

Dear Chris,

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

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

It is also important to note that, while I do not accept the concept of a 'universal assembler' which will be able to build 'virtually anything' (as repeatedly espoused by Dr. Drexler and others at the Foresight Institute), I have a *genuine interest* in the fundamental mechanosynthesis ideas outlined by Freitas and Merkle and believe that their willingness to at least accept the key significance of proof-of-principle experiments is a big step forward. I also wholeheartedly endorse the following statement in your e-mail: "Also, if it's theoretically workable but practically near-impossible, then it may take a long time to develop--and again, CRN would need to modify its message." While I am open to the idea of attempting to consider routes towards the development of an implementation pathway for Mann et al.'s Si/Ge-triadamantane dimer placement reaction, even this most basic reaction in

mechanochemistry is practically near-impossible. For example, how does one locate one tool with the other to carry out the dehydrogenation step which is so fundamental to Mann et al.'s reaction sequence? In my correspondence with Dr. Drexler, I have put forward similar arguments re. reaction sequences previously described by Merkle and co-workers:

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

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

Dr. Drexler's response to this type of comment during our correspondence last year was that molecular manufacturing would not be based on SPM technology. My question remains: to implement computer-controlled atomic precision positioners, if SPM technology is not to be used then what's the alternative? As I discuss in more detail in the following sections, arguments and analogies based on the Apollo Moon landings simply don't address this question. If CRN and the Foresight Institute want to succeed in attracting public funding for the development of MNT then:

- (i) a coherent strategy/ pathway to assembler development must be outlined. ['Stick' diagrams such as those shown in Fig. 8.14 of *Nanosystems* convince no-one. At least Freitas et al. are attempting to address the key technical issues rather than "stonewalling" on the precise details of the assembler and tip technology].
- (ii) 'proof-of-principle' experiments must be attempted – this has been tacitly accepted by researchers at the Foresight Institute (see <http://www.foresight.org/stage2/project1A.html>).

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

### What is mechanosynthesis?

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

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

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

- (i) The beautiful STM work of Lyding et al. on atomic hydrogen desorption involves either E field- or tunnel current (vibrational heating)-induced removal of adsorbed H atoms from Si(100). This is not *mechanical* positioning. If E fields are to be employed within Drexlerian assemblers then this obviously opens up a broad new parameter space.
- (ii) The work of Becker et al. [1987], Avouris et al. [173], and Aono et al. [1993] on STM-induced atomic manipulation does not involve reactive (and re-chargeable) molecular tools. Furthermore, as all of this work involved STM on semiconductors, electric fields of order  $10^9 \text{ Vm}^{-1}$  were again present. (It is worthwhile referring to TT Tsong's papers on electric field-assisted atomic manipulation when considering STM-based manipulation). Whitman et al. have also published some extremely nice work on field-induced diffusion of Cs atoms on GaAs(110). Ho and Lee's breathtaking work in 1999 *explicitly* involves tunnelling electrons and is thus outside the realm of mechanosynthesis.
- (iii) While Oyabu et al.'s exciting experiment (PRL 90 176102) is AFM-based and therefore involves purely mechanical forces, it still doesn't fall within the scope of the definition above. There is no placement of a

reactive *molecule* to drive the 'abstraction' process – rather, an atom from the AFM tip forms a bond with the surface. One might argue that this is simply “splitting hairs”, i.e. that the experiment is clearly an example of mechanical interactions driving a surface modification and thus this exemplifies the 'essence' of mechanosynthesis. I cannot accept this argument. Mechanosynthesis necessitates the manipulation of *pre-chosen* reactive molecules and, moreover, will require the application of *rechargeable* tools.

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

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

### **Implementation pathways and “sticky fingers”**

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

*“The overall deposition reactions are endothermic and, therefore, thermodynamically unfavorable for both Si and Ge tools. Retraction of the tool from the diamond substrate will retain the carbon dimer to the placement tool the vast majority of the time, so the proposed tools are inefficient at their designated task. However, depositing a C2 dimer onto the diamond surface may occur a finite*

*percentage of the time, which might be an adequate performance for early experimental proof-of-concept demonstrations. "*

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

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

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

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

This is precisely what Merkle, Freitas, and Mann et al. find in their work and, if we're honest, at the most fundamental level this represents an alternative statement of Smalley's "sticky fingers" argument. That is, the detailed chemistry of each system provides a fundamental obstacle to the construction of a universal assembler that can handle all the technologically important elements in the periodic table.

### **SPM and alternative (?) technologies**

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

surround the tool-tip. The growth process will also be complicated by surface reconstruction of the various facets of the handle structure. I'd appreciate it if you could let me know what I'm missing – i.e. why will the nanocrystal grow in a fashion whereby the tool tip remains “isolated” at the bottom of the grown structure?

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

While I can seemingly identify flaws in Freitas' proposed methods, at least he (and Merkle) are attempting to outline a strategy (based around technology that to me looks as if it's fundamentally based on current SPM methods). Dr. Drexler, however, does not agree with Freitas and Merkle's suggestion that SPM might be used to achieve positional control. He has stated: *“no one has argued that molecular manufacturing can be performed using today's crude scanning probes”*. My question to Dr. Drexler – raised time and time again during our correspondence last year - remains: if not scanning probe technology then what? Why are Freitas and co-workers devoting so much time to a consideration of SPM methods if these are not ultimately relevant to mechanosynthesis? The ‘Drexlerian’ vision of mechanosynthesis necessitates computer-controlled actuation and positioning – *just how will these operations be carried out if SPM-type positioning and SPM-type tips are not to be used?* [I plead that you don't refer me to Chapter 16 of *Nanosystems* – I've read this and there is no coherent workable strategy capable of producing a prototype device described there].

The question of outlining workable strategies and formulating ‘proof-of-principle’ experiments was at the core of my argument with Dr. Drexler last year. In the final section of this letter/document, I outline why I feel that ‘proof-of-principle’ experiments are essential to illustrate that even the most basic steps in mechanosynthesis are possible. While I am more than aware that Dr. Drexler is fundamentally opposed to this approach, it seems that Freitas and Merkle appreciate the relevance of defining appropriate strategies that might be tested by experiment.

### **Proof-of-principle experiments**

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

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

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

*“You mistake the situation. Molecular manufacturing will result from a series of advances in molecular machine systems, much as the first Moon landing resulted from a series of advances in liquid-fuel rocket systems. We are now in a position like that of the British Interplanetary Society of the 1930s which described how multi-stage liquid-fuelled rockets could reach the Moon and pointed to early rockets as illustrations of the basic principle. Your query is like a suggestion that we use 1930s rockets to bring back just a tiny sample of lunar material, as a proof of concept for the larger system”.*

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

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

Moreover:

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

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

Best wishes,

Philip