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Future of Mechanochemistry**

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Complete List of Authors:	Craig, Stephen; Duke University, Department of Chemistry

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ARTICLE

Concluding Remarks: Fundamentals, Applications and Future of Mechanochemistry

Stephen L. Craig*^a

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This paper provides a summary of the *Faraday Discussion* on “Mechanochemistry: Fundamentals, applications, and future” in the context of broad themes whose exploration might contribute to a unified framework of mechanochemical phenomena.

Introduction

Elena Boldyreva’s Introductory Remarks to this Discussions meeting included a forward-looking list of nine contemporary challenges for the field of mechanochemistry. I will focus my Concluding Remarks on the two items that topped her list:

1. Unification of mechanochemical phenomena
2. Identify parameters that guide reactivity

These two challenges, respectively, succinctly summarize what is required for a comprehensive conceptual and practical implementation of mechanochemistry. Once these pieces are in hand, the additional important challenges from Boldyreva’s list (selection of treatment, preparation of reactants, role of fluids, role of melting, impact of material relaxation, etc...) will immediately become much more tractable.

The challenge, as we have seen throughout the meeting, is that experimental observations in the field are the result of a complex integration of reaction probabilities across location, time, temperature, composition, and force or pressure distribution. And, as we have also seen, the effects of a single parameter are often difficult to unentangle, because one parameter influences another. In many ways, a statement that Ken Suslick made in his Concluding Remarks to the prior incarnation of this meeting,¹ now eight years ago, still holds:

“In mechanochemistry, the progression from descriptive questions to more mechanistic concerns is still at an early stage. We do not yet have a firm grasp of the underlying conditions created during most mechanochemical events; indeed we do not

even have a fully resolved theory of the underlying quantum mechanics that connects chemical and mechanical phenomena.”

While Suslick’s statement is certainly still true, however, I have been struck over the course of the meeting that the status of this statement is starting to change. One can argue that many historical challenges in the field are either tractable or close to becoming so. Broad challenges of such complexity are very rarely, if ever, solved in a single investigation. Instead, the route to general principles is often found in the aggregated exploration of more specific questions. It is perhaps useful, therefore, to look at the content of the meeting’s papers in terms of the kinds of broad themes whose exploration might ultimately lead to a more global picture of mechanochemical phenomena. Here, I offer some thoughts along those lines. It is perhaps appropriate that the meeting has been held on the banks of the Cam, as any endeavor of this flavor is truly “taking a punt,” albeit in a very different connotation than that of the flat-bottomed boats that have glided into and out of sight through the meeting room windows to the rear of our speakers over the days of the Discussion meeting.

Some caveats.

The sub-themes employed in this paper, and as well even the classification of individual papers with those sub-themes, are more subjective than objective, and almost certainly not uniquely appropriate for the task at hand. My own view is very much a function of my experience in covalent polymer mechanochemistry,² whereas the papers that have been presented in this meeting are dominated by work in ball-mill grinding, resonant acoustic mixing, tribology, and shock wave propagation. My thinking is highly influenced by approaches and frameworks that I have found to be useful in my own work. In particular, Boldyreva noted the core question of reactivity

^a Department of Chemistry, Duke University, Durham, NC 27708-0346

that occurs “during” vs. “between” the imposition of mechanical energy, and I will focus primarily on the question of what occurs “during,” which is taken here to include the mixing that is necessary even for reactivity that may occur “between” events.

The hope is that the differences in perspective between the two fields, whether stark or subtle, might encourage and support a richer understanding and motivate new ideas and approaches within each. Mechanochemistry in granular or crystalline solids and that in polymers under tension are quite easily contrasted on the basis of their differences, but general principles and frameworks of mechanochemistry should unite them. There may be value in actively promoting more meetings that target the combined community.

Discussion

I structure my discussion in terms of a very general and hierarchical framework, beginning with the mechanics being imposed macroscopically and progressing down to the dynamics of chemical reactivity at the molecular level.

What continuum mechanical states characterize the system?

In some cases, continuum mechanical states of a system are defined relatively easily. For example, in covalent polymer mechanochemistry a rubber band or other elastomeric film held under constant tension can be characterized by a single stress and strain that remains invariant for long periods of time at constant temperature. Even repeated stretching and relaxing macroscopically leads to repeated stretching and relaxing of the constituent strands within a covalent elastomer.³ A snapshot of a ball mill, however, would be characterized by a high stress at the collision point between the surfaces of the ball and vessel and no stress elsewhere. Different geometries of polymeric material and methods of imposed strain (e.g., tensile vs. compressive vs. torsional) can also lead to a distribution in the effective continuum stresses that would, for example, be captured in finite elements modelling.

Characterizing the energetic inputs into mechanochemical processes now enables the ability to quantify the efficiency gains relative to traditional thermal methods, as demonstrated nicely in the work of Leon et al.⁴ Pétry et al. showed how specific experimental conditions influence overall reaction efficiency in sydnone synthesis.⁵ But what do the experimental parameters mean for what is experienced by the sample and how is that mediated by the reactant phase itself? Vugrin et al. provide a compelling example of the potential utility of this line of questioning, using modelling to derive a direct correlation between the energy of an impact event of reactivity.⁶ Further advances are likely possible when the energy is broken into various mechanical contributions, such as stress vs. shear, as explored by Fang et al. in the context of zinc dialkyldithiophosphate tribofilm formation.⁷

In situ methods of force, stress, or strain generation are therefore quite useful. In covalent polymer mechanochemistry, these quantities can often be measured directly either as part of the mechanical testing device used to deliver the strain, or through the use of imaging.⁸ Such methods are not amenable to, for example, a ball mill, and so approaches with embedded sensors such as presented by Marrero et al. present a rich set of opportunities.⁹ One speculates that the use of piezoelectric particles^{9, 10} as threshold indicators of mechanical stress might also be useful in this regard, similar to the use of mechanochromic mechanophores in polymer mechanochemistry.¹¹ The continued advancement of in situ characterization methods^{12, 13} may be particularly important when the property changes that accompany reaction have a significant impact on the mechanical energy being delivered, for example as the products occupy a different phase (liquid vs. solid) from the reactants, or simply make up materials with different moduli. Thorough characterization of the specific molecular and mesoscopic details of the transformations induced^{14, 15} will also give important physical insights into mechanically induced transport and phase changes, as well as reactivity.

What is the distribution of molecular mechanical environments for a given continuum stress/strain?

In polymer mechanochemistry, a bulk material or local volume within the bulk might be accurately characterized by a single stress, but the tension is distributed unevenly at the molecular level throughout the material. Similarly, the reactants between contacting surfaces in impact or grinding, or within a gap under tribological mechanical stimulus, might be characterized in the ensemble by an effect stress or force, but still have a wide range of mechanically coupled molecular states due to variations in the position and/or orientation of one particle within a jammed multi-particle aggregate, within the contact area or intersurface gap, or even of a specific molecule within a given particle.

Such effects are implicitly addressed in multi-scale simulations, as seen in the papers by Bhuiyan et al.¹⁶ and Michalchuk.¹⁷ The ability to connect simulations to well-characterized physical environments and outcomes⁷ is particularly empowering. Mechanochemical molecular transformations that result in significant changes in photophysical^{4, 18, 19} or electrochemical^{9, 10} properties are the focus of several of the meeting's reports. The continued development of such systems might empower in situ monitoring of spectroscopic changes as a reporter of the more local stress environment, and the stress-sensitive spectroscopy of nitrogen-vacancy diamond was proposed by Batteas during discussions as another attractive option for this purpose. To be as informative as possible, the stress-dependent response should be quantified by theory or experiment. Quantitative characterization of molecular behaviour under quasi-static tension by single molecular force spectroscopy has been particularly enabling for polymer mechanochemistry,^{20, 21} and diamond anvil presses²² might prove to be useful for similar

characterization relevant to granular and crystalline solids mechanochemistry.

How does the probability of a reaction outcome depend on the specific mechanical state of the reactant?

As the distribution of mechanical states is better characterized, the relative contribution of a given mechanical state to the overall conversion observed in a mechanochemical reaction becomes the next focus. Computations now allow for force-modified potential energy surfaces of reactions to be calculated at high precision, and excellent agreement is observed when well-controlled forces are applied through single molecular polymer mechanochemistry.²³⁻²⁶ The inference that similar methods should capture the fundamentals of mechanochemical coupling at the molecular under other mechanical potentials seems reasonable, and these types of computational approaches contributed to multiple talks in the meeting.^{16, 27} One of the difficulties of ball mill grinding and related work is that the interpretation of experimental data is complicated by the fact that the medium that transduces the applied force is also the reactant medium, and so pulling out the contributions of one or the other aspect of its participation becomes difficult. Polymer mechanochemistry in the bulk benefits from the fact that the transducer (the polymer or polymer network) and the reacting species (the mechanophore) are distinct, and the mechanophore can be varied at dilute quantities within an otherwise constant polymer matrix. Alternatively, the same mechanophore can be used to probe the transduction efficiency of different polymers. As quantitative tools are increasingly applied in the granular/crystalline solids space, there may be a role for less practical studies of dilute reactants within chemically inert "transduction" media.

Do reactants interchange mechanical environments? In particular, do they do so faster or slower than the relevant timescales of chemical reaction?

Given that a given continuum mechanical state might have a broad distribution of molecular mechanical states,²⁸ it is likely that a subset of reactants experiences privileged, "high reaction probability" mechanochemical coupling while others remain effectively inert. If reactants do not change their molecular mechanical state, even after very long times the only reactions that will have occurred come from that (potentially very small) subset of reactants. In contrast, if the mechanical force or stress is continuously redistributed among the reactants, the reactive "hot spots" might be exchanged so that all reactants eventually convert to products. For example, in a rubber band held under constant tension, there is almost certainly a wide range of molecular strand tensions, but each individual strand maintains its particular tension more or less indefinitely. A detonating crystalline material, however, involves a peak stress and temperature whose magnitudes and positions change with time as an explosion propagates rapidly through the material; both

the distribution of states and the specific state of any given molecule change dramatically throughout the process.

The consequences of dynamic force distributions and bulk dynamics for overall reaction kinetics are considerable, and would complicate interpretation of even the most fundamental kinetic observations, because the force that corresponds to the average reaction probability over a given time is not necessarily equal to the average force of the system over that time;²⁸ in fact, the two might diverge considerably, especially at high stresses and strains. This and other interplays of reaction dynamics and mechanical dynamics contribute to the compelling nature of some of the more fundamental investigations of mechanochemical propagations presented during the meeting.^{7, 16, 17} Dynamic effects at high strain rates beyond the quasi-static limit (e.g., shock waves) represent a particularly intriguing area of investigation in mechanochemical reactivity.

Conclusion

A remarkable aspect of contemporary mechanochemistry is its breadth. The contributions from the meeting include advances in polymer synthesis,²⁹ catalytic coupling,^{30, 31} crystal polymorphism,³² CuS phases,³³ and broad questions of mechanochemical methodology.^{34, 35} That breadth has continued potential to expand, and the discussions during the meeting inspired two thoughts as to areas of future promise that were not represented in the contributions.

First, the intermittent nature of localized high force events has been noted as a challenge for characterization, but might also provide opportunity in new forms of catalysis. Many catalytic cycles comprise a series of discrete steps, and the optimal catalyst for one step is not necessarily the optimal catalyst for another. When considered in this light, the intermittent application of high mechanical forces to an active catalyst might be used to allow the catalyst to toggle between two distinct states, each of which is better matched to a unique, distinct step in the catalytic cycle. For example, tension applied to bis-phosphine ligands has been shown to accelerate reductive elimination³⁶ and to decelerate oxidative addition.³⁷ The intermittently generated high forces delivered by sonication of polymer solutions or impact during ball mill grinding are examples of mechanical inputs that could be used to switch a given catalyst between states better suited to oxidative addition and reductive elimination, increasing the overall efficiency of a reaction.

Second, the complexity of mechanochemical reaction systems is of the sort where contemporary methods in machine learning seem well suited to add value. I have been fortunate in recent years to interact with Brad Olsen and the Community Resource for Innovation in Polymer Technology (CRIPT), which is developing an approach for polymer chemistry that I believe has numerous similarities to the needs of the mechanochemistry community. The algorithms for this sort of effort are not the

barrier; the key lies in data. I think it is a good time for the community to be thinking about the kinds of data structures and practices that preserve and communicate the richest set of primary data and its associated metadata. Schemas that allow characterization to be directly associated with traditional compositional data, as developed for polymers,³⁸ are likely to be quite useful here as well. Several comments were made in discussions during the week with respect to the subtle effects of how a sample is prepared before mechanochemical treatment, or the difficulty of reproducing conditions (or even identifying how conditions are different) from one lab to another, or maybe even within a given lab. The same data collection, storage, and sharing procedures that address these kinds of concerns are the types of data handling procedures that are likely to best serve machine learning methods.

It has been a truly stimulating meeting. One should always encourage a bit of skepticism in such things, but I find it easy to be more optimistic at the opportunity than pessimistic at the challenge presented by the complexity that is inherent to most mechanochemical reactions. It will be interesting to see how the status of the field is summarized at the next Discussions meeting on this topic some years down the road.

Author Contributions

S. L. Craig conceived and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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