

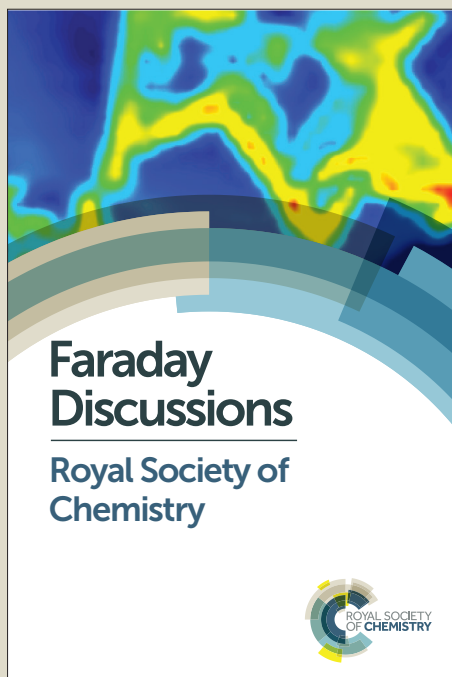
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Mechanochemistry and Sonochemistry: Concluding Remarks

Kenneth S. Suslick

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5 This paper offers a perspective on mechanochemistry and offers
summarizing commentary on the *Faraday Discussion* 170,
“Mechanochemistry: From Functional Solids to Single Molecules”. The
connection between the mechanical and the chemical worlds dates to our
earliest written records and beyond, but its renaissance over the past decade
10 or so has had impact on a huge swath of modern science and engineering:
from metallurgists to polymer scientists to synthetic organic and inorganic
chemists to cellular biologists. Connections among the different subfields
of mechanochemistry (tribochemistry, trituration, macromolecular, and
sonochemistry) are drawn out and the common themes and open questions
15 are enumerated.

1 Introduction

The use of friction to make fire takes our connection between the mechanical and
the chemical worlds back to the dawn of our species. The written records on
mechanochemistry date back to the ancient Greeks, when Theophrastus (one of
20 Aristotle’s students) wrote “On Stones” in ca. 315 BCE and referred to the reduction
of cinnabar to mercury by grinding in a copper mortar and pestle.¹ 2100 years later,
Faraday described the reduction of silver chloride by grinding with various metals,
his “dry way” of inducing chemical reactions.² The full history of mechanochemistry
is fascinating and has been delightfully examined by Laszlo Takacs elsewhere.³

25 While the chemical consequences of mechanical actions have a long heritage, it
was Ostwald (the ninth Nobel Laureate) who systemized chemistry in 1919 into the
branches of thermochemistry, electrochemistry, photochemistry and
mechanochemistry.⁴ It is only the past decade or so, however, that
mechanochemistry has gained a notable focus in the chemical community with the
30 coming together of a huge diversity of related but quite different specialties, ranging
from metallurgists to polymer scientists to synthetic organic and inorganic chemists
to cellular biologists.⁵⁻¹⁸

This very recent renaissance, moreover, makes this symposium (FD170,
“Mechanochemistry: From Functional Solids to Single Molecules”) the first
35 significant appearance of mechanochemistry in the *Faraday Discussions*. The 26
papers and 48 posters presented at FD170 spanned most of the modern topics of
mechanochemistry, with the notable exception of bio-mechanochemical topics (i.e.,
cellular motion, biomolecular motors, and intracellular active transport^{16, 19, 20}).
While the relationship between mechanochemical and the bio-mechanical is clear,
40 the latter is sufficiently complex to require its own, future *Faraday Discussion*.

The diversity of mechanochemistry reflects the multitude of ways in which
mechanical phenomena can bring about chemical consequences; I provide one useful
organizational chart in Fig. 1. One may break mechanochemistry into four areas:
tribochemistry (the chemistry of surfaces in contact), trituration (chemistry induced
45 by grinding and milling), macromolecular mechanochemistry (from breakage of
polymer chains to molecular motors and biological motion), and sonochemistry (the

chemistry generated from the mechanical consequences of sound). One might also add shock-induced solid-state chemistry as a fifth subfield, but one note included in these discussions. These separate categories have each developed largely independently of one another in different communities and often with different goals and concerns. One may hope that FD170 will have contributed substantially to a convergence of these diverse areas under the more general rubric of mechanochemistry.

My role in FD170 was two-fold: I was given the honour of presenting the summary lecture, but I was also the principal representative of a related branch of non-traditional chemistry dealing with the chemical effects of ultrasound. With apologies to Churchill, sonochemists and mechanochemists are one people, separated by a common phenomenon. That common phenomenon is the conversion of mechanical energy into chemical consequences. As such, my commentary below will first draw out the similarities among all forms of mechanochemistry (with some focus on my own sonochemical interests) and second will provide an overview of the presentations and discussions of FD170. I do not intend to provide a blow-by-blow summary of all the presentations and the accompanying discussions: obviously, this can be far better gained by reading the Discussion volume. I will, however, attempt to bring out common themes and unresolved questions that the Discussions developed.

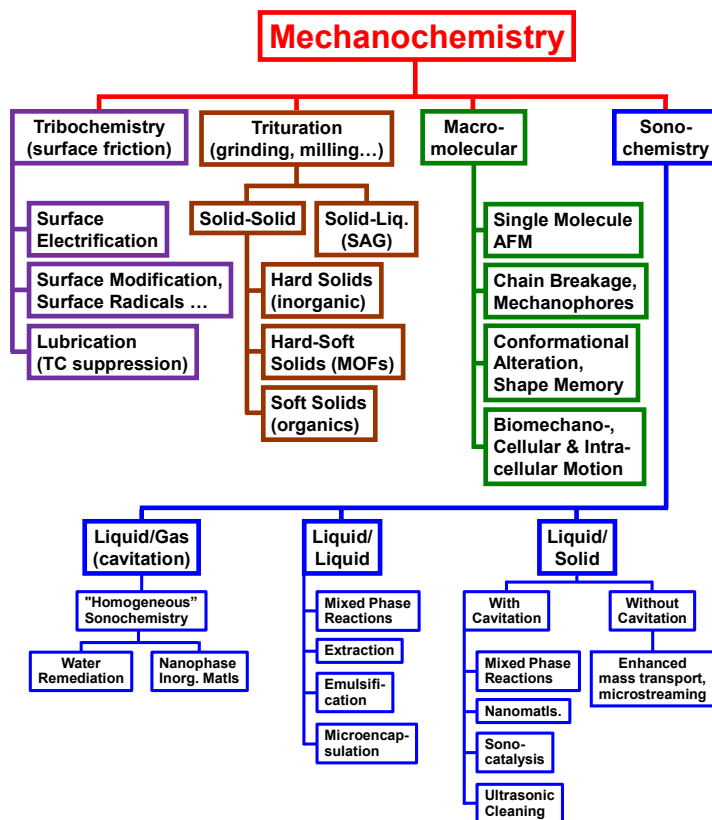


Fig. 1 Mechanochemistry may be divided into four distinct, but related arenas.

2 The Sonochemical-Mechanochemical Connection

Sonochemistry is a consequence of the mechanical effects of sound on liquids and originates from acoustic cavitation (the formation, growth, and implosive collapse of bubbles in liquids, Fig. 2).²¹⁻²⁴ The bubble collapse creates intense compressional heating within the bubble and generates extreme transient conditions in the resultant hot spots that can achieve temperatures above 5,000 K, pressures exceeding 1,000 atmospheres, and heating and cooling rates in excess of 10^{10} K/sec.^{22, 25-28} These conditions are distinct from other conventional synthetic techniques such as photochemistry, wet chemistry, or hydrothermal synthesis (Fig. 3).

Sonochemical reactions can be categorized as primary sonochemistry (gas-phase chemistry occurring inside collapsing bubbles), secondary sonochemistry (solution-phase chemistry occurring outside the bubbles from species produced in or near the bubble interface), and physical modifications (caused by high-speed jets of liquid driven at extended surfaces (Fig. 4a) or by shock waves in the liquid created by bubble collapse, Fig. 4b).^{21, 29, 30}

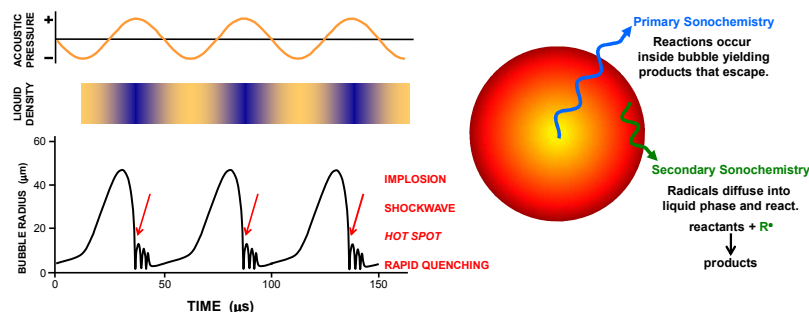


Fig. 2 Schematic illustration of the process of acoustic cavitation: the formation, growth and implosive collapse of bubbles in a liquid irradiated with high intensity ultrasound. Homogeneous sonochemistry derives from the reactions that occur within the hot spot generated by the collapsing bubble. In liquid-solid systems, acoustic cavitation can have other mechanochemical consequences due to shockwaves, interparticle collisions in slurries, and microjetting near surfaces.

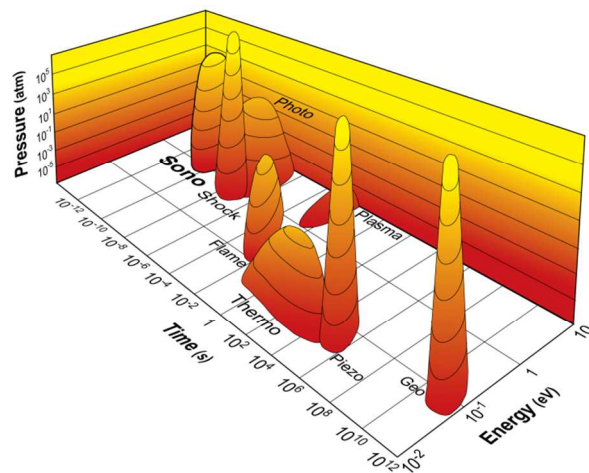


Fig. 3 Islands of chemistry as a function of time, pressure, and energy. Sonochemistry occupies a unique short-time, high-energy, and high-pressure space. Reprinted with permission from ref. ²². Copyright 2008 Annual Reviews.

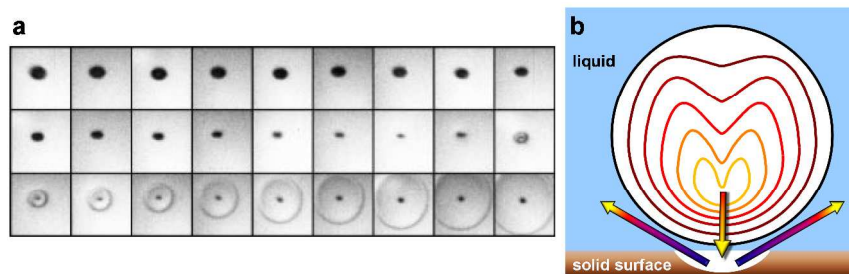


Fig. 4 (a) A spherical shock wave launched from laser-induced cavitation. The rebound of the collapsing bubble generates a shock wave in the surrounding liquid that can reach 60 kBar with velocities of 4 km/s (frame size 1.5 x 1.8 mm², 5 ns exposure, 20.8 million fps). Reprinted with permission from ref. ³¹. Copyright 1999 The Royal Society. (b) Cavitation near an extended solid surface is highly asymmetric and generates liquid jets with velocities of hundreds of m/s. The jets cause pitting, erosion, and remove of passivating surface coatings and can thus enhance surface reactions on reactive surfaces, such as Grignards and lithiations.

10 It is the physical effects of sonochemistry that are most reminiscent of other forms of mechanochemistry. For example, the shock waves created by bubble rebound can accelerate solid particles suspended in the liquid. Interparticle collisions in slurries can reach velocities of hundreds of meters per second, causing changes in particle size distributions, particle morphologies, and surface compositions.³²⁻³⁴ Particle agglomeration (for malleable materials, Fig. 5), particle fragmentation (for brittle materials, Fig. 6), and exfoliation of layered materials into 2D layers have all been observed.^{21, 29, 35, 36} The consequences of cavitation lend themselves readily to the production of novel nanomaterials (especially since every bubble is an isolated nanoreactor) and provide an unusual route to novel materials
 20 without bulk high temperatures, high pressures, or long reaction times.^{21, 29}

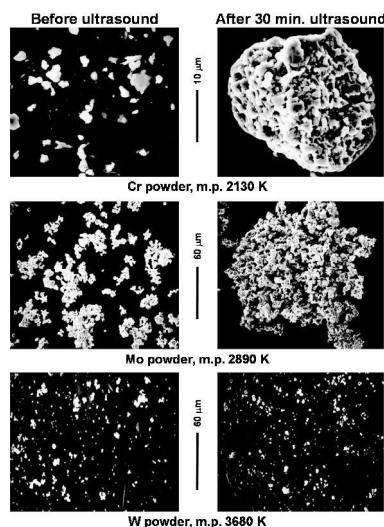


Fig. 5 Effects of ultrasonic irradiation on slurries of fine metal powders (~5 µm diameter). Sonicated in decane slurries of 2.5% metal v/v. Reprinted with permission from ref. ³². Copyright 1990 AAAS.

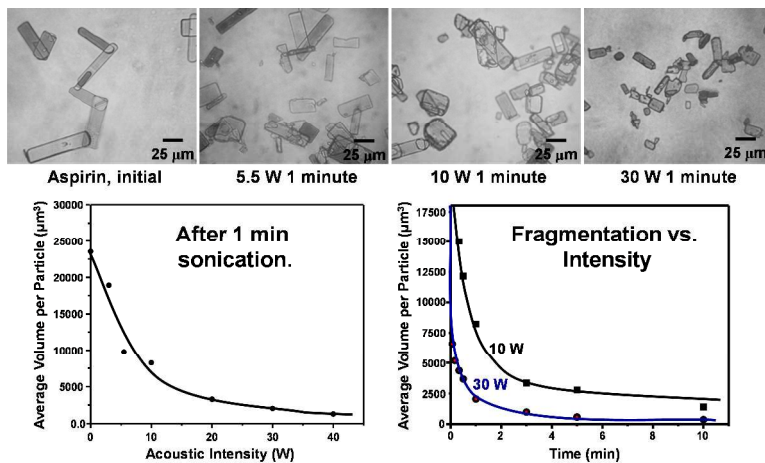


Fig. 6 Effects of ultrasonic irradiation on slurries of fine metal powders ($\sim 5 \mu\text{m}$ diameter). Sonicated in decane slurries of 2.5% metal v/v. Reprinted with permission from ref³⁵.

5 Given the similarities in mechanical effects of cavitation of slurries and trituration (grinding, milling) of powders, there is an inevitable convergence of chemical consequences. As an example, if one examines the chemical and physical consequences of sonochemical and mechanochemical (specifically grinding) of inorganic materials, one arises at exactly the same list for both, as given below.

10

- Bulk Heating
- Local Heating & pressure/shock
- Crystal deformation
- Formation of many defects
- 15 ▪ Shear stresses
- Phase transitions
- Amorphization
- Reduction of crystallite sizes
- Aggregation of crystallites
- 20 ▪ Acceleration of diffusion processes
- Emission of light (common)
- Emission of electrons (uncommon)
- Chemical bond breaking

25 **3 Summarization of Mechanochemistry: From Functional Solids to Single Molecules**

As at any *Faraday Discussion*, the contributed papers formed a complementary web of topics with an associated wealth of specific questions and comments, among
 30 which several recurring themes and issues can be identified. The Introductory Lecturer (Professor Bill Jones, University of Cambridge) provided a masterly overview of the current state-of-the-art of mechanochemistry, touching on its history, areas of application, and mechanistic aspects.³⁷

As was clear from the start of the Discussions, the technological and industrial
 35 applications of mechanochemistry are diverse. The earliest studies of

mechanochemistry dealt with the effect of grinding on minerals and have already resulted in real applications. Mechanical activation of minerals and mechanical alloying (for example, oxide dispersions) have been produced commercially on the ton scale.³ Fine milling of lignocellulosic biomass is already coming into use for biofuel production³⁸ and higher value added materials, including graphene.³⁹ Applications of mechanochemical activation to inorganic and ceramic synthesis are increasingly abundant at the laboratory scale, where ball milling becomes a common primary step. The use of mechanochemical methods for organic and organometallic synthesis remains a relatively new, but extremely active research area. Mechanochemistry is often viewed as a “greener” alternative because it often avoids the use of solvents.

One may break the applications discussed in FD170 into perhaps five categories: (1) inorganic compounds, metal coordination and organometallic complexes and extended coordination polymers (e.g., MOFs),⁴⁰⁻⁴³ (2) organic synthesis with the making and breaking of covalent bonds,^{41, 44-47} (3) supramolecular and pharmaceutical reactions and the making of co-crystals;^{37, 42, 48} (4) inorganic and organic nanomaterials;^{39, 40, 49-51} and (5) polymer chain scission, intra- and inter-chain reactions.⁵²⁻⁵⁵

Mechanochemical preparation of co-crystals of pharmaceuticals became a prominent theme that emerged in multiple papers during FD170.^{37, 42, 48} Co-crystals are one example of the broader issues of supramolecular solid state chemistry, but one that has important biomedical application for drug delivery, pharmaceutical efficacy, and admittedly pharma intellectual property extension. The use of twin screw extruders for this purpose was particularly well received.⁴⁸

The production of nanomaterials (i.e., particles no more than a few nm in size) and nanoscaled materials (i.e., bulk materials with features or crystallites at the few nm scale) through mechanochemical means was another major theme of the Discussions. There are two general approaches to such nanomaterials: top down or bottom up, as illustrated in Fig. 7. Inherently, sufficient application of trituration (i.e., comminution, grinding, or milling) will lead to amorphization. One may expect that such processes will take crystalline materials and induce defects and fragmentation, followed by agglomeration and formation of mosaic particles, to finally amorphous products, but the meanings of these terms implies a length scale: from mm to μm to nm to \AA . And one must realize that the ultimate defect of any crystal is its outer surface. The meaning of “amorphous” is inherently unclear unless one states a length scale. In discussions of mechanochemistry and crystallinity of products, the community must take more care to specify the relevant length scales.

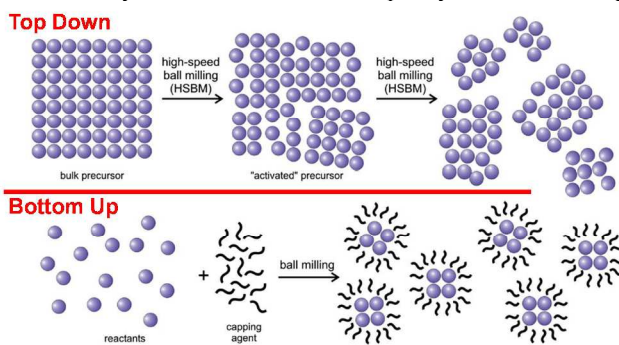


Fig. 7 Mechanochemical synthesis of nanomaterials and nanoscale materials through amorphization, comminution, and grinding can occur either from bulk (i.e., mm scale) materials down or from molecular or quantum dot precursors.⁵¹

The continued expansion of the use of mechanophores in polymer mechanochemistry was another significant aspect of FD170.^{53, 54} The use of well-defined “weak-links” in polymer chains as a means of controlling bond scission has developed well over the past decade.^{8, 56} Progress towards coupling mechanical forces into more general chemical reactions will be an important aspect of mechanochemistry over the next decade.

Surprisingly, mechanistic aspects of mechanochemical reactions induced by trituration, grinding, or milling were not heavily discussed in FD170. For both experimentalists and theorists, understanding the fundamental nature of mechanochemical reactions remains an important but largely unsolved problem.⁵⁷ Mechanochemical processes are complex; they involve very wide length and time scales; they are diverse and often system specific. Among these we have surface modification, crack propagation, surface electrification and even plasma-like transients, dislocations and amorphization, formation of metastable polymorphs, and localized impulse heating at points of impact, all occurring simultaneously with timescales ranging from ns to minutes.⁵⁷ Clear definition of the relative importance of these phenomena has not yet emerged and indeed is likely to vary substantially from system to system.

Some mechanistic aspects of mechanochemistry, however, were part of our Discussions. While macroscopic experimental investigations, empirical models, and the characterization of mechanically activated materials have provided the lion's share of our empirical knowledge of mechanochemistry, single molecule studies using atomic force microscopy⁵⁴ is a very promising tool to address fundamental questions on the atomic scale. In situ XRD characterization of milling processes received particular attention using new techniques available through the high intensity x-ray beams available at the European Synchrotron Radiation Facility.⁴³ The sudden onset of solid state phase transitions during milling was particularly striking, and especially so in light of Takacs' extremely interesting paper on exothermic mechanochemical reactions, where again, sudden and reproducible onset of reaction (e.g., between Sn and Se powders) was observed.⁵⁸ The electrification of surfaces was also discussed, and Galembeck's paper introduced the participants to the current state of the art of the closely related field of tribochemistry;⁵⁹ comparisons between high resolution electrostatic potential maps (using a non-contact Kelvin scanning electrode) were compared with SEM images of the same regions of polymer films after tribocharging (i.e., rubbing of surface), and it was argued that surface electrification occurs through transfer of tribochemical reaction products.

Within the context of mechanistic concerns, it is obvious that computer simulations have become an increasingly important component of all theoretical investigations, from modelling the macroscopic operation of milling devices to molecular dynamics and quantum chemical calculations.^{13, 60, 61} The difficulties in such approaches, particularly for MD-QM calculations under mechanochemical conditions, reveals the underlying complexity of such systems, and it may be some time before such results prove predictive.

The issues of mechanochemical equipment and scale-up were a plentiful source of discussions. A significant practical problem remains in the field of mechanochemistry: how does one compare results that use different apparatuses, how does one interpret changes in procedures (e.g., different grinding balls), how does one compare ball mills to jet impact mills to planetary mills, and so on? There are no well-defined mechanochemical equivalents of actinometry. It seems to me that the sharp onset that is observed for highly exothermic solid-solid reactions,⁵⁸ however, provides a real possibility of using such self-sustaining reactions as a

means of calibrating different mechanochemical apparatuses with respect to one another. This would be a major advance to mechanochemical experimentalists.

In terms of equipment itself, a wide range of apparatus studies were discussed, from the small to the very large. A clever and simple small-scale photo-mechanochemical apparatus was described by MacGillivray based on a modification of a common vortex mixer.⁴⁵ Improvements in efficiency and scale-up were examined for a variety of different larger scale laboratory equipment for both organic and inorganic systems.^{39, 47, 55, 62} Blair's use of finite element modelling of ball milling apparatus provided some visual insights into more effective operation of commercially available devices.³⁹ Excitingly, the work of Daurio et al.⁴⁸ on twin-screw extruders (Fig. 8) for solid state manufacturing of pharmaceutical co-crystals provides a new route to large scale, continuous flow mechanochemical processing; while such extruders are common for polymer blending and food processing, their chemical consequences have only rarely been examined.⁶³ The development of such extruders for a wider range of other mechanochemical reactions will be very interesting.

Finally, let me end this discussion with a list of a dozen open issues and questions that I see, at least within the context of FD170, as worthy of further investigation in the field of mechanochemistry.

- 20 ▪ The ability to predict mechanochemical reactions is still mostly missing.
- Our fundamental QM understanding of mechanical breakage of chemical bonds during mechanical stress remains to be further developed.
- 25 ▪ Initial conditions at point of impact during milling or grinding (i.e., temperature and pressure resolved at ns timescale) are generally unknown.
- Role of materials hardness: fracture vs. defects vs. plastic deformation vs. agglomeration vs. local eutectic/glassy solid/solid solution.
- Why do supramolecular rearrangements dominate with organics vs. covalent/ionic rearrangements with inorganics?
- 30 ▪ How wide is the range of molecular chemistry and synthesis that can be done mechanochemically, especially without the use of organic solvents?
- Can endothermic mechanochemical reactions dissipate energy from shocks?
- Control of selectivity of macromolecular chemistry using mechanophores. How generally can one change the specificity of macromolecular chemistry mechanochemically?
- 35 ▪ What are the connections between chemistry and luminescence in mechanoluminescence? Can mechanoluminescence serve as a probe of conditions during mechanochemical reactions?
- What are the mechanisms of triboelectrification (e.g., surface chemistry, electron transfer, proton transfer, ion transfer...)?
- 40 ▪ Can self-propagating reactions be used for calibration of mechanochemical apparatuses?
- Scale-up issues: energy efficiency vs. mechanochemical apparatuses, improvements beyond the kg scale, and flow vs. batch processing.

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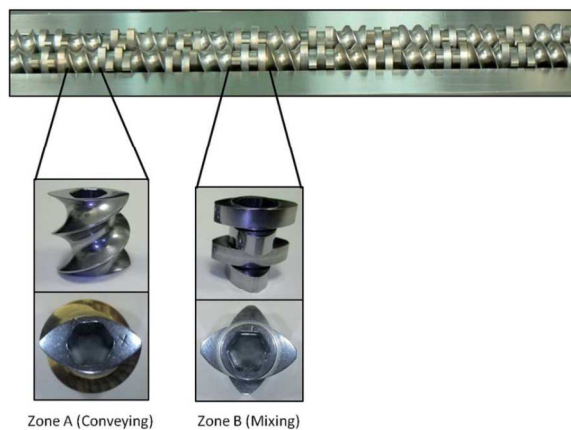


Fig. 8 A Prism PharmaLab twin screw extruder showing conveying and mixing elements.⁴⁸

4 Conclusions

It became clear during the Discussion that the field of mechanochemistry is still
5 in extremely active development. In a very real sense, human knowledge
recapitulates our anthropological evolution: We start as hunter-gatherers and ask
“Where?” as in “Where’s the food?” We develop into naturalists and ask “What?”
as in “What’s that long-toothed creature and is it good to eat?”. We progress further
and become engineers asking “How?” as in “How do we keep that long-toothed
10 creature from eating us?”, and finally only as scientists do we turn to “Why?” as in
“Why did that spear work so well to puncture that long-toothed creature?”. 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
15 have a fully resolved theory of the underlying quantum mechanics that connects to
chemical to the mechanical.

The fundamental importance of the connection between the chemical and the
mechanical makes it certain that, although this was the first Faraday Discussion
dealing with mechanochemistry, it is unlikely to be the last. So let me conclude by
20 congratulating, and thanking, the organizers and scientific committee of FD170—
Tomislav Friscic, Elena Boldyreva, James Mack, Stuart James, Carsten Bolm, and
Jonathan Steed—for proposing and coordinating such an interesting, diverse, and
thought-provoking meeting.

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^a School of Chemical Sciences, University of Illinois at Urbana-Champaign, 600 S. Mathews Av., Urbana, IL 61801 USA; Tel: 1-217-333-2794; E-mail: ksuslick@illinois.edu

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