ARMY RESEARCH LABORATORY

Slow Processes: The Accumulation of Molecular Events Leading to Failure on Macroscale

A Report on a Workshop Organized by the U.S. Army Research Office 9–11August 2000

Robert W. Shaw (editor)

ARL-SR-16 February 2001

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Army Research Laboratory

Research Triangle Park, NC 27709

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Abstract

A U.S. Army Research Laboratory workshop was held in preparation for a new initiative to support long-term reliability. Chemists, engineers, and physicists from universities, Department of Energy, National Institute of Standards and Technology, the Navy, and the Army met to develop research recommendations to provide a fundamental understanding of the chemistry of processes that lead to materials failure. The workshop was held at Duke University during 9–11 August 2000 and was the first of its kind. This report presents the papers given by participants and the results of their discussions and outlines a new research initiative that can lead to the design of materials for a longer, useful life and enable a rational basis for programmed maintenance. Specific recommendations for experimental and theoretical research are included.

Contents

1. Introduction **1**

2. Summary of Conclusions and Recommendations for Research **3**

3. Workshop Background **5**

3.1 Previous Meetings and Reports 5

3.2 Discussions at Princeton 6

4. Workshop Presentations **7**

4.1 Chairman's Remarks 7

4.2 Summary of Participants' Talks 8

Responses to Questions posed before the workshop (Anna Balaza) 11

Monitoring the effects of ageing on the mechanical properties of polymer bonded explosives (H. T. Goldrein) 15

Thoughts on aging of materials and methods to understand the slow reactions underlying aging processes (Richard Behrens). *31*

Atomic-Level Modeling and Rate calculations of Slow Processes in Complex Materials (Donald Thompson) 45

Controlling activated transitions: theory and experiment (Mark Dykman et al) 49

Aging of materials (Dana Dlott) 55

Methods for Slow Processes (Arthur Voter) *61*

Some Remarks on "Slow Chemistry" (Wing Tsang) *75*

Observation of the First Kinetic Steps in the Activation of Molecules Adsorbed on Surfaces (John Yates) *81*

Notes on Ultraslow Chemical Dynamics (Peter Weber) 83

5. Reports of Focus Groups **89**

5.1 Alpha Group Report and Recommendations 89

5.1.1 Identify Classes of Slow Phenomena and Systems 89

5.1.2 Identify Experimental/Theoretical Tools to Study Phenomena 90

5.2 Omega Group Report and Recommendations 92

5.2.1 Identify Classes of Slow Phenomena and Systems ... 92

5.2.2 Identify Experimental and Theoretical Tools 93

Distribution **103**

Report Documentation Page **107**

Appendix

A. Participants **97**

B. Summary of 1997 Princeton Preliminary Meeting **99**

Figures

Goldrein, Monitoring

1. Standard compression and tensile testing geometries 16
2. Dogbone specimen of binder for mechanical testing 16
3. The Brazilian test 17
4. Failure stress/failure strain graph comparing aged and unaged specimens of a PBX 19
5. Experimental arrangement used to manufacture gratings 21
6. Experimental arrangement for moiré interferometry 22
7. Schematic of a moiré interferometer 23
8. Diffraction at the specimen surface 23
9. Result from a moiré experiment on a PBX being quasistatically deformed in the Brazilian test 25
10. Post failure optical micrograph of the specimen shown in figure 9 26
11. ESEM image of unaged failed PBX 27
12. ESEM image of aged failed PBX 27
13. ESEM image of the same region of aged failed PBX at higher magnification 28

Behrens, Thoughts on aging

1. Chart illustrating material properties and reactive processes that control the behavior of an energetic component as it ages 33
2. First order decomposition reaction 34
3. Autocatalytic reaction without stabilizer 35
4. Autocatalytic reaction without stabilizer and faster rates for reaction R2 and R3 36
5. Autocatalytic reaction without stabilizer and faster rate for reaction R2 and very slow rate for reaction R3 37

Figures (cont'd)

6. Autocatalytic reaction without stabilizer and faster rate for reaction R2 and very slow rate for reaction R3 38
7. Autocatalytic reaction with stabilizer and faster rate for reaction R2 and very slow rate for reaction R3 39
8. Autocatalytic reaction with and without stabilizer and faster rate for reaction R2 and very slow rate for reaction R3 40
9. Schematic of STMBMS apparatus 41
10. Cross-section of STMBMS reaction cell 41
11. Ion signals of the decomposition products formed during the thermal decomposition of RDX at 180°C 42
12. Reaction processes that control the thermal decomposition of RDX and HMX between 160°C and 270°C 43
13. Schematic of microprobe/FTICR mass spectrometry system 44

Dykman et al, Controlling

1. The prehistory probability distribution of the scaled radiation intensity I for experimentally observed dropout events in a semiconductor laser 50
2. The logarithm of the time-average rate of activated escape W as a function of the scaled amplitude $2|F_1|/D$ of the driving field $F(t) = 2\mathrm{Re}\,[F_1 \exp(i\omega_F t)]$ for an overdamped Brownian particle in a potential $U(q) = 1/2\, q^2 - 1/3\, q^3$ 51
3. Rendering of two focused laser beams, the equilibrium positions of the particle, and a transitional path between the beams. The coordinate of a particle that switches at random between the equilibrium positions $\mathbf{r}_1$ and $\mathbf{r}_2$ 51
4. Plots of the time-dependent switching probabilities out of a symmetrical double-well potential over a cycle ωF_t of the modulating waveform $F(t) = 2F_1 \cos \omega F_t + 2F_2 \cos(2\omega F_t + \phi)$ for $F_2 = F_1 = 2$ 52

Dlott, Aging

1. Part of the energy landscape of a supercooled liquid 55

Voter, Methods

1. Illustration of the hyperdynamics method 64
2. Schematic illustration of the temperature-accelerated dynamics method 68
3. Selected snapshots illustrating the structure of 1/4 monolayer of Cu on Cu(111) at different times during a TAD simulation at 150 K ... 71
4. Simulations of vapor-deposited Cu growth on Cu(100) performed using hyperdynamics combined with parallel replica dynamics ... 72

Tables

1. Three systems that exhibit aging 89
2. Slow phenomena 90

1. Introduction

This workshop focused on failure and aging of molecular (covalently bonded) materials. We think that the characterization and understanding of the fundamental, underlying processes will contribute significantly to predictive models of aging, degraded performance, and failure. Valid models of the aging process will enable the design of new materials with longer useful lifetimes and enable the development of rational maintenance and replacement schedules. These schedules will anticipate the need for maintenance and for replacement before the part fails. The consequent improvements in safety and cost savings for the U.S. Army and for society, in general, will be enormous.

Our planning for this workshop identified a list of issues. For example, can we accelerate aging to enable experimental measurements (and theoretical calculations) to proceed in practical times? Past practice has been to increase temperature to accelerate aging. But this method will not work unless all-important aging processes have the same temperature dependence. Various possible competitive modes of slow change may occur: covalent bond breaking, tunneling, oxidation/reduction, diffusion to the aging site, and catalysis by impurities (especially H_2O). These processes may depend differently on temperature.

Measurements may be difficult: Experimental methods must have high sensitivity and selectivity to detect very slow changes. The long times required for aging also complicate some theoretical approaches; for example, the usual chemical dynamics calculations with femtosecond steps cannot describe processes occurring over long times.

This workshop brought together a small number of experts (app A) with a wide range of skills. We asked them to prepare talks based on the workshop focus, to outline how current computational and experimental tools could contribute to the understanding of slow processes and to recommend specific studies. The participants then separated into two groups (called "Alpha" and "Omega" (see sect. 5)) to discuss and develop recommendations for research on slow processes. This report comprises the participants' background papers and the reports of the research groups.

Short-Term Workshop Objectives

- Identify characteristics of needed tools to study slow changes.
- Choose the most promising current tools to study long-term processes.
- Choose an experimental system for initial studies:

- Simple enough to yield results within a reasonable time (1–3 years). Results mean information that provides increasing focus on experimental and theoretical approaches.
- Relevant to Army interests.

Long-Term Research Objective

Establish experimental and theoretical tools to characterize chemical processes that cause aging. Aging means slow changes leading to degraded performance. Slow means 10^6–10^9 s (10 days to 30 years). Focus on processes at the molecular level in molecular materials (not metals).

2. Summary of Conclusions and Recommendations for Research

Workshop discussions did not reveal substantial disagreements; hence, this summary represents the participants' consensus:

1. A useful definition of "slow" is a process with at least two timescales (τ_1, τ_2) such that $\tau_1/\tau_2 \gg 1$, and events at these scales speak significantly to each other simultaneously.
2. The principal problem is how to bridge the gap between femtosecond atomic-scale events and processes that take seconds, hours, years, etc. Can the timescale of slow processes be accelerated while not altering the basic mechanisms? Can the accelerated model and/or experimental results be "inverted" to deduce the true events?
3. Related to consensus 2—Is there a relation between timescales and length scales? At the molecular scale, can slow motion subspaces be identified? Expressed another way: What is the role of long-range (many atom-collective motions) states on chemistry (which tends to be very local—only involving directly a few atoms)?
4. The system is most likely to fail at surfaces, around internal impurities, and at the boundaries between amorphous and crystalline phases, because of phase changes (e.g., changes in a polymer character).
5. Multiple and changing potential energy barriers may be studied by following the diffusion of particles through the energy landscape: Create a set of point defects in a crystal or on a prepared surface, and dope a polymer with small gas molecules. Observe diffusion or change.
6. Processes that are likely important in aging: cyclic processes (thermal, mechanical stress); energy exchanged into complex molecules in bulk and at surfaces; photoinduced changes in materials; diffusion, transport, and nucleation processes; and structure and evolution of polymers in solution.
7. Perturbations to induce aging behavior include periodic disturbances, high field excitations of defects and excited states, low field effects on molecular dynamics, and pressure (both static and fast shocks).
8. Promising experiments to study the chemical basis of aging include reactive molecular beams scattered off surfaces and reactive molecules generated in bulk solid materials.
9. Processes must be studied in well-characterized materials in controlled environments where surface and impurity effects have been eliminated.

10. A library of well-characterized samples should be begun and maintained over long periods (decades) for periodic study and validation of accelerated experiments and models.
11. Because their role is uncertain, systems with strong quantum effects (microscopic processes/elementary steps) should be chosen for study.
12. The workshop did not identify new phenomena involved in slow processes. Study may show that, for aging systems, chemical-rate models currently used, plus corrections to be determined, will be adequate.
13. Considerable work has been done on multiple timescales, but chemistry is missing. For example, current treatments of protein folding are physical.
14. The participants agreed that further exploration of this topic promises to provide a capability to assess and manage long-term materials evolution and to enhance long-term reliability of materials and equipment.

3. Workshop Background

3.1 Previous Meetings and Reports

Materials aging and degradation have been the subjects of considerable study; the results of which appear in many reports and meetings proceedings. These results rarely touch on the role of underlying fundamental processes at the molecular level—the subject of our workshop.

The 1995 symposium, "Long-Term Performance Issues in Polymers-Chemistry and Physics,"[1] explored photooxidation and thermooxidative degradation, role of stabilizers, and evironmental and other factors thought to affect aging of materials. This meeting, concerned mostly with phenomenology, did not have discussions on the underlying fundamental molecular processes, although various speakers pointed to problems with Arrhenius rate equation extrapolations and transport models. We note here that failures of Arrhenius expressions, used to extrapolate rates measured at high temperatures (to accelerate aging) down to temperatues of interest, are not surprising—simple use of these expressions cannot model aging processes with more than one temperature dependence.

The JASONs issued their report, "Signatures of Aging"[2] in 1998, providing recommendations for assessing potential aging problems that could affect performance of energetic materials, organics and plastics, and other parts of nuclear weapons. The JASONs give an especially clear description of important goals of aging assessment. These goals are establishing—

- Diagnostics for aging in which readily measurable physical quantities can be uniquely related to the required functional performance of the materials.
- Diagnostics for aging in which readily measurable physical quantities can be uniquely related to the safety of the materials.
- The stage of materials aging at which decomposition products endanger the performance of other components of the weapon.
- Criteria and procedures for the replacement of the materials and components.

The JASONs refer to historical surveillance programs that have generated information on aging of explosives by measuring density, binder molecular

[1] Proceedings of the 1995 Fall Meeting of the Materials Research Society (dns.mrs.org/meetings).

[2] S. Drell, R. Janloz, et al, "Signatures of Aging," *JASON Report*, The Mitre Corporation, January 1998.

weight, tensile strength, etc, and they recommend correlation of these data with manufacturing history, performance studies, etc. They also remark that "archiving of data, characterization of materials, and preservation of samples lacked proper attention…." The JASONs do not discuss the fundamental processes of aging. Participants at our workshop also emphasized the importance of data archives based on measurements over time on well-characterized and carefully chosen samples.

The International Conference on Aging Studies and Lifetime Extension of Materials[3] was held July 1999 at St. Catherine's College, Oxford, England. The sessions included Experimental Techniques, Modeling and Theoretical Studies, Lifetime Prediction and Validation, Lifetime Extension, and Material Design for Aging. Participants described work on polymers, metals, glasses, ceramics, explosives, and nuclear and structural materials. No work on the underlying fundamental processes at the molecular level was discussed.

3.2 Discussions at Princeton

The workshop of this report was preceded by a small group discussion at Princeton University in September 1997. The participants at the Princeton meeting were Herschel Rabitz, Princeton, a theoretician working on chemical dynamics and familiar with U.S. Army research; John Yates, University of Pittsburgh, a surface chemist, also familiar with U.S. Army research; Richard Behrens and Leanna Minier, Sandia-Livermore, experimentalists who study the decomposition of energetic materials and work in the Department of Energy (DOE) program on aging of nuclear weapons; and Robert W. Shaw of the U.S. Army Research Office.

Behrens talked about the Sandia "Enhanced Surveillance Program" for the aging nuclear stockpile and about his own studies on the chemical and physical degradation of energetic materials. Minier spoke about the aging of propellants and provided copies of two studies on "Service Life Prediction Techniques." Yates discussed new experimental techniques to study molecular motion at surfaces—these methods may provide information on the slow chemistry occurring at normal temperatures, i.e., under normal "aging" conditions. Rabitz described new theoretical methods related to the aging problem but emphasized that new tools were needed. These tools include methods to exploit cooperative motion in complex systems and management of extreme noise fluctuations that may drive systems over potential energy barriers. Appendix B provides more details of the 1997 Princeton meeting.

[3] L. G. Mallinson (chairman), "International Conference on Aging Studies and Lifetime Extension of Materials," *AWE/Hunting-BRAE*, St. Catherine's College, Oxford, England, 12–14 July 1999.

4. Workshop Presentations

4.1 Chairman's Remarks

To begin the workshop, Rabitz posed the principal problem: We must bridge the gap between femtosecond atomic-scale events and processes that take seconds, hours, years, etc. Systems that exhibit these disparate timescales include aging energetic materials, folding proteins, defects propagating through solids, and phase changes in amorphous, glassy materials. Understanding these phenomena may enable alteration of long-time evolutionary behavior—we may be able to design materials with longer useful lives. Rabitz then presented a list of issues and questions to the participants in considering long-timescale chemical evolution:

1. Molecular dynamics or chemical kinetics—Where can we start?
2. Nature of the evolution: (a) the activated, infrequent event (i.e., barrier crossing), (b) a long sequence of slow complex processes, or (c) both together?
3. Is transition state theory a valid model?
4. Are special stochastic models or techniques relevant?
5. At the molecular scale, can slow motion subspaces be identified? Can issue 4 be included?
6. Are hybrid discrete-continuum models suitable?
7. Can automated molecular substructuring methods be found for dynamics?
8. Is there a relation between timescales and length scales?
9. Do quantum phenomena (e.g., H-atom tunneling) play a role?
10. Does initiation occur at local defects in solids?
11. With molecular dynamics, can we live with modest (moderate) potential errors?
12. For molecular dynamics, does fast motion contribute to the slow motion?
13. Will it be necessary to swing from one model to another as different time regimes are entered?
14. Can multiple timescale (nonperturbative) theories lead to systematic modeling at a hierarchy of timescales?
15. Can the timescale of slow processes be accelerated while not altering the basic mechanisms? Can the accelerated model and/or experimental results be "inverted" to deduce the true events?

16. What laboratory techniques are needed to identify infrequent, but fast, events?
17. Can kinetic models be directly generated by inversion from concentration observations?
18. Can experiments be devised to hone in on small parts of the mechanism?
19. Are suitable archival samples readily available for analysis?
20. What observation techniques are suitable for different timescale regimes?
21. Will "pump and probe" experiments be useful?
22. Can special closed-loop learning experiments be adapted to unravel the underlying complex processes?

Current molecular dynamics cannot cover the needed range of timescales. Molecular vibrations occur on the femtosecond scale. Even with 10^6 steps, we only reach the nanosecond scale. Can we find a systematic means of filtering out the high-frequency jitter during the dynamics? Early work indicates that a low-frequency subspace exists, which is nearly invariant over long times, and the dynamics in which we are interested are mostly in that subspace. One may also take a hybrid dynamics approach (discrete continuum).

4.2 Summary of Participants' Talks

Participants wrote extended abstracts on which they based their talks. Those extended abstracts follow this section. The opening talks focused on modeling and measurements of specific systems. Balazs described her models for the properties and fracture of polymer interfaces. Goldrein outlined new methods for rather complete measurements of strain in composite materials consisting of crystalline explosives bonded in polymer matrices. Behrens provided a general framework for thinking about aging and failure of energetic components ranging from the underlying physics and chemistry of reactive processes to the performance and safety of components.

Other talks provided more general perspectives on studying slow processes. Thompson proposed theoretical and computational studies for atom-scale modeling of pathways and rates. Dykman presented some new work on the surprising influence of thermal fluctuations on particles trapped in potential wells and the control of these fluctuations. Dlott discussed the power of the "energy landscape" picture of structural evolution and proposed fast, short shock waves to push the system high on the landscape followed by a study of its relaxation. Voter discussed the power of transition state theory as a framework for characterizing infrequent events and described several approaches to enable calculations to cover greater timescales.

Tsang spoke from the kineticist's perspective about characterizing chemical reaction mechanisms in polymers. Yates described tools for measuring properties of weakly and strongly bound molecules on well-defined surfaces and proposed these systems as models for studies of slow processes. Weber estimated the time required to perform experiments on slow processes.

Prof. Anna Balazs
University of Pittsburgh

Responses to Questions posed before the workshop:

A. ARE THE MODELS AND APPROXIMATIONS WE USE TO DESCRIBE FAMILIAR PHENOMENA GOOD FOR SLOW PROCESSES?

As I describe below, with certain modifications or within certain limits, Brownian dynamics simulations and self-consistent field theory can be used to describe slow processes involved in the failure of polymer reinforced interfaces.

B. CAN YOUR SKILLS AND TOOLS BE USED TO STUDY SLOW PROCESSES? HOW?

Fracturing Copolymer Reinforced Interfaces

We recently developed a Brownian dynamics simulation for fracturing copolymer-reinforced polymer/polymer interfaces [1]. The copolymers, or "connectors", in our simulations are modeled as chains of freely-jointed rigid rods. Beads placed at the junctions of these rods "feel" the tension in the neighboring rods and a force from the surrounding medium. The force is composed of the following components: a viscous drag and a thermal force arising from the random motion of the surrounding chains. In addition, we model the homopolymer matrix as an infinite array of obstacles or repulsive force centers. The potential is adjusted so that the connector chain is prevented from crossing any force center. The motion of the beads is friction limited, that is, the inertia of each bead is negligible. Therefore, Newton's equations reduce to Langevin equations (which are computationally less demanding to solve).

Given an initial configuration of the connector chain, and a series of constraint equations, which fix the length of the rods at each time step, the fracture event can be simulated. In essence, we separate the interface at constant velocity, and monitor the force that must be supplied to fully separate the junction.

Using this model, we investigated the role molecular weight and architecture plays in the effectiveness of the connectors [1]. In particular, we contrasted the effectiveness of "single-stitch" connectors (e.g. AB diblock copolymers at an A/B interface) with "multi-stitch" compatibilizers, which can cross the interface many times (e.g. a random AB copolymer at an A/B interface). Furthermore, we determined the effect of side chains (or branches) within the connector on the toughness of the interface. Since random copolymers are significantly less costly to synthesize than diblocks, our prediction that these copolymers are more effective at improving the strength of the blend can have a technological and economic impact.

In the previous studies, we assumed a relatively fast pulling rate, where the obstacles do not move on the time scale of the chain pullout. We can model "slower" events or slow fracture by allowing theobstacles (which represent regions of entanglement points in the polymermatrix) to move on the same time scale as the chain pullout. These changes will, however, make the calculations more computationally intensive.

Fracture in Polymer/Solid Interfaces

In recent studies [2], we investigated the adsorption of copolymers onto heterogeneous surfaces, which represent the surface of the influenza virus. The copolymers contain "stickers" that are highly attracted to receptors on the viral surface. We varied the sticker concentration and determined the conformation of the adsorbed chains on the heterogeneous substrate. We then calculated the interaction energy as a function of distance between this polymer-coated surface and a bare interface, which represents the surface of a red blood cell. The results show that there is an optimal range of the sticker concentrations that sterically inhibit contact between the two surfaces. The findings help rationalize recent experiments, which show that extent of inhibition depends on the fraction of stickers in adsorbing copolymer [3].

We can use our self-consistent field (SCF) calculations to consider a related problem. Here, two solid surfaces are bound with a layer of adhesive. The chains in the adhesive layer contain stickers that are attracted to the surfaces. Recent fracture studies on similar systems reveal that there is an optimal sticker concentration for enhancing the strength of the joint [4]. Through our model, we can systematically vary the separation between the coated solids, establishing the location of the stickers and the conformation of the chains as the surfaces are pried apart. These SCF calculations are equilibrium calculations; thus, we can model "slow" fracture where the separation between the surfaces is essentially quasi-static. That is, the chains have sufficient time to reach equilibrium conformations at each surface separation.

Through these calculations, we can add a new twist. We can introduce a sticker-sticker attraction in addition to the sticker-surface interaction. Thus, the stickers can bind and form clusters in the adhesive layer. As the surfaces are forced apart and the polymer layer is stretched, some stickers will be pulled away from the surface. These stickers can then bind with others localized in the gap. Some clusters will involve chains that are still bound to a surface. The presence of clusters in the interfacial region could provide additional reinforcement between the surfaces. By varying the sticker concentration, the relative values of the sticker-surface and sticker-sticker interaction energies and calculating the free energy profiles, we can isolate conditions where the chains provide optimal resistance to the stress (fracture) and are the most effective in strengthening the interface.

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Monitoring the effects of ageing on the mechanical properties of polymer bonded explosives

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Introduction

The focus of my work in our laboratory has been on the study of the mechanical properties of Polymer Bonded Explosives (PBXs). A typical PBX will contain between 60 and 95% of some mix of crystalline explosives bound in a matrix of an organic binder, giving the system strength, toughness, extensibility, and importantly also altering its sensitivity.

There seems to be little evidence that the typical explosives (HMX and RDX) are affected by age, but there is plenty of evidence that most binder systems are indeed affected. In our laboratory, we have a variety of sensitive techniques for measuring the mechanical properties of PBXs on the microstructure scale and we have applied several of these to search for variations with age in the failure mechanisms at work in deforming PBXs. In general, we have found that there are no significant variations in failure mechanisms, though we know the mechanical properties of the binder vary significantly. Thus, we ascribe the effects of ageing to the deterioration of the binder. However, we see evidence only of incremental deterioration, and not of any step-changes which might suggest serious threat to the integrity of a charge.

Since the focus of this meeting is not on the PBXs we have studied, nor even necessarily on PBXs generally, I present below a summary of the techniques I see as relevant for sensitive study of the microstructure of composite materials, together with some examples where possible. Necessarily, since this is the realm of my experience, PBXs will figure largely in what follows!

Mechanical Testing

Various mechanical tests have been used to study the mechanical properties of PBXs. The easiest to interpret are the standard tension and compression tests used throughout engineering practice. However, these tests usually involve large specimens, requiring remote operation of testing apparatus, and consequently high costs of setting up and running testing facilities. Typical geometries are illustrated in Figure 1.

To determine compressive strengths, a right cylindrical specimen is compressed between the two flat, parallel anvils of a universal testing machine. For this type of test, it is important that the specimen be machined accurately, in particular with flat and parallel end faces. If this is not achieved, the specimen will fail prematurely, and invalidate the test. For tensile

strengths, a dog-bone specimen can be used, as illustrated in Figure 1, or a cylindrically symmetrical equivalent. Machining tolerances are, if anything, even more important here, since any slight nick along the gauge length will cause premature failure. The loading system is usually designed with flexible joints in the load train to allow a straight pull. Any torsion due to poor alignment will cause premature failure, and invalidate the test.

It is fair to say that both these types of test are widely used in most laboratories to gain baseline data regarding the strengths of their compositions. Many laboratories have also carried out similar tests on binder systems alone, again, to provide baseline data. A tensile dogbone specimen of a polyurethane-based binder system is illustrated in Figure 2.

A means of testing which we have used extensively in our laboratory is the "Brazilian test", also known as the "diametral splitting test" or the "concrete splitting test." The "Brazilian Test"[1] has been used to great effect on PBXs, since it overcomes some of the problems experienced with the simpler uniaxial tests (see Huntley, Palmer, Field, 1987[2], and also Field, Parry, Palmer, Huntley 1989[3] and Palmer, Field & Huntley, 1993[4]). The test involves the diametral compression of a disc of PBX, which induces a uniform tensile stress perpendicular to the loading axis. The sample fails in tension across the line of compression by formation of a vertical crack through the centre of the disk. The set-up is illustrated in Figure 3. There are no large clamping jaws which could cause an accidental initiation, and

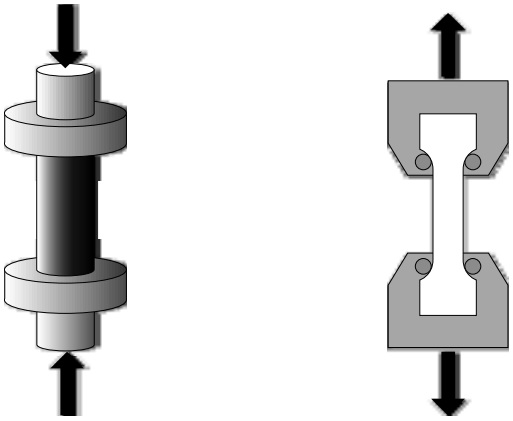
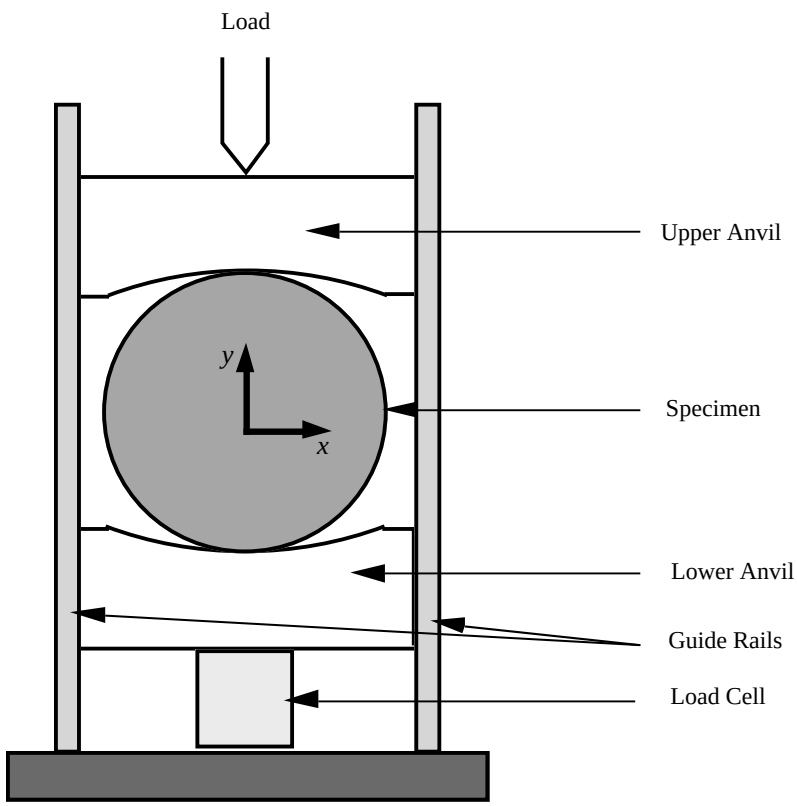


Figure 1. Standard compression and tensile testing geometries.

Figure 2. Dogbone specimen of binder for mechanical testing.

Figure 3. The Brazilian test.



the sample can be made sufficiently small that the hazard would be acceptable should such an initiation event take place. The samples are typically about 10 mm diameter, and 2.5 – 4 mm thick, giving a net explosive mass of approximately 0.5 g, which presents a sufficiently small risk in the case of accidental initiation to be acceptable in our laboratory.

As described by Palmer et al.[4], the curved anvils in use prevent the premature onset of edge failures. When the ratio of the contact half width b to the disc radius R is small, the tensile strength is linearly dependent on b/R, up to a value of 0.27, after which it is independent, as shown by Awaji & Sato[5]. The manifestation of this is that as the contact half width reduces, the shear stress at the loading points increases, and thus influences the tensile strength by initiating a premature mode II failure at the disc edge. With larger values of b/R, the stresses near the contact points become compressive, and so the tensile stress at the disc centre controls the failure. For point loads, the tensile stress σ_{xx} at the centre of the disc is calculated from

$$\sigma_{xx} = \frac{2P}{\pi D t} \tag{1}$$

where P is the applied load, D the sample diameter, and t, the sample thickness. Awaji & Sato show that for a finite contact zone, the stress at the specimen centre is given by

$$\sigma_{xx}^{*} = \left\{1 - \left(\frac{b}{R}\right)^2\right\}\sigma_{xx} \,. \tag{2}$$

In the geometry in common use in our laboratory, the upper anvil was moved downwards at a constant rate of 0.83 μm s^{-1}, which gives rise to a straining rate of approximately 10^{-4} s^{-1}.

The test does have some disadvantages, and these include the fact that this is a biaxial test, compared with the more conventional uniaxial tests. This means that the results of the test are more difficult to interpret, and certain assumptions have to be made about the properties of the sample which may or may not be valid.

The most serious assumption is that the sample is linearly elastic. If it is assumed that the stress distribution under the anvils remains constant (and this in effect means that the contact area under the anvils remains constant), then the assumption can be relaxed slightly to include specimens which are linearly visco-elastic according to the visco-elastic correspondence principle[6]. If the stress distribution under the anvils has no time-dependence, the stress and strain distributions can be shown to be identical to the elastic case, but for a time-dependent multiplier. There is known to be some departure from linear visco-elastic behaviour, but this departure is usually assumed to be small. In general, the more brittle binders will adhere more closely to this assumption than softer binders.

The Brazilian test also presents several other advantages in the studies of PBXs which were carried out. As well as enabling tensile tests to be performed, there is the useful side-effect of localising the eventual failure site much more than is possible with a conventional dumb-bell test. A common problem experienced with such tests is failure at the clamping point at one end of the sample. This is of relevance when high-resolution (and therefore small field of view) optical studies are made of a region of the sample as it deforms, as is described later. Whilst the failure will not always pass exactly through the geometrical centre of the sample, the failure point is much more predictable in this geometry than in dumb-bell geometries attempted in other laboratories.

Simply-instrumented mechanical tests such as these are essential if any measure of the deterioration of a PBX with age is to be gained. There is ample evidence than such tests are sufficiently sensitive, and can easily distinguish important factors. For example, consider the graph shown in Figure 4. Here, aged and unaged samples of a particular PBX were tested in the Brazilian test, the aged specimens having been subjected to accelerated ageing equivalent to many decades of natural ageing. Strains were calculated simply from measurements made using a clip-gauge to measure the diametral dilatation. The lowered stresses and strains at failure in the aged material are easy to detect.

Failure Mechanisms

As has been described, is rather easy to show that ageing has an effect. It is rather harder to explain why this should be. For these reasons, we have

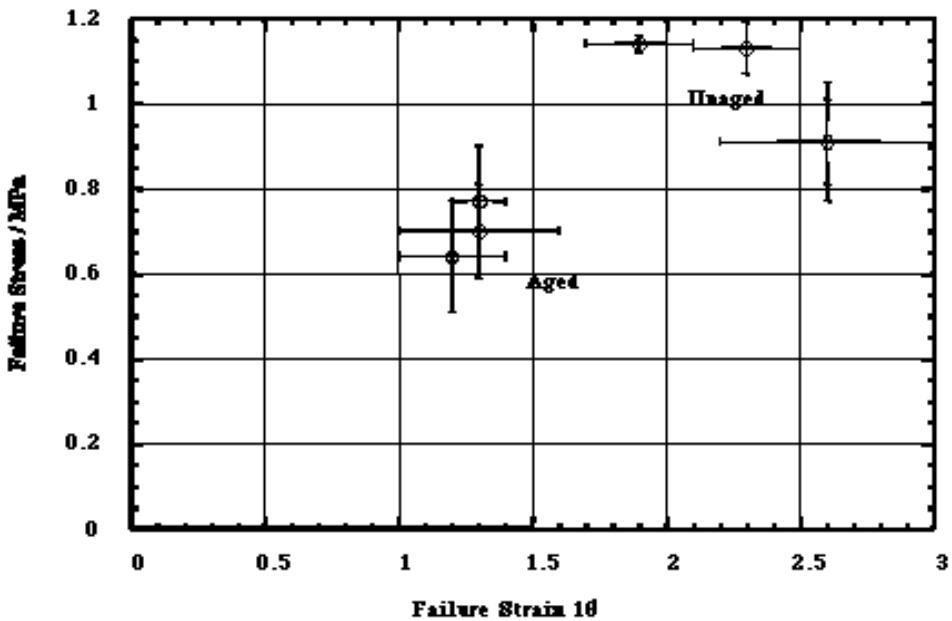


Figure 4. Failure stress/failure strain graph comparing aged and unaged specimens of a PBX.

investigated extensively the failure mechanisms which operate in PBXs, and we have looked for changed mechanisms in the aged specimens. Two main approaches have been used. In the first place, we have used high-resolution, high sensitivity optical displacement measurement techniques to allow us to measure the way strain is distributed though the microstructure of the specimen. This has been supported by finite-element modelling work. Secondly, using environmental scanning electron microscopy (ESEM), we have carried out higher-resolution experiments, albeit without the quantitative information gained otherwise.

Moiré Interferometry

Conventionally, the moiré technique in experimental mechanics has come to be applied to the superposition of two line gratings, one in some way moving with the specimen (the specimen grating), and the other stationary (the reference grating). The resulting fringe pattern which is formed represents a contour map of the displacement of the specimen grating in a direction normal to the lines of the gratings. The contour interval is equal to the pitch of the specimen grating. The name "moiré" comes from a type of silk, imported into France from China, with a regular weave which showed these effects.

In the conventional geometric moiré technique, often known as moiré photography, the fringe patterns that are analysed are produced geometrically, by superposing two gratings. For a fuller discussion of the technique the reader is referred to chapter 6 of the Handbook on Experimental Mechanics[7]. The everyday example of this phenomenon is the patterns seen when the line of vision is through two layers in the folds of a net curtain, or when looking at the railings on either side of a motorway bridge moving relative

to each other as the observer drives underneath. Fringes such as these might be produced in the laboratory by drawing fine lines on a sample which is to be deformed, and then observing the fringes though a second grating of similar pitch. If the specimen and reference gratings are identical, then there will be a null field, with no fringes present, and any strain will be revealed by the production of fringes as a mismatch in the grating spacings occurs. There is no way of knowing whether the strain is compressive or tensile, however, since identical fringe patterns will be produced either side of the null field in either case. To prevent this, some known slight mismatch is usually introduced at the outset, so that the experiment begins with some fringes visible. The sign of the strain can then be determined by observing whether the fringe spacing increases or decreases, assuming the direction remains constant throughout the experiment. It is this method that has been used to measure deformation in such diverse structures as bridges, and Victorian terraced houses and wooden structures[8], hollow spheres subjected to large elastic strains[9], or even notched polycarbonate tensile specimens[10]. Many of these experiments enhanced the sensitivity of the technique by adapting the lens of the camera used to photograph the fringes so as to tune its spatial sensitivity carefully to the spatial frequency of the moiré grating (see Burch & Forno, 1975[11]). This was the method used in our laboratory to study dynamic systems including stress pulses crossing a stationary crack tip in PMMA[12], and composite disc specimens modelling artillery shells[13].

Much more sensitive are the techniques which rely not on the mismatch of physical gratings, but on the interrogation of a higher frequency specimen grating (typically ~1000 l mm^{-1}, compared to a maximum of about 75 l mm^{-1}) by interfering laser beams, often referred to as moiré or grating interferometry. The interferometric method will give a sensitivity of order 1 μm/fringe, compared with a typical 25 μm/fringe for the simpler photographic method. Moiré interferometry is thus the most suitable for measuring the very small deformations of small samples used when studying PBXs.

The specimen gratings used in moiré interferometry are typically of the order of 500–1500 l mm^{-1} (i.e. a grating pitch of order 1 mm). For a detailed description of this process, the reader should refer to section 7-6 of Handbook on Experimental Mechanics[14], or Baschore & Post[15]. Such gratings are cast from master gratings, which can be (and historically have been) produced by the following procedure.

The light from a laser beam is split using a half-silvered mirror. The two beams traverse different paths and are subsequently made to diverge by passing through beam expanders, and are then collimated using photographic quality lenses. The two beams are then recombined in an image plane on the surface of a holographic plate. The difference in the path lengths must be small, and in any case less than the coherence length of the laser light. The fringe patterns which are produced are used as the basis of the grating. By altering the angle at which the two beams interfere, the spacing

of the grating can be altered. The pitch d of the grating will be given as shown in equation (3).

$$d = \frac{\lambda}{2\sin\alpha} \qquad (3)$$

where: λ = wavelength of laser light

α = angle of incidence measured from normal

The experimental set-up is shown in Figure 5.

When the holographic plate is developed, the exposed areas which correspond to the bright lines of the interference pattern swell slightly, so that the surface topology of the holographic plate will consist of a series of ridges and troughs which are of the same spacing as the original fringe pattern. As the final stage in the development of the plates, they are rinsed in a weak surfactant solution, the effect of which is explained subsequently. The plates are then dried, and a thin layer of aluminium is deposited on the plate surface by evaporation.

Recently, however, master gratings of almost perfect quality have become commercially available at reasonable prices (for example, from Ealing Electro Optics, Watford), and these are used in preference to gratings produced in house.

An epoxy or a silicone-rubber compound is then used to duplicate the grating onto the specimen. The epoxy or rubber is spread onto the surface of the master grating, and allowed to cure with the specimen held in place in the pool of curing replica material. It is then peeled off. The separation takes place at the surfactant layer, since it reduces the adhesion of the aluminium to the photographic emulsion. The duplicate then has the form of a finely-spaced grating, aluminised on one side. A slightly different route may involve aluminising the replica after separation from a non-aluminised master grating, though the eventual product is similar.

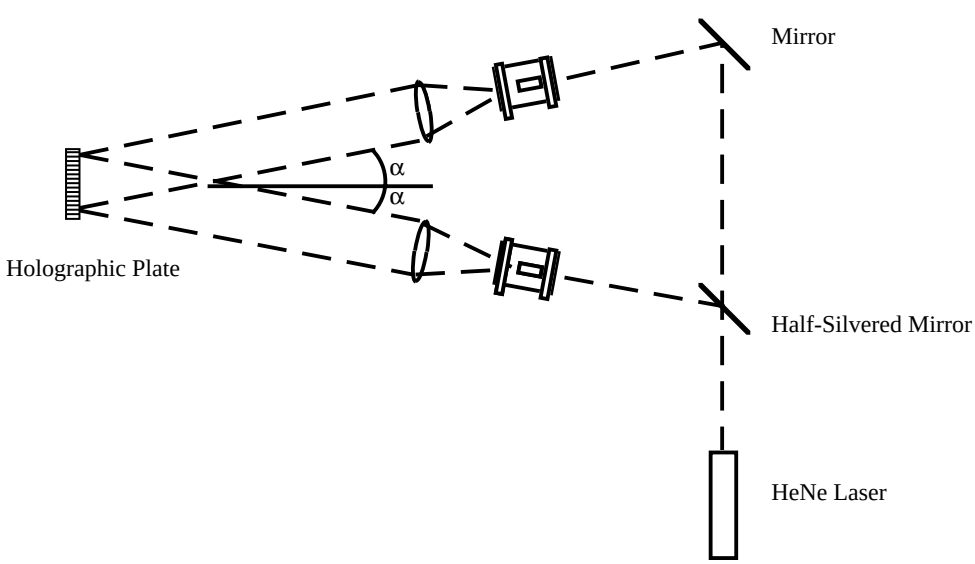


Figure 5. Experimental arrangement used to manufacture gratings.

The reference grating is not a real grating, but is produced by two more laser beams in much the same way as before. The two beams are allowed to interfere on the surface of the specimen grating. Each of the two beams must be lined up so that the first order diffracted beam (diffracted by the specimen grating) enters the camera. These two beams interfere in the camera to produce a fringe pattern which can be analysed by computer at some later time. It is also possible to take a computer picture of this pattern directly, using a video camera and a fast analogue-to-digital converter, or "frame-grabber". This is illustrated in Figure 6.

The characteristics of the fringe pattern can be derived thus (as shown in the Handbook on Experimental Mechanics).

As illustrated in Figure 7, the specimen grating intercepts two beams of coherent light, A and B, incident at angles of $\pm\alpha'$. To prevent phase inversions caused by reflection, it is important that the light is polarised either parallel or perpendicular to the plane of the diagram. The grating diffracts these two beams such that the diffracted beams A'' and B'' propagate back towards the camera, where they interfere to form an interference pattern.

Diffraction at the grating surface takes place as illustrated in Figure 8.

If the frequency of the specimen grating is given as F, the angle of incidence α'. is arranged correctly, and the grating lines are exactly parallel, the first order diffracted beam from beam A emerges with angle β=0, and equivalently, light from the -1 order of beam B also emerges with β=0. Two coherent beams coexist in space, but their angle of intersection is zero, so the interference pattern produced will have uniform intensity throughout the field—a null field.

Suppose the specimen is now subjected to a deformation that stretches it uniformly in the $+x$ direction, producing a uniform strain ε_{xx}. The spacing of the grating is no longer F, but is now F', where

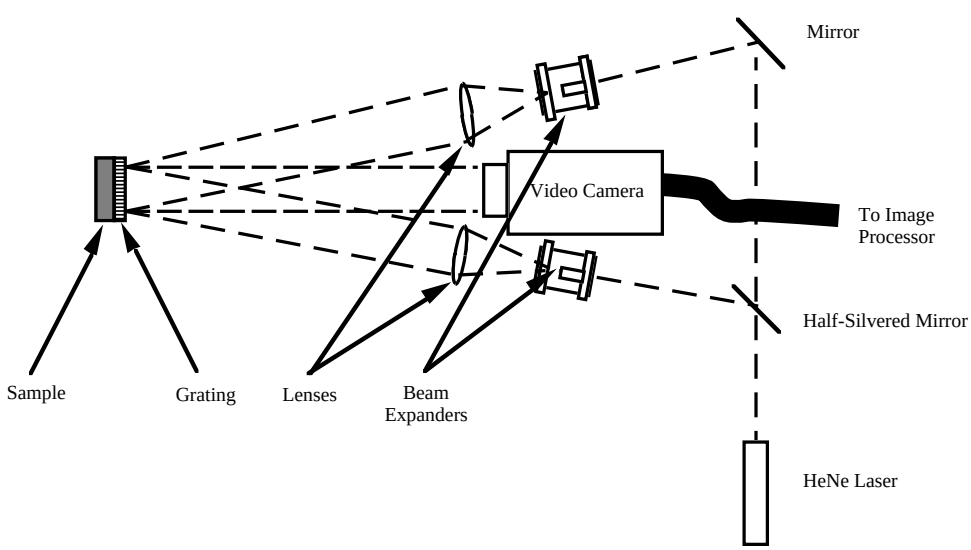


Figure 6. Experimental arrangement for moiré interferometry.

Figure 7. Schematic of a moiré interferometer.

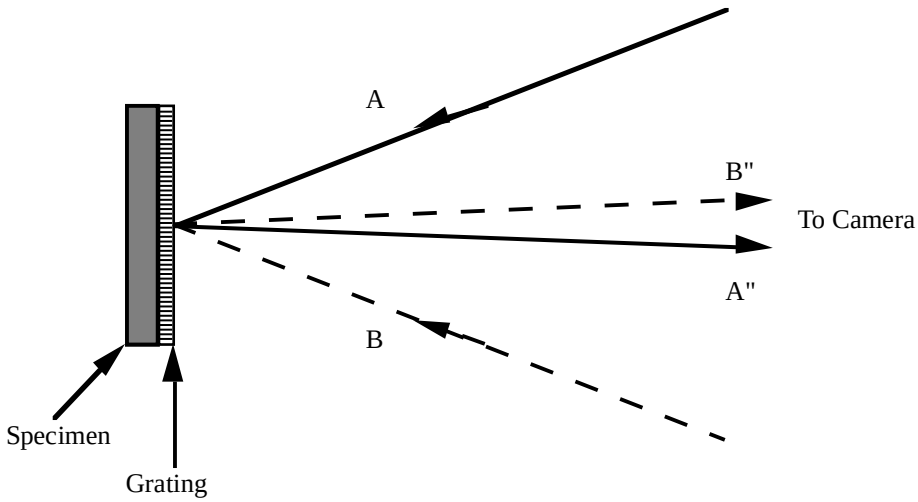
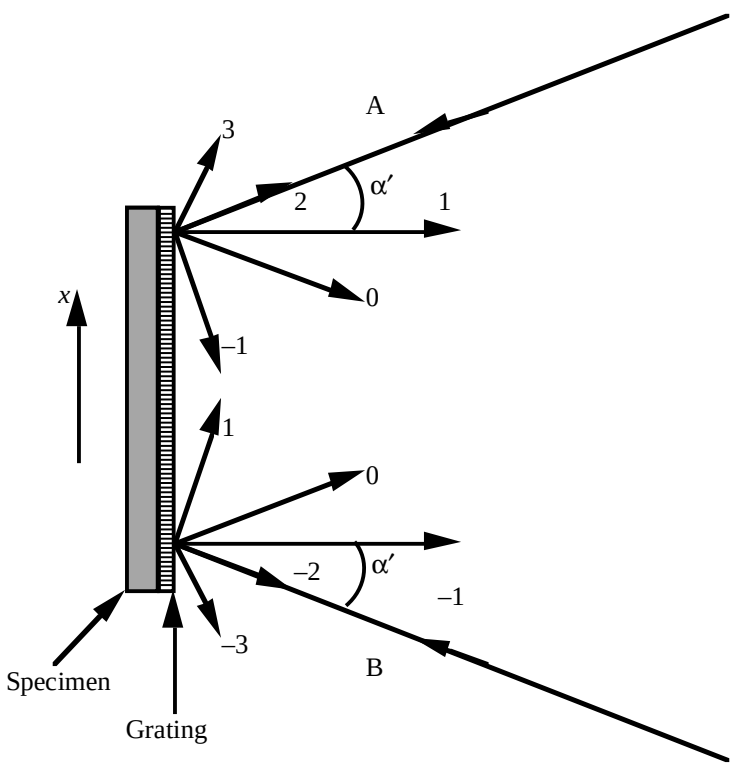


Figure 8. Diffraction at the specimen surface. Diffracted beams from the incident beams A and B are numbered.



$$F' = \frac{F}{1+\varepsilon_{xx}} \tag{4}$$

Light from the first order beam of A does not now emerge perpendicular to the grating, but will emerge at an angle β_1, such that

$$\beta_1 = -F\lambda\varepsilon_{xx}\,. \tag{5}$$

Similarly, light from the –1 diffraction order of beam B will emerge so that

$$\beta_{-1} = -F\lambda\varepsilon_{xx} . \qquad (6)$$

Hence we can see that the two beams are now propagating towards the camera with an angular separation of $2\beta_1$. The Handbook of Experimental Mechanics shows that the result of this situation is an interference pattern with uniformly spaced, parallel fringes. This is, in fact, exactly equivalent to the situation illustrated in Figure 5. The fringe gradient F_{xx} (which is obviously $\partial N_x/\partial x$) is proportional to the angle of intersection of the two beams, $2\beta_1$. Now in general, if two beams of wavelength λ interfere separated by a half-angle θ, the fringe gradient F will be given by $F = 2/\lambda \sin\theta$. Since β_1 is very small, we can substitute $\sin\theta = \beta_1$ to obtain the relation

$$F_{xx} = 2F\varepsilon_{xx} . \qquad (7)$$

This gives us the important result that the fringe spacing is proportional to twice the reference grating frequency, and also the strain. It can be seen that each fringe will represent a displacement of one half the grating pitch, in a direction perpendicular to the grating lines. This is the fundamental on which all the subsequent image processing is based. Various computerised methods have been developed to allow accurate quantitative interpretation of the images of fringe patterns acquired in experiments such as this, and a sensitivity approximately one hundredth of a fringe can be achieved.

In our laboratory, we have built an interferometer which allows exciting new possibilities over and above the design outlined above. We have designed an interferometer which allows us to view a specimen with the resolution of optical microscopy, with a field of view of approximately 0.5 $\times$ 0.5 mm^2, and giving a spatial resolution of approximately 1 µm. For this reason, we learnt to cast very thin gratings (~1 µm also) on our specimens, so that any local concentrations of strain were not blurred out through the thickness of the grating. Further, we can make the grating semi-transparent so that whilst it is possible to obtain high-contrast interference fringes in red HeNe laser light, it is also possible to see through the grating in white light to obtain pictures of the underlying polished and stained microstructure. Thus it is possible to obtain high-resolution displacement maps with a spatial resolution of about 1 µm a displacement sensitivity of a few tens of nanometres in direct registration with images of the underlying microstructre. One example taken from a loading sequence is shown below in Figure 9.

This is a good example of the type of information that can be gained from experiments such as this. The HMX-based PBX has been polished and the polyurethane binder stained to appear darker, so the larger crystals included in the bimodal crystal-size distribution are very easy to see. The view is near the centre of a specimen which is being compressed vertically, so here we are measuring the horizontal component of displacement. The strains are tensile. If the strain were uniform, the 0.5 µm contours would be parallel, vertical and evenly spaced. Instead, they reveal that the strain-distribution is

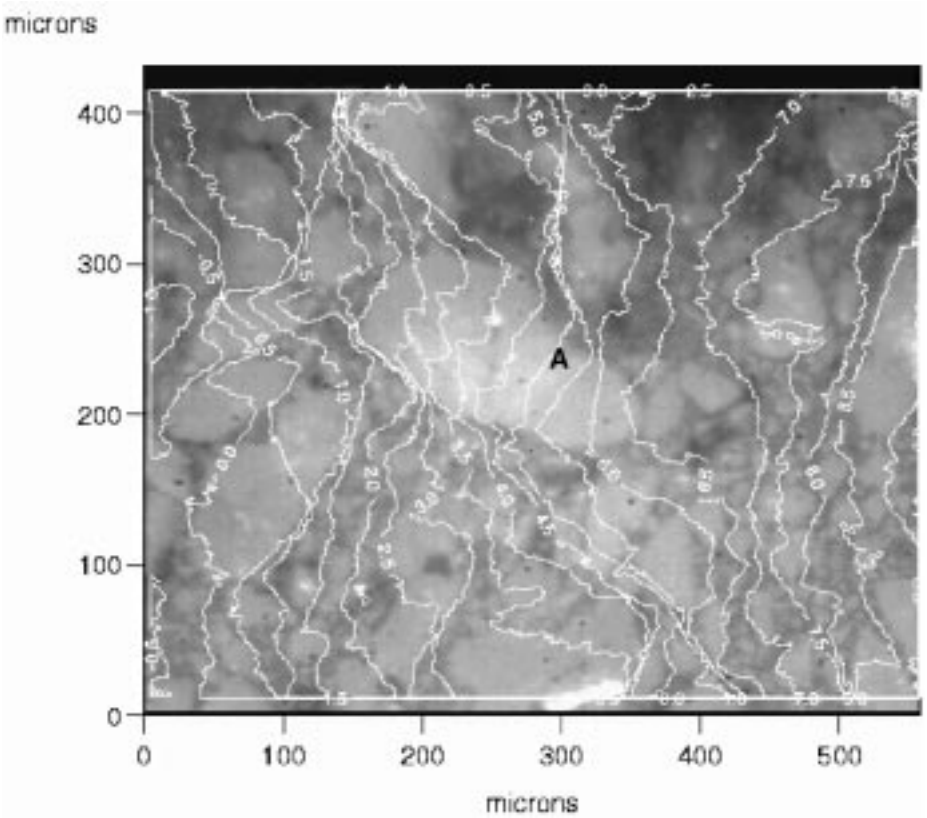


Figure 9. Result from a moiré experiment on a PBX being quasistatically deformed in the Brazilian test. The contours are at 0.5 μm intervals, and represent horizontal displacement. Crystal 'A' is labelled near the centre of the image.

significantly influenced by the locations of the larger crystals. In some places, the contours get extremely close together. These are the locations where cracks will begin to form. It can be seen that such strain concentrations largely appear around the near-vertical edges of the larger crystals. In fact, post-failure analysis in a conventional microscope confirms that this is in fact the case, as illustrated in Figure 10. This photograph was taken with a high-quality optical photomicroscope using Nomarski contrast enhancement. In Figure 9 there are also regions where there is a lack of large crystals, where the fine crystals and binder matrix appear to support very large strains. In places, we have seen such regions support strains up to twice those which one would expect the bulk explosive to support. Since the modulus of the filler particles is roughly four orders of magnitude greater than that of the binder, one might expect that the filler particles would accommodate rather little strain. In fact, there is clear evidence of significant strain in some of the crystals. The reason for this can be deduced from study of the crystal labelled 'A' both in Figure 9 and Figure 10. Here, the almost vertical contours kink, with sections running almost horizontally. There are parallel rows of kinks running from top left of the crystal to bottom right. This is due to the crystal undergoing deformation twinning. The measurement technique is sufficiently sensitive to detect the surface displacement as the crystal structure rearranges itself as the twinning occurs. In Figure 10, there are other twinned crystals which don't stand out in the moiré picture in Figure 9 This is because the twin planes are much closer to the horizontal, and so there is little displacement in the direction of sensitivity of the moiré measurement.

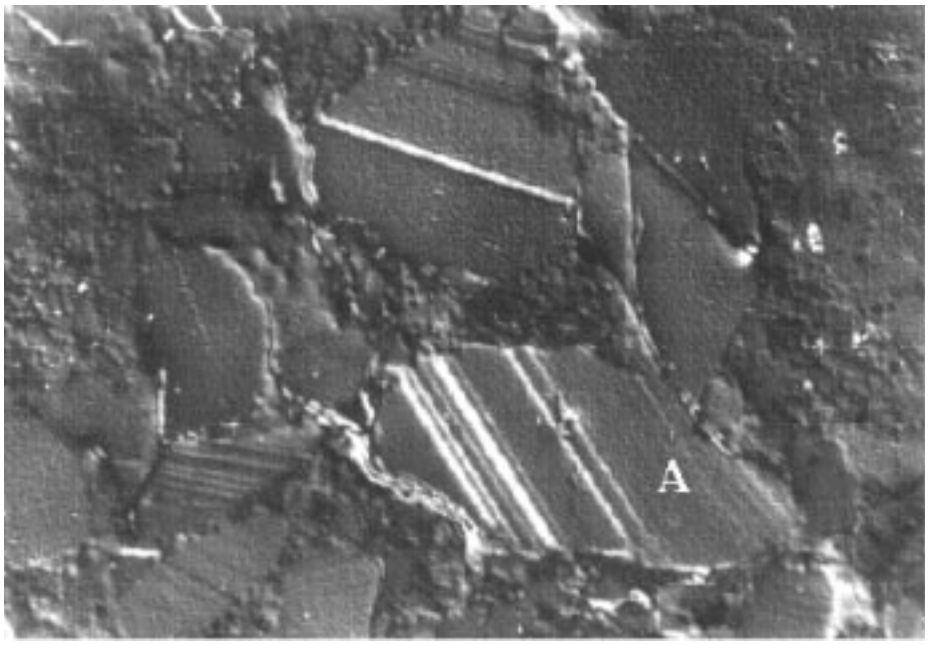


Figure 10. Post failure optical micrograph of the specimen shown in figure 9.

In brief summary, the moiré interferometry experiment allows measurement of strains in direct correlation with the underlying microstructure. Whilst the spatial resolution is of order 1 μm, the displacement sensitivity is of order tens of nanometres. One can quantify the strains, and gain insight into the factors which affect the distribution of strain throughout the composite. Further, and perhaps most importantly, one can examine samples of virgin and aged composites to see if there are any changes in the failure mechanisms one can detect, or if the strain distributions vary significantly.

Environmental Scanning Electron Microscopy (ESEM)

Environmental Scanning Electron Microscopy is now becoming a widely used technique in the study of insulating materials. Historically, there has always been a problem with conventional SEM that insulating materials charge in the electron beam of the instrument. The conventional solution has been to sputter or evaporate a thin conducting layer of, say, gold onto the specimen to carry away the collecting charge, and this works very well so long as the specimen is unchanging. However, if the specimen is, for example, yeast growing, or, more topically, a PBX cracking *in-situ* inside the microscope, new surfaces are exposed which have not been coated, and so these charge and become invisible. It is often not possible to carry out the kind of experiment where a mechanical test is interrupted by trips to the sputterer. Hence the invention of the ESEM. In this instrument, by virtue of a sophisticated system of differential pumping apertures, a significant pressure of some gas is kept in the specimen chamber, compared with the more familiar, quite hard vacuum in the column of a traditional SEM. This gas is ionised by the electron beam, and by processes which are still not fully understood, these ions will discharge the specimen, and allow high-resolution electron microscopy to take place. The main thrust of all this is that it is now possible to visualise newly opened cracks in insulating materials.

We have been studying *in-situ* Brazilian tests of various PBXs in the ESEM for a number of years, and one of the topics we have looked at is the variation with age of the failure mechanisms observed. Compare the images shown in Figure 11, Figure 12 and Figure 13.

Cracks can be seen to run around the large, smooth faces of larger crystals, much as predicted by the moiré experiments. Where there are regions of finer-grained material, the binder appears to pull out in thin whiskers. The failure appears largely to be due to debonding of the larger crystals, with a small amount of fracture toughness being endowed on the composition by the extending binder whiskers pulling the crack walls together. Smaller secondary failures can be seen parallel to the main failure in both aged and unaged compositions. Note that this is in fact a slightly different composition from that shown in the moiré experiments, and this factor is special to

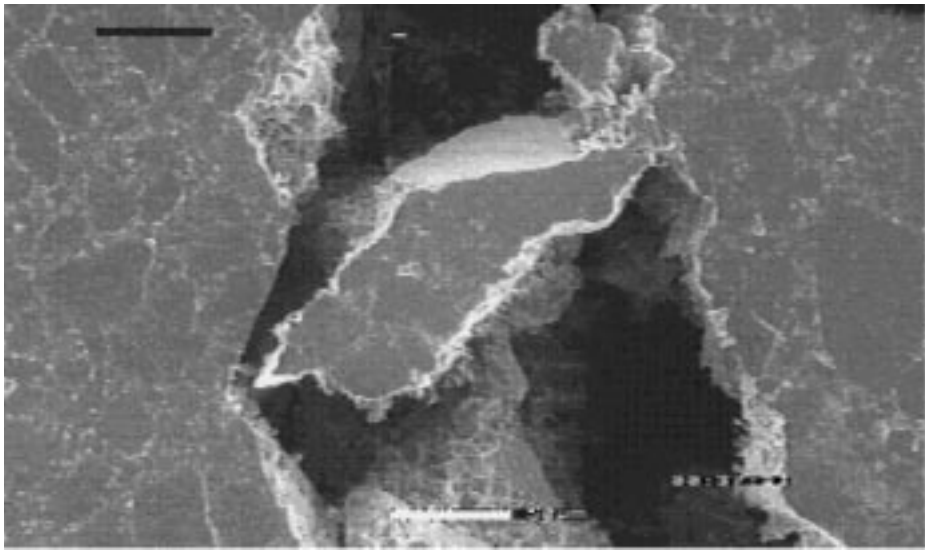


Figure 11. ESEM image of unaged failed PBX.

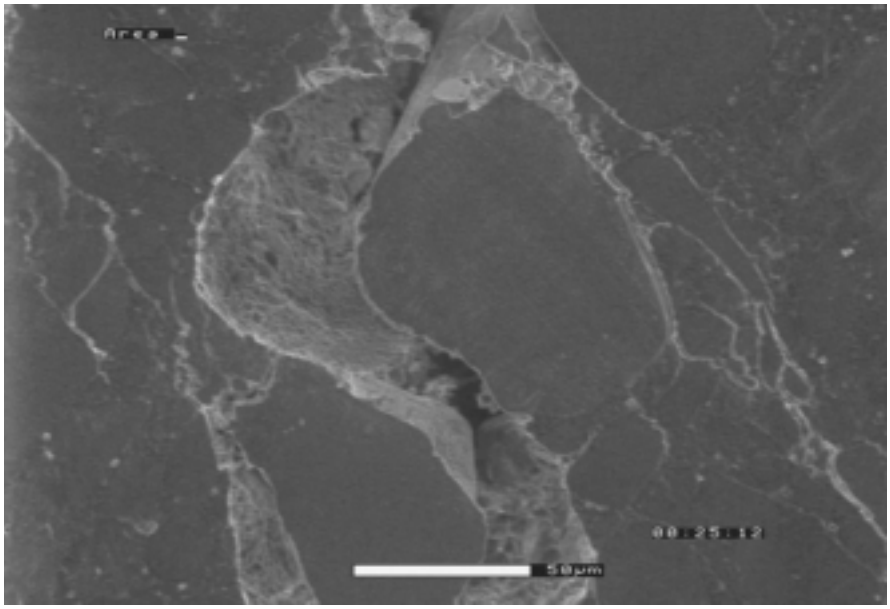


Figure 12. ESEM image of aged failed PBX.

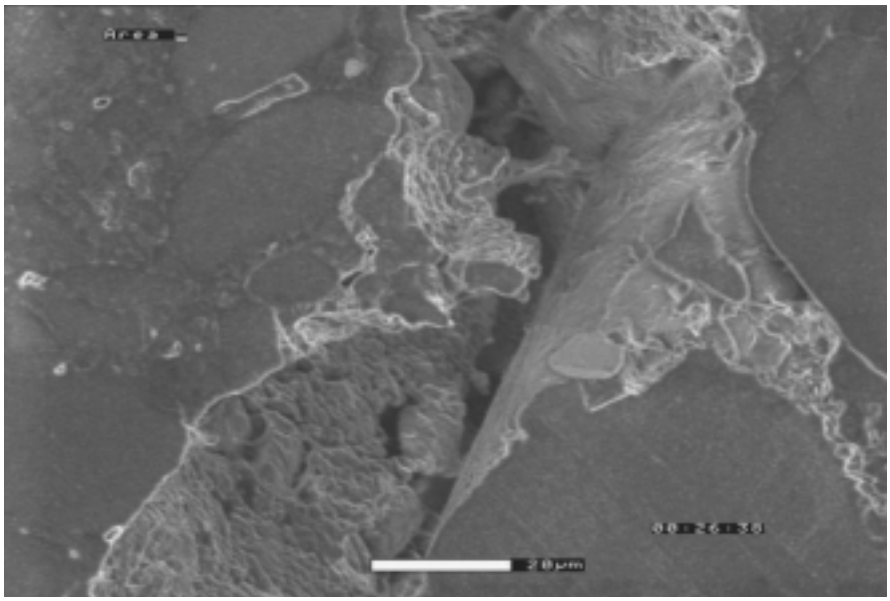


Figure 13. ESEM image of the same region of aged failed PBX at higher magnification.

this composition. There are many other similarities between the unaged and aged specimens. However, with extensive experience of watching cracks grow through both virgin and aged PBX in real time, we have not been able to detect any differences in the failure mechanisms at work.

In essence, the ESEM provides yet higher resolution images of the PBX failing, with greater clarity and depth of field than in optical microscopy or in the moiré interferometer. A detailed *qualitative* view of failure is gained, and when this is combined with the slightly lower-resolution but *quantitative* measurements from the interferometer, great insight into the mechanisms of failure can be achieved.

Summary

Despite the power of these techniques, we have not been able to detect any significant changes in the failure mechanisms with ageing of the composite. In many ways, this is reassuring, but there remains the nagging question of the cause of the significant reduction in overall strength with age. In fact, this is not so hard to explain. It is well known that the filler crystals show negligible changes with age. The component of the binder in this system which is known to degrade with age is nitrocellulose. Separate work has shown clearly that the average molecular weight of nitrocellulose deteriorates with time. Equally, the strength of nitrocellulose is known to reduce with reduced molecular weight. There is an excellent correlation between the reduction of strength of the explosive and the reduction of molecular weight of the included nitrocellulose. It seems that the reduction in strength of the composite can be explained completely by the variation in just one of its constituents.

Conclusions

In what precedes, I have given an example of how some of the available methods for studying the mechanical properties of composites have been used to gain insight into the effects of ageing. There are many techniques I have not described, and not all the techniques are applicable to all types of PBX, let alone all types of composite or materials in general.

Some of the advantages of this type of mechanical study are these:

- Quantification of mechanical properties;
- Understanding of the mechanisms of failure;
- Understanding of deformation processes;
- Identification of alterations in these processes with age;
- Identification of failure mechanisms which may become a significant threat to the integrity of the material in service;
- Identification of the most appropriate means to improve the properties of a composite.

Some of the disadvantages of this type of mechanical study are these:

- Some of the studies are not straightforward, and can thus consume time and money;
- Finite element modelling of the microstructure of composites like this is not yet sufficiently advanced to behave as a useful predictive tool.

Where the mechanical properties of a material may vary with age, and where the variation in these properties may have some adverse effect on the system into which the material is built, at least some understanding of these changes will probably be necessary. Whilst it is clear that the underlying causes of all these changes may be explained by a chemistry-based approach, the impact of these changes will very likely have to be approached by at least some of the techniques described above.

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Thoughts on aging of materials and methods to understand the slow reactions underlying aging processes.

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Army Research Office workshop on Slow Processes, August 9–11, 2000

The failure of manufactured items as they age is a long-standing problem. The root cause of the problem usually stems from changes that occur in the constituent materials with time. Designs of new articles are typically based on properties of newly fabricated materials, not taking into account how the properties may change with time. In some cases, properties of the constituent materials are available as a function of time, making it possible to estimate how the manufactured item may change as it ages. However, once the materials are selected for a design, the materials may be altered in the manufacturing process, creating new materials and new material interfaces. Thus, the assembled system becomes significantly more complex. In these cases, although information on aging of specific materials used for building an article may be available, the failure of the item may be determined by interactions between materials that are unknown to the designer. To address these types of issues, engineers have resorted to accelerated aging tests to obtain advanced warning of incipient failures. For some specific failure modes, such as fatigue failure, the item can be tested at an accelerated rate, thus providing advanced warning of failures. To assess failure of items due to chemical reactions that occur at very slow rates, the items are typically stored at elevated temperatures and periodically removed for testing. This method of testing often provides erroneous results.

It is not surprising that accelerated aging tests, based on storage of articles at higher temperatures, do not provide reliable estimates of aging behavior. For a typical item comprised of a number of different types of materials, many different possible chemical reactions may take place. Each reaction will have a characteristic rate and characteristic temperature dependence. In addition, changes that occur in different materials, or at different material interfaces, will most likely lead to different modes of failure. Thus, conventional aging experiments will fail for two main reasons. First, the rate-limiting reactions that occur at elevated temperatures of the aging test, are not necessarily the same reactions that will be dominant at lower temperatures. Second, the failure mode, and hence the change in the material that leads to the failure mode, at higher temperature may not be the same as the failure mode at lower temperatures. Given these two limitations, the

question arises of how to improve our ability to achieve advanced warning of incipient failures of systems due to slow changes in materials.

Basic requirements for aging predictions. To assess the likelihood of failure of a system requires understanding both the chemical reactions that can occur within the system at normal storage temperatures and how these chemical reactions can lead to failures of the system. This requires a level of understanding of the system that is not usually available. Figure 1 shows a chart that illustrates the understanding required to assess a component containing energetic materials, such as a rocket motor or detonator. The chart illustrates the range of items that must be understood in order to predict the life expectancy of an energetic material component. The top level of the chart shows that for energetic materials, understanding changes that affect both performance and safety must be understood. For more common items, predicting changes in performance usually suffices. The bottom level of the chart lists the various types of phenomena that must be understood. For example, to understand how the materials change with age, the energetic material properties and the reactive processes that control the changes of the materials must be understood. To understand the failure modes, the reactive processes that control the combustion in the device must be understood. If one understands the material characteristics and the material properties, listed on the chart, and has constructed mathematical models representing these processes, then it should be possible to predict the failure modes and estimate the time to failure. This is a difficult task. While developing this predictive capability is a good long-term goal and is useful for guiding research relevant to achieving the goal, it is clear that obtaining simpler and alternative pathways for assessing the effects of aging should be investigated.

Aging research program approaches. Two alternative approaches for establishing a research program on the aging of materials involve 1) developing new tools that can be used to detect small changes in materials that may affect the performance of a system and/or 2) focusing on simple well-defined systems for study.

The first approach can be illustrated with the chart in Fig. 1. For example, it is known that double-base propellants, containing nitrocellulose (NC) and nitroglycerine, decompose releasing NO_2. NO_2 is known to undergo subsequent reactions with the NC, leading to further decomposition. To inhibit this nonlinear reaction, a stabilizer is added to the propellant that reacts with NO_2, providing a sink for the reactive intermediate. In this case the failure mode of the propellant is the rapid decomposition of the nitrate esters comprising the propellant and the state of the propellant can be monitored by measuring the degree of nitration of the stabilizer. Thus, by knowing some information about the energetic material properties and how they are qualitatively related to the performance of the propellant, an experimental testing method can be devised to evaluate the state of the propellant. This is a standard procedure for evaluating aging of double-base propellants. In this case the failure mode is relatively obvious from direct

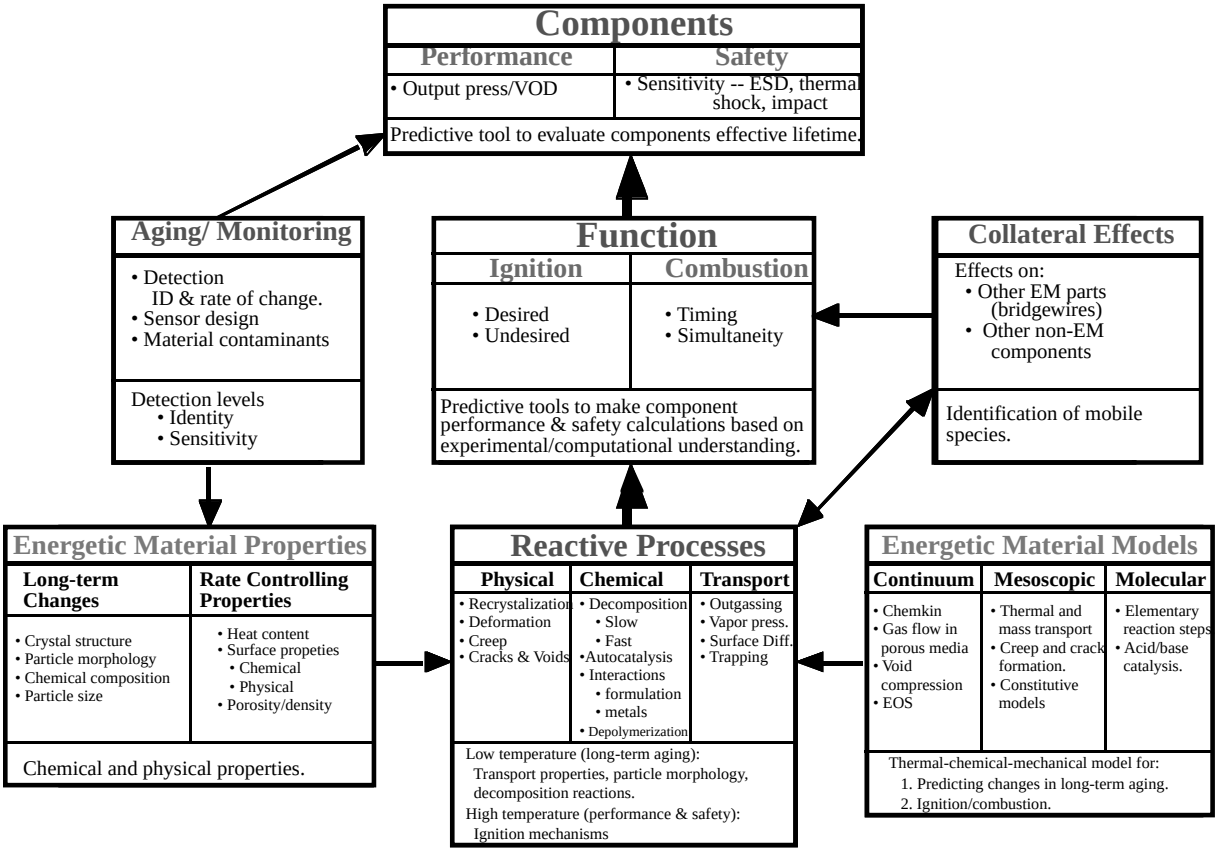


Figure 1. Chart illustrating material properties and reactive processes that control the behavior of an energetic component as it ages.

observations of the behavior of the propellant under normal storage conditions. It should be noted that this method of of monitoring aging focuses on only one failure mode of the double-based propellants (there may be others that go unnoticed) and it is only applicable to nitrate ester based materials in which decomposition to form NO_2 is an issue. In contrast, for ammonium perchlorate (AP) based propellants, macroscopic chemical decomposition is not observed and there is not a clear and obvious chemical indicator of aging. AP-based propellants exhibit changes in the mechanical properties of the propellant grain which show some correlations with changes in ballistic performance. Thus, understanding the chemical reactions that alter the mechanical properties of AP-based propellants may provide a better basis for understanding the effects of age on this class of solid rocket motors. The mechanical properties may be affected by changes in the polymeric bind (i. e., hardening, oxidation) and interfacial debonding between the binder and the solids contained within the propellant (AP and aluminum). Thus, the one approach to establish a research program that addresses aging issues is to develop better diagnostic tools that can probe changes in polymers and interfacial reactions of organics and polymers that occur on very slow time scales.

The second approach to establish a research program is to focus on important, yet simpler chemical systems. Several opportunities come to mind. One area focuses on the behavior of adhesives and how they fail with age. Adhesive technology has a long history and plays an important role in many systems. Are there some underlying features of adhesives that would form the basis of a research program to study slow processes in materials? Another area focuses on small micromachines. New technologies, such as silicon micromachines (SMM), are being developed and incorporated into new microsensor systems. While these new technologies present new and inexpensive methods for developing sensors for a wide variety of applications, there is little known about how the performance of these devices will change with age. For example, the high surface area to volume ratio of these microdevices suggests that changes in frictional forces may have a very large effect on their performance. Thus, understanding how changes in either the surface characteristics or the nature of adsorbates may influence the frictional characteristics of the devices would be important. If the static friction forces become too large with time, the devices may cease to function after being left in a dormant state. Numerous aging issues can be postulated for these SMM.

Basic aging kinetics. One fundamental question with regard to investigating slow processes is how slow is slow? What rate of change needs to be detected? What level of change must be detected to provide enough advanced warning of incipient failure? Even for relatively simple systems it is dependent on the type of reactions that occur and their relative rates of reaction. For a relatively simple first order reaction such as

$$A \rightarrow D \qquad (R1 - k1)$$

where A decomposes to an inert product D with a rate constant k1. The long-term rate of reaction is illustrated in Figure 2. This decomposition reaction is gradual. If the system fails when 5% of the material decomposes (~ 35 years) then a significant amount of advanced warning can be obtained. The sample can be simply analyzed for the amount of degraded material. Measuring a change of several percent should be relatively simple.

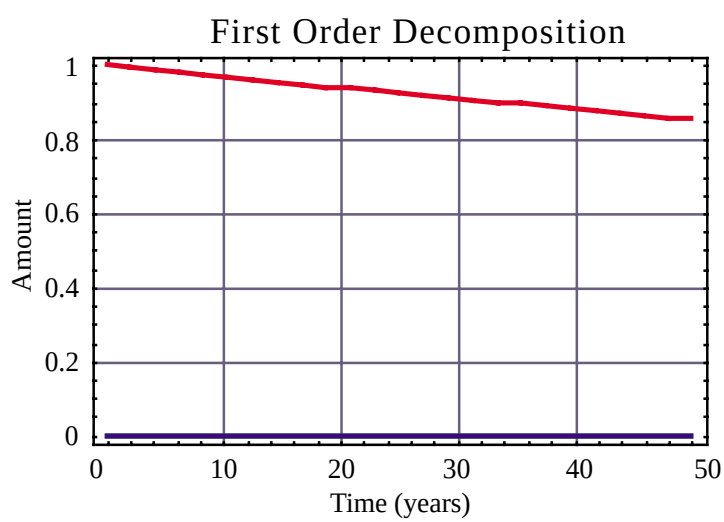


Figure 2. First order decomposition reaction. Rate constant k1 = 1×10^{-10}.

The situation becomes more complex when nonlinear processes are added to the reaction scheme. For example, consider the following scheme:

$A \rightarrow D$	(R1 – k1)
$A + B \rightarrow 2B + E$	(R2 – k2)
$A \rightarrow B$	(R3 – k3)
$C + B \rightarrow F$	(R4 – k4)

where the reactant A decomposes to an inert product D and a reactive product B. Reaction R2 is between A and B producing an additional intermediate B and inert products E. Reactant C is a stabilizer that reacts with the intermediate B, forming an inert product F. The stabilizer may be either deliberately added to the material or may be present in the material as a determined or undetermined impurity.

The behavior of the decomposition process for a range of different reaction rates is illustrated in Figures 3 through 8.

Figure 3 shows the result when there is no stabilizer (C) present and the reaction rate is controlled by a combination of reactions R2 and R3. The rate

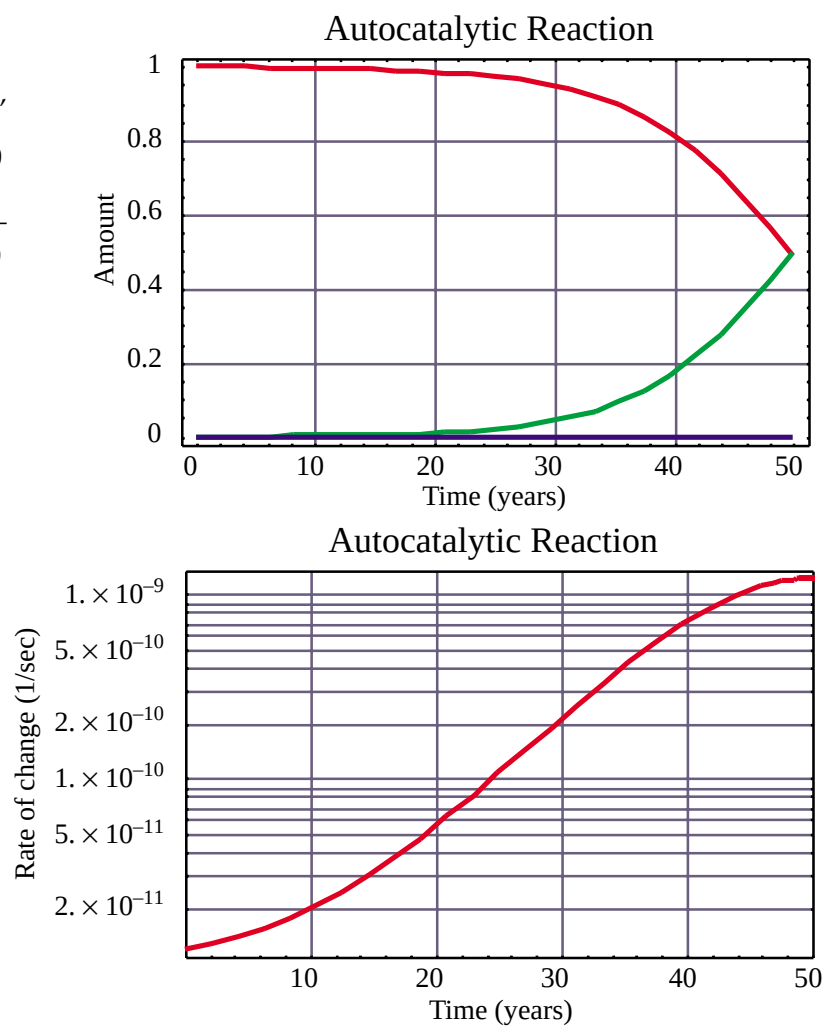


Figure 3. Autocatalytic reaction without stabilizer. $k1 = 1. \times 10^{-11}$, $k2 = 5. \times 10^{-9}$, $k3 = 2. \times 10^{-12}$, $k4 = 1. \times 10^{-30}$; $A0 = 1.$, $c0 = 1. \times 10^{-30}$. Legend: A – red line, B – green line, C (stabilizer) – blue line. Lower plot: rate of change of A (sec^{-1}).

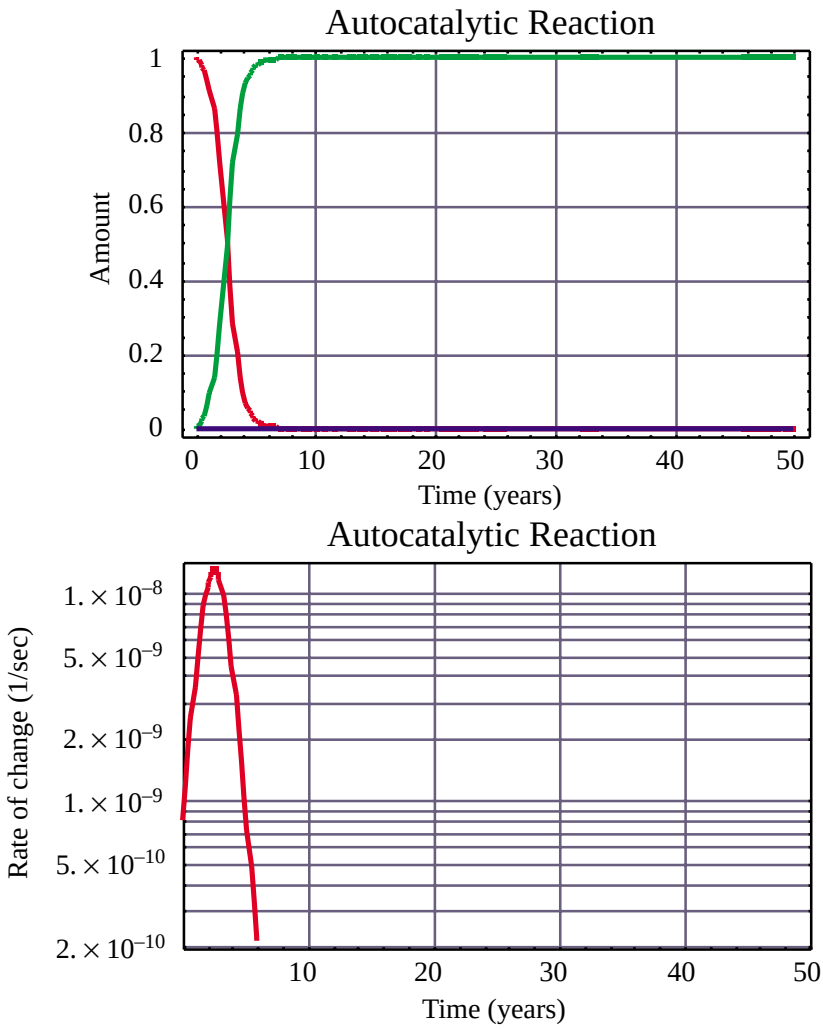


Figure 4. Autocatalytic reaction without stabilizer and faster rates for reaction R2 and R3. k1 = $1. \times 10^{-1}$, k2 = $5. \times 10^{-8}$, k3 = $8. \times 10^{-10}$, k4 = $1. \times 10^{-30}$; A0 = 1., c0 = $1. \times 10^{-30}$. Legend: A – red line, B – green line, C (stabilizer) – blue line. Lower plot: rate of change of A (sec^{-1}).

constants used in the calculation are listed in the figure caption. In this case the growth of the nonlinear reaction is relatively slow. If 5% degradation of A is again used as the criteria for failure, then failure occurs at ~ 30 years and the growth of the reactive intermediate, B, starts to appear ~ 10 years prior to failure. With a reasonable surveillance program it should be possible to identify the failure mode and estimate the time of failure.

Figure 4 shows the results from a case that is similar to that shown in Figure 3, but in which the rate constants for reactions R2 and R3 are larger. In this case the device will reach the 5% decomposition level shortly after it is placed in service. In this type of a situation, it is likely that the failure mechanism may have been discovered during the design of the item.

Figure 5 represents a significantly different case from those shown in Figures 3 and 4. In this case the reaction rate for R2 is slightly higher but the direct production rate of B from reaction R3 is very slow. In this case little change is observed for a long period of time (~ 20 years). Note the slight decrease in A prior to the runaway reaction is due to reaction R1. This case presents the most challenging situation for predicting failure. Little change is observed until just prior to catastrophic failure. In this case there is about

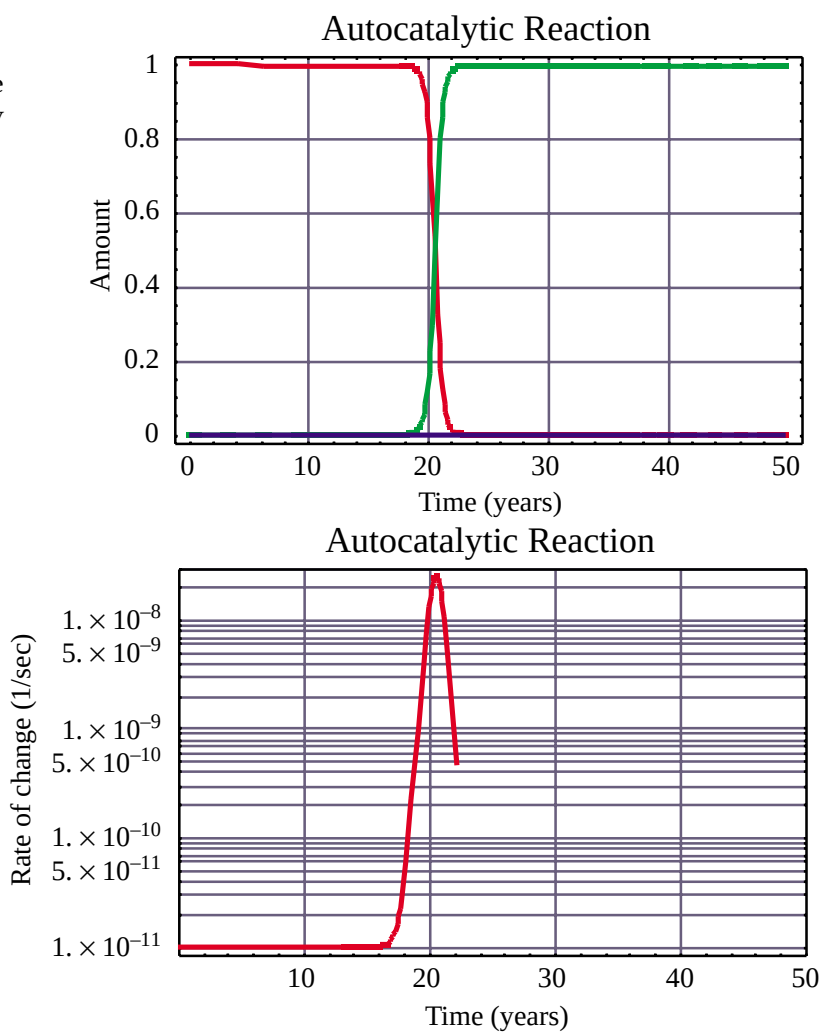


Figure 5. Autocatalytic reaction without stabilizer and faster rate for reaction R2 and very slow rate for reaction R3. k1 = $1. \times 10^{-11}$, k2 = $1. \times 10^{-7}$, k3 = $8. \times 10^{-30}$, k4 = $1. \times 10^{-30}$; A0 = 1., c0 = $1. \times 10^{-30}$. Legend: A – red line, B – green line, C (stabilizer) – blueline. Lower plot: rate of change of A (sec^{-1}).

1/ 2-year lead time between the onset of the reactions leading to failure and the failure event. Figure 6 shows an even more dramatic case in which the rate constant for reaction R3 has been slowed even further. In this case there is even less time from the onset of the reactions leading to failure and the failure event. In a normal surveillance situation, in which the behavior of a large number of units are monitored, this may be interpreted as a random event in which one of the units for some unknown reason failed.

Figure 7 shows how the presence of a stabilizer, C, delays the onset of the rapid reaction seen in Figure 6, but does not substantially change the time between the onset of the reactions leading to failure and the failure event.

Figure 8 shows the effect of a stabilizer, C, for a combination of rate constants for reactions R2 and R3 that produce a more gradual decomposition. In this case the delayed onset of reaction due to the stabilizer is as expected. This case illustrates that the presence of an unknown stabilizer will delay the onset of reactions leading to failure. In this case the reactions leading to failure may not become apparent until after the stabilizer is depleted.

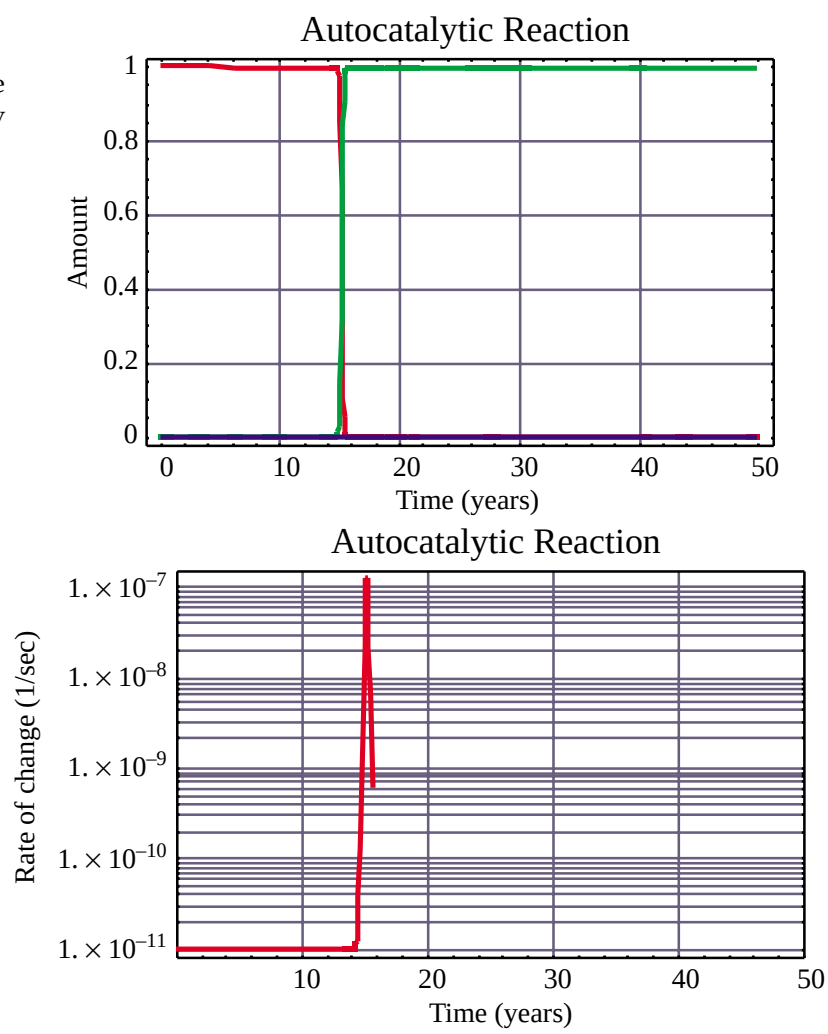


Figure 6. Autocatalytic reaction without stabilizer and faster rate for reaction R2 and very slow rate for reaction R3. k1 = $1. \times 10^{-11}$, k2 = $1. \times 10^{-7}$, k3 = $8. \times 10^{-33}$, k4 = $1. \times 10^{-30}$; A0 = 1., c0 = $1. \times 10^{-30}$. Legend: A – red line, B – green line, C (stabilizer) – blueline. Lower plot: rate of change of A (sec^{-1}).

Suggestions for areas of investigation. The different types of reaction conditions that lead to changes in materials that comprise a particular article and lead to its failure suggest several general areas of investigation that can improve our ability to identify and monitor these changes. These general observations suggest the following:

1. The reaction mechanisms that control the aging processes that lead to failure will depend very strongly on the specific materials used in the article. Finding general reactions that characterize different materials will be difficult.

2. Identifying different possible reaction mechanisms at elevated temperatures will provide insight into types of reactions that can occur in a particular type of material. This will provide more information and understanding than is obtained through conventional accelerated aging tests.

3. Methods to measure the behavior of slow reactions of organics, polymers and inorganics and their interactions are required. The methods should not only provide information on the chemical reaction

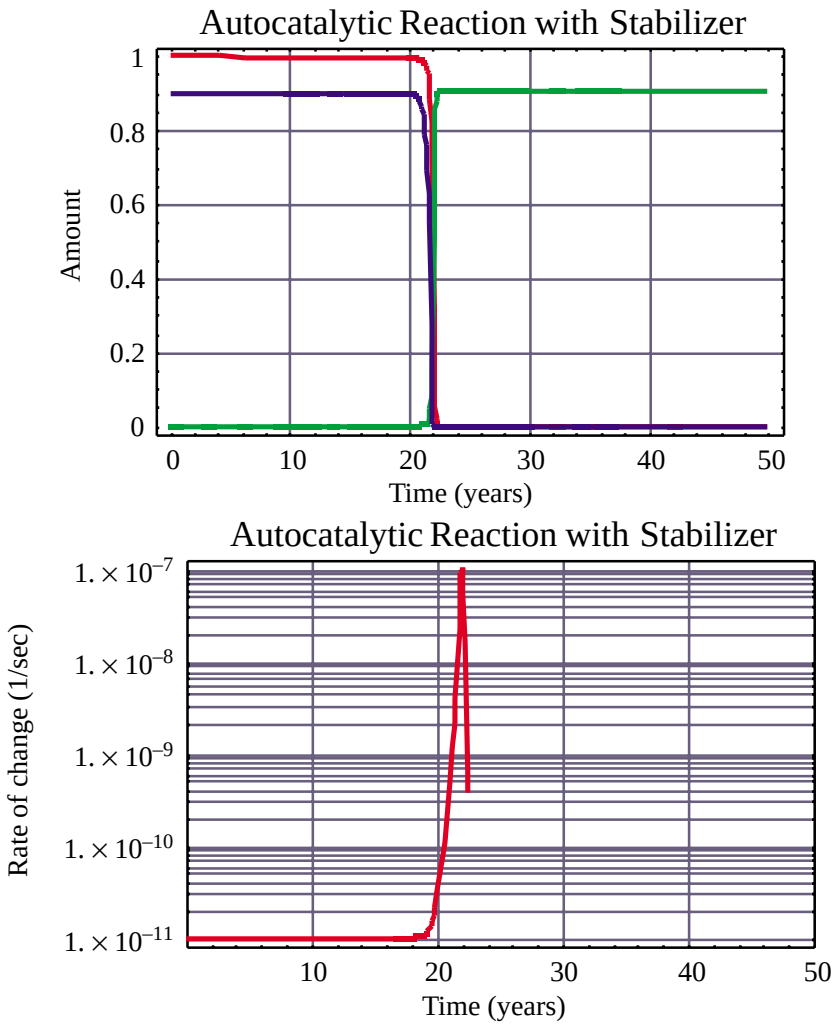


Figure 7. Autocatalytic reaction with stabilizer and faster rate for reaction R2 and very slow rate for reaction R3. k1 = $1. \times 10^{-11}$, k2 = $1. \times 10^{-7}$, k3 = $8. \times 10^{-33}$, k4 = 4.4×10^{-6}; A0 = 1., c0 = 0.09. Legend: A – red line, B – green line, C (stabilizer) – blue line. Lower plot: rate of change of A (sec^{-1}).

mechanism but also the morphological changes induced by the slow chemical reactions. This requires making measurements in which not only the time-dependent chemical changes can be measured but also the spatial features of the chemical changes.

4. Understanding the possible failure mechanisms of a particular article is important for assessing the effects of aging on the article. All sources of information should be used to assess the possible failure modes. These should include statistical databases of failures and engineering models of failure modes.

5. Several well-defined systems should be defined to provide a basis for a research program on slow reaction processes that underlie the aging and failure of materials.

Sandia/CA programs. Sandia has large number of projects addressing issues of materials aging in system components. Two of the approaches being used at the Combustion Research Facility at Sandia, California are described here.

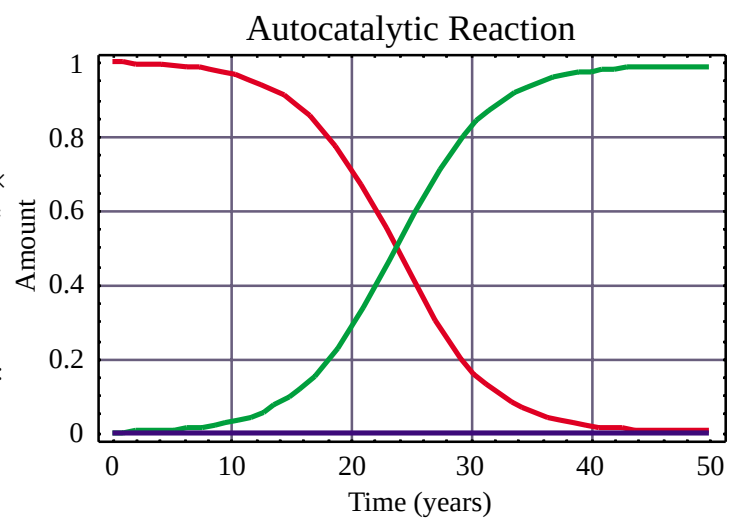
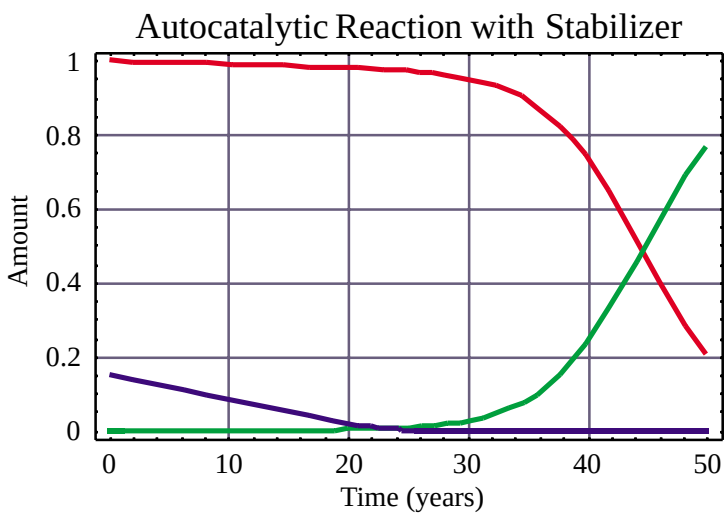


Figure 8. Autocatalytic reaction with and without stabilizer and faster rate for reaction R2 and very slow rate for reaction R3. k1 = $1. \times 10^{-11}$, k2 = $8. \times 10^{-9}$, k3 = $2. \times 10^{-11}$, k4 (upper) = $1. \times 10^{-30}$, k4 (lower) = 1.0×10^{-5}; A0 = 1., c0 (upper) = $1. \times 10^{-30}$, c0 (lower) = 0.015. Legend: A – red line, B – green line, C (stabilizer) – blue line.



STMBMS. The simultaneous thermogravimetric modulated beam mass spectrometer (STMBMS) apparatus has been used to study the reaction processes that control the thermal decomposition of energetic materials. A schematic diagram of the apparatus is shown in Fig. 9 and a cross section of the reaction cell used to conduct the thermal decomposition experiments is shown in Figure 10. In these experiments the energetic material is place in the reaction cell and sealed with a gold foil containing a pinhole orifice with a diameter between 2.5 µm and 1000 µm. The reaction cell is place in the STMBMS apparatus where the reaction cell is radiatively heated in a high vacuum environment. The reaction cell is mounted on a thermocouple probe that is seated in a microbalance. As the sample is heated, gas evolves through the orifice. Part of the gas flow from the reaction cell passes through two beam defining orifices, forming a molecular beam. The molecular beam is modulated with a chopping wheel and passes through an electron-bombardment ionizer where a small fraction of the molecules is ionized. The ions of selected m/z values are transmitted through a quadrupole mass

Figure 9. Schematic of STMBMS apparatus.

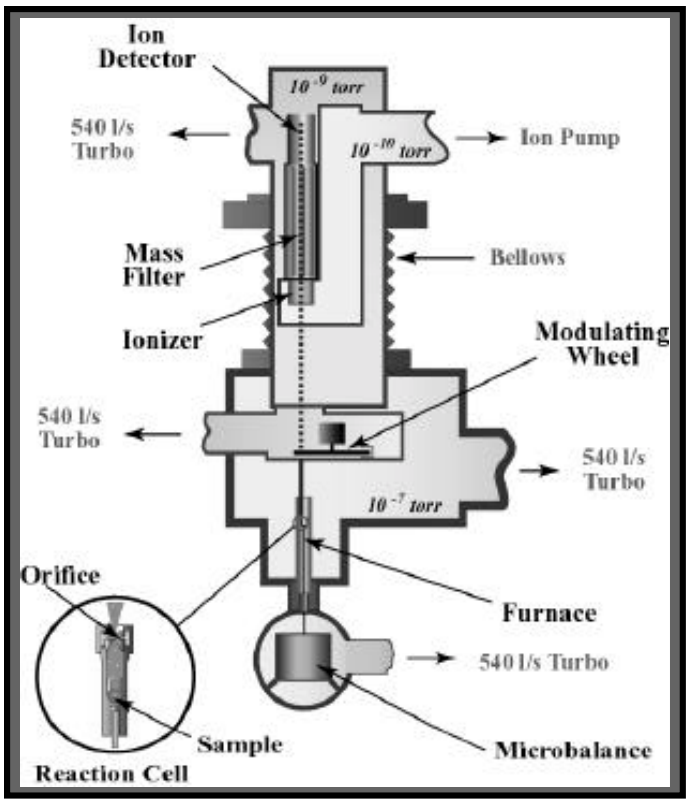
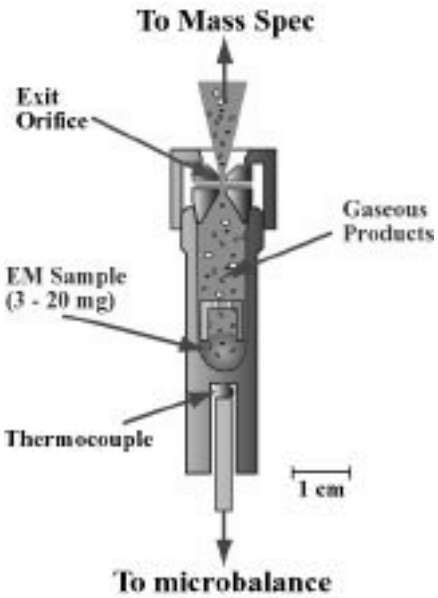


Figure 10. Cross-section of STMBMS reaction cell.



filter and counted with a Daly-type ion detector. The rate of force change due to gas exiting the reaction cell is measured with the microbalance. The simultaneous measurement of the rate of force change (mostly due to mass loss) and the ion signals measured with the mass spectrometer allow the rate of formation of the gaseous products to be determined as a function of time.

The decomposition of two cyclic nitramines, RDX and HMX, have been extensively studied using the STMBMS. An example of the nonlinear reaction behavior is shown in Fig. 11 for the case of decomposition of RDX in the solid phase. In this case the first reaction involves the slow decomposition of RDX and the nucleation of a nonvolatile residue (NVR) on the surface of the solid RDX. After nucleation of the NVR, the rate controlling reaction involves the reaction of RDX on the surface of the NVR, leading to the formation of gaseous decomposition products and the growth of the residue. This leads to an increasing rate of reaction as the sample continues to decompose. This reaction is similar to reactions R2 and R3 in the simple reaction scheme presented above.

Based on the results from a large number of experiments with RDX and HMX a general reaction scheme that characterizes the decomposition of these two cyclic nitramines was developed and is shown in Figure 12. The main point of presenting this reaction scheme at this workshop is to illustrate how the STMBMS method can be used to identify the underlying reaction processes that are involved in controlling the thermal decomposition of energetic materials. Separating the various reaction channels and determining the reaction kinetics for each channel allows the relative importance of each channel to be estimated at lower temperatures. While these

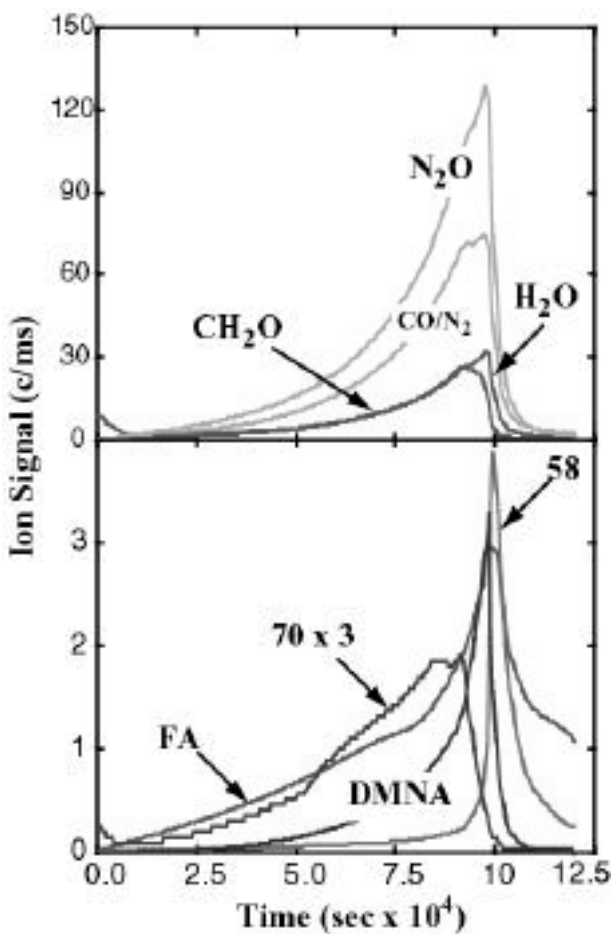


Figure 11. Ion signals of the decomposition products formed during the thermal decomposition of RDX at 180°C. Products: formamide (FA), dimethylnitrosamine (DMNA).

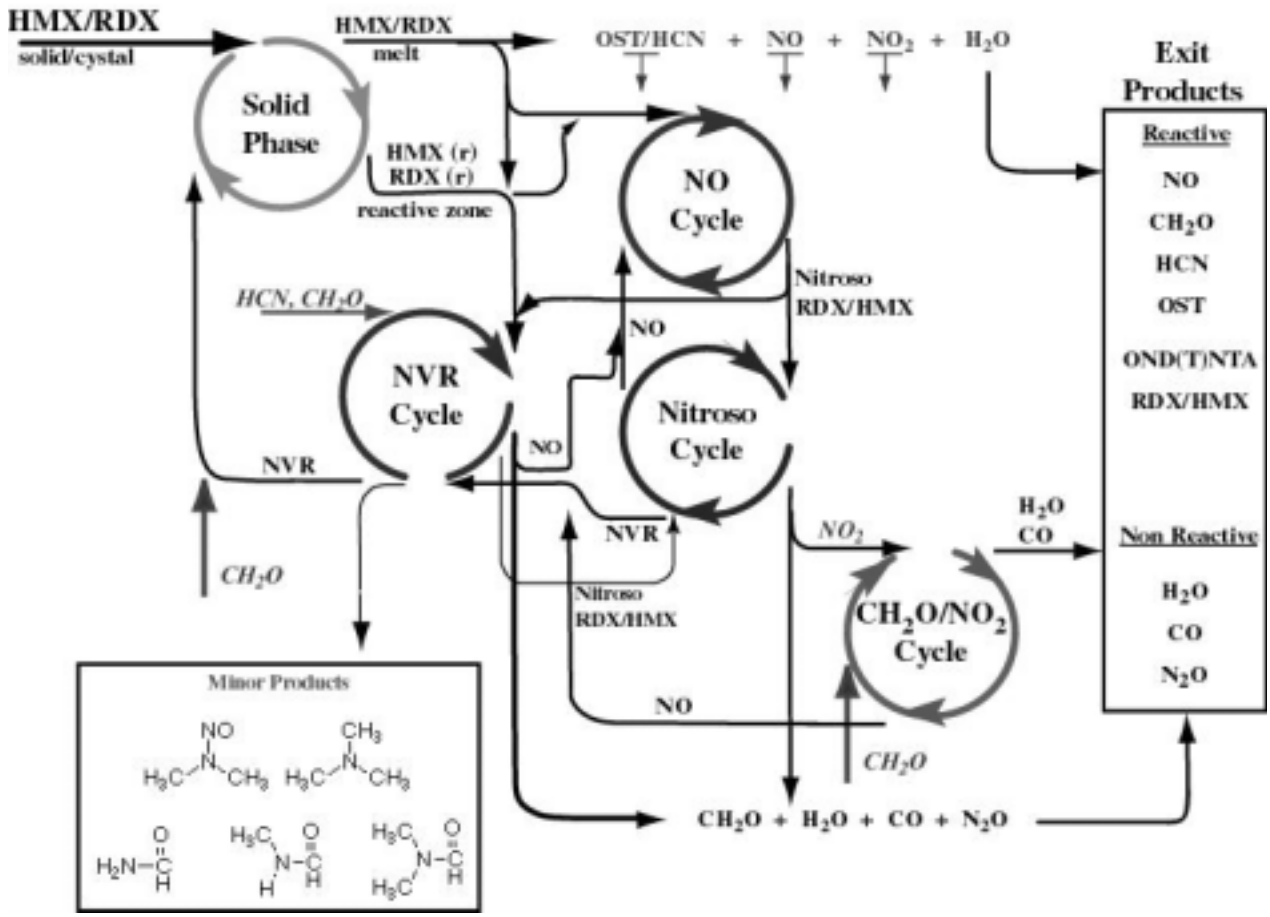


Figure 12. Reaction processes that control the thermal decomposition of RDX and HMX between 160°C and 270°C.

experiments provide new insight into the types of reactions that may be important in assessing the slow changes that may occur at lower temperatures, they do not provide a sufficient amount of information to evaluate how a component composed of a nitramine-based explosive or propellant will change with age.

<u>*Microprobe/ FTICR mass spec*</u>. To identify slow reactions that may occur in materials found in actual components a new instrument has been designed and constructed to examine these materials. A schematic of the instrument is shown in Figure 13. The instrument consists of a Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer coupled with an ion and laser beam surface analysis microprobe system. The FTICR mass spectrometer provides the ability to identify complex high molecular weight compounds (50,000 Daltons) via its high resolution (m/Dm from 100,000 to 3,500,000) and its ability to conduct MS n experiments. The surface analysis system can accommodate samples up to 1" square and can move and position the sample to within 10 nm. The 25kv Ga+ ion gun, with a beam diameter of 50 nm, provides the ability to both image the sample by collecting secondary electrons and generate secondary ions for high resolution

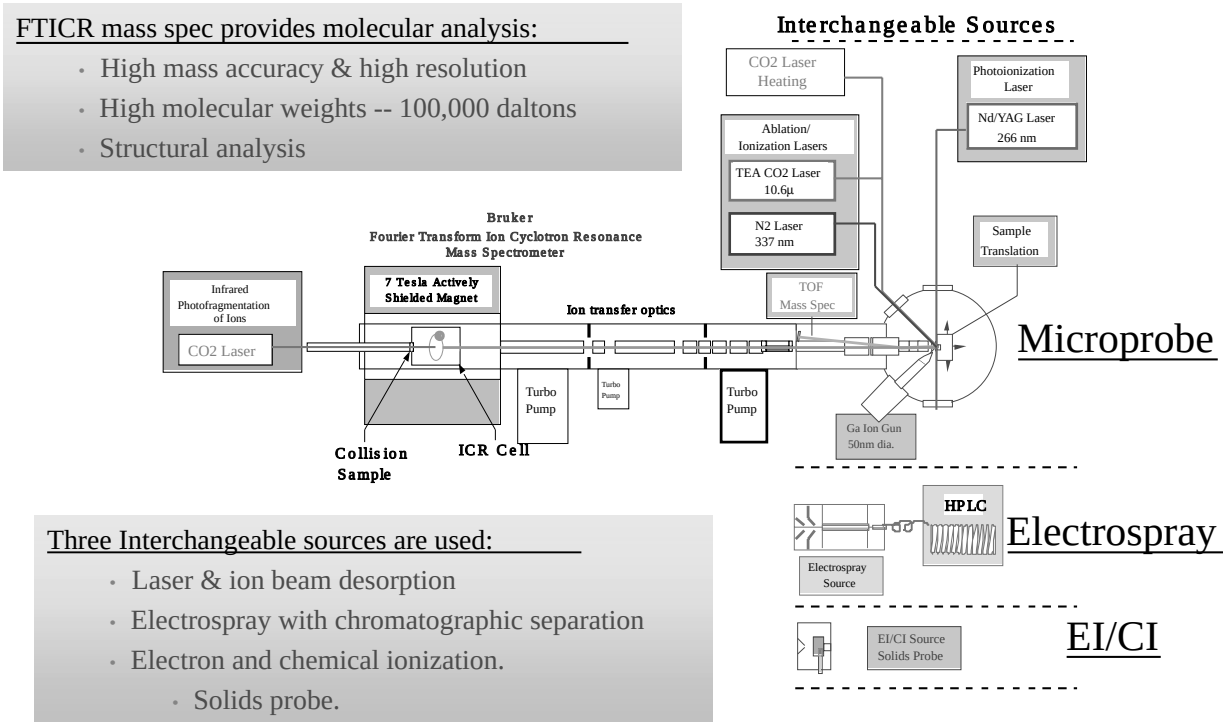


Figure 13. Schematic of microprobe/FTICR mass spectrometry system.

analysis with the FTICR mass spec or rapid imaging with a linear TOF mass spectrometer. UV and IR laser microprobes provide additional methods to either directly generate secondary ions or ablate neutral species that are subsequently ionized using the 266 nm UV pulse from a Nd/YAG laser. The system will be used to examine the materials present in cross sections prepared from various types of components. Samples will be prepared with both standard sectioning procedures and the new femtosecond laser machining facility at LLNL. The microprobe/FTICR mass spec system will be used to identify chemical compounds and measure the spatial distribution of the various constituents.

Atomic-Level Modeling and Rate calculations of Slow Processes in Complex Materials

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Oklahoma State University
July 2000

Our research focuses on theoretical/computational studies of elementary rate processes. Our studies have dealt with gas/surface chemistry, gas-phase unimolecular and bimolecular reactions, collisional energy transfer, intramolecular vibrational energy redistribution (IVR), cluster growth, atom and molecule migration on surfaces and in solids, electronically nonadiabatic processes, proton tunneling, and reactions and conformational transitions in liquids and dense gases. Our focus has been on simulations and rate calculations using realistic models of large systems. We have developed methods for constructing PESs to describe chemical reactions and condensed phase systems (particularly, molecular and ionic crystals). We have also developed a set of methods for computing rates for processes ranging from statistical (*i.e.*, slow) to nonstatistical (*i.e.*, fast). These are primarily based on classical mechanics, but also include practical methods for treating some quantum effects by semiclassical approximations. Some of the kinds of materials that might be studied by our techniques are crystalline molecular solids, crystalline ionic solids, energetic polymers, and composites of crystals and polymers (e.g., energetic materials).

The precise definition of aging will depend on the type of material and its function. A general definition might be: Any physical or chemical change that modifies the macroscopic properties that are essential for the proper functioning of the material. More specific definitions would be based on the microscopic changes that lead to structural changes such as separations, voids, cracks, etc. The elementary processes that may lead to aging include chemical reactions, chemical (mass) migration, tunneling (when H-atom transfer is the critical step), and phase transitions and other "large scale" rearrangements. For example, in composite materials structural changes due to debonding or separation of the components may be the critical process of aging, and thus we would want to determine the rate at which this occurs. In pure materials, phase transitions such as crystalline phase changes may be the important aging mechanism, and then one would need to compute or measure the rate at which these large-scale rearrangements occur.

For the sake of designing studies, one might begin with the assumption that aging occurs in stages. Identifying the initial step would be important for understanding the process and for designing ways to inhibit it. Identifying rate-determining steps that separate the assumed major stages in aging would also be critical for understanding the overall aging process. (Question: Is there a "critical step" as in nucleation and similar processes?) The

major stages can be viewed in terms of the system existing in relatively deep local potentials (which result in slow steps), which may include a number of shallow local minima (which may be "visited" only briefly by the system, and thus result in fast steps). That is, we assume there are a range of rates as the system makes it way among multiple pathways between the "pristine" and "aged" states.

Given the time scales and non-extreme conditions it is reasonable to assume that the system will pass along well defined pathways within the "maze" of minima in the PES that must exist for complex materials. In other words, the system will tend to hop between the minima along a few paths near the MEP. I would not expect the system to sample all the wells, and certainly not to behave ergodically. That is, the overall process, absent strong perturbations and stresses, should be statistical, with the system making its way through the saddle points separating local minima along the MEP as it moves towards the global minimum. There could be some "non-statistical" behavior where the system does not take the lowest pathway, but this seems unlikely to me unless there is applied stress or rapid, strong perturbations. This would argue that aging will always result in very similar final conditions of the material if we start with identical samples and subject them to identical conditions. This, of course, is difficult to do under normal conditions, but experiments might be designed to study specific aspects of it.

The overall process could be approached as is often done for other macroscopic processes; that is, use phenomenological modeling of the overall aging processes with input for specific elementary processes provided by theoretical and experimental studies. It is probably not necessary to accurately model the system passing through all of the stages, but rather to model and predict transitions between certain stages. It would be sufficient to understand the properties and functioning of the material at selected stages, and the transitions between them. This information could be then be used in a global model, as is done in modeling of processes such as combustion.

Theoretical and computational studies that we could do:

- Develop atomic-level models for condensed phase systems.
- Use Monte Carlo methods to locate critical points on the PESs. (More refined methods such as those developed by David Chandler, Jim Doll, and others may be useful.)
- Perform MD simulations to probe the fundamental behavior of the systems and to compute "fast" rates. (The new methods developed by Art Voter will be useful here.)
- Develop PESs and perform reaction dynamics studies for key elementary reactions (e.g., simple bond fission to produce radicals).
- Perform Monte Carlo variational transition-state theory (MCVTST) calculations of rates.
- Compute tunneling rates if appropriate.

Overview of Methods

It is often necessary or desirable to use classical methods for the problems involving a large number of atoms. However, there are limitations to their applicability - due to the breakdown of the classical approximation or the practical problem of performing the calculations for long-time (rare event) processes. Thus, other methods are needed when MD is not valid or feasible. We have developed practical, accurate TST methods for calculating rates in the statistical regimes where it is usually not feasible to integrate the classical equations for sufficiently long times to obtain reaction rates. This approach, MCVTST, can be used to efficiently calculate rates using realistic potentials and for energies near reaction thresholds. MCVTST provides an advantage over standard VTST methods in that it can employ exactly the same PES as used in MD. This allows it to be used in the development of the atomic-level models and to obtain results that are directly comparable to MD results for the PES. Also, we have recently developed another very useful approach that can be used to calculate rates in the non-statistical (IVR-limited) regime where classical trajectory calculations are often not feasible. In the *intramolecular dynamics diffusion theory* (IDDT) method, the rates of energy transfer calculated from very short-time (on the order of a few fs) trajectories are used in a diffusion theory formalism to predict the dynamical rates for reactions. We have also shown that the dynamical parameter in IDDT can be determined from the rate at a single energy. The rates involved in materials aging are expected to be statistical, and thus IDDT would only be useful in extrapolating dynamics results to lower energies and temperatures. We have also developed methods for using semiclassical approximations for treating quantum effects (tunneling and curve crossings) in multidimensional systems. The basic idea in this approach is to incorporate quantum mechanical effects in standard MD simulations; thus multidimensional effects are included. One of the motivations of this work is to develop methods for introducing quantum effects in MD generally, tunneling being a convenient process for testing the methods against experimental data. The formulation of accurate models is a crucial part of this work since the main goal is realistic simulations to predict properties and rates for large, complex systems. We have investigated various functional forms and methods for fitting empirical and *ab initio* data, and studied the sensitivity of results to the details of potentials.

The combination of these methods provides the means to accurately calculate both slow and fast rates of complex processes in large systems, and to study the mechanistic details of how they occur. This would require some modifications and refinements for the problems of interest here, and in some cases the methods developed by others might be more useful. The practical problems in materials aging are considerably more complicated than those we have attacked in the past; however, the methods and approaches we have developed could be extended to treat some of them. However, the fundamental problems of interest in aging are the kinds that are at the core

of our work. As in our work on energetic materials, our methods could be used to explore the underlying fundamental dynamical behavior of the systems as well as to simulate some of the complex aging processes with realistic models.

Controlling activated transitions: theory and experiment

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In the presentation, we will briefly review recent theoretical and experimental results on the consequences of ac fields on the motion of particles trapped in double, or multiple, potential wells, and discuss prospective ways of controlling this motion [1]-[8]. A quantum particle can tunnel between the wells, whereas a classical particle, in the presence of thermal fluctuations, will experience activated overbarrier transitions from one well to another. Response of both quantum and classical multistable systems to an alternating field may display dramatically strong nonlinearity, even for comparatively weak fields. We have been investigating this response over a broad spectral range, from frequencies of order of interstate transition rates up to the characteristic intrawell frequencies of the trapped particle. The effect of a high-frequency field on the rates of activated transitions is most counterintuitive, as one would expect that the field would just average out, whereas in fact it is in this range that the most striking control over particulate motion can be exercised. We have predicted and demonstrated that, by judicious choice of the field characteristics, the diffusion of the particles in a multiwell periodic potential can be directed. Both the direction of the flux and its strength are exponentially sensitive to the parameters of the field.

These ideas, although fundamental, can have practical consequences in several areas of applied science and technology. One of the most significant may occur in control of nonequilibrium crystal growth, where surface diffusion plays a crucial role. The degradation of materials brought about by defect and impurity migration in the presence of oscillating fields, is another. Also, chemical and biological separation, an area of immense growth, depend on discriminating among species diffusing in strong fields and field gradients.

The theoretical approach is based on the idea that, although large fluctuations are infrequent and happen at random, the motion of a system in a large fluctuation is in some sense deterministic. On its way from a metastable state to a given state q_f, the system is exponentially more probable to move along a certain optimal path than along any other trajectory. Following our earlier suggestion [9], such optimal paths have been recently directly observed in the experiment [7], by investigating the distribution of fluctuational paths to a state q_f (the prehistory probability distribution), see Fig. 1. The peak of the distribution gives the optimal path.

Even a small control field may produce an exponentially strong influence upon fluctuations if it affects the motion along the optimal path. The key idea here is that the field can **synchronize** fluctuations which would

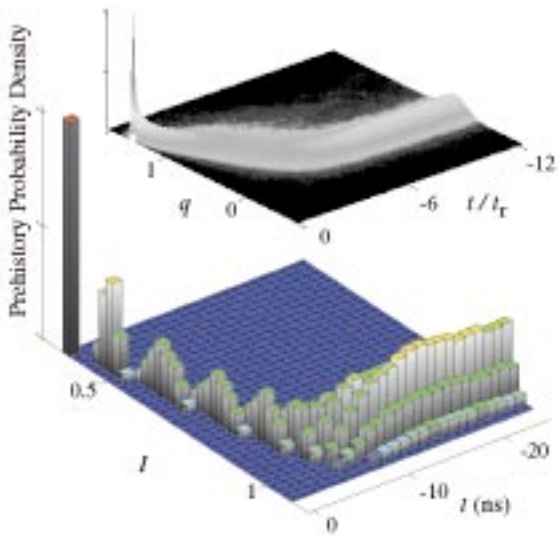

Figure 1. The prehistory probability distribution (PPD) of the scaled radiation intensity I for experimentally observed dropout events in a semiconductor laser [7]. Inset: the PPD obtained by simulating the motion of an overdamped Brownian particle in a potential $U(q) = \frac{1}{2}q^2 - \frac{1}{3}q^3$ for the ratio of the barrier height to the noise intensity $\Delta U/D = 10$, for particles that arrive at a point $q_f = 1.2$ behind the barrier.

otherwise occur at any time. Furthermore, the work done by the field on the system as it moves along the optimal path changes the activation barrier. As a result, the fluctuation probability is exponentially sensitive to the amplitude and frequency spectrum of the field.

In a broad parameter range, the probability of activated escape in a driven system can be found in a closed form, including both the exponent and the prefactor [3]. The results are illustrated in Fig. 2.

To test these ideas experimentally we used an archetypal system, a mesoscopic particle suspended in a liquid and confined within a potential with metastable minima. The potential is made with strongly focused laser beams which create an optical gradient trap, i.e. "optical tweezers", as shown in Fig. 3. Because of thermal fluctuations in the liquid, the particle does not stay at the potential minima located close to the waists of the beams, but fluctuates about these minima and occasionally makes transitions between them. We could restore experimentally, with high precision, the self-consistent confining potential of a particle. This enabled us to provide the first direct quantitative test of the classical theory of escape rates [4].

We could modulate the confining potential by modulating the intensity of one of the beams. The results of such modulation are shown in Fig. 4 [5].

The most interesting situation, from the point of view of numerous applications in material science, is the one where the double-well potential is symmetric in the absence of modulation. In this case one can obtain the effect of **dynamic localization**: by applying a zero-mean non-sinusoidal driving, one can by choice localize the particle in one of the two equivalent wells [8]. We have demonstrated that the localization occurs not only for a slow modulation, as in Fig. 4, but also for a high-frequency modulation. In this latter

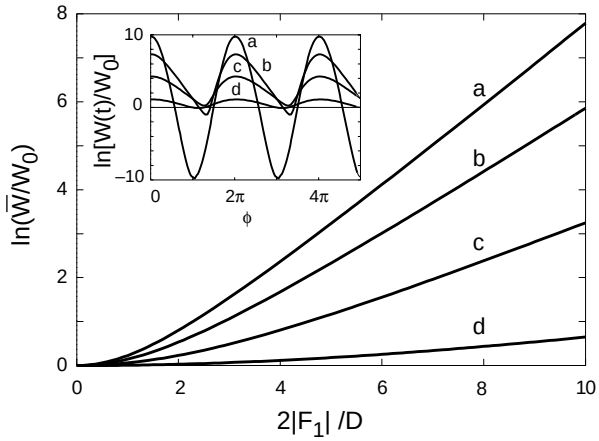

Figure 2. The logarithm of the time-average rate of activated escape $\bar{W}$ as a function of the scaled amplitude $2|F_1|/D$ of the driving field $F(t) = 2\mathrm{Re}\,[F_1 \exp(i\omega_F t)]$ for an overdamped Brownian particle in a potential $U(q) = \frac{1}{2}q^2 - \frac{1}{3}q^3$ (D is the noise intensity) [3]. The curves a to d refer to the dimensionless field frequency $\omega_F = 0.1; 0.4; 0.7; 1.2$. Inset: time dependence of the logarithm of the instantaneous escape rate for the same frequencies and $2|F_1|/D = 10$ ($\phi = \omega_F t$), illustrating loss of synchronization of escape events with increasing ω_F.

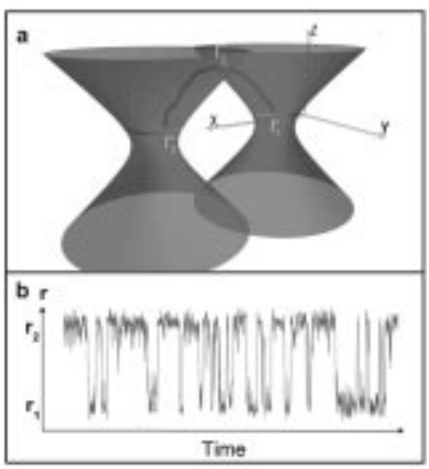

Figure 3. (a) Rendering of two focused laser beams, the equilibrium positions of the particle (rings), and a transitional path between the beams. (b) The coordinate of a particle that switches at random between the equilibrium positions $\mathbf{r}_1$ and $\mathbf{r}_2$ [4].

case, a change of populations > 20% was achieved experimentally for a small-amplitude biharmonic modulation (cf. Fig. 4) which, according to the "standard" theory, should give a population change < 0:5%.

In the case of a system fluctuating in a periodic potential, the same modulation will give rise to directed diffusion. It is remarkable that, as follows from the theoretical analysis [10] and the experimental data, the diffusion direction is controlled just by the phase shift between the harmonics of the ac force.

The results of this research suggest that ac forces can be used for a highly effective control of activated processes, including switching from a metastable state, diffusion, and nucleation. In contrast to other techniques, external energy is used only to direct fluctuations, the actual work is done by the fluctuations themselves. This is a new type of control that may lead to significant technological advances. We have demonstrated that its implementation does not require a priori knowledge of the system dynamics.

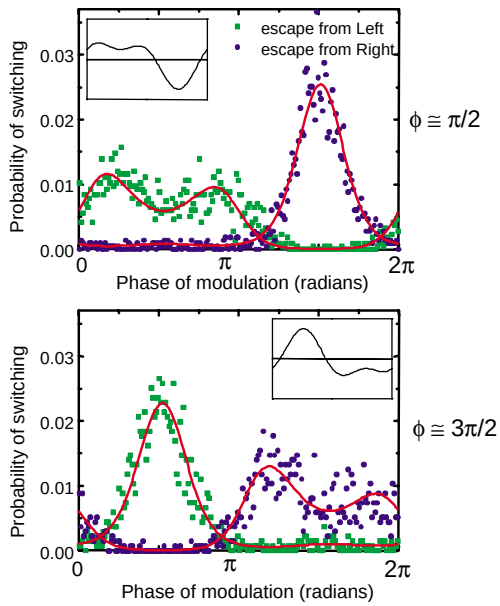

Figure 4. Plots of the time-dependent switching probabilities out of a symmetrical double-well potential over a cycle $\omega_F t$ of the modulating waveform $F(t) = 2F_1 \cos \omega_F t + 2F_2 \cos(2\omega_F t + \phi)$ for $F_2 = F_1 = 2$. The data refer to the modulation frequency ω_F small compared to the intrawell relaxation rate. The upper and lower panels show the role of the phase angle ϕ between the components in controlling the transition rates. Solid lines show the theoretical results. Insets show the instantaneous di er ence between the heights of the potential barriers in the two wells.

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Aging of materials

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Introduction

Aging is usually viewed in terms of a slow and steady degradation of a useful material property as the result of an external factor such as chemical reaction, drying, accumulation of defects created by absorption of light or ionizing radiation, or mechanical fatigue. However so-called "physical aging" will occur without any external factor whatever. Disordered systems such as supercooled liquids (glasses and glassy polymers), compacted granular media, biological materials, etc., are characterized by continuously evolving structures. Structural evolution, according to Stillinger, is viewed as the system wandering around a complicated "energy landscape" (see Fig. 1), and it can have a large effect on material properties. A knowledge of aging behavior is needed for the prediction of the long-time behavior from the short time behavior. For instance I am always being told the mean-time-to-failure of the diode lasers I buy is 96,000 hrs. However that's ten years *on the average*. Some lasers must be lasting 20 or 30 years. Those lasers have only been around for a few years, so how do they know that? They use torture tests conducted in an oven at elevated temperatures and some Arrhenius model to extrapolate back to ambient temperature. Ridiculous.

I would like to distinguish between four types of slow processes. (1) Systems *with extremely high barriers*. For example it takes 4 billion years for an α-particle to tunnel out from a ^{238}U nucleus. These are simply elementary processes and need no fancy theoretical treatment. However in cases such as radiation damage, they might be the ultimate source of some more complicated aging processes. (2) Physical aging with *spontaneous structural evolution*. An amorphous material is quenched at temperature T ages for a time t_w. That means it is temporarily stuck at some point on the energy landscape well above the global minimum (Fig. 1). As the system evolves along the landscape toward the global minimum, it spontaneously produces entropy and "ages". During physical aging, the physical properties evolve in

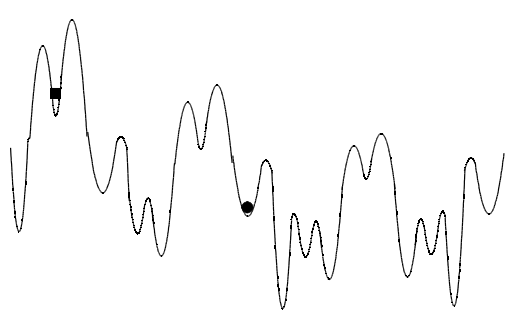

Figure 1. Part of the energy landscape of a supercooled liquid. The circle refers to a system prepared by cooling to Tg after a time tw. The square is obtained by using a laser-driven shock on the circle system.

time. (3) *Physical aging induced by external perturbations*. A material expands and contracts as it heated and cooled by sunrise and sunset. It is a part in a strained mechanical assembly. It is surrounded by an oxidizing medium. It is banged around by rough handling. This is viewed as motion along an energy landscape *away from the global minimum*, accompanied by an increase in the system's entropy. The physical properties evolve in time. (4) *Fluctuating barriers*. Structural evolution causes the barrier heights associated with various mechanical and chemical processes to fluctuate in time. Aging processes are elementary barrier-crossing events, but they occur when the barriers happen to be lower rather than higher.

Of the four processes mentioned above, (1) is theoretically trivial; (2) is a timely topic in physics that has received much attention but is far from solved; (3) has been treated to a limited extent in the context of *weak perturbations*, and (4) has hardly been discussed in the context of aging, although it is an important current topic in biomolecular dynamics and single-molecule spectroscopy.

In recent experimental work, most attention has been paid to physical aging. For example a glass is prepared by quenching at temperature T. As it moves toward the global minimum, the fraction of crystalline character increases with time, causing the viscosity to increase and the elasticity to decrease. These properties can be measured by many methods including acoustic attenuation or by the dielectric constant. Viscosity or elasticity can be measured as a function of quenching rate, waiting time t_w, etc. Many interesting results have been obtained. For instance, believing that going over high barriers causes aging suggests that slowly quenching the glass (spending a lot of time at high temperature) will result in an "older" glass. Interestingly, it turns out that is exactly wrong for spin-glasses. Temperature cycling experiment might be expected to "rejuvenate" old glasses but that does not always happen. Systems that would otherwise age have been kept in a stationary yet far from equilibrium regime of "youth" by external perturbations. Other intriguing results are the spontaneous development of shear bands in granular media and the development of grain boundaries in systems with defects.

Problems

There are three problems I have considered: (1) fluctuation dissipation theorem; (2) energy landscape; (3) large amplitude perturbations

Fluctuation-dissipation theorem. The fluctuation-dissipation theorem states that the return to equilibrium is governed by the same laws as the regression of spontaneous fluctuations. For a dynamical variable R, both are governed by the correlation function $<R(t)R(0)>$. In the derivation of the fluctuation-dissipation theorem, it is assumed that $<R(t+t_w)R(t_w)> = <R(t)R(0)>$. This *is not true* for an aging system. The correlation function slowly changes as t_w increases. This is fundamental to the way we measure and think about aging. We usually measure the (fast) response to a perturbation and then

see how this response evolves with t_w (or log t_w). Generalized forms of the fluctuation-dissipation theorem has been derived that have different dependences on t_w. If we know this dependence, *we can predict the aging behavior from the short time behavior*. Some progress has been made in physical aging but hardly anything is known about this problem with other kinds of aging.

Energy landscapes. The energy landscape view is the most powerful method of understanding the nonequilibrium behavior and physical properties of supercooled liquids and other disordered systems. The energy landscape $\phi(r_1,r_2,r_3,...r_n)$ describes the energy of the system as a function of many configurational coordinates r_1-r_n. The landscape (see Fig. 1) is typically very rugged with many deep basins that themselves are very rugged with shallower basins. We need better ways of understanding the energy landscape in aging materials. Suppose I have some aging polymer that is developing cross-links and losing elasticity. I can take two approaches. Either I can say the *energy landscape is changing with time* as cross-linking increases, or I can say there is a *super energy landscape* with one coordinate that represents the fraction of cross linking. When this coordinate is zero, I see the energy landscape for non cross-linked polymer. When it is unity, I see the landscape for fully cross-linked polymer. This latter grand view is nicer, but in either case we need quantitative measures of *how the energy landscape changes as a material undergoes complicated aging processes*.

Large amplitude perturbations. In the physical aging literature, there are several assertions to the effect that large amplitude perturbations destroy the aging effect. For instance if we heat a glass far above Tg, it becomes 'rejuvenated". Similar effects have been observed for "large" magnetic fields, large AC electromagnetic fields, etc. Something seems fundamentally wrong with this. It is not "large" perturbations that are destroying the aging effect, it is "moderate" perturbations. A "large" perturbation is where I smash a material with a big hammer or shock wave or cook it in an oven with oxygen. That definitely does not destroy the aging effect! For practical problems, more attention needs to be paid to how large amplitude perturbations (the "slings and arrows of outrageous fate") affect aging.

Proposed experiments

Here are two types of novel experiments which are directed toward finding out how the energy landscape changes with time, and how changes in the landscape cause barriers to chemical reactions to fluctuate. Optical hole-burning (or its time domain equivalent stimulated echo spectroscopy) is a powerful tool for understanding the energy landscape. Ligand rebinding after flash photolysis is a powerful tool for understanding chemical reactivity on energy landscapes. Ordinarily aging studies would involve using these probes to understand the effects of thermal history. A unique new idea that originates from our work with laser-driven shock waves is to combine these probes with shock compression.

Referring to Fig. 1 once again, temperature studies refer to motion along the landscape. In Fig. 1, the state of the system is denoted by the circle. The location of the system is determined by the thermal history. The faster the cooling rate, in general the higher up on the landscape. The rate of moving among local minima depends on temperature through the rate of barrier crossing. We have recently shown that a short duration laser-driven shock (a "nanoshock") can produce extremely fast compression and heating effects. A polymer can be heated several hundred degrees and then cooled back to room temperature in just a few ns. That corresponds to putting the system very high on the energy landscape. Aging studies often put the sample in an oven to make aging occur faster. With nanoshocks, *we put the system much higher up on the energy landscape*, which presumably also makes aging faster. Thus *we can speed up the aging process in a new way, without using elevated temperatures*, making it more amenable to study.

In hole burning or stimulated echoes, an ensemble of chromophores is dissolved in a disordered medium. The optical spectrum is massively inhomogeneously broadened by structural disorder. A narrow band laser burns sharp holes in the absorption, thereby tagging chromophores in certain environments. As the environment ages, the hole fills in. The rate of hole filling and hole broadening can be related to structural evolution along the energy landscape. Exciting hole burning experiments have been performed, that look at structural dynamics with thermal cycling and pressure cycling. Hole burning technology, which is very well developed and which is extremely sensitive to even tiny structural changes, can be used to study accelerated aging after nanoshock, or as a result of oxidation, radiation damage, etc.

In ligand rebinding experiments, a small ligand bound to a colored molecule is dissociated with a flash of light. Weak light is used to monitor the rebinding kinetics. A common system is CO bound to iron porphyrin PFe, which has many practical advantages and has enough chemical versatility to be incorporated into almost anything. The reaction may be written:

$$\text{PFe-CO} + h\nu \rightarrow \text{PFe} + \text{CO} \rightarrow \text{PFe-CO}$$

In amorphous materials, ligand rebinding is highly nonexponential in time. It is believed that *every individual ligand sees a single barrier* and rebinds in an elementary barrier-crossing process. However the ensemble of rebinding ligands see a broad distribution of barrier heights. By mapping the nonexponential kinetics of rebinding, the distribution of barriers (enthalpic and entropic) can be measured. This has been done a lot. The new feature is to look at how this distribution of barriers changes as the sample ages, in other words how the barriers to chemical reactions change with time as aging occurs. Aging can be accomplished by many methods such as thermal cycling, pressure cycling, repeated impacts, radiation damage or slow oxidation, or with nanoshocks. The idea of this experiment is to understand at a fundamental level how the likelihood of a chemical reaction changes

with time as a result of the aging process. Of particular interest is understanding what kind of aging processes result in dramatic lowering of activation barriers.

Responses to Shaw's questions

1. MRI. MRI seems like the best possible technique to study aging. Ideally as a sample ages, one could measure the spatial distribution of different chemical species throughout the sample. In practice there are some limitations to MRI: (1) low sensitivity, (2) poor spatial resolution (~10 mm) and poor time resolution (milliseconds). The poor time resolution seems like the least important limitation. So let's discuss the issues that create problems for MRI: Things that involve a small concentration of defects, such as defect pinning of grain boundaries, or the formation of nucleation centers. Things occurring on short spatial length scales. Things that raise and lower the barriers on the energy landscape that might have practically no effect on the MRI signal. The initial stages of crack growth. Loss of elasticity.

2. Arrhenius equation. As mentioned above, aging need not involve slow processes going over very high barriers, but rather slow structural evolution that causes barrier heights to fluctuate or decline with time. Also with very high barriers, tunneling might end up being significant. A better rate equation might include a random walk or driven random walk along the energy landscape, a barrier height that depends on this random walk, a viscosity that depends on the random walk, and Arrhenius barrier crossing as well as tunneling.

3. Transition state theory: TST seems OK for aging problems. TST describes the very fast process of barrier crossing. Corrections for TST are based on problems that occur at very short times, not slow processes. I think aging is described by a slow variation in local properties such as density, viscosity, barrier heights, and so forth, but the 1 picosecond of crossing the barrier that is treated by TST is just a function of the local properties at that instant.

4. Surface probes: Not all aging takes place at surfaces. Physical aging occurs very well in an infinite sample. Even when surfaces are crucial, a lot of phenomena is occurring at buried interfaces.

METHODS FOR SLOW PROCESSES

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ABSTRACT

Methods for describing very slow processes are discussed. This document was prepared for the Army Research Office Workshop on Slow Processes at Duke University, August 9-11, 2000. The first section addresses questions suggested in preparation for the workshop. Transition state theory (TST) is proposed as the appropriate framework for describing slow (activated) processes. It offers a way to compute accurate rate constants without dynamics. Dynamical corrections are easily incorporated, if desired, to obtain classically exact rate constants. In complicated systems, there is often a problem with identifying the relevant reaction mechanisms. In these cases, newly developed acceleration methods, based on TST, offer a way to achieve much longer simulation times, so that reaction paths can be directly observed. Three such methods are described in the following sections with two brief examples of applications to metallic surface diffusion and growth. With some modifications, these methods may be powerful for the types of polymeric systems of interest in this workshop.

I. ISSUES AND INTRODUCTION

As I understand it, we are interested in infrequent-event systems, in which the relevant dynamical evolution consists of transitions from one potential basin (i. e., state) to another, with a large (perhaps extremely large) number of vibrational excursions within each basin before the next transition occurs.

Yes, I think the models and approximations we usually use should be appropriate for very slow processes. In my view, the main workhorse (unless we are interested in quantum effects such as tunneling) is transition state theory (TST). In TST, the rate constant for escape from a state along a particular pathway is given by the absolute flux through the dividing surface. This is equivalent to the exact classical rate if there are no correlations between dividing-surface crossings. Whether or not the TST-violating correlated dynamical events are important depends on the nature of the system and the level of accuracy sought. If desired, the TST rate can be corrected for these correlated dynamical events [1,2], but in the following we will usually assume that this issue is of secondary importance.

In applying TST, it should not matter whether the system spends thousands of vibrational periods or trillions of periods in a basin before it escapes. The memory of how it entered the state is lost after the first few vibrational

periods. After that, the probability of exiting along any particular pathway is a purely statistical property of the system.

In fact, the TST approximation, that transitions are uncorrelated, may be even better satisfied for very slow systems, but is at least unlikely to be worse.

The Arrhenius approximation: This form emerges automatically when the TST rate is evaluated within the harmonic approximation. The activation energy is then simply the energy difference between the saddle point and the minimum, and the preexponential factor (from Vineyard theory [3]), is the product of all the $3N$ normal mode frequencies at the minimum divided by the product of the $N-1$ nonimaginary normal mode frequencies at the saddle point. For the metal systems we have typically focused on, this is a good approximation for most rates up to about half the melting point. (Occasionally the Vineyard prefactor is artifically high, an effect we are investigating.) Above this temperature the anharmonic effects can become more pronounced, causing the true rate to be either higher or lower than the Arrhenius (harmonic TST) prediction from the Vineyard theory. For a process that is particularly slow due to the energy barrier being high relative to k_BT, I see no reason why the rate is more likely to deviate from Arrhenius behavior.

On the other hand, deviations from Arrhenius behavior will result from a process that is not an elementary basin-to-basin transition, but rather is made up of a combination or sequence of transitions with differing barrier heights. Thus, we may need to be clear about how the quantity we are measuring relates to the underlying atomistic processes.

So, given a reaction mechanism, we can apply the TST approach, either in harmonic form or exactly (e. g., using Monte Carlo [2,4]), to compute a rate constant. This rate constant may correspond to a time between reactive events (i. e., the inverse of the rate constant) that is far longer than the nanoseconds accessible to molecular dynamics. In this sense, we have used TST to beat the time scale problem. However, this is not the whole story.

The more difficult part for realistic systems is determining the relevant mechanisms. This has certainly been the case for metallic systems we have studied. For example, during vapor-deposited film growth of copper, the surface diffusion events (which are important in determining the final film morphology) can be surprisingly complicated. Often they involve three or more atoms, and violate our intuition about how metal atoms will move and interact. As a result, if we try to guess in advance what diffusive events are important, we misdescribe the behavior of the surface in a qualitative way.

Recently, we have been developing methods that side-step this problem of having to guess the relevant reaction mechanisms. The basic idea is to exploit the infrequent-event nature of the dynamics in a way that shortens the required simulation time between diffusive events. Building on transition

state theory, we have now developed three methods along these lines: hyperdynamics, temperature accelerated dynamics, and parallel replica dynamics.

In the hyperdynamics method [5,6], the potential energy surface is modified with a bias potential that raises the energy within each basin, so that the trajectory spends less time near the minimum and finds an escape path sooner. The accelerated simulation time, which becomes a statistical property of the system, is estimated as the trajectory proceeds. The key to effective implementation of hyperdynamics is designing a bias potential that can sense the location of dividing surfaces based only on local properties of the potential surface.

The temperature accelerated dynamics (TAD) method [7,8] is an alternative to hyperdynamics that is in some ways simpler. It is based on the concept that events occur more frequently when the temperature is raised. The key is to filter the events (i. e., rejecting many events) in a way that gives the proper evolution of the system. We have developed an extrapolation procedure that extracts the correct transition, and the correct transition time, from the high-temperature run, thus giving the correct state-to-state dynamical evolution. Assuming a few requirements are met, TAD is easy to implement and achieves boost factors roughly comparable to hyperdynamics.

In the parallel replica method [9], the power of parallel processing is applied to extend the molecular dynamics (MD) simulation time. This is in contrast to the usual parallel MD algorithms, which extend the length scale. This approach can be used in combination with either the hyper-dynamics method [10] or with TAD. Used on its own, it even provides a correct description of the correlated dynamical events; i. e., it gives the classically exact state-to-state evolution of an infrequent-event system.

In our experience so far, which has been primarily on metal systems described with embedded atom method (EAM) interatomic potentials [11], these methods look very promising. We have achieved simulation times in the microseconds and milliseconds, and sometimes even longer. The methods work best when the lowest barriers in the system are fairly high. It remains to be seen how effectively these methods can be applied to the systems of interest in this workshop, such as solid polymers, because low barriers may be a significant problem. The remaining sections introduce each of these methods, while details can be found in the original papers.

II. TRANSITION STATE THEORY AND HYPERDYNAMICS

We seek to characterize the dynamics of a system that makes infrequent transitions from one potential basin to another. In transition state theory (TST), the rate constant for escape from one state (A) to another (B) is given by the flux through the dividing surface separating the two states. This is an equilibrium property of the system, in the following sense. We could, in

principle, run a dynamical simulation for a very long time, so that the system makes many transitions back and forth between states A and B, giving an average time spent in each state that is proportional to the partition function for that state. Analyzing this trajectory, we can count the number of forward (A to B) crossings of the dividing surface. This count, divided by the total time the trajectory resided in state A, gives the TST rate constant $k^{TST}_{A\to B}$. If the successive crossings of the dividing surface are not dynamically correlated, i. e., if many vibrational periods occur between crossings, then the TST rate constant is equivalent to the exact rate constant. However, the real beauty of TST is that $k^{TST}_{A\to B}$ can be computed without ever running a trajectory. In the canonical ensemble, $k^{TST}_{A\to B}$ is proportional to the ratio of the partition function of the dividing surface "state" to the partition function of state A. For solid state systems, TST tends to be a very good approximation to the exact rate. Even the harmonic approximation to TST [3] is reasonably accurate; this is employed below for the temperature-accelerated dynamics.

In the traditional application of TST, one must first define the dividing surface, or find the saddle point (in the case of harmonic TST), after which the rate constant is computed. However, transition state theory, and its implications for the dynamical properties of the system, are far more general. The methods described here exploit these general properties of TST to give accelerated escape from each basin without advanced knowledge of the dividing surfaces or the events that might occur.

In hyperdynamics, the dynamical simulation is run on a potential energy surface that has been modified in a specific way. A nonnegative "bias" potential $\Delta V_b(\mathbf{R})$, which is zero at all dividing surfaces and also meets a few other requirements [5], is added to the original potential. A schematic example of this type of modification is shown in Fig. 1.

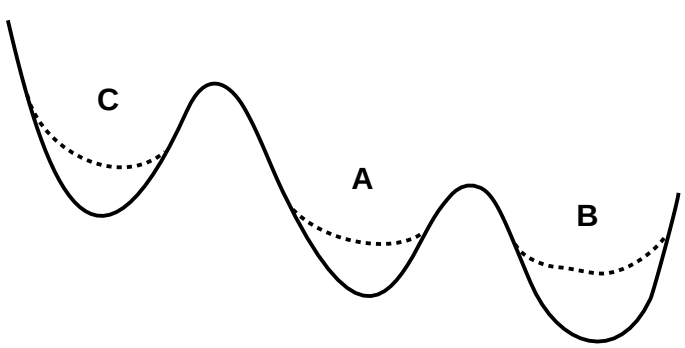

Figure 1. Illustration of the hyperdynamics method. A trajectory is evolved on the biased potential (dashed line) rather than the original potential (solid line). Relative escape probabilities are preserved because the bias potential is zero at the dividing surfaces. The accelerated time scale is calculated as the simulation proceeds.

As discussed in detail elsewhere [5], appealing to TST, one can show that the dynamical evolution on this modified potential surface has some desirable properties. First, and most obvious, is the fact that escape from each state will occur, on average, more quickly than for the regular dynamics (dynamics on the unbiased potential surface). Second, the relative escape rates to different possible adjacent states (e. g., A → B vs. A → C in Fig. 1) are exactly the same as for the original surface. This means that the system evolves from state to state in a sequence that is indistinguishable from the regular dynamics. Third, an estimate of the (accelerated) time that the system has evolved after n_{step} MD steps can be computed from

$$t_{hyper} = \sum_{i=1}^{n_{step}} \Delta t_{MD} \exp[\Delta V_b(\mathbf{R}_i) / k_B T] , \qquad (2-1)$$

where Δt_{MD} is the MD time step, $\mathbf{R}_i$ is the configuration-space position of the trajectory at the ith MD step, k_B is the Boltzmann constant, and T is the temperature. While this definition for the accelerated time (or "hypertime") is meaningless on times comparable to a vibrational period, it converges on the exact value (with vanishing relative error) at long times. It thus gives a realistic estimate, with error bars, for the time at which each transition occurs. Note that Eq. (2-1) reduces to the expression for normal MD if ΔV_b is zero everywhere.

Defining an effective bias potential is a key requirement for application of the hyperdynamics method. $\Delta V_b(\mathbf{R})$ must be zero (or nearly so, for the method to be useful) at all the dividing surfaces, even though we do not know in advance where the dividing surfaces are. As shown elsewhere [6], the distance from a position in **R**-space to a dividing surface (or a possible dividing surface) can be determined by examining the local slope and curvature properties. A suitable bias potential is created by designing a function of these properties that goes smoothly to zero as the dividing surface is approached and gives a controllable maximum value within the basin. The necessary slope and curvature quantities (based on the gradient and eigenvalues of the Hessian) are evaluated using an iterative procedure that requires only first derivatives of the potential. In this approach, the bias potential, and its derivatives, are computed using a few tens of calls to the MD force routine at each position of the hyperdynamics trajectory. This implementation of hyperdynamics requires a roughly 30 times more work per integration step than direct MD. There are also ongoing efforts to develop simpler bias potentials [12–15], that exploit locality and/ or fixed-energy bias forms.

If the average boost factor (the ratio of hypertime to MD time) is greater than this extra work factor, hyperdynamics is computationally faster than direct MD. In tests so far, mostly on metal systems using EAM interatomic potentials, boost factors from 10^0 to 10^6 have been observed [6,10]. For a given system and a fixed bias potential definition, the boost increases dramatically as the temperature is lowered, due to the exponential dependence in Eq. (2-1).

For a system at fixed temperature, the attainable boost is limited by the lowest barrier in the system. Loosely speaking, the bias potential must not raise the potential higher than this lowest barrier. For a system in which the transition pathways and barriers are unknown, one can choose a safe strength for the bias potential by using the time the simulation has progressed since the last transition to place a lower bound on the lowest barrier in the system. As the simulation proceeds, accumulating more hypertime, this estimate of the lowest barrier height can be successively increased. This, in turn, causes the hypertime to accumulate more rapidly [10]. In this approach, the bias strength must be reset to zero, or a very low value, after each transition.

III. TEMPERATURE-ACCELERATED DYNAMICS

As in hyperdynamics, the goal in temperature-accelerated dynamics (TAD) [7,8] is to stimulate rapid escape from each potential basin. In TAD, this is accomplished by raising the temperature of the system from the desired temperature (T_{low}) to some higher temperature (T_{high}). Although raising the temperature is a well-known and often-used approach for accelerating diffusive events, it does not give the correct state-to-state evolution for temperature T_{low} because the relative escape probabilities change with temperature. However, if, from among the transitions occurring rapidly at T_{high}, the correct T_{low} transitions can be selected and the others prevented, then the system will evolve from state to state appropriately for temperature T_{low}. This is the essence of TAD.

Consider a system trapped in a potential basin with n escape paths, and a rate constant, k_i, associated with each escape path. The total escape rate (k_{tot}) is given by the sum of these rates,

$$k_{tot} = \sum_{i=1}^{n} k_i \ . \qquad (3-1)$$

Because this is an infrequent-event system, escape from this basin is a first-order process. The probability distribution for the time until the first escape is thus given by the exponential distribution

$$p(t) = k_{tot} \exp(-k_{tot} t) \ . \qquad (3-2)$$

Similarly, if we consider each of the escape paths individually, the probability distribution for the time to first escape for each escape path i is given by

$$p_i(t) = k_i \exp(-k_i t) \ . \qquad (3-3)$$

In essence, the goal of any accelerated dynamics method is to answer the question: which path will the system choose to escape from the current basin, and when will that escape occur? If we have the set of rates $\{k_i\}$, one way to find the answer is to draw one random number from each of the n distributions in Eq. (3-3). Each of these numbers corresponds to the time at which that transition would first occur. We then select the lowest of these

times and the pathway to which it corresponds. The remaining times can be discarded, as the system moves to a new state at the instant of the first transition. Because we are considering an infrequent event system that obeys transition state theory, in which all memory of the previous transition is lost before the next one occurs, this is an *exact* way to determine the state-to-state dynamics. (In fact, although inefficient, this would be one way to construct a kinetic Monte Carlo algorithm.)

Now consider evolving this system using molecular dynamics. After a number of vibrational excursions (perhaps a huge number), the trajectory passes through a dividing surface, taking the system into a new state. In essence, the simulation "picks" one of the escape paths. The time of this transition can be precisely determined by dropping steepest-descent paths from successive positions along the trajectory to identify the time at which these steepest descents begin to fall into the new state instead of the old state. The key point is this: the escape path and escape time determined in this way are indistinguishable from the random-number method described in the previous paragraph. In either method the probability of choosing a particular escape path is k_i/k_{tot}. Applied repeatedly, either method yields a distribution of first passage times given by Eq. (3-2), and an average escape time of $1/k_{tot}$.

We can extend this concept by considering a "basin constrained" trajectory, in which all transitions out of the basin are blocked, e. g., by reflecting the trajectory back into the basin at the instant of each attempted escape. In a basin-constrained trajectory, the set of all escape attempts and associated times (the first escape time for each pathway) will be indistinguishable from a set of times chosen randomly from exponential distributions as described above. In this sense, a molecular dynamics simulation can be viewed as a very expensive random number generator.

We now assume that each escape rate k_i is well described using the harmonic approximation to TST [3]. The rate constant then takes on an Arrhenius form,

$$k_i = \nu_i \exp[-\Delta E_i/k_B T] \,, \qquad (3-4)$$

where ΔE_i is the energy difference between the basin minimum and the saddle point, k_B is the Boltzmann constant, and ν_i is a *temperature-independent* pre-exponential factor that depends on the vibrational spectrum at the minimum and the saddle point [3]. This is an excellent approximation for many diffusive processes in materials, although if the temperature is raised high enough, the anharmonicities cause a deviation from this ideal behavior. A consequence of Eq. (3-4) is that the ratio of rate constants at two temperatures (T_{high} and T_{low}) is given by

$$k_i(T_{high})/k_i(T_{low}) = \exp[-\Delta E_i(1/k_B T_{high} - 1/k_B T_{low})] \,, \qquad (3-5)$$

The above discussion leads us to the following key concept: the set of first-escape times $\{t_i^{high}, i = 1, 2, \ldots, n\}$, resulting from a basin-constrained

simulation at temperature T_{high}, maps onto a valid set of low-temperature first-escape times $\{t_i^{low}, i = 1, 2, \ldots, n\}$via the following transformation:

$$t_i^{low} = t_i^{high} \exp[\Delta E_i(1/k_B T_{low} - 1/k_B T_{high})] \,, \qquad (3-6)$$

In other words, by running a simulation at high temperature, we can generate a list of first-escape times for the low temperature case from Eq. (3-6) that is indistinguishable (in a probabilistic sense) from a list generated by a simulation at low temperature. No statistical test could distinguish whether the list was generated by an actual low-temperature simulation or by the transformation of a high-temperature list.

Appealing to a visual construct, an Arrhenius plot, we note that the ordinate can be thought of as either the logarithm of the rate or as the logarithm of inverse time. In the inverse-time view, the time progression of a simulation (at temperature T) corresponds to logarithmic motion *downward* along a vertical line. On such a plot, the transformation of Eq. (3-6) maps a point (a transition) on the T_{high} time line onto a point on the T_{low} time line by a simple extrapolation along a line with slope $-\Delta E_i/k_B$. Figure 2 shows an example after two attempted transitions have occurred at T_{high}.

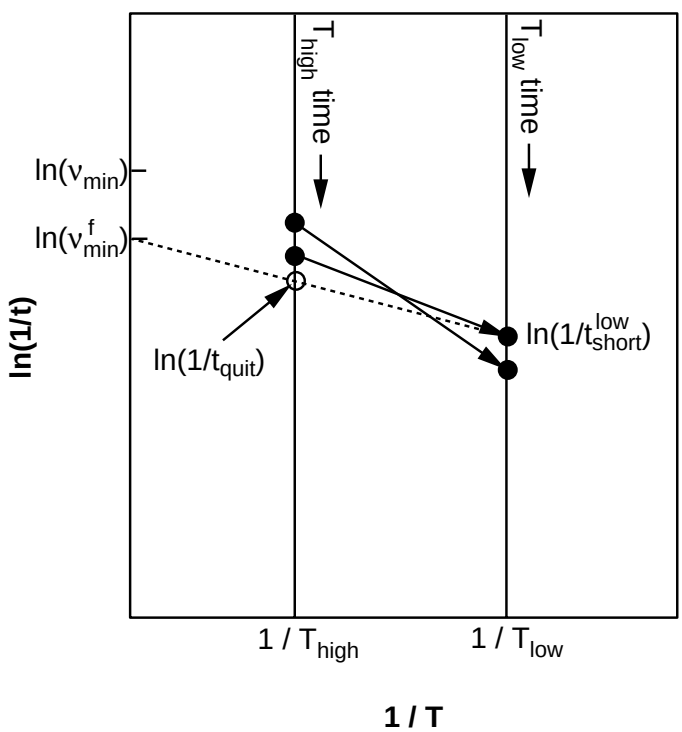

Figure 2. Schematic illustration of the temperature-accelerated dynamics method. Progress of the high-temperature trajectory can be thought of as moving down the vertical time line on the left. For each transition detected during the run, the trajectory is reflected back into the basin, the saddle point is found, and the time of the transition (solid dot on left time line) is transformed (arrow) into a time on the low-temperature time line on the right. Plotted in this Arrhenius form, this transformation is a simple extrapolation along a line whose slope is the negative of the barrier height for the event. The dashed termination line connects the shortest-time transition recorded so far on the low temperature time line (solid dot) with the confidence-modified minimum pre-exponential ($\nu_{min}^f = \nu_{min}/\ln(1/(1-f))$) on the y axis. The intersection of this line with the high-T time line gives the time (t_{quit}) at which the trajectory can be terminated. With confidence f, we can say that any transition observed after t_{quit} could only extrapolate to a shorter time on the low-T time line if it had a pre-exponential lower than ν_{min}.

The last step in designing the method is determining when we can stop the high temperature, basin-constrained trajectory and accept the shortest-time transition at the low temperature. To accomplish this we make one additional approximation: we assume that there is a minimum value for the prefactor, ν_{min}, which is a lower bound on all the prefactors in the system. For metal systems, $5\text{x}10^{11}$ s^{-1} is a reasonable choice. It is then easy to show that we can stop the trajectory at a time

$$t_{quit} = \frac{1}{\nu^f_{min}} \left(t^{low}_{short} \nu^f_{min} \right)^{T_{low}/T_{high}} , \tag{3–7}$$

knowing that, to a desired confidence level f (e. g., f=0.99), no later transition we would observe by continuing the trajectory would change the first transition at low temperature. Here ν^f_{min} is a "confidence-modified" preexponential factor,

$$\nu^f_{min} = \nu_{min} / \ln(1/(1-f)) . \tag{3–8}$$

This quitting time can also be determined graphically, as shown in Fig. 2. Note that in the limit as T_{high} approaches T_{low}, Eq. (3-6) reduces to t_{quit} = t^{low}_{short}, which is identical to direct molecular dynamics – every transition is immediately accepted. Thus, the TAD approach is completely compatible with direct MD, in the sense that the high temperature, basin-constrained sampling can be turned on and off at any time (with a suitable warming or cooling period) without corrupting the state-to-state dynamics.

Inspection of Eq. (3-6) shows that low barriers limit the available boost in this method, a problem also seen in hyperdynamics. In TAD, it results from the fact that t_{low}/t_{high} depends exponentially on the barrier height. This problem can be reduced in TAD by applying a special treatment ("synthetic mode" [8]) to transitions that have occurred many times. This modification still gives the correct dynamics (to the extent that the basic approximations in TAD are valid), but reduces the time wasted on these fast transitions.

IV. PARALLEL REPLICA DYNAMICS

In parallel replica dynamics, we appeal to the first-order nature of infrequent-event dynamics to develop a parallel method [9] for extending the time scale. In this approach, a replica of the entire system is placed on each processor, and each trajectory is evolved independently until a transition occurs. This is in contrast to the usual parallel implementation in large-scale MD programs, in which the system is spatially divided over a grid of processors.

For an M-processor computer, the method works as follows: On each processor, an independent trajectory for the entire system is propagated. The trajectories are made independent by performing repeated, random Maxwellian momentum assignments during an initial period of time. This de-phasing stage takes about 1 ps for metals. On each processor, constant

monitoring is performed to detect any transition. This is achieved by simply interrupting the trajectory every few ps to follow a steepest descent path to the minimum of the current potential basin. The geometry thus obtained will abruptly change if a transition has occurred since the last check. When a transition to a new basin is detected (on processor i, say), the other processors are stopped, and the master simulation clock is advanced by the sum of the trajectory times accumulated on all the processors up to the time of the transition. The trajectory on processor i is then continued for a short time (a picosecond or two) to allow completion of correlated dynamical events. This additional correlation time is added to the simulation clock, and the procedure is repeated by replicating the new geometry of processor i onto all M processors.

As shown elsewhere [9], this method gives the correct probability distribution for the time between escapes, and preserves the relative probabilities of the different possible escape paths. The state-to-state dynamical evolution is thus exact, and proceeds nearly M times faster than a single-processor trajectory, provided the average time between transitions is much longer than time for the dephasing stage or the time required to evolve the correlated events on one processor. Communication time is typically insignificant, although it could become important in implementations on hundreds of processors.

Combining this approach with the hyperdynamics method gives a total boost (the increase in simulation time per wall-clock time) that is the product of the hyperdynamics boost with the parallel boost. Simulations on hundreds of processors have been performed in this fashion, achieving millisecond time scales [10]. More recent results have employed over a thousand processors. Soon we will be testing an implementation of TAD with parallel replica.

V. EXAMPLE CALCULATIONS

Here I briefly describe two example calculations performed using these new acceleration methods. Figure 3 shows a simulation performed with TAD [8] using a couple of weeks of processor time on a single workstation. On a Cu(111) surface with periodic boundary conditions transverse to the surface normal, 1/4 monolayer of Cu adatoms were placed at random positions. Atomic interactions were described with an EAM potential. At first we used normal molecular dynamics, because free adatom diffusion has a very low barrier (~ 0.05 eV). After all the adatoms formed into clusters, TAD was turned on, using $\nu_{min} = 5 \times 10^{11}\text{s}^{-1}$ and $f = 0.99$. T_{high} was adjusted automatically to give about six for the ratio of the lowest barrier to k_BT.

The clusters diffused and rearranged via concerted mechanisms, and the coalescence led to higher barriers and hence larger boosts. The overall boost factor was 2.4×10^9; A total of 2793 transitions occurred and 48 different states were visited; the vast majority of the transitions occurred in the special synthetic mode. The boost in TAD depends strongly on temperature.

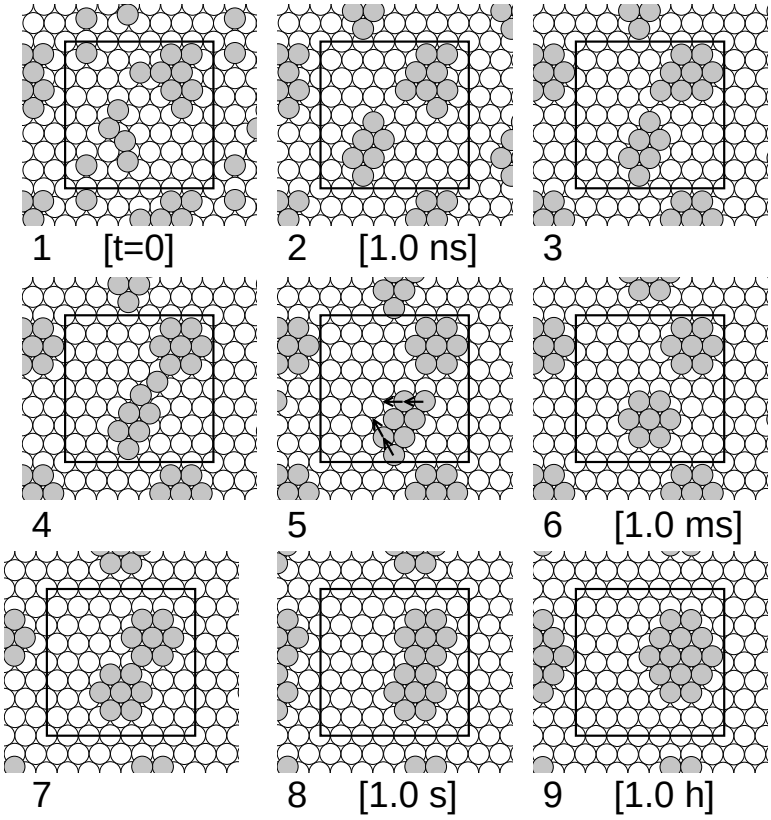

Figure 3. Selected snapshots illustrating the structure of 1/4 monolayer of Cu on Cu(111) at different times during a TAD simulation at 150 K. The frame indicates the size of the simulation cell. Between pictures 5 and 6, two dimer shears have taken place (shown by arrows). Between pictures 6 and 7, the upper island has glided twice.

At 300 K, starting from the same configuration as above, a compact 14-atom cluster was formed after only 50 μs, giving an average computational boost of 260.

Figure 4 shows the simulation of vapor-deposited films of Cu on Cu(100) [16]. These were per-formed using hyperdynamics combined with parallel-replica dynamics, as described in the figure caption. The simulation at the slowest deposition rate took 24 hours on 1000 processors.

ACKNOWLEDGMENTS

Collaborations with Tim Germann and Mads SΔrensen are gratefully acknowledged. This work was supported by the United States Department of Energy, Office of Basic Energy Sciences, and by a CRADA with Intel Corporation. The Cu/Cu(100) growth simulations were performed on the massively parallel ASCI-Red computer at Sandia National Laboratory.

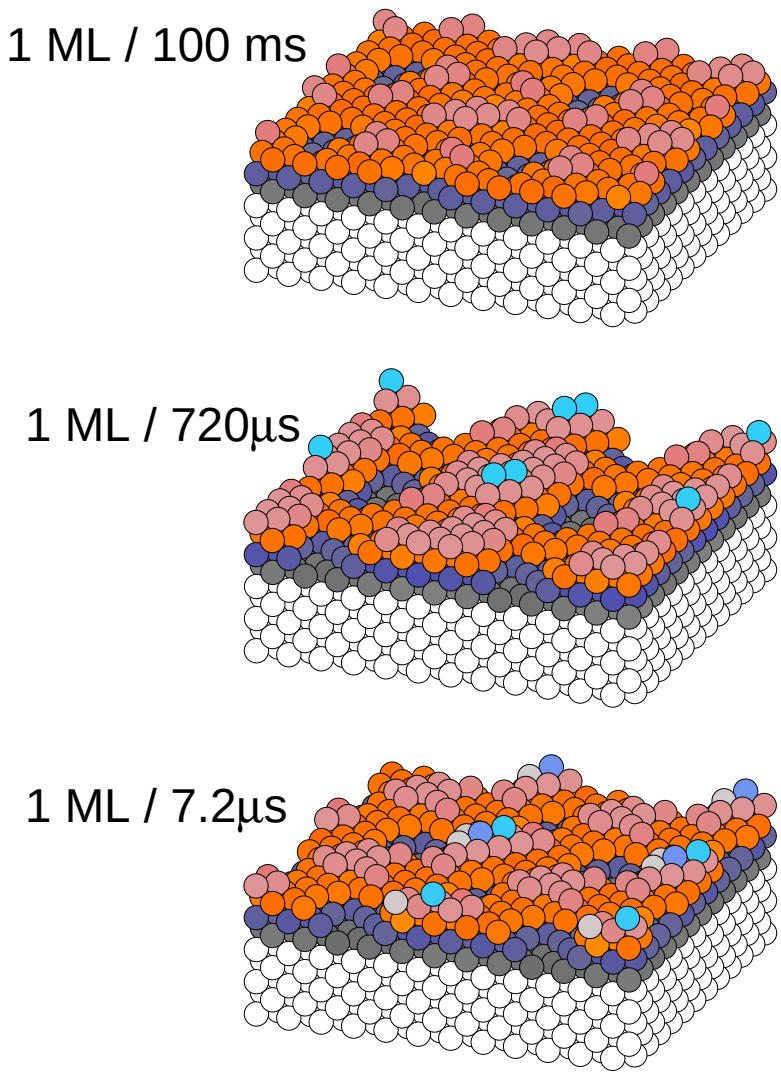

Figure 4. Simulations of vapor-deposited Cu growth on Cu(100) performed using hyperdynamics combined with parallel replica dynamics. The deposition of each new adatom was performed using regular molecular dynamics, after which the accelerated dynamics was used to traverse the long time until the next deposition. The periodic simulation cell had 72 atoms per layer; four cells are displayed for clarity. Snapshots after deposition of three monolayers (ML) are shown for three different deposition rates. Even the fastest (bottom) is too slow to be achieved with regular molecular dynamics. The slowest (top) deposition rate (10 ML/s) is typical for fast deposition of a copper seed layer using a plasma reactor during semiconductor processing.

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SOME REMARKS ON "SLOW CHEMISTRY"

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Preliminary Considerations

The following are some comments based on the directions for the meeting. It will be assumed that the types of substance of interest are energetic materials and plastics under ambient conditions and that the chief properties of interest are the changes in sensitivity for the former and macroscopic property changes brought about by auto-oxidation for the latter. We assume that the aim of this program is to obtain sufficient fundamental information regarding the possible chemical transformation of these materials so that "slow" changes can be quantitatively predicted from their physical and chemical properties.

With the focus on materials under ambient conditions the reaction media will probably be in the solid state. Practically all our fundamental understanding of chemical reactivity deal with molecules in isolation and semi-isolation and with very little constraints on their motion. The effect of cooperative effects on chemical reactivity is a true research frontier.

The time scales have been defined in terms of 10^6 to 10^9s or 10 days to 30 years. Since for any rate process, time can be traded off against extent of reaction. Thus for a reaction time of 1 second one would need the detection capability of ppm to ppb in the products. These detection limits are well within the capability of modern analytical instrumentation for of stable species. For reaction intermediates on surfaces and in the bulk their shorter lifetimes may require higher sensitivity if real time determinations are to be made.

Reaction Mechanisms

The quantitative description of any process involving chemical transformations must begin with the specification of the reaction mechanism. For simple systems this is never a problem. The mechanism for the decomposition of hydrogen molecules in the gas phase can only involve hydrogen atom production. This is never the case for complex organic molecules. For the subjects of present interest, there is much uncertainty in the mechanism of decomposition of energetic materials. The general directions for the oxidative decomposition of many plastics are known on a qualitative basis. Much of this has been based on extensive past work where the reactions are in the liquid or gas phase. The fact that the general mechanism appears to be unchanged in going over to the solid state and to lower temperatures is extremely encouraging.

The key test for the validity of any mechanism is the proper accounting of all the products detected during the course of a series of experiments over as wide a range of conditions as possible. This includes not only temperature and pressure but also the effect of species concentrations. The ideal situation will involve detection of all products and intermediates. This is not practicable especially with respect to intermediates. Thus one usually postulates a mechanism of the basis of the more easily detectable compounds and then use the yields of the intermediates to test, confirm and fine tune the mechanism. In the course of this work where one seeks to match laboratory and pilot scale data one will have developed the input data (rate expressions for kinetic processes) necessary for simulations in the global sense. Such work is aided by our increased knowledge relating ranges of acceptable rate parameters and that the rate expressions for the same or similar reactions have been determined in other contexts.

In the case of energetic materials, for all except the simplest of compounds there is no certainty regarding the low or for that matter the high temperature decomposition mechanism. The special molecular groupings characteristic of energetic materials means that there is a much smaller data base of results on related compounds. Thus estimates are less reliable. Some data are beginning to appear. The coupling of mass spectrometers to decomposing energetic materials has given some indication of the nature of the products. Unfortunately, all the data are at higher than ambient temperatures and in the gas phase. The results of Behrens and coworkers [1] may in fact be the only ones that may have pertinence to the present application. They represent the intermediate regime between fast and slow region. It is clear that the products observed by them are the results of complex rearrangements. Their labeling experiments must be considered the first step on the development of decomposition mechanisms. Furthermore, temperature dependencies have not yet been determined, thus it is not possible to extrapolate the results to lower temperatures. An additional complication is whether the highly polar media has any effects on the direction of the decomposition reactions. One would like to clearly distinguish between gas and condensed phase processes.

For the auto-oxidation of standard plastics, there is an enormous amount of data[2]. Many of the standard analytical tools have been employed. Results have been obtained under ambient conditions and for very long times. The principal slow decomposition mode has been described in terms of peroxy radicals and hydroperoxides and the step wise decomposition of the organics going to unsaturates and carbonyl compounds. A very encouraging factor has been the correspondence between what has been observed in solids and films and predictions derived from studies in homogeneous media in the gas and liquid phases. Apparently there is no startlingly new chemistry. It would appear that for energetic materials, the use of tools and methodology applied to the analysis of the stability and degradation of plastics can yield rich dividends and begin to lay the foundation of fundamental knowledge that is essential for understanding.

MODEL DEVELOPMENT

With the type of information that can now be obtained on the auto-oxidation of e plastics, one can build an essentially empirical or semi-empirical model so as to expand the results to a wider range of conditions. It is suspected that this is what is being done. Nevertheless advances in simulation technology can now lead to models that have more direct connections between fundamental microscopic inputs and macroscopic results. Such models have of course a greater range of predictive capabilities. It is suspected that their absence is indicative of the pressing needs for short term practical solutions and the lack of direct input data. It has been noted earlier that most of the data used in describing auto-oxidation processes are based on results from homogeneous systems. A key and extremely important issue is how such data can be quantitatively carried over to solids where molecular motion is constrained. In this regard it is interesting that gas phase kinetic data are relatively unaffected when transferred to non-polar liquid media after account is taken of the limited mobility of the molecular fragments (cage effects).

In the past, the capability for properly modeling the type of process of interest was limited. In recent years there has been much work on modeling gas surface processes such as etching and diamond growth. There is SURFACE CHEMKIN[3] and calculations have been carried out with kinetic Monte Carlo procedure[4]. It would appear that these techniques, particularly the latter can be readily adapted to model chemical transformations in the organic materials of interest. Although the ultimate aim of the models is to make predictions for macroscopic properties, they can also serve the very important role of identifying the controlling reactions for a particular process. In the case of auto-oxidation it must first involve the relative importance of physical (diffusion of oxygen) as opposed to chemical processes.

In the case of energetic materials models of the high temperature decomposition or flame chemistry processes exist. However for the low temperature processes of interest, there is uncertainty regarding species and reaction pathways Thus any modeling efforts would be extremely speculative.

RESEARCH DIRECTIONS

Based on the earlier discussion it is clear that understanding of the slow chemistry for the auto-oxidation of plastics is far in advance of that for energetic material. For the former there is the need to establish reaction mechanisms. Specifically, the chain of reactions which lead ultimately to a particularly undesirable property. In the case of energetic materials we presume it is its increasing sensitivity. For the auto-oxidative properties of plastic it is the use of the large array of existing or tools to be developed to supplement the extensive experimental results in terms of truly fundamental chemical and physical interactions.

The major technical challenge is undoubtedly in the area of energetic materials. Nevertheless the extensive tools and procedures developed in the course of studies on the durability of plastics should prove to be a very satisfactory starting point. A great deal of the work must be on the energetic material in the bulk, perhaps in the form of thin films. Thus methodology for following reaction processes under such conditions must be developed. This must be in parallel with by studies of the individual molecules by themselves or in the bulk. A key uncertainty will be the degree to which the very polar media characteristic of the energetic material may change the nature of the reactions. It is suspected that a major problem is such studies will be the identification of the possible new products and reaction intermediates. Finally we note that a whole host of new surface techniques has been developed in the context of micro-electronics. A close look at the applicability of these techniques for the present application will be worthwhile.

POSSIBLE NIST CONTRIBUTIONS

The following represent some possible contributions from the research groups at NIST.

(a) Determination of the mechanism and rates of reactions of complex organic molecules.

We have considerable experience in this area [5,6]. This is particularly important for studying energetic materials. It will involve a variety of studies where the reaction media is changed from very dilute and to highly concentrated. At the same time attempts will be made to accelerate the process through the addition of likely products. A very likely candidate will be nitrogen dioxide. It will be extremely interesting to observe effects arising from its presence in large quantities. Every effort will be made to detect all stable products. GC-MS and HPLC-MS will be used. Probably the most challenging problem will be the identification of products.

(b) NIST has long developed data base for modeling the transformation of organic compounds in homogeneous mixtures[7]. We have applied these to the simulation of combustion related phenomena. We have noted that the available observations on the auto-oxidation of plastics are in qualitative agreement with mechanistic results from homogeneous systems. It would be extremely interesting to develop a complete quantitative model for a selected plastic involving gas, surface and bulk phenomena building on our knowledge of homogeneous chemistry. For this purpose we will collaborate with Prof. Frenklach in the application of the kinetic monte carlo procedure which he has successfully employed in defining many of the properties of diamond growth and other surface phenomena.

(c) NIST has recently developed an exceedingly sensitive technique based on cavity ring down spectroscopy and the evanescent wave from a

total reflection minicavity[8]. The consequence is the capability of determining fractional monolayers on surfaces. This may have the capability of determining initial decomposition processes under ambient conditions. Here again, one would like to apply it auto-oxidation processes before its use in determine energetic material degradation.

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OBSERVATION OF THE FIRST KINETIC STEPS IN THE ACTIVATION OF MOLECULES ADSORBED ON SURFACES

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Understanding of the slow kinetic processes which result in the degradation of materials depends upon the separation of the elementary kinetic steps from each other so that they may be individually studied. The adsorption and activated decomposition of molecules on surfaces represents one example where sequential elementary steps are present. Modern experimental methods are now able to separate and study the elementary surface processes which constitute the sequence of chemical changes, and this talk will illustrate these methods and results.

Adsorption on surfaces may be divided into two types- physical adsorption where only van der Waals forces are dominant in the molecule-surface interaction, and chemisorption, where electron exchange and bond rerrangement occurs as the chemisorbed species becomes chemically bound to the surface. It is now well accepted that many chemisorption processes occur via the formation of a physically-adsorbed mobile precursor molecule. This weakly-bound species often exhibits large lateral motion as it moves across the surface seeking a site where chemisorption will occur. By working at low temperatures, the kinetics of the adsorption of the mobile precursor species may be manipulated such that the rate of chemisorption is optimized, and kinetic studies of this phenomenon will be illustrated by studies of acetylene chemisorption on Si(100).

The mobile precursor, a transient and weakly-bound species may, in favorable cases, be trapped at very low surface temperatures, and its structure and kinetic behavior may be observed. An example of the trapping of precursor NH3 species on a single crystal surface will be given as well as its unusual structure. In addition, the activated conversion from the precursor species to the chemisorbed NH3 species has been witnessed as covalent bonding takes place via an activated surface process.

The activation of chemisorbed species, producing a surface reaction, involves the absorption of thermal energy from the phonons of the solid. The absorption of the small quantities of thermal energy by a chemisorbed acetate species has been witnessed directly by the observation of the onset of rotational motion of the dangling methyl group. At low temperatures, the methyl group is frozen azimuthally; at higher temperatures, hindered rotation is observed to occur. The barrier to rotation is about 10 meV, which is one-half the barrier to rotation in the free acetic acid molecule. A speculation on the electronic factor responsible for this softening effect within the chemisorbed molecule will be presented.

Notes on Ultraslow Chemical Dynamics

Peter M. Weber
Brown University
October 18, 2000

Ultraslow chemical reactions are poorly understood and characterized, because their existence is not evident on the time scale of typical laboratory experiments. Nonetheless, reactions on a megasecond time scale could be important. Examples of well-known ultraslow reactions include:

* crystallization of glasses
* aging of metals; hardening
* slow changes in atmospheric composition

Beyond those examples, there may be numerous ultraslow reactions of molecular materials. Some of these reactions could be of prime practical importance. Materials that would be worth looking at might include:

Pharmaceuticals: decay of medicines while in storage?

Plastics: decay of optical information storage media?

Decay of insulators in wiring?

Hydrocarbons: is there a shelf life for fuels, gasoline, and lubricants?

Chloro-and fluoro-compounds:

Is there a lifetime for liquid fillings of capacitors?

Shelf life for refrigerants?

Photochemical processes:

Decay of paints and other surface coatings?

Glasses and crystalline optical materials: photochemical stability?

The build-up of high technology during the recent decades has made heavy use of advanced molecular materials. It is important now to investigate the life expectancy of the materials used. As just one example, billions of dollars will be spent during the next decade on fiber optic networks. It might be important to investigate the aging characteristics and long-term photochemical stability of the glasses that are used.

I am an experimentalist. Thus I concentrate on questions relating to the measurement of ultraslow reactions.

Instrumental requirements to study ultraslow reactions:

To establish guidelines for measurements, let us review some elementary chemical kinetics.

1. First order reactions

Assume for simplicity a simple first order reaction, A ◊ B. Assume also that at time zero, one starts with a clean sample of substance A only. In general, A could be one component of a multi-component system. The question is posed about the decay of substance A to form substance B. For the purpose of a calculation about instrument requirements we take the reaction to be first order, with a rate k_f. From elementary chemical kinetics it follows that the fraction of B, with respect to A, as a function of time is given by:

$$\frac{[B](t)}{[A](t)} = e^{k_f t} - 1 \approx k_f t + \frac{1}{2}\left(k_f t\right)^2 + \ldots$$

For the very slow reactions of interest here we truncate the expansion after the linear term. Suppose then, that the detection limit of an instrument for substance B, in the presence of a large amount of substance A, is L_1. The B molecule can then be detected if the elapsed time is longer than:

$$\frac{[B](t)}{[A](t)} \approx k_f t + \ldots \geq L_1$$

$$t \geq L_1 / k_f$$

Example: If an instrument can detect substance B, in the presence of a large amount of substance A, to 100 ppm, then $L_1 = 1 \cdot 10^{-4}$. A reaction with a rate of $k_f = 1 \cdot 10^{-9}\ s^{-1}$ (half-life: 22 years) will lead to a detectable B-signal after a time of $t > 1 \cdot 10^5$ s, or 1 day.

2. Complex reactions

It is not the purpose of this exposé to review all possible reaction schemes that might be important. In general, complex reactions feature a time dependence for the B concentration that does not follow the simple exponential form. Similar to the first order reaction, however, the initial rise of B is often linear with time. Therefore, to observe the difference between a first order reaction and complex reactions, or to elucidate complex reaction schemes, one must be able to measure at least the quadratic term in the expansion of the time dependence of B. Details depend, of course, on the specific reaction mechanism.

A measurement of the quadratic term imposes more stringent requirements on the instrument. Suppose that the accuracy with which the concentration of B is measured is given by L_2. Deviations from the linear part of the expansions will be noticed if the elapsed time exceeds:

$$\frac{[B](t)}{[A](t)} \approx k_f t + \frac{1}{2}\left(k_f t\right)^2 + \ldots \geq k_f t + L_2$$

$$t \geq \frac{\sqrt{2L_2}}{k_f}$$

In our example of a reaction with a rate of $k_f = 1 \cdot 10^{-9}\ s^{-1}$ we find that, if we take L_2 to be 10^{-4} as well, the elapsed time must exceed $1.4 \cdot 10^7$ s, or 163 days. While this seems not too daunting, realize that most instruments will probably have an L_2 that is higher than L_1. Longer observation times will therefore be required.

Summary: Evidence of chemical reactions can be observed within a relatively short time, even when the reactions occur on a Gigasecond time scale. While the full extent of the reaction will take a long time to unfold, the early parts of the reaction should be observable within a reasonably short amount of time, given suitable instrumentation. However, a measurement of a kinetics scheme, or even a verification that the reaction is indeed first order, requires a much longer observation time.

Instrumental requirements:

Instruments to study slow reactions should meet the following requirements:

- High detection limits in the presence of large amounts of reactants (L_1).
- High degree of accuracy for measuring small concentrations (L_2).
- Good linearity
- Stability; reproducible calibration over extended periods of time.

It is important to recognize that the choice of instrument must go hand in hand with the system to be studied. Here I suggest two types of experiments that I could imagine performing in order to study ultraslow reactions.

1. Materials with a reasonable vapor pressure

If the reactants and products are expected to have a reasonably large vapor pressure, and can be transferred to the gas phase, then a mass spectrometer would be a useful instrument to observe the slow rise of the products. Ideally one would choose an instrument that uses an ionization scheme that minimizes fragmentation, so that little confusion arises about the origin of small peaks observed in the mass spectrum

Mass spectrometers could be well suited to study reactions where reactants and products have distinct masses. Thus, isomerization reactions would be difficult. However, this problem could be addressed if the instrument possesses in addition to the mass resolution some form of spectral resolution that can distinguish the isomers.

Our femtosecond photoionization instrument at Brown University:

- Excellent S/N: exceeding $L_1=10^5$ with short data acquisition (minutes).
- L_2 is at the theoretical limit: the limits are imposed by the shot noise of the observed product mass, or, if masses overlap, the shot noise from the residual fragmentation of the reactant. Our instrument shows a fragmentation in the range of 1% or less.

- Digital counting system; high degree of linearity.
- Can be calibrated; possibly run simultaneously a sample of reaction products.
- Can be applied to many substances.
- Very little fragmentation; provides clean identification of reaction products.
- Possibility of added spectral resolution via a photoelectron spectrum.

Notes on the choice of molecular systems:

- Best and easiest if the reactant has some reasonable vapor pressure (>1Torr; heating is fine.)
- Product should ideally have a vapor pressure not too different from the reactant.
- For starters, let's stay away from isomerization reactions; for example, an electrocyclic ring opening reaction will not show up in a mass spectrum.

Applicability:

* Hydrocarbons

* chlorinated and fluorinated compounds

* some pharmaceuticals

First prototype systems:

- CCl_4, CF_4, and mixed molecules: CCl_3F, CCl_2F_2, etc.
- Fluorinated and chlorinated benzenes

2. Transparent solid materials

A different class of materials to investigate for ultraslow chemical reactions involves transparent solids materials, such as glasses or certain polymers. For these materials one could use light scattering to investigate the appearance of impurities or crystallites. In an experiment one would transmit laser light through the glassy material, and observe the time dependence of the intensity of scattered radiation. Depending on the setup, one could use a simple photomultiplier to detect the scattered light.

In a variation of this scheme, one could explore the photochemical stability of the material by exposing the material to an intense laser beam for extended periods, and observe the time evolution of the scattering centers arising from this exposure.

Applicability:

* glasses

* molecular crystals; e.g. nonlinear optical materials.

* Transparent plastics

* possibly fiber optics

Notes:

To avoid spurious signals from dust accumulation, one may have to keep the materials in a vacuum. However, one must make sure that there is no pump-oil deposition, and that there are no energetic particles in the vacuum (this likely excludes ion pumps).

Note: This experiment will not measure reactions that maintain the transparency of the medium; such reactions would require a measurement of a spectrum.

Possible model systems

- Optical crystals; nonlinear crystals such as BBO, KTP
- Clear plastics (e.g. CD's).
- Glasses

Further notes and thoughts:

- One may anticipate that the kinetics of ultraslow reactions in the solution phase depends strongly on the presence of container walls, and on impurities or particulate inclusions. (Example: the reaction $H_2 + {}^1/_2\, O_2 \lozenge H_2O$ wouldn't happen without such initiators.) Thus, one needs to be extremely careful in establishing procedures that allow reproducible results.
- It will be important to investigate to what extent very small impurities act in a catalytic fashion. A careful analysis of trace contaminations of all reactants will be required.
- Are there 'suspects'? I.e., reactions in systems that appear stable, but are suspected to undergo slow reactions?
- For solution phase chemistry: the products should not evaporate, precipitate, or bind as 'crud' to the container walls. Instead, they should be dissolved in the reactant.

Finally, a question: How do we define 'success'? Is it important to indeed find a slow reaction in a system that previously had been considered stable? Or, do we have specific systems that we would like to know the stability of? If the latter, then success might indeed be the verified absence of a reaction or decomposition!

5. Reports of Focus Groups

5.1 Alpha Group Report and Recommendations

5.1.1 Identify Classes of Slow Phenomena and Systems

Aging Pathways

- High-energy barriers: a long time elapses before a thermal fluctuation enables the system to surmount the barrier.
- Entropic barriers: the system explores many degrees of freedom before encountering a decomposition path.

Table 1 identifies three practical systems that exhibit aging.

Studies should focus on aging of a filled polymer composite (with the simplest system showing almost all processes that are needed to understand the general problem of aging). Some classes of slow phenomena and their causes for material change are identified in table 2.

Table 1. Three systems that exhibit aging.

Systems for study	Criteria to determine aging	Processes leading to aging
PBXs (plastic bonded explosives)—crystalline explosives embedded in a polymer matrix	Mechanical strength Performance Sensitivity (premature explosion)	Degradation of binder adhesion Plasticiser migration Crack growth Coupling/bonding agents
Filled polymers Fiber-reinforced composites	Strength Failure under stress or tension Evolution of meso-structure (e.g., aggregation of filler particles) Sedimentation	Diffusion Crack growth Chemical degradation Surface phenomena Coupling/bonding agents
Energetic materials (PETN particle-size variation with age)	Organic crystal morphology	Structural evolution of granular materials Particle growth Formation of bulk defects Crack initiation and growth

Table 2. Slow phenomena.

Classes of slow phenomena	Cause for material change
Polymer chemical degradation	Thermal Reaction with environment or evolved gases Photochemical
Polymer surface interfaces	Loss of adhesion (e.g., polymer for filler)
Physical aging	Polymer crystallization causing loss of strength
Diffusion	Nucleation causing change in meso-structure Sedimentation

5.1.2 Identify Experimental/Theoretical Tools to Study Phenomena

Discovery of Phenomenology

One should search for stockpiles of progressively aged materials with well-documented compositions and histories. One should begin archives of materials for study at regular intervals and perform chemical and mechanical testing of new and aged materials. Finally, one should develop methods for accelerated aging (experimental methods are suggested in the following paragraphs; theoretical methods were described in the presentation by Voter (p 61)).

Calculation of Rates

Quantum chemical calculations for energies at minima of the potential energy surface are good, but calculations of rates require accurate barrier heights, and more development is needed.

Monte Carlo techniques may be the only feasible means of calculating extremely slow-rate processes.

Use of Gas Phase Data to Describe Condensed Phase Kinetics

Theories of chemical kinetics in the gas phase have been very successful, and they are backed by a vast experimental literature. What of this gas phase knowledge can be transferred to the condensed phase? For example, can liquid phase reactions be treated as perturbed gas phase reactions or do many body effects require new approaches? This issue is crucial because time does not permit one to perform experiments on every system of interest; rather, progress depends on developing general formalisms that can be parameterized with a smaller set of good experiments. To begin, we need to understand simple chemical reactions in solids. For the aging problem, we must also understand the effects of structural evolution of solid-state chemistry.

Can we find well-defined solid-state experiments that can be used to determine whether gas phase data are relevant? Considerable data exists for simple gas phase, e.g., reactions in noble gas matrices. For more complex

matrices (e.g., molecular crystals, polymers), few measurements have been made. We should compare related systems: oxygen + ethane in the gas phase versus oxygen reacting with solid polyethylene.

Experiments Suggested To Understand Chemical Basis of Aging

1. Beams of reactive molecules (e.g. oxygen) can be reactively scattered off polymer surfaces (gas-surface scattering) with techniques of gas-phase reaction dynamics and kinetics.

2. Reactive molecules (radicals) can be generated in the bulk of a solid by photolysis or radiolysis of the material or of impurities (e.g. peroxides), and by chemical reactions studied in the solid-state with the use of spectroscopic probes. Besides being interesting, this has possibilities for accelerated aging.

3. Very slow evolution of gas from polymers (e.g., NO_2 outgassing from nitrocellulose or fluorocarbon outgassing from fluoropolymers) can be measured with a sensitive spectroscopic probe hovering near the surface. Cavity ring-down spectroscopy seems well suited to these measurements.

4. One can periodically use mass spectroscopy, high-performance liquid chromatography, and nuclear magnetic resonance to analyze bits of archived samples to determine very slow chemical degradation.

Aging and Failure: Mechanical and Chemical Properties of Interfaces

Make a model interface (e.g., by gluing two flat or curved pieces together) and measure the critical failure stress and strain with aging. Vibrational sum frequency generation may be a useful real-time probe of molecular dynamics at the failure interface.

Micromechanics: Probing Mechanical Processes in Real Time

Experimental methods include (1) laser-driven nanoshock waves to explore fast structural relaxation under large mechanical strain (see presentation by Dlott (p 55)); (2) electron, optical, and x-ray microscopy and laser and ion microprobes to provide spatial images of mechanical degradation (e.g., cracking) and of chemical changes; (3) Real-time measurements of strain with the use of moiré, etc (see presentation by Goldrein (p 15)); and (4) Finite element modeling will help interpret these tests.

Modeling

1. Map energy landscapes of chemical aging, strain, and density changes.

2. Develop best possible physical/chemical model of polymer degradation for a selected system from literature to identify weakness in understanding and gaps in data.

Suggested Research Program

1. Provide a reasonably faithful model system with the use of a filled polymer; it is not too simple. Choose a model composite, e.g., a filled polymer such as SiO_2 in hydroxy-terminated polybutadiene or polyethylene. Although SiO_2 is relatively inert, one can functionalize the surface. One can buy well-characterized shapes and sizes of SiO_2, and properties of the crystal surfaces are well known. One can characterize the silica surface reactions with various monomers using the tools of surface science. This model system comprises multiple length scales; potential energy surfaces for filled polymers may be, however, difficult to develop.

2. Characterize the basic failure mechanisms: Failure on mesoscale (possibly early consequences of polymer-filler interactions), failure on the macro scale (later, cumulative failure–cracking), and failure of model joints.

3. Characterize failure mechanisms with naturally aged and artificially aged materials. Induce artificial aging using light, heat, vibration, impact, and reactive atmospheres.

4. Through observations, suggest new diagnostic and modeling tools as aging continues.

5. Identify critical effects of age—What changes? What is important?

6. Use analytical tools to determine composition and structure of aged material.

7. Relate composition and structure to mechanical changes.

5.2 Omega Group Report and Recommendations

5.2.1 Identify Classes of Slow Phenomena and Systems

Characteristics of Slow Phenomena To Be Studied

1. The system is likely to fail: at surfaces, around internal impurities, and at boundaries between amorphous and crystalline phases, because of phase changes (e.g., changes in polymer character). So studies of these system properties should be emphasized. The role of stress is especially important.

2. Different slow processes may have very different kinetics. The processes may be governed by a single critical step or multiple steps with their own timescales and contributions to the temporal evolution of the systems. These processes may be fit by Arrhenius expressions or not. The coupling of chemical processes to slow transport may be crucial to a range of slow processes (e.g., the diffusion of reactive species to a reaction site); chemical engineering has already developed tools to manage this coupling.

3. To succeed, we must link atomistic behavior and macroscopic phenomena or, equivalently, link fast and slow timescales. This problem is commom to many phenomena where one must understand atomic- and molecular-

scale processes to model correctly the origins and behavior of long timescale events. Progress will be improved by better communications between chemists and molecular scientists on the one hand and engineers and polymer scientists on the other.

Processes and Systems That May Be Important in Aging

1. Various cycling processes (thermal, mechanical stress) cause material degradation.

2. Energy exchange into complex molecules in bulk and at surfaces.

3. Photoinduced changes in materials.

4. Diffusion, transport, and nucleation processes.

5. Slow chemical processes/cumulative or collective processes, e.g., structure and evolution of polymers in solution. Workers should take advantage of considerable current work on biopolymers.

6. Slow processes should be studied in well-characterized materials in controlled environments where surface and impurity effects have been eliminated. We cannot emphasize enough the need for well-defined, well-characterized systems to obtain a basic understanding of multitimescale phenomena. Modern analytical techniques are well capable of detecting minute amounts of materials that arise from slow processes. However, to learn anything, one needs to perform experiments under extremely well-controlled conditions. This is especially so in the "single critical step" scenario. Beyond surfaces and impurities, this scenario might include temperature, pressure, light, dissolved gasses, and possibly, nature of the surfaces involved. Any experimental study of slow processes must be capable of identifying the sources of reactions to connect to a theoretical understanding.

7. Some aging processes may not occur on the ground potential energy surface. Transitions may occur between different electronically excited states (e.g., radicals diffusing together). Hence, nonadiabatic processes should be included. This issue is related to photoinduced changes.

8. Quantum effects may be important; hence, systems with strong quantum effects (microscopic processes/elementary steps) should be chosen for study.

5.2.2 Identify Experimental and Theoretical Tools

Materials

1. Design and synthesis of homologous series of molecules with a tailor-made range of barriers. This topic deals with molecular materials tailored to cover a broad window of timescales by including conformational barriers of different magnitudes. The demands on material designs are only modest, because they just need to reasonably suggest the likely barrier mag-

nitudes. The experimental observations of conformational changes over various timescales could provide rich data for modeling and analysis, with feedback to additional syntheses as desired.

2. Materials enabling the study of critical nucleation. This and the following item 4 address the general class of phenomena where migration in materials, and especially of defects, can strongly influence the long timescale evolution of the materials. It seems possible to develop well-defined experiments to explore this class of phenomena.

3. Materials with free radical traps.

4. Materials to study production, stabilization, and transport in condensed phases.

Experiments To Study Response to Perturbations

All the items for this topic have some overall relevance for one to attain a better understanding of long-time dynamics phenomena by using a variety of disturbances and observing their impact.

1. Periodic disturbances to synchronize slow processes: lock-in discrimination, frequency spectrum, matched filtering.

2. High field excitation of defects and excited states leading to materials decomposition (sharp tips with high fields can create defects and induce chemical processes). The development of scanning tunneling methods will enable a wide range of experiments.

3. Low field effects on internal molecular dynamics leading to slow processes. This topic addresses how very low fields may work in cooperation with naturally present fluctuations to enhance the rate of barrier crossings. The capability to have minimal disturbance enhancement would be significant for accelerating slow processes in the most benign fashion. In addition, theoretical arguments suggest that basic information may also be learned about the dynamics of infrequent critical events by this approach (see presentation by Dykman and Golding (p 49)).

4. Static pressure effects on materials can increase diffusion into condensed phases and change transition states.

5. Effect of medium on transition states.

6. Creation of artificially induced slow processes, including nanosecond shocks and photoexcitation. These experiments use the pump-probe method. The pump step could be a photoexcitation, a pressure wave, etc.

7. Unraveling multiple barrier processes by low-temperature studies of kinetic phenomena.

Measurement and Detection

1. Coherent determination of trace species-enhanced detection sensitivity. We wish to exploit the progress in coherent control to enhance the detection limits of specific species. The capability to detect trace species is a rather generic problem in many long timescale problems involving chemical reactions. Besides the traditional techniques of detection, the recent developments in the field of coherent laser manipulation of molecules may offer a new means for high finesse detection of trace species. This comment arises from the observation that these techniques inherently rely on enhancing discrimination between one chemical versus another, and this capability should be transferable to also enhance detection sensitivity.

2. Detection of single molecule reaction products in a macroscale sample with the use of noninvasive methods, e.g., single photon emission. Identification of single molecule transformation in a bulk medium is a very important and challenging task for measuring infrequent events. For high sensitivity, we must arrange for individual, reacting molecules to signal their transformation. Molecules designed to contain absortive or chemiluminescent chromophores may provide these signals.

3. Insert microdevices sensitive to aging, e.g., detection of NO_2 from degradation of nitrocellulose. The DoD Smart Materials Program may provide directions for this approach.

Modeling

1. Revealing the underlying dynamics of slow fluctuational processes (infrequent events).

2. Dimensionality reduction-retaining slow processes (see presentation by Rabitz for details.

3. Accelerated dynamics simulation methods (see presentation by Voter for details (p 61)). This item and the previous two items (1 and 2) speak of basic theoretical computational issues that are necessary to bridge between slow and fast processes. The nature of modeling in this dynamic simulation is very much open for development with achieving computational reliability and efficiency as central criteria. These developing capabilities will interface with all the aforementioned phenomena and key experiments.

4. Interplay of diffusion and conformational changes and chemical reactions.

The Omega group suggested that this field of study be called "Diagnostics and Control of Slow Processes."

Appendix A. Participants

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Appendix B. Summary of 1997 Princeton Preliminary Meeting

B-1. Richard Behrens on Sandia Enhanced Surveillance Program

1. Long term effects of aging are largely unknown.

2. Energetic materials aging is highly and potentially likely to have a bad consequence.

3. Materials aging at atomic scale is a precursor to performance changes.

4. Goals include identifying critical degradation early; forecasting safety, performance, service life; providing signatures for monitoring; and providing tools for age-tolerant design.

5. Computational power required to model at macroscale, but with microinformation base.

B-2. Richard Behrens on Chemical/Physical Degradation of PETN-Based Energetic Materials

Observations about PETN:

1. Frequently used in stockpile, lots of components (20–30 years old) available for study.

2. Preliminary observations of aged PETN show no significant changes.

3. Literature values for PETN decomposition show great variability.

4. Energetic materials in use may be complex mixtures—binder, etc.

5. Simultaneous thermogravimetric modulated beam-mass spectrometry (STMBMS) is being used to analyze decomposition from accelerated aging (elevated temperature) experiments—these experiments are highly relevant to safety issues—consequences of a fire. Isotopic labeling suggests solid-phase decomposition products; LC/MS identifies products.

6. Acidic and hydrolytic conditions cleave the nitrate ester (yielding NO_2—the common degradation product for nitrate esters).

7. Binder degradation is more complex.

B-3. Leanna Minier on Aging Issues with Solid Rocket Motor (SRM) Propellants

Most rocket catastrophes attributed to increased surface area—cracks in grains, grain unbonding from walls, etc—of combusting materials leading to accelerated burning rate.

Fundamental processes are not understood:

1. Chemical aging of individual constituents and how they affect each other.

2. Chemistry at particle/binder and binder/liner interfaces.

3. Initiation of chemistry: applied stress/strain initiation of chemistry and correlation of chemistry to microstructural change.

Potential System for Study of Hydroxy-Terminated Poly Butadiene (HTPB):

1. Most SRM propellants are HTPB; more are being developed.

2. Can transfer information, models, etc, to other propellants.

3. Propellant is low energy (not detonable) and provides inert base.

4. Formulation is not difficult.

Leanna's Handouts include:

1. Pritchard on service-life prediction: discussion of Joint Army-Navy-Air Force program to predict solid rocket motor life. Various codes and approaches are available; those that use chemistry depend on elevated temperatures to derive heats of activation for gas generation, solubility, and stabilizer depletion for example. Associate chemistry of aging with cracking, unbonding, etc.

2. Oberth on solid propellant aging: Slow chemical reactions lead to softening, hardening, and fissuring. Accelerates aging by raising temperature. Deriving activation energies from Arrhenius behavior neglect gas diffusion, humidity, autocatalysis, and chain reactions. Gas fissuring is seen as major problem.

B-4. John Yates on Tracking Molecular Motion at Surfaces

1. Can observe the zero point motion of chemisorbed molecules and thermal excitation leading to surface diffusion using momentum resolved—electron stimulated desorption ion angular distribution. This gives information about constraints at surface site to motion. Can infer shape of potential energy surface from motion deep in well.

2. Perhaps can observe early onset of surface reactions.

3. First stages of surface oxidation show unusual self-organization effects—insight to surface passivation.

B-5. Herschel Rabitz on Long Timescale Dynamics

Situation: Individual atom motions (o) 10^{-15} s; computer calculations can reach 10^6 steps (o) 10^{-9} s.

Dilemma: So how does one handle long timescale motion? How does one focus on slow (important) events and not on atomic jitter? Also not clear is the notion if slow dynamics includes, or is separate from, the picture of an infrequent but locally fast process in time (i.e., a rapid barrier crossing that seldom happens).

Possible and complementary approaches:

1. Develop long timescale dynamics and collective/cooperative atomic motion—compare to Born-Oppenheimer approximate.

One approach—reduce degrees of freedom to lower dimensional space, but how does one find this space? Use dynamics equations, derive Jacobian matrix, and diagonalize collective degrees of freedom ordered by their frequencies—select low frequencies to lower dimension space of slow equations.

2. Develop tools to incorporate the role of noise-driven large fluctuations (i.e., barrier crossings or bond-breaking events).

B-6. Group Discussion

1. What should the phenomenon be called? Possibilities are aging → failure, very slow reactions, infrequent events, etc. Choice was "molecular dynamics on long timescales."

2. Are there other means to identify the subspace of slow variables?

3. What are promising systems for study? Possibilities are energetic materials polymers, especially very thin layers, e.g., by spin-coating diffusion on surfaces or in solids.

4. What communities should be involved?

- Experimental: surface scientists (especially those using various atom-probe microscopies), condensed-matter chemists, polymer degraders.
- Theorists: protein folders, nucleators.

5. What are the key experiments? Besides the development of the slow dynamics/kinetics tools, a reasonable goal would be to identify particular experiments that could verify the theoretical concepts. One could study either simple unimolecular decompositions or even slow diffusion processes.

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A U.S. Army Research Laboratory workshop was held in preparation for a new initiative to support long-term reliability. Chemists, engineers, and physicists from universities, Department of Energy, National Institute of Standards and Technology, the Navy, and the Army met to develop research recommendations to provide a fundamental understanding of the chemistry of processes that lead to materials failure. The workshop was held at Duke University during 9–11 August 2000 and was the first of its kind. This report presents the papers given by participants and the results of their discussions and outlines a new research initiative that can lead to the design of materials for a longer, useful life and enable a rational basis for programmed maintenance. Specific recommendations for experimental and theoretical research are included.

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