this (as would be required in a grant proposal, for example?))

In Nottingham we carried out the first room temperature, sub-nanometre precision, single molecule positioning experiments almost a decade ago. I'll leave you to search the literature for other examples of room temperature molecular manipulation (with sub-nanometre precision) in vacuum on the surface of an $sp^3$-bonded crystal – let me know what you find. [The state of play with regard to room temperature single molecule manipulation as of 2001 is outlined in Rep. Prog. Phys. **64** 297 (2001)].

*"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"*

I suggest that you read *Nanosystems* Section 6.4.6 (in particular, the last paragraph) for a concise and well-argued explanation as to why unpassivated surfaces are a big problem in mechanosynthesis. This also relates to your comment *"if a surface reconstructs, we simply choose another surface"* which I've discussed in the comments under the *"Is mechanosynthesis feasible?"* thread on Soft Machines. I would once again suggest that you visit www.nottingham.ac.uk/~ppzpjm/ amshome.htm and consult any of the textbook references on surface physics listed there (e.g. Lueth, Prutton, Venables, Woodruff and Delchar, etc..): only a very small subset of surfaces don't reconstruct. Drexler knew exactly what he was doing

---

[†] Your comment that each "atom would be bonded to a molecule" (which is transparently obvious to me) suggests that you perhaps define atomic manipulation as the assembly of molecules from individual atoms "floating" in free space?

when he chose H-passivated diamond as his prototypical mechanosynthesis 'platform'!! (And yet, as Freitas et al. have found, even this extremely well-chosen system is fraught with problems).

*"The first thing I note is that your list is not complete; it does not require high throughput…if it doesn't have high throughput then it isn't Stage 4".*

Yes, you're completely correct – this is by far your strongest argument. Without a throughput/ bandwidth of ~ 1 MHz (as outlined in table 16.1, *Nanosystems*) then what I've described as Stage 4 simply isn't Stage 4 (although, as you state, the list of conditions is *necessary* but not complete). As noted above, however, I simply don't care about bandwidth at the moment: as must be very clear by now, I'm focussed on the basic chemistry underlying the low level mechanosynthesis 'machine language'. I've obviously (and sloppily) transferred this dismissal of bandwidth issues to my appraisal of Stage 4. I wholly concur with you - SPM is not sufficient for Stage 4. Please accept my apologies for this stupid error.

Nevertheless, I don't believe that bandwidth was at the heart of my disagreement with Drexler. I raised with him the same issue I bring up on the following page with regard to proof-of-principle experiments. That is, if a molecular manufacturing technology is to be with us within "one to three decades" (as Drexler asserted in 2001) then surely a demonstration of a rudimentary mechanosynthesis step (using a reactive molecule and a rechargeable tool) within the near future (i.e. 3 to 5 years) is not too much to ask for? (I reiterate: bandwidth is not an issue for me). [*Reference to e-mail correspondence with Drexler removed – PJM*]. My counter-argument is that a technology which enables positioning of molecules with atomic precision *is* available (SPM): why not use this to implement basic mechanosynthesis steps at a bandwidth of a few per week (at most)? I stress again that Drexler cites this strategy as an alternative Stage 1 in Nanosystems (as we both agree: *"if you were arguing that they might be useful for earlier stages, then I don't think anyone disagrees with you"*). If you, CRN, and the Foresight Institute want to convince the nanoscientific community at large (and particularly critics such as myself) that the molecular manufacturing vision is remotely viable, then I strongly suggest that you very carefully consider Freitas and Merkle's proposal† at http://www.foresight.org/stage2/project1A.html. They suggest a strategy which is very similar to what I'm asking of you (except that their focus is solely on computational chemistry – this won't be enough).

*"My discussion of electric fields was prompted…considering the reasons why they might fail in singular systems is "beyond the scope""*

OK, I'm glad that you've seemingly taken on board the problems with electric field-based manipulation I've raised (see also my discussion of the Basu et al. paper below). I don't fully understand what you mean by a "singular system", however, nor am I clear on why considering electric field mechanisms is 'beyond the scope' in these systems?

*"As to Drexler's providing or not providing blueprints….architectural concepts"*

Richard's comments in his e-mail of 2nd January 2005 to you are extremely pertinent here [*e-mail not included in this transcript – PJM*]. Note that the Cambridge dictionary defines "blueprint" as *"an early plan or design which explains how something might be achieved"*. I think that this covers your understanding of the term. Early plans or designs which explain how something might be achieved are precisely what Drexler provides. I'll agree with you, however – compared to the other issues raised in my letter, this point *is* a triviality. I note, nevertheless, that it's the definition of 'blueprint', rather than my comments regarding the lack of detailed specification of the mechanosynthesis chemistry, which you address. What has also not been addressed are the following (raised either in my previous letter or in my comments in the Soft Machines blog):

---

† Although overall I applaud Merkle and Freitas' proposal, I still have key difficulties with a number of their claims. See, for example, Comment #16 under http://www.softmachines.org/wordpress/ index.php?p=50#comments

(i) the error rate for Stage 4 is suggested to be $10^{-15}$ in Nanosystems. This doesn't compare at all favourably with Freitas et al.'s 20% success rate. How will this problem be surmounted? (No, let me guess – we choose a different system with a much higher success rate? OK – which system (which, as you admit, also must fulfil the 4 criteria listed in my previous letter?)) Are you still expecting that the *lowest level* mechanosynthetic steps will be error free?

(ii) To carry out computer-controlled atomic precision positioning of reactive molecules piezoelectric devices (i.e. SPM-type technology) will be required. Are you aware of an existing alternative technology that will enable this? (I'm returning to the point I raised in my last letter: if not SPM then what?) You have stated that Drexler's pressure actuators (Nanosystems, Chapter 16) are so simple that you couldn't see how they wouldn't work: has there been *any* effort towards the implementation of these devices?

*"Your desire to see these drawings as blueprints…speaks volumes about your mindset and intentions – not about Drexler".*

This is a remarkable passage. First, I thought that you wanted to stay clear of a discussion of perception. However, as you've raised the issue, let me now "put my cards on the table"! You seem to think that there's something wrong about attempting to prove that Drexler's ideas may be flawed. This, in case you'd forgotten, is how we progress in science – a theory is proposed and it's tested thoroughly against experimental (and other theoretical) data. Only when a theory has survived rigorous critique from both experimentalists and theorists is it accepted (and even then effectively only provisionally (i.e. we don't know that a theory which supersedes the accepted theory isn't 'round the corner'!)). *Nanosystems* is not some type of 'received wisdom' which can't be criticised. If you're not interested in detailed critiques of Drexler's work (which encompass the 'game' of trying to prove him wrong) then you're not behaving like a scientist. This may also explain your all-too-easy acceptance of Freitas' proposal before you 'had time' to consider the physics in detail. There is a process whereby ideas and results are scrutinised before they're disseminated to the scientific community – it's called peer review. Some proponents of molecular manufacturing do not help their cause by rushing to publish work on the web before that research has received even one round of peer review. (Has your nanofactory paper been submitted for publication in a peer-reviewed journal?)

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

See my comments on the (7x7) surface in my "addendum to second letter" e-mail. I'm still trying to work out why Merkle brought the (7x7) structure up and, moreover, why he referred to it as an "intermediate" structure. The (7x7) reconstruction is the ground state of the Si(111) surface but, as I've mentioned, it's the (kinetically limited) (2x1) structure which forms at room temperature. You're also neglecting Drexler's (and Merkle's) design criterion that prohibits completely unpassivated surfaces. [In addition to the section from Nanosystems I've cited above, consider: *"a simple strategy, therefore, is to ban intermediate structures with many dangling bonds. Thus, we deem the non-hydrogenated silicon (111) surface as "too complex to analyze."",* Ralph Merkle, http://www.foresight.org/SciAmDebate/SciAmResponse.html). There's a wealth of work on hydrogen-passivated silicon surfaces that I'm not going to re-hash here. See, for example, John Boland's authoritative review [Advances in Physics **42** 129] and work by both John [Surface Science **244** 1] and others [e.g. Surface Science **324** 211].

*"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".*

Atom-by-atom construction of fullerenes? Where is the literature on this? What size of a graphene 'sheet' do you start with? How do you stop that graphene unit from folding so as to reduce its dangling bond density? Do you start with a large 'bulk-like' graphene sheet and then add atoms to its edges? How does this enable you to make "desired shapes" – you're constrained by the symmetry of the lattice. The most recent relevant literature of which I'm aware is that of Andre Geim's group at Manchester (http://grendel.ph.man.ac.uk/~geim/graphene-in-science/science2004.pdf) but this is a far cry from 'atom-by-atom' construction of graphene or fullerenes. The solution-phase chemistry you cite in your original letter is also not relevant to the mechanosynthesis/molecular manufacturing debate: you need to move well beyond conventional chemistry/self-assembly to implement even Stage 1 of Drexler's molecular manufacturing strategy. (A key element of Drexler's Table 16.1 is labelled "Instructions" – this explicitly indicates computer-directed assembly).

*"Yes, by chromophore pairs I did mean FRET…basic research has succeeded".*

You still haven't addressed the question of which particular chromophore pair you wish to include in the tip structure. In addition, how will you embed the chromophore (some details of the proposed mechanochemistry would be helpful) *and* how will you prevent the chromophore interfering with the growth of the diamondoid lattice?

*"In a two-tip scenario…can pre-rotate the tips to be aligned correctly"*

For someone who has previously carried out STM experiments (see comments below), the idea that you can pre-rotate the tip so that its perfectly aligned to do the type of mechanochemistry required for Freitas' proposal is naïve to say the least. Note that a small tilt in the tip will completely change the reaction coordinates – I thought that we were attempting effectively error-free chemistry (Chapter 16 of *Nanosystems*)? My 5 DOF per tip suggestion was based upon your argument that you were going to use a FRET-type mechanism – you require a donor-acceptor pair and also need to be able to separately embed a molecule in each lattice. Doing this mechanochemistry (how? – see comment above) *and* returning to the appropriate site on the workpiece will be *greatly facilitated* by having 5 DOF *per tip*. (I'd also not rule out that sixth degree of freedom – having the ability to 'tilt' the molecule at the end of the tip (independently of the $\phi$–$\theta$ coordinates) would be an invaluable capability).

*"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."*

It's a shame that your strong point on bandwidth is accompanied in your letter by far the weakest argument you have yet put forward. Your original statement was: *"It would not surprise me if someone developed a polymer-based molecular manufacturing system before 2010"* and I asked you to provide evidence to support your **opinion** that molecular manufacturing would be with us before 2010. I didn't ask you to prove that the technology **will be** with us, rather simply to give me some indication as to why the appearance of molecular manufacturing on this exceptionally short time scale would not surprise you. It would certainly surprise the hell out of me! You have also previously voiced similar opinions as to the extremely rapid appearance of molecular manufacturing (on, for example, the CRN website) – my question remains: on what basis do you justify these opinions? Furthermore, in just what sense was I not focusing on the science? I asked you to provide me with references to the literature which supported your opinion. That you respond in the most unconvincing fashion on this does nothing to convince me that your 5 year timeline is even remotely viable.

Indeed, if you were to suggest a 5 year timeline for a proof-of-principle experiment to demonstrate the following rudimentary diamondoid mechanosynthesis steps to build up a 3 dimer 'block' on a hydrogen-passivated diamond surface (let alone implement full scale molecular manufacturing) I'd argue that this was hopelessly optimistic.

1. Depassivate site on hydrogen-passivated diamond surface for addition of C dimer.
2. Put down hydrogen abstraction tool.
3. Pick up dimer addition tool.
4. Relocate depassivated site and add dimer. (Do not underestimate that 'relocate' step!).
5. Recharge and put down dimer addition tool (or put down and recharge dimer addition tool – order not important).
6. Pick up hydrogen abstraction tool and move to site neighbouring dimer.
7. GOTO 1.

Why do I think that demonstrating the steps above within 5 years is 'hopelessly optimistic'? Because I'm well aware of the current state-of-the-art in scanning probe technology and the associated extreme practical difficulties with putting into practice rudimentary mechanosynthesis steps. Freitas et al. find a 20% success rate in an **ideal** system (i.e. an 'in silico' simulation) – do you really think that an experiment will get anywhere near this success rate?

You could argue, however, that as we've discussed in previous correspondence, there are currently two proposed contenders for Stage 1 of the Drexlarian molecular manufacturing vision (as outlined in Chapter 16 of Nanosystems): Freitas' implementation of the basic mechanosynthesis steps and Drexler's "polymer-based" strategy. If Freitas' strategy fails to work then we switch to Drexler's proposal. I ask again: where is the research towards implementing Drexler's computer-controlled polymer synthesis strategy?[‡] The atomic and molecular manipulation work cited by Freitas in his bibliography of "mechanosynthesis" (see my first letter) was carried out completely independently of *Nanosystems* (just how many of the experimental papers cited in Freitas' bibliography mention Drexler's work?). Development of the SPM technology underlying that work (for example, the construction of five degree of freedom/ multi-tip instruments) will continue to occur naturally without any input from proponents of the Drexler 'vision'. Freitas et al. have made a very wise decision to choose the UHV/diamondoid mechanosynthesis/SPM option – just what other coherent strategy (that doesn't involve SPM-type control) has been proposed?

*"The polystyrene work was done at Northwestern…."*

OK, I was aware of this but didn't know that this was the paper to which you were referring. This builds on really neat earlier work by Lopinski, Wolkow et al. (Nature **406** 48(2000)) but involves a combination of STM-based hydrogen abstraction (using tunnelling electrons and *not* a "hydrogen abstraction tool") with self-assembly rather than molecule-by-molecule mechanosynthesis. (This is an extremely important distinction – please don't claim that Basu et al.'s work provides any semblance of an 'existence proof' for mechanosynthesis). Note the statement on the first page of the paper re. 'proximity' effects:

---

[‡] I've re-read Chapter 15 of Nanosystems and have a technical question on Drexler's discussion of the polymer bead approach. He argues at the start of Section 15.4.5 that *"on a large scale, scanning the primary bead provides a low resolution image of the array of flat-side beads"*. I can't be interpreting the model outlined in 15.4.2 correctly because I don't see how this will be the case. The imaging process is controlled by the highest radius of curvature point regardless of whether that's on the tip or on the substrate (i.e. 'primary' or 'flat-side' bead). SPM operators are sometimes plagued by 'tip imaging' artefacts where the substrate images the tip and not vice versa. If the imaging geometry is as shown in Fig. 15.3(a) then the result on large scales won't be a low resolution image of the array of flat-side beads, it'll either be an image of the surface of the primary bead (if there's only one molecular tip 'active') or, more likely, it'll be an extremely complicated, convoluted image comprising a number of overlapping images of the primary bead surface as the imaging centre changes from molecular tip to molecular tip.

*"In order to achieve this goal, a second FCL* [feedback-controlled lithography] *pattern must be atomically registered with the original FCL patterned molecules. A further difficulty presents itself when the second FCL pattern is positioned in close proximity (e.g., at an adjacent lattice site) to a preexisting molecule. Since many organic molecules are susceptible to electron stimulated desorption, the second FCL step can unintentionally induce desorption of the originally patterned organic molecule, thus disrupting the desired heteromolecular nano-structure."*

Another good reason to avoid current flow in mechanosynthesis!

*"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."*

The comments in my previous e-mail re. tapping mode and sensing a 'molecule capture' event have not been addressed here. Why would you ever want to try the reaction "blind"?! This makes absolutely no sense. You have the ability to measure forces but you decide to switch that off when approaching the surface and do the reaction 'blind'? Why? This is akin to doing a single molecule force-distance spectroscopy measurement without measuring the force on the cantilever! You're cutting off an extremely important information channel. For example, by measuring the force you will most likely be able to detect when you'd picked up the molecule (as I've pointed out before).

*"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."*

I'm glad that you have some experience with scanning probes – it's helpful to know this. Nevertheless, if it's your intention to indicate how straight-forward you find scanning probe manipulation experiments by telling me just how little time (in your opinion) it took you to reproduce the gold cluster experiment then please forgive me for not being particularly impressed. I would expect a good physics undergraduate to reproduce those experiments over a similar time frame (particularly with a commercial instrument). Indeed, your experience with Au dot creation seems to have given you a somewhat false impression of how easy it is to controllably manipulate matter with scanning probes.

There is a vast difference between voltage pulsing a gold tip in air to produce clusters of Au atoms and using scanning probes to manipulate molecules with sub-nanometre precision. I've done both types of experiment and single molecule manipulation at room temperature is tedious, time-consuming and difficult. Why? *Because the tip structure and chemistry are so important and so difficult to control*. (Note that as the Au pulsing experiment relies on electric fields to produce the nanoclusters the constraints on tip structure are much, much weaker and it's really only the radius of curvature that's of importance). Achieving a tip that is capable of both good atomic resolution *and* reliable single molecule positioning (note that the Nottingham group works with buckyballs on surfaces of covalently bound materials (Si(111) and Si(100)) at room temperature) requires a lot of time and patience. Even when a good tip is achieved, I've lost count of the number of experiments which went 'down the pan' because instead of a molecule being pushed/pulled across a surface it "decided" to *irreversibly* stick to the tip. In this context, Freitas et al.'s relatively low success rate for dimer transfer (~ 20%) is rather interesting.

On the related theme of error correction, and before we leave the question of the 'machine language' of mechanosynthesis, perhaps if you get a chance you could respond to my comment on this topic at http://www.softmachines.org/wordpress/index.php?p=50#comments (Comment #25).

*"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,…"*

I've already outlined my thoughts on whether or not the issues are "trivialities" at a number of points in this letter. I have no doubt that you think that the topics in your essay are "more interesting" than considering the fundamental mechanosynthesis chemistry in detail. While I think that the discussion *has* been (incrementally) moved forward (you now at least seem to accept that Freitas' "tool handle" CVD growth mechanism is flawed), I remain disappointed that you still cling to the idea that the detail of the lowest level mechnosynthesis steps is not required when considering the design of a nanofactory. I've presented a wide range of arguments which I had hoped would persuade you that this is a very narrow-minded view. I don't see the point in pursuing discussions of the lowest level steps in mechanosynthetic chemistry with you further and instead will pursue the topic directly with Freitas. (This is particularly the case if you're not going to invest the time and effort to read in sufficient detail the work of molecular manufacturing proponents).

At this juncture, I've addressed your original queries regarding my problems with the Drexlarian 'vision' of molecular manufacturing and have given you a detailed critique of Freitas' proposal: this is a good point at which to draw a line under this particular element of the debate. However, please, of course, feel free to address the questions I've raised in this letter.

It appears that you are more comfortable with discussions based on the 'higher level' elements of molecular manufacturing – you certainly claim that you find these more interesting. This is a topic that I will pursue with you in the future but, for now, I have an extremely busy semester coming up and will not have a huge amount of "free time" on my hands in order to pursue our debate.

Finally, I was extremely disappointed to see that you did not credit/thank Richard Jones for his extremely useful feedback on your Science & Technology essay at http://www.crnano.org/essays05.htm#1,Jan. In peer-reviewed work there is generally an "Acknowledgements" section so that those who have made an important contribution in the form of discussion/criticism are credited. Perhaps you could bear this in mind for future essays?

Best wishes,

Philip

**Subject:** Addendum to my 3rd letter
**Creation Date** 04/01/2005 14:39:55
**From:** Philip Moriarty
**To:** Chris Phoenix

Chris,

Apologies - I neglected to include the following passage in my letter in relation to the Basu et al. paper.

From your first letter:-

"*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.*"

Of course the dehydrogenated spot doesn't diffuse around the surface - the barrier for H hopping is of order 1.7 eV (along the dimer rows [Phys. Rev. B 60, 15896-15900 (1999)]). I'll leave you to do the calculation to determine what hopping rate this represents at room temperature. Could you tell me who has ever suggested that "intuitions" of diffusion rates on metals would be a reliable guide to diffusion rates of hydrogen on semiconductors? (Looks suspiciously like a straw man to me...)

Philip

**Subject:** Re: Publishing the discussion
**Creation Date** 04/01/2005 21:53:38
**From:** Chris Phoenix
**To:** Philip Moriarty

I don't have time right now to address your letter in well-formated and complete detail. I started with the intention of just answering a few urgent points, but have now spent nearly all day on it. Some points will remain unanswered, at least in this response. And I will not format the answers in the same sequence that the topics appeared in your letter.

As you will see, much of this response consists of clearing up misunderstandings and answering accusations. I wish I could have spent more time breaking new technical ground.

I do not consider the technical or scientific issues "trivialities." I do consider some of them "beyond the scope," and reluctantly (because I'm always curious) set them aside. What annoyed me enough to use that word was the bickering over words and phrases. Perhaps there are real issues hidden in some of those words and phrases. If so, I'm more than willing to explore them.

For example, you said, "*You seemingly argue that the distinction between a reaction such at that shown in Fig. 8.14 of Nanosystems and the dimer placement chemistry described in Freitas et al.'s work is "trivial". There is an exceptionally "non-trivial" difference in the chemistry required! In Fig. 8.14 of Nanosystems an individual atom has been transferred via a chemical reaction. In Freitas' work, a dimer is transferred. Building "atom-by-atom" is a considerably different process from building "molecule-by-molecule".*"

I'm not sure how to interpret this statement. Are you saying that reactions which transfer one atom are so fundamentally different from reactions which transfer two atoms that they should be studied as separate classes of technique and carefully distinguished by language? Obviously, any two particular reactions will be very different. But is a carbon-atom deposition more different from a carbon-dimer deposition than from, say, a fluorine-atom deposition?

If there is no fundamental difference between the class of single-atom transfers and the class of dimer transfers, then an insistence on classifying mechanosynthetic systems based on whether the structures will be built "atom by atom" or "molecule by molecule" would seem to be merely confusing, because it would prevent classification of a system which used some reactions that transferred one atom at a time and some reactions that transferred two.

It may clarify things to know that I have been talking about a different issue all along. Some critics of Drexler's ideas, such as Bill Atkinson, have argued that building "atom by atom" can't work because the atoms would immediately react with the tool tip. In other words, for them, "atom by atom" implies that the atom is unbonded: in other words, that Drexler expects single physisorbed atoms to be transported and transferred. It is trivially obvious (to anyone who is not abjectly incompetent, and who doesn't think that Drexler is abjectly incompetent) that Drexler has never proposed such a thing. So when we started to get into discussion of whether Drexler proposed "atom by atom" or "molecule by molecule" and whether that mattered, I thought we were discussing a triviality. Again, if there is a useful categorical difference between reactions which transfer one atom and reactions which transfer more than one atom, I look forward to learning about it. If there is not a useful categorical distinction, then I don't (yet) see that there is anything non-trivial to talk about--and this is why I complained about discussing "whether we all know the difference between atoms and molecules."

You said, "*there has yet to be a single experimental demonstration of a mechanosynthetic reaction carried out by positioning reactive molecules with atomic precision despite the availability of a technology which in principle should enable these experiments to take place*." If someone duplicated Oyabu's results with a well-structured molecule on his scanning tip, would that qualify as a mechanosynthetic reaction? (Note that Oyabu could recharge his tip by picking up an atom from elsewhere on the surface.)

On electric fields: In your first letter to me, you wrote, "*If E fields are to be employed within Drexlerian assemblers then this obviously opens up a broad new parameter space*." Then you stated that the use of E fields didn't scale, so they couldn't be used in nanofactories. I started discussing ways to make them scale. Then you started explaining why E fields wouldn't work. If E fields don't work, then why did you say their use "obviously opens up a broad new parameter space"? That statement of yours is why I started talking about them. I think it's more useful to talk about ways that they could work than reasons why they couldn't. If you don't see any way that they could work, then we should stop talking about them.

You have complained several times about my glossing over problems. If I had been the one to propose the use of E fields, then my desire to refrain from defending them would reflect badly on me. So let's be clear: you brought them up first, implying that they could be useful, and that's why I was talking about them at all. If you now say they are not useful, then there is nothing wrong with my lack of interest in discussing the details of why they are not useful.

On the issue of Richard Jones's comments: I considered whether to give him credit, and decided not to for several reasons. One is that I did not use information from him; I simply dropped the paragraph. If I had used information, I definitely would have given him credit. Another reason is that it was not a formal review. A third reason is that I thought he would likely not even want his name associated with that essay, since it takes a position opposite to his, and listing him as a reviewer could imply endorsement. Perhaps I should have delayed publication (though it was already late) and asked him. So, Richard, do you want me to append "Thanks to Richard Jones for helpful comments on an earlier version" to the web-archived essay?

On the blueprint topic: I heartily encourage "attempting to prove that Drexler's ideas may be flawed"--as you should already know. What I do not have any use for is attempts to prove that Drexler's presentation was flawed. Criticizing his illustrations for being too detailed appears to be an instance of the latter. When I objected to your criticism of Drexler's presentation, you gave me a paragraph of "*This, in case you'd forgotten, is how we progress in science*" and "*If you're not interested in detailed critiques of Drexler's work ... then you're not behaving like a scientist*" and "*There is a process whereby ideas and results are scrutinised before they're disseminated to the scientific community – it's called peer review*." Do you talk to your colleagues that way? Do you take that tone with your students? Tell me, Philip--what class of people do you feel justified in answering with such snide rudeness, and what have I done to earn a position in that class?

On the timeline, you said: "*It's a shame that your strong point on bandwidth is accompanied in your letter by far the weakest argument you have yet put forward. Your original statement was: "It would not surprise me if someone developed a polymer-based molecular manufacturing system before 2010" and I asked you to provide evidence to support your opinion that molecular manufacturing would be with us before 2010. I didn't ask you to prove that the technology will be with us, rather simply to give me some indication as to why the appearance of molecular manufacturing on this exceptionally short time scale would not surprise you*."

Let's review what actually happened. After I said it "would not surprise me", your response was in this tone: "This will be with us in 5 years or less? .... How can you be so confident that polymer-based molecular manufacturing will be with us on such a short time scale?" I responded by objecting to your attributing to me opinions that I do not have. I did not bother to give any argument defending my actual opinions. So your claim that I put forward a weak argument is quite unfair. I put forward no argument at all. That was the best response I could give to an unreasonable question. If you want to see my argument, you must ask a reasonable question--and not simply claim that you have previously asked it. If you were to ask, "Why do you think it is possible to develop molecular manufacturing in five years?" then I would be very happy to explain. But if you continue to pretend that I said 'It will happen,' or to pretend that you did not say 'why are you so confident that it will happen,' or to pretend that I gave a weak argument when I did no such thing, then I will simply drop the topic.

On my chromophore suggestion, you ask how to deposit it and which particular pair to use. I will not be able to answer such questions in detail working alone. And before they can be answered, I think there are some other questions that should be answered first. For example: How does the attainable positional measurement accuracy vary with distance? How is the signal strength affected by the relative orientation of the chromophore molecules? Can the frequency or responsiveness of a chromophore be affected by how it is bound? Can silicon nanoparticles be used to reduce problems of bleaching?

One rough-draft suggestion that occurs to me for binding chromophores to the tip is to deposit a chromophore-adhesive material on the entire tip, then use an e-beam to etch it away except for a few patches, then dip the tip in a mixture of different chromophores, then characterize it to see which colors have stuck where. If the chromophores are placed a few nm back from the tip of the tip, they might not interfere with the deposition reaction.

You wrote, "*(This is an extremely important distinction – please don't claim that Basu et al.'s work provides any semblance of an 'existence proof' for mechanosynthesis)*." That was not why I brought up the work. I brought it up because it was an example of an atomically precise operation done at room temperature, and because it was a useful data point that the missing H didn't diffuse around the surface.

But you raise an interesting question. If a system did a positionally controlled mechanochemical reaction which was followed by self-assembled deposition reactions in limited number and predictable position, would that count as mechanosynthesis or not? For example, suppose a mechanochemical deprotection step at a certain point on a covalent lattice was followed by self-assembled deposition of a protected molecular building block. I can imagine such a system being useful for building molecular machine systems, productive nanoscale fabrication systems, maybe even scalable integrated manufacturing systems.

I don't see a clear dividing line between a deprotection system like I've outlined and a variant of Basu's work that used purely mechanical H abstraction. And I don't see a useful dividing line between a deprotection system and a system in which every reaction involves direct positional control. This is why I am suspicious of early attempts to define molecular manufacturing on the basis of exactly what reaction families it includes or excludes. We do not yet know which reaction families will support the functionality necessary for large-scale productive nanosystems.

Our discussion of measuring force during AFM operations has not been efficient. I'll try to get it back on track by reviewing the context. When discussing the logistics of picking up a molecule with a broken diamond shard, you had asked, "just how does one measure and control/tune the force during the "insert-bind" phase (or indeed during any of the mechanosynthesis steps)?" This implied to me that you thought that measuring and controlling the contact force in a feedback loop would be difficult. So my answer was, "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."

You then misunderstood me, asking: "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..."

What I was proposing was a two-step process. In the first step, tapping mode is used to establish with high accuracy the 3D coordinates of the tip. In tapping mode, one senses the non-contact force indirectly via its effect on resonant frequency; one could, if it were useful (as it frequently is), control the non-contact force by adjusting the height. But one does not control contact forces, because there are no contact forces. And I have never heard of someone using tapping mode to apply a deliberately varied (controlled) force to the surface. It looks like you made a leap from 'not controlling the force' to 'refusing to use anything involving forces.' I was not suggesting that at all, and I'm not sure why you thought I was. And were you thinking that I was suggesting lowering the cantilever while still in tapping mode? It's obvious that that wouldn't work. I think if you had given me credit for just a little deeper understanding of AFM, you would have realized that your interpretation of my proposal couldn't be what I intended.

In my second proposed step, the position is changed by a predetermined amount to bring the tip and the molecule into contact with a precalculated amount of force. The force would not be measured and controlled via a feedback loop during this second step. Instead, the positional change would be directly controlled (by changing the voltage on the piezo) and the resulting force would be pre-calculated. This would require modeling informed by experimentation. There would be at least one clue: the nonlinear change in cantilever deflection as the tip moves into contact with the molecule. This might be useful to adjust the positional control via a feedback loop, or it might be unnecessary.

And yes, this constitutes an observation of force--I don't say "a measurement of force" because I don't know whether the observation would be quantitative. The point is that rather than programming the control loop to produce a certain force-vs-time profile, the control loop would be producing a certain position-vs-time profile. That seems probably sufficient to bring the shard in contact with the molecule in a way that causes some bonding. And it eliminates the need to derive quantitative measurements of the force during the contact process, which would be necessary to control force-vs-time--which, I thought, was the objection you were raising.

I really hope that makes it clear what I was proposing and why. I don't understand why we had such trouble communicating. How would you have described my two-step proposal so as to make it clearer?

You wrote, "*If molecular manufacturing doesn’t necessarily involve molecule-by-molecule mechanochemistry – a distinction which, as you state, is contrary to Drexler’s and CRN’s current definitions - then don’t you think that the CRN message re. molecular nanotechnology should be modified (so as not to mislead those of us who are actually attempting to critically consider just what is required to implement the process at the molecular and atomic levels)? The radical nanotechnology/molecular manufacturing ‘vision’ is fundamentally based on molecule-by-molecule control – if there are forms of molecular manufacturing that will not involve the construction of “gram quantities of atomically precise, functional product that is heterogeneous and engineered at all scales” [Phoenix, 2004] then please make the appropriate distinctions in your writing*."

I have quoted you at length because you listed several different criteria for molecular manufacturing, and I do not think they are equivalent. For example, I am honestly not sure whether a hypothetical process involving mechanically-programmably-guided non-covalent assembly, presumably followed by a (likely non-guided) cross-linking step, should count as molecular manufacturing or not. It would not involve molecule-by-molecule mechanochemistry. It would involve molecule-by-molecule control. The position of the crosslinking reactions would be pre-planned, but probably not individually controlled. Speaking hypothetically, it would be capable of scaleup, and so would be able to make gram quantities of precise functional product.

So does it count as molecular manufacturing, or not? I don't know. It's a gray area. It does fit my five criteria. It does not fit the letter of Drexler's definition. It could be a transformative general-purpose technology, though probably not as high-performance as diamondoid machines for several reasons. Much of the higher-level system design work could apply to it. So I would argue that it fits the spirit of Drexler's work.

Is it really necessary to you to know whether this example is or is not officially considered molecular manufacturing, in the sense that you can't pursue the technical conversation until this point is settled? I don't see much point in settling it now; in fact, I think settling it either way would artificially constrain and confuse the discussion.

If we are trying to answer the question, "Is molecular manufacturing likely to be a transformative technology in the next 20 years?" then of course it is crucial to know what "molecular manufacturing" means. But I am trying to answer a different question: "Can an approach based on engineered molecular shapes, nanoscale machine systems, massively parallel productive nanosystems, the digital nature of covalent chemistry, and simple engineering practice--can such an approach be the basis of a transformative technology that could be relatively quick to develop if sufficient resources were spent?"

You may say that, since "molecular manufacturing" has been defined in terms of a certain class of chemical processes, I should either stick to that or lobby for a formal change of definition. At the moment, making sure that all extant definitions of "molecular manufacturing" agree in every detail is a rather low priority for me. Does this justify your calling me lazy? The other question is whether I should make sure that CRN's web site agrees with me rather than with Drexler on the few cases where we might disagree. That would be premature right now, since we have no solid definition, though I will keep it in mind as an issue to be resolved.

Let me go into a bit more detail on the hypothetical blocks with physisorbed protective caps. Suppose we build a class of molecules that has six roughly planar "faces" corresponding roughly to the faces of a cube. Call this the "core." Each core is a single molecule. The core has a pattern of regions--positive and negative (not ions) or hydrogen bonding--on each face that make it strongly self-assemble with other core molecules. The faces are not reactive--not radical--just attractive to other molecules with the right patterns. If a bunch of uncapped cores were dissolved, they would self-assemble into a random blob.

Now we build a second class of molecules that I'll call "cap." Each cap has a pattern that makes it stick to a face of the core. Again, this is self-assembly--physisorption--not reaction. If a cap is pulled off, the face does not become reactive, and does not reconstruct. An uncapped face will of course attract solvent molecules, but will have stronger affinity for a correspondingly patterned cap or face.

Now we design a machine that can hold a core/cap complex, remove caps from selected faces, remove selected caps from a shape composed of stuck-together cores, and position the uncapped core on the uncapped shape so that it sticks. The trick is that the machine is built of shapes that have been built up from cores. So when the machine finishes building a shape, something is done to crosslink it (perhaps a dose of photons), and the shape then becomes a single, relatively strong molecule--a suitable component for the previously-mentioned construction machine.

This is the proposal that I was trying to present with the description: "*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*." I'm not sure why you thought that the faces would be reactive or crystalline or would reconstruct when the caps were pulled off--I stated that they were physisorbed, not chemisorbed.

I've now thought of a simplification: instead of pulling the caps off and then pushing the uncapped cores together, push the capped cores together so that the caps are squeezed out sideways. This substantially reduces the mechanical complexity, and also eliminates the possibility that something will self-assemble to an uncapped face before the core can be put on the surface.

The nanofactory paper was peer-reviewed. The Journal of Evolution and Technology, where I first published it, is peer-reviewed--in fact, one of the reviewers was quite critical of my first version, and what you see is much improved because of it. At the end of the paper, I thanked seven people for reviewingit, including "two anonymous reviewers." Why did you say that it wasn't peer-reviewed? I do not appreciate spending time to answer hasty and incorrect accusations, but I am also not willing to have a conversation in which such accusations go unchallenged.

You misunderstood what I meant when I said in the Nanofactory paper that "diamondoid fabrication chemistry need not be completely understood."http://www.jetpress.org/volume13/Nanofactory.htm#s2.1 What I wrote was, "Diamondoid fabrication chemistry need not be completely understood--a basic set of a few reliable deposition reactions, with motions parameterized to account for edges and other discontinuities, should be sufficient to build bulk diamond." In other words, even if we don't know everything there is to know about diamond-building chemistry, as long as we know enough to do the reactions we need, then we can make the nanofactory work. I was not suggesting that we would not even have to know that much.

I do think that the architecture of my nanofactory is compatible with a variety of possible mechanosynthetic reactions. It doesn't even have to be diamondoid; most of my paper would not need to be re-written for cubic boron nitride or even silica. So in that sense, I don't mind--for the purposes of that paper!--leaving the reactions as a "black box." However, I am certainly very interested in all levels and aspects of molecular manufacturing, including developing a good understanding of which materials and reactions will be useful.

Was I too hasty in promoting Freitas's proposal? I thought I understood CVD better than it appears that I do. I had thought that it was easier to achieve ballistic deposition than it now sounds like it is, and I had not expected fractional methane radicals to physisorb and diffuse for significant distances on any surface at reasonably high temperature before either desorbing or bonding. Based on that, and also on knowing how cautious and thorough Freitas is, it seemed to me that the CVD idea was well worth trying. And trying it, whether or not it worked, would have taken molecular manufacturing research "a big step closer to the lab."

I wrote, "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, ...." This was in response to a series of questions you asked me referring to particular slides in his presentation. Given that Freitas is presumably available for you to ask him questions directly, I did not want to take the time to review his presentation yet again, find the slides, understand your question, and try to give you a third-party explanation of his thinking.

This does not give you any grounds for accusing that I "now admit to “not having time” to fully understand the physics underlying Freitas’proposal." I will defer any more discussion of what I actually think about Freitas's proposal until you ask reasonable questions rather than accusing me of opinions that I do not hold.

If you want to stop talking now, that's fine with me. I'm sure you think you've been far more patient with me than I deserve. And I certainly think I have been very patient with you. If we cannot find a better basis for communication than snide comments, unfounded accusations, excessive demands for certainty and detail, and unnecessary misunderstandings that drag on through repeated exchanges, then continuing this conversation would not do either of us any good.  I had hoped we might have a chance to do some fun stuff like brainstorming about ways to mechanosynthetically deposit cubic boron nitride or curved graphene (with 5- and 7-member-ring dislocations).  Or even discussing superlubricity--you've stated you support Richard's arguments, but you haven't added anything to them, and I was hoping to understand them better.

The best criticism does not come from a desire to attack, but from a desire to understand.  I do not see that in your writing.  Instead, I see lack of respect, hasty conclusions and accusations, and willingness to be uncivil.  To your credit, you do seem to be motivated to instruct me in things I don't know.  But that is not enough for a productive discussion.

At this time, I don't plan to read your letter again, because large parts of it are needlessly unpleasant.  If there are technical or scientific questions in it that I did not answer, and you would like me to answer, please feel free to copy the text into a subsequent letter.

Chris

**Subject:** Re: Publishing the discussion
**Creation Date** 05/01/2005 13:07:03
**From:** Philip Moriarty
**To:** Chris Phoenix

Chris,

Thanks for your e-mail and my sincere apologies if I've offended/insulted you (see below). I'd appreciate it if you would let me offer a few (relatively) brief responses to key elements of your e-mail. Remarkably, despite your misgivings about my letter, I finally feel that we've made some (more than incremental) progress!

*I do not consider the technical or scientific issues "trivialities." I do consider some of them "beyond the scope," and reluctantly (because I'm always curious) set them aside.*

Unfortunately, what is "beyond the scope" to you may be crucially fundamental for others. I am keenly focussed on the molecular level details of mechanosynthesis whereas you apparently see this as a secondary issue or "beyond the scope".

*Perhaps there are real issues hidden in some of those words and phrases....*

Yes, absolutely.

*....I'm not sure how to interpret this statement. Are you saying that reactions which transfer one atom are so fundamentally different from reactions which transfer two atoms that they should be studied as separate classes of technique and carefully distinguished by language?*

Now we're making progress! My argument is that Drexler's statement 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"

is logically inconsistent if a mechanosynthetic reaction involves the transfer of an atom. Reactive molecular positioning (molecule-by-molecule construction) and atom-by-atom building are definitely, as you say, "two separate classes of technique" which should be "carefully distinguished by language".

*[It has been necessary to remove a paragraph containing a quote from Drexler’s e-mail correspondence with PJM here. The following quote (from) PJM was included (at this point) in the e-mail response to Phoenix and is taken from an e-mail to Drexler dated July ’03 - PJM]*

PJM: "In our discussion some time ago I had asked whether you could clarify the following passage in your 1981 paper: "...molecular devices can characterize a frozen cell in essentially arbitrary detail by removal of successive layers of material (atomically thin layers) if desired"”

*[Drexler’s response to the quote above has been removed - PJM]*

*Obviously, any two particular reactions will be very different. But is a carbon-atom deposition more different from a carbon-dimer deposition than from, say, a fluorine-atom deposition?*

An interesting question - I'd argue that all three reactions are very different from each other.

*If there is no fundamental difference between the class of single-atom transfers and the class of dimer transfers, ...*

...but there is - the chemistry is completely different. (**And** there's no "class" of single-atom transfers or "class" of dimer transfers - the details of the chemistry (e.g. potential energy landscape) will be completely different from materials system to system. See also my comments on Universal Assemblers at http://www.softmachines.org/wordpress/index.php?p=50#comments)

*...then an insistence on classifying mechanosynthetic systems based on whether the structures will be built "atom by atom" or "molecule by molecule" would seem to be merely confusing, ...*

No - this is my entire (and now extremely well-worn/ tired) argument: "atom by atom" and "molecule by molecule" are distinct chemical processes.

*It may clarify things to know that I have been talking about a different issue all along. Some critics of Drexler's ideas, such as Bill Atkinson, have argued that building "atom by atom" can't work because the atoms would immediately react with the tool tip. In other words, for them, "atom by atom" implies that the atom is unbonded: in other words, that Drexler expects single physisorbed atoms to be transported and transferred. It is trivially obvious (to anyone who is not abjectly incompetent, and who doesn't think that Drexler is abjectly incompetent) that Drexler has never proposed such a thing.*

Chris, you spend some considerable time in your comments below berating me for immoderate language. Are you accusing Bill Atkinson of "abject incompetence" here? It certainly seems like it. Could I ask you the same question you ask of me: "Do you talk to your colleagues that way?". (You *know* that I don't think that Drexler is abjectly incompetent and I would not be spending many hours writing letters to you if I thought that you were abjectly incompetent.)

*You said, "there has yet to be a single experimental demonstration of a mechanosynthetic reaction carried out by positioning reactive molecules with atomic precision despite the availability of a technology which in principle should enable these experiments to take place." If someone duplicated Oyabu's results with a well-structured molecule on his scanning tip, would that qualify as a mechanosynthetic reaction? (Note that Oyabu could recharge his tip by picking up an atom from elsewhere on the surface.)*

Mechanosynthesis, as defined by Drexler in his open letter to Smalley, requires the positioning of reactive **molecules** not the manipulation of individual atoms. If Oyabu et al. recharge their tip by picking up an atom from elsewhere on the surface then, no, they haven't carried out a mechanosynthetic step.

And "*having a well-structured molecule on his scanning tip*"? In Nottingham, we've done an experiment somewhat similar to that you suggest. Read Surf. Sci. 407 27 (1998) - where a $C_{60}$ molecule from Si(100) was picked up and dropped back down elsewhere on the surface (note the probability of successful transfer was ~ 0.2% - i.e. two orders of magnitude down on Freitas et al.'s result). Is this mechanosynthesis in the "Nanosystems" sense? No. Why? Simply because, as mentioned in my first e-mail, we start with a reactive (not passivated) substrate. (That is, there's no hydrogen abstraction step using a reactive molecular tool). You might argue that I'm once again just "quibbling" but I can't agree. To convincingly demonstrate a mechanosynthetic reaction as described in "Nanosystems", I argue that at least one iteration of the 7 step sequence described in my most recent letter to you must be carried out. As I stress in the letter, do not underestimate how difficult repeated iterations will be.

I note that, once again, my comments re. steric hindrance in Fig. 8.14 of "Nanosystems" (and associated figures) have been ignored (as has been my discussion of Fig. 15.3). These are direct scientific criticisms of "Nanosystems" - I would appreciate a response at some point.

*On electric fields: In your first letter to me, you wrote, "If E fields are to be employed within Drexlerian assemblers then this obviously opens up a broad new parameter space." Then you stated that the use of E fields didn't scale, so they couldn't be used in nanofactories.*

Chris, this is your **interpretation** of my comment - I didn't mention nanofactories. What I meant was that E fields are prone to induce non-local diffusion processes and this - just as for the electron-stimulated desorption process described by Basu et al - is problematic for the local (molecule-by-molecule) chemistry as required for mechanosynthesis.

*If you don't see any way that they could work, then we should stop talking about them*.

Can E-fields and the associated current flow be used to do atomic scale chemistry? Yes - check the literature on H:Si(100) listed in Freitas' bibliography. Is this chemistry via "the positioning of reactive molecules" as defined by Drexler? No.

*On the issue of Richard Jones's comments: ... Perhaps I should have delayed publication (though it was already late) and asked him.*

In my opinion, that would have been the courteous thing to do.

*When I objected to your criticism of Drexler's presentation, you gave me a paragraph of "This, in case you'd forgotten, is how we progress in science" and "If you're not interested in detailed critiques of Drexler's work ... then you're not behaving like a scientist" and "There is a process whereby ideas and results are scrutinised before they're disseminated to the scientific community - it's called peer review." Do you talk to your colleagues that way? Do you take that tone with your students? Tell me, Philip- what class of people do you feel justified in answering with such snide rudeness, and what have I done to earn a position in that class?*

As mentioned above, my sincere apologies if these comments offended you. You ask, however, "what have I done to earn a position in that class?" and accuse me of snide rudeness. Consider:

1. "And yes, it's eloquent; that's its main virtue, because it's wrong", (http://crnano.typepad.com/crnblog/2004/11/mainstream_acce.html) in response to comments on Richard Jones' "Soft Machines" textbook.

and, more recently:

2. "There are plenty of opinions. Almost without exception, the opinions are shallow." from http://crnano.typepad.com/crnblog/2005/01/creativity_and_.html#c3329453

See also my comments re. your use of the term "abject incompetence" above.

Although I wholeheartedly apologise if you find my comments insulting, I note that - to the best of my knowledge - you have yet to extend a similar courtesy to Richard regarding point 1 above.

*On the timeline, you said...*

Chris, all I asked is that you justify your "I would not be surprised" statement with reference to current capability. Perhaps you could add an essay on the CRN website justifying just why you think that the timeline you suggest is plausible (with reference to current literature and technological capability).

*On my chromophore suggestion, you ask how to deposit it and which particular pair to use. I will not be able to answer such questions in detail working alone. And before they can be answered, I think there are some other questions that should be answered first. For example: How does the attainable positional measurement accuracy vary with distance? How is the signal strength affected by the relative orientation of the chromophore molecules? Can the frequency or responsiveness of a chromophore be affected by how it is bound? Can silicon nanoparticles be used to reduce problems of bleaching?*

All good questions. Back to the timeline issue: at the very least, five years work is required to address/implement the problems outlined in the paragraph above, let alone develop a full scale molecular manufacturing process on this time scale!

*But you raise an interesting question. If a system did a positionally controlled mechanochemical reaction which was followed by self-assembled deposition reactions in limited number and predictable position, would that count as mechanosynthesis or not?*

No - you've not got computer-controlled molecule-by-molecule synthesis.

*This is why I am suspicious of early attempts to define molecular manufacturing on the basis of exactly what reaction families it includes or excludes.*

You're either doing computer-controlled molecule-by-molecule chemistry or you're not. If you're not then just make clear that the experiment/technology falls outside the scope of "Nanosystems" and the Drexler "vision".

*We do not yet know which reaction families will support the functionality necessary for large-scale productive nanosystems.*

And yet you (or CRN) are willing to write: "exponential general-purpose molecular manufacturing... might become a reality by 2010, likely will by 2015, and almost certainly will by 2020." ?

*Our discussion of measuring force during AFM operations has not been efficient. I'll try to get it back on track by reviewing the context. When discussing the logistics of picking up a molecule with a broken diamond shard, you had asked, "just how does one measure and control/tune the force during the "insert-bind" phase (or indeed during any of the mechanosynthesis steps)?" This implied to me that you thought that measuring and controlling the contact force in a feedback loop would be difficult. So my answer was, "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."*

*You then misunderstood me.....*

No, I didn't - see comments below.

*What I was proposing was a two-step process. In the first step, tapping mode is used to establish with high accuracy the 3D coordinates of the tip. In tapping mode, one senses the non-contact force indirectly via its effect on resonant frequency; one could, if it were useful (as it frequently is), control the non-contact force by adjusting the height. But one does not control contact forces, because there are no contact forces.*

Chris, consider this: why is "tapping mode" called "tapping mode"?

*And I have never heard of someone using tapping mode to apply a deliberately varied (controlled) force to the surface.*

Read the literature Chris. Think about just how much of the force-distance curve is traversed during one cycle of tapping mode AFM. See the following website: http://www.spmtips.com/products/cantilevers/catalog/tapping/. Note how "tapping mode" is frequently called "intermittent contact mode". Note in particular the sentence: "Softer cantilevers can be used in Tapping mode as compared to Noncontact as the problem of the tip sticking to the surface can be circumvented by increasing the amplitude of oscillation".

These comments apply to much of your discussion of AFM.

*I think if you had given me credit for just a little deeper understanding of AFM...*

See preceding comments.

*For example, I am honestly not sure whether a hypothetical process involving mechanically programmably-guided non-covalent assembly, presumably followed by a (likely non-guided) cross-linking step, should count as molecular manufacturing or not. It would not involve molecule-by-molecule mechanochemistry....*

Then it's not molecular manufacturing as defined by Drexler and CRN needs to modify its message.

*...It does not fit the letter of Drexler's definition...*

So don't mislead your readers. Ensure that the appropriate distinctions are made.

*Is it really necessary to you to know whether this example is or is not officially considered molecular manufacturing, in the sense that you can't pursue the technical conversation until this point is settled?*

I'm an experimental physicist whose background is in SPM, UHV-based imaging and spectroscopy techniques, and single molecule manipulation/ self-assembly. My primary concern is that we consider at length what's required for the basic low level mechanosynthesis steps. I will not deviate from this! If you want to get more experimentalists interested in attempting some research related to mechanosynthesis as outlined in Nanosystems, then you need to accept that many others will focus on precisely the issues I have.

*If we are trying to answer the question, "Is molecular manufacturing likely to be a transformative technology in the next 20 years?" then of course it is crucial to know what "molecular manufacturing" means.*

Good, we agree.

*You may say that, since "molecular manufacturing" has been defined in terms of a certain class of chemical processes, I should either stick to that or lobby for a formal change of definition. At the moment, making sure that all extant definitions of "molecular manufacturing" agree in every detail is a rather low priority for me.*

"Molecular manufacturing (MM) means the ability to build devices, machines, and eventually whole products with every atom in its specified place" (http://www.crnano.org/timeline.htm). If this is NOT what molecular manufacturing means then I would consider it rather a high priority that you modify CRN's message.

*The nanofactory paper was peer-reviewed. The Journal of Evolution and Technology, where I first published it, is peer-reviewed--in fact, one of the reviewers was quite critical of my first version, and what you see is much improved because of it. At the end of the paper, I thanked seven people for reviewing it, including "two anonymous reviewers." Why did you say that it wasn't peer-reviewed?*

Chris, there's a question mark at the end of the sentence to which you refer. However, in the context of the preceding paragraph of my letter, I very much take your point. My sincere and deepest apologies. It was lazy of me to ask you whether the paper was peer-reviewed rather than take the time to check the literature directly.

*In other words, even if we don't know everything there is to know about diamond-building chemistry, as long as we know enough to do the reactions we need, then we can make the nanofactory work. I was not suggesting that we would not even have to know that much.*

But you have quite specifically stated (as pointed out in my letter) that you feel that the detailed chemistry is not an issue and that the engineering issues are higher priority.

*I do think that the architecture of my nanofactory is compatible with a variety of possible mechanosynthetic reactions. It doesn't even have to be diamondoid; most of my paper would not need to be re-written for cubic boron nitride or even silica. So in that sense, I don't mind--for the purposes of that paper!--leaving the reactions as a "black box."*

...this is the crux of our argument.

*The best criticism does not come from a desire to attack, but from a desire to understand. I do not see that in your writing.*

Chris, I spent a long time mulling over your many points and queries. I am critical of molecular manufacturing and will of course naturally look for flaws in proposals. Does that mean that I don't want to understand? If I didn't want to understand I would not hunt out Freitas, Merkle et al.'s work and read it in detail. I've also recently downloaded your Nanofactory paper and have spent some time considering the proposals contained there.

*Instead, I see lack of respect, hasty conclusions and accusations, and willingness to be uncivil.*

Chris, I've pointed out a few places above where similar criticism can be applied to your writing. Of course, two wrongs don't make a right and I apologise for the more "over-heated" passages in my letter.

*If there are technical or scientific questions in it that I did not answer, and you would like me to answer, please feel free to copy the text into a subsequent letter.*

I'd be very grateful if you could please address the comments re. Fig. 8.14 and Fig. 15.3 I've raised.

Once again, let me apologise for my sometimes immoderate language. As I mention above, I feel that at this point we have actually made progress and, in the future, if you would still like, I am more than happy to consider the "higher level" aspects discussed, for example, in your Nanofactory paper.

Philip

---

Following this e-mail message, a short e-mail and a short response were exchanged between Phoenix and Moriarty (PJM). Unfortunately, both the e-mail and the response contained discussion of quotes from Drexler's earlier (2003) e-mail messages to PJM. These quotes are deleted from the transcript above (see comments in blue type) and the final e-mails (between Phoenix and Moriarty) are therefore not reproduced here.

While it is disappointing that the debate became acrimonious in its final stages, it should be noted that a very positive outcome has been the initiation of discussions between Frietas and Moriarty. The following statement has been agreed by both Freitas and Moriarty:

*"Freitas and Moriarty have recently agreed to continue discussions related to the fundamental science underlying mechanosynthesis and the experimental implementation of the process. These discussions will be carried out in a spirit of collaboration rather than as a debate and, therefore, will not be published on the web. In the event that this collaborative effort produces results that impact (either positively or negatively) on the future of mechanosynthesis, those results will be submitted for publication in a peer-reviewed journal*".